

Corrosion study of the BR1 fuel in highly alkaline conditions

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Content

Contents	i
List of Figures	v
List of Tables	xv
List of Acronyms	xvii
List of Symbols	xix
Chapter 1. Context of the thesis.....	1
1.1. BR1	2
1.2. BR1 fuel	3
1.3. Waste and disposal.....	7
1.4. Objectives of the thesis.....	10
1.5. Outline	11
Chapter 2. State of the art	13
2.1. 1xxx series aluminium alloys	14
2.2. Impact of alloying elements in aluminium alloys	15
2.3. Corrosion of aluminium and aluminium alloys.....	19
2.4. Cementitious materials for waste encapsulation	25
2.5. Corrosion inhibitors for aluminium alloys	31
2.6. Li-Al layered double hydroxide.....	40
2.6.1. Synthesis of LDH on aluminium and aluminium alloys.....	41
2.6.2. Corrosion protection of LDH on aluminium and aluminium alloys	46
2.7. Cement paste porosity	51
Chapter 3. Experimental procedures and methods	57
3.1. Sample preparation	58
3.2. Electrochemical methods	60
3.2.1. Electrochemical Impedance Spectroscopy.....	60

3.2.2.	Tafel plot.....	63
3.2.3.	Corrosion rate.....	65
3.3.	Gas chromatography.....	66
3.4.	Scanning electron and energy – dispersive X - ray spectroscopy.....	68
3.5.	General effective medium theory	70
3.5.1.	Percolation threshold of the capillary pores ϕ_c	71
3.5.2.	Critical exponent t	72
3.5.3.	Conductivity of capillary pore phase σ_p	72
3.5.4.	Conductivity of solid-gel phase σ_s	73
3.5.5.	Conductivity of overall cement paste σ_{eff}	74
3.6.	Pore solution extraction.....	75
3.7.	Mercury intrusion porosimetry	76
Chapter 4. Corrosion inhibition of AA1100 in Portland cement pastes by lithium salts.....		79
4.1.	Introduction.....	80
4.2.	Methods	81
4.3.	The validity of EIS results.....	81
4.4.	Impedance spectra.....	85
4.5.	Equivalent circuit model analysis	86
4.5.1.	Wire inductance and uncompensated resistance	87
4.5.2.	Modelling of the cement paste part.....	101
4.5.3.	Modelling of the interface	110
4.5.4.	Discussion on the modelling	116
4.6.	Fitting	116
4.6.1.	Wire inductance and uncompensated resistance	116
4.6.2.	Cement paste.....	116
4.6.3.	Interface	120
4.6.4.	Discussion about the fitting results	121
4.7.	Corrosion rates	123
4.7.1.	Determination of R_t	123
4.7.2.	Determination of β_a and β_c	126
4.7.3.	Determination of the produced hydrogen volume	129
4.7.4.	Determination of the corrosion product layer thickness.....	131
4.7.5.	Comparison of the corrosion rate obtained by EIS, GC and SEM	132
4.8.	Resistance of the corrosion product film (R_p)	139
4.9.	Characterization of the Al/corrosion product film/cement paste interface by SEM	142

4.10. Mechanisms of formation of corrosion product film	151
4.11. Conclusions	153
Chapter 5. Analysis of the cement paste porosity using EIS coupled with GEM.....	155
5.1. Introduction	156
5.2. Methods	157
5.3. Impedance spectrum results.....	158
5.4. Equivalent circuit model	159
5.5. Conductivity and pH of pore solution.....	162
5.6. Cement paste porosity	164
5.7. Conclusion.....	170
Chapter 6. Conclusions.....	175
Chapter 7. Perspectives.....	181
Appendix	185
A.1. The electrochemical cell setup	184
A.2. Preselection of the model for cement paste	190
A.3. The comparison of W_{cem2} and CPE_{cem2}	193
A.4. Fitting results.....	208
A.5. The link between the microstructures and the spectra	229
A.6. Uncertainty of the measurements	238
Bibliography	249

List of Figures

Figure 1.1 Outlook of Belgian Reactor 1.....	2
Figure 1.2 Schematic view of the BR1 reactor [1].	3
Figure 1.3 Belgian Reactor 1 fuel structure [1].	4
Figure 1.4 Schematic of the flux-alpha canning process. The uranium slugs are first coated (a), then rinsed (b) and finally inserted into an Al can (c) [2].	6
Figure 1.5 SEM micrographs showing (a) the top part of the BR1 fuel rod in cross section, (b) the anti-diffusion layer (ADL) and the bonding layer (BL) [4].	6
Figure 1.6 Near surface Belgian nuclear waste system for Category A waste (a) [6] and indicative diagram of the geological repository envisaged for B&C waste and of the surface facilities for the production of the supercontainers (b) [7].	9
Figure 1.7 Overall (a) [8] and localized (b) configuration of geological disposal.	10
Figure 2.1 Schematic of the mechanism leading to loss of particles from the surface. (A) Cathodic reactions at particle sites. (B) Pitting around a particle. (C) Repassivation of a particle-free pit [20].	16
Figure 2.2 Schematic of particle-induced pitting corrosion [21].	17
Figure 2.3 Optical microscopy micrographs of AA1100 (a) being polished and (b) after etching using Keller's reagent for 15s [39].	19
Figure 2.4 (a) SEM micrographs of polished AA1100 and (b) EDS maps of Al (red) and Fe (green) distribution on the framed area [39].	19
Figure 2.5 TEM micrograph of an oxide layer on a subsection of a lamella of AA6016 [40].	20
Figure 2.6 Pourbaix diagram for aluminium–water system [42].	21
Figure 2.7 Corrosion rates of commercially pure aluminium with exposure time at 30 °C determined by weight loss method [44].	22
Figure 2.8 Pitting potentials of AA1100 (a) and AA6061 (b) as a function of the temperatures in the corresponding NaCl+MgCl ₂ ·6H ₂ O solutions at the relative humidities (Φ) [45].	22
Figure 2.9 Example of pitting corrosion on the surface of AA1100 which was corroded in a 0.1 kmol·m ⁻³ NaCl solution [46].	23
Figure 2.10 Schematic of crevice corrosion mechanism [47].	24

Figure 2.11 Galvanic corrosion between aluminium and copper [48].	24
Figure 2.12 Corrosion inducing cracking initiation in AA6xxx during a stress corrosion cracking test [49].	25
Figure 2.13 Schematic diagram illustrating the evolution of pH at 25 °C in hydrated cement pore fluid as a result of cement degradation [57].	27
Figure 2.14 Pourbaix diagram for iron-water system [58].	28
Figure 2.15 Schematic diagram of a cross-section of supercontainer for vitrified high level nuclear waste emplaced in disposal [59].	28
Figure 2.16 Visible cracks formed at the (a) surface and (b) cross-section of the BFS/OPC sample with encapsulated Al [62].	29
Figure 2.17 pH evolution of simulated pore solutions of OPC and MKPC mortars (a), comparison of the corrosion current density (i_{corr}) (b) and the volume of H_2 (c) evolved versus time for pure AA1050 and AA5754 in OPC and MKPC mortars [64].	30
Figure 2.18 pH of PC (blended with blast furnace slag (BFS)) and MSH samples (a) and the volume of H_2 (b) evolved versus time for pure aluminium in OPC and MSH samples [66].	31
Figure 2.19. Schematic of the Tafel plot showing the effect of a cathodic inhibitor on corrosion [68].	32
Figure 2.20 Schematic of the Tafel plot showing the effect of an anodic inhibitor on corrosion [68].	33
Figure 2.21 Schematic of the Tafel plot showing the effect of a mixed inhibitor on corrosion [68].	33
Figure 2.22 Side (a) and top (b) view of the most stable configurations for adsorption of 2-MBT on the Al(111) surface in an acidic medium [69].	34
Figure 2.23 Corrosion protection mechanism of chromate controlled by the electrochemical potential and solubility of chromium oxide as a function of valence state and pH [79,80].	35
Figure 2.24 Schematic illustration of the inhibition mechanisms of MoO_4^{2-} in simulated concrete pore solutions with moderate MoO_4^{2-} concentration (10 mM) and high MoO_4^{2-} concentration (30 mM) [91].	36
Figure 2.25 Schematic mechanism of corrosion inhibition on AA2024 by zinc phosphate (ZP) in the epoxy matrix [97].	37
Figure 2.26 Schematic of cerium precipitation mechanisms on the AlCuMg (S-phase) intermetallic particles in aluminium alloys [111].	38
Figure 2.27 Structure of common layered double hydroxide [127].	41
Figure 2.28 Schematic structure of $LiAl_2(OH)_6Cl$. Li, Al, Cl, O, and H are represented by purple, gray, green, red, and white balls, respectively [139].	41
Figure 2.29 Synthesis steps of Zn–Al LDH by co-precipitation method [142].	42
Figure 2.30 Schematic illustration of the steps in the Li-Al LDH formation [149].	43
Figure 2.31 Schematic representation of the formed layers. Region I and Region II indicate the areas under different solution chemistry in the neutral salt spray experiment [152].	44
Figure 2.32. SEM images of Mg-Al LDH films developed at various reaction temperatures and crystallization times [154].	44

Figure 2.33 Schematic representation of the structure of the LDH based film [141] and FIB-SEM image of MgAl-LDH coating on AA6082 [167].....	48
Figure 2.34 Impedance plots of CaAl-LDH: (I) as-prepared, (II) after 4 days, (III) after 7 days immersion in 0.1 mol·L ⁻¹ NaCl solution [153].	48
Figure 2.35 Potentiodynamic polarization curves for AA2024-T3 aluminium alloy immersed in 0.05 mol·L ⁻¹ NaCl solution with and without corrosion inhibitor [176].	50
Figure 2.36 SEM micrographs of the polished alloy (a); SEM micrograph of the alloy after immersion in a mixed solution containing 0.05 M Zn(NO ₃) ₂ ·6H ₂ O and 0.3 M NH ₄ NO ₃ for 0.5 h (b); (c)~(f) are the framed regions in (b) [177].	50
Figure 2.37 Schematic of the inhibition mechanism of Li ₂ CO ₃ on AA2024 substrate (a) [176] and the corresponding SEM micrograph (b) [151].	51
Figure 2.38 Relationship between compressive strength and the capillary porosity of cement pastes with low water-to-cement ratios fitting by Balshin function [183].....	52
Figure 2.39 Schematic of the pore structure of hardened cement paste [198].	53
Figure 2.40 Fundamental analytical models for effective properties of two-component materials [206]. 55	
Figure 3.1 Schematics of EIS (a), SEM & GC & MIP (b) and pore solution (c) specimens.....	59
Figure 3.2 Schematic of (a) condition 1 and (b) condition 2 for the curing of samples.	60
Figure 3.3 Sinusoidal current response in a linear system.....	61
Figure 3.4 A. Equivalent circuit; B. Nyquist; C. Bode plots with impedance vector for the parallel RC circuit [226].	62
Figure 3.5 Electrical equivalent circuit characteristic of the Al corrosion mechanism [126].	63
Figure 3.6 Example of a Tafel plot [229].....	64
Figure 3.7 Example of the Tafel plot of an OPC+LiNO ₃ sample after 121 days in condition 1.	65
Figure 3.8 Schematic of a gas chromatograph and its main components [235].....	66
Figure 3.9 Schematic of a gas specimen extraction.	67
Figure 3.10 Example of gas chromatography result.....	68
Figure 3.11 Signals excited by electron beam (a) and the interaction volume and the regions of signals (b) [236].	69
Figure 3.12 Relationship between the effective conductivity and porosity in cement pastes.	71
Figure 3.13 Porosity and conductivity of cement pastes determined by Tumidajski et al [216].....	72
Figure 3.14 Different saturation conditions of capillary pores.	73
Figure 3.15 EIS test setup (a), Nyquist plots (b) and the equivalent circuit model (c) of the cell in saturated Ca(OH) ₂ solution over one month.	75
Figure 3.16 Accessories (a) and the setup (b) of pore solution extraction.	76
Figure 3.17 Schematic representation of pores [255].....	77

Figure 4.1 Nyquist and Bode plots, including both the high-to-low and low-to-high frequency scans, of AA1100 in the OPC paste after 29 days in condition 1 (a) (b), in the OPC+LiNO ₃ paste after 79 days in condition 2 (c) (d) and in the OPC+Li ₂ CO ₃ paste after 92 days in condition 1 (e) (f).....	83
Figure 4.2 Comparison between the experimental data and the result calculated using the Kramers-Kronig transforms for AA1100 in the OPC paste after 29 days in condition 1, in the OPC+LiNO ₃ paste after 79 days in condition 2 and in the OPC+Li ₂ CO ₃ paste after 92 days in condition 1.	84
Figure 4.3 Nyquist (a) and Bode (b) plots of AA1100 aluminium alloy in the OPC paste in condition 1. ...	85
Figure 4.4 Variation of Nyquist (a) and Bode (b) plots of AA1100 in the OPC+Li ₂ CO ₃ paste in condition 2.	86
Figure 4.5 Variation of Nyquist (a) and Bode (b) plots of AA1100 in the OPC+LiNO ₃ paste in condition 1.	86
Figure 4.6 Electrical equivalent circuit used to fit the EIS spectra for the corrosion of Al in cement pastes.	87
Figure 4.7 Example of the Nyquist (a), (b) and Bode (c) plots of an OPC+Li ₂ CO ₃ sample in condition 1. ...	89
Figure 4.8 Dummy cell used (a) and the corresponding equivalent circuit (b).	90
Figure 4.9 Nyquist plot of the dummy cell in the glovebox with the 5 m wire connection.	91
Figure 4.10 Nyquist plot with $R_s = 10 \Omega$, $R_{ct} = 100 \Omega$, $L_1 = 10 \mu\text{H}$, $C_{dl} = 100 \mu\text{F}$ reported in literature [262].	91
Figure 4.11 Bode plots of the same dummy cell of different wire lengths.	92
Figure 4.12 Fitting results of the dummy cell in the glovebox with the 5 m wire connection (a), out of the glovebox with the 1.5 m wire connection (b) and out of the glovebox with the 1 m wire connection (c).	93
Figure 4.13 Resistance of the aluminium rod measured (a) and the holes and cracks present in the cement paste.	94
Figure 4.14 EIS fitting results (Nyquist (a), (b), Bode (c) plots and the fitting parameters (d)) of an OPC+LiNO ₃ sample in condition 2 after 51 days.	96
Figure 4.15 EIS fitting results (Nyquist (a), (b), Bode (c) plots and the fitting parameters (d)) of the equivalent circuit with a free L_1 of an OPC+Li ₂ CO ₃ sample after 62 days in condition 1.	97
Figure 4.16 EIS fitting results (Nyquist (a), (b), Bode (c) plots and the fitting parameters (d)) of the equivalent circuit with a fixed L_1 of an OPC+Li ₂ CO ₃ sample after 62 days in condition 1.	98
Figure 4.17 EIS fitting results (Nyquist (a), (b), Bode (c) plots and the fitting parameters (d)) of the equivalent circuit without L_1 of an OPC+Li ₂ CO ₃ sample after 62 days in condition 1.	99
Figure 4.18 EIS fitting results (Nyquist (a), (b), Bode (c) plots and the fitting parameters (d)) of an OPC+Li ₂ CO ₃ sample in condition 1 after 48 days.....	100
Figure 4.19. Equivalent circuit of the cement paste proposed in literature.	101
Figure 4.20 Equivalent circuit used in preliminary study for the EIS fitting.	101
Figure 4.21 Example of a case with 'n' value of CPE_{cem2} lower than 0.5.	102
Figure 4.22 Three possible models with physical meanings.	103

Figure 4.23 Typical impedance spectrum of a Warburg element with a reflective boundary (a), simulated impedance spectra of porous microstructures with closed ends [280] (b) and the porous microstructure of C-S-H on the surface of the cement grains [281,282] (c).	105
Figure 4.24 Equivalent circuit model (a) used for the fitting of the mortars reported by Marriaga et al. and the corresponding fitting results of non-conductive pore capacitance [283] (b).	106
Figure 4.25 Schematic diagram of the ITZ (a) [284] and average porosity in ITZ at various age (b) [285].	107
Figure 4.26 Typical impedance spectra of a Warburg element with a reflective boundary produced with: $W_o-R = 1000$; $W_o-T = 0.1$; $W_o-P = 0.5$	109
Figure 4.27 Impedance spectra of a Warburg element with a reflective boundary produced with: $W_o-R = 2.0 \times 10^6$; $W_o-T = 150$; $W_o-P = 0.7$	110
Figure 4.28 Equivalent circuit used in the study for describing the interface.	112
Figure 4.29 EIS fitting results only using a parallel R_t and C_{dl} (Nyquist (a), (b), Bode (c) plots and the fitting parameters (d)) of an OPC+LiNO ₃ sample after 63 days in condition 1.	113
Figure 4.30 EIS fitting results (Nyquist (a), (b), Bode (c) plots and the fitting parameters (d)) of an OPC+LiNO ₃ sample after 63 days in condition 1.	114
Figure 4.31 EIS fitting results (Nyquist (a), (b), Bode (c) plots and the fitting parameters (d)) of an OPC+Li ₂ CO ₃ sample after 79 days in condition 1.	115
Figure 4.32 Equivalent electrical circuit of the cementitious composites (a) and the corresponding fitting results for different SMS concentrations and curing ages (b) [276].	118
Figure 4.33 Equivalent electrical circuit reflecting the phenomenon at the steel/mortar interface (a), the fitting parameters from EIS spectra of the carbon steel embedded in mortar after different W/D cycles without (b)/with (c) the addition of 8 wt.% <i>MgAl-LDHs-NO₂⁻</i> [293].	119
Figure 4.34 Equivalent circuits used to fit the EIS spectra: (EC1) unexposed defect areas and defect areas with few or no corrosion products; (EC2) defect areas with voluminous porous corrosion products; (EC3) defect areas with protective layer generated (a) and corresponding fitting results of AA2024 (b) [303].	121
Figure 4.35 EIS fitting results of an OPC sample after 7 days in condition 1.	122
Figure 4.36 Evolution of R_t as a function of time of (a) OPC samples in condition 1, (b) OPC samples in condition 2, (c) OPC+LiNO ₃ samples in condition 1, (d) OPC+LiNO ₃ samples in condition 2, (e) OPC+Li ₂ CO ₃ samples in condition 1, (f) OPC+Li ₂ CO ₃ samples in condition.	124
Figure 4.37 Tafel polarization plots of (a) OPC samples in condition 1, (b) OPC samples in condition 2, (c) OPC+LiNO ₃ samples in condition 1, (d) OPC+LiNO ₃ samples in condition 2, (e) OPC+Li ₂ CO ₃ samples in condition 1, (f) OPC+Li ₂ CO ₃ samples in condition 2.	126
Figure 4.38 Example of the determination of Tafel slopes in different potential ranges for an OPC+LiNO ₃ sample after 121 days in condition 1.	128

Figure 4.39 Evolution of H_2 concentration measured from GC as a function of time of (a) OPC samples in condition 1, (b) OPC samples in condition 2, (c) OPC+LiNO ₃ samples in condition 1, (d) OPC+LiNO ₃ samples in condition 2, (e) OPC+Li ₂ CO ₃ samples in condition 1, (f) OPC+Li ₂ CO ₃ samples in condition 2.	130
Figure 4.40 Variation of the film thickness as a function of time for OPC+LiNO ₃ and OPC+Li ₂ CO ₃ samples from SEM characterisation.....	132
Figure 4.41 Variation of the corrosion rates as a function of time of (a) OPC samples in condition 1, (b) OPC samples in condition 2.....	133
Figure 4.42 Pictures showing (a) the breach of a GC sample in condition 1 after 133 days and (b) a crack in an EIS sample appeared in condition 2 generated after 8 days.....	134
Figure 4.43 Variation of the corrosion rates as a function of time of (a) OPC+LiNO ₃ samples in condition 1, (b) OPC+LiNO ₃ samples in condition 2.	136
Figure 4.44 Variation of the corrosion rates as a function of time of (a) OPC+Li ₂ CO ₃ samples in condition 1, (b) OPC+Li ₂ CO ₃ samples in condition 2.....	138
Figure 4.45 Evolution of R_f as a function of time of (a) OPC samples in condition 1, (b) OPC samples in condition 2, (c) OPC+LiNO ₃ samples in condition 1, (d) OPC+LiNO ₃ samples in condition 2, (e) OPC+Li ₂ CO ₃ samples in condition 1, (f) OPC+Li ₂ CO ₃ samples in condition 2.	140
Figure 4.46 SEM micrographs of (a) the pure OPC sample after 28 days, (b) the pure OPC sample after 79 days, (c) the OPC+LiNO ₃ sample after 28 days, (d) the OPC+LiNO ₃ sample after 79 days, (e) the OPC+Li ₂ CO ₃ sample after 28 days, (f) the OPC+Li ₂ CO ₃ sample after 79 days. All samples were aged in condition 2. .	143
Figure 4.47 SEM micrographs of (a) the pure OPC sample after 28 days, (b) the pure OPC sample after 79 days, (c) the OPC+LiNO ₃ sample after 28 days, (d) the OPC+LiNO ₃ sample after 79 days, (e) the OPC+Li ₂ CO ₃ sample after 28 days, (f) the OPC+Li ₂ CO ₃ sample after 79 days. All samples were aged in condition 1. .	144
Figure 4.48 EDX line scan results (Al, O, Ca and Si) of the cross-section of an OPC+LiNO ₃ sample after exposure in humid Ar atmosphere (condition 1) for 81 days.	146
Figure 4.49 EDX line scan results (Al, O, Ca and Si) of the cross-section of a OPC+Li ₂ CO ₃ sample after exposure to saturated Ca(OH) ₂ (condition 2) for 79 days.....	148
Figure 4.50 Example of EDX line scan results (Al, O, Ca and Si) of the cross-section of a OPC+Li ₂ CO ₃ sample after exposure to saturated Ca(OH) ₂ (condition 2) for 79 days.	149
Figure 4.51 Example of EDX line scan results (Al, O, Ca and Si) of the cross-section of a OPC+Li ₂ CO ₃ sample after exposure to saturated Ca(OH) ₂ (condition 2) for 79 days.	150
Figure 4.52 Proposed scenario for the corrosion process of Al in the pure OPC paste.	152
Figure 4.53 Proposed scenario for the corrosion process of Al in the OPC paste with the addition of LiNO ₃ or Li ₂ CO ₃	152
Figure 5.1 Variation of Nyquist plots of AA1100 with time in pure OPC paste under condition 1.	159
Figure 5.2 Electrical equivalent circuit employed to fit EIS spectra for the corrosion of Al plate in cement pastes.	160

Figure 5.3 Evolution of R_{cem1} as a function of time of (a) OPC samples in condition 1, (b) OPC samples in condition 2, (c) OPC+LiNO ₃ samples in condition 1, (d) OPC+LiNO ₃ samples in condition 2, (e) OPC+Li ₂ CO ₃ samples in condition 1, (f) OPC+Li ₂ CO ₃ samples in condition.	161
Figure 5.4 Variation of the conductivity of cement pore solution as a function time for different conditions with or without inhibitors.	163
Figure 5.5 Variation of the pH of cement paste pore solutions as a function of time.	164
Figure 5.6 Variation of the porosity as a function of time measured by EIS and MIP of (a) 0.36 OPC samples in condition 1, (b) OPC samples in condition 2, (c) OPC+LiNO ₃ samples in condition 1, (d) OPC+LiNO ₃ samples in condition 2, (e) OPC+Li ₂ CO ₃ samples in condition 1, (f) OPC+Li ₂ CO ₃ samples in condition 2.	166
Figure 5.7 SEM and EDX line scan results of the Al element of the cross-section of an OPC sample in condition 1 for 28 days.	167
Figure 5.8 Tiny cracks appeared in one of the three replicate 0.36 OPC samples after 133 days in condition 1.	168
Figure 5.9 Methodology for the study the cement paste porosity using a combination of EIS and GEM.	171
Figure 6.1 Summary of the methods used in the thesis.	175
Figure A.1 Schematic of (a) two-electrode, (b) three-electrode, and (c) four-electrode cell configurations (WE is the working electrode, CE is the counter electrode, RE1 and RE2 are the reference electrodes).	185
Figure A.2 Schematic of (a) two-electrode and (b) four-electrode cell configurations and (c) the corresponding impedance spectra in the literature [319].	186
Figure A.3 Schematic of the two-electrode cell configuration and the corresponding equivalent circuit [213].	187
Figure A.4 Schematic of electrochemical noise analysis setup of two identical corroding electrodes [323].	187
Figure A.5 Schematic of one big electrode (a) and two electrodes (b) in cement paste (A, B, C and D have the same area).	189
Figure A.6 BSE image of the Portland cement paste sample milled by FIB [337] (a), the hydrated cement particle after 21 days curing time, C-S-H needles with diameter approx. 5 nm [338] (b) and the schematic structure of the calcium-silicate-hydrate (C-S-H) paste on the meso- and nano-scale (white cement paste) [339] (c).	191
Figure A.7 Schematic illustration of pore network in the cementitious system.	192
Figure A.8 Excluded models because of bad fitting.	192
Figure A.9 Temperature dependence of DC conductivity for C-S-H and C ₄ AF [277].	193
Figure A.10 Typical impedance spectrum of a Warburg element with a reflective boundary i.e. W_o (a), simulated impedance spectra of porous microstructures with closed ends [280] (b) and the porous microstructure of C-S-H on the surface of the cement grains [281,282] (c).	195
Figure A.11 Current flow on the capillary/gel interface.	196

Figure A.12 Equivalent circuit model used for a lithium-ion battery [337].....	196
Figure A.13 Equivalent circuit model used for the fitting of the mortars reported by Marriaga et al. and the corresponding electrical behaviour of non-conductive pore capacitance [283].	197
Figure A.14 Schematic diagram of ITZ (a) [284] and average porosity in ITZ at various age (b) [285].	198
Figure A.15 Simplification of the equivalent circuit of a mixed conductor which applies for low frequencies [343].	199
Figure A.16 Schematic of the electrical conduction in soils (a) and the corresponding equivalent circuit of soils (b) [344].	199
Figure A.17 Equivalent circuit with a Warburg element describing the diffusion in the solid phase path.	200
Figure A.18 Typical impedance spectra of a Warburg element with a reflective boundary produced with: $W_o-R = 1000$; $W_o-T = 0.1$; $W_o-P = 0.5$	201
Figure A.19 Impedance spectra of a Warburg element with a reflective boundary produced with: $W_o-R = 2.0 \times 10^6$; $W_o-T = 150$; $W_o-P = 0.7$	202
Figure A.20 EIS fitting results using a CPE (a) and using a W_o (b) of an OPC sample after 29 days in condition 1.	204
Figure A.21 EIS fitting results using a CPE (a) and using a W_o (b) of an OPC+Li ₂ CO ₃ sample after 49 days in condition 2.	205
Figure A.22 EIS fitting results using a CPE (Nyquist (a), (b), Bode (c) plots and the fitting parameters (d)) of an OPC+LiNO ₃ sample after 79 days in condition 1.	206
Figure A.23 EIS fitting results using a CPE (Nyquist (a), (b), Bode (c) plots and the fitting parameters (d)) of an OPC+LiNO ₃ sample after 86 days in condition 1.	207
Figure A.24 EIS fitting results of an OPC sample after 7 days in condition 2.	209
Figure A.25 EIS fitting results of an OPC sample after 13 days in condition 1.	210
Figure A.26 EIS fitting results of an OPC sample after 13 days in condition 2.	211
Figure A.27 EIS fitting results of an OPC sample after 29 days in condition 1.	212
Figure A.28 EIS fitting results of an OPC sample after 30 days in condition 2.	213
Figure A.29 EIS fitting results of an OPC sample after 41 days in condition 1.	214
Figure A.30 EIS fitting results of an OPC+LiNO ₃ sample after 7 days in condition 1.	215
Figure A.31 EIS fitting results of an OPC+LiNO ₃ sample after 7 days in condition 2.	216
Figure A.32 EIS fitting results of an OPC+LiNO ₃ sample after 28 days in condition 1.	217
Figure A.33 EIS fitting results of an OPC+LiNO ₃ sample after 28 days in condition 2.	218
Figure A.34 EIS fitting results of an OPC+LiNO ₃ sample after 79 days in condition 1.	219
Figure A.35 EIS fitting results of an OPC+LiNO ₃ sample after 120 days in condition 1.	220
Figure A.36 EIS fitting results of an OPC+LiNO ₃ sample after 120 days in condition 2.	221
Figure A.37 EIS fitting results of an OPC+Li ₂ CO ₃ sample after 8 days in condition 1.	222

Figure A.38 EIS fitting results of an OPC+Li ₂ CO ₃ sample after 8 days in condition 2.	223
Figure A.39 EIS fitting results of an OPC+Li ₂ CO ₃ sample after 30 days in condition 1.	224
Figure A.40 EIS fitting results of an OPC+Li ₂ CO ₃ sample after 30 days in condition 2.	225
Figure A.41 EIS fitting results of an OPC+Li ₂ CO ₃ sample after 79 days in condition 1.	226
Figure A.42 EIS fitting results of an OPC+Li ₂ CO ₃ sample after 121 days in condition 1.	227
Figure A.43 EIS fitting results of an OPC+Li ₂ CO ₃ sample after 121 days in condition 2.	228
Figure A.44 EIS fitting results of an OPC sample after 22 days in condition 1.	229
Figure A.45 The simulation of EIS results of an OPC sample after 22 days in condition 1 with $CPE_{cem1}-T$ decreasing by ten times.	230
Figure A.46 Simulation of EIS results of an OPC sample after 22 days in condition 1 with R_{cem1} decreasing by 2000 Ω	231
Figure A.47 Simulation of EIS results of an OPC sample after 22 days in condition 1 with R_{cem2} decreasing by 2000 Ω	232
Figure A.48 Simulation of EIS results of an OPC sample after 22 days in condition 1 with $W_{cem2}-R$ increasing by an order of magnitude.....	233
Figure A.49 Simulation of EIS results of an OPC sample after 22 days in condition 1 with CPE_f-T increasing by an order of magnitude.....	234
Figure A.50 Simulation of EIS results of an OPC sample after 22 days in condition 1 with R_f decreasing by 1000 Ω	235
Figure A.51 Simulation of EIS results of an OPC sample after 22 days in condition 1 with C_{dl} decreasing by 0.002.....	236
Figure A.52 Simulation of EIS results of an OPC sample after 22 days in condition 1 with R_t decreasing by 2000 Ω	237
Figure A.53 Evolution of R_t (with the average values and the error bars) as a function of time of (a) OPC samples in condition 1, (b) OPC samples in condition 2, (c) OPC+LiNO ₃ samples in condition 1, (d) OPC+LiNO ₃ samples in condition 2, (e) OPC+Li ₂ CO ₃ samples in condition 1, (f) OPC+Li ₂ CO ₃ samples in condition 2.....	239
Figure A.54 Evolution of H ₂ concentration (with the average values and the error bars) as a function of time of (a) OPC samples in condition 1, (b) OPC samples in condition 2, (c) OPC+LiNO ₃ samples in condition 1, (d) OPC+LiNO ₃ samples in condition 2, (e) OPC+Li ₂ CO ₃ samples in condition 1, (f) OPC+Li ₂ CO ₃ samples in condition 2.....	240
Figure A.55 Variation of the film thickness (with the average values and the error bars) as a function of time for OPC+LiNO ₃ and OPC+Li ₂ CO ₃ samples from SEM characterisation.	241
Figure A.56 Evolution of corrosion rates (with the average values and the error bars) as a function of time of (a) OPC samples in condition 1, (b) OPC samples in condition 2, (c) OPC+LiNO ₃ samples in condition 1,	

(d) OPC+LiNO ₃ samples in condition 2, (e) OPC+Li ₂ CO ₃ samples in condition 1, (f) OPC+Li ₂ CO ₃ samples in condition 2.....	242
Figure A.57 Evolution of R_f (with the average values and the error bars) as a function of time of (a) OPC samples in condition 1, (b) OPC samples in condition 2, (c) OPC+LiNO ₃ samples in condition 1, (d) OPC+LiNO ₃ samples in condition 2, (e) OPC+Li ₂ CO ₃ samples in condition 1, (f) OPC+Li ₂ CO ₃ samples in condition 2.....	243
Figure A.58 Evolution of R_{cem1} (with the average values and the error bars) as a function of time of (a) OPC samples in condition 1, (b) OPC samples in condition 2, (c) OPC+LiNO ₃ samples in condition 1, (d) OPC+LiNO ₃ samples in condition 2, (e) OPC+Li ₂ CO ₃ samples in condition 1, (f) OPC+Li ₂ CO ₃ samples in condition 2.....	244
Figure A.59 Variation of the porosity (with the average values and the error bars) as a function of time measured by EIS and MIP of (a) 0.36 OPC samples in condition 1, (b) OPC samples in condition 2, (c) OPC+LiNO ₃ samples in condition 1, (d) OPC+LiNO ₃ samples in condition 2, (e) OPC+Li ₂ CO ₃ samples in condition 1, (f) OPC+Li ₂ CO ₃ samples in condition 2.	246

List of Tables

Table 1. Calculated effective neutron absorption cross section (Barns) and yield strength (MPa) for pure elements [3].....	4
Table 2. Chemical composition of AA1100.....	5
Table 3. Aluminium alloy designation numbers [9].....	14
Table 4. Chemical composition of 1xxx Series Alloys (wt.%) [10].	15
Table 5. Open circuit potential of intermetallic compounds (NaCl, H ₂ O ₂ solution, ASTM G 69) [13].....	18
Table 6. Possible corrosion inhibitors, their aluminium corrosion inhibition mechanism and explanation of their non-practical use in the geological disposal facility.	39
Table 7. Synthesis approaches to LDHs at various synthetic conditions with various precursors [141]. ...	45
Table 8. Classification of pore sizes in hydrated cement pastes [191].	53
Table 9. Chemical composition of the cement.....	58
Table 10. Methods for the corrosion study.....	81
Table 11. Calculated β_c , β_a and B from Tafel polarization tests.	129
Table 12. Methods for the porosity study.....	157
Table 13. Pore solution conductivities (S/m) used in the GEM for each cement paste system.	163

List of Acronyms

AA1100	Aluminium alloy 1100
AC	Alternating current
AFm	Aluminoferriite monosulphate
AFt	Ettringite
ASR	Alkali silica reaction
BR1	Belgian reactor 1
BTA	Benzotriazole
CEM I	Portland cement
CEM II	Portland-composite cement
CEM III	Blast furnace cement
CEM IV	Pozzolanite cement
CEM V	Composite cement
CEM VI	Portland-composite cement containing less clinker
CH	Portlandite
C–S–H	Calcium-silicate-hydrate
C₂S	Dicalcium-silicate
C₃A	Tricalcium-aluminate
C₃S	Tricalcium-silicate
C₄AF	Tetracalcium-aluminoferriite
DC	Direct current
EDX	Energy-dispersive X-ray spectroscopy
EEC	Electrical equivalent circuit
EIS	Electrochemical impedance spectroscopy
EMT	Effective medium Theory
GC	Gas chromatography

GEM	General effective media theory
IADS	International Alloy Designation System
ITZ	Interfacial transition zone
K-K	Kramers-Kronig
LDH	Layered double hydroxide
LILW	Low and intermediate level waste
MKPC	Magnesium potassium phosphate cement
MSH	Magnesium silicate hydrate
MIP	Mercury intrusion porosimetry
OCP	Open circuit potential
OPC	Ordinary Portland cement
SEM	Scanning electron microscope
SMSs	Sugar beetroot-based micro sheets
1xxx series	Aluminium, purity higher than 99%
2xxx series	Copper-addition alloys
2-MBT	2-mercaptobenzothiazole
3xxx series	Manganese-addition alloys

List of Symbols

A_w	Warburg coefficient
B	Stern Geary Constant
C	Capacitance
C_{dl}	Double layer capacitance
χ^2	Chi-square test of independence
CPE	Constant phase element
CPE_{cem1}	Constant phase element of the solid phase in the cement paste
CPE_f	Constant phase element of the corrosion product film
$CPE-n/CPE-T$	Constant phase element parameter
$CPE-Q/CPE-P$	Constant phase element parameter
D	Effective diffusion coefficient of the particle
d	Diameter of the capillary
EW	Equivalent weight
I_{corr}	Corrosion current
I_{appl}	Applied current
K	Cell constant
L	Effective diffusion thickness
L_1	Inductance of external wires
M	Molar mass
P	Pressure
R_{cem1}	Resistance of connected capillary pores
R_{cem2}	Resistance of the disconnected pores
R_{eff}	Effective resistance of the system
R_f	Resistance of the corrosion product film
R_t	Charge transfer resistance

R_u	Overall uncompensated resistance
S	Exposed surface area
T	Mean thickness values of the corrosion product film
t	Critical exponent
V	Volume
W	Warburg element
W_{cem2}	Warburg element of the solid phase in disconnected pore path
W_o	Warburg element with a reflective boundary
$W-P$	Warburg element parameter
$W-R$	Warburg element parameter
$W-T$	Warburg element parameter
β_a	Anodic Tafel slope
β_c	Cathodic Tafel slope
γ	Surface tension of the liquid
$\Delta\Phi$	Applied voltage
θ	Contact angle of the liquid
v_{corr}	Corrosion rate
ρ	Metal density
σ_p	Conductivity of capillary pore phase
σ_s	Conductivity of solid-gel phase
σ_{eff}	Effective conductivity of the system
Φ_c	Percolation threshold of the capillary pores
ω	Angular frequency

1

Context of the thesis

Chapter 1. Context of the thesis

This thesis study revolves around geological disposal of the Belgian Reactor 1 (BR1) fuel. The basic information about this reactor and nuclear fuel is presented first followed by the introduction of the waste disposal routes in Belgium.

1.1. BR1

The reactor BR1, shown in Figure 1.1, was the first nuclear reactor in Belgium and has been operational since 1956. It is an air-cooled reactor that uses graphite (carbon) as moderator. The moderator is used to slow down the energetic fission neutrons. The reactor is surrounded by a heavy barite concrete construction of about 2 m thickness. This construction mainly serves as a biological shield against radiation. It enables workers to perform experiments on and around the reactor without exposure to irradiation doses. For the past 20 years, the reactor worked for 3 days per week at a power of 700 kW for a maximum of 8 hours a day. Owing to the cooling way of forced air convection with the help of a fan, the working temperature of BR1 is controlled to stay well below 200 °C. After more than 60 years, the average fuel element burn-up is calculated to be only 0.07% fissions per initial metal atom [1].

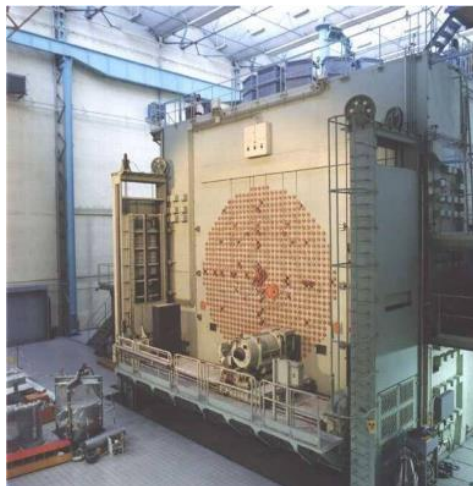


Figure 1.1 Outlook of Belgian Reactor 1.

BR1 possesses 829 channels, which have a square section of $5 \times 5 \text{ cm}^2$, passing through these 14500 graphite blocks. Only 569 of these channels are loaded with fuel and each channel contains 23 fuel elements. A fuel element has a cylindrical geometry with a length of 20.3 cm and a diameter of 2.54 cm. The overall structure of BR1 is provided in Figure 1.2 [1].

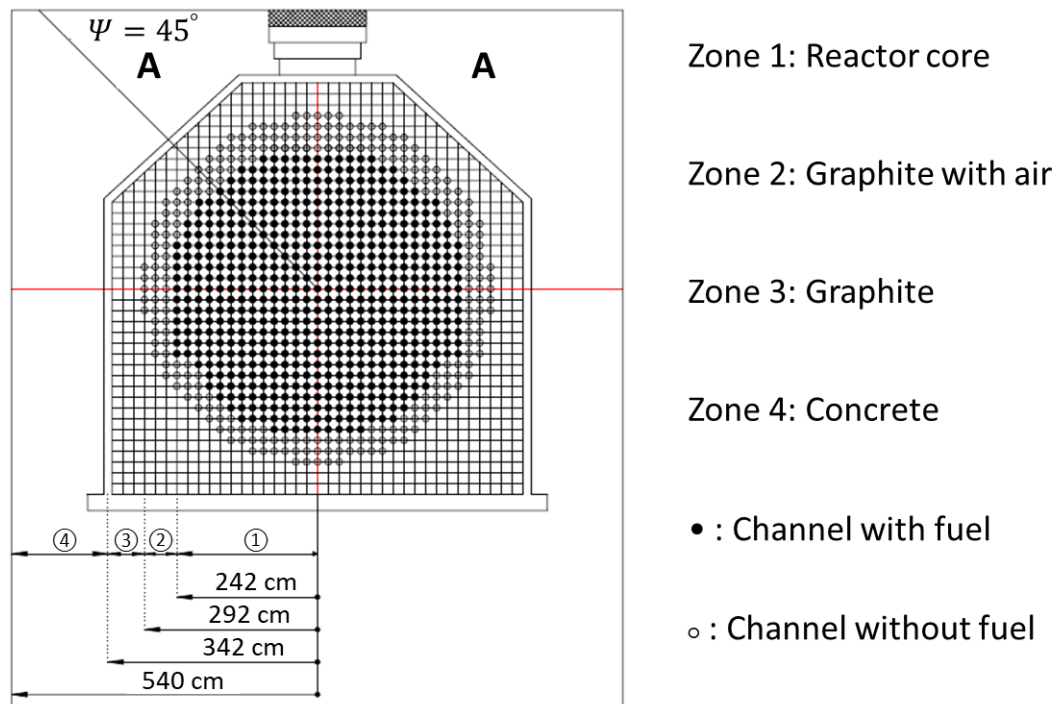


Figure 1.2 Schematic view of the BR1 reactor [1].

At the beginning, BR1 was used primarily for research on reactor and neutron physics and for the production of medical radioisotopes. Now, it still has a variety of applications including the irradiation of components, the calibration of measuring instruments, some neutron activation analysis and the training of nuclear experts.

1.2. BR1 fuel

BR1 uses natural metallic uranium (0.7% $^{235}\text{U}/\text{U}_{\text{tot}}$) as nuclear fuel [2]. Figure 1.3 indicates that the fuel core is composed of natural unalloyed metallic uranium, coated with an $\text{U}(\text{Al},\text{Si})_3$ anti-diffusion layer and an aluminosilicate (AlSi) alloy bonding layer. The $\text{U}(\text{Al},\text{Si})_3$ anti-diffusion layer is applied to limit the interaction between the uranium and the aluminium cladding. The AlSi bonding layer is applied not only to assure good thermal bonding between the uranium rod and the aluminium can but also to provide intimate contact between the aluminium cap and can. Then, the fuel is encapsulated in an aluminium can (i.e. the cladding) [2]. Aluminium alloy, AA 1100, was chosen as cladding material because of its low thermal neutron absorption cross-section (see Table 1) and good corrosion resistance [3].

Aluminium was used as the fuel cladding in early nuclear reactors. The investigation of aluminium cladding of uranium bars for research reactors dates back to 1942. The Metallurgical Laboratory of the

Chapter 1

University of Chicago used uranium slugs sealed in Al cans inside Al tubes for a water-cooled reactor and created the fuel cladding concept. The B Reactor constructed in 1944 at the Hanford site and the BR1 constructed in 1956 in SCK CEN both adopted the aluminium fuel cladding. However, the maximum service temperature at 200 °C, which is limited by oxidation and mechanical strength, led to the gradual phase-out of the use of aluminium cladding [3].

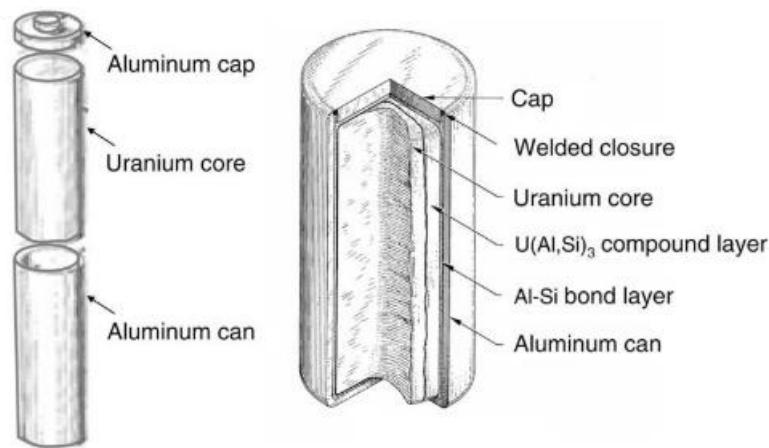


Figure 1.3 Belgian Reactor 1 fuel structure [1].

Table 1. Calculated effective neutron absorption cross section (Barns) and yield strength (MPa) for pure elements [3].

Elements	Neutron absorption cross section (Barns)	Yield strength (MPa)
Be	0.009	200–350
C	0.004	24–28
Mg	0.063	65–100
Si	0.160	165–180
Zr	0.185	135–310
Al	0.231	30–40
Mo	2.480	170–350
Cr	3.050	185–280
Nb	1.150	75–95
Fe	2.550	110–165
Ni	4.430	80–280
V	5.040	125–180
Sn	0.630	7–15

The aluminium can of BR1 fuel was deep-drawn from the aluminium alloy 1100 (AA1100), which has the chemical composition given in Table 2:

Table 2. Chemical composition of AA1100.

Composition	Al	Cu	Fe	Mn	Si	Zn
wt. %	99.0–99.95%	0.05–0.20%	0.95% max	0.05% max	0.95% max	0.1% max

The uranium slugs were machined from rods, degassed and heat treated to provide a randomly oriented grain structure. An Al–Si coating bath was applied to deposit an $U(Al, Si)_3$ anti-diffusion layer on the U slug. The coated slugs were then rinsed in molten Al–Si alloy to avoid contaminations for the next steps. In the canning operation, the U slug was inserted into an Al can submerged in molten Al–Si alloy, followed by a seal of an Al cap. The completed assembly was finally taken out of the bath with the removal of the excess Al–Si. The technical details of the molten metal bath process are provided as follows (see also Figure 1.4 [2]) [4]:

1. The Al–Si coating bath to form the anti-diffusion layer, i.e. $U(Al, Si)_3$.

Bath temperature: 590 °C - 615 °C

Bath composition (3 layers):

- a. Lead layer to preheat the slugs
- b. Intermediate layer of Al–Si alloy (11.2 - 11.5 wt.% Si)
- c. Flux layer to provide protective cover of the bath

2. Al–Si alloy (11.2 - 11.5 wt.% Si) rinse bath to avoid contaminations of the final Al–Si canning bath.

Bath temperature: (595 ± 5 °C)

3. Al–Si (11.2 - 11.5 wt.% Si) canning bath to form an AlSi bonding layer.

Bath temperature: (593 ± 3 °C)

Canning procedure:

- a. The Al can was submerged and filled with Al–Si
- b. The U slug was submerged
- c. The U slug was inserted into the can
- d. The aluminium cap was submerged and inserted into the top of the can and pressed against the uranium slug

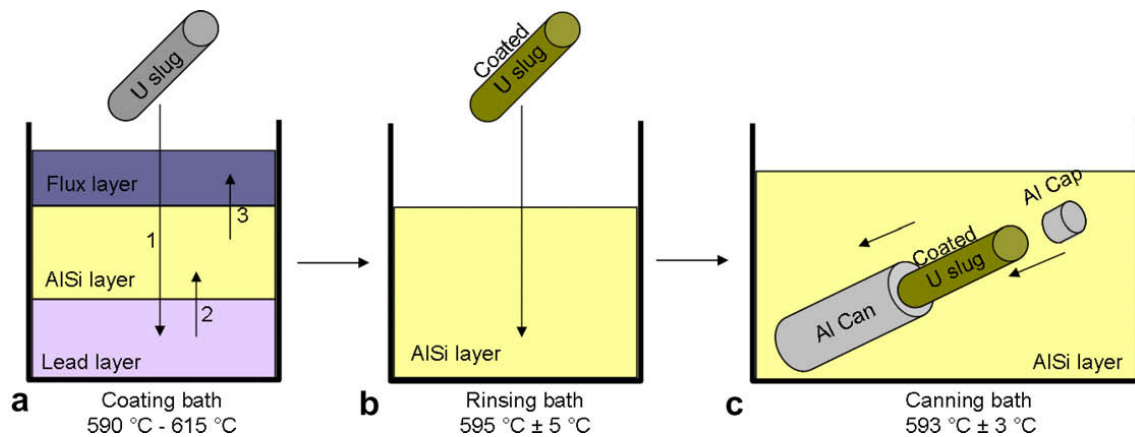


Figure 1.4 Schematic of the flux-alpha canning process. The uranium slugs are first coated (a), then rinsed (b) and finally inserted into an Al can (c) [2].

SEM micrographs of the BR1 fuel are provided in Figure 1.5. Figure 1.5(a) provides the overview of the fuel structure, while Figure 1.5(b) shows the $U(Al,Si)_3$ anti-diffusion layer and the AlSi bonding layer on the uranium surface [4].

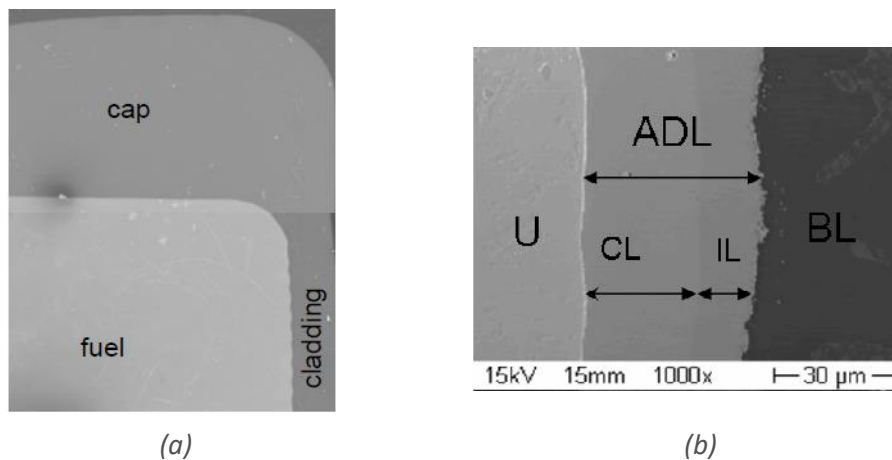


Figure 1.5 SEM micrographs showing (a) the top part of the BR1 fuel rod in cross section, (b) the anti-diffusion layer (ADL) and the bonding layer (BL) [4].

There are different long-term management solutions proposed for these fuels, which will eventually become waste. At present, no disposal route is predetermined for the metallic waste. A series of disposal routes can be discussed:

- The easiest and less expensive method is the direct disposal of the whole fuel capsule in a cement-based material;

Chapter 1

- Because aluminium could react fast in contact with cement pastes, an alternative method is the mechanical removal of the Al cladding, AlSi and $U(Al,Si)_3$ outer layers, followed by mixing the metallic uranium with a cement-based material;
- The disposal of metallic uranium in cementitious materials could also be problematic due to the generation of corrosion products. For example, H_2 and uranium oxides could produce an extra pressure resulting in the stress problem and UH_3 can ignite in contact with water and oxygen. To avoid this problem, pre-oxidation of the metallic uranium including an iteration of calcination steps to oxidise the metallic uranium can be performed before disposal;
- If the disposal of UO_2 is still problematic, reprocessing and/or collection of pure UO_2 (after removal of the impurities, fission products,...) for a possible recycle can be another option.

This doctoral thesis focuses from a scientific viewpoint on the first route to be launched in regards to the disposal of the BR1 fuel because other routes involving the pre-treatments of BR1 fuel are commercially unbeneficial. More information regarding the details of disposal of nuclear waste in Belgium is introduced in the next section.

1.3. Waste and disposal

In Belgium, radioactive waste is classified in three categories: (i) category A is the short-lived (half-life less than 30 years) low and intermediate level waste (LILW), (ii) category B is LILW containing long-lived radionuclides and (iii) category C is the high level waste containing long-lived radionuclides and with heat emission [5].

Radioactive waste classified as Category A mainly originates from industrial activities, medicine and scientific research. In Belgium, a near-surface storage concept is applied for this waste without any risk to the public health and the environment. The drums with radioactive waste are first encapsulated in concrete monoliths, which are then stored in an underground concrete bunker, which is further covered with a sequence of protective layers. The facility used for this near-surface disposal is shown in Figure 1.6(a) [6].

Highly radioactive and/or long-lived nuclear waste (Category B&C wastes) includes fissile materials from nuclear power plants and residual products from the processing of fuel. This waste needs to be safely stored for a long term (up to hundreds of thousands of years). A geological disposal concept currently is the most promising way for this type of waste. Alternatives such as disposal at seabed, in an ice cap or in space have been evaluated, weighed and finally given up because of political and safety reasons. In geological disposal, the isolation of these wastes is implemented by disposal in a stable geologic environment (typically hundreds of meters below the ground). It entails a combination of natural and engineered barriers. For example, clay, as an important natural barrier, has the property of preventing

Chapter 1

water flow and retaining radioactive particles, allowing them to migrate only very slowly. The engineered barriers mainly refer to the specially designed disposal containers (i.e. concrete supercontainers with steel envelope) stored in backfilled concrete galleries. Figure 1.6(b) describes the layout of the current reference repository envisaged for geological disposal of Belgian B&C waste, as developed by ONDRAF/NIRAS [7]. It should be noted that the final political decision has yet to be taken in Belgium.

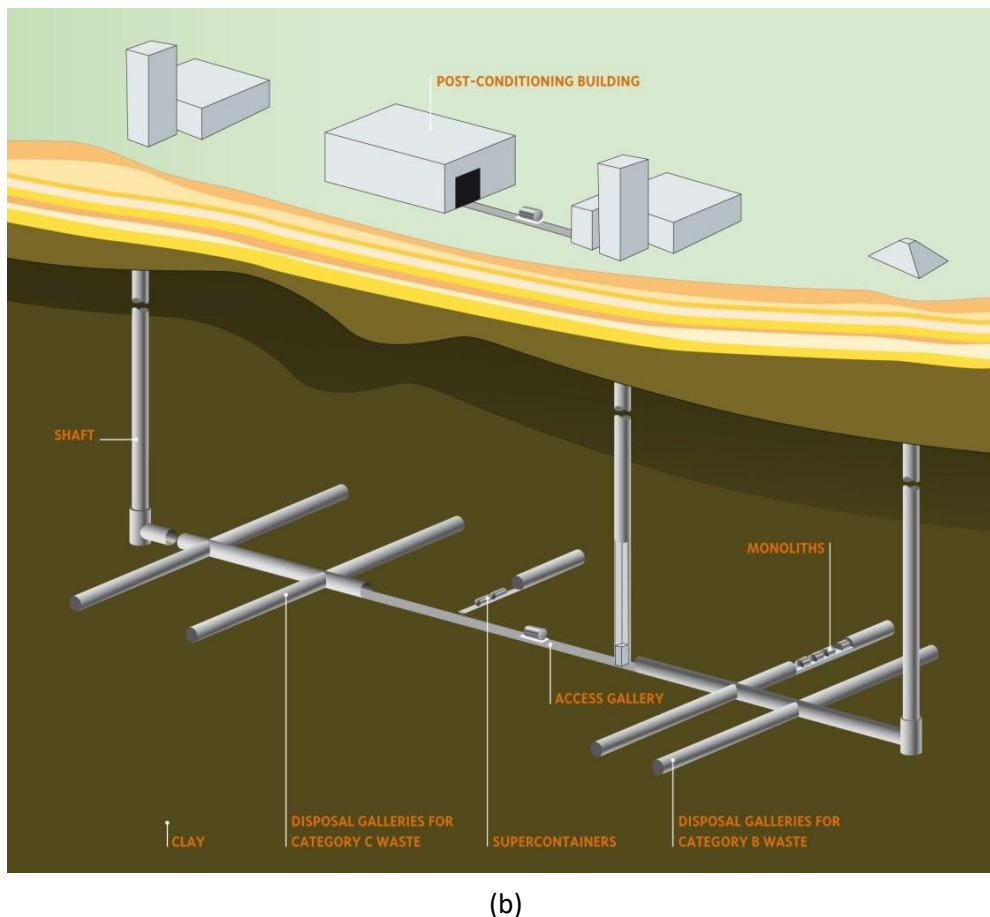
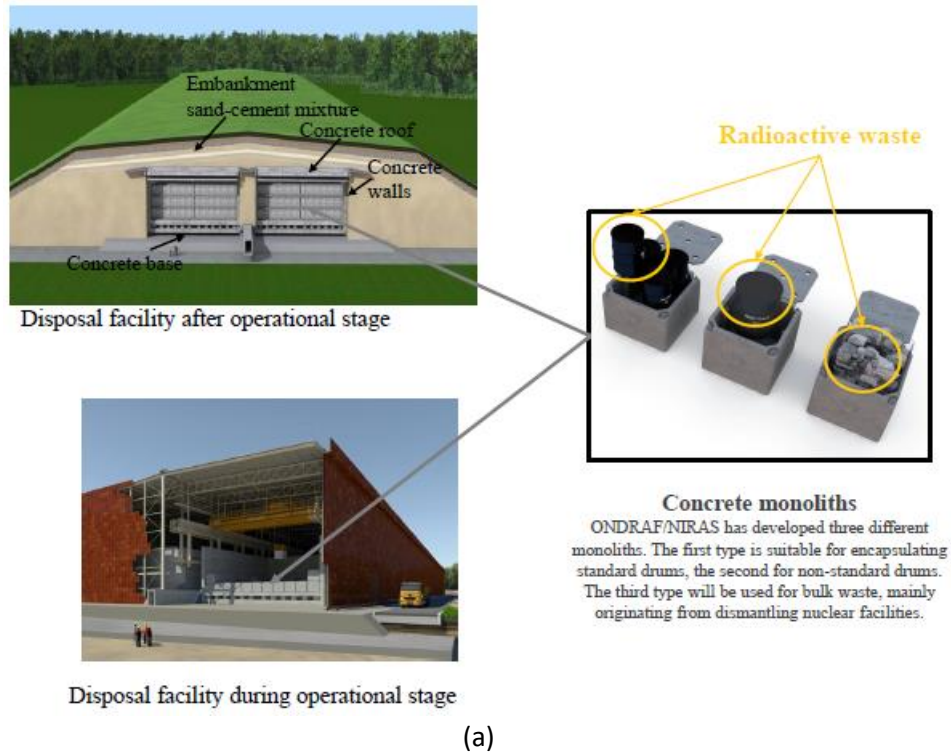


Figure 1.6 Near surface Belgian nuclear waste system for Category A waste (a) [6] and indicative diagram of the geological repository envisaged for B&C waste and of the surface facilities for the production of the supercontainers (b) [7].

Chapter 1

One feasible long-term management route for BR1 fuel, belonging to category B, is the geological disposal with a proposed monolith configuration consisting of several concrete and steel barriers that contain the waste as shown in Figure 1.7(a) [8]. The primary packages of B-waste are immobilised in cementitious supercontainers based on Portland cement and are constructed at the surface before being transported underground for disposal. In this configuration, the outermost Al cladding of BR1 fuel inside drums with cementitious backfill will have a direct contact with cement paste (Figure 1.7(b)). Therefore, it is of utmost importance to study the corrosion rate and mechanism of metallic aluminium in such conditions, as well as the methods to inhibit as much as possible the metallic corrosion. This is the main reason why this doctoral study has been conducted.

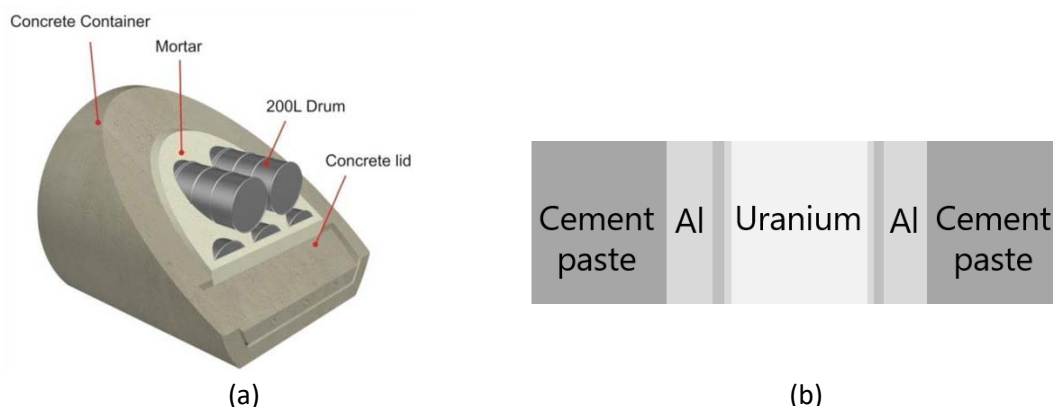


Figure 1.7 Overall (a) [8] and localized (b) configuration of geological disposal.

1.4. Objectives of the thesis

This study firstly aims at finding a solution for the corrosion problem of the aluminium cladding of BR1 fuel in geological disposal. Because of the high corrosion rate of aluminium in the highly alkaline cementitious environment, this thesis revolves around the investigation of lithium salts for inhibiting the corrosion of aluminium in Portland cement (OPC) pastes (see Chapter 2). The corresponding objectives are defined as follows:

1. The corrosion inhibition effect of LiNO_3 and Li_2CO_3 on AA1100 embedded in OPC pastes will be investigated to evaluate whether they can effectively retard the high corrosion rate. This corrosion rate study needs to be accomplished by different techniques in order to examine the validity of the results.
2. The corrosion inhibition mechanisms of LiNO_3 and Li_2CO_3 need to be fully understood. Consequently, the corrosion process of aluminium embedded in Portland cement pastes with/without lithium addition needs to be known.

Chapter 1

3. The advantages and disadvantages of using LiNO_3 and Li_2CO_3 inhibitors need to be compared and the better option for the engineering application of geological disposal needs to be determined.
4. The influences of different experimental curing conditions and cell configurations on the corrosion process need to be understood.

Besides, because of the significant impact of the capillary pores on the mechanical and transport properties of cement paste, the porosity evolution of cement pastes during the hydration and corrosion process needs to be investigated (see Chapter 5). The aims of the porosity study are identified as follows:

5. To innovatively combine General Effective Media (GEM) theory and Electrochemical impedance spectroscopy (EIS), in order to characterize the cement paste porosity. Mercury Intrusion Porosimetry (MIP) measurements will be performed to examine the reliability of this new combined methodology.
6. To determine the relationship between the porosity variation of cement paste and the corrosion evolution of aluminium need to be understood.

1.5. Outline

The thesis consists of 7 chapters.

Chapter 1 introduces the context of this study including some basic information on BR1 and its fuel and on the disposal methods proposed for nuclear waste in Belgium. The objectives of the thesis are also summarized.

Chapter 2 reviews the state of the art on the 1XXX Series aluminium alloys, the influence of the alloying elements, the corrosion of aluminium, cementitious materials for waste encapsulation, corrosion inhibitors for aluminium, the formation of Li-Al layered double hydroxides and cement paste porosity. It provides a literature overview of previous researchers and points out the remaining difficulties, to which this doctoral study needs to bring new insights.

Chapter 3 presents the methods used in this doctoral research. First, the experimental materials and sample preparation procedures are introduced. Then, the electrochemical techniques for the corrosion study, including electrochemical impedance spectroscopy (EIS) and Tafel extrapolation, are explained. Gas chromatography (GC) and Scanning Electron Microscopy (SEM) are two other techniques used in this study to better understand the corrosion rate variations and the corrosion mechanisms. Next, the General Effective Media (GEM) model is explained. We innovatively link this model to the EIS analysis to quantitatively determine the cement paste porosity. Pore solution extraction of cement pastes is performed to provide the conductivity values of the pore solution for the GEM calculation. Finally, mercury

Chapter 1

intrusion porosimetry (MIP) is introduced, which will provide the porosity variation of cement pastes in view of a validation of the reliability of the new GEM method.

Chapter 4 revolves around the corrosion study. First, the impedance spectra obtained by EIS are analysed to get corrosion variation results. Secondly, the equivalent circuit model constructed for EIS fitting is explained. This fitting separates the electrochemical responses from different elements of the cell and provides two important parameters, i.e. the charge transfer resistance (R_t), and the resistance of the formed corrosion product film (R_f). Afterwards, the corrosion rates determined from R_t values are compared with the corrosion rates calculated from the hydrogen generation measured by GC and from the SEM micrographs, while the R_f values are compared with the data reported in literature. The morphology of the cement paste/corrosion product film/Al interface is further studied by SEM, combined with Energy-dispersive X-ray spectroscopy (EDX) characterisation of the element distribution at the interface. According to the corrosion results and the mechanisms proposed in literature, the corrosion mechanisms of aluminium embedded in Portland cement pastes with/without lithium inhibitors are hypothesized. Conclusions involving the main findings of the corrosion study in this thesis are finally presented.

Chapter 5 first presents the impedance spectrum analysis and the equivalent circuit model constructed for EIS fitting. After obtaining the resistance of ionic conduction through the connected capillary pores (R_{cem1}) from EIS fitting, the pore solution conductivity values of cement pastes are measured to determine the cement paste porosity. The pH values of the pore solutions are also measured incidentally. The porosity results are compared with the ones obtained by MIP and with data from literature. A conclusion is given at the end of the chapter.

Chapter 6 formulates general conclusions summarizing the doctoral research and the main findings.

Chapter 7 provides some suggestions for possible improvements and research directions left for future works.

2

State of the art

Chapter 2. State of the art

As addressed above, the aluminium cladding of BR1 fuel could be in contact with cement paste in the currently proposed geological disposal design. The corrosion performance of the aluminium alloy in cement paste is one of the key issues involved in the long-term safety of waste disposal. This chapter introduces the influential factors of aluminium corrosion and the relevant physicochemical properties of the cementitious materials.

2.1. 1xxx series aluminium alloys

Aluminium alloys include different alloys with various combinations of mechanical strength, ductility, corrosion-resistance, etc. They can be categorized into the casting alloys and the wrought alloys [9]. Cast alloys are produced by casting techniques and usually contain larger percentages of alloying elements when compared to wrought aluminium. The wrought alloys indicate the aluminium alloys which are originally available in the form of worked products, e.g. sheet, plate and wire. According to the different main alloying elements, the wrought alloys can be designated by a four-digit number as shown in Table 3 [9]. Besides, the wrought alloys can be further classified into other categories: non-heat-treatable and heat-treatable [10].

Table 3. Aluminium alloy designation numbers [9].

	Designation no.
Aluminum, 99.00 percent and greater	1xxx
Aluminum alloys grouped by major alloying elements	
Copper	2xxx
Manganese	3xxx
Silicon	4xxx
Magnesium	5xxx
Magnesium and silicon	6xxx
Zinc	7xxx
Other element	8xxx
Unused series	9xxx

AA1100 used for the aluminium cladding of BR1 fuel belongs to the family of "commercially pure" wrought aluminium alloys (1000 or 1xxx series according to the International Alloy Designation System (IADS) [11]). The 1xxx series alloys contain a minimum of 99 wt.% aluminium without other major alloying elements. Hence, these alloys are also referred to as commercially pure aluminium. Even if no alloying elements is purposely added into the aluminium matrix, the pure aluminium can be still called as an alloy

Chapter 2

because of the small amount of elements present as impurities, whose contents need to be quantitatively limited. Such Al alloy does not contain hardening precipitates but is harder than most alloys of 1xxx series owing to cold working leading to dislocation hardening. The yield strength can reach typically 100 MPa which remains still much smaller than the 600 MPa attained in some high strength Al alloys. The ductility is good. Table 4 [10] provides the chemical composition of some commercial 1xxx series wrought alloys registered with the Aluminum Association.

Table 4. Chemical composition of 1xxx Series Alloys (wt.%) [10].

AA Designation	Si Fe	Cu	Mn	Zn	Ti	Al (min)
1050	0.25 0.40	0.05	0.05	0.05	0.03	99.50
1060	0.25 0.35	0.05	0.03	0.05	0.03	99.60
1100	0.95 Si+Fe	0.05-0.20	0.05	0.10	-	99.00
1145	0.55 Si+Fe	0.05	0.05	0.05	0.03	99.45
1175	0.15 Si+Fe	0.10	0.02	0.04	0.02	99.75
1200	1.00 Si+Fe	0.05	0.05	0.10	0.05	99.00
1230	0.70 Si+Fe	0.10	0.05	0.10	0.03	99.30
1235	0.65 Si+Fe	0.05	0.05	0.10	0.06	99.35
1345	0.03 0.40	0.10	0.05	0.05	0.03	99.45
1350	0.10 0.40	0.05	0.01	0.05	-	99.50

2.2. Impact of alloying elements in aluminium alloys

The chemical composition of the aluminium alloys is one of the most important parameters governing the corrosion resistance. For example, the corrosion resistance performance of the 2xxx series (copper-addition alloys) is very different from that of the 3xxx series (manganese-addition alloys). The corrosion resistance is strongly influenced by the microstructure of the alloys including the grain size, the composition, the distribution of intermetallic phases and of hardening precipitates.

In terms of elements present in the form of solid solution, they mainly affect the open circuit potential of the alloy. For example, the addition of copper and zinc respectively raises and decreases the open circuit potential, while the addition of magnesium has little influence [12]. As for elements present in the form of

Chapter 2

intermetallic particles, their influence on the corrosion resistance mainly relies on the electrochemical corrosion between the aluminium matrix and the intermetallic particles.

In 1xxx series alloys, as shown in Table 4, iron and silicon are the major impurities, which cannot be refined out of aluminium for economic reasons. Because iron (0.04 wt.% [10] or 0.05 wt.% [13]) and silicon (0.01 wt.% at 200 °C [13]) are practically insoluble (<0.05 wt.%) in the solid aluminium matrix at room temperature, the excess of iron and silicon, which are above the solid solution limit, precipitates in the form of intermetallic phases [13]. These intermetallic phases include Al_3Fe , $\alpha\text{-AlFeSi}$ and $\beta\text{-AlFeSi}$. The binary Al_3Fe phase crystallizes in the form of long prisms or needles and appears mostly in alloys containing less than approximately 0.5 % silicon [10]. The ternary $\alpha\text{-AlFeSi}$ and $\beta\text{-AlFeSi}$ phases refer to $\text{Al}_8\text{Fe}_2\text{Si}$ and Al_5FeSi , respectively. Aziz and Godard [14] reported the negative effect of iron-containing intermetallic particles on the pitting corrosion resistance of aluminium. The Fe-rich intermetallic particles work as favoured sites for the cathodic reaction, typically i.e. oxygen reduction in an aerated environment [15], resulting in the local alkalisation around intermetallic particles [16,17]. Meanwhile, the galvanic coupling between the intermetallic particles and the aluminium matrix leads to dissolution of the Al matrix surrounding the particles, while the particles themselves remain inert [18-20]. As a result, the intermetallic particles become detached from the surface (see Figure 2.1 [20]). Hence, the particles are preferential sites for nucleation of pits. Liao et al. [21] (see Figure 2.2) indicated that the pits caused by intermetallic particles can be categorized to two types: (i) independent fine pits of a diameter of less than 20 μm , which are normally regarded as generalized surface corrosion; (ii) pits of a diameter larger than 20 μm , due to the aggregation of particles on and near the surface, which are classified as pitting corrosion.

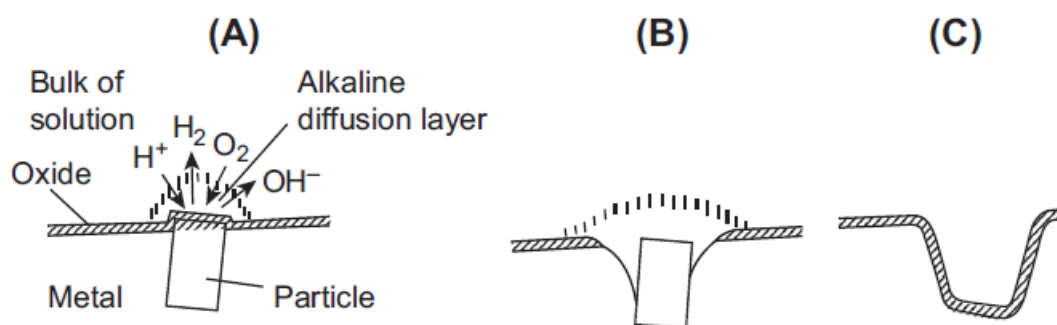


Figure 2.1 Schematic of the mechanism leading to loss of particles from the surface. (A) Cathodic reactions at particle sites. (B) Pitting around a particle. (C) Repassivation of a particle-free pit [20].

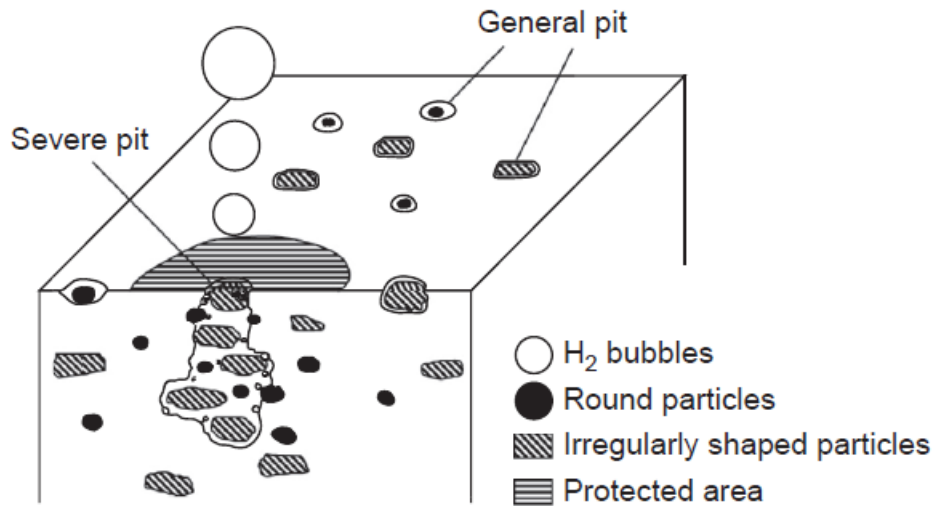


Figure 2.2 Schematic of particle-induced pitting corrosion [21].

Copper has the highest content level after iron and silicon (normally 0.05-0.1 wt.%). For AA1100, higher amounts of copper (up to 0.20 wt.%) are added to increase strength through solid solution effect. However, this addition leads to a decrease in corrosion resistance [10,22], which can be attributed to the Cu-rich intermetallic particles providing cathodic sites [23,24], similar to Fe-rich intermetallic particles. Besides, the addition of copper is reported to affect the aluminium oxide film. Brock and Prior [25] mentioned that the addition of copper leads to the reduction of the crystal nucleation density of γ - Al_2O_3 alumina and the increase of the amorphous alumina between γ - Al_2O_3 crystals. Compared with the Cu-rich intermetallic particles, the minor changes of the aluminium oxide film do not play a primary role in the poor corrosion resistance of copper-addition alloys. Copper in the form of intermetallic particles mainly includes Al_2Cu (θ -phase), Al_2CuMg (S-phase) and $\text{Al}_7\text{Cu}_2\text{Fe}$ [13]. $\text{Al}_7\text{Cu}_2\text{Fe}$ is three times more active in accelerating the oxygen reduction compared with Al_2Cu [26].

Magnesium and zinc are the two most soluble elements in aluminium in the solid state [13]. In the solid solution state, magnesium has little influence on the open circuit potential of aluminium but slows down the cathodic reaction [27]. When excess amount of magnesium is added into the alloy or when the alloy takes a long term exposure to elevated temperature, magnesium will precipitate in the form of Al_8Mg_2 or Al_3Mg_2 along the grain boundaries [28,29]. These particles are reported to be anodic compared to the Al matrix and therefore prone to localized corrosion [30-33]. The addition of zinc accelerates the anodic dissolution of aluminium [34,35]. Besides, the addition of zinc to 5xxx alloy was reported to reduce the intergranular corrosion by the formation of Al-Mg-Zn (τ phase) instead of Al_3Mg_2 (β phase) at grain boundaries [36,37].

Chapter 2

As discussed above, these intermetallic phases (either binary A_nX_m or ternary $A_nX_mY_p$) significantly influence the corrosion resistance [11]. Sometimes, alloying elements can even combine together without aluminium. For example, magnesium and silicon form the intermetallic Mg_2Si , magnesium and zinc form $MgZn_2$. The intermetallic particles are either anodic or cathodic compared with the aluminium matrix [38], i.e.: (i) cathodic intermetallic particles with an open circuit potential higher than that of the matrix, hence the aluminium matrix is dissolved; (ii) anodic intermetallic particles with open circuit potential lower than that of the matrix, hence the particles are dealloyed. The values of the open circuit potential (OCP) of some intermetallic particles are provided in Table 5 [13].

Table 5. Open circuit potential of intermetallic compounds (NaCl, H_2O_2 solution, ASTM G 69) [13].

Position	Intermetallic compounds	Open circuit potential (mV vs. SCE)
Cathodic intermetallic particles	Cu	-110
	Si	-170
	Al_3Ni	-430
	Al_3Fe	-470
	Al_2Cu	-640
	Al_7Cu_2Fe	-650
AA1050	Al	-750
Anodic intermetallic particles	Al_6Mn	-760
	Al_3CuLi_3	-760
	Al_5CuLi_3	-785
	Al_2CuLi	-800
	Al_2CuMg	-910
	$MgZn_2$	-960
	Al_3Mg_2	-1150
	Mg_2Si	-1200
	AlLi	-1350

For AA1100, intermetallic particles can be directly observed near the grain boundaries as shown in Figure 2.3 [39]. The elongated intermetallic particles possess a length lower than $5\text{ }\mu\text{m}$ with an aspect ratio of about 5:1. According to Figure 2.1(a), the area fraction of particles is low (3.96 % reported in literature [39]). Besides, the SEM/EDS image shown in Figure 2.4 [39], illustrates that the particles observed on the aluminium surface are Fe-rich intermetallic particles.

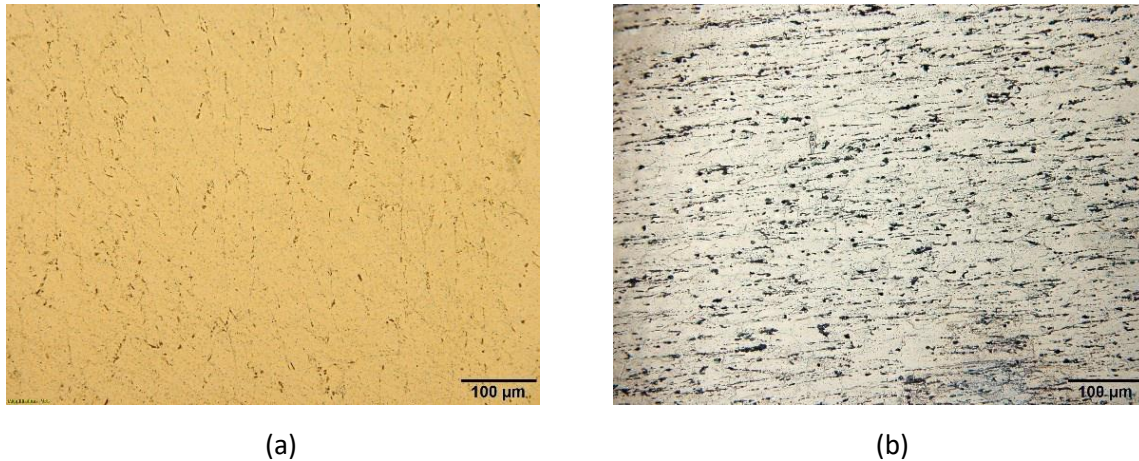


Figure 2.3 Optical microscopy micrographs of AA1100 (a) being polished and (b) after etching using Keller's reagent for 15s [39].

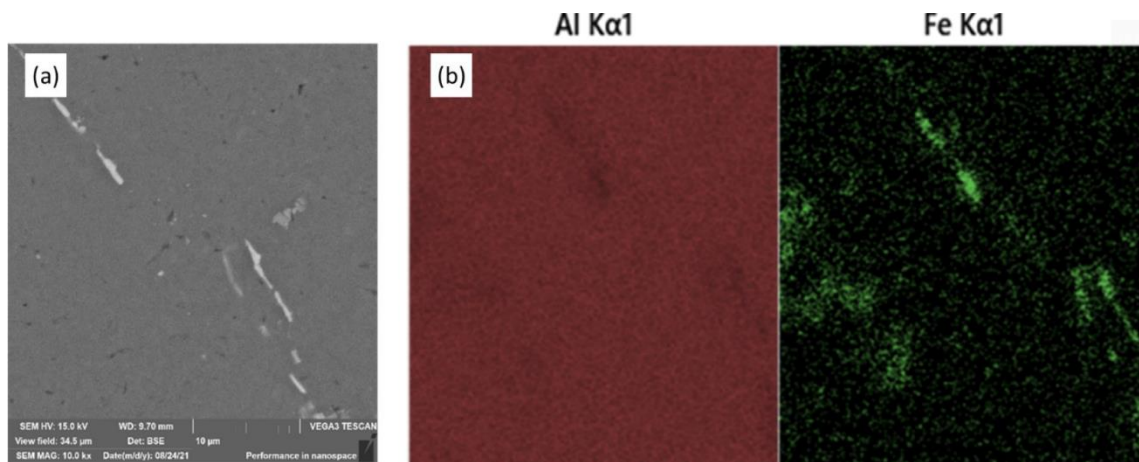


Figure 2.4 (a) SEM micrographs of polished AA1100 and (b) EDS maps of Al (red) and Fe (green) distribution on the framed area [39].

2.3. Corrosion of aluminium and aluminium alloys

Because the BR1 fuel consists of multiple layers as mentioned in Section 1.2, the corrosion of the BR1 fuel in the geological disposal can be categorized into two steps: (i) the corrosion of the aluminium cladding and (ii) the corrosion of the inner fuel structure, which contains the vast majority of the radionuclides. After the breach of the aluminium cladding, the corrosion of Al-Si bond layer, $U(Al,Si)_3$ compound layer and uranium happens in sequence while the galvanic corrosion between different layers could also occur simultaneously, with the release of radionuclides into the environment. Hence, the aluminium cladding as the first barrier is of major importance for preventing any potential leakage of radiation emitting elements into the environment.

Chapter 2

Aluminium, including its alloys, is a very reactive material that is widely used in many building and construction domains, such as for windows and frames, roof structures, facade claddings, photovoltaic panels. One of the main reasons for this broad range of applications is the formation of a very adherent and protective oxide film when it is in contact with air. An example of this oxide film is shown in Figure 2.5 [40]. Such a film of 1 nm thickness is already highly effective in protecting the aluminium from corrosion, while this oxide film generally grows to a thickness much greater than 1 nm in normal atmosphere. Usually, a dynamic equilibrium between the opposing forces building up and breaking down this film can be established at a thickness ranging from 20 to 200 nm [41]. This corrosion process is normally categorized as uniform corrosion, in which aluminium oxidizes as follows:

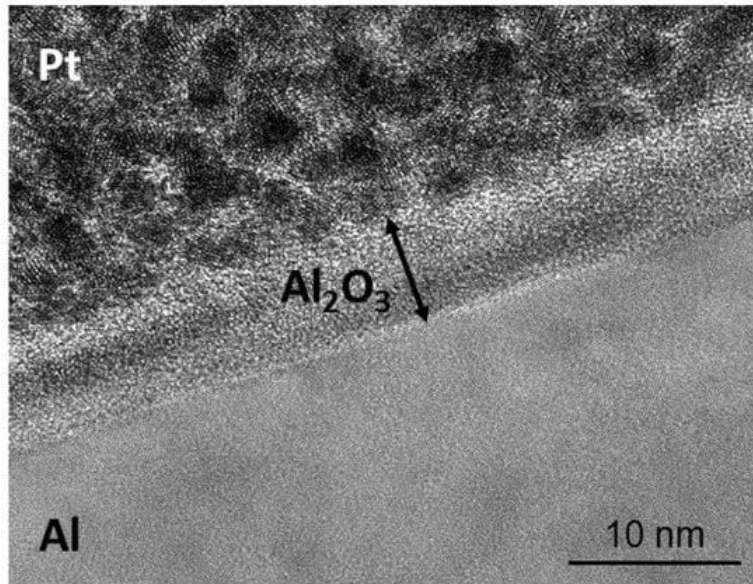
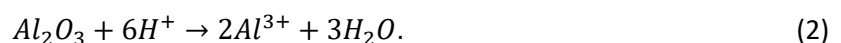
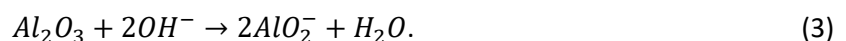


Figure 2.5 TEM micrograph of an oxide layer on a subsection of a lamella of AA6016 [40].

However, the oxide layer formed on the surface of Al is amphoteric and, as such, it is not resistant to corrosion in both acidic and alkaline conditions. The passive aluminium oxide layer cannot be steadily maintained on the surface of Al when pH is above 8.6 or below 3.8 as shown in the Pourbaix diagram in Figure 2.6 [42]. In a solution with a pH value lower than 3.8, the oxide film is dissolved with the formation of aluminium ions and water:



If the pH is higher than 8.6, the oxide film is also dissolved but with production of aluminate ions and water:



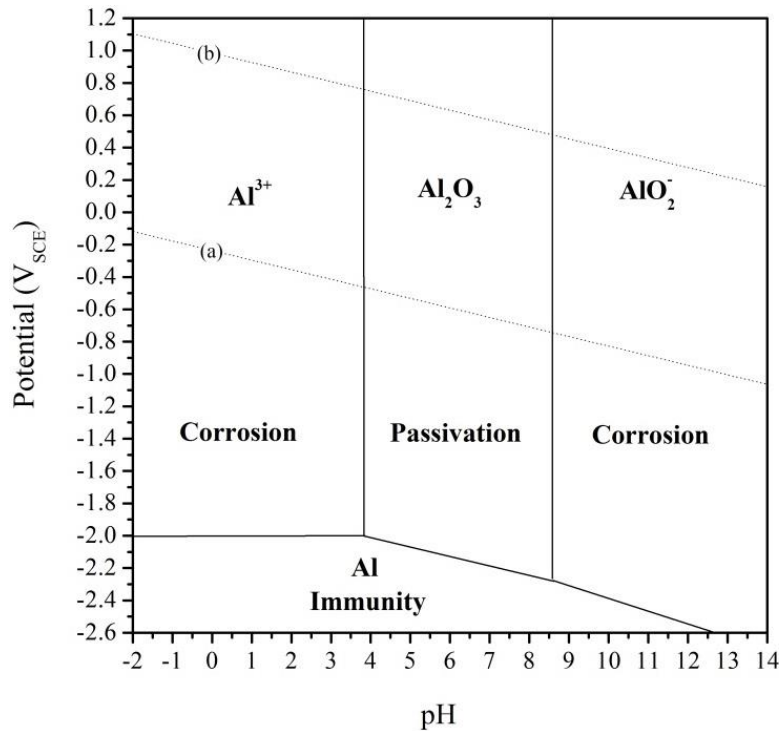


Figure 2.6 Pourbaix diagram for aluminium–water system [42].

Therefore, the oxide film will be rapidly dissolved in either acid or alkaline solution. Afterwards, the corrosion process on the surface will proceed into the aluminium matrix with the formation of Al^{3+} at low pH values and the formation of AlO_2^- at high pH values. Meanwhile, H^+ or H_2O is reduced simultaneously in the acid or alkaline solution, respectively. Note that the Pourbaix diagram does not reveal the passivation phenomenon of aluminium, i.e. the formation of the passivating film in strongly acid solutions of high redox potential such as concentrated nitric acid [43]. Besides pH, the corrosion of aluminium also depends on many other factors. For example, the anaerobic or aerobic condition directly decides the types of corrosion products. In the anaerobic condition, because of lack of oxygen, normally it is water that works as the electron acceptor and is reduced to hydrogen:



In the aerobic condition, oxygen is reduced:



Moreover, the reaction time is an important factor that affects the corrosion rate. The average corrosion rate decreases as a function of time, which is attributed to the accumulation of aluminate ions on the sample surface. This process is controlled or partially controlled by the mass transfer rate between the sample surface and the bulk solution, hence it does not work for a flowing system. An example of corrosion rates influenced by the exposure time is provided in Figure 2.7 [44], in which the corrosion rates in different alkaline conditions all decrease as a function of time ($1 \text{ g}\cdot\text{m}^{-2}\cdot\text{y}^{-1} \approx 0.37 \text{ }\mu\text{m}\cdot\text{y}^{-1}$). Another example is the effects of environmental factors on atmospheric corrosion. Compared with the corrosion in solution,

Chapter 2

atmospheric corrosion, which typically occurs beneath very thin electrolyte layers, is more complex. Dan et al. [45] proved that the relative humidity and temperature influence the atmospheric corrosion of AA1100 and AA6061 by affecting the chemical composition and the evaporation rates of the surface electrolyte, respectively (see Figure 2.8).

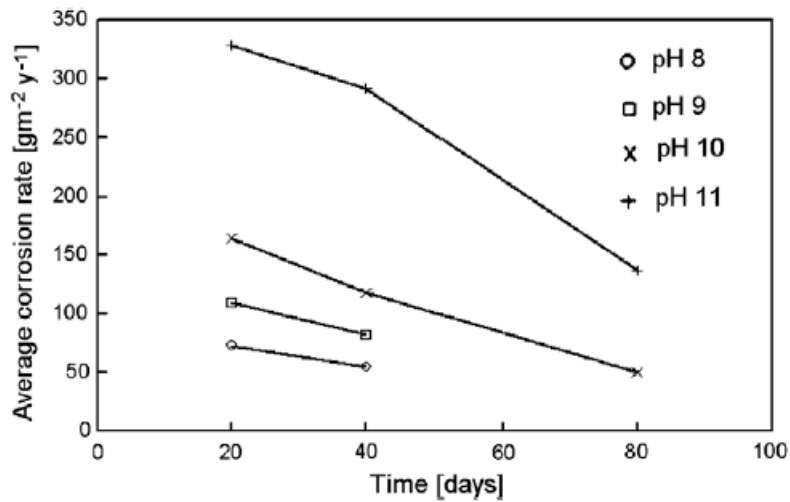


Figure 2.7 Corrosion rates of commercially pure aluminium with exposure time at 30 °C determined by weight loss method [44].

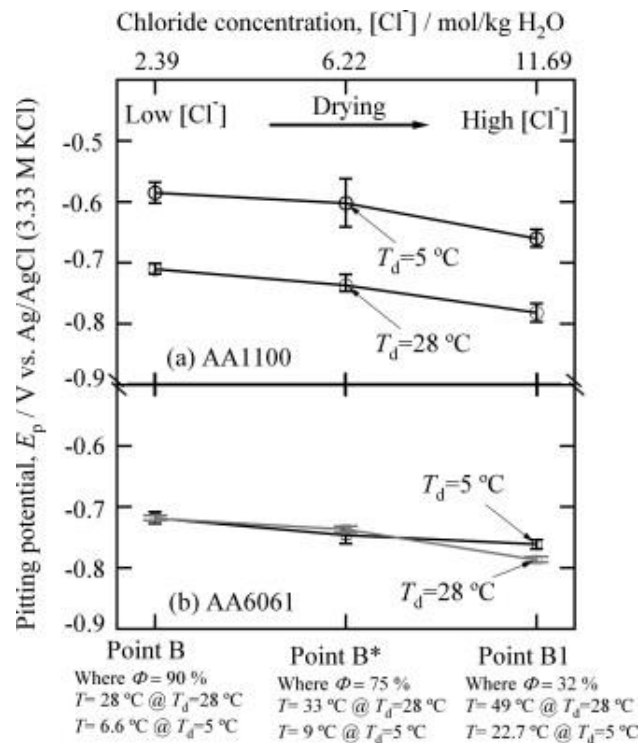


Figure 2.8 Pitting potentials of AA1100 (a) and AA6061 (b) as a function of the temperatures in the corresponding $\text{NaCl}+\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ solutions at the relative humidities (Φ) [45].

Chapter 2

Besides uniform corrosion, pitting corrosion is another common form of corrosion for aluminium alloys. Pitting corrosion usually occurs when aggressive environments locally break down the protective film on the aluminium surface. For example, solutions containing chlorides are harmful and create local potential gradients between the metal surface and occluded regions (i.e. within a pit) where the chloride is concentrated. Chlorides work by forming AlCl_3 , which contributes to the breakdown of the film [43]. An example of pitting corrosion is shown in Figure 2.9 [46]. According to its definition, i.e. a local loss of passivity, pitting only appears in the near neutral pH range because the oxide film is unstable in both acidic and alkaline conditions. As introduced in Section 2.2, intermetallic particles in aluminium alloys are likely to lead to pitting corrosion.

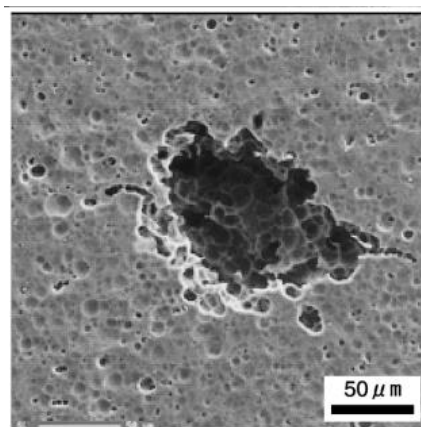


Figure 2.9 Example of pitting corrosion on the surface of AA1100 which was corroded in a $0.1 \text{ kmol}\cdot\text{m}^{-3}$ NaCl solution [46].

Moreover, other types of corrosion such as crevice corrosion, galvanic corrosion and stress corrosion cracking might occur when aluminium is situated in different conditions.

Crevice corrosion requires the presence of a crevice such as the gap between a bolt and a structure. The uncovered surface acts as the cathode, while the crevice interior is the anode because of its lower oxygen concentration compared with the uncovered surface. The lower oxygen concentration in the crevice is caused by the geometry constrain. As the anodic part, the crevice interior is subjected to the corrosive attack. The crevice corrosion mechanism is depicted in Figure 2.10 [47].

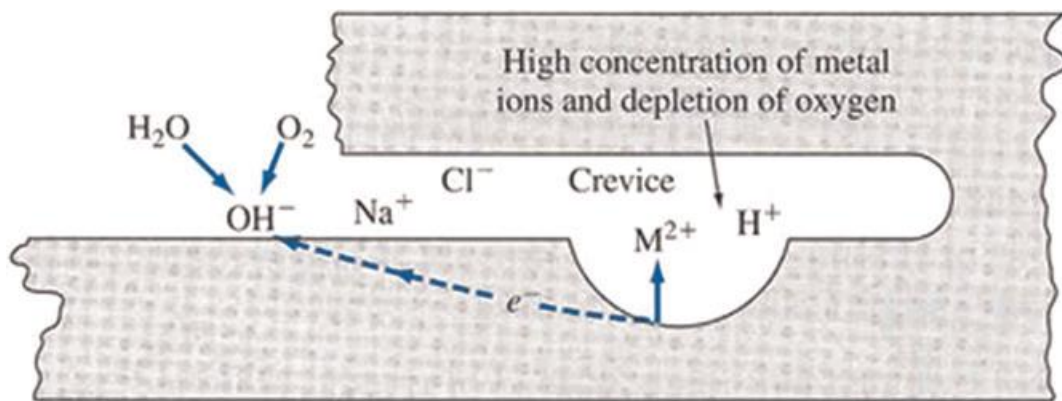


Figure 2.10 Schematic of crevice corrosion mechanism [47].

Galvanic corrosion occurs when aluminium connects to a more noble metal and both metals are in contact with the same electrolyte. As an example, in contact with copper, aluminium is the anode while copper is the cathode. The corrosion of aluminium is then accelerated, while the corrosion of the more noble metal decreases (cathodic protection). An example of the galvanic coupling between aluminium and copper is shown in Figure 2.11 [48].

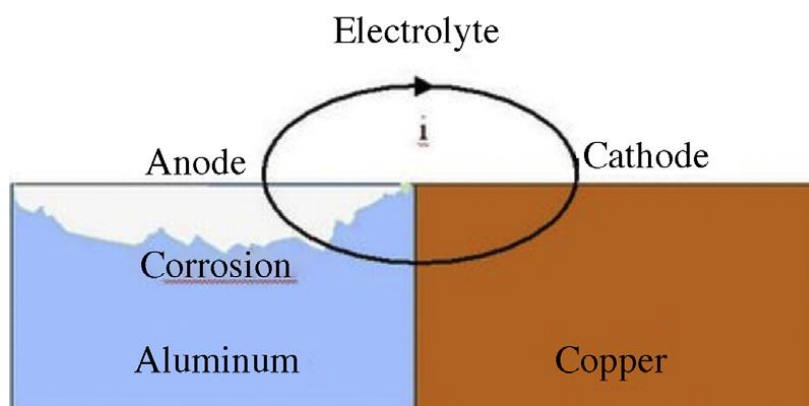


Figure 2.11 Galvanic corrosion between aluminium and copper [48].

Besides, aluminium alloys are susceptible to stress corrosion cracking, which results from the joint action of tensile stress and a corrosive environment. The alloying elements, i.e. copper, magnesium, silicon, and zinc in aluminium alloys can lead to cracking along grain boundaries when simultaneously exposed to specific environments and sufficient magnitude of stresses. An example of the cracks formed in AA6xxx created by a stress corrosion cracking test is shown in Figure 2.12 [49].

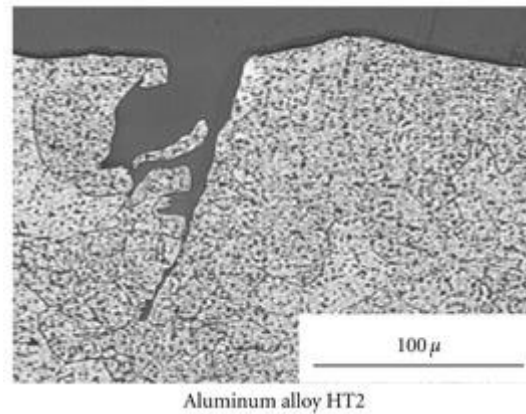


Figure 2.12 Corrosion inducing cracking initiation in AA6xxx during a stress corrosion cracking test [49].

In the case of the corrosion of aluminium in high pH conditions, such as the ones met in contact of cementitious matrices, the dense aluminium oxide layer does not protect the surface from corrosion and thus the continuous corrosion process increases the breach risk of the aluminium cladding, potentially leading to the leakage of inner radioactive materials. Therefore, the encapsulation environment of BR1 fuels directly determines the corrosion rate of the aluminium cladding.

2.4. Cementitious materials for waste encapsulation

The application of cementitious materials i.e. cement paste, grouts and concretes to immobilise radioactive wastes is complicated. On the one hand, there are a large number of cementing agents, which provide all sorts of properties; on the other hand, the working environments and the waste species are also multifarious. This means that each case should be considered individually.

Ordinary Portland cement (OPC) is the most widely used cement type and a candidate for the waste encapsulation. OPC is processed by heating limestone (CaCO_3) with small quantities of other materials (such as clay) to 1450°C in a kiln. The resulting hard substance, called 'clinker', is then ground with a small amount of gypsum into a powder. Non-hydrated Ordinary Portland cement mainly consists of the oxides of calcium, silica, alumina and iron, these elements exist in the form of compounds such as tricalcium-silicate ($3\text{CaO}\cdot\text{SiO}_2$), dicalcium-silicate ($2\text{CaO}\cdot\text{SiO}_2$), tricalcium-aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$), and tetracalcium-aluminoferriate ($4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$) which are abbreviated as C_3S , C_2S , C_3A and C_4AF in cement chemistry terminology. Furthermore, a limited amount of gypsum is added to control the set time. [50-52] The constituents' content and function are:

Chapter 2

- **Alite** (50 - 70%), i.e. tricalcium silicate (C_3S^1 or Ca_3SiO_5). Alite reacts with water to form Calcium Silicate Hydrate (C-S-H) gel and portlandite ($Ca(OH)_2$, or CH in short notation). Alite is considered to be the most significant constituent phase with respect to strength development at the early stage of cement hydration up to 28 days.
- **Belite** (20 - 30%), i.e. dicalcium silicate (C_2S or beta Ca_2SiO_4). Belite reacts with water to produce also C-S-H and portlandite (CH), but at a slower rate. The strength development by belite hydration is only attained after a longer time period.
- **Aluminate** (5 - 12%), which is present as ferrite (see next bullet) and tricalcium aluminate (C_3A^2 or $Ca_3Al_2O_6$). If there is no gypsum, C_3A shows a very fast reaction with water, to form calcium aluminate hydrate (C-A-H). As this would lead to 'flash setting' in concrete, already during mixing, some gypsum needs to be added, controlling the reaction of C_3A to first form calcium aluminotrisulphate (AFt³). When the gypsum gets exhausted, AFt is gradually converted to calcium aluminomonosulphate (AFm), while now also C-A-H is formed.
- **Ferrite** (5 - 12%), i.e. calciumaluminoferrite (celite, C_4AF , $Ca_2(AlFe)_2O_5$), with a high substitution of Fe for Al. C_3A The reaction of C_4AF is very complex, and not yet fully understood. As it is not specifically relevant in the context of this thesis, further reference is made to cement literature [53].
- **Gypsum** (~2%), i.e. calcium sulphate (e.g. $CaSO_4 \bullet 2H_2O$). Gypsum is added to slow down the setting time and to permit a period of workability. See the introduction of C_3A above.

While interacting with water, the cement hydration reactions start and the interlocking hydration products give strength to the cement paste. The main hydration products of cement paste include calcium silicate hydrate (C-S-H), calcium hydroxide (CH) and other phases containing aluminium, iron, and sulphate. [50-52] Their chemical constituents are:

- **C-S-H**: Calcium-silicate-hydrate is a mixture of poorly crystallised products. The Ca to Si molar ratio (C/S) varies between 1.5 and 2.0, depending on factors such as initial water/cement ratio, the age of paste, the curing conditions and impurities; C-S-H has a layered geometry with calcium silicate sheet structure separated by an interlayer space. The space gives a high surface area and is filled with interlayer water. It also often incorporates partial substitution of Si by Al, which is then called C-A-S-H.
- **CH**: $Ca(OH)_2$, or portlandite.

¹ C = CaO and S = SiO₂.

² A = Al₂O₃.

³ F = Fe₂O₃.

Chapter 2

- **AFt**: Ettringite is a group of calcium sulfoaluminate hydrates, with $[\text{Ca}_3(\text{Al,Fe})(\text{OH})_6 \cdot 12\text{H}_2\text{O}]\text{X}_3 \cdot \text{H}_2\text{O}$ as general formula, where X denotes a double-charged anion (typically sulphate) or two units of a single-charged anion. In Portland cement paste, ettringite is typically seen in needle-like structure.
- **AFm**: aluminoferrite monosulphate— with $[\text{Ca}_2(\text{Al,Fe})(\text{OH})_6]\text{X} \cdot \text{H}_2\text{O}$ as general formula.
- **Hydrogarnet**: $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$.

To satisfy specific engineering requirements, supplementary cementitious materials, such as fly ash, blast furnace slag, or silica fume, can be added to OPC. According to cement constituents, the European Committee for Standardization defines six kinds of common cements containing OPC as a main constituent (i.e. CEM I = Portland cement; CEM II = Portland-composite cement; CEM III = Blast furnace cement; CEM IV = Pozzolanic cement; CEM V = Composite cement and CEM VI = Portland-composite cement containing less clinker).

OPC-based materials have a considerable advantage when encapsulating steel materials (geological disposal includes a series of steel structures such as the supercontainer envelope), which is the highly alkaline pore solution (pH usually above 12.5 [54-57] as shown in Figure 2.13). Because iron is passivated in a high pH environment as shown in Figure 2.14 [58], the corrosion rate of carbon steel is normally lower than one micro-meter per year [59-60], while the corrosion rate of stainless steel under an anaerobic environment could even be as low as one nanometre per year [61]. Hence, the combination of OPC-based materials and steel is a good candidate for the encapsulation of nuclear wastes. Figure 2.15 provides an example of the supercontainer design proposed for radioactive wastes classified as Category C in the Belgian radioactive waste management, in which a stainless steel envelope and a carbon steel overpack are in direct contact with the OPC-based concrete buffer directly.

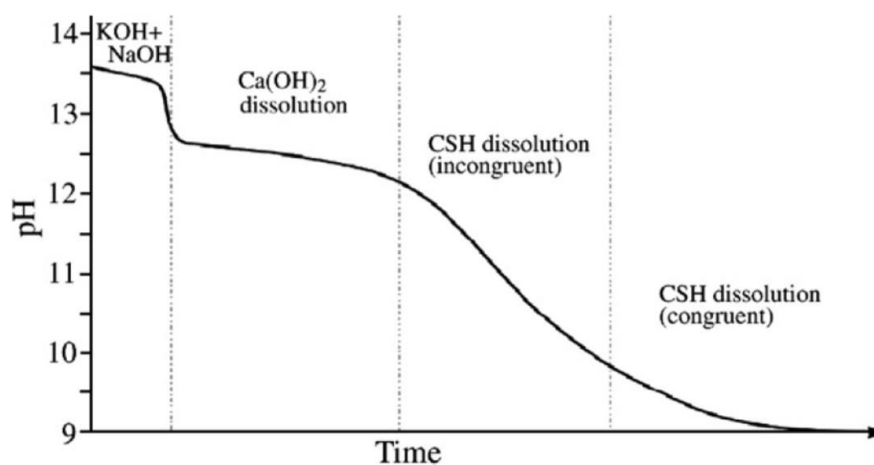


Figure 2.13 Schematic diagram illustrating the evolution of pH at 25 °C in hydrated cement pore fluid as a result of cement degradation [57].

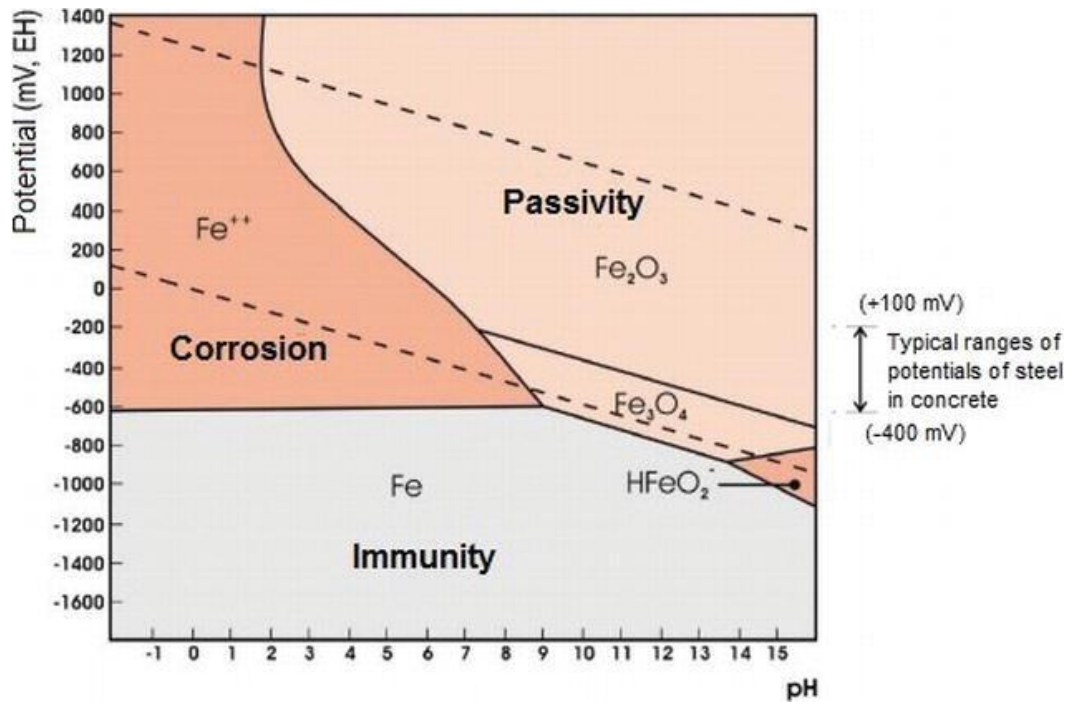


Figure 2.14 Pourbaix diagram for iron-water system [58].

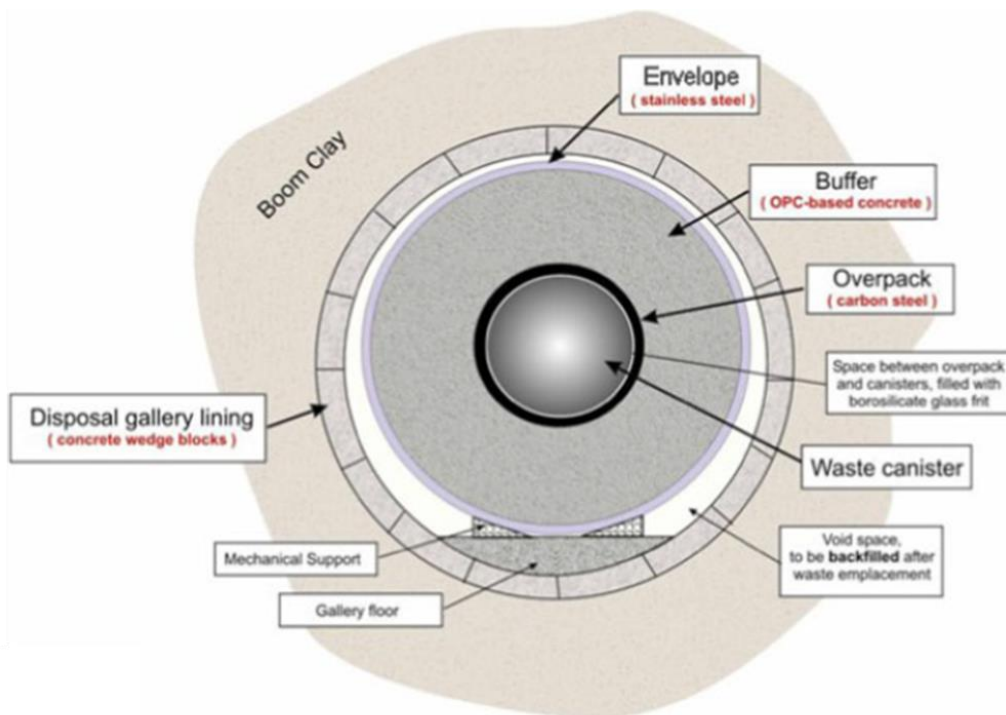


Figure 2.15 Schematic diagram of a cross-section of supercontainer for vitrified high level nuclear waste emplaced in disposal [59].

Chapter 2

By contrast, the highly alkaline pore solution in the OPC-based materials can lead to a high corrosion rate of aluminium alloy 1100 (AA1100), because the protective aluminium oxide film cannot be steadily maintained in the highly alkaline environment. Moreover, the production of H_2 gas and the fast accumulation of corrosion products, which results in volume changes compared to the metallic aluminium, raises the residual stress level and consequently induces cracks in the cementitious matrix. Such a cracking phenomenon was reported by L.M. Spasova et al. [62] and Q. Zhou et al. [63] for the corrosion of Al embedded BFS/OPC system (see Figure 2.16 [62]).

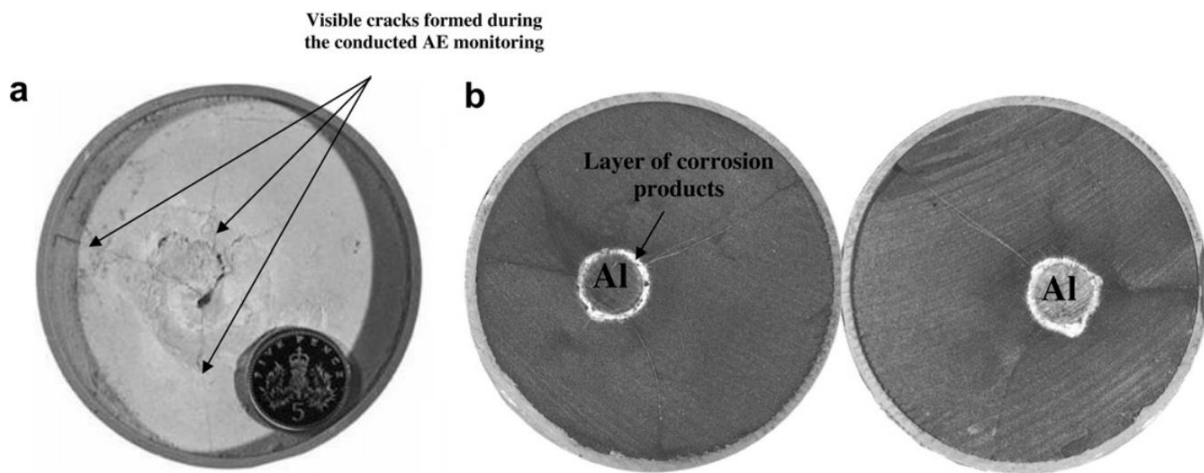


Figure 2.16 Visible cracks formed at the (a) surface and (b) cross-section of the BFS/OPC sample with encapsulated Al [62].

Therefore, to avoid this problem when embedding metallic aluminium in cement paste matrices, the application of other cementitious materials for the aluminium corrosion could be helpful for enhancing the safety of the geological disposal. A lot of researches have been carried out on other types of cement pastes with a lower pH (it should be within a suitable pH range also good for the corrosion protection of steel) for the immobilization of aluminium and its alloys. For example, magnesium potassium phosphate cement (MKPC) [64,65] and magnesium silicate hydrate (MSH) cement [66,67] were reported to possess a good compatibility with aluminium. Perona et al. [64] studied the immobilization of pure aluminium in MKPC mortars. Their pH measurements of the simulated pore solutions show that the MKPC mortar has a much lower pH than that of the OPC mortar and its pH value is close to neutral (see Figure 2.17(a)), which benefits to the stability of the oxide film on aluminium. Consequently, both the corrosion current and the H_2 generation (the gaseous corrosion product) of pure aluminium (AA1050) and of aluminium alloys e.g. (AA5754) in MKPC mortar are apparently lower than that of specimens in OPC mortar as shown in Figure 2.17(b) and (c), limiting the build-up of stress and the formation of cracks. Tingting et al. [66] also indicated that MSH specimens have a lower pH value and less H_2 generation caused by aluminium

Chapter 2

corrosion compared with OPC specimens (see Figure 2.18). If also considering the corrosion protection of the steel structures in geological disposal, MSH appears more appropriate than MKPC because steel is passivated in the pH range of MSH.

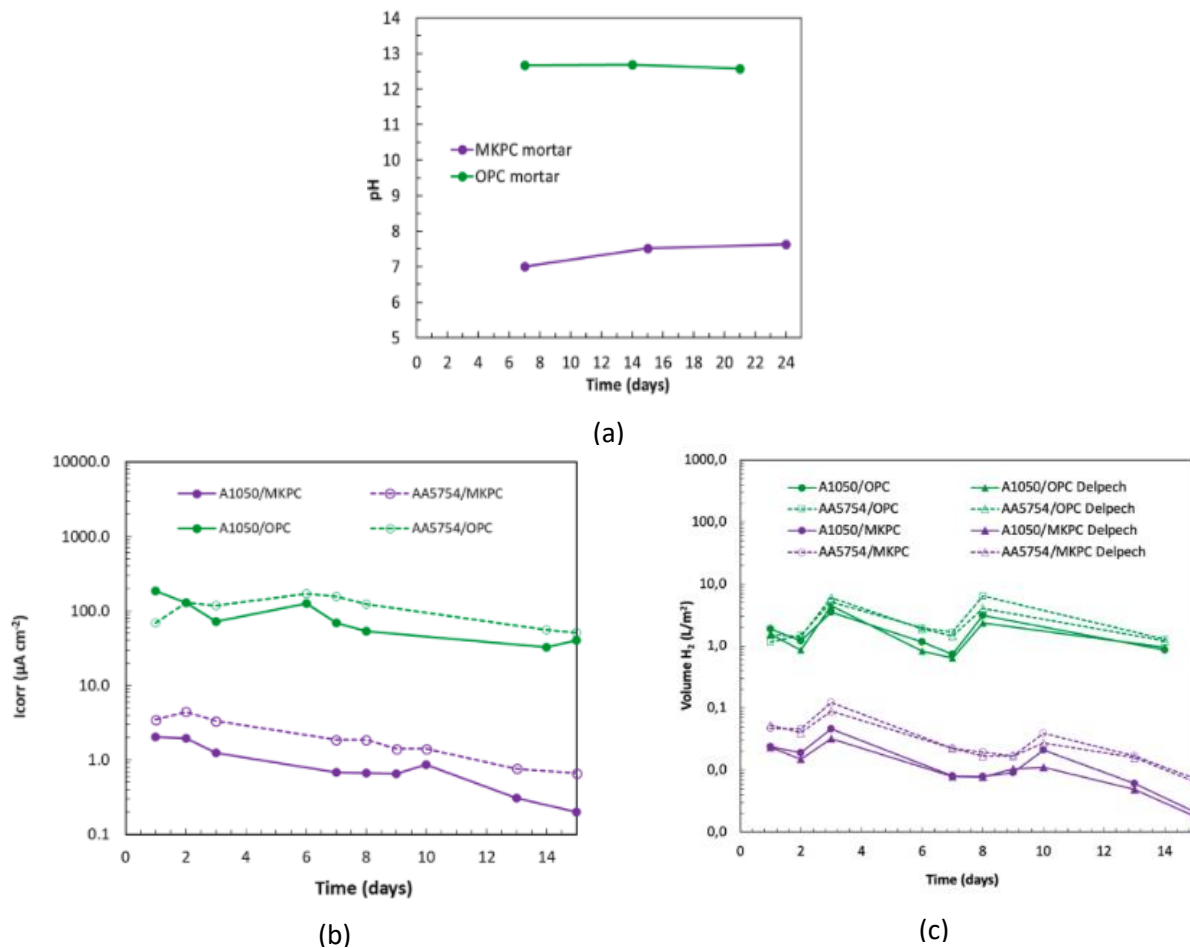


Figure 2.17 pH evolution of simulated pore solutions of OPC and MKPC mortars (a), comparison of the corrosion current density (i_{corr}) (b) and the volume of H_2 (c) evolved versus time for pure AA1050 and AA5754 in OPC and MKPC mortars [64].

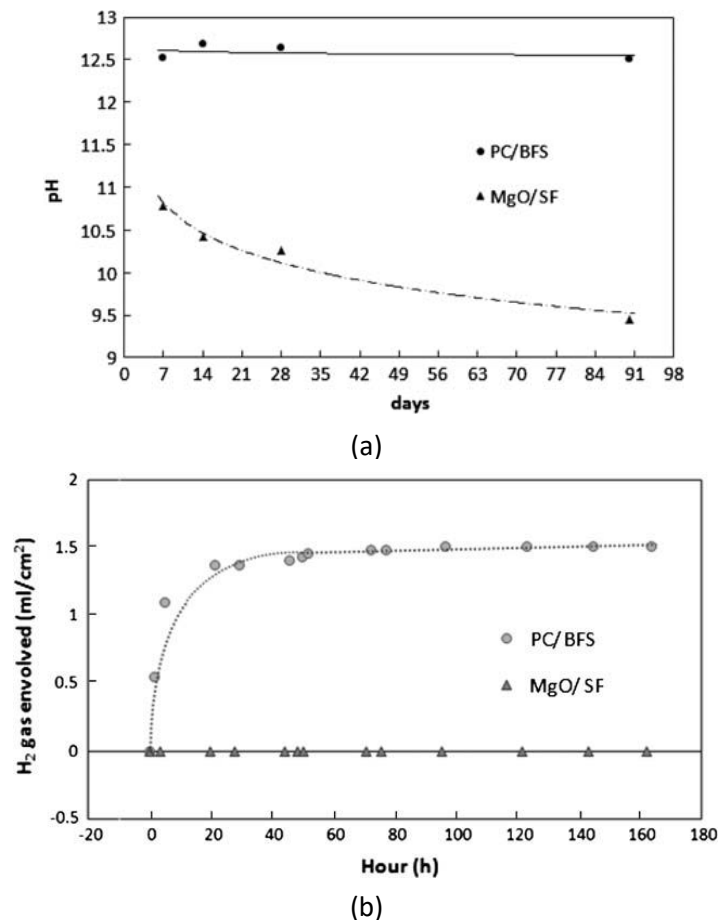


Figure 2.18 pH of PC (blended with blast furnace slag (BFS)) and MSH samples (a) and the volume of H₂ (b) evolved versus time for pure aluminium in OPC and MSH samples [66].

2.5. Corrosion inhibitors for aluminium alloys

Besides the use of low pH cements, another possible route is the application of inhibitors in OPC-based materials for the encapsulation of aluminium, which is economically attractive. For closed systems, as in the case of geological disposal of nuclear waste, it is convenient to make use of corrosion inhibitors owing to a relatively stable concentration over a long timescale with a low possibility of dilution. The corrosion inhibitor is defined as “a chemical substance that, when added in small concentration to an environment, effectively decreases the corrosion rate” [68]. In general, corrosion inhibitors can be categorized into cathodic inhibitors, anodic inhibitors and the mixed inhibitors according to their electrochemical influences.

Cathodic inhibitors either slow the cathodic reactions (i.e. the reduction reactions which occur at the cathode) directly or precipitate on cathodic areas to increase the surface impedance. The inhibition can be achieved by three different mechanisms: (i) cathodic poisons hindering the hydrogen atoms from

Chapter 2

forming hydrogen gas (note that cathodic poisons can also increase the susceptibility of a metal to hydrogen induced cracking), (ii) oxygen scavengers reacting with the dissolved oxygen to decrease the reduction reaction, (iii) cathodic precipitates e.g. zinc, calcium and magnesium precipitating on the surface of the metal to form a protective layer decreasing the effective area for cathodic reactions. Meanwhile, their effect on the anodic reactions is generally negligible. Cathodic inhibition will give a decrease in the electrochemical potential of the cathodic reaction. Consequently, the anodic and cathodic branches in the Tafel plot will intersect at lower corrosion potential and lower corrosion current as shown in Figure 2.19 [68].

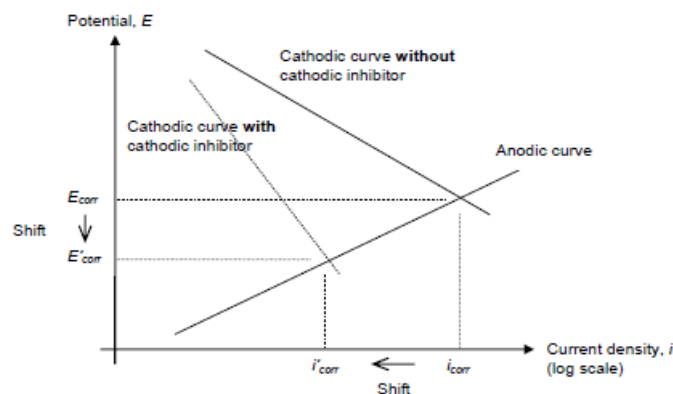


Figure 2.19. Schematic of the Tafel plot showing the effect of a cathodic inhibitor on corrosion [68].

Anodic inhibitors form a protective oxide film on the surface of the metal, which retards the anodic reactions (i.e. the oxidation reactions), making the metallic surface passivated. Thus, they are also known as passivators. Meanwhile, they have little effect on the cathodic reactions. In the Tafel plot with anodic inhibition (see Figure 2.20 [68]), the anodic branch is shifted upward resulting in higher corrosion potential and lower corrosion current. For aluminum alloys, anodic inhibitors typically increase the pitting potential, or suppress the onset of pitting in exposure testing.

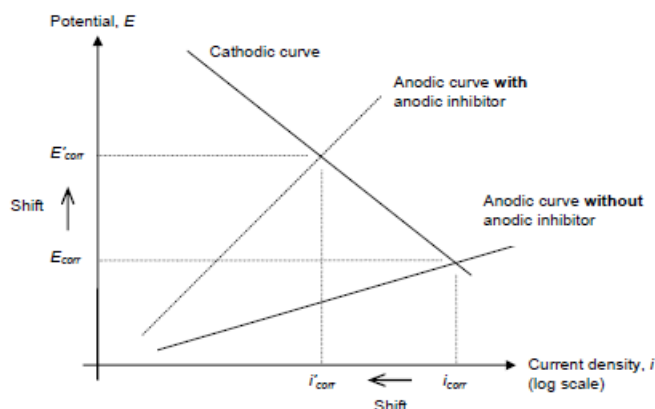


Figure 2.20 Schematic of the Tafel plot showing the effect of an anodic inhibitor on corrosion [68].

Mixed inhibitors inhibit both anodic and cathodic corrosion reactions. They typically precipitate on the surface forming a protective film and thus blocking both anodic and cathodic sites indirectly. Mixed inhibitors decrease the corrosion rate without a significant influence on the corrosion potential (Figure 2.21). The corrosion potential probably shifts towards either the anodic or the cathodic side, depending on which half-cell reaction is more affected, but the change is usually negligible.

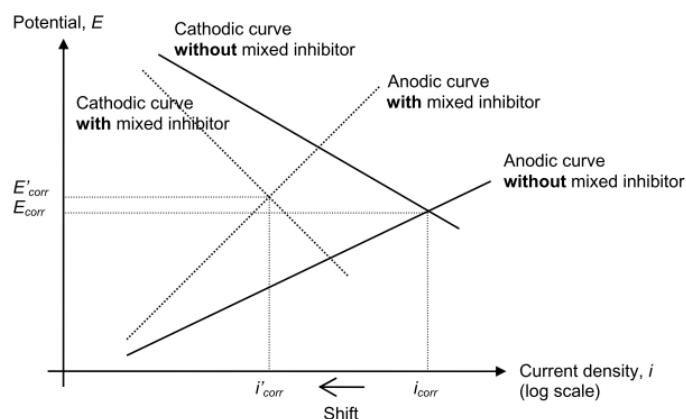


Figure 2.21 Schematic of the Tafel plot showing the effect of a mixed inhibitor on corrosion [68].

Besides, corrosion inhibitors can be categorized in other ways. For example, they can be divided into organic inhibitors and inorganic inhibitors according to the type of chemical composition. One inhibitor can simultaneously belong to two categories. For instance, an organic inhibitor can be also categorized as the mixed inhibitor because of its electrochemical effect on both the anodic and cathodic reactions.

Many investigations focused on studying organic inhibitors in order to develop “green” solutions. Heterocyclic compounds such as 2-mercaptobenzothiazole (2-MBT) and benzotriazole (BTA) were

Chapter 2

reported to possess an excellent corrosion inhibition property for aluminium alloys, which can be mainly attributed to their physical adsorption on the Al surface to form a protective layer [69,70]. Figure 2.22 illustrates the adsorption mode of 2-MBT on the aluminium surface. The planarity and the heteroatoms such as the nitrogen atom are the playmakers in the adsorption process [69]. Besides, for aluminium alloys containing intermetallic particles, 2-MBT and BTA inhibit the oxygen reduction at intermetallic particles (cathodic sites) by forming a complex layer or a polymeric film. The coverage of these sites is constructed by the physisorption or chemisorption of inhibitor molecules on the surface. For example, Bokati et al. [70] reported that BTA molecules form complex films on the surface of iron-containing intermetallic particles in AA1050 decreasing the number of available sites for oxygen reduction. 2-MBT is also reported to form precipitates on the copper-rich intermetallic inclusions of the AA2024 surface via stable covalent Cu–S bonds [71]. However, in a geological repository environment (radioactivity, high temperature, high pH...) of nuclear wastes, organic inhibitors for the corrosion of aluminium can potentially deteriorates and can consequently lead to the failure of the corrosion inhibition.

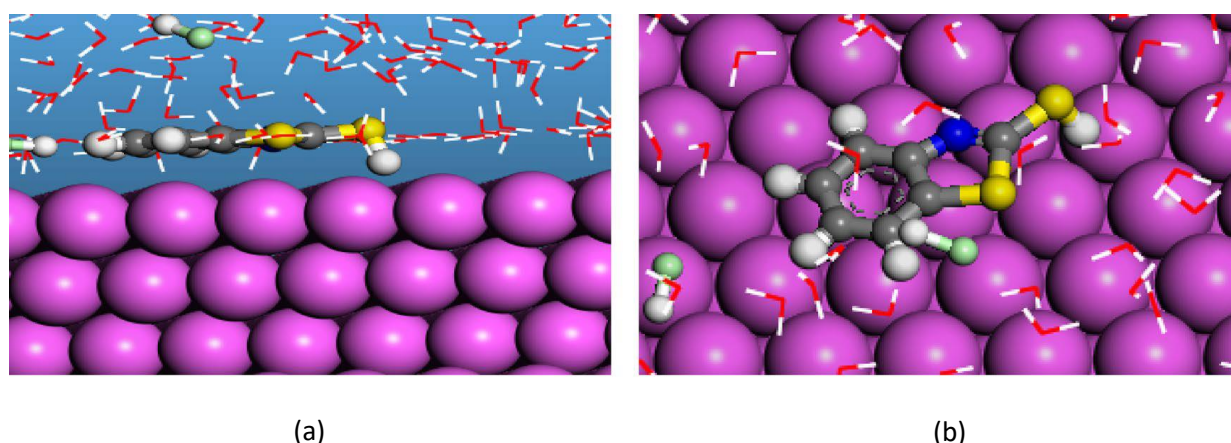


Figure 2.22 Side (a) and top (b) view of the most stable configurations for adsorption of 2-MBT on the Al(111) surface in an acidic medium [69].

The use of inorganic salts is therefore practically favoured. A large number of studies researched effective inorganic corrosion inhibitors of aluminium alloys, e.g. chromates [72-84], silicates [85-88], molybdates [89-91], phosphates [92-97] and metal cation salts (mainly rare earth elements) [98-105]. However, not all of them are appropriate for the corrosion inhibition of aluminium in cement pastes.

Chromate inhibitors such as strontium chromate [76], sodium chromate [77] and zinc chromate [78] were reported to possess an excellent corrosion inhibition ability. In terms of the corrosion inhibition of aluminium alloys, chromate ions are reduced to form a Cr(III) film (see Figure 2.23 [79,80]), which not only inhibits cathodic reactions by covering the Cu-rich intermetallic particles in the alloys but also adsorbs on aluminium oxides inhibiting anodic activities [81,82]. Llevbare et al. [83,84] indicated that chromium species significantly decrease the rate of oxygen reduction and moderately hinder anodic dissolution

Chapter 2

kinetics of AA2024. However, the application of Cr(VI) species for corrosion protection needs to be limited or banned because of high toxicity [74,106,107].

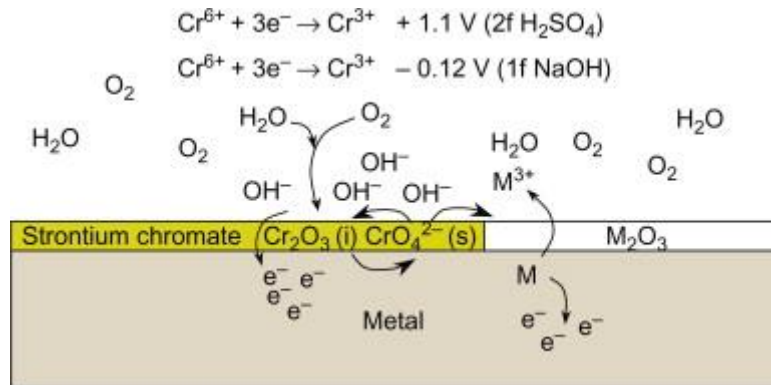


Figure 2.23 Corrosion protection mechanism of chromate controlled by the electrochemical potential and solubility of chromium oxide as a function of valence state and pH [79,80].

Sodium silicate is reported to provide effective anodic inhibition for AA2024 in high alkaline conditions at a concentration above 0.01 M, which is attributed to the formation of the protective film on the aluminium matrix by adsorption of aluminosilicate anions [108]:



For a near-neutral pH condition, silicate ions partially inhibit the dissolution of the intermetallic particles by the precipitation of silica- and silicate-based derivatives. In an acidic solution, a porous mixed silica/aluminosilicate film is formed showing little corrosion protection [85]. Nevertheless, silicates used in OPC pastes are likely to become part of the calcium silicate hydrate (C–S–H) phase of cement pastes instead of impacting the corrosion process as silicate anions.

Li et al. [90] indicated that sodium molybdate acts as a good anodic inhibitor for aluminium in H₃PO₄ solution. Wang et al. [91] studied the inhibition effect of sodium molybdate on corrosion of AA6061 in simulated concrete pore solutions and also reported the anodic inhibition ability of sodium molybdate. They attributed the inhibition mechanism to the adsorption of Mo species on the surface of AA6061 forming a protective Al–Ca–Mo(V)–O(H) oxide layer. However, in the high concentration of MoO₄²⁻, the intermetallic particles of AA6061 leads to the formation of Al–Mg–Si–O(H), which reduces the inhibition efficiency (see Figure 2.24 [91]). Although molybdates involve a good corrosion inhibition ability, Shi et al. [109] reported reduced mechanical properties and accelerated diffusion of chloride ions for mortars containing molybdate compared with those without molybdate, which may be attributed to the delayed cement hydration and the possible consumption and decomposition of hydration products caused by molybdate.

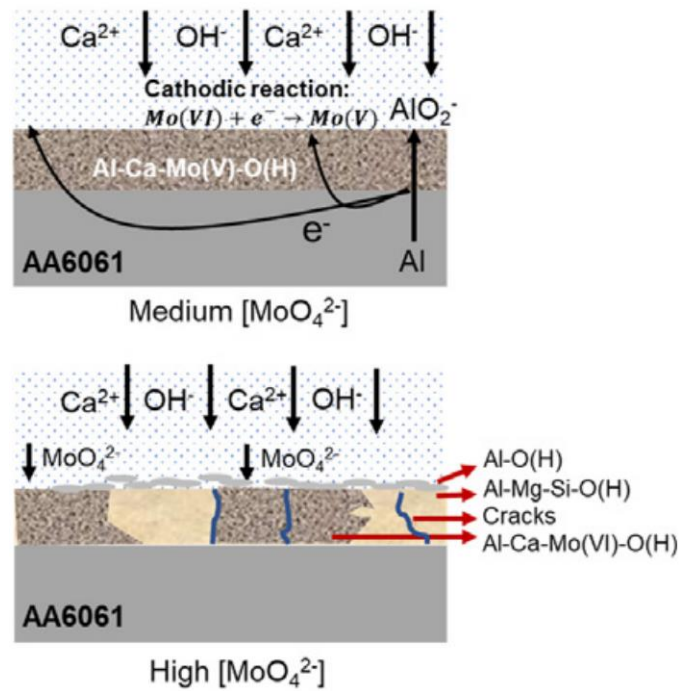


Figure 2.24 Schematic illustration of the inhibition mechanisms of MoO_4^{2-} in simulated concrete pore solutions with moderate MoO_4^{2-} concentration (10 mM) and high MoO_4^{2-} concentration (30 mM) [91].

Literature reported that phosphates are effective in inhibiting the pitting corrosion of aluminium [94,95]. Korniy et al. [96] and Dagdag et al. [97] studied the corrosion inhibition mechanisms of zinc dihydrogen phosphate and zinc phosphate for AA2024, respectively. Both studies concluded that both Zn^{2+} and PO_4^{3-} ions play a role in the corrosion inhibition of the alloy by forming an insoluble protective film. Zn^{2+} ions interact with hydroxyl ions and form sparingly soluble compounds at the intermetallic particles suppressing the cathodic reaction, while PO_4^{3-} ions form a protective film of insoluble aluminium/zinc phosphates on the alloy surface (mainly in the anodic area) hindering the anodic reaction (Figure 2.25 [97]). The problem of the application of phosphates in this study is that phosphates lead to an increase of the chloride release in cement pastes [110], which is detrimental for the corrosion protection of aluminium.

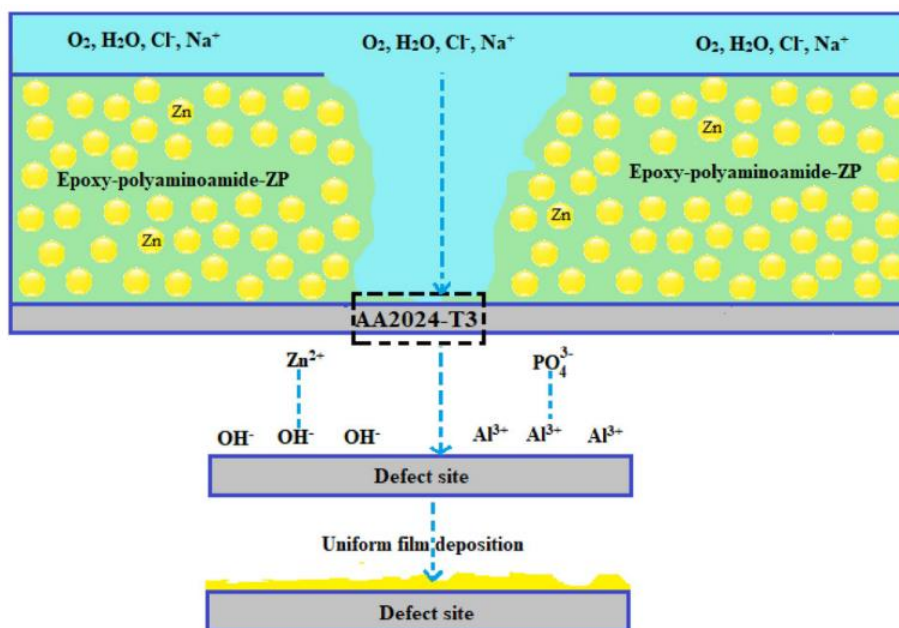


Figure 2.25 Schematic mechanism of corrosion inhibition on AA2024 by zinc phosphate (ZP) in the epoxy matrix [97].

Besides, some rare earth metal salts, such as cerium salts [99] and lanthanide salts [100, 101], are excellent corrosion inhibitors and non-toxic. The corrosion inhibition mechanism of aluminium alloys by Ce and La ions is mainly attributed to the precipitates of oxides/hydroxides of lanthanum and cerium on the intermetallic particles [101]. This precipitation covers the cathodic intermetallic sites and hence inhibits the cathodic reactions. An example is provided in Figure 2.26, in which Kosari et al. [111] showed the preferential precipitation of cerium species on the cathodic sites (e.g. AlCuMg intermetallic particles). The inhibition mechanism of cerium inhibitors also depends on the type of anion, the composition of intermetallic particles and pH. For example, Rodic and Milosev [112] mentioned that $CeCl_3$ and $CeAc_3$ inhibit the anodic reaction of pure aluminium and AA2024 as well as the cathodic reaction. Although rare earth metal salts are good corrosion inhibitors, they are economically unacceptable for geological disposal of nuclear waste due to their high prices.

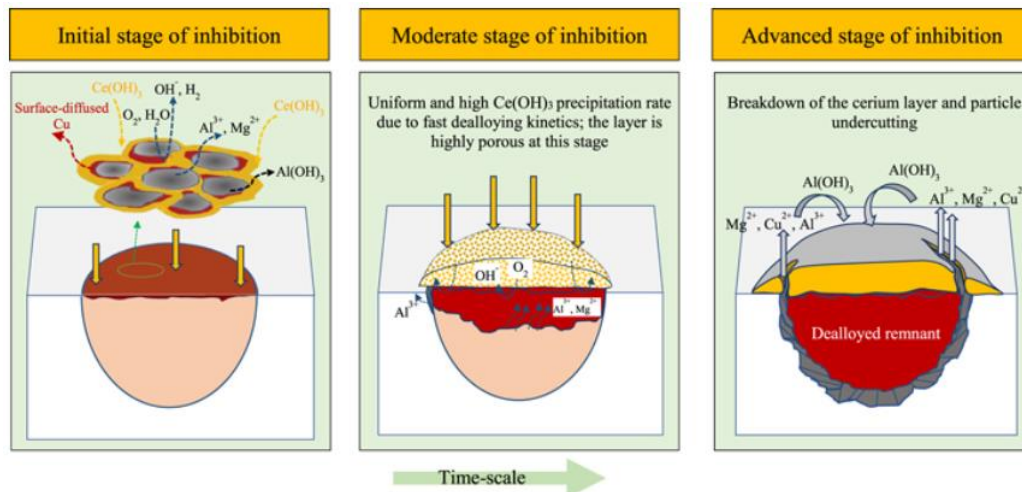


Figure 2.26 Schematic of cerium precipitation mechanisms on the AlCuMg (S-phase) intermetallic particles in aluminium alloys [111].

Table 6 lists all the corrosion inhibitors described above, as well as a summary of the corrosion mechanism explaining the inhibiting effect and the reason why they cannot be used in a geological disposal facility.

Chapter 2

Table 6. Possible corrosion inhibitors, their aluminium corrosion inhibition mechanism and explanation of the non-practical use in the geological disposal facility.

Name	Inhibitor mechanism	Reason of non-practical use in the geological disposal facility
2-MBT and BTA	2-MBT and BTA are not only physically adsorbed on the Al surface inhibiting anodic activities, but also inhibit the oxygen reduction at intermetallic particles (cathodic sites) in the alloys by forming a complex layer or a polymeric film	Incompatibility in a geological repository environment of nuclear wastes with high radioactivity, high temperature, high pH...
chromates	chromate ions are reduced to form a Cr(III) film not only inhibiting cathodic reactions by covering the Cu-rich intermetallic particles in the alloys but also adsorbing on aluminium oxides inhibiting anodic activities	high toxicity
silicates	the anodic inhibition is attributed to the formation of the protective film on the aluminium matrix by adsorption of aluminosilicate anions	possibility of becoming part of the calcium silicate hydrate (C–S–H) phase of cement pastes
molybdates	the adsorption of Mo species on the alloy surface forming a protective Al-Ca-Mo(V)-O(H) oxide layer inhibits the anodic reaction	the reduced mechanical properties and the accelerated diffusion of chloride ions in mortars
phosphates	PO_4^{3-} ions form a protective film of insoluble aluminium/zinc phosphates on the alloy surface (mainly in the anodic area) hindering the anodic reaction	an increase of the chloride release in cement pastes
rare earth metal salts	oxides/hydroxides of rare earth metals precipitate on the cathodic intermetallic particles and hence inhibit the cathodic reactions	economically unacceptable

Chapter 2

Considering the environmental protection, the compatibility with cementitious environments and the economic feasibility, lithium salts could be a good choice for the corrosion inhibition of aluminium in cement pastes. They are lowly toxic [113] and possess an acceptable price [114-116]. Moreover, they are already studied for mitigating alkali silica reaction (ASR) in OPC mortar and concrete systems [117-119], which indicates their good compatibility with cementitious materials. Many investigations focused over the last decades on studying different lithium salts, such as LiNO_3 and Li_2CO_3 , as potential inhibitors for the corrosion of Al alloys in alkaline systems [120-123]. For aluminium encapsulated in cementitious materials, researchers reported that mixing LiNO_3 with cement resulted in the inhibition of hydrogen gas generation produced during the corrosion of Al in cement pastes and mortars [124-126]. This is the subject of the next section.

2.6. Li-Al layered double hydroxide

The inhibition effect of lithium salts on the corrosion of aluminium in high pH conditions is attributed to the formation of a Li-Al layered double hydroxide (LDH) preservation film on the aluminium surface.

Layered double hydroxides belong to anionic clay family and many investigations focused on their unique characteristics. Most LDHs possess a basic structure with a fraction of the divalent cations in brucite-like ($\text{Mg}(\text{OH})_2$) layers substituted by trivalent cations, in which the extra positive charge is balanced by intercalation of anions (also accompanied by water) between the hydroxide layers as shown in Figure 2.27 [127]. The general formula of LDHs can be represented by: $[\text{M}_{1-\chi}^{\text{M}^{2+}}\text{M}_{\chi}^{\text{M}^{3+}}(\text{OH})_2]_n^{\chi+} \cdot [\text{A}^{n-}]_{\chi/n} \cdot m\text{H}_2\text{O}$, where M^{2+} (e.g. Mg^{2+} , Ni^{2+} , ...) and M^{3+} (e.g. Al^{3+} , Fe^{3+} , Cr^{3+} , ...) are the divalent and trivalent cations, while A^{n-} represents anions such as NO_3^- , CO_3^{2-} , Cl^- [127, 128]. The cationic radius of the trivalent cations should not differ much from that of Mg^{2+} [129,130] and the pure hydrotalcite phase can be reasonably stable when $0.2 < \chi < 0.33$, i.e. with the $\text{M}^{2+}/\text{M}^{3+}$ ratios of 2–4 [131-134]. The change of the χ values leads to the formation of pure hydroxides or other compounds with different structures [135-137]. Besides, the different combinations of M^{2+} and M^{3+} ions can produce ternary, even quaternary LDHs [138] and the range of LDHs is larger than what the formula shows. For example, the LDH film results from the facile substitution of lithium ions with aluminium ions in the aluminium hydroxide layer to form $[\text{LiAl}_2(\text{OH})_6]_n^{1+} \cdot \text{A}^{n-} \cdot m\text{H}_2\text{O}$ (an example of $\text{LiAl}_2(\text{OH})_6\text{Cl}$ is shown in Figure 2.28 [139]), where A^{n-} is the counter anion (NO_3^- or CO_3^{2-} when LiNO_3 or Li_2CO_3 is respectively added into the cement paste as the corrosion inhibitor) [122,140].

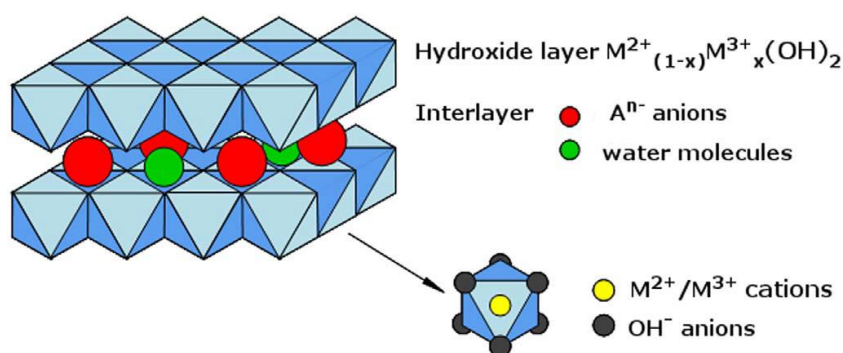


Figure 2.27 Structure of common layered double hydroxide [127].

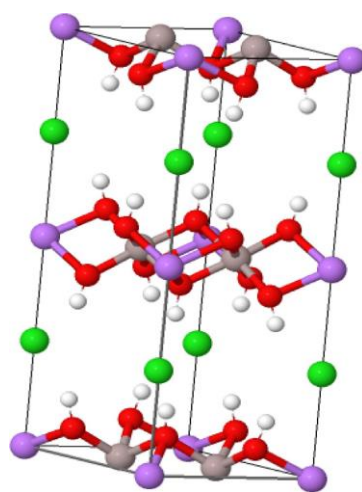


Figure 2.28 Schematic structure of $LiAl_2(OH)_6Cl$. Li, Al, Cl, O, and H are represented by purple, gray, green, red, and white balls, respectively [139].

2.6.1. Synthesis of LDH on aluminium and aluminium alloys

Iqbal et al. [141] classified the preparation methods of Al-based LDHs into the co-precipitation and the in-situ growth methods. The co-precipitation synthesis is an ex-situ method in which the LDH precursors are prepared in the form of powder in advance and then applied on the aluminium surface. The co-precipitation LDH precursors are prepared in the divalent and trivalent cationic salt solutions (see Figure 2.29 [142]). In order to exclude the presence of CO_2 in air, which leads to the carbonate forms of LDHs, the preparation process can be complemented under CO_2 -free conditions [143,144]. Because the experimental conditions can be artificially controlled, the co-precipitated LDHs have a high purity, a high crystallinity, a controlled chemical composition, and an excellent interaction with inhibitors. Rao et al. [145] reported that the urea hydrolysis as a modification of the hydrothermal treatment for the co-precipitation can yield uniform, small-sized and well-crystallized LHDs. However, the final adhesion of the precursors is difficult to be homogeneous on the surface. For example, in the sol-gel method to deposit LDHs on the

Chapter 2

substrate, the as-prepared LDHs by the co-precipitation is dispersed in sols and then the substrate (e.g. aluminium alloys) is dipped in the sol-gels, followed by drying and curing [146,147]. It is difficult to ensure the consistent formation of the LDH film on the substrate. Bukhtiyarova [127] focused on the co-precipitation method of LDHs and discussed the factors, significantly affecting the formation of LDHs, such as the pH, the salt concentration, the nature of the solutions, the aging time, the reaction temperature, and the molar cationic ratios. Salak et al. [148] studied the synthetic conditions of Zn–Al LDHs including the initial concentration of salts, crystallization time, solution pH, precipitating agents and the divalent/trivalent cations' ratio. These factors significantly affect the LDH structure, functional properties and chemical compositions.

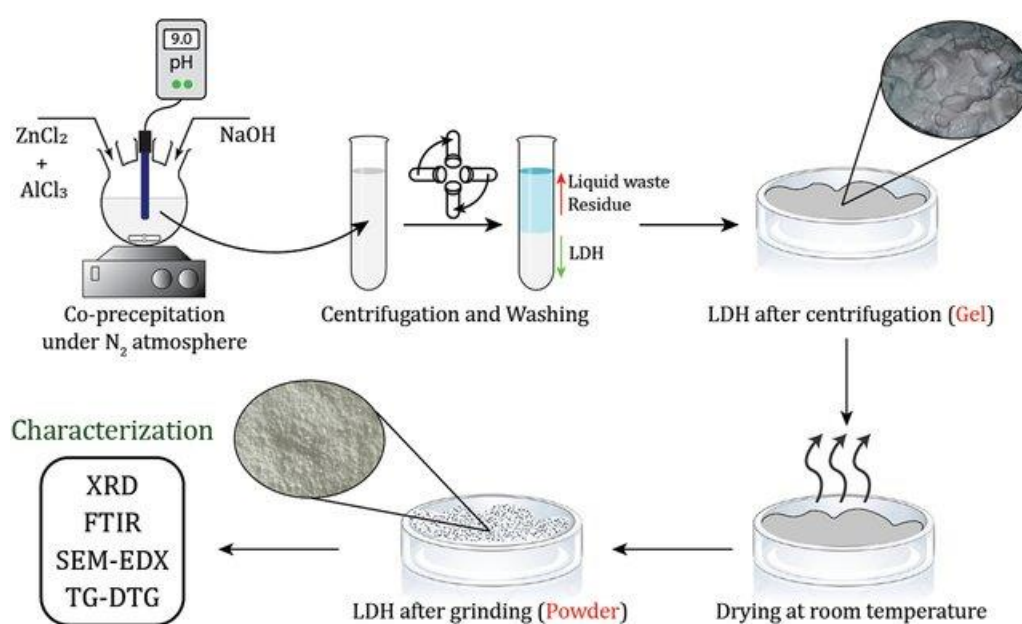


Figure 2.29 Synthesis steps of Zn–Al LDH by co-precipitation method [142].

In the in-situ method, LDHs are directly grown on the substrate, which provides a controlled film/thickness size and a strong adhesion between LDH and the substrate. Visser et al. studied the in-situ growth of Li–Al LDH on the AA2024-T3 substrate and proposed the mechanism of the layer formation as shown in Figure 2.30 [149]. The aluminium alloy performs as the source of Al^{3+} to establish a competitive growth and dissolution process of $\text{Al}(\text{OH})_3$ on the alloy surface, when the aluminium surface begins to be dissolved in an alkaline solution [150]. Then Li^+ cations in the solution enter the $\text{Al}(\text{OH})_3$ gel. The substitution of Li^+ cations with Al^{3+} ions results in the LDH structure (Figure 2.28). In the later characterizations of the film, the newly-born film was found to consist of the dense region, the porous region and the columnar region outwards [151]. The dense region in direct contact with the substrate is an amorphous lithium-containing pseudoboehmite phase, i.e. Li-pseudoboehmite; the porous region is the complex combination of crystalline Li–Al LDH, amorphous Li-pseudoboehmite and amorphous $\text{Al}(\text{OH})_3$;

Chapter 2

the columnar region consists of single-crystal pillars of Li-Al LDH (see Figure 2.31) [152]. The Li^+ concentration and pH play an important role in the formation of the different layers. Besides, other synthetic conditions such as the number of cations, pH, reaction temperature, aging time, alkali solution and so on [127], strongly control the crystallinity and geometry in the in-situ growth of LDHs [153-157]. For example, Iqbal et al. [154] reported that the film thickness of the Mg-Al LDH film increases as a function of the reaction time and temperature. The corresponding different morphologies of Mg-Al LDHs are shown in Figure 2.32. Usually, the thickness of LDHs ranges from a few microns to several micrometres according to different experimental conditions [141]. Liang et al. [155] also reported that the compactness of Mg-Al LDH film rises with the increase of the reaction temperature according to the microscopy characterization.

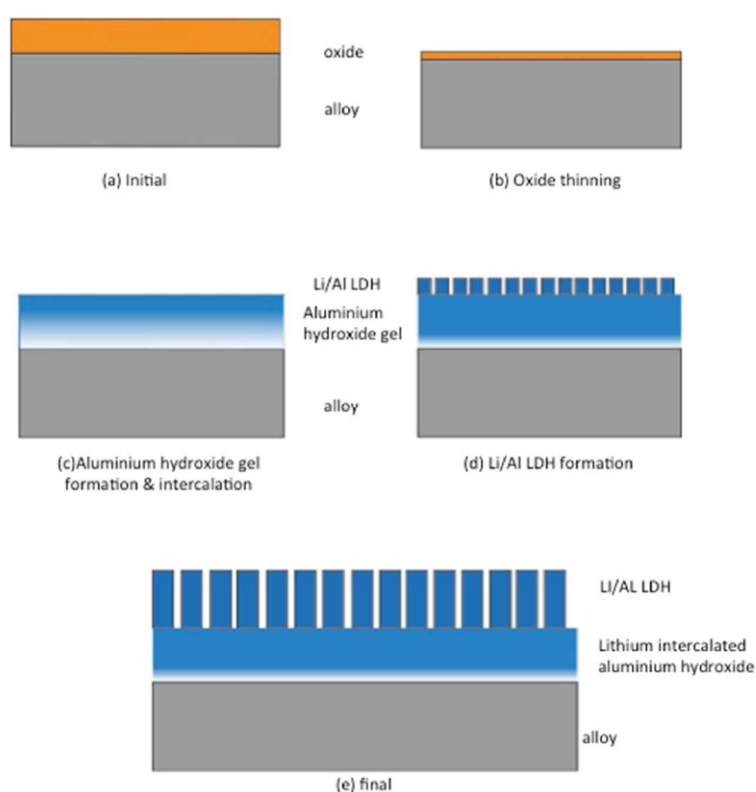


Figure 2.30 Schematic illustration of the steps in the Li-Al LDH formation [149].

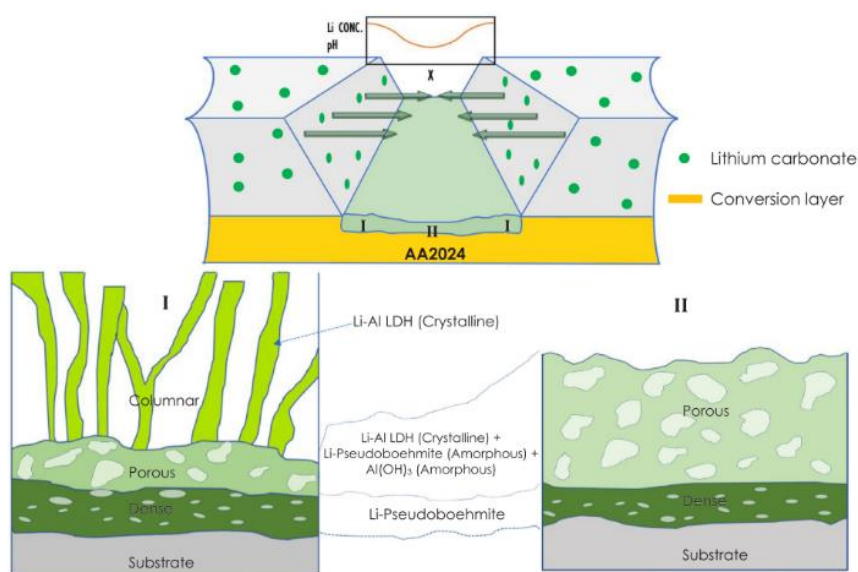


Figure 2.31 Schematic representation of the formed layers. Region I and Region II indicate the areas under different solution chemistry in the neutral salt spray experiment [152].

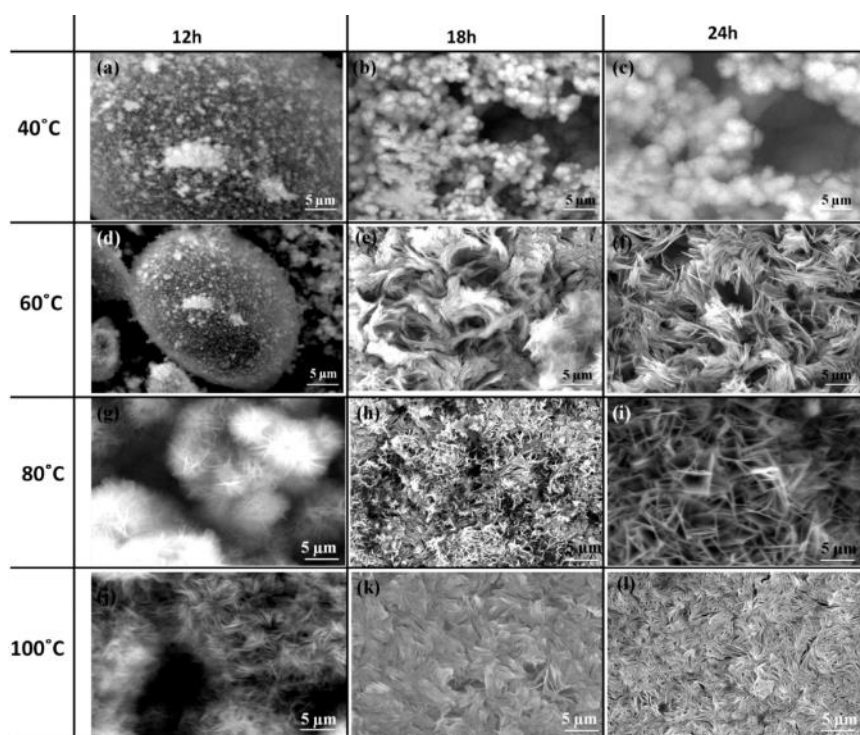


Figure 2.32. SEM images of Mg-Al LDH films developed at various reaction temperatures and crystallization times [154].

Chapter 2

Iqbal et al. [141] summarized some synthesis methods of LDHs reported in literature in Table 7 including both the co-precipitation method and the in-situ method. It proves the presence of different synthesis methods even for the same type of LDH.

Table 7. Synthesis approaches to LDHs at various synthetic conditions with various precursors [141].

LDH	Anion- Exchanger	Precursors	Alkaline Media	Method	Al Alloy	Synthetic Condition		
						°C	pH	Aging Time (h)
ZnAl	V	ZnCl ₂ , AlCl ₃	NaOH	coprecipitation	2024	55	6.3-6.5	12
ZnAl	V	ZnCl ₂ , AlCl ₃	NaOH	coprecipitation	2024	55	6.3-6.5	12
MgAl	(MBT)/(QA)	Mg(NO ₃) ₂ , Al(NO ₃) ₃	NaNO ₃	coprecipitation	2024	65	10	24
ZnAl		Zn(NO ₃) ₂ , Al(NO ₃) ₃			2024	65	10	24
ZnAlVO ₃	-	Zn(NO ₃) ₂ , Al(NO ₃) ₃ , NaVO ₃	NaOH	coprecipitation	2024	65	9.5	24
MgAlVO ₃	-	Mg(NO ₃) ₂ , Al(NO ₃) ₃ , NaVO ₃	NaOH	coprecipitation		65	9.5	24
ZnAl	V	Zn(NO ₃) ₂ , Al(NO ₃) ₃	NaNO ₃	coprecipitation		65	10	24
MgAl	V	Zn(NO ₃) ₂ , Al(NO ₃) ₃	NaNO ₃	coprecipitation		65	10	24
ZnAl	4-ABSA, 3-ABSA and 3,4-HHBA	ZnCl ₂ , AlCl ₃	NaOH	coprecipitation	2024	30	9	12
ZnAl	-	ZnCl ₂ , AlCl ₃	NaOH	coprecipitation	2024	30	10	12
ZnAl	Na ₂ CO ₃	ZnCl ₂ , AlCl ₃	NaOH	coprecipitation	2024	30	9	12
ZnAl	K ₂ CrO ₄	ZnCl ₂ , AlCl ₃	NaOH	coprecipitation	2024	30	10.5	12
ZnAl	Na ₂ C ₁₀ H ₁₄ N ₂ O	ZnCl ₂ , AlCl ₃	NaOH	coprecipitation	2024	30	10	12
ZnAlCe	-	Zn(NO ₃) ₂ , Al(NO ₃) ₃ , Ce(NO ₃) ₃	NaNO ₃	coprecipitation	2024	65	10	18
ZnAl	V	Zn(NO ₃) ₂	-	In situ	2024	<100	7	-
ZnAl	Laurate	Zn(NO ₃) ₂	NH ₄ NO ₃	In situ	Al	45	6.5	36
MgAl	8HQ	Mg(NO ₃) ₂	NH ₄ NO ₃	In situ	Al	100	9	48
MgAl	C ₆ H ₅ COON	Mg(NO ₃) ₂ , urea	NH ₄ NO ₃	In situ	6061	45	10	24
ZnAl	V	Zn(NO ₃) ₂	NH ₄ NO ₃	In situ	2198	45	7	-
ZnAl	V	Zn(NO ₃) ₂	NH ₄ NO ₃	In situ	2024	95	6.5	0.5
ZnAl	V	Zn(NO ₃) ₂	NH ₄ NO ₃	In situ	2024	95	6.85	0.5
MgAl	-	Mg(NO ₃) ₂ , NH ₄ NO ₃	NH ₄ NO ₃	In situ	6082	60/80	10	24
MgAl	-	Mg(NO ₃) ₂	NH ₄ NO ₃	In situ	6082	60/80/100	10	18/24
ZnAl	-	Zn(NO ₃) ₂ , NH ₄ NO ₃	NH ₄ NO ₃	In situ	6082	60/80	6/6.5/7	18/24
CaAl	-	Ca(NO ₃) ₂	NaOH	In situ	6082	140	10	18/24/72
ZnAl	Laurate	Zn(NO ₃) ₂ , NH ₄ NO ₃	-	In situ	Al	85	6.5	12
NiAl	-	Ni(NO ₃) ₂	NaOH	In situ	6082	130	10	24
NiAl	-	Ni(NO ₃) ₂ , NH ₄ NO ₃	NH ₄ NO ₃	In situ	Al	85	-	40
MgAl	-	Mg(NO ₃) ₂ , NH ₄ NO ₃	-	In situ	5005	125	8-10.5	1-8
MgAl	Laurate, stearate, oleate	Mg(NO ₃) ₂ , urea	-	In situ	Al	70	-	24
ZnAl	-	Zn(NO ₃) ₂ , NH ₄ NO ₃	NH ₄ NO ₃	In situ	Al	120	6.5	-
MgAl	Stearic acid	Mg(NO ₃) ₂ , NH ₄ NO ₃	NH ₄ NO ₃	In situ	5005	125	10	4
ZnAl-RGO	RGO	Zn(NO ₃) ₂ , NH ₄ NO ₃ , Al(NO ₃) ₃ , RGO	NH ₄ NO ₃	Hydrothermal continuous flow	A6N01	130-80	5.6	0.75-2
ZnAl	Mo, graphene	Zn(NO ₃) ₂ , NH ₄ NO ₃	-	In situ	2024	45	8.8	6
MgAl	Sol gel	Mg(NO ₃) ₂ , Al(NO ₃) ₃	NaOH	coprecipitation	2024	70	-	18
ZnAl	Stearic acid	Zn(CH ₃ COO) ₂	NH ₄ OH	In situ	Al	60	-	4
ZnAl	V	Zn(NO ₃) ₂	NH ₄ OH	In situ	2024	95	6.5	0.5
MgAl	PFDTMS	Mg(NO ₃) ₂		In situ	2198	45	7	80
CoAl		Co(NO ₃) ₂						
NiAl		Ni(NO ₃) ₂						
ZnAl		Zn(NO ₃) ₂						
ZnAl	MBT/8HQ/V/PA/Mo	Zn(NO ₃) ₂	-	coprecipitation	2024	60	-	20
LiAl	Vanillin, aspartic acid	LiNO ₃	-	In situ	A6N01	60	-	0.33

Chapter 2

In terms of the in-situ growth of Li-Al LDH expected in this study, the formation of the Li-Al LDH does not seem to be a problem. Bravo-Suárez et al. [158] reported that Li^+ ions are thermodynamically favoured to form Li-Al LDHs with Al^{3+} ions, because Li-Al LDHs are estimated to have a small and negative standard Gibbs free energy of formation, which means the formation of the Li-Al LDHs is spontaneous. Wan et al. [159] mentioned a simple synthesis method of Li-Al LDH by dissolving aluminium in LiOH solution in 10 °C water baths (in order to reducing the temperature because the reaction releases heat). Buchheit et al. [122] reported that Li-Al layered double hydroxide can be prepared by the direct immersion of aluminium alloys (AA1100, AA6061 and AA7075) in a $0.1 \text{ mol}\cdot\text{L}^{-1}$ Li_2CO_3 solution at room temperature, in which LiOH is used to adjust the pH to the range between 11.5 and 13.5. Visser et al. [149,151,160] and Kosari et al. [152] indicated that Li_2CO_3 leached from an organic coating can react with the AA2024 substrate to form a protective layer including a Li-Al LDH structure in NaCl solutions. The hydrolysis of CO_3^{2+} ions leads to the formation of OH^- ions, which can be used for the growth of Li-Al LDH [160,161]. The pore solution of Portland cement pastes contains a great amount of OH^- (pH around 12, see Section 2.4 and Section 5.5), which can therefore facilitate the formation of Li-Al LDHs. Matsuo et al. proved the insolubility of the Li-Al LDH film both theoretically [162] and experimentally [125] and investigated the influence of underground water on the stability of the Li-Al LDH film in geological disposal conditions [163,164]. In addition, the concentration of Li^+ ions in mortars is also discussed [163]. Hence, the formation of Li-Al LDHs in the cement paste is theoretically possible.

However, the presence of other ions in the cement paste pore solution (Ca^{2+} , Mg^{2+} , etc. (see Section 2.7)) possibly leads to the formation of other types of LDHs. For example, Iqbal et al. [153] reported that Al can react with $\text{Ca}(\text{NO}_3)_2$ solution in alkaline condition (pH 10) to form Ca-Al LDHs at a temperature of 140 °C. Iqbal et al. [154] also studied the growth of Mg-Al LDHs by directly immersing the AA6082 substrate in the mixed $\text{MgNO}_3\text{-NH}_4\text{OH}$ solution within the temperature range of 40-100 °C. Although the hydration of the cement paste releases heat and increases the temperature, it is difficult to determine whether or to what extent these LDHs (Ca-Al LDHs, Mg-Al LDHs, etc.) can form. This might be a research direction in the future. Furthermore, lithium inhibitors are usually directly mixed with cement powders before hydration. Consequently, the lithium ions diffuse from the cement paste bulk to the aluminium surface through the connected pores inside the cement paste. Related factors such as the diffusion of Li^+ and OH^- ions in the cement paste, which involve the formation of LDHs, are not discussed in this research.

2.6.2. Corrosion protection of LDH on aluminium and aluminium alloys

The excellent corrosion resistance performance of LDHs is essentially attributed to the physical barrier against water and ion migration. Most LDHs have a multi-layered structure as shown in Figure 2.33, i.e. an inner relatively dense layer and an outer porous layer (sometimes the structure could be further divided

into more different layers as shown in Figure 2.31). The physical barrier effect of LDHs is reported via two mechanisms:

- The inner layer works as a dense impermeable protective layer, which hinders the migration of water and ions. Iqbal et al. [141] mentioned that the inner dense layer is responsible for the physical barrier effect. Visser et al. [149] and Liu et al. [165] reported the barrier effect of the inner dense layer in the study of Li-Al LDH, while Wu et al. [166] indicated that the dense inner layer of Mg-Al LDH provides better protection than the porous outer layer.
- The outer porous layer was reported to induce the 'air valley' effect caused by LDHs' nest-like morphology (see Figure 2.33 [141,167]). Literature reported that the superhydrophobic ability of different LDHs e.g. Li-Al LDHs [168-170], Mg-Al LDHs [171,172], Zn-Al-La LDH [156] benefits the corrosion resistance. This superhydrophobic ability is attributed to the 'air valley' effect caused by the surface morphology of LDHs. The nest-like LDH surface can trap air bubbles in the pores of the LDH surface impeding the ingress of the outer electrolyte and the aggressive ions. The 'air valley' effect is controlled by many factors, e.g. the surface roughness and the film thickness, and can be improved by surface modifications [156,168,169,172] such as the introduction of the low surface-energy species. However, when LDHs are in contact with the electrolyte, the hydraulic pressure causes the trapped air bubbles to break away from the constrain of pores and the electrolyte will fill the porous structure of LDH, thus losing the protective effect. This phenomenon is always accompanied by a decrease of the LDHs impedance, which has been widely observed in different LDHs [153,154,156,171]. For example, Iqbal et al. [153] studied the impedance evolution of CaAl-LDH being immersed in 0.1M NaCl solution. In the first 7 days of immersion, a decrease by an order of magnitude in the low-frequency range was observed (see Figure 2.34). According to the results reported in the literature [153,154,156,171], this decrease normally occurs in the first month of the immersion.

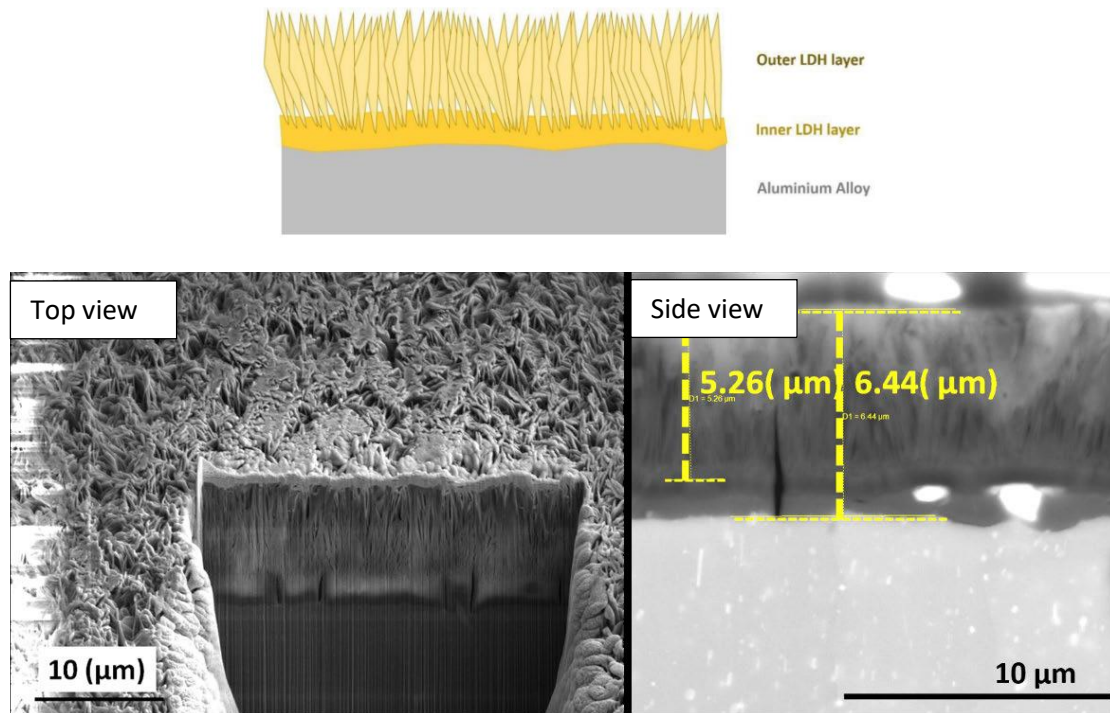


Figure 2.33 Schematic representation of the structure of the LDH based film [141] and FIB-SEM image of MgAl-LDH coating on AA6082 [167].

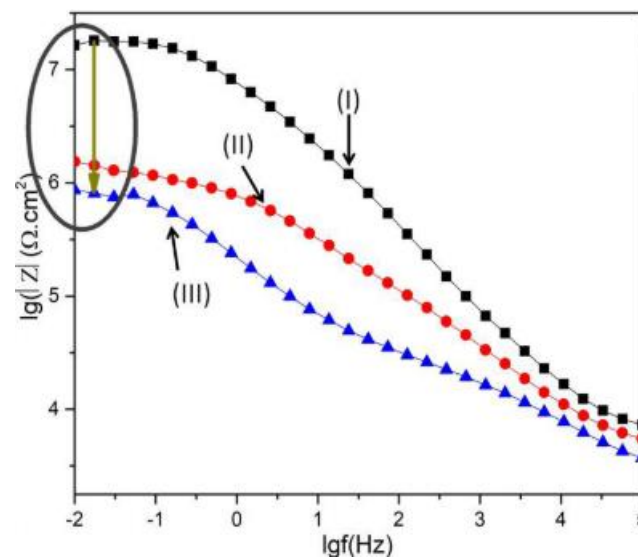


Figure 2.34 Impedance plots of CaAl-LDH: (I) as-prepared, (II) after 4 days, (III) after 7 days immersion in 0.1 mol·L⁻¹ NaCl solution [153].

Another mechanism involving the corrosion protection by LDHs is the ion exchange reactions. Due to the anion exchange capability of LDHs, various anions can be easily intercalated into the LDH interlayer to modify the chemistry of LDH for specific applications, meanwhile some anions would be released from the

Chapter 2

interlayer to balance the charge. This exchange process can trap some aggressive ions such as Cl^- in the interlayer, thus reducing the attack of these ions [141]. For example, considering the ion exchange equilibrium constant in LDH based films, the value decreases in the following order: $\text{CO}_3^{2-} > \text{SO}_4^{2-} > \text{OH}^- > \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^- > \text{I}^-$ [173]. Therefore, the exchange of I^- and/or NO_3^- (if present in the LDH film) by outer aggressive species (e.g. Cl^- , F^- , Br^- and SO_4^{2-}) is favoured, which benefits the corrosion protection by entrapping the harmful anions in the film [141,153,154]. Besides, other species such as metal ions, inorganic complex, organic molecules working as corrosion inhibitors can be intercalated into the LDH interlayer to enhance the corrosion resistance properties [174,175].

In terms of the corrosion protection of aluminium alloys, Li-Al LDHs are reported to possess an excellent corrosion protection ability. Visser et al. [149,151,160] and Kosari et al. [152] reported that Li_2CO_3 reacts with the AA2024 substrate to form a protective layer including a Li-Al LDH structure in NaCl solutions. This layer provides both the anodic inhibition and the cathodic inhibition for AA2024 as shown in Figure 2.35 [176]. The polarization curve of AA2024 aluminium alloy with Li_2CO_3 addition shows that both anodic and cathodic current densities are significantly decreased compared with that in the blank solution, while E_{corr} remains almost the same magnitude. The effect of Li_2CO_3 on the corrosion current and the corrosion potential proves that it works as a mixed inhibitor for the corrosion of AA2024. According to literature, some LDHs can preferentially form on the site of the intermetallic particles. For example, Liang et al. [177] studied the formation of LDHs on AA2099 Al–Cu–Li alloy. Al–Fe–Mn–Cu intermetallic particles are preferential sites for the formation of nucleation and growth of Zn–Al LDHs (see Figure 2.36), which may be attributed to the fact that the particles serve as cathode in a localized corrosion increasing the local pH. However, this has not been found in Li–Al LDH studies. Visser et al. [176] reported that, unlike organic inhibitors such as benzotriazole and 2-mercapto-benzothiazole, the protective layer including a Li–Al LDH structure, which is attributed to the effect of Li_2CO_3 , covers both cathodic and anodic areas of the aluminium matrix, limiting the reduction and oxidation reactions. The intermetallic particles as cathodic sites are also uniformly covered as shown in Figure 2.37.

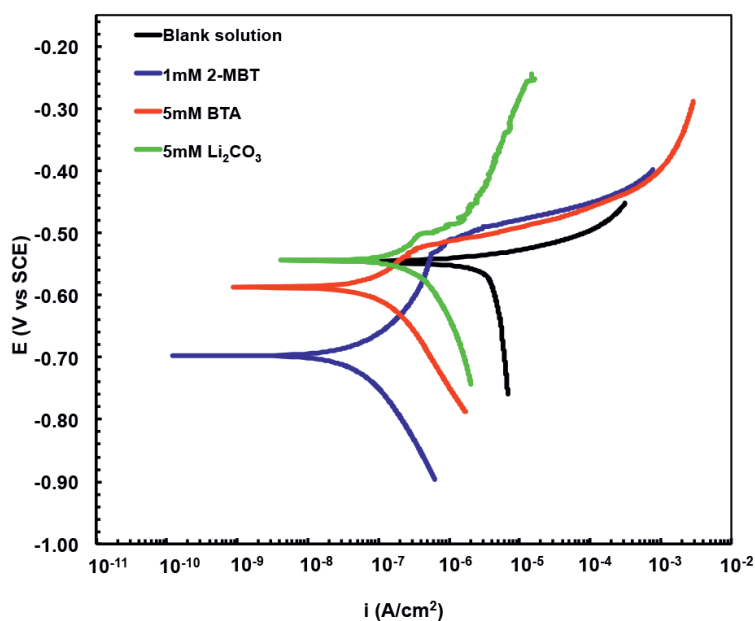


Figure 2.35 Potentiodynamic polarization curves for AA2024-T3 aluminium alloy immersed in $0.05 \text{ mol} \cdot \text{L}^{-1}$ NaCl solution with and without corrosion inhibitor [176].

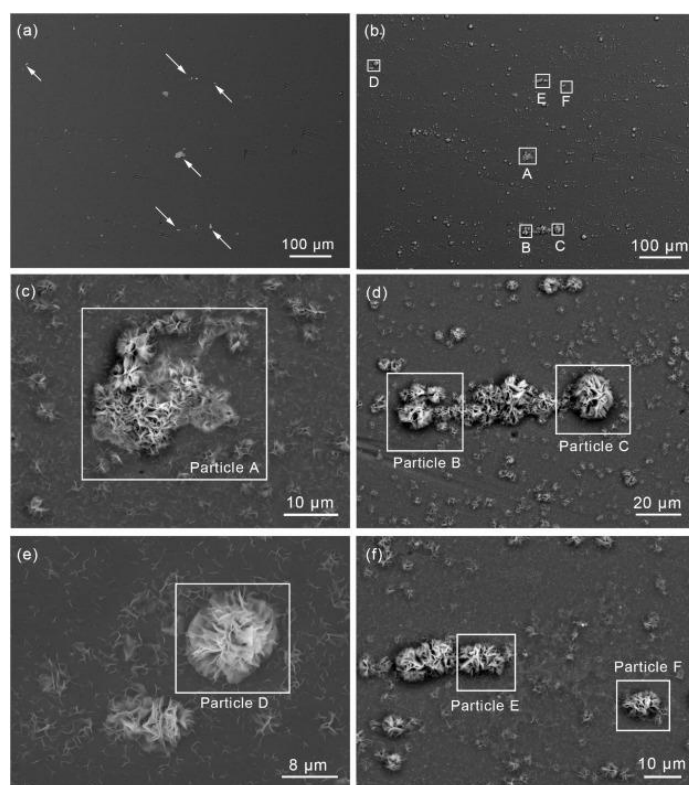


Figure 2.36 SEM micrographs of the polished alloy (a); SEM micrograph of the alloy after immersion in a mixed solution containing $0.05 \text{ M Zn(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $0.3 \text{ M NH}_4\text{NO}_3$ for 0.5 h (b); (c)~(f) are the framed regions in (b) [177].

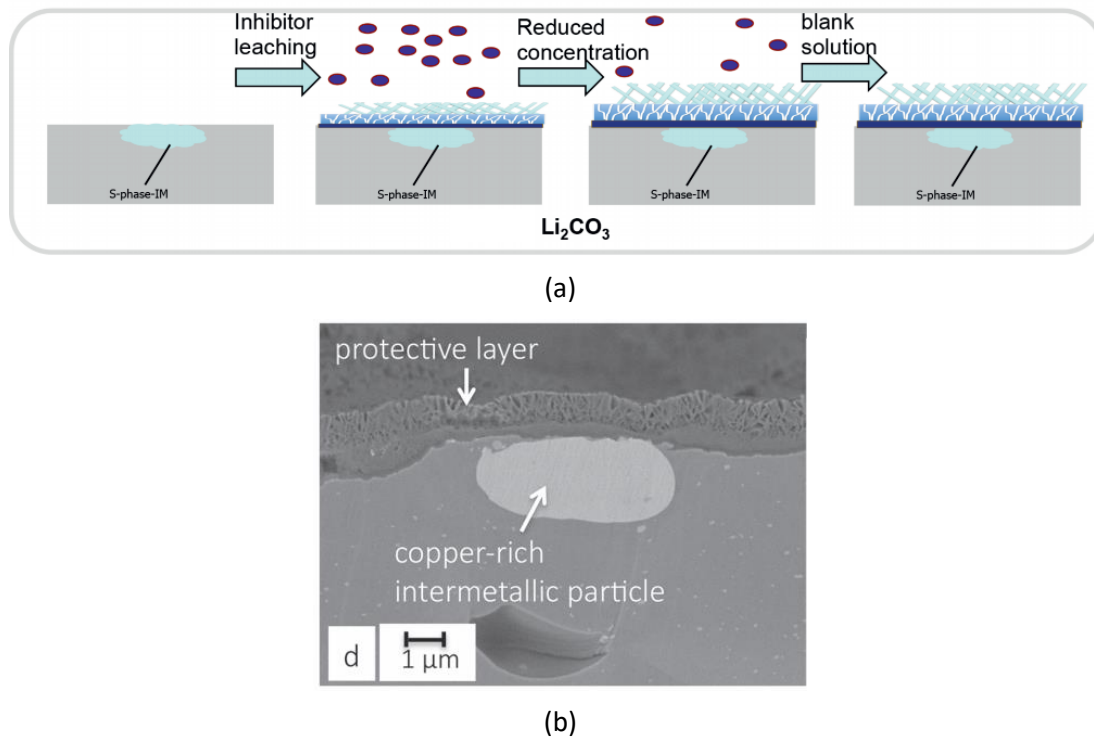


Figure 2.37 Schematic of the inhibition mechanism of Li_2CO_3 on AA2024 substrate (a) [176] and the corresponding SEM micrograph (b) [151].

The hydrogen production during the corrosion of Al in cement pastes was also found to be inversely proportional to the amount of added LiNO_3 , but a dosage higher than 3% of the cement weight does not further improve the inhibition ability [125]. However, Delpech et al. [126] explained that the decrease of the H_2 production is likely attributed to the formation of ammonia instead of to a direct inhibition effect on the corrosion. Indeed, the corrosion current obtained from impedance analysis indicated a much higher H_2 production compared to that actually collected by gas chromatography. According to Fanning [178], Al indeed reacts with NO_3^- to form ammonia gas in an alkaline solution. Li_2CO_3 also shows inhibition ability regarding Al corrosion in alkaline solutions [149,165, 176,179]. While being added into cement paste, the CO_3^{2-} ions are also likely to affect the corrosion process by changing the microstructure of cement paste through a carbonation reaction. Although Li_2CO_3 is a possible corrosion inhibitor for Al in cement paste, no related works have been reported to our knowledge.

2.7. Cement paste porosity

OPC-based materials normally include cement pastes (cement + water), mortars (cement + sand + water) and concretes (cement + sand + gravel + water). In order to simplify the studied system, i.e. decrease the number of variables, the cement paste system was chosen for this study.

Chapter 2

Hardened cement paste contains a large number of pores, which play an important role in the mechanical and transport properties of cement paste. Changes of the pore structure significantly influence the mechanical properties such as the hardness [180], Young's modulus [181,182], compressive strength [183,184]. For example, the compressive strength of cement pastes is inversely correlated with the capillary porosity. The capillary porosity is the main factor affecting the compressive strength and the quantitative relationship between the capillary porosity and compressive strength can be well fitted by different models such as Balshin function as shown in Figure 2.38 [183]. Literature also shows that transport properties, including diffusion [181,185,186] and permeation [187-189], are related to porosity, pore size, connectivity, and tortuosity of cement pastes. Because of the significant influences on the properties, pores are usually an important factor for the study of metallic corrosion occurring in cement pastes.

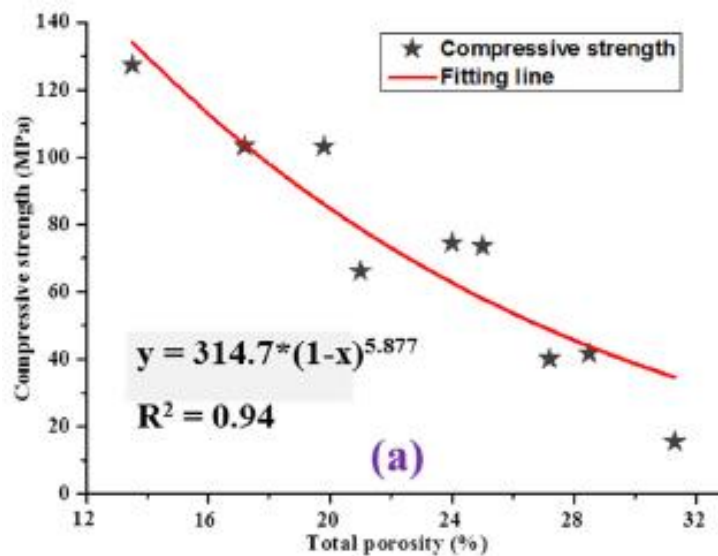


Figure 2.38 Relationship between compressive strength and the capillary porosity of cement pastes with low water-to-cement ratios fitting by Balshin function [183].

According to the size of the pores, a classification is made into two categories (see Table 8): gel pores smaller than 10 nm and capillary pores with size between 10 nm and 10 μm [190,191]. The gel pores are inner pores within the structure of hydration products such as C-S-H, CH, AF_t ($\text{Al}_2\text{O}_3 - \text{Fe}_2\text{O}_3 - \text{tri}$) and AF_m ($\text{Al}_2\text{O}_3 - \text{Fe}_2\text{O}_3 - \text{mono}$). They are normally regarded as part of these hydration products [192]. Capillary pores are the remnant of initially water-filled space [193], whose volume fraction decreases with the increase of hydration degree [194]. In this study, only capillary pores are considered because of their dominant role in transport properties at micro-scale [195-197]. The gel pores and capillary pores are illustrated in Figure 2.39.

Table 8. Classification of pore sizes in hydrated cement pastes [191].

	Size	Subordinated category
Gel pores	≤ 0.5 nm	Interlayer spaces
	0.5-2.5 nm	Micropores
	2.5-10 nm	Small isolated capillaries (small mesopores)
Capillary pores	10-50 nm	Medium capillaries (large mesopores)
	0.05-10 μ m	Large capillaries (macropores)

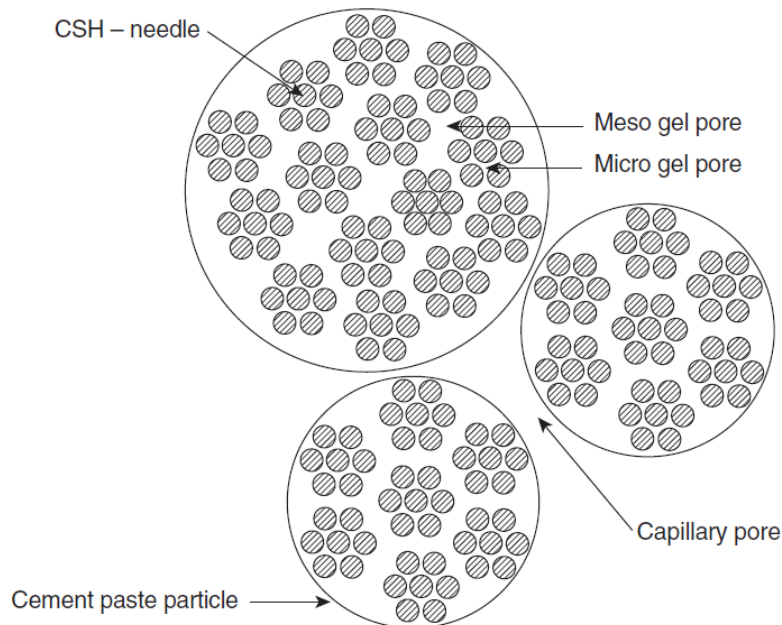


Figure 2.39 Schematic of the pore structure of hardened cement paste [198].

The cement paste porosity can be determined from electrical conductivity measurements. First, the cement paste system can be roughly considered as a two-phase system with one solid-gel phase and one capillary pore phase [199-201]. Hydration products of the cement paste include C-S-H gel, CH, and other minor phases. The gel pores in the C-S-H gel are filled with physically adsorbed water, which could provide a certain level of conductivity. Other hydration products and unhydrated cement grains are normally regarded as insulators. Thus, the solid-gel phase is considered as the low-conductivity phase. The pore solution inside the capillary pore phase contains ionic species such as OH^- , K^+ , Na^+ , Ca^{2+} , Fe^{2+} , Mg^{2+} and SO_4^{2-} [202] which dominate the charge transport process. Therefore, the conductivity of the capillary pore phase mainly depends on the amount and conductivity of the capillary pore solution [203,204]. The amount and conductivity of capillary pore solution can be influenced by many factors, such as initial water/cement ratio, humidity, setting time and temperature [205]. Normally, the conductivity of the

Chapter 2

capillary pore phase is much higher than that of the solid-gel phase. Hence, the capillary pore phase is regarded as the high-conductivity phase. For a randomly distributed two-phase composite such as a cement paste, there are already numerous models dealing with the relationship between the effective physical properties including the conductivity and the phase content as shown in Figure 2.40. On the basis of the Effective Medium Theory (EMT), the General Effective Media (GEM) theory, proposed by McLachlan et al. [207-210], provides a better theoretical basis to build up a physical relationship between the electrical conductivity and the porosity. Thus, the experimental determination of the electrical conductivity is firstly needed to determine the porosity of cement-based materials through the GEM methodology [200,201,211]. More details of GEM are provided in Section 3.5. Depending on the type of media present in between the electrode surface and the sample surface, the different approaches for determining the electrical conductivity of the cement-based materials can be categorised as: the direct contact method without extra medium, the indirect contact method with an insulating or conductive medium and the non-contact method with a thin air layer [212]. Either the direct contact method [213,214] or the indirect contact method [200,214-216] may provide the needed information entangled with a large contact impedance at the electrode/sample interface. Even if the non-contact method is reported to reduce the interface effect, some effects associated with the interface (e.g. the impedance of filling media air) cannot be completely neglected or separated [217-218]. Hence, the influence of the electrode/sample interface is always problematic when characterizing the electrical conductivity for the study of the porosity of a cement-based material.

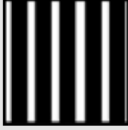
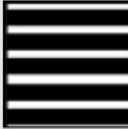
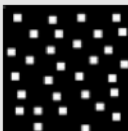
Model	Structure schematic ^a	Expressions ^b
Parallel model		$\lambda_e = (1 - \phi)\lambda_1 + \phi\lambda_2$
Series model		$\lambda_e = \left[\frac{1-\phi}{\lambda_1} + \frac{\phi}{\lambda_2} \right]^{-1}$
EMT model		$(1 - \phi) \frac{\lambda_1 - \lambda_e}{\lambda_1 + 2\lambda_e} + \phi \frac{\lambda_2 - \lambda_e}{\lambda_2 + 2\lambda_e} = 0$
Maxwell model		$\frac{\lambda_e}{\lambda_1} = 1 + \frac{3(\alpha-1)\phi}{(\alpha+2) - (\alpha-1)\phi}$
Hamilton model		$\frac{\lambda_e}{\lambda_1} = \frac{\alpha + (n-1) + (n-1)(\alpha-1)\phi}{\alpha + (n-1) + (1-\alpha)\phi}$
Reciprocity model		$\frac{\lambda_e}{\lambda_1} = \frac{1 + (\sqrt{\alpha}-1)\phi}{1 + (\sqrt{1/\alpha}-1)\phi}$

Figure 2.40 Fundamental analytical models for effective properties of two-component materials [206].

3

Experimental procedures and methods

Chapter 3. Experimental procedures and methods

This chapter introduces the sample preparation procedures and the techniques applied in the thesis.

3.1. Sample preparation

The aluminium alloy 1100 used in the experiments was coming from Alfa Aesar, with a nominal chemical composition consisting of a minimum of 99.0% Al and 1.0% Si + Fe. Test specimens were cut from a 1.0 mm thick sheet with two different dimensions depending on the type of experiment: larger Al plates (30x30 mm) were used for the electrochemical measurements, while smaller Al plates with 2.25 cm² surface area (15x15 mm) were used for GC and SEM measurements. These sheets were polished with successive grades of SiC paper up to 1200 grid, and then cleaned with acetone, ethanol, and distilled water, respectively before to be dried by air flow.

Ordinary Portland Cement (CEM I 52.5 N class according to EN 197-1) was used to produce the cement pastes. Its chemical composition is provided in Table 9.

Table 9. Chemical composition of the cement.

Composition	SO ₃	Cl	Na ₂ Eq	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	Na ₂ O	K ₂ O	MgO	Others
wt.%	2.60	0.04	0.66	21.3	5.2	3.3	63.1	0.33	0.50	2.19	0.78

Three different OPC pastes were prepared in this study: pure OPC, OPC+LiNO₃ and OPC+Li₂CO₃. The pure OPC paste was used as a reference and possessed a low water-to-cement ratio (w/c) equal to 0.36. For the production of the OPC+LiNO₃ pastes, 3 wt.% of LiNO₃ was added to the cement because this concentration can effectively inhibit the generation of hydrogen and a higher dosage cannot further improve the inhibiting effect [125]. The w/c was equal to 0.36. For the production of OPC+Li₂CO₃ pastes, 1.607 wt.% of Li₂CO₃ was added to the system to keep the same lithium ions concentration. The addition of Li₂CO₃ increased the viscosity of the cement paste. Therefore, the w/c was increased up to 0.5 to improve the workability of this cement paste.

For all systems, cement powder and milli-Q water were manually mixed with a rubber spatula for 10 minutes in a steel mixing bowl. Milli-Q water was added into cement powder in two steps during mixing. This procedure ensures the homogeneity of the paste. All manipulations were performed in a glove box under argon atmosphere in order to create an anaerobic system (less than 1 ppm O₂), which simulates the environment of the geological disposal in the long term.

Chapter 3

The electrochemical experiments (EIS & Tafel) were performed using a two-electrode (Al-Al) configuration, whose feasibility for electrochemical tests was already examined elsewhere [219-221]. The working electrode and the counter/reference electrode were identical. To allow an easy connection of the electrodes embedded in the cement paste, an aluminium wire was spot-welded at the back of the 30x30x1 mm Al plates. The electrodes were covered by a non-conductive and waterproof tape and the Al wires were surrounded by a Teflon® heat shrinkable tube, leaving an exposed surface area of 2.26 cm². Finally, the Al plates were positioned in parallel at a distance of 5.5 mm apart by means of Teflon® screws and plastic rods. Once the fresh cement paste was poured into a 40x40x40 mm³ cubic mould, the two-electrode system was immediately inserted into the middle of the cement paste as shown in Figure 3.1(a) and covered by a plastic sheet on the surface to avoid too fast water evaporation.

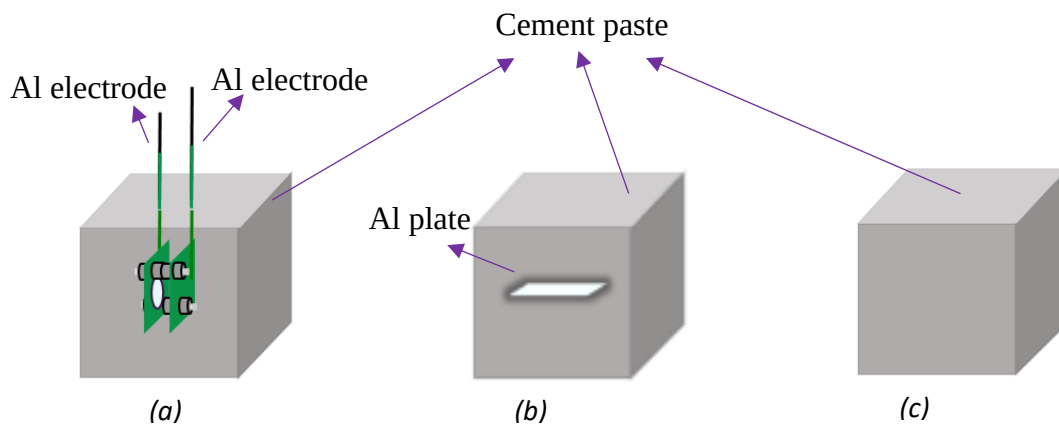


Figure 3.1 Schematics of EIS (a), SEM & GC & MIP (b) and pore solution (c) specimens.

Samples prepared for the SEM, GC and MIP analyses used the same cubic mould. The fresh cement paste was firstly poured into the mould and then a 15x15x1 mm Al plate was inserted into the centre of the mould (Figure 2.16(b)).

Moreover, pure cement paste samples were processed for the collection of pore solution (see Figure 2.16(c)).

All specimens were de-moulded after 24 h and were cured in two types of conditions (see Figure 3.2). In condition 1, the specimens, were placed in a humid Ar atmosphere. The humid atmosphere is produced by placing the specimens on a holder above the water level in a closed cell. This environment also simulates the humid and anaerobic underground environment in the real geological disposal. After about 80 days, when the corrosion rates clearly reach a steady state for OPC+LiNO₃ and OPC+Li₂CO₃ samples, these samples were transferred into a saturated Ca(OH)₂ solution i.e. limewater to simulate the resaturation of the cement paste after possible breaching of the waste protective barrier. In condition 2, the specimens were directly immersed and cured in saturated Ca(OH)₂ solution from the beginning. For electrochemical and GC tests, three repetitive samples were prepared for each condition to ensure the reproducibility of

the results. For SEM and MIP characterization, one sample was made for each selected time point to reveal the corrosion variation as a function of time. For pore solution collection, three samples were made for each time point to collect enough amount of solution for the conductivity and pH measurements.

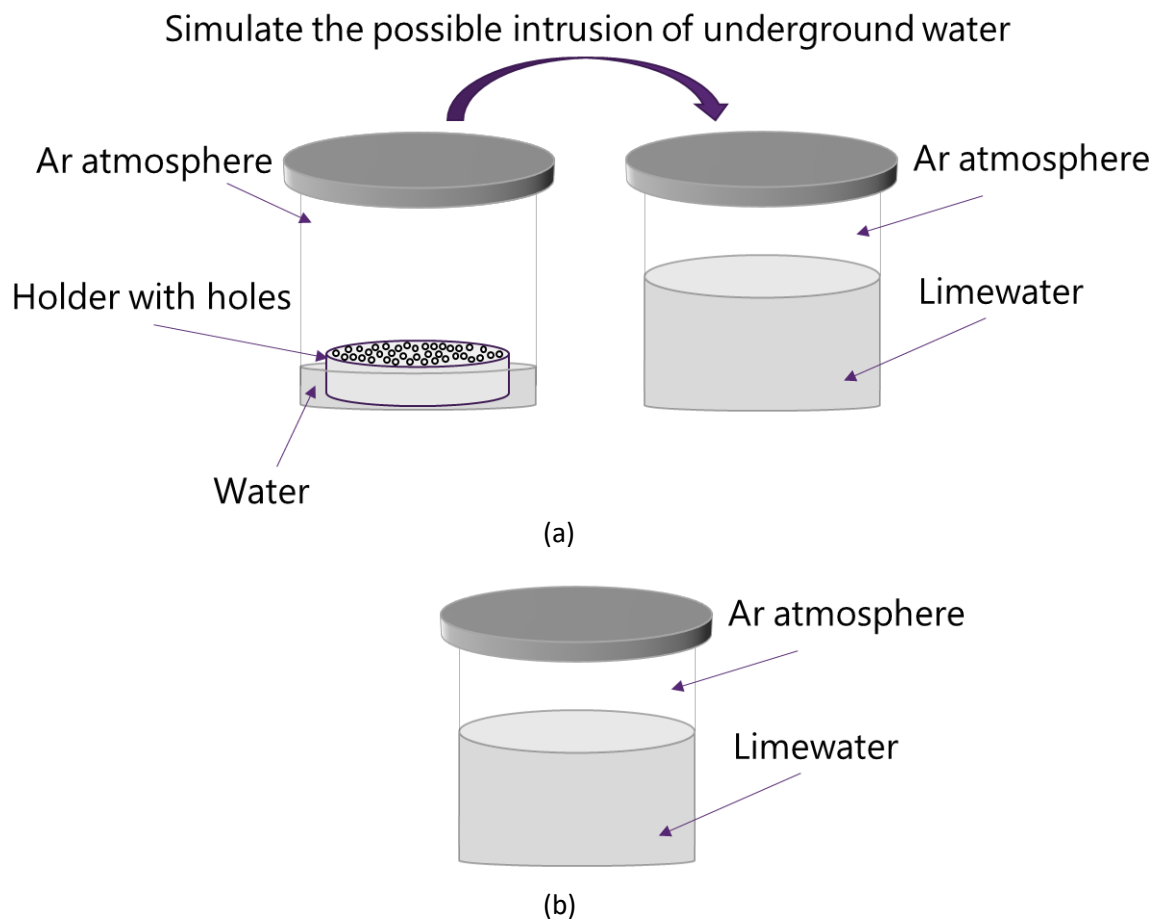


Figure 3.2 Schematic of (a) condition 1 and (b) condition 2 for the curing of samples.

3.2. Electrochemical methods

The electrochemical measurements were performed using an Autolab PGSTAT 30 potentiostat combined with the NOVA 1.8 version software.

3.2.1. Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) measures the variation of the cell or electrode impedance as a function of frequency (Figure 3.3).

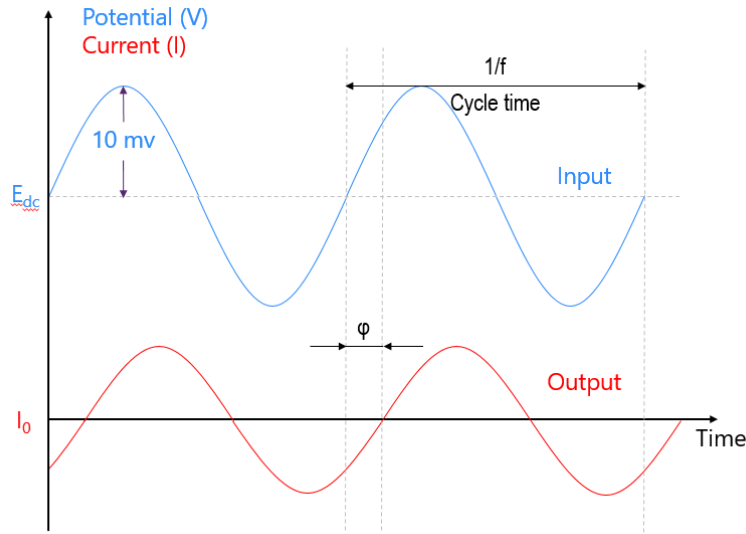


Figure 3.3 Sinusoidal current response in a linear system.

In an electrochemical cell, the potential imposed on the working electrode is a direct current (DC) mean value, E_{dc} , which is the equilibrium potential of the electrode, plus a sinusoidal alternating current (AC) component, E_{ac} , of 10 mV peak-to-peak amplitude. Such an AC signal, $E(\omega)$, can be expressed as:

$$E(\omega) = E_0 \sin(\omega t), \quad (7)$$

where E_0 is the amplitude of the input signal, ω is the frequency of the signal and t is time.

The responses measured by the electrochemical working station are the resulting current ($I(\omega)$) at the same frequency of $E(\omega)$ and its phase angle (ϕ) with respect to $E(\omega)$. Similar to $E(\omega)$, $I(\omega)$ has the form:

$$I(\omega) = I_0 \sin(\omega t + \phi), \quad (8)$$

where I_0 is the amplitude of the output signal.

Based on the expression for $E(\omega)$ and $I(\omega)$, the impedance ($Z(\omega)$) can be calculated as:

$$Z(\omega) = \frac{E}{I} = Z_0 \exp(j\phi) = Z_0(\cos \phi + j \sin \phi). \quad (9)$$

When the frequency (ω) of $E(\omega)$ changes, the corresponding variation of impedance and of phase angle can be recorded. [222]

EIS is applied to indirectly monitor electrode processes and interface states. In a general sense, an electrochemical cell can be characterised by the variation of its impedance (Z) to a series of sinusoidal excitations of different frequencies. To quantitatively analyse the cell by fitting, an equivalent circuit model is commonly constructed consisting of several electrical elements (such as resistors (R) and capacitors (C)), that have the same (for both the amplitude and phase angle) current or potential response, to a small amplitude of potential or current stimulation, as the real cell [222]. This equivalent circuit model can be

Chapter 3

regarded as the abstract expression of the cell in electrical field and all the equivalent circuit components should have a practical meaning in the physical electrochemistry (electrolyte, films, reactions, etc.) of the cell [222-225]. According to Equation (9), the expression for $Z(\omega)$ is composed of a real and an imaginary part. When the real part is plotted on the X-axis and the imaginary part is plotted on the Y-axis of a chart, a Nyquist plot is produced.

An alternative representation is the Bode plot that expresses the variation of $\log |Z|$ and ϕ as a function of $\log |\omega|$. For example, a RC parallel equivalent circuit model, Nyquist and Bode plots are shown in Figure 3.4 [226]. In practice, the equivalent circuit is always constructed according to the structure and processes of the cell. The fitting of measured EIS results determines the parameters of the components of the circuit. On the other hand, if the fitting gives abnormal parameter values to the circuit components or cannot match the Nyquist and Bode plots well, it is most likely because the equivalent circuit model is inappropriate.

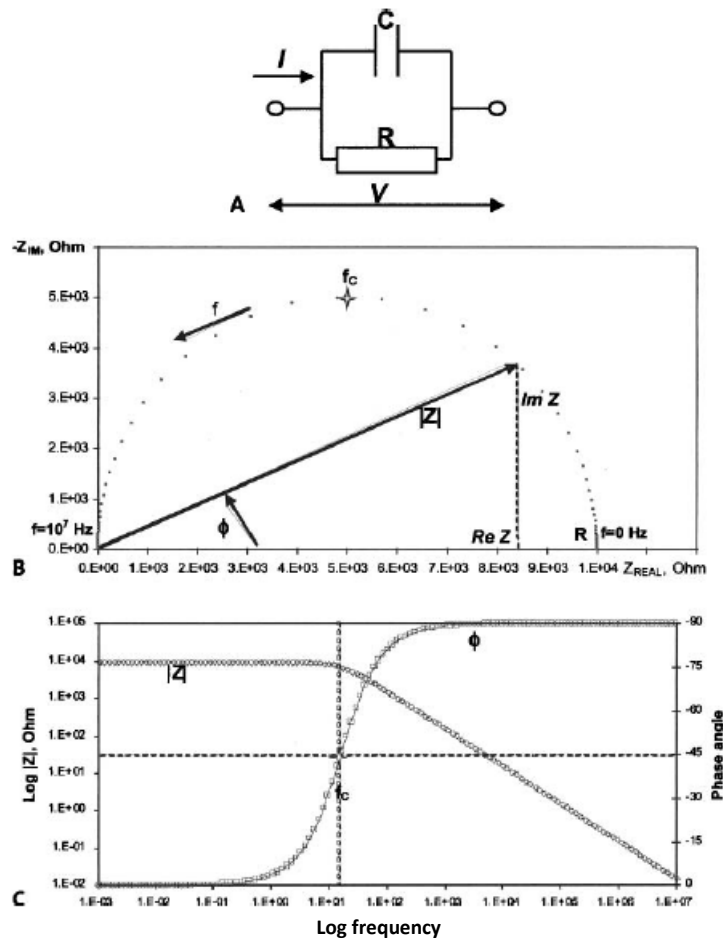


Figure 3.4 A. Equivalent circuit; B. Nyquist; C. Bode plots with impedance vector for the parallel RC circuit [226].

Chapter 3

Compared to the model in Figure 3.4, the real situation is always more complex, as shown in Figure 3.5 [126], which shows one model of aluminium corrosion in cement paste. In terms of the corrosion study, R_t (the sum of R_{t1} and R_{t2}), as the charge transfer resistance, is one of the key parameters for the corrosion rate calculation.

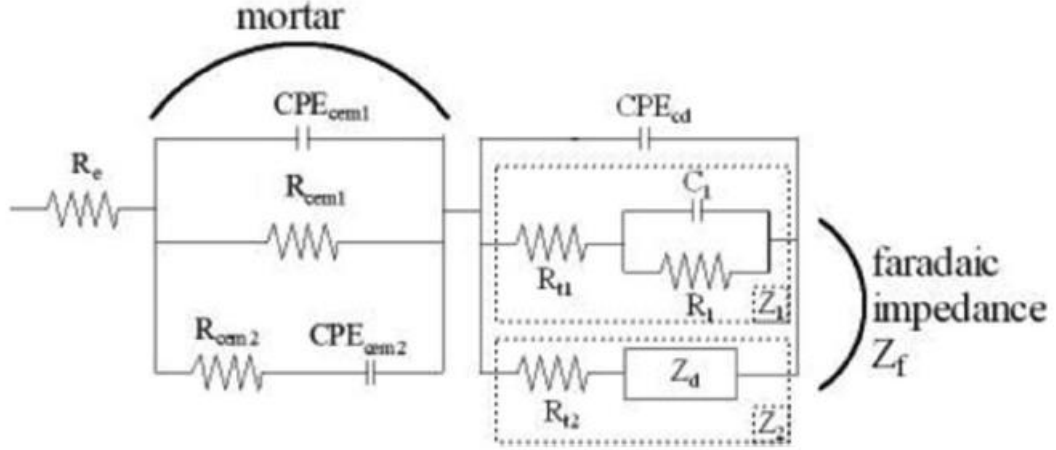


Figure 3.5 Electrical equivalent circuit characteristic of the Al corrosion mechanism [126].

In this research, the EIS spectra were recorded at the open circuit potential with a 10 mV amplitude. The frequency ranged between 10^6 Hz to 10^{-2} Hz, with 10 frequency values per logarithmic decade. The analysis and the fit of the spectra were performed using the software 'Zview'.

3.2.2. Tafel plot

The potential of a corroding electrode is related to the applied current density (and vice versa) by the following relationship (known as the Butler-Volmer equation [222,227,228]):

$$i = i_0 \left[e^{\frac{2.303\eta}{\beta_a}} - e^{\frac{-2.303\eta}{\beta_c}} \right], \quad (10)$$

where $\eta = E_{applied} - E_{corr}$, i is the current density, i_0 is the exchange current density, β_a and β_c are the anodic and the cathodic Tafel parameter.

In the Tafel extrapolation method (TP), the test electrode is polarized around 250-300 mV either side of the open-circuit potential. This can be accomplished either potentiostatically by changing the potential of the electrode by a fixed amount and monitoring the current, or galvanostatically by applying a small fixed current and measuring the resulting potential. The obtained polarization curve is called a Tafel plot.

A Tafel plot provides the variation of the resulting current i (A) as a function of the applied potential E (V) as shown in Figure 3.6 [229]. The anodic branch above E_{corr} and the cathodic branch below E_{corr}

Chapter 3

can be distinguished. When $|E - E_{corr}| > 50 \text{ mV}$ [229], the anodic branch with slope β_a and cathodic branch with slope β_c both follow the Tafel equation as

$$\eta = a + \beta \log i. \quad (11)$$

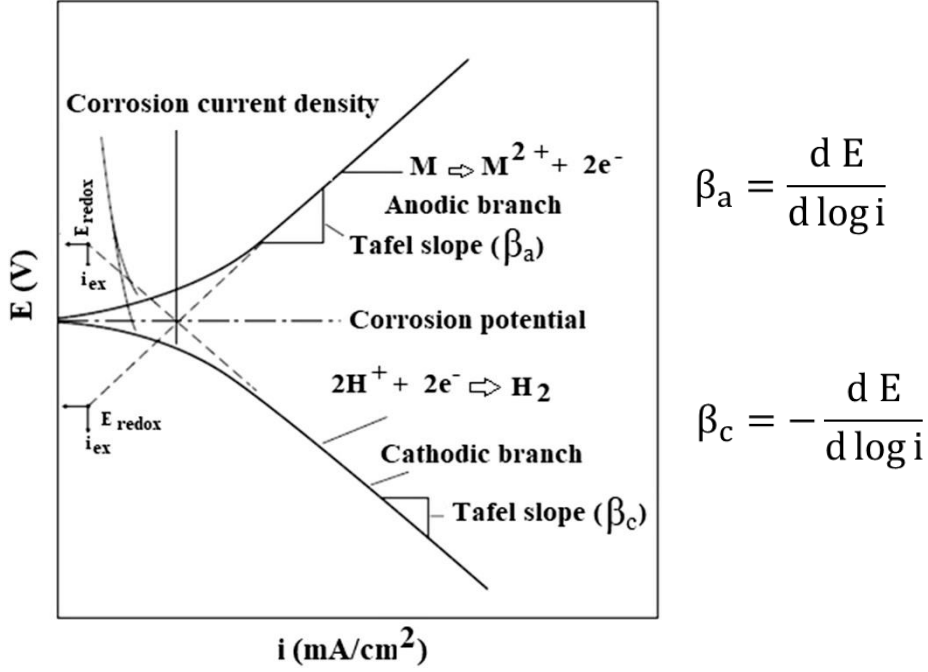


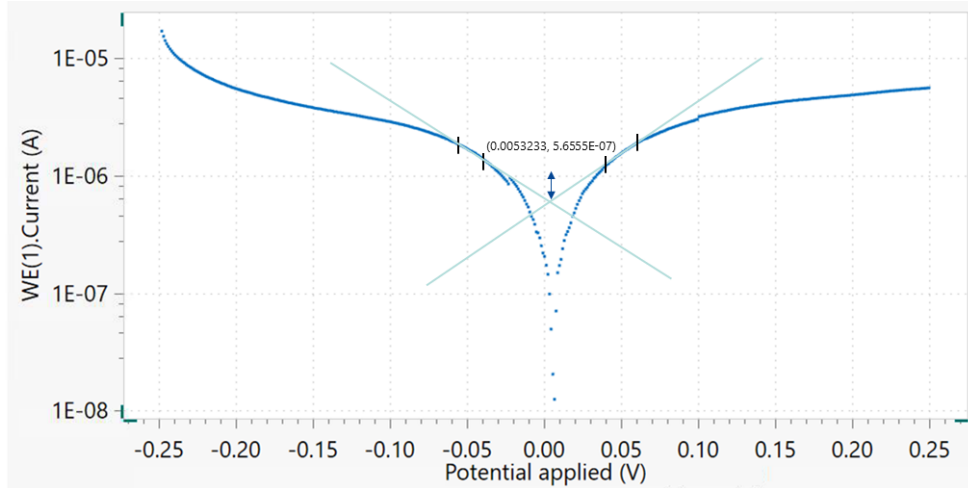
Figure 3.6 Example of a Tafel plot [229].

Then β_a and β_c can be determined from the Tafel plot and used for the calculation of the Stern Geary Constant (B) by:

$$B = \frac{1}{2.303} \left(\frac{\beta_a \times \beta_c}{\beta_a + \beta_c} \right). \quad (12)$$

The Stern Geary constant (B) was eventually used together with R_t values, obtained from EIS fitting to calculate the corrosion rate. Commonly, the Tafel slopes β_a and β_c are usually fixed in a certain system which means they nearly do not change with time. Since the Tafel plot measurement modifies the surface state, it is measured at the end of electrochemical experiments [230].

A typical example of how the values of β_a and β_c were deduced from the Tafel plots is illustrated in Figure 3.7, Tafel regions (always around $\pm 60 \sim 120 \text{ mV}$ to the E_{corr} [231]) were chosen manually to calculate the slopes β_a and β_c . (The results are provided and discussed in Section 4.7.2)



Results

Ecorr, Obs 0.0066136 V
 jcorr 2.5136E-07 A/cm²
 icorr 5.6555E-07 A
 Corrosion rate 0.0027403 mm/year
 Polarization resistance 41833 Ω
 Ecorr, Calc 0.0053233 V
 |ba| 0.10361 V/dec
 |bc| 0.11487 V/dec
 E Begin -0.052795 V
 E End 0.059357 V

Figure 3.7 Example of the Tafel plot of an OPC+LiNO₃ sample after 121 days in condition 1.

Tafel plots in this study were measured potentiodynamically from -0.25 V to +0.25 V vs. OCP with a scanning rate of 0.167 mV/s.

3.2.3. Corrosion rate

The corrosion current (I_{corr}) can be estimated by:

$$I_{corr} = \frac{I_{appl}}{2.3\Delta\phi} \left(\frac{\beta_a\beta_c}{\beta_a+\beta_c} \right) = \frac{B}{R_t}, \quad (13)$$

where R_t and B are the charge transfer resistance and Stern Geary Constant, respectively. As introduced in Section 3.2.1 and 3.2.2, these parameters can be obtained from EIS and Tafel respectively. Then, I_{corr} can be used to calculate the corrosion rate as:

$$V_{corr} (in m \cdot y^{-1}) = 3.27 \times \frac{I_{corr}}{\rho} \times EW, \quad (14)$$

with ρ as the metal density (g·cm⁻³, $\rho_{Al} = 2.7$ g·cm⁻³) and EW as equivalent weight, respectively. EW is calculated by dividing the atomic weight of an element with the valence of the metal, in this case the Al atomic weight is 27 and the valence is 3, so $EW_{Al} = 27/3 = 9$.

3.3. Gas chromatography

Gas chromatography (GC) is one type of chromatography techniques used for the separation and analysis of gas compounds. Typical applications of GC include qualitative and quantitative analysis of gaseous specimens such as hydrogen measurement in the context of the present research [232]. Besides, GC can be used to purify chemical species from a mixture in preparative chromatography [233,234]. A schematic of a GC setup is shown in Figure 3.8 [235]. When transported into the column, placed in an oven, the injected sample will be immediately eluted by the carrier gas. However, the movement of the sample through the column is inhibited by the adsorption of the molecules onto the packing materials (i.e. the stationary phase) in the column. Since each type of molecule will pass through the column at a different rate, the various components of the injected sample are separated and thus they will reach the end of the column at different times (retention time). The column is placed in an oven, which is heated during the analysis to elute the less volatile components. The outlet of the column is inserted into a detector in which the various components are analysed (i.e. the amount of each component and the time at which each component reaches the outlet of the column). The retention time of a specific molecule depends on the strength of gas adsorption, which is essentially determined by the type of molecule and on the stationary phase materials. Besides the adsorption, other parameters that can influence retention time, including the carrier gas flow rate, the column length and the temperature.

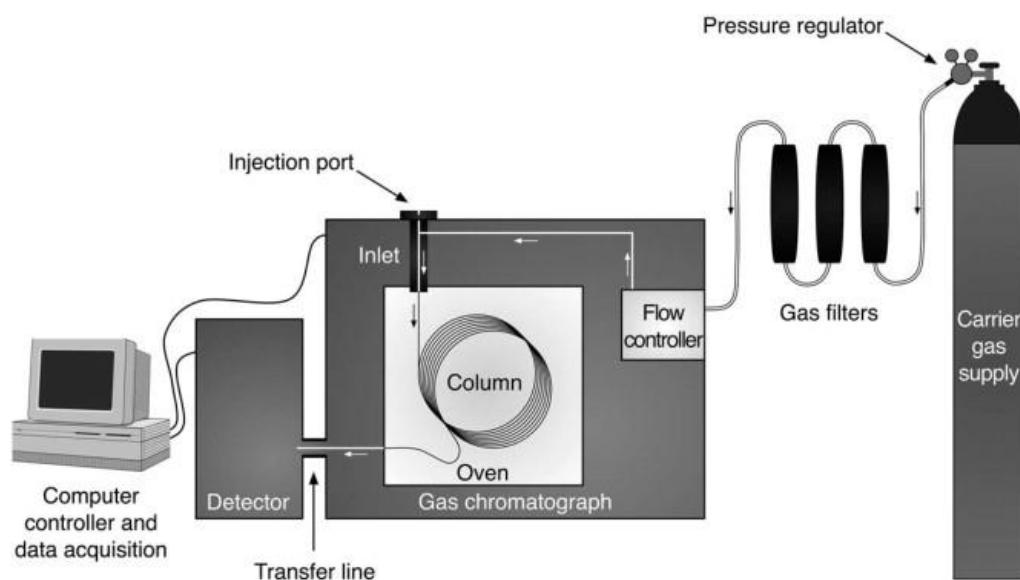


Figure 3.8 Schematic of a gas chromatograph and its main components [235].

In this study, GC technique was used on a regular basis to monitor the volume of hydrogen produced with time. The specimens were stored in a gas-tight container. After certain period of time, a gas specimen was extracted into a 50 ml vessel (see Figure 3.9) and injected in a Shimadzu GC-2010 Plus type GC

Chapter 3

equipment, using a ShinCarbon ST column and a Barrier Discharge Ionisation Detector (BID). The H_2 concentration was quantified by comparing the area under the H_2 peak with a calibration curve obtained by injecting argon gas containing 1 to 10000 ppm H_2 . At the beginning and at the end of a day of measurements, a 100 ppm H_2/Ar gas was injected into the GC for quality control. Because the container volume is known, the amount of hydrogen generation over a given time interval can be determined and correlated to the corrosion rate of Al plates in cement pastes. In order to lower as much as possible the volume of H_2 gas trapped in the cement paste or adsorbed on the wall of the container, the containers were slightly patted several times before sampling. The atmosphere in the container was thoroughly refreshed by Ar every time after the measurement to remove the residual hydrogen generated during the previous period.

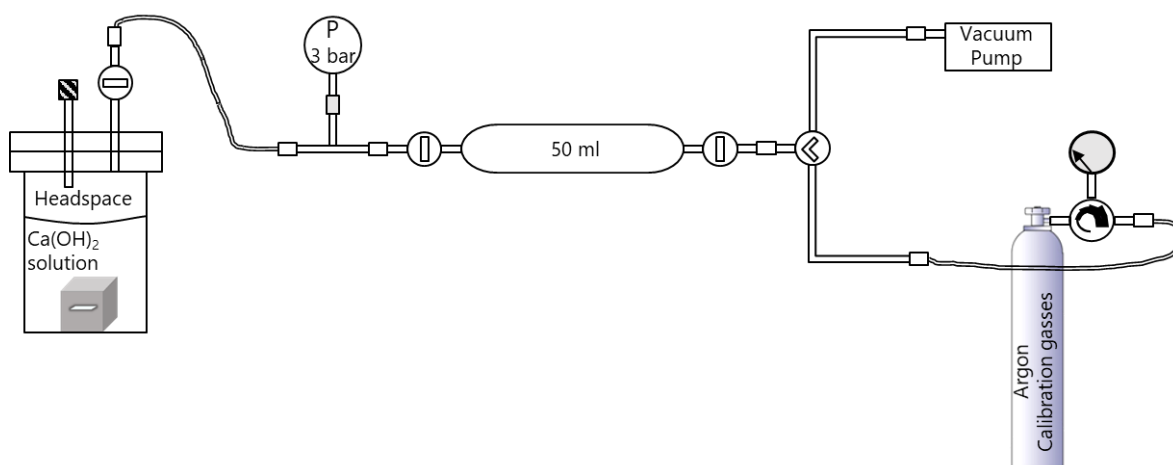


Figure 3.9 Schematic of a gas specimen extraction.

A typical example of a gas chromatogram is given in Figure 3.10. In this study, the characteristic peak of hydrogen is located at about 0.55 min (the huge peak afterwards is attributed to the carrier gas). The area under the H_2 gas peak is proportional to the concentration of H_2 present in the injection vessel. Because the concentration values of H_2 in the injection vessel and in the sample container are the same, the volume of H_2 in the sample container can be obtained. Then the volume of H_2 generated in the sample container under normal pressure can be obtained by Boyle's law:

$$P_1 V_1 = P_2 V_2, \quad (15)$$

where P_1 and V_1 are the pressure and the volume of H_2 in the sample container, P_2 and V_2 are the pressure and the volume of H_2 under normal pressure. Since the density of H_2 under normal pressure ($0.08988 \text{ g}\cdot\text{L}^{-1}$) is already known, the mass and the amount of H_2 generated by Al in the sample container can be determined from the volume of H_2 under normal pressure.

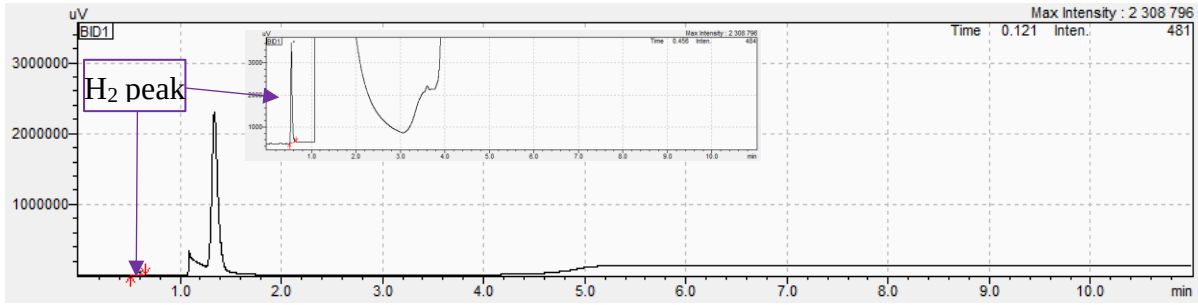
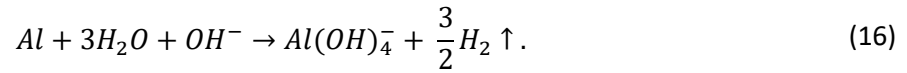


Figure 3.10 Example of gas chromatography result.

In the condition of these tests, i.e. high pH systems under anaerobic atmosphere (the pH of the cement paste pore solution is usually above 12.5 and GC samples were prepared and stored in Ar atmosphere), the amount of the consumed aluminium is linked to that of the formed hydrogen by the following reaction [160]:



Therefore, the consumed Al (mol) can be quantitatively determined and the average corrosion rate over a certain period can be calculated as follow:

$$v_{corr} = \frac{Al \text{ corroded} \times M}{\rho \times S \times time} \times 10^6 (\mu m \cdot y^{-1}), \quad (17)$$

where M is the molar mass of aluminium ($\text{g} \cdot \text{mol}^{-1}$, $M_{Al} = 26.98 \text{ g} \cdot \text{mol}^{-1}$), ρ is the metal density ($\text{g} \cdot \text{cm}^{-3}$, $\rho_{Al} = 2.7 \text{ g} \cdot \text{cm}^{-3}$) and S is the exposed surface area (m^2).

3.4. Scanning electron and energy – dispersive X - ray spectroscopy

Scanning Electron Microscopy (SEM) produces images by scanning the surface with a focused electron beam. The electrons interact with atoms on the surface, creating signals such as secondary electrons (see Figure 3.11 [236]). The surface topography can be imaged owing to the variation of the intensity of the detected signal.

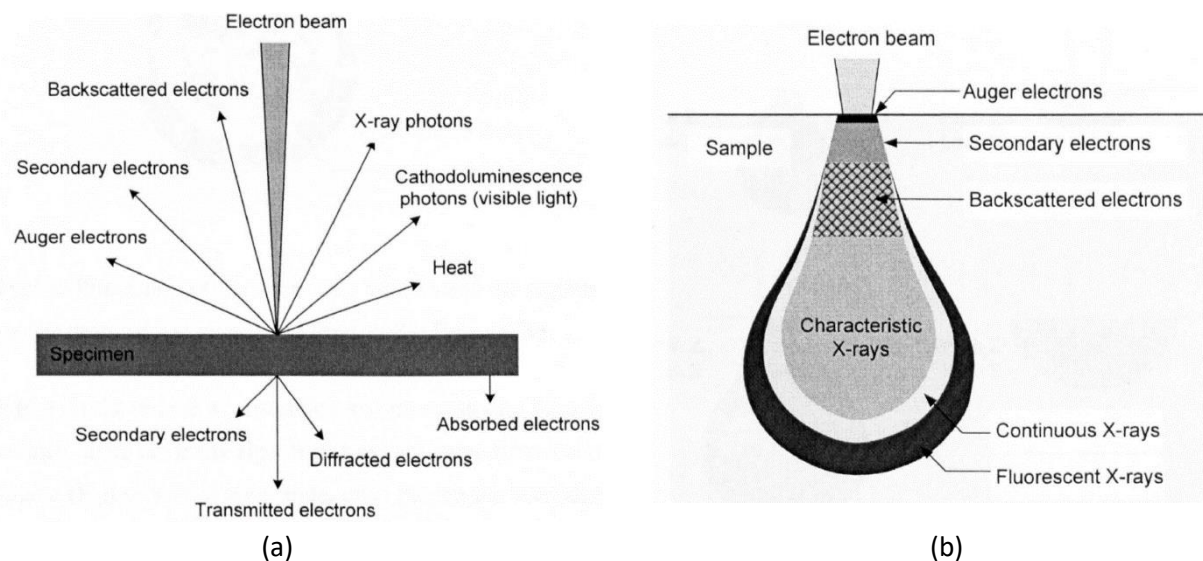


Figure 3.11 Signals excited by electron beam (a) and the interaction volume and the regions of signals (b) [236].

In this study, SEM is used to determine the thickness of the corrosion product film formed on Al, which can be considered as a direct indicator of the corrosion rate. Furthermore, analysis of the aluminium/corrosion product film/cement interfaces can provide valuable information such as the morphology of the corrosion attack, the initiation of cracks and the delamination of the corrosion product film.

Energy-dispersive X-ray spectroscopy (EDX) provides qualitative or semi-quantitative element analysis. A series of X-ray photons are ejected by atoms when excited by an energy source (such as the electron beam of an electron microscope). The energy difference of X-ray provides a characteristic spectrum based on the atom species. The position of the peaks in the spectrum enables the identification of the element species, while the intensity of the peak corresponds to the element content. In this study, EDX is mainly used to investigate the elemental composition and distribution at the aluminium/corrosion product film/cement paste interface. The EDX results help to understand the chemical compositions of corrosion products and the diffusion of elements at the interface.

After one SEM-EDX specimen was cut and prepared at each selected time point, SEM-EDX characterization was then carried out with a Phenom Pro X apparatus using an accelerating voltage of 15 kV and a working distance fixed automatically. As there is no internal standard in the apparatus, EDX only provides semi-quantitative analysis.

The thickness variation of the corrosion product film extracted from SEM micrographs is then used to calculate the corrosion rate. The mean thickness at each time point is determined from 12 thickness

measurements performed at different locations of a SEM sample. Then, the average corrosion rate during a time interval can be calculated using:

$$v_{corr} \text{ (in } \mu\text{m} \cdot \text{y}^{-1}) = \frac{T_{t_2} - T_{t_1}}{t_2 - t_1}, \quad (18)$$

where T_{t_1} , T_{t_2} are the mean thickness values of the corrosion product film at times t_1 and t_2 .

Note that the SEM method is not suitable for pure OPC samples, because severe cracks emerge in the cement paste just after a few days, which interfere with the normal growth of corrosion product film. Meanwhile, it is difficult to identify the boundary between the corrosion product film and the cement paste in some pure OPC samples, which brings some uncertainty in the determination of the film thickness. More details, e.g. regarding the cracks in the cement paste and the delamination of the corrosion product film, from SEM analysis are provided in Section 4.9, while the study of v_{corr} using the SEM method is provided together with EIS and GC in Section 4.7.

3.5. General effective medium theory

A methodology is proposed to determine the cement paste porosity based on EIS results. The first step is the construction of an appropriate model to relate the electrical resistivity and the cement paste porosity. Considering the complexity of cement paste as a compound system, the model has to be simplified compared to reality by retaining only the dominant micro-structural parameters, e.g. porosity and tortuosity.

A large number of two-phase models [206], which provide the relationship between effective properties (electric conductivity, thermal conductivity, etc.), already exist as presented in the state of art. Among them, the Effective Medium Theory (EMT) tackles materials with a completely random distribution of the constituents, which is the case for the cement paste. However, EMT cannot deal with some special cases, e.g. a conductor-insulator composite close to the percolation threshold of the conductive phase [237].

To overcome this drawback, the General Effective Media (GEM) model, proposed by McLachlan et al. [207-210], further combines percolation and EMT theories and puts forward a relationship between the electrical conductivity (= 1/resistivity) and the microstructure parameters, given by [207,237]:

$$\phi = \frac{\left[\left(\frac{\sigma_p}{\sigma_{eff}} \right)^{\frac{1}{t}} + \left(\frac{1-\phi_c}{\phi_c} \right) \right] \times \left[\left(\frac{\sigma_s}{\sigma_{eff}} \right)^{\frac{1}{t}} - 1 \right]}{\left[\left(\frac{\sigma_p}{\sigma_{eff}} \right)^{\frac{1}{t}} + \left(\frac{1-\phi_c}{\phi_c} \right) \right] \times \left[\left(\frac{\sigma_s}{\sigma_{eff}} \right)^{\frac{1}{t}} - 1 \right] - \left[\left(\frac{\sigma_p}{\sigma_{eff}} \right)^{\frac{1}{t}} - 1 \right] \times \left[\left(\frac{\sigma_s}{\sigma_{eff}} \right)^{\frac{1}{t}} + \left(\frac{1-\phi_c}{\phi_c} \right) \right]}, \quad (19)$$

where ϕ is the volume fraction of the low-resistivity phase, i.e. porosity, ϕ_c is the percolation threshold of the capillary pores, t is the critical exponent characterizing the conductivity of the conducting regions in

the microstructures, σ_p is the conductivity of the capillary pore phase, and σ_s is the conductivity of the solid-gel phase. These different parameters are discussed one by one hereafter to explain how the identification is performed based on literature data or on experimental results.

3.5.1. Percolation threshold of the capillary pores ϕ_c

The percolation threshold of the cement system is the point at which the capillary pores first span the system, i.e., the first appearance of long-range connectivity. It can be seen in Figure 3.12 that the effective conductivity of the cement paste increases significantly at around ϕ_c due to the connection of individual pores. According to literature [194, 238-246], ϕ_c is independent of the water/cement ratio and can range from 0.05 to 0.22. Garboczi et al. [243] studied the percolation of the cement paste by modeling their studied system with a three-dimensional digital image. When a high resolution of 400^3 pixels ($0.25 \mu\text{m}/\text{pixel}$) is chosen, the threshold is 0.12, which corresponds with the result obtained in the multi-scale model of Prabhu et al. [244]. Besides, ϕ_c decreases in this model with the increment of the digital resolution, meaning that the smaller the pores taken into account, the smaller the ϕ_c . Navi et al. [245] also found a similar relationship between the percolation threshold and the resolution in their mathematical model. They reported that in normal cement pastes, with a 10% total porosity, more than 95% of capillary pores are connected under a $2 \mu\text{m}/\text{pixel}$ resolution. Tumidajski et al. [246] experimentally tested the porosity and the electrical resistivity of different cement pastes. Figure 3.13 was drawn according to their results. Figure 3.13 shows that the conductivity (1/resistivity) changes most significantly at around 10.4%, which fulfils the definition of the percolation threshold. Hence, $\phi_c = 0.104$ was selected in the present study.

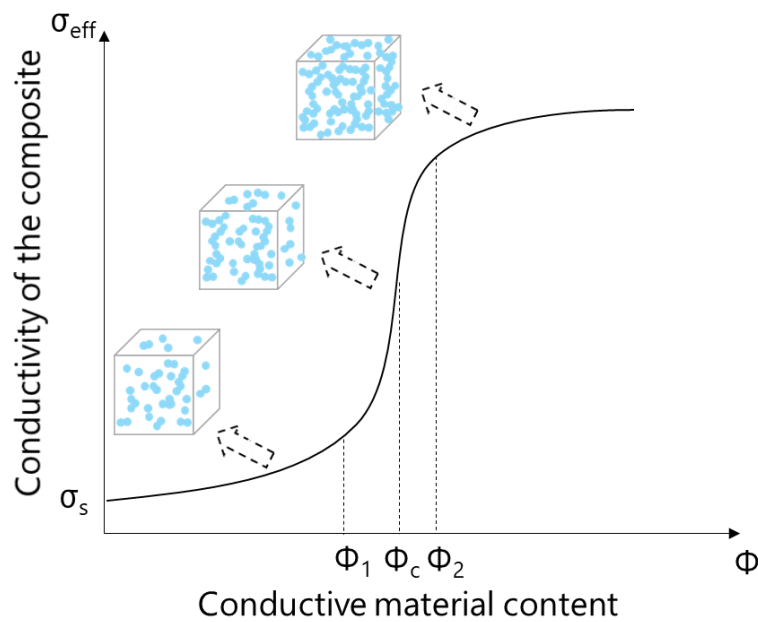


Figure 3.12 Relationship between the effective conductivity and porosity in cement pastes.

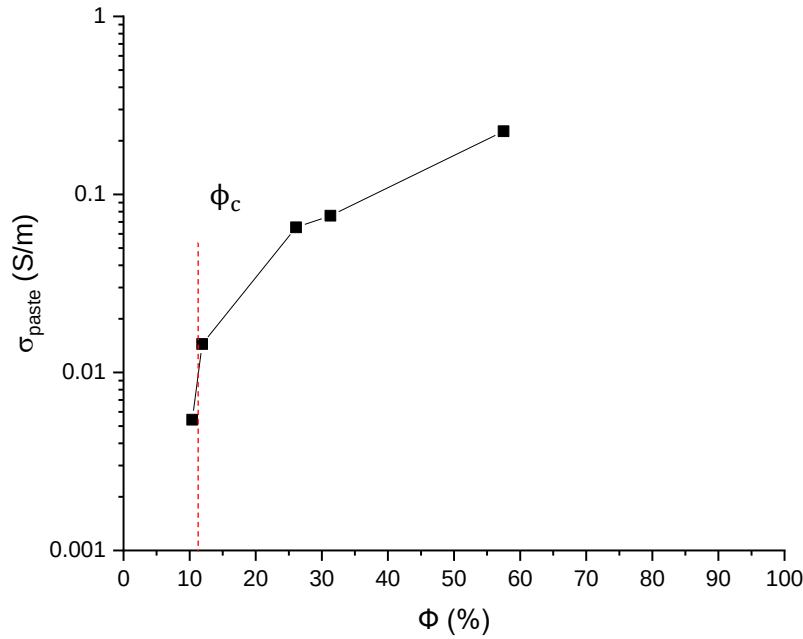


Figure 3.13 Porosity and conductivity of cement pastes determined by Tumidajski et al [216].

3.5.2. Critical exponent t

The larger the t value, the more tortuous the network, or the rougher the surface of the conductor. Different ranges of t are reported in literature. Theoretical lattice models are used to predict t in an ideal 3D lattice system providing a t value equal to 2 [247]. McLachlan et al. [207] and Isichenko [248] reported that t ranges between 1.4 and 2.46 for composites based on computational simulations. Note that Neithalath et al. [201] reported that the best fitting values of t should range from 2-5 for different cement pastes by simply trying different t values in the GEM model. Other researchers adopted $t = 2$ directly [200,242]. In the present study, we retain the value $t = 2$ for all cement pastes.

3.5.3. Conductivity of capillary pore phase σ_p

When the cement paste is fully saturated, the capillary pores are entirely filled with pore solution and σ_p is equal to the conductivity of the pore solution. When the capillary pores are partly saturated, σ_p is lower than the conductivity of the pore solution until reaching zero when the capillary pores are dry. The different saturation conditions are illustrated in Figure 3.14. The pore solution conductivity can be directly determined from experiments that extract and measure the pore solution [202]. Buenfeld et al. [249] reported that the pore solution resistivity is in the range of 0.3-0.4 $\Omega \cdot m$ (i.e. 2.5-3.3 S/m for the σ_p conductivity), with a small change over 4-20 weeks for OPC mortar of 0.4 and 0.6 water/cement ratios. Neithalath et al. [201] used a model [250,251] that utilizes the change in non-evaporable water to predict the conductivity of simulated pore solutions. This model reported that the pore solution conductivities of OPC pastes possessing a water/cement ratio of 0.32 and 0.42 are respectively equal to 17 S/m and 13 S/m

Chapter 3

after the initial rapid increase during the first 10 days [201]. However, limited validation of this method to determine the electrical conductivity of cement paste pore solution is reported in the literature [203]. In this study, the conductivity of the pore solutions was experimentally measured as addressed in Chapter 5.5 and was used for the value of σ_p . Note that the use of the conductivity of the pore solution for σ_p leads to an underestimation of the calculated porosity when the pores are not fully saturated. It is as if only the space occupied by the pore solution is taken into account, while the empty pore space is regarded as part of the solid-gel phase.

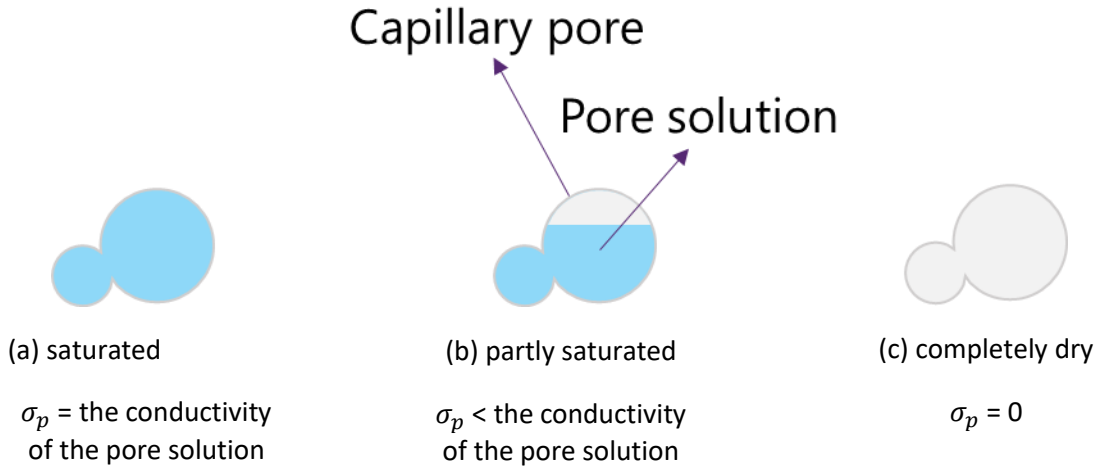


Figure 3.14 Different saturation conditions of capillary pores.

3.5.4. Conductivity of solid-gel phase σ_s

The conductivity σ_s for OPC pastes is difficult to be directly measured. Zhang et al. [200] proposed that the appropriate value of σ_s/σ_p ranges from 10^{-3} to 10^{-2} and chose a value of 0.0025 in their model. Neithalath et al. [201] used $\sigma_s = 0.0075$ S/m, which is close to the value in the study of Ma et al [252]. Christensen et al. [253] reported that σ_s is estimated as equal to $(1 - \phi) \times 10^{-3}$ S/m. The work of Garboczi et al. [242] estimated that σ_s/σ_p varies continuously between 0.001 and 0.0025. Oh et al. [239] deduced the value of σ_s/σ_p according to the relationship between the effective diffusivity and the conductivity. They reported that the value of σ_s/σ_p is about 2.0×10^{-4} for OPC pastes. In this study, σ_p will be shown to be in the range from 7 to 16 S/m (see Chapter 5.5) and hence σ_s should range from 0.00035 to 0.0008 S/m. In fact, it is very likely that σ_s slightly fluctuates. On the one hand, many factors e.g. the setting time, the composition and the curing condition, can play a role, which lead to different σ_s values. On the other hand, the main contribution for the solid-gel phase conductivity should always come from the C–S–H phase in all types of OPC pastes, which means that the σ_s range is limited. In this study, 0.0008 S/m has been selected as a fixed σ_s value. In fact, σ_s and σ_p have a relatively low influence on the porosity compared with ϕ_c , t and

σ_{eff} . Trials on different values indicate that there is just an insignificant effect on the porosity result no matter 0.001 S/m, 0.0008 S/m or even 0.00035 S/m is chosen.

3.5.5. Conductivity of overall cement paste σ_{eff}

The effective conductivity σ_{eff} is regarded as a homogenized material property. The relationship between the resistance and the conductivity is given by Eq. (20):

$$\sigma_{eff} = \frac{K}{R_{eff}}, \quad (20)$$

where K is the cell constant and R_{eff} is the effective resistance of the system. The value of K only depends on the geometry of the electrochemical cell and is fixed for a specific cell, irrespective of the type of electrolyte. Hence, in order to determine the K value, an impedance experiment was carried out in saturated Ca(OH)_2 solution using the same two-electrode cells as the ones cast in the cement pastes (Figure 3.15(a)). EIS tests were then carried out in a frequency range of 1 MHz to 10 mHz using a 10 mV peak-to-peak AC potential signal. The results as a function of time are summarised in the Nyquist plots shown in Figure 3.15(b). Regardless of the experimental time, these Nyquist plots all have the trend to intersect the Z' axis at around 100 Ω in the high frequency region, which is the left part of the graph. This Z' value could be roughly regarded as the R_{eff} of the cell in saturated Ca(OH)_2 solution because the equivalent circuit of the cell system presented in Figure 3.15(c) can be simplified to be R_s , which is the solution resistance, in a high frequency region. The conductivity σ_{eff} of the saturated Ca(OH)_2 test solution was experimentally measured by a conductivity meter and was found to be 1.03 S/m. Therefore, the K value was calculated to be equal to 103 as determined by Eq. (20) using R_{eff} in saturated Ca(OH)_2 solution and σ_{eff} of saturated Ca(OH)_2 solution. Then R_{eff} of the cement paste is still needed to calculate σ_{eff} of the cement paste. R_{eff} is approximated by the resistance of connected capillary pores (R_{cem1}) determined by the fitting of the equivalent circuit in Section 4.5

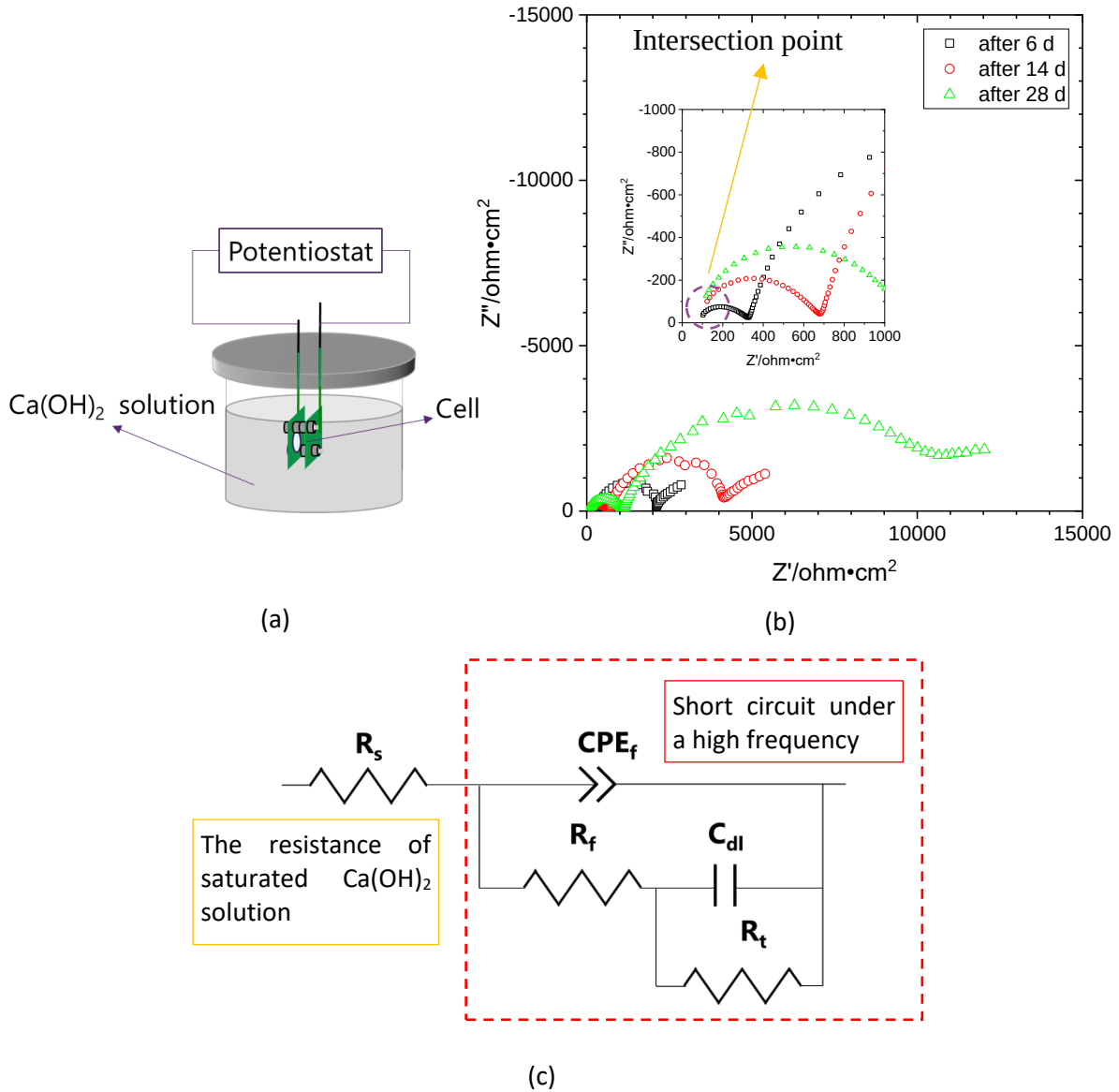


Figure 3.15 EIS test setup (a), Nyquist plots (b) and the equivalent circuit model (c) of the cell in saturated Ca(OH)_2 solution over one month.

3.6. Pore solution extraction

Because the conductivity of the cement pore solution needs to be known for the application of the GEM theory, the cement pore solution was experimentally collected from the cement paste samples. A universal testing machine with corresponding accessories (a plunger, a hollow steel tube and a pedestal) as shown in Figure 3.16 was used to extract solution from the samples. The paste sample was placed in the hollow tube, then the testing machine imposed a compressive force up to 900 kN on the plunger. The pore solution squeezed out from the paste sample was collected in a ring-like reservoir in the pedestal. A series

of cement samples were produced and squeezed to collect cement pore solutions during 120 days, followed by conductivity and pH measurements (see Section 5.5).

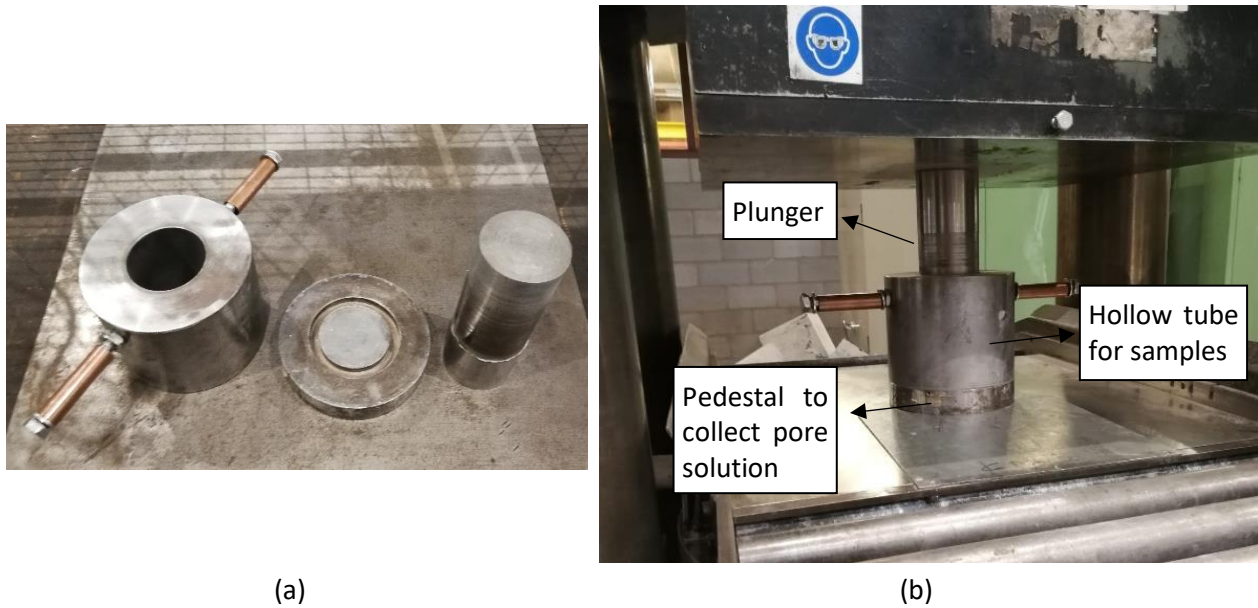


Figure 3.16 Accessories (a) and the setup (b) of pore solution extraction.

3.7. Mercury intrusion porosimetry

Mercury intrusion porosimetry (MIP) is a characterization technique for porous materials. MIP is capable of providing a series of information, e.g. the pore size distribution, the total porosity, the skeleton and apparent density.

The prepared sample, which can be pellets, granules, other pieces, or powder, is placed into a holder or cell called a penetrometer. The cell is then installed into a pressurized chamber. In the chamber, the cell is evacuated, and backfilled with mercury. After that, the chamber will gradually increase the cell pressure to force mercury to intrude into the pores in the porous material. With the increase of pressure, the filling proceeds from large pores to small pores.

The Washburn Equation (Eq. (21)) [254] relates the applied pressure to pore diameter according to the premise of the non-wetting liquid (mercury in this case):

$$P = \frac{-4\gamma \cos \theta}{d}, \quad (21)$$

where P is pressure, γ is surface tension of the liquid, θ is contact angle of the liquid, and d is diameter of the capillary.

The pore size distribution can be determined from the volume intruded at each pressure increment. Total porosity can be easily determined from the total volume intruded. For obvious reasons, MIP cannot

be used to analyse closed pores, because the mercury has no way of entering that pore. In Figure 3.17 [255], the closed pores and blind pores cannot be measured by MIP.

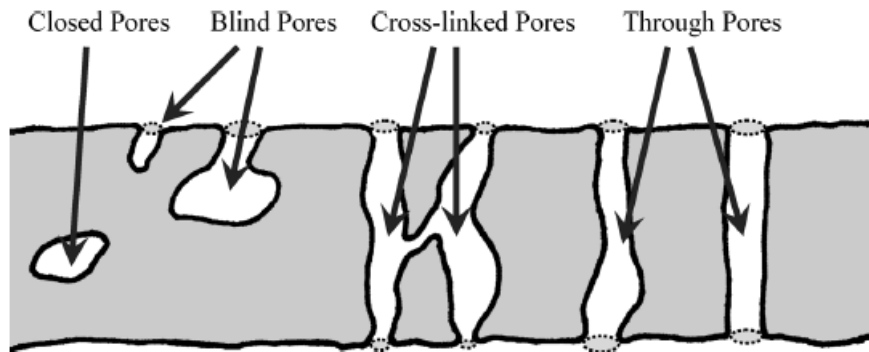


Figure 3.17 Schematic representation of pores [255].

In this work, MIP experiments were performed using a PASCAL 140/440 porosimeter in which the mercury pressure is monotonically increased linearly up to a maximum pressure of 200 MPa. To prepare dry samples with little microstructural damage for MIP tests, the cubic elements were immediately immersed in diethyl ether for 24 hours at each selected time point. Then, the used ether solution was replaced and the sample was immersed in fresh ether for another 24 hours. Finally, the sample was placed in a vacuum chamber for 24 hours to evaporate the ether out of the sample. This immersion procedure into ether is applied in order to remove the water inside the cement paste and hence to stop the corrosion process and cement hydration. Afterwards, samples were cut into pieces with irregular shapes of approximately 1.5 g, taken from a corner of a specimen.

4

Corrosion inhibition of AA1100 in Portland cement pastes by lithium salts

The corrosion results have been organised and already published in the paper “Li, X., Caes, S., Pardoen, T., De Schutter, G., Hauffman, T., & Kursten, B. (2023). Inhibition effect of lithium salts on the corrosion of AA1100 aluminium alloy in ordinary Portland cement pastes. Corrosion Science, 111325.” This chapter is based on the aforementioned publication with several additions and changes.

Preamble: The goal of this chapter is to answer the primary question of this study, i.e. whether the application of LiNO_3 or Li_2CO_3 is a viable solution for mitigating the corrosion of BR1 aluminium cladding when embedded in a Portland cementitious material.

Chapter 4. Corrosion inhibition of AA1100 in Portland cement pastes by lithium salts

4.1. Introduction

In the context of geological disposal of BR1 fuel, one of the possible options is the direct disposal of the fuel capsules, leading to a direct contact of the aluminium cladding with Portland cement pastes. In order to decrease the corrosion rate of aluminium in such alkaline medium, the corrosion inhibition effect of LiNO_3 and Li_2CO_3 on AA1100 embedded in OPC pastes is investigated by a combination of different methods in this chapter.

First, the corrosion rates are investigated by electrochemical techniques i.e. Electrochemical Impedance Spectroscopy (EIS) and Tafel polarization tests. The EIS results as a function of time are normally summarised in the Nyquist and Bode plots (called impedance spectra). Some information involving the properties of the cell system such as the corrosion variation can be directly identified. However, because of the overlapping of the electrochemical responses from different cell components, a quantitative analysis is difficult.

Therefore, an equivalent circuit model is constructed for EIS fitting to quantitatively understand the corrosion process. This equivalent circuit is established based on the physical structures of the cell and the fitting enables the separation of different components from the impedance spectra. This corrosion study only focuses on the charge transfer resistance (R_t) and the resistance of the formed corrosion product film (R_f), obtained by EIS fitting. R_t is used together with the Stern Geary constant (B) obtained from Tafel polarization to determine the corrosion rate by the method addressed in Section 3.2.3. The corrosion product film thickness determined by SEM and the hydrogen gas produced during the corrosion reaction measured by GC are also used to calculate the corrosion rates and were compared together with the results obtained from EIS. Furthermore, because the R_f value reveals the protection ability of the corrosion product film to some extent, it is also analysed and compared with the results reported in the literature. This study mainly focuses on studying the effectiveness of LiNO_3 and Li_2CO_3 as corrosion inhibitor for AA1100 in OPC pastes and on identifying the influence of two different curing conditions of the cement pastes on the corrosion process of AA1100.

Furthermore, the morphology and the chemical composition of the aluminium/corrosion product film/cement paste interface was studied by SEM and EDX, respectively. In the EDX analysis, attention was mainly focused on obtaining the element distributions of Al, O, Ca and Si, because Al and O are the main elements of the corrosion products and Ca and Si are typical elements of the cement paste. These analyses should help us understanding the corrosion mechanisms.

Chapter 4

Finally, the corrosion processes of aluminium embedded in Portland cement pastes with/without lithium are hypothesized on the basis of the results obtained by experiments and the mechanisms proposed in literature.

4.2. Methods

This chapter uses different methods to investigate both the corrosion rate and the corrosion product film. These techniques are classified in Table 10. The details of these methods were presented in Chapter 3.

Table 10. Methods for the corrosion study.

	Parameter investigated	
Tafel	Stern Geary constant (B)	
EIS	The charge transfer resistance (R_t)	The resistance of the corrosion product film (R_f)
GC	The amount of H_2 generated	
SEM	The thickness of the corrosion product film	The morphology of the corrosion product film
EDX	The chemical composition of the corrosion product film	

4.3. The validity of EIS results

In order to ensure the validity of EIS measurement data, some conditions involving the measured system have to be fulfilled according to the Linear Systems Theory [256-258]:

- Linearity: the output response exhibits a linear relationship to the perturbation applied.
- Causality: the output response of the system is only caused by and is solely a function of the perturbation (input signal) applied.
- Stability: the electrochemical system does not change with time over the duration of the test, and the system immediately returns to its initial state without further oscillations once the measurement is terminated.

- Finiteness: the impedance data are finite for all values of frequency.

In this research, the quality of the EIS data was first examined experimentally by running the measurement first in the descending frequency step direction, i.e. from high (1 MHz) to low (0.01 Hz) frequencies, followed by the measurement in the ascending direction, i.e. from low to high frequencies, to confirm the stability constraint of the system. If the stability condition is satisfied, the two results should be close regardless of the scanning direction. An example of EIS plots, for both high-to-low and low-to-high frequency directions, is given in Figure 4.1. For OPC+LiNO₃ and OPC+Li₂CO₃ samples, the scanning direction has little influence on the EIS results. For the OPC sample, there are some tiny differences between the results obtained from the two frequency scan directions, especially in the low and middle frequency regions. This can be attributed to the fact that the corrosion process in the OPC sample changes the system relatively faster. However, neither the shapes of the two plots nor the corresponding EIS fitting results are significantly changed. Therefore, the OPC sample could still be regarded as a stable system during the measuring period.

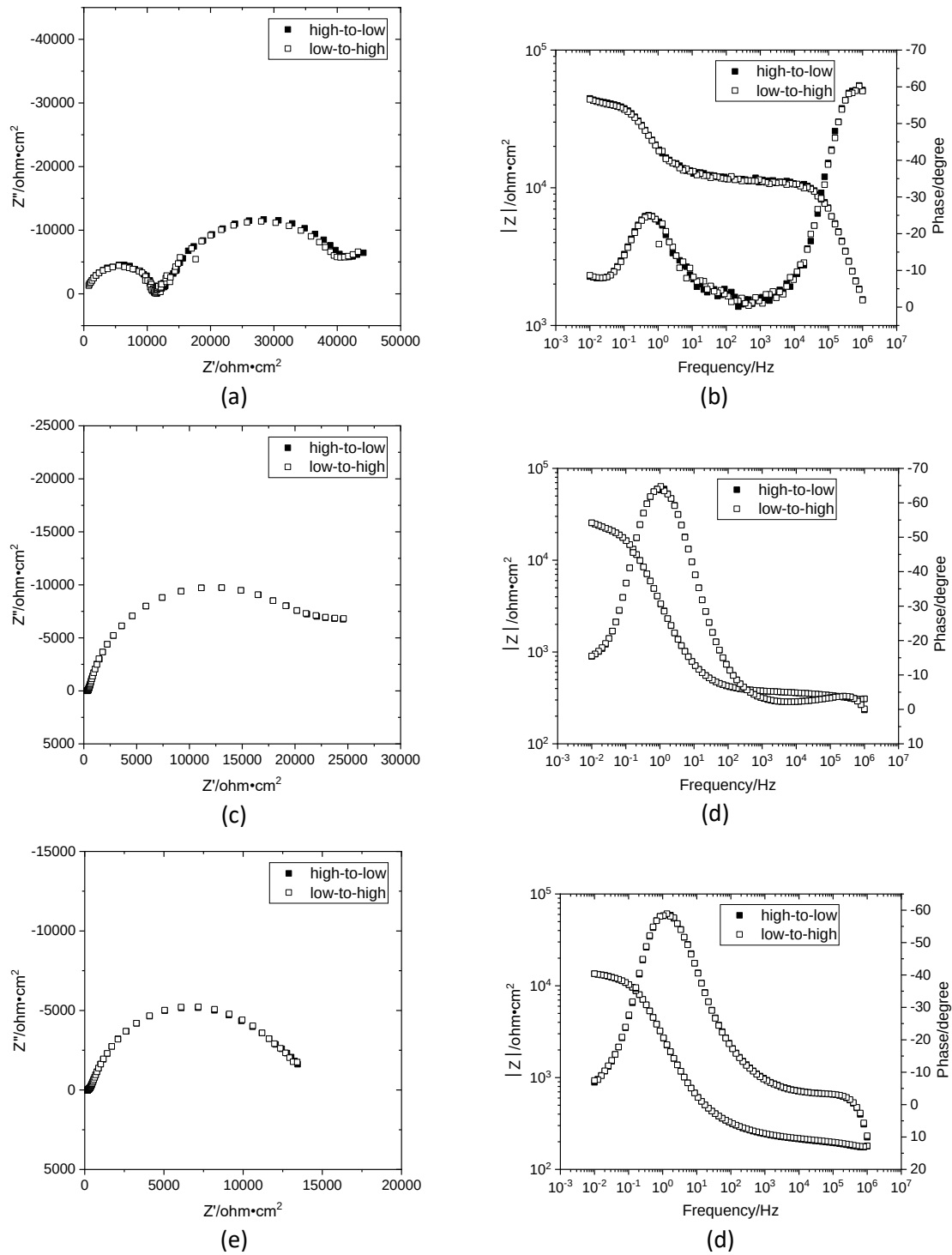


Figure 4.1 Nyquist and Bode plots, including both the high-to-low and low-to-high frequency scans, of AA1100 in the OPC paste after 29 days in condition 1 (a) (b), in the OPC+LiNO₃ paste after 79 days in condition 2 (c) (d) and in the OPC+Li₂CO₃ paste after 92 days in condition 1 (e) (f).

The data quality was also theoretically validated by using the Kramers-Kronig (K-K) transforms to check the linearity, causality and stability of the system. The K-K transforms is a mathematical procedure

Chapter 4

to calculate the imaginary (or real) part of the impedance from the experimentally measured real (or imaginary) part and then the measured part is compared with the corresponding experimental part. If the measured real or imaginary part has a good agreement with the K-K relations, the linearity, causality and stability of the system are confirmed. More details about the K-K relations can be found in the literature [259]. The K-K transforms for the EIS data was performed using the Autolab Nova 1.8 software. Figure 4.2 provides an example of K-K transforms obtained in this study. A good agreement between the experimental data and the K-K results is shown and hence the validity of the experimental data obtained by EIS is confirmed. Besides, the accuracy of the K-K transforms is also evaluated by the sum of squares of the relative residuals (χ^2), which depends on the number and the value of data points. The larger the χ^2 value is, the lower the data quality is. As a rule of thumb, values lower than 10^{-6} represent an excellent data quality, a reasonable result ranges from 10^{-5} to 10^{-6} , an acceptable margin is around 10^{-4} . Normally, the χ^2 values of OPC+LiNO₃ samples and OPC+Li₂CO₃ samples are very low (for example, it is 3.686×10^{-6} and 4.2986×10^{-6} for AA1100 in the OPC+LiNO₃ paste after 79 days in condition 2 and in the OPC+Li₂CO₃ paste after 92 days in condition 1, respectively), while OPC samples have a relatively larger χ^2 value (the χ^2 value for AA1100 in the OPC paste after 29 days in condition 1 is 1.2119×10^{-4}). As addressed above, Al exposed to OPC corrodes relatively fast, which can cause increasing internal stresses and consequently lead to cracks growing. This explains the higher χ^2 values for these samples. Because the χ^2 values for the OPC samples are still around 10^{-4} and can be further decreased by a removal of some outlier points, the corresponding data are considered to be acceptable.

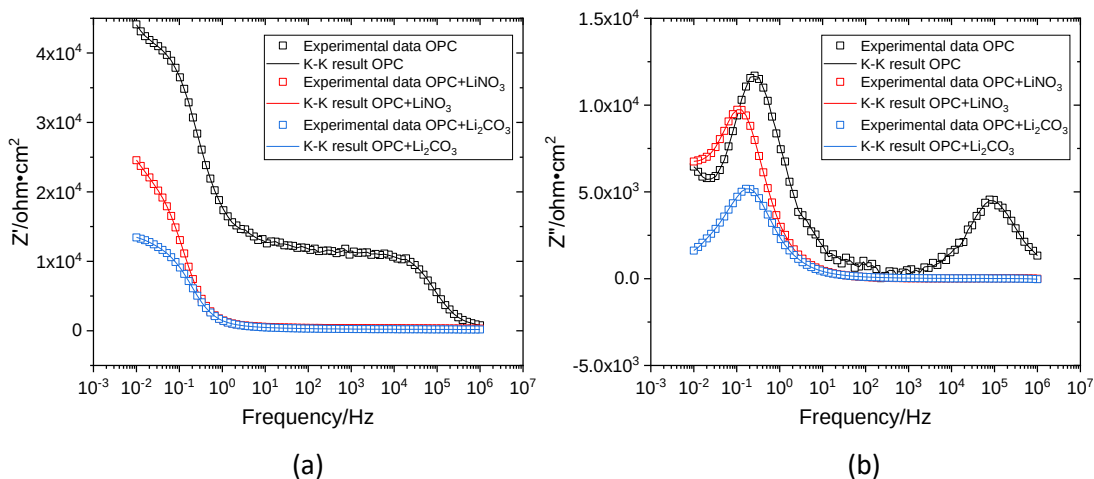


Figure 4.2 Comparison between the experimental data and the result calculated using the Kramers-Kronig transforms for AA1100 in the OPC paste after 29 days in condition 1, in the OPC+LiNO₃ paste after 79 days in condition 2 and in the OPC+Li₂CO₃ paste after 92 days in condition 1.

4.4. Impedance spectra

The impedance spectra of pure OPC samples (Figure 4.3) show that three time constants can be visibly distinguished. Generally, the responses of the cement paste part are mainly revealed in the higher frequency regions, while the lower frequencies reveal the responses of the interface between the aluminium and cement paste, including a corrosion product film (More discussions are provided in Appendix A.5).

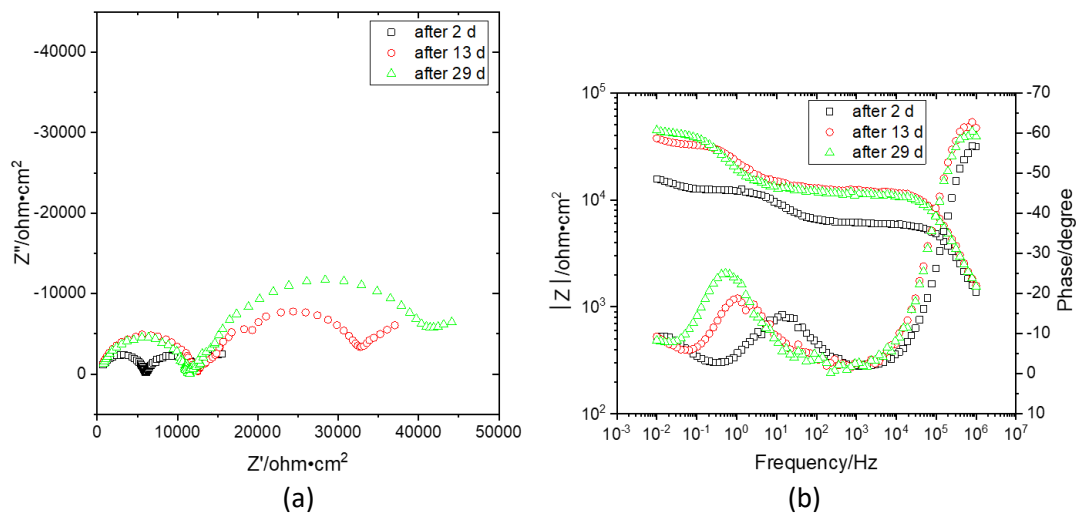


Figure 4.3 Nyquist (a) and Bode (b) plots of AA1100 aluminium alloy in the OPC paste in condition 1.

For samples with the addition of LiNO_3 or Li_2CO_3 , the three time constants are also found in the high-frequency domain, around 1 Hz and in the low-frequency domain, respectively. Exceptionally, for one $\text{OPC}+\text{Li}_2\text{CO}_3$ sample, a fourth time constant in the range of 1 kHz to ~ 10 kHz is occasionally observed at the early stage of the tests. This time constant is gradually overlapped by the other time constants with the increase of time (see Figure 4.4(b)). The impedance spectra evolve as a function of time, increasing the difficulty of distinguishing each time constant as shown in Figure 4.4(a). On the one hand, at the early stage of the tests, with ongoing cement hydration, thickening of the corrosion product film and increasing charge transfer resistance, the magnitude of the impedance of $\text{OPC}+\text{Li}_2\text{CO}_3$ samples at the low-frequency limit increases monotonically (see Figure 4.4(a)); on the other hand, other factors e.g. the ingress of cement pore solution into the corrosion product film, can lead to a drop of the impedance magnitude at the low-frequency limit as shown in Figure 4.5(a) for $\text{OPC}+\text{LiNO}_3$ samples.

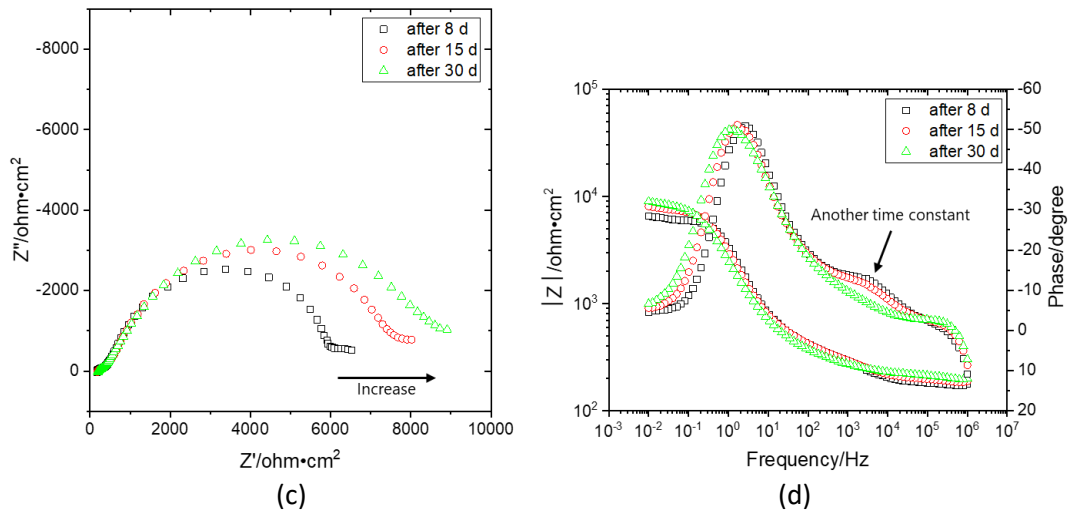


Figure 4.4 Variation of Nyquist (a) and Bode (b) plots of AA1100 in the OPC+Li₂CO₃ paste in condition 2.

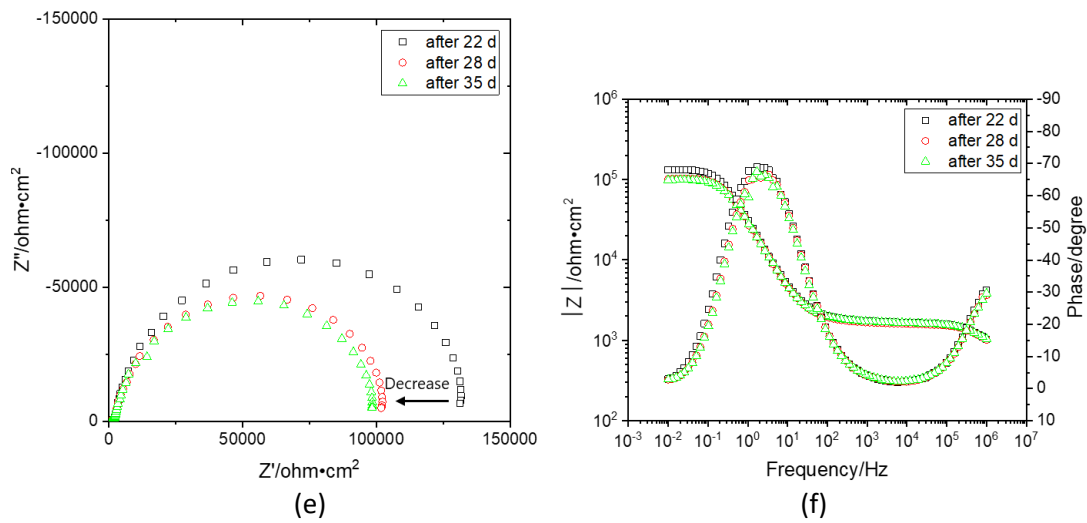


Figure 4.5 Variation of Nyquist (a) and Bode (b) plots of AA1100 in the OPC+LiNO₃ paste in condition 1.

4.5. Equivalent circuit model analysis

To quantitatively analyse the recorded EIS data, the EIS fitting was performed using the electrical equivalent circuit (EEC) shown in Figure 4.6, which was established based on the physical structures of the cell. This circuit can be divided into three different parts:

- The wire inductance and uncompensated resistance part,
- The cement paste part,

- The Al/corrosion product/cement paste interface part.

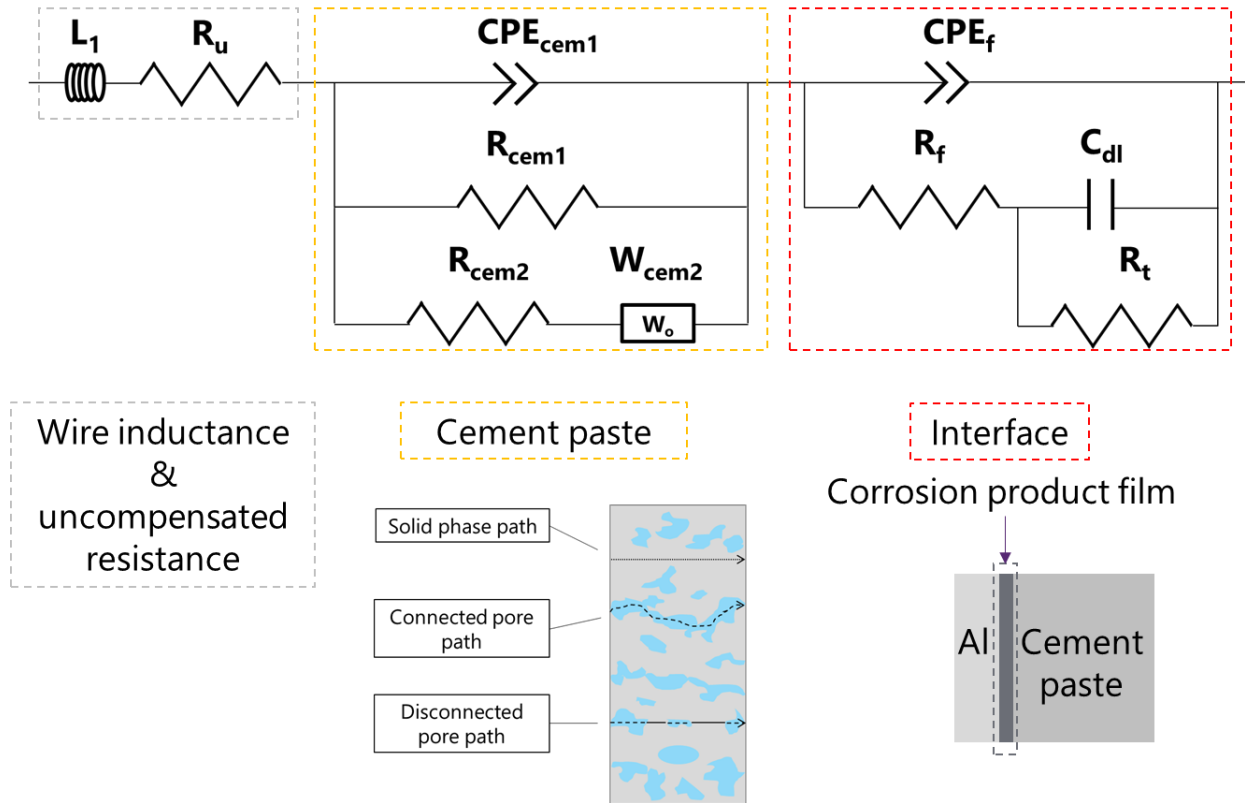


Figure 4.6 Electrical equivalent circuit used to fit the EIS spectra for the corrosion of Al in cement pastes.

In the following sections, the three different parts of the EEC will be further elaborated.

4.5.1. Wire inductance and uncompensated resistance

First, an inductor (L_1) and a resistor (R_u) are placed in series. L_1 represents the inductance of the external wires. This term was used when the high frequency (1 MHz), adopted to collect the information of the cement paste, activates the inductance response in some samples. R_u , an overall uncompensated resistance, includes the resistance of the solution that exists in macro holes or crevices, the resistances of the Al plate matrix, Al rods, the external circuit, etc. L_1 and R_u can be selected or not according to the appearance of a specific impedance spectrum and such an adjustment has little influence on the other sub-circuit parameters.

4.5.1.1. Justification of the wire inductance L_1

Chapter 4

Initially, a frequency in the range of 100 kHz to 0.01 Hz was chosen for our EIS measurements. It was thought wide enough for the corrosion study. However, it failed to provide more information about the cement paste (the measuring frequency for the cementitious material study is normally up to 1 MHz). Hence, the frequency was increased to 1 MHz. This increase brought some impedance points below the X axis (positive imaginary part of the impedance) in the high frequency region of the Nyquist plots of some samples and the corresponding phase angles are above 0. An example is shown in Figure 4.7, in which the blue points represent the measured values and the red line represents the fitting results. A new time constant appeared and made the fitting more difficult. To better match the impedance curve when fitting, an inductor has to be added into the equivalent circuit model.

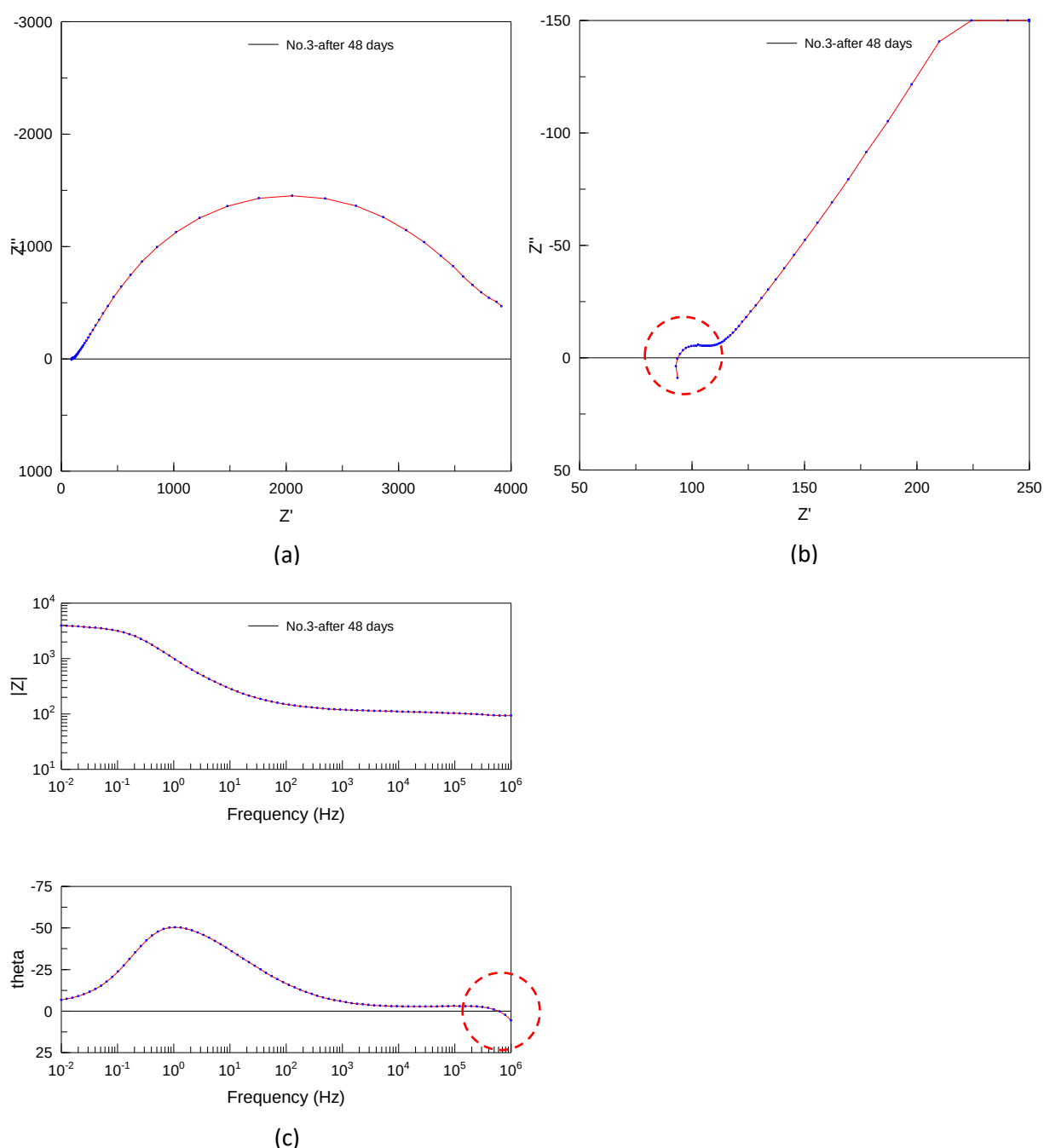


Figure 4.7 Example of the Nyquist (a), (b) and Bode (c) plots of an OPC+Li₂CO₃ sample in condition 1.

To understand the meaning of this inductor, the potentiostat was first changed to carried out the EIS measurements again. Because the new potentiostat provided similar results and correspondingly the possibility that it was coming from the potentiostat was excluded.

Second, when the inductor was added in the fitting, the inductance of the inductor normally ranged from 1 μ H to 4 μ H. If it was caused by a phenomenon coming from the specimen, such as the adsorption of H₂ gas, it should vary with time. Therefore, the most likely source of this inductance should come from

Chapter 4

the wires between the electrodes and the potentiostat. Indeed, to create anaerobic conditions, our samples were stored in a glovebox. Because the potentiostat was located out of the glove box, long wires (about 5 meters long) had to be used between the electrodes and the potentiostat together with an electrical feed-through connecting the electrical wires used inside the glove box to the wires outside the glove box.

To experimentally prove that these wires were the cause of the inductance, EIS measurements on a dummy cell (see Figure 4.8) were performed. Three measurements on the same dummy cell were performed. The first one measured the response of the dummy cell placed in the glovebox and connected to the potentiostat with a long wire connection (about 5 m and a connector connecting the inner part and the outer part of the glovebox); the second test measured the dummy cell out of the glovebox using a 1.5 m wire connection; the third measurement recorded the dummy cell out of the glovebox using an 1 m wire connection.

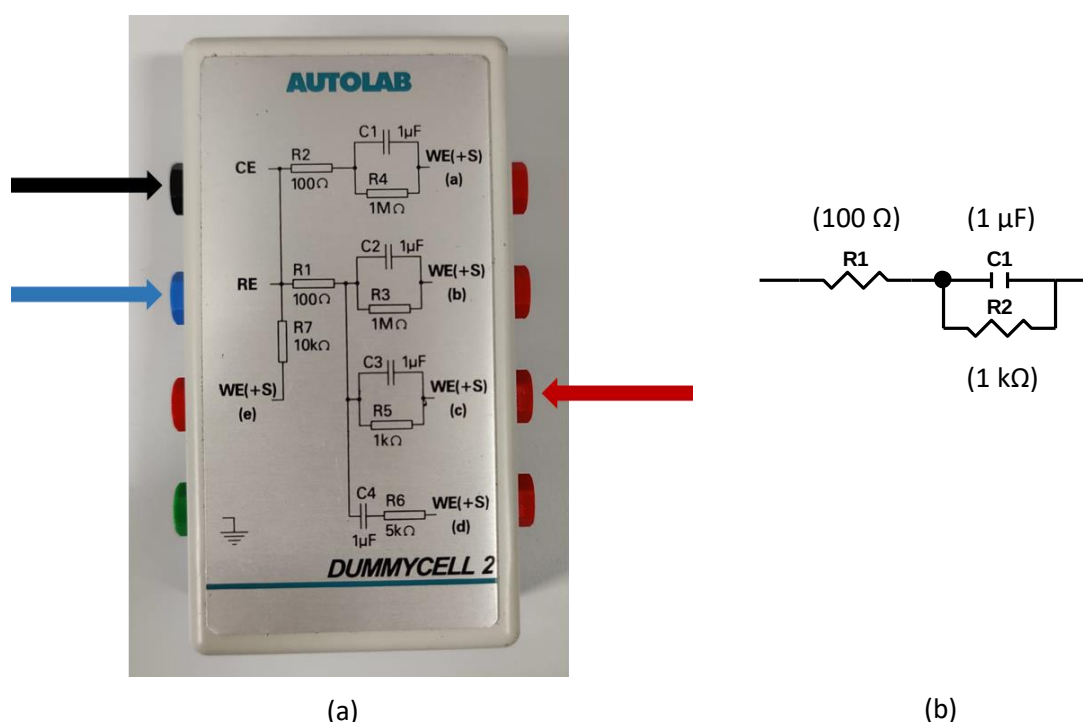


Figure 4.8 Dummy cell used (a) and the corresponding equivalent circuit (b).

The Nyquist plot of the dummy cell in the glovebox with the 5 m wire connection is given in Figure 4.9, which clearly shows a few points below the X axis in the high frequency region. In addition, the overall curve is close to that of an equivalent circuit reported in the literature [262], which includes an inductor (See Figure 4.10). This means that the presence of the inductor even in the circuit of the dummy cell. Hence, the inductor is assumed not to be related to the samples. Because the possibility of deriving from the potentiostat has been excluded, the source of the inductor is preliminarily confirmed to be the wires.

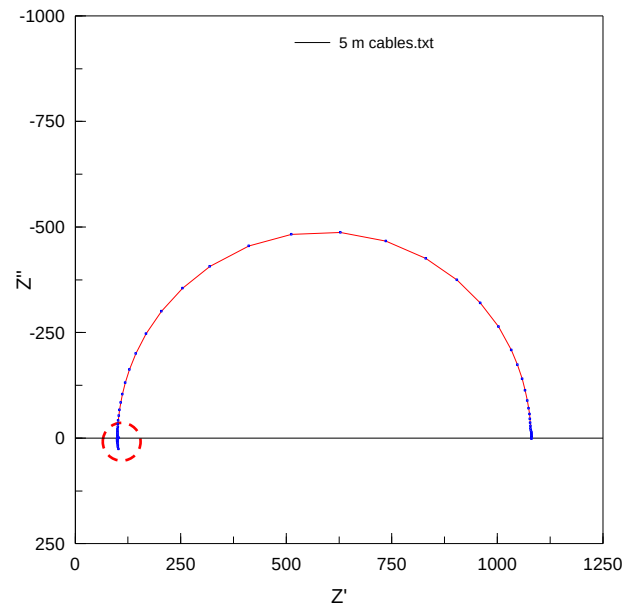


Figure 4.9 Nyquist plot of the dummy cell in the glovebox with the 5 m wire connection.

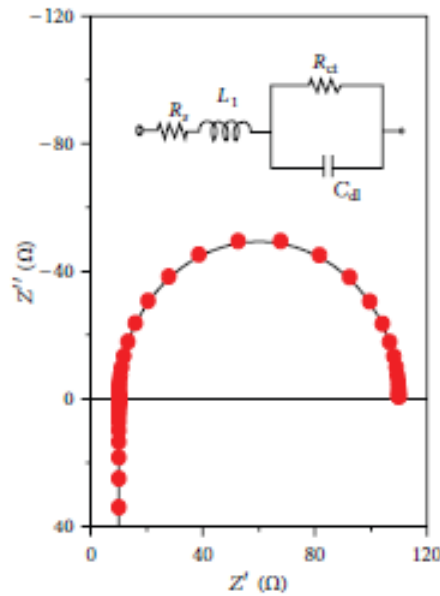


Figure 4.10 Nyquist plot with $R_s = 10 \, \Omega$, $R_{ct} = 100 \, \Omega$, $L_I = 10 \, \mu\text{H}$, $C_{dl} = 100 \, \mu\text{F}$ reported in literature [262].

Then, the Bode plots of the same dummy cell with different wire lengths are compared. It was found that the phase angle decreases with a shortening of the cables gradually shifting towards 0 degrees. This indicates that the effect of the inductor disappears gradually with the decrease of the wire length. The effect of the length of the wires is more apparent in the Bode plots than in the Nyquist plots (Figure 4.11).

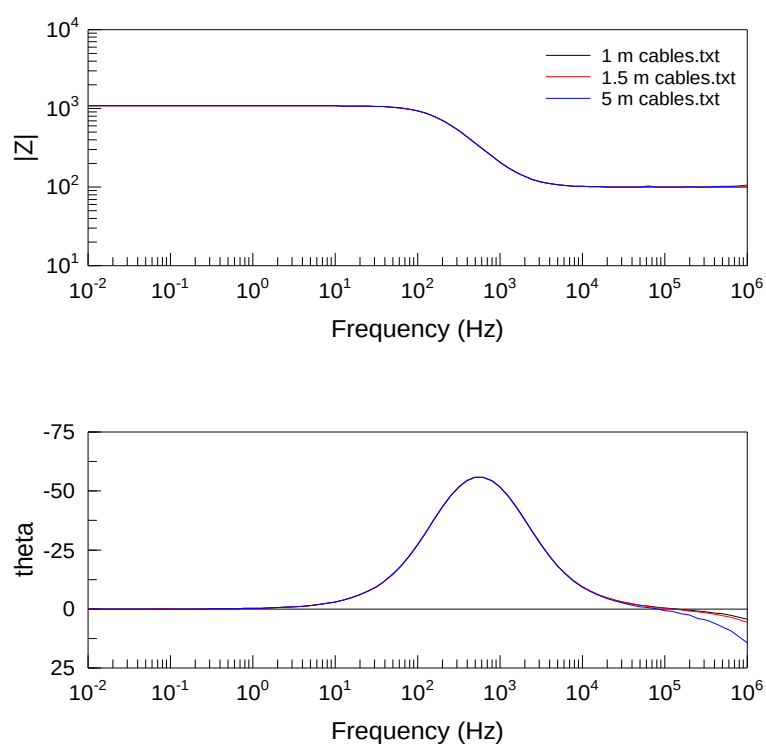
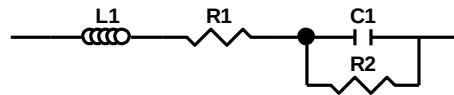


Figure 4.11 Bode plots of the same dummy cell of different wire lengths.

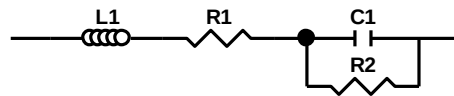
Finally, the EIS fitting was also performed on the EIS results obtained with the dummy cell using different wire lengths to determine the L_1 associated to the wires. The fitting results are provided in Figure 4.12. The L_1 value decreases with the decrease of the wire length, which implies that L_1 is, as already explained, caused by the wires.



Element	Freedom	Value	Error	Error %
L1	Free(±)	4.2604E-06	3.642E-08	0.85485
R1	Free(±)	100.5	0.057224	0.056939
C1	Free(±)	9.4885E-07	9.6011E-10	0.10119
R2	Free(±)	979.7	0.48746	0.049756

Chi-Squared: 0.00034752
Weighted Sum of Squares: 0.054214

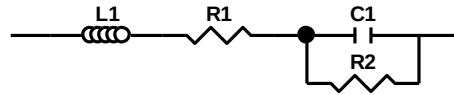
(a)



Element	Freedom	Value	Error	Error %
L1	Free(±)	1.6114E-06	1.4308E-08	0.88792
R1	Free(±)	100.1	0.022711	0.022688
C1	Free(±)	9.4803E-07	3.8217E-10	0.040312
R2	Free(±)	979.9	0.19432	0.019831

Chi-Squared: 6.0753E-05
Weighted Sum of Squares: 0.0094775

(b)



Element	Freedom	Value	Error	Error %
L1	Free(±)	1.2528E-06	1.4359E-08	1.1462
R1	Free(±)	100.1	0.022808	0.022785
C1	Free(±)	9.4786E-07	3.8377E-10	0.040488
R2	Free(±)	979.8	0.19514	0.019916

Chi-Squared: 6.1986E-05
Weighted Sum of Squares: 0.0096698

(c)

Figure 4.12 Fitting results of the dummy cell in the glovebox with the 5 m wire connection (a), out of the glovebox with the 1.5 m wire connection (b) and out of the glovebox with the 1 m wire connection (c).

Besides, Mason et al. [263] specifically studied the influences of cables on impedance spectroscopy of cement-based materials and attributed the severe inductive distortion at high frequencies to the inductor caused by the cables and leads. In their paper, the inductor has an inductance equal to $1.5 \mu\text{H}$, which is comparable to the one applied in this study. Wang et al. [212] also discussed the influences of the

wires (the stray impedance) in the EIS measurements of cementitious materials and attributed the inductor in the circuit to the wire/cable.

4.5.1.2. Justification of the uncompensated resistance R_u

As for L_1 , a resistance R_u is sometimes needed for a better fitting in the high frequency region. R_u can come from many sources, such as the aluminium rod (the rod is welded for electrical conduction) and the defects in the cement paste as shown in Figure 4.13. Figure 4.13(a) provides an example of the resistance experimentally measured, which comes from the aluminium rod and the welding point. However, as for L_1 , the information of R_u can be sometimes masked by the responses of the cement paste and L_1 . Correspondingly, R_u cannot be clearly separated in the EIS fitting in some cases.

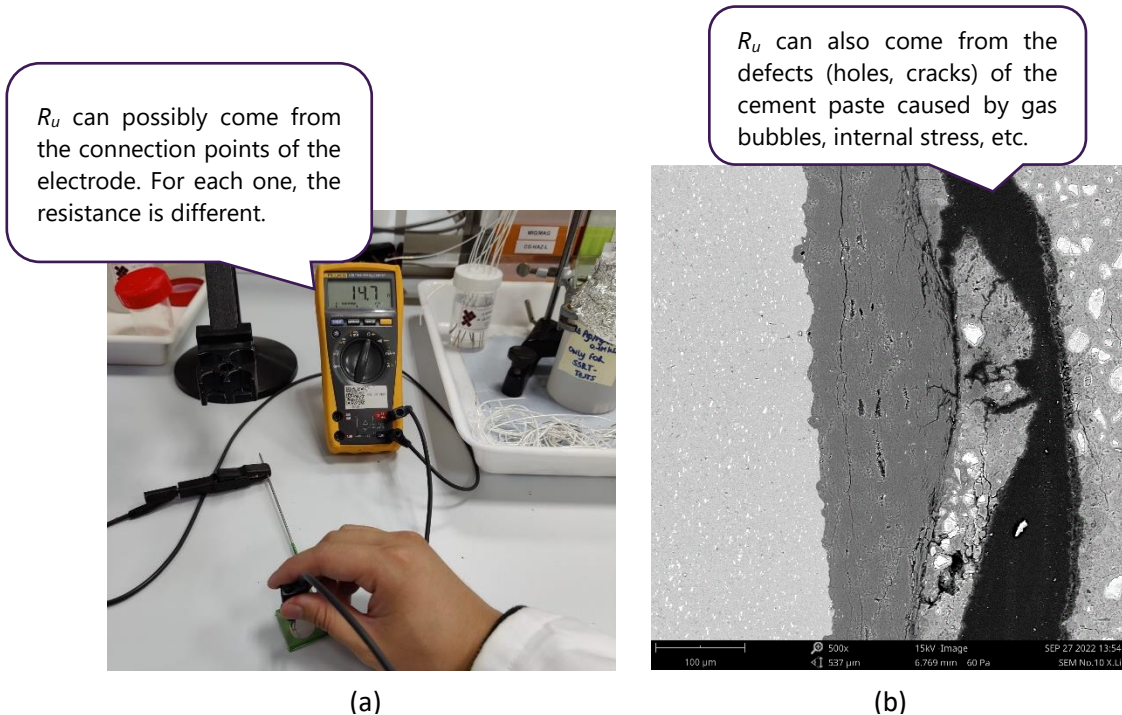


Figure 4.13 Resistance of the aluminium rod measured (a) and the holes and cracks present in the cement paste.

4.5.1.3. Discussion on L_1 and R_u

Because the appearance of the inductance and the resistance is not always observed in the EIS curves, the systematic use of these L_1 and R_u is probably not necessary. Fitting of the EIS data can be hampered because the electrochemical responses of L_1 and R_u overlap with the responses from other parts of the system (mainly the cement paste).

Chapter 4

Especially for L_1 , its electrochemical response always occurs in the high frequency domain, which overlaps with the information of the cement paste. This overlap results in the difficulty of correctly separating the different information in the EIS fitting. An example is shown in Figure 4.14, in which the first two or three points in the high frequency region seem to be dominated by L_1 . However, due to a lack of a sufficient number of corresponding points in the high frequency region, a good fitting of L_1 cannot be supported. And because the circuit without L_1 and R_u already provided good enough fitting results, L_1 and R_u are not consistently used in the equivalent circuit. Correspondingly, the drawback is that the high frequency region cannot be well fitted and some fitting parameters (mainly CPE_{cem1}) could be partly distorted because of the negligence of L_1 and R_u (the error of CPE_{cem1} is relatively large and the n value (i.e. P value in the software) is low in Figure 4.14).

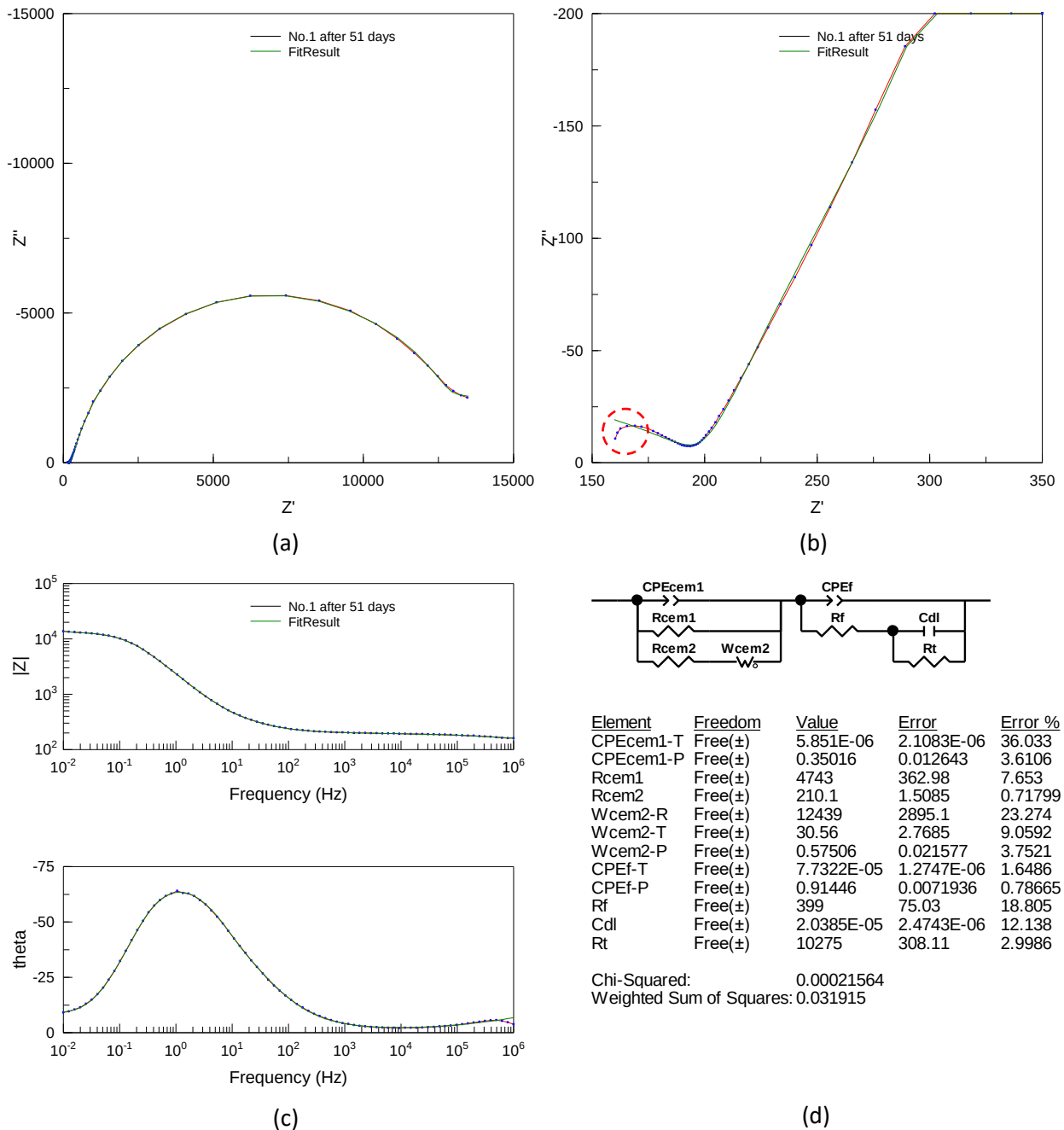


Figure 4.14 EIS fitting results (Nyquist (a), (b), Bode (c) plots and the fitting parameters (d)) of an OPC+LiNO₃ sample in condition 2 after 51 days.

The more extreme situation is that the electrochemical responses associated to L_1 is fully masked by the one of the cement paste in the impedance plots. In this case, the addition of L_1 just gives a wrong L_1 through fitting as shown in Figure 4.15 where negative values are obtained. L_1 indeed exists in the system, but the fitting cannot properly give the correct value due to the interferences with the cement paste. Therefore, the L_1 was removed from the electrical equivalent circuit in such cases.

Chapter 4

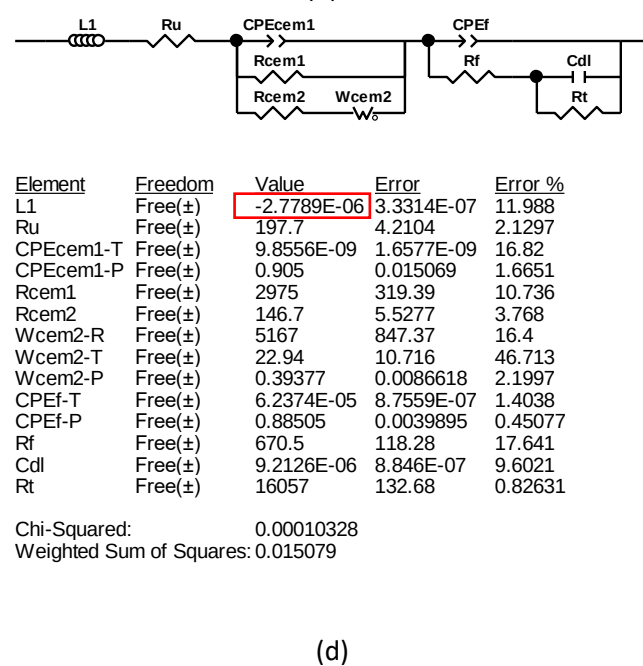
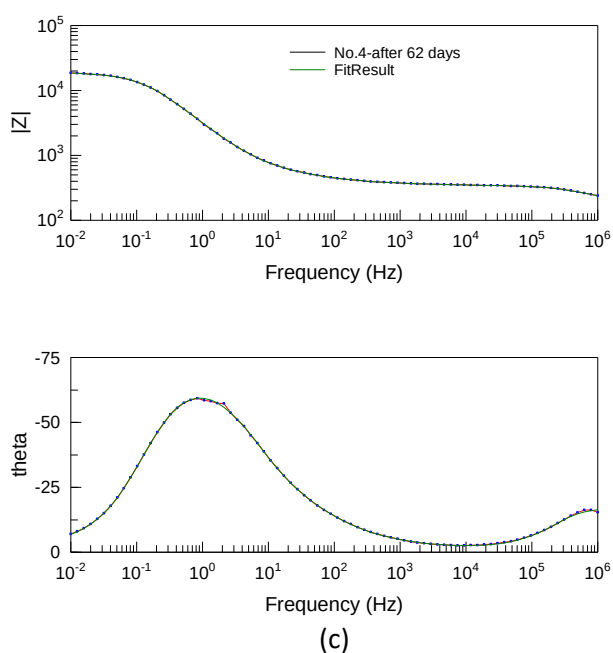
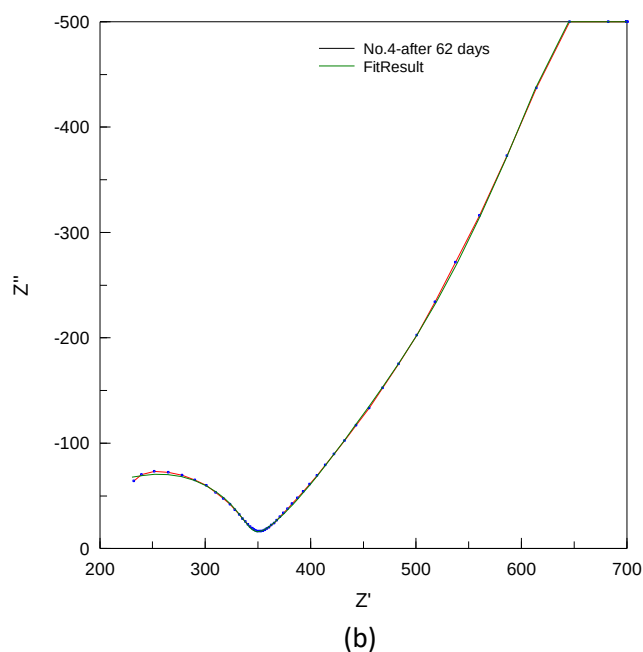
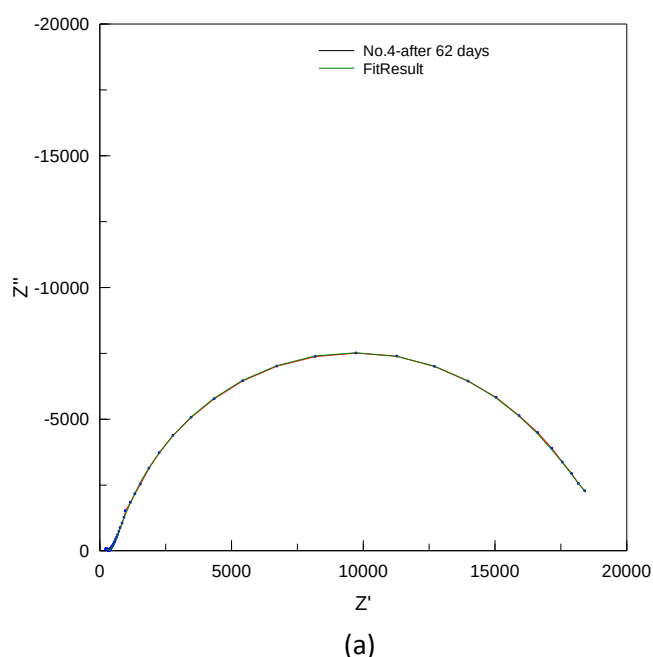


Figure 4.15 EIS fitting results (Nyquist (a), (b), Bode (c) plots and the fitting parameters (d)) of the equivalent circuit with a free L_1 of an OPC+Li₂CO₃ sample after 62 days in condition 1.

Chapter 4

One possible solution for this case is to fix the value of L_1 as shown in Figure 4.16. However, it is difficult to give the precise value of L_1 , as only an approximate range of L_1 is known and this value can change within this range. For example, the position and the connection of the cables affect L_1 . Besides, the addition of a fixed L_1 , when its electrochemical influences cannot be seen in the plots, will induce significant uncertainty.

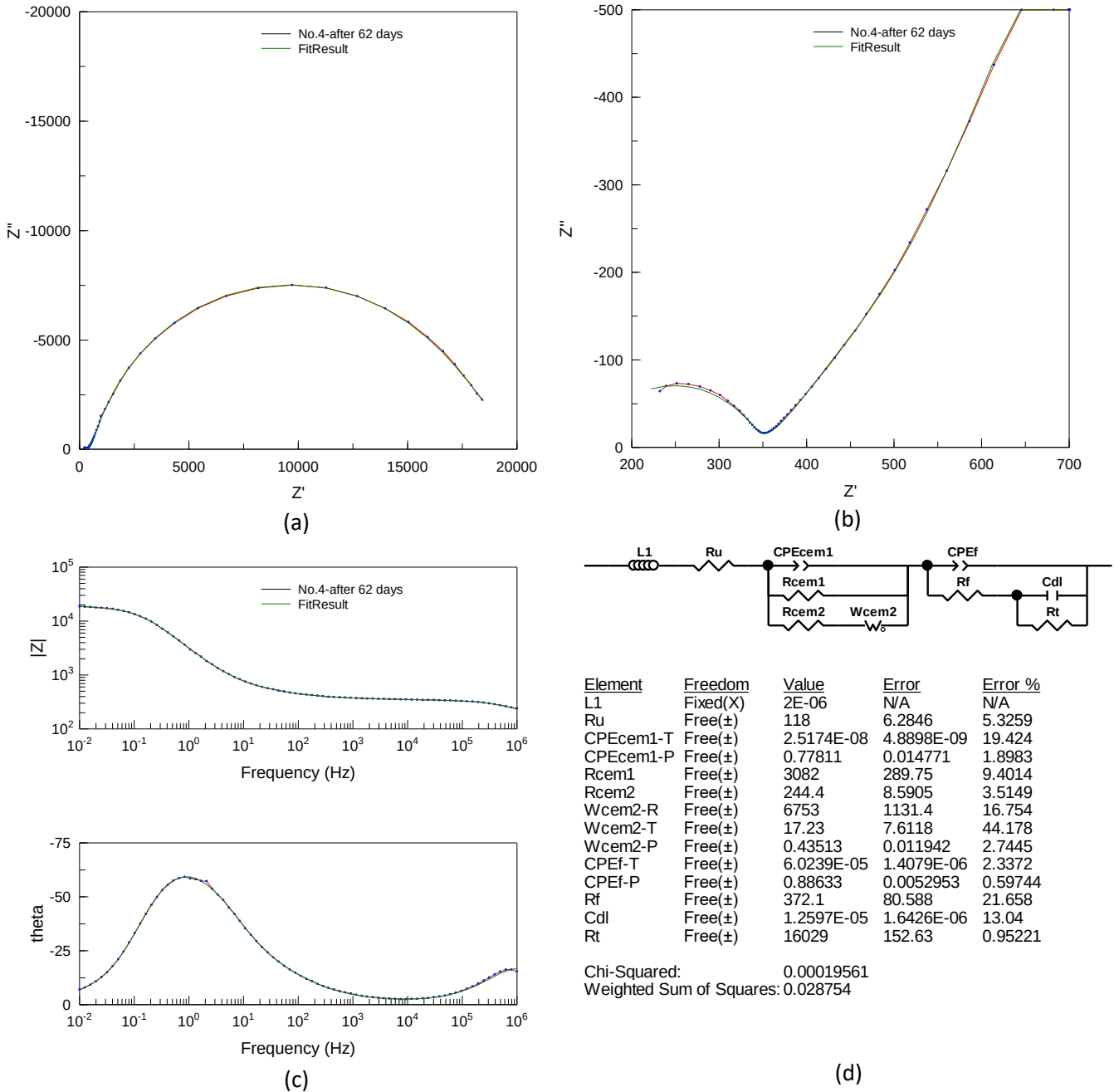


Figure 4.16 EIS fitting results (Nyquist (a), (b), Bode (c) plots and the fitting parameters (d)) of the equivalent circuit with a fixed L_1 of an OPC+Li₂CO₃ sample after 62 days in condition 1.

Another solution is to directly ignore the influence of L_1 in the equivalent circuit (Figure 4.17(d)), because it cannot be identified from the plots. Compared with the equivalent circuit with a free/fixed L_1

Chapter 4

(Figure 4.15 and Figure 4.16), this does not change significantly the fitting values of the other parameters. Hence, for the samples in which the information of L_1 is fully covered by that of the cement paste, L_1 is ignored (Figure 4.15).

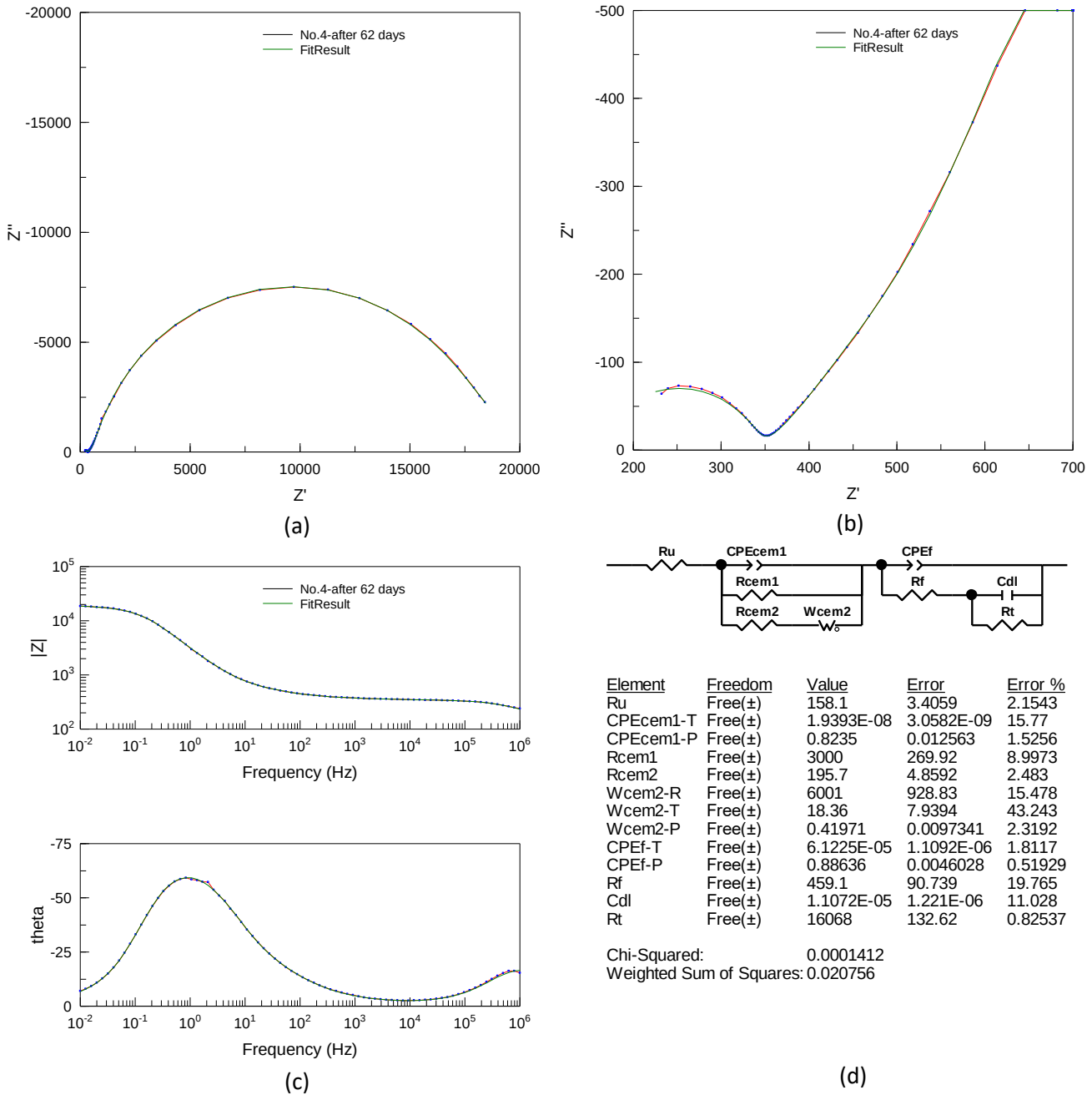
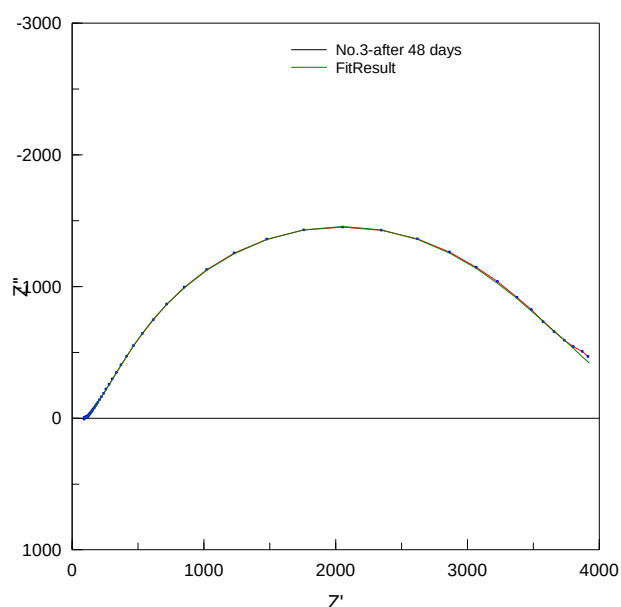


Figure 4.17 EIS fitting results (Nyquist (a), (b), Bode (c) plots and the fitting parameters (d)) of the equivalent circuit without L_1 of an OPC+Li₂CO₃ sample after 62 days in condition 1.

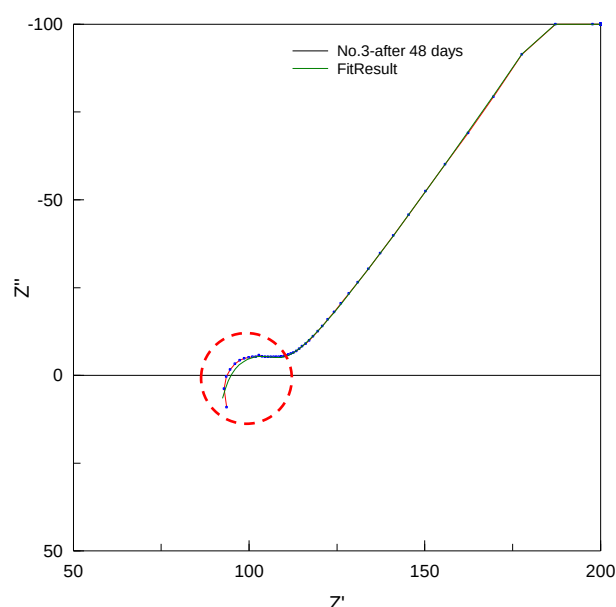
Generally speaking, if the equivalent circuit without L_1 and R_u can still give good fitting results i.e. the matching of the fitting curves and the small fitting errors, it was decided to avoid the introduction of L_1

Chapter 4

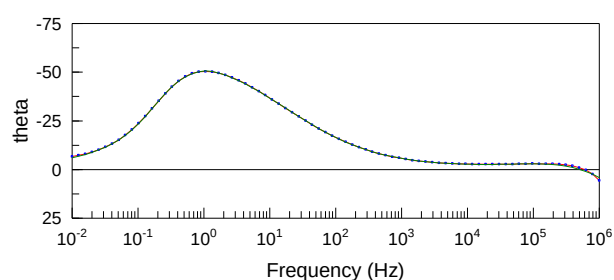
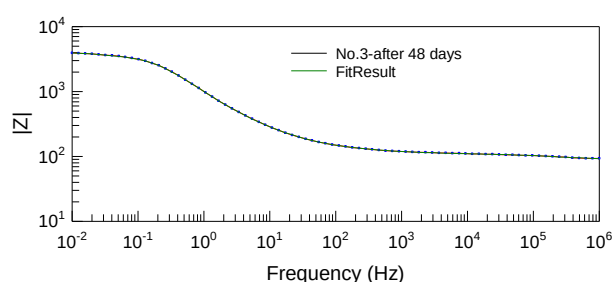
and R_u to use a simpler model. Only when they are really needed to fit a curve e.g., in Figure 4.18 in which a clear corresponding time constant can be observed, they are added.



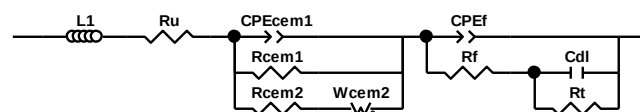
(a)



(b)



(c)



Element	Freedom	Value	Error	Error %
L1	Free(±)	1.7936E-06	8.3395E-08	4.6496
Ru	Free(±)	87.92	1.1696	1.3303
CPEcem1-T	Free(±)	0.0004911	1.0383E-05	2.1142
CPEcem1-P	Free(±)	0.53862	0.0081729	1.5174
Rcem1	Free(±)	2391	24.39	1.0201
Rcem2	Free(±)	64.56	20.505	31.761
Wcem2-R	Free(±)	18523	4789.9	25.859
Wcem2-T	Free(±)	1.32	0.074522	5.6456
Wcem2-P	Free(±)	0.63431	0.017684	2.7879
CPEf-T	Free(±)	3.1648E-06	7.4499E-07	23.54
CPEf-P	Free(±)	0.68059	0.03606	5.2983
Rf	Free(±)	20.23	1.5883	7.8512
Cdl	Free(±)	0.00034784	4.7525E-06	1.3663
Rt	Free(±)	1841	17.012	0.92406

Chi-Squared: 0.00010034
Weighted Sum of Squares: 0.01465

Data File: C:\Users\xlii\Desktop\Experimental data handli
Circuit Model File: C:\Users\xlii\Desktop\Experimental data handli
Mode: Run Fitting / Freq. Range (0.01 - 1000000)
Maximum Iterations: 100
Optimization Iterations: 10
Type of Fitting: Complex
Type of Weighting: Calc-Modulus

(d)

Figure 4.18 EIS fitting results (Nyquist (a), (b), Bode (c) plots and the fitting parameters (d)) of an OPC+Li₂CO₃ sample in condition 1 after 48 days.

Moreover, Mason et al. [263] and Wang et al. [212] mentioned some remediation strategies (e.g. geometric adjustment and null corrections) dealing with the inductance problem coming from the

wires/cables in the EIS studies of cementitious materials, apart from eliminating/shortening the lengths of cables or wires. This could be the research direction of future works.

4.5.2. Modelling of the cement paste part

The second part of the EEC ($CPE_{cem1} // R_{cem1} // R_{cem2} - W_{cem2}$) is composed of three branches in parallel (see Figure 4.6) corresponding to the electrochemical properties of the cement paste between the two electrodes. CPE_{cem1} represents the capacitance properties of the solid phase in the cement paste; R_{cem1} is the resistance of ionic conduction through the connected capillary pores; the disconnected pore path is composed of a resistor (R_{cem2}) in series with a Warburg element (W_{cem2}), which correspond to the charge transfer processes of the pore phase and solid phase, respectively. At a preliminary stage of the study, the equivalent circuit reported in the literature [261,264,265], shown in Figure 4.19, was employed as part of the overall circuit (Figure 4.20) for the EIS fitting to describe the cement paste between the two electrodes. However, the adoption of a constant phase element (CPE_{cem2}) would provide an 'n' value of CPE_{cem2} lower than 0.5 in some samples (Figure 4.21).

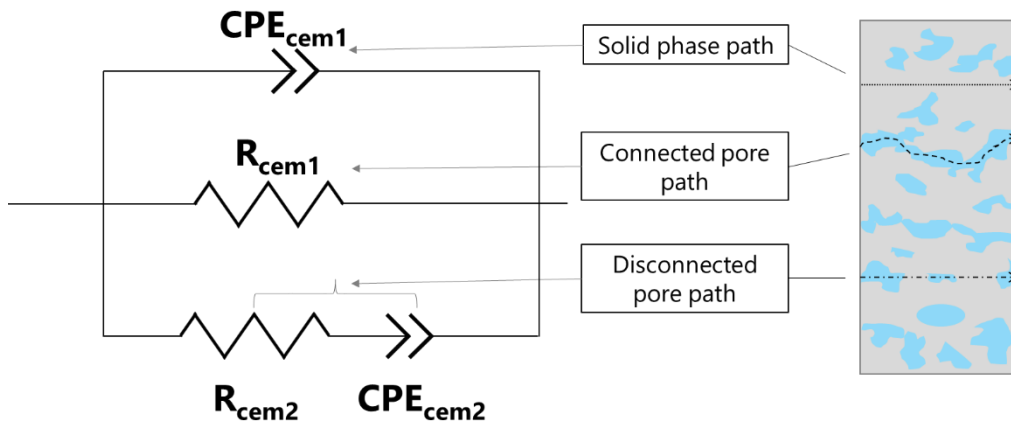


Figure 4.19. Equivalent circuit of the cement paste proposed in literature.

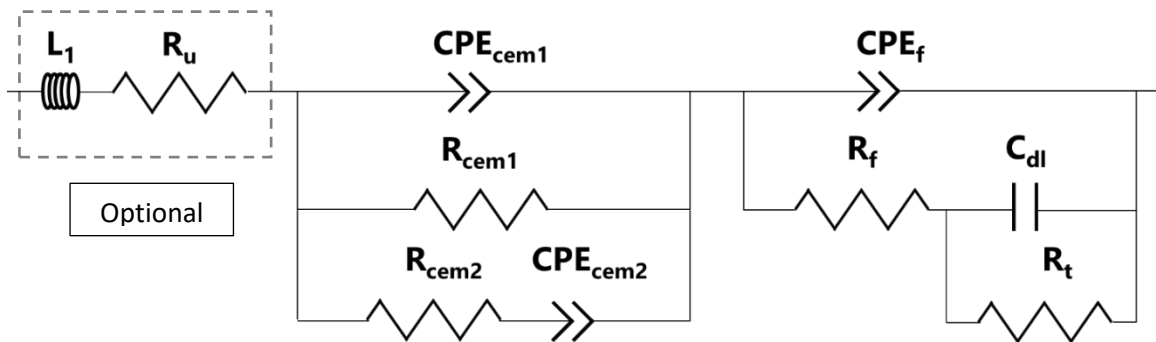


Figure 4.20 Equivalent circuit used in preliminary study for the EIS fitting.

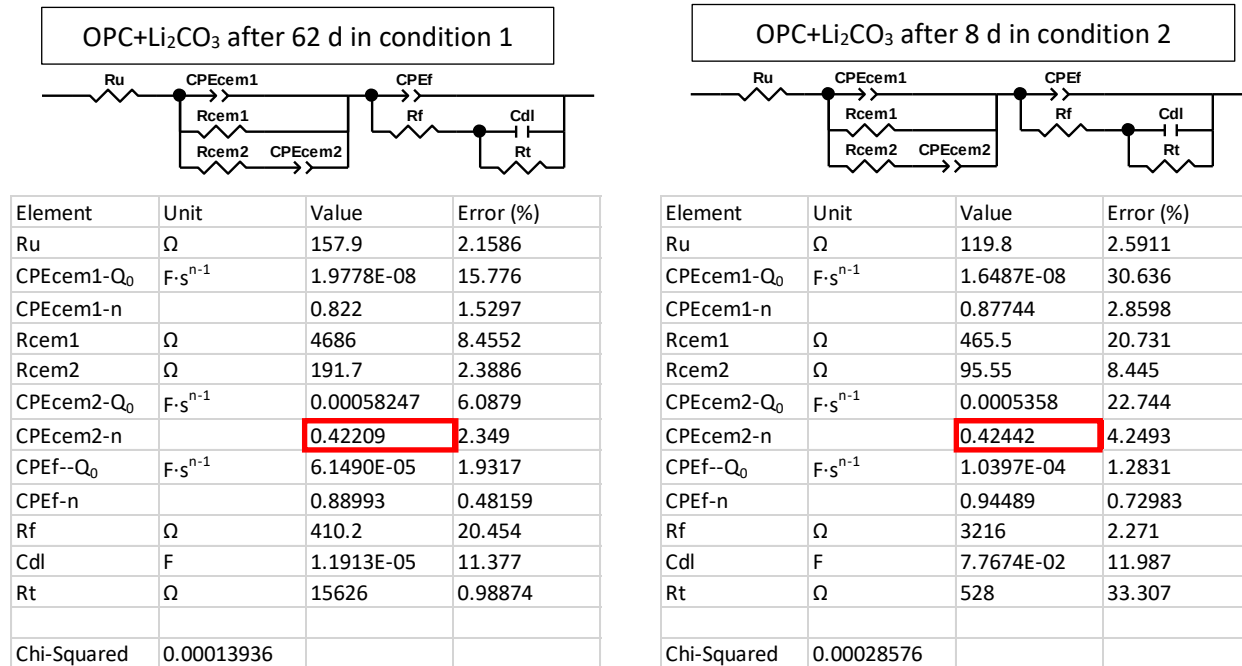


Figure 4.21 Example of a case with 'n' value of CPE_{cem2} lower than 0.5.

As a rule of thumb, when n is close to 0.5, the system is more likely to be controlled by a diffusion process. The ion diffusion in cementitious materials was also mentioned in the literature [266-269] suggesting that a Warburg element might be more suitable than a constant phase element, while all other elements of the electrical circuit remain identical, as shown in Figure 4.6. Before the model was finally decided, a systematic discussion had been performed.

According to the cement paste microstructure, various equivalent circuit models are reported as Hu et al. classified in the literature [270]. On this basis, a series of models were preliminarily tested. Most models were first excluded because of bad fitting results and some others were directly rejected due to lack of physical meanings. Only three models showed the possibility of good fitting with clear physical meanings (Figure 4.22). More details on all these models are provided in Section A.2.

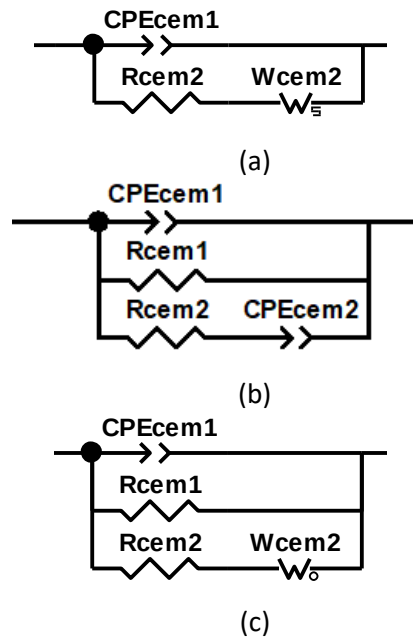


Figure 4.22 Three possible models with physical meanings.

The equivalent circuit shown in Figure 4.22(a) is widely accepted for the fitting of cementitious materials in literature [271-276]. In this model, CPE_{cem1} corresponds to the dielectric capacitance related to solid phase, R_{cem2} is the resistance of the pores filled with the pore solution and W_{cem2} describes the ion diffusion in the cementitious material. The problem with this model is that the literature does not clearly explain the source of the ion diffusion (the ion diffusion might occur in C-S-H gel, which will be discussed in detail later in this section) nor does it include the connected pore path, which also contributes to the electrical conductivity. Moreover, some tests were performed using this model and only the use of a Warburg element with a transmissive boundary (W_s) is suitable for the fitting of our samples, while the Warburg element with a reflective boundary (W_o) did not lead to good fitting of the curves.

In the equivalent circuits shown in Figure 4.22(b) and (c), CPE_{cem1} represents the capacitance properties of the solid phase in the cement paste, R_{cem1} is the resistance of ionic conduction through the connected capillary pores and R_{cem2} corresponds to the resistance of the disconnected pores. The only difference between both models is that the model in Figure 4.22(b) used a constant phase element (CPE_{cem2}) to describe the electrochemical responses of the solid phase between disconnected pores, while the model in Figure 4.22(c) used a Warburg element with a reflective boundary (W_{cem2}). If CPE_{cem2} is used, it means that the solid phase between disconnected pores is non-conductive and behaves closer to a capacitor with surface roughness. If W_{cem2} is used, it implies that the electrical conductivity of the solid phase between disconnected pores relies on the ions' diffusion. According to the results of a literature

Chapter 4

review, W_{cem2} was selected in this doctoral research. A detailed discussion involving this selection process is provided below.

The primary key to make the selection is to understand whether the solid phase involves the ion diffusion (if not, the use of Warburg element is not appropriate). Many papers reported ionic diffusion in the solid phase of the cement pastes. The gel pores of C-S-H (the main constituent of the solid phase) are filled with the solution containing hydroxyl ions, calcium ions, etc. Nagao et al. [277] measured experimentally (both by DC and AC methods) the conductivity of C-S-H, which ranges from 10^{-4} to 10^{-3} S/cm in humidified air at temperatures between 60 and 100 °C. They indicated that indicated that the hydroxide ion is the major charge carrier in C-S-H. Patel et al. [278] reported that the inter-layer of C-S-H does not contribute to the diffusion in C-S-H, while all gel pores contribute to the ion diffusivity in terms of electric resistivity measurements. Yogarajah et al. [279] studied the influence of the gel porosity and of the tortuosity on the ion diffusion in C-S-H. Hence, the ion diffusion in the solid phase of the cementitious materials is a fact and accounts for the conductivity of the solid phase.

Second, W_{cem2} used here is the Warburg element with a reflective boundary i.e. W_o (the Warburg element with a transmissive boundary does not provide good fitting, e.g. leading to an error more than 100%), which is typically associated with the diffusion where one of the boundaries is blocking, such as in a porous electrode. W_o is more complex than the conventional Warburg element ($Z = A_W \cdot \sqrt{\omega} \cdot (1 - j)$) and can be written as:

$$Z = \frac{W_o - R \cdot \coth((j \cdot W_o - T \cdot \omega)^{W_o - P})}{(j \cdot W_o - T \cdot \omega)^{W_o - P}}, \quad (22)$$

where $W_o - R$ is related to the resistance, $W_o - T = \frac{L^2}{D}$ (L is the effective diffusion thickness and D is the effective diffusion coefficient of the particle), $W_o - P$ ranges from 0 to 1. A typical impedance spectrum of a Warburg element with a reflective boundary i.e. W_o is provided in Figure 4.23(a). Cooper et al. [280] simulated the impedance spectra of diffusion in porous microstructure and reported the results as shown in Figure 4.23(b) for the closed-end systems. Figure 4.23(a) and (b) clearly show that the application of a Warburg element with a reflective boundary for the diffusion in closed-end pores is appropriate. Indeed, the physical microstructure of C-S-H has a corresponding geometry i.e. closed-end pores. For example, in the hydration of the cement grain, the C-S-H phase is first formed on the outer surface of the cement grain while the inner part of the cement grain remains unhydrated as shown in Figure 4.23(c) [281,282]. On one hand, the gel pores (the inter-C-S-H pores in Figure 4.23(c)) on the surface are in contact with the capillary pores; on the other hand, the gel pores are closed by the unhydrated cement grain or by the C-S-H needles. Hence, the microstructure of C-S-H can be correlated with W_o .

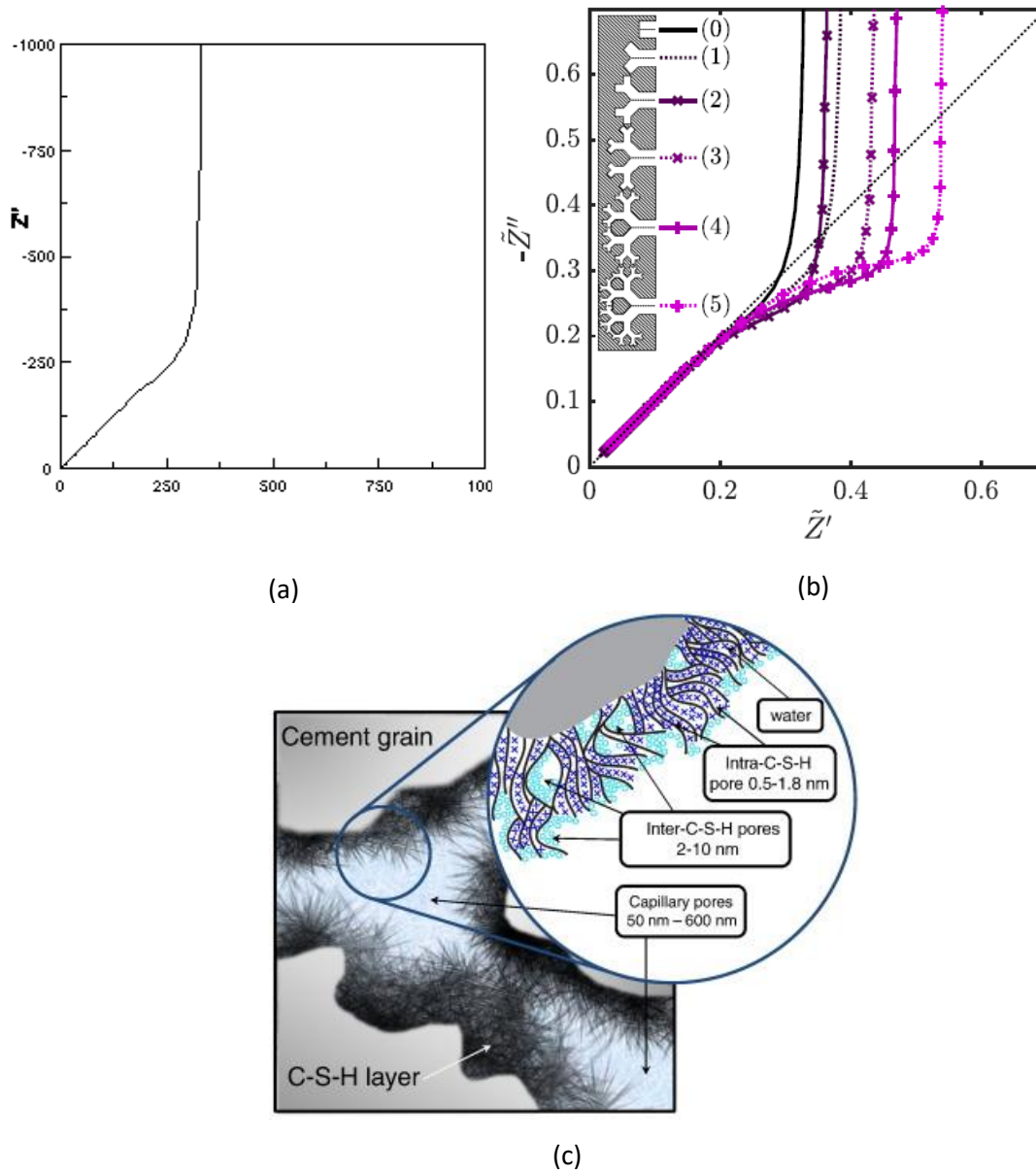
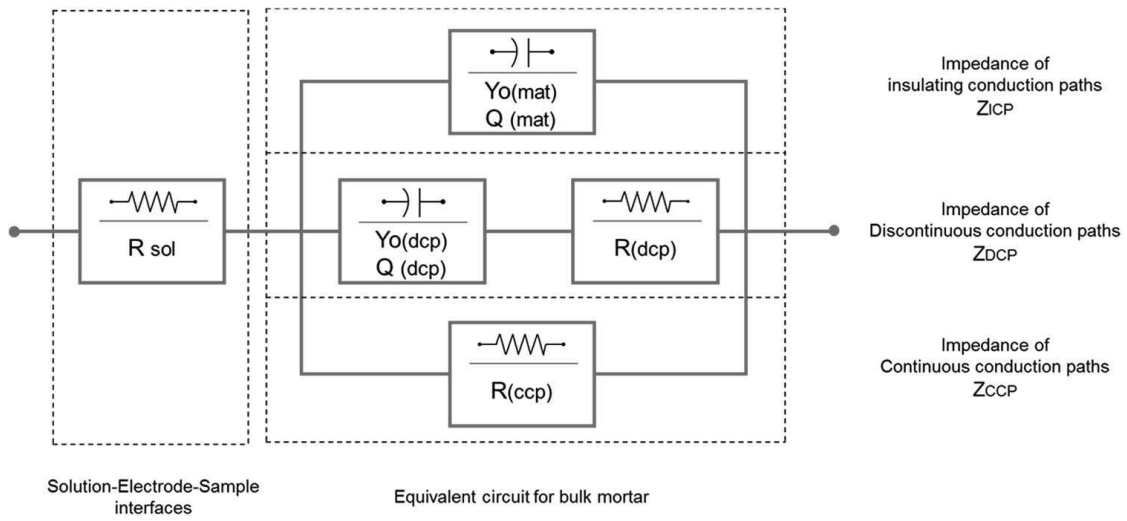


Figure 4.23 Typical impedance spectrum of a Warburg element with a reflective boundary (a), simulated impedance spectra of porous microstructures with closed ends [280] (b) and the porous microstructure of C-S-H on the surface of the cement grains [281,282] (c).

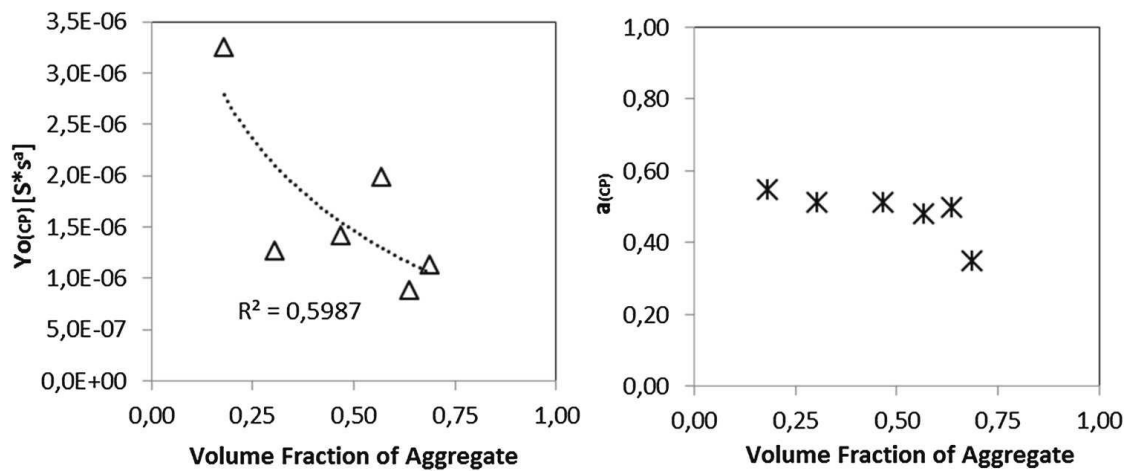
Finally, the same selection has been reported in the literature by Marriaga et al. [283]. They first used the equivalent circuit model (see Figure 4.24(a)), which is the same as the model shown in Figure 4.22(b), for the EIS fitting of OPC mortars. The n value (a in their paper) of the CPE in the non-conductive paths is close to 0.5 (Figure 4.24(b)). Correspondingly, they proposed to replace the CPE element with the Warburg element defining the diffusion behaviour of the non-conductive paths. The only difference between Marriaga et al. and the present work in terms of the Warburg element is that they justify the use of the Warburg element from the mass transport in the Interfacial Transition Zone (ITZ) (the surface of the aggregate), while in this work, it is assumed that it is derived from the ion diffusion in the gel pores of C-S-

Chapter 4

H (the surface of the cement grain). Like the gel pore structure in C-S-H, the ITZ has also a porous structure as shown in Figure 4.25 [284-285].



(a)



(b)

Figure 4.24 Equivalent circuit model (a) used for the fitting of the mortars reported by Marriaga et al. and the corresponding fitting results of non-conductive pore capacitance [283] (b).

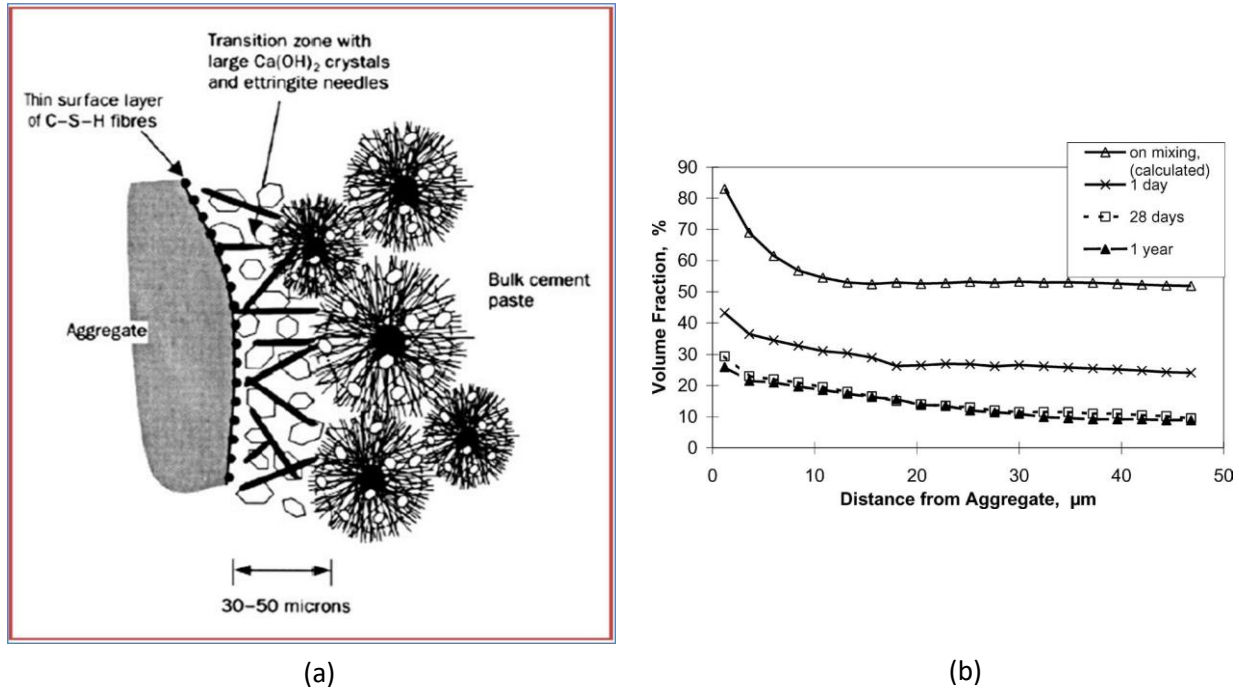


Figure 4.25 Schematic diagram of the ITZ (a) [284] and average porosity in ITZ at various age (b) [285].

Sometimes, a CPE with the n value close to 1 also fits well, which seems to be contradictory to the application of W_o to describe the electrochemical responses of the solid phase (C-S-H). Indeed, this can be attributed to the characteristics of W_o . For a Warburg element with a reflective boundary, its electrochemical responses can be roughly separated into two frequency domains. The typical impedance spectrum is shown in Figure 4.26. In the high frequency domain, the phase angle of W_o is fixed at -45° , which corresponds to the diffusion controlled process. In the low frequency domain, the phase angle of W_o is fixed at -90° , indicating that it behaves like a capacitor. The impedance spectra of porous microstructures with closed ends (Figure 4.23) are expected to have such electrochemical responses. In terms of the gel pores in C-S-H, the physical meaning of two frequency domains is that the ion transport in the gel pores follows different rules under different frequencies. In the high frequency region, the ion transport direction alternates fast and the process of ion migration towards one direction is short, then it is a diffusion controlled process because of the geometry constraint. By contrast, in the low frequency region, the long duration associated with ion migration towards one direction, leads to the accumulation of anions/cations on the surface of the closed end in the gel pores, which works like an electrical double layer. Between the two frequency domains, there is a transition zone. In terms of the gel pores of C-S-H, there are many influential factors e.g., the cement hydration, the humidity and the temperature. Even the addition of lithium salts is reported to change the C-S-H structure [286-291]. Therefore, the gel pores of C-S-H can have different pore sizes, pore shapes, ion concentrations, etc., corresponding to distinct ion diffusion behaviours. Considering the replacement of W_o by a CPE , if the diffusion controlled process of W_o with a phase angle at -45° (the high frequency part) is predominant in the measured frequency range,

Chapter 4

the n value of a CPE is 0.5; if the capacitor behaviour of W_o with a phase angle at -90° (the low frequency part) is predominant in the measured frequency range, the n value of a CPE is 1. However, when both domains cannot be neglected in fitting the electrochemical responses of C-S-H, the replacement of W_o with a CPE leads to the failure of good fitting in the entire frequency range. By contrast, W_o always works regardless of the variation of C-S-H. Even if the electrochemical responses of C-S-H show a capacitor behaviour, W_o can fit appropriately by behaving like a CPE with an n value higher than 0.5 (this also explains why sometimes the n value of W_o in the fitting is higher than 0.5). An example is provided in Figure 4.27. Note that the small deviation from a standard CPE in the low frequency region can be avoided by adjusting the values of W_o .

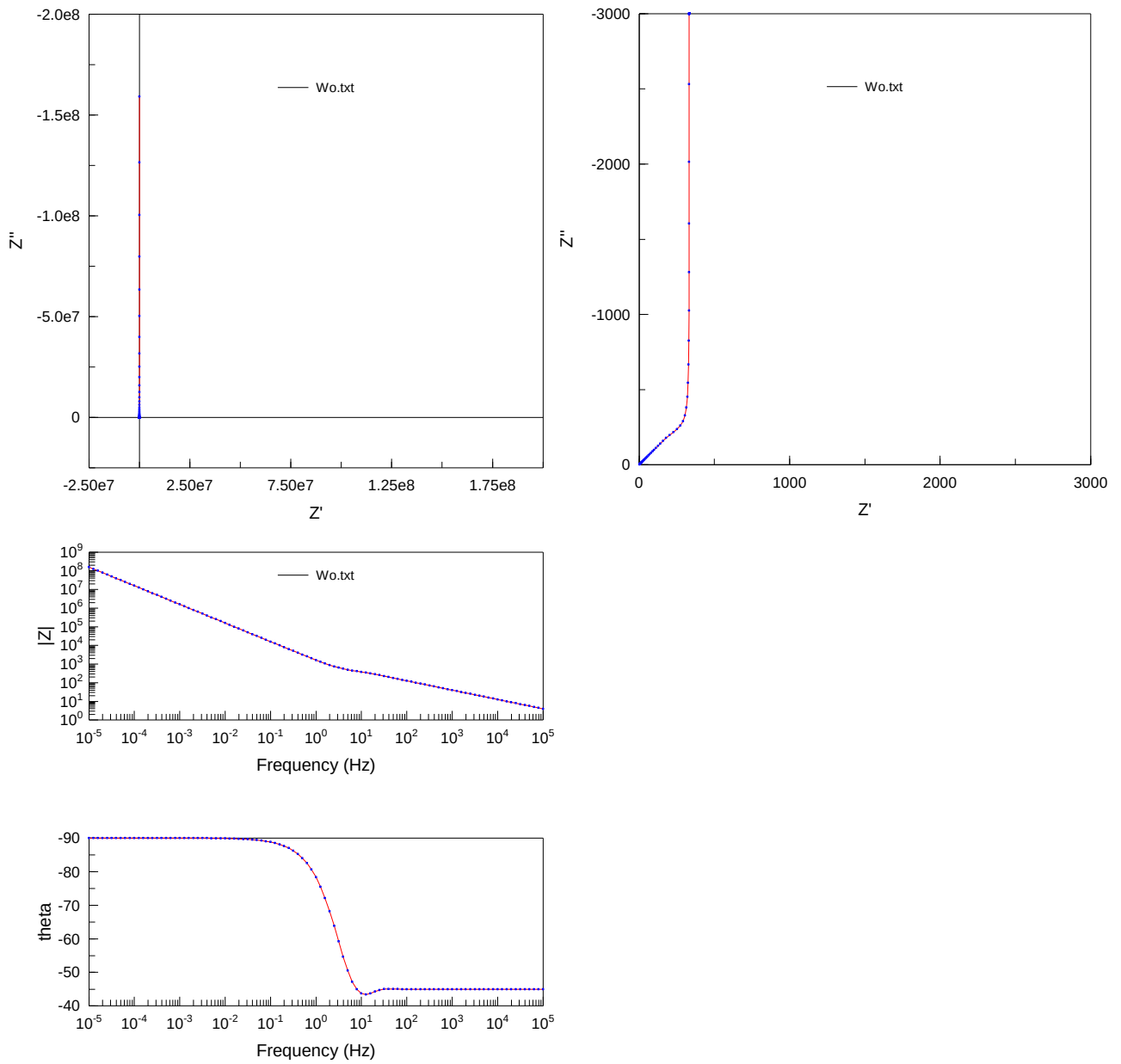


Figure 4.26 Typical impedance spectra of a Warburg element with a reflective boundary produced with: $W_o-R = 1000$; $W_o-T = 0.1$; $W_o-P = 0.5$.

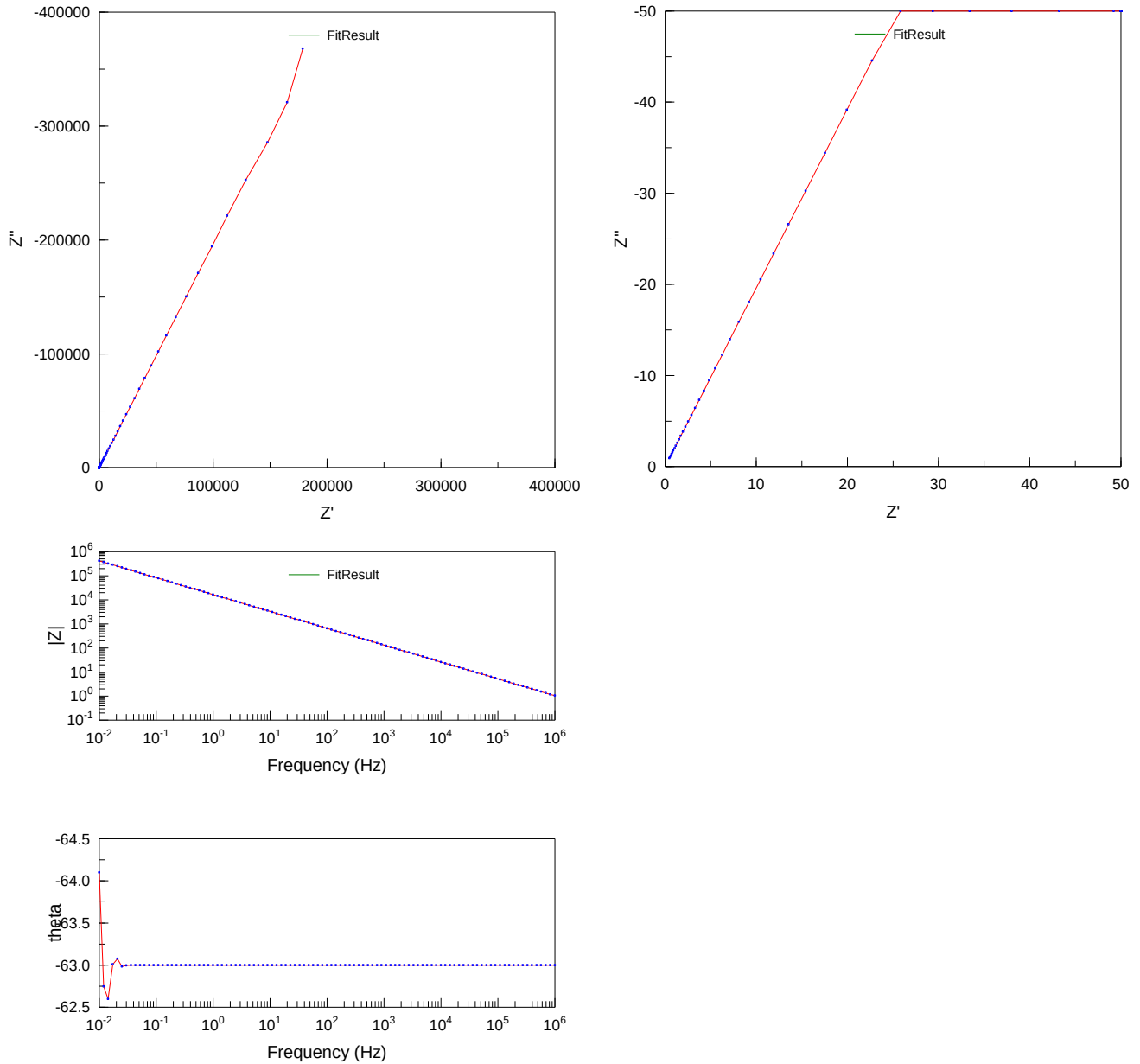


Figure 4.27 Impedance spectra of a Warburg element with a reflective boundary produced with:

$$W_o-R = 2.0 \times 10^6; W_o-T = 150; W_o-P = 0.7.$$

At the end, the equivalent circuit shown in Figure 4.22(c) with W_{cem2} was adopted. More details involving the comparison of CPE_{cem2} and W_{cem2} are provided in Section A.3.

4.5.3. Modelling of the interface

The third part accounts for the electrochemical response of the aluminium/corrosion product film/cement paste interfaces of the two electrodes. The same EEC was adopted by Visser et al. [160] for the corrosion study of aluminium alloy 2024 in alkaline lithium carbonate solution. The capacitance and the resistance properties of the corrosion product film are represented by CPE_f (C_f is occasionally used

Chapter 4

when the ' n ' value of CPE_f is above 1, which is physically unacceptable) and R_f , respectively. C_{dl} is the double layer capacitance. R_t is the charge transfer resistance, which describes the charge transfer process. In the corrosion study, R_t is used to calculate the corrosion rate and R_f is an important parameter revealing the evolution of the corrosion process. Considering the setup composed of two identical electrodes, the magnitude of the resistances (R_f and R_t) in this part is actually the sum of two individual elements coming from both electrodes. Thus, the real R_f and R_t in each electrode are half of the fitted value. For the same reason, the real Q/C parameters of CPE_f and C_{dl} are twice as high as the fitted value.

At the beginning of the fitting study, a simpler circuit with R_t and C_{dl} in parallel (Figure 4.28(a)) was used to describe the interface. They are commonly used to study the processes at the electrochemical interface. However, it does not fit well in the low frequency region as shown in Figure 4.29(c). The curve in the low frequency region mainly corresponds to the electrochemical responses of the interface part, thus the mismatch means the problem of the corresponding equivalent circuit part. Meanwhile, the presence of the corrosion product film can be visibly observed as discussed in Section 4.9. According to Chapter 2, this corrosion product film is expected to work as a physical barrier. Hence, the electrical contribution including the resistance (R_f) and the capacitance (CPE_f) of the film is considered in the equivalent circuit model as shown in Figure 4.28(b). This model gives a better fitting curve and a lower Chi-squared value (Figure 4.30). Moreover, a Warburg element next to R_t (a Randles circuit), which represents the ion diffusion of reactants and products, was also tested. This is to examine whether the diffusion process could occur at the interface instead of in the cement paste (W_{cem2}), correspondingly W_{cem2} was replaced with CPE_{cem2} . Nevertheless, neither a Warburg element with a reflective boundary nor a Warburg element with a transmissive boundary fits well. Even if the model with a Warburg element next to R_t sometimes provides comparable fitting curves, the fitting errors are incredibly high (Figure 4.31). It should be noted that the n value of CPE_f could also be low sometimes, which means that W_f might be more suitable than CPE_f in some cases. This matches the diffusion behaviour observed in Section 4.9. However, this is not discussed because it increases the complexity of the model and it goes beyond the scope of this study.

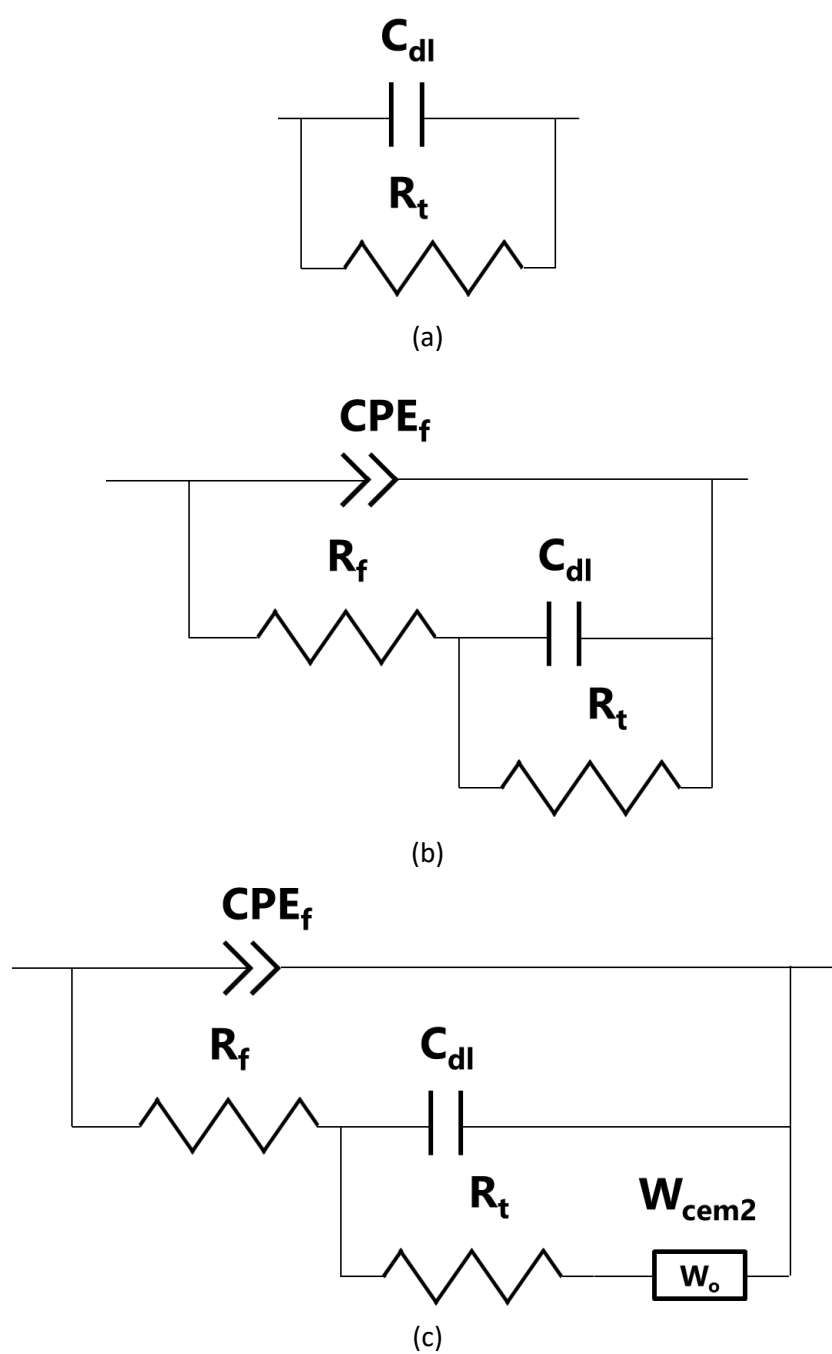
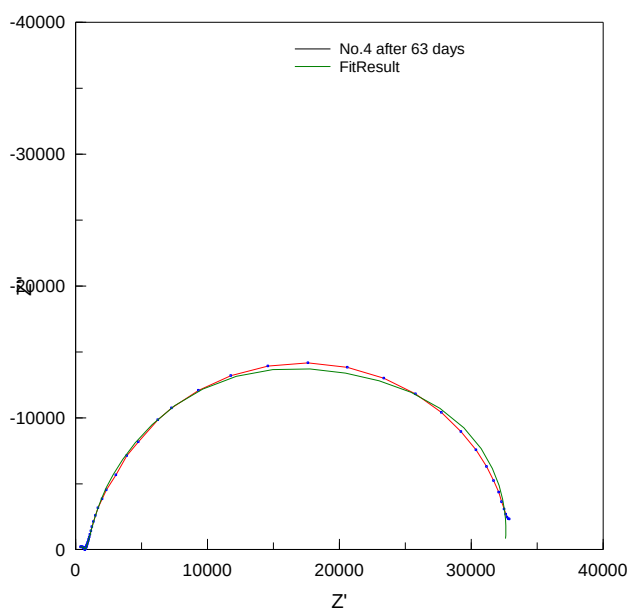
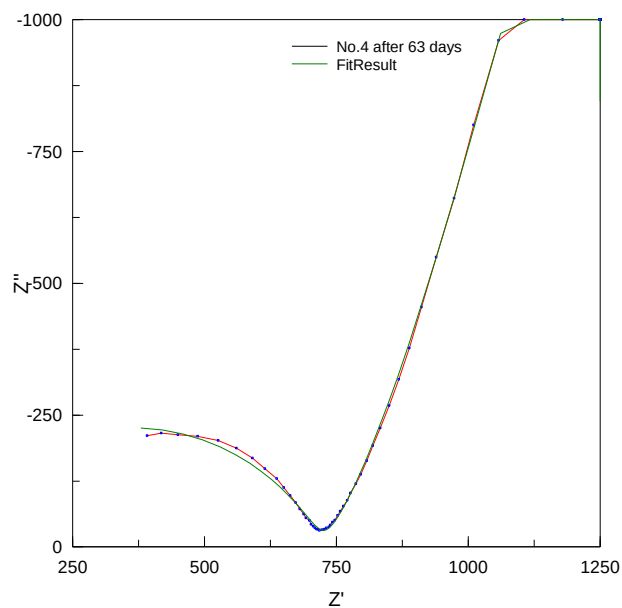


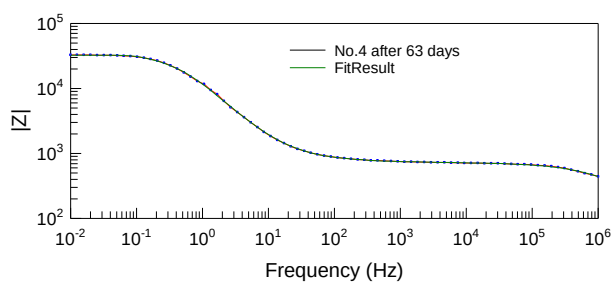
Figure 4.28 Equivalent circuit used in the study for describing the interface.



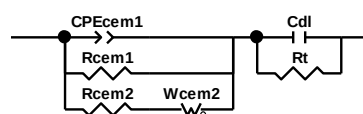
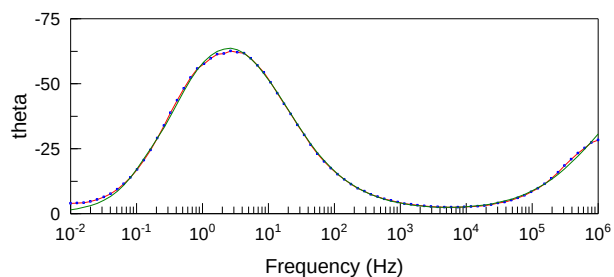
(a)



(b)



(c)



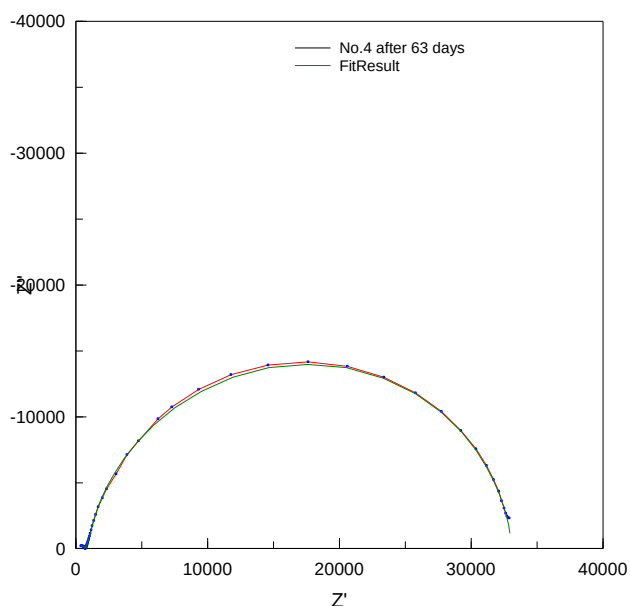
Element	Freedom	Value	Error	Error %
CPEcem1-T	Free(±)	1.878E-08	2.1718E-09	11.564
CPEcem1-P	Free(±)	0.71131	0.0075581	1.0626
Rcem1	Free(±)	10136	564.9	5.5732
Rcem2	Free(±)	778.1	5.0954	0.65485
Wcem2-R	Free(±)	6576	1254.2	19.072
Wcem2-T	Free(±)	0.60363	0.1364	22.597
Wcem2-P	Free(±)	0.57384	0.010363	1.8059
Cdl	Free(±)	1.5288E-05	2.4676E-07	1.6141
Rt	Free(±)	22423	549.7	2.4515

Chi-Squared: 0.00096265
Weighted Sum of Squares: 0.14536

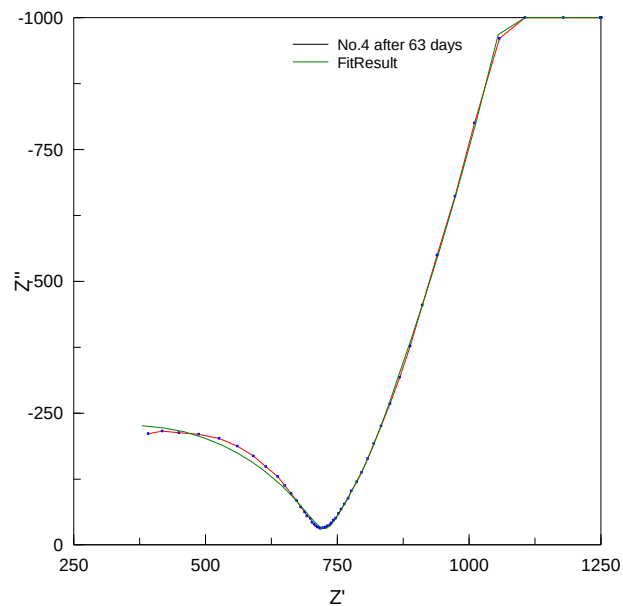
(d)

Figure 4.29 EIS fitting results only using a parallel R_t and C_{dl} (Nyquist (a), (b), Bode (c) plots and the fitting parameters (d)) of an OPC+LiNO₃ sample after 63 days in condition 1.

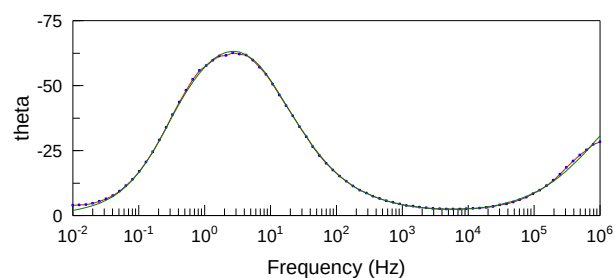
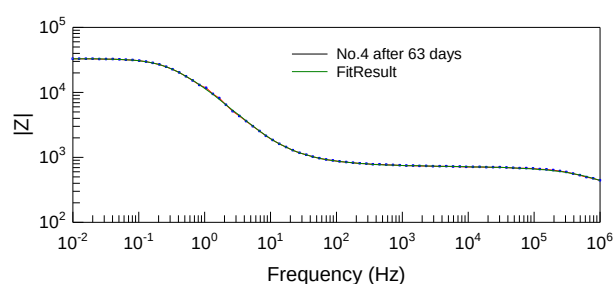
Chapter 4



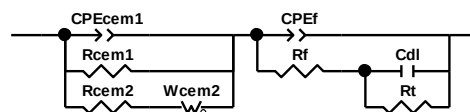
(a)



(b)



(c)



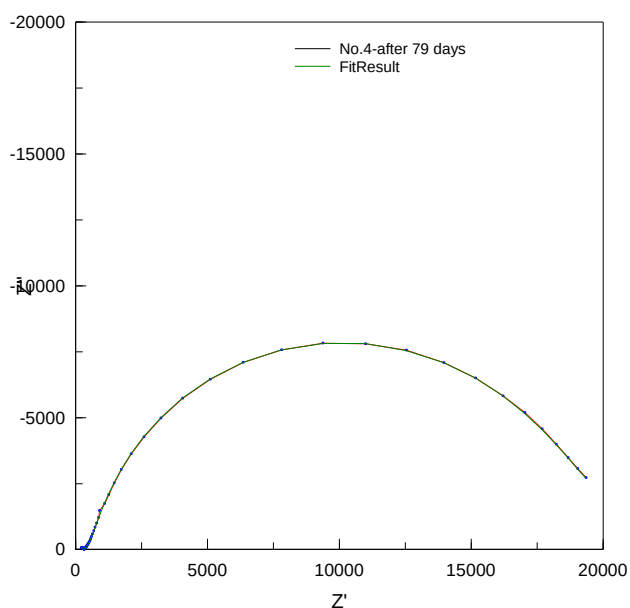
Element	Freedom	Value	Error	Error %
CPEc1-T	Free(±)	1.8431E-08	2.0911E-09	11.346
CPEc1-P	Free(±)	0.71243	0.007162	1.0053
Rcem1	Free(±)	18481	3080.8	16.67
Rcem2	Free(±)	751.1	9.0562	1.2057
Wcem2-R	Free(±)	219.8	84.737	38.552
Wcem2-T	Free(±)	0.0061165	0.004058	66.345
Wcem2-P	Free(±)	0.48967	0.0080945	1.6531
CPEf-T	Free(±)	2.1538E-05	2.2725E-06	10.551
CPEf-P	Free(±)	0.85115	0.021298	2.5023
Rf	Free(±)	2390	1236.5	51.736
Cdl	Free(±)	4.1261E-06	1.0969E-06	26.584
Rt	Free(±)	12253	2565.5	20.938

Chi-Squared: 0.00066607

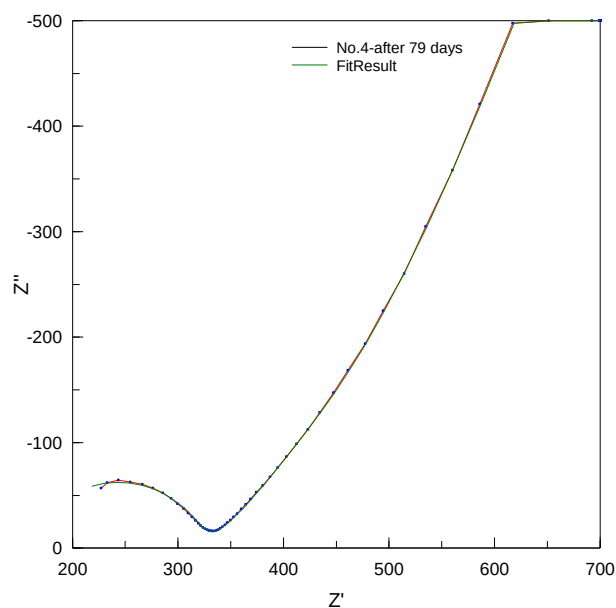
Weighted Sum of Squares: 0.098578

(d)

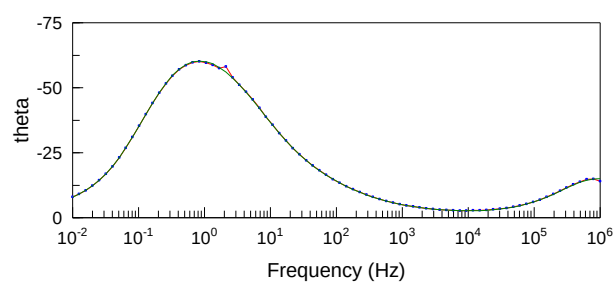
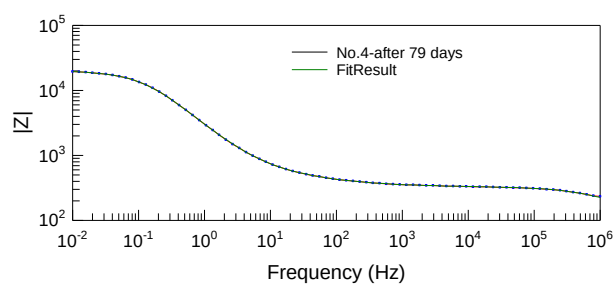
Figure 4.30 EIS fitting results (Nyquist (a), (b), Bode (c) plots and the fitting parameters (d)) of an OPC+LiNO₃ sample after 63 days in condition 1.



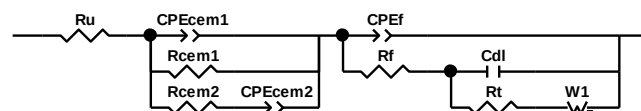
(a)



(b)



(c)



Element	Freedom	Value	Error	Error %
Ru	Free(±)	159.9	3.5659	2.2301
CPEcem1-T	Free(±)	2.2801E-08	6.4851E-09	28.442
CPEcem1-P	Free(±)	0.82215	0.013155	1.6001
Rcem1	Free(±)	6241	753.85	12.079
Rcem2	Free(±)	168	4.6456	2.7652
CPEcem2-T	Free(±)	0.00050164	6.245E-05	12.449
CPEcem2-P	Free(±)	0.43668	0.021368	4.8933
CPEf-T	Free(±)	6.4257E-05	2.1154E-05	32.921
CPEf-P	Free(±)	0.93147	0.12148	13.042
Rf	Free(±)	296.2	84.082	28.387
Cdl	Free(±)	1.1359E-05	1.5181E-05	133.65
Rt	Free(±)	13570	3967.8	29.239
W1-R	Free(±)	2420	3981	164.5
W1-T	Free(±)	3.652	0.25241	6.9116
W1-P	Free(±)	0.41338	0.01797	4.3471

Chi-Squared: 0.00011074
Weighted Sum of Squares: 0.016058

(d)

Figure 4.31 EIS fitting results (Nyquist (a), (b), Bode (c) plots and the fitting parameters (d)) of an OPC+Li₂CO₃ sample after 79 days in condition 1.

4.5.4. Discussion on the modelling

Ignoring the contribution of the first part (L_1 and R_u), which only emerges occasionally, the EEC model used in this study normally involves four time constants related to CPE_{cem1} , W_{cem2} , CPE_f and C_{dl} . However, in general, most of the spectra only show 3 time constants (an example is shown in Figure 4.3), which matches the results reported in literature [126]. This apparent contradiction between the numbers of the time constants is attributed to the convolution of electrochemical phenomena happening at closeby frequencies with an amplitude in the same order of magnitude.

The validity of the EIS fitting results needs to be supported by other evidences. Because the experimental determination of the resistance is easier than that of the capacitances or the Warburg elements, we focused on R_{cem1} , R_f and R_t and compared them (or some results calculated from them) with the ones from other sources to examine the accuracy of the fitting as introduced in Section 4.7.5, 4.8 and 5.6 (R_{cem1} and R_t were respectively used to determine the porosity and the corrosion rate, which were compared with the results determined from other techniques, instead of a direct comparison of R_{cem1} and R_t).

4.6. Fitting

The ranges of the fitting parameters should be roughly predetermined because the fitting software needs close starting values. Besides, the results provided by the fitting should not only be physically acceptable but should also be supported by other sources.

4.6.1. Wire inductance and uncompensated resistance

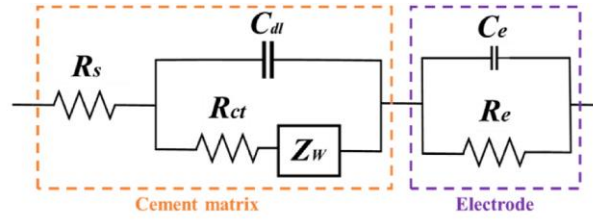
The existence of L_1 and R_u was experimentally studied and discussed earlier. According to the discussion in Section 4.5.1.1, if the influence of the inductance cannot be ignored, the starting value of L_1 is chosen as equal to 2 μH . Similarly, R_u is normally started at 100 Ω . The fitting procedure will provide the most suitable values automatically.

4.6.2. Cement paste

It turned out to be difficult to directly compare the elements of the cement paste part with literature data because of the differences of cell geometry (the area, the shape, the distance between electrodes), cement constituent, and equivalent circuit model. For example, the larger the electrode area is, the higher the capacitance is. However, some specific cases reported in the literature, such as the variation of these elements, can still provide valuable information.

CPE_{cem1} corresponds to the capacitance properties of the solid phase in the cement paste. Some literature reported that the capacitance of the cementitious matrix can be as low as $\mu\text{F} \sim \text{nF}$ [126, 292-

296]. This matches the fitting results of most samples in this study. However, an exception occurs in some OPC+Li₂CO₃ samples, in which CPE_{cem1} can be relatively high (hundreds of μF). Chen et al. [297] and Carter et al. [298] reported that the capacitance of the cementitious bulk matrix could be more than 1 mF, but it should be noted that their equivalent circuit models are different from the one applied here. Besides, literature reported many factors that can change the capacitance of the cementitious bulk matrix. Huang et al. [276] reported that the capacitance of the cement matrix is increased by the addition of sugar beetroot-based micro sheets (SMS). With ongoing curing time, the influence of the SMS concentration is more and more obvious. After 28 days, the cement paste containing 0.3 wt.% SMS reveals a cement matrix capacitance almost 1000 times higher compared to that without the addition of SMS (see Figure 4.32). Cao et al. [293] showed that the addition of MgAl-LDHs-NO₂⁻ into mortar increased the capacitance of the cementitious bulk matrix. The increase of matrix capacitance (C_{mat}) of mortar samples with the addition of MgAl-LDHs-NO₂⁻ is shown in Figure 4.33. Besides, the addition of steel fibers [295], aggregates [296] or the different curing conditions [299] are reported to affect the capacitance of the cementitious bulk matrix. In terms of OPC+Li₂CO₃ samples, the addition of Li₂CO₃ probably leads to the carbonation of the cement paste and hence change the constituents of the cement paste matrix. Some changes are indeed observed during the preparation of OPC+Li₂CO₃ samples. The addition of Li₂CO₃ accelerated the hardening process of the cement paste, which complicated the preparation of these samples. Therefore, the w/c ratio of these samples was increased up to 0.5. Therefore, the high capacitance of the bulk matrix in OPC+Li₂CO₃ samples might be attributed to the addition of Li₂CO₃. Besides, other factors such as omitting L_1 and W_{cem1} (see Figure 4.14 and Figure A.17) for simplification are likely to affect CPE_{cem1} . Further research is needed to better understand the influence of these factors.

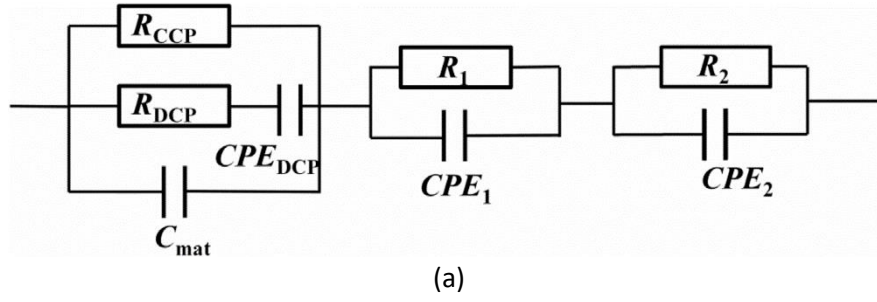


(a)

Day	SMS (wt%)	R_s (Ω)	C_{dl} (μF)	R_{ct} (Ω)	Z_w (Ω/cm^2)	C_e (μF)	R_e (Ω)
7	0	928.9	4.84E-01	156.5	2.02E-04	1.28E-03	231.6
	0.1	1004	5.92E-01	141.2	2.91E-04	1.58E-03	234.8
	0.2	1074	1.58	87.65	9.55E-04	4.70E-4	298.3
	0.3	1163	8.68	148.6	7.71E-04	7.53E-4	258.7
14	0	1041	1.30E-03	295.7	1.34E-04	7.42	337.4
	0.1	1113	5.39E-02	113.3	3.81E-04	3.22E-4	436.6
	0.2	1239	2.54E-01	84.95	5.21E-04	3.66E-4	439.1
	0.3	1313	1.67	140.5	6.04E-04	7.73E-4	306.9
28	0	1142	7.895E-04	421.7	1.148E-04	7.512	337.3
	0.1	1222	1.40E-03	320.2	2.800E-04	2.30	353.7
	0.2	1335	1.53E-03	279	3.320E-04	5.04	367.8
	0.3	1348	6.68E-01	166.9	3.920E-04	5.58E-4	421.6

(b)

Figure 4.32 Equivalent electrical circuit of the cementitious composites (a) and the corresponding fitting results for different SMS concentrations and curing ages (b) [276].



(a)

W/D cycles	$R_{CCP}/k\Omega$ μm^2	C_{mat}/pF cm^{-2}	$R_{DCP}/k\Omega$ cm^2	CPE_{DCP} $Y_{DCP}/(10^{-6} \Omega^{-1} cm^{-2} s^n)$	n_{DCP}	$R_1/k\Omega$ cm^2	CPE_1 $Y_1/(10^{-6} \Omega^{-1} cm^{-2} s^n)$	n_1	$R_2/k\Omega$ cm^2	CPE_2 $Y_2/(10^{-6} \Omega^{-1} cm^{-2} s^n)$	n_2
2	2.689	65.52	3.394	216.1	0.689	1.742	589.8	0.130	188.8	623.6	0.867
7	2.938	83.14	4.383	147.0	0.715	2.683	321.3	0.186	254.0	330.5	0.826
8	2.200	84.46	8.116	106.8	0.814	2.317	288.3	0.184	18.46	1650	0.818
10	2.446	76.54	12.29	75.34	0.883	2.930	249.7	0.185	12.36	2014	0.877
11	2.002	85.10	33.54	0.246	0.804	2.670	244.0	0.161	23.30	1364	0.658
12	2.360	77.65	49.21	0.177	0.833	3.711	201.2	0.137	47.08	701.8	0.668

(b)

W/D cycles	$R_{CCP}/k\Omega$ cm^2	C_{mat}/pF cm^{-2}	$R_{DCP}/k\Omega$ cm^2	CPE_{DCP} $Y_{DCP}/(10^{-6} \Omega^{-1} cm^{-2} s^n)$	n_{DCP}	$R_1/k\Omega$ cm^2	CPE_1 $Y_1/(10^{-6} \Omega^{-1} cm^{-2} s^n)$	n_1	$R_2/k\Omega$ cm^2	CPE_2 $Y_2/(10^{-6} \Omega^{-1} cm^{-2} s^n)$	n_2
2	1.127	108.3	3.836	68.92	0.624	0.532	234.9	0.168	1539	280.7	0.858
7	1.381	129.4	3.729	67.02	0.653	0.433	170.5	0.302	2197	218.4	0.851
8	1.409	130.5	4.710	62.40	0.685	0.576	216.2	0.279	2340	230.3	0.840
10	1.780	113.4	7.224	48.68	0.738	1.032	224.4	0.257	2763	211.4	0.846
11	1.612	111.8	7.374	48.66	0.791	1.116	254.4	0.258	2446	213.3	0.848
12	1.888	269.3	17.49	14.40	0.897	1.267	208.2	0.276	2654	202.1	0.839

(c)

Figure 4.33 Equivalent electrical circuit reflecting the phenomenon at the steel/mortar interface (a), the fitting parameters from EIS spectra of the carbon steel embedded in mortar after different W/D cycles without (b)/with (c) the addition of 8 wt.% $MgAl-LDHs-NO_2^-$ [293].

R_{cem1} is the resistance of ionic conduction through the connected capillary pores. Literature reported different variation trends. For instance, Cao et al. [293] provided the fitting results of a relatively stable resistance of the connected capillary pores during the first 12 days. Delpech et al. [126] reported a continuously increasing R_{cem1} . Nevertheless, because the pore solution conductivity of the cementitious materials is stable (see Section 3.5.3 and Section 5.5), the resistance of the connected capillary pores should be proportional to the number of the connected pores. According to the physical variation of the pores in cement paste, R_{cem1} should increase at the beginning of the first 28 days and then remain almost stable. Thanks to the relationship between the number of the connected pores and R_{cem1} , the cement paste porosity was analysed using R_{cem1} (see Section 3.5 and Chapter 5) and this study proves the reliability of the fitting results in return. The range of R_{cem1} reported in the literature is usually between hundreds of ohms and thousands of ohms [126,264], but a further direct comparison with literature is meaningless because of different experimental conditions.

Chapter 4

A resistor (R_{cem2}) and a Warburg element (W_{cem2}) form the disconnected pore path. Similar to R_{cem1} , R_{cem2} is expected to change rapidly at the beginning of the cement hydration (normally in the first 28 days), followed by a relative steady state. As addressed in Section 4.5.2, W_{cem2} describes the electrochemical responses of the ion diffusion in the gel pores of C-S-H. In terms of the gel pores of C-S-H, there are many influential factors e.g. the cement hydration, the humidity and the temperature. Besides, the addition of $LiNO_3$ or Li_2CO_3 and the curing conditions are also likely to change the gel pores. Therefore, it is difficult to predict the variation of W_{cem2} . The only requirement for W_{cem2} in the fitting is that the parameters are physically acceptable (e.g. the parameters should be positive and should be finite).

4.6.3. Interface

CPE_f (C_f is occasionally used when the ' n ' value of CPE_f is above 1, which is physically unacceptable) and R_f represent the capacitance and the resistance properties of the corrosion product film, respectively. The capacitance of the oxide film formed on a pure aluminium in the NaOH solution is reported to be several $\mu F \cdot cm^{-2}$ [300]. In terms of the capacitance of LDH films, literature reported that the capacitance values of different types of LDH films e.g. Li-Al LDH [160], Mg-Al LDH [154] and Zn-Al LDH [156] range from a few $\mu F \cdot cm^{-2}$ to tens of $\mu F \cdot cm^{-2}$. Therefore, either in the pure OPC samples or in the samples with lithium addition, the capacitance of the corrosion product film is expected to exhibit values in the order of $\mu F \cdot cm^{-2}$. One typical characteristic of R_f of LDHs is the 'air valley' effect. At the beginning, R_f can be as high as thousands of $\Omega \cdot cm^{-2}$ because of the air bubbles trapped in the film. Afterwards, R_f plunges rapidly with the ingress of the outer electrolyte, which usually occurs during the first 28 days, replacing the trapped air in the porous structure of the LDH film. This decrease has also been discussed in Section 2.6.2 and Section 4.8. Therefore, the decrease of R_f at the beginning should be observed in the fitting.

C_{dl} is the double layer capacitance. For OPC samples, the aluminium is in direct contact with the pore solution of the cement paste. The pore solution is detrimental to the corrosion protection of aluminium, because it is not only highly alkaline (Section 2.4 and Section 5.5) but also contains a series of aggressive ions such as Cl^- (Section 2.7 and Section 3.1). Abdel-Gaber et al. [301] reported that aluminium has a high C_{dl} (up to tens of $mF \cdot cm^{-2}$) in NaOH solution with/without the addition of NaCl. Abdallah et al. [302] also mentioned that C_{dl} of aluminium in a $0.1 \text{ mol} \cdot L^{-1}$ NaOH solution is $14.98 \text{ mF} \cdot cm^{-2}$. Visser et al. [303] studied the corrosion of AA2024 in $0.05 \text{ mol} \cdot L^{-1}$ NaCl solution, in which C_{dl} can be more than $1 \text{ mF} \cdot cm^{-2}$ when no inhibitor is added (see Figure 4.34(b)). Besides, Figure 4.34(b) shows that the value of C_{dl} significantly decreases when lithium carbonate is added. The high C_{dl} value of aluminium or aluminium alloys without inhibitor in an aggressive condition (NaOH and/or NaCl solution) should be attributed to the fact that the fast corrosion reaction significantly increases the surface area. The fitting results of C_{dl} in this study matches that reported in the literature. C_{dl} of samples without lithium addition is in the range of $mF \cdot cm^{-2}$,

Chapter 4

while C_{dl} of samples with lithium addition is in the range of $\mu\text{F}\cdot\text{cm}^{-2}$. Other factors such as the cement hydration and the curing conditions possibly influence C_{dl} as well. R_t is the charge transfer resistance, which is inversely proportional to the corrosion rate. It ranges from hundreds of ohms to thousands of ohms in this study. R_t was used to calculate the corrosion rate. Note that this corrosion rate is compared with the one determined from other techniques (Section 4.7.5), to examine the reliability of R_t results.

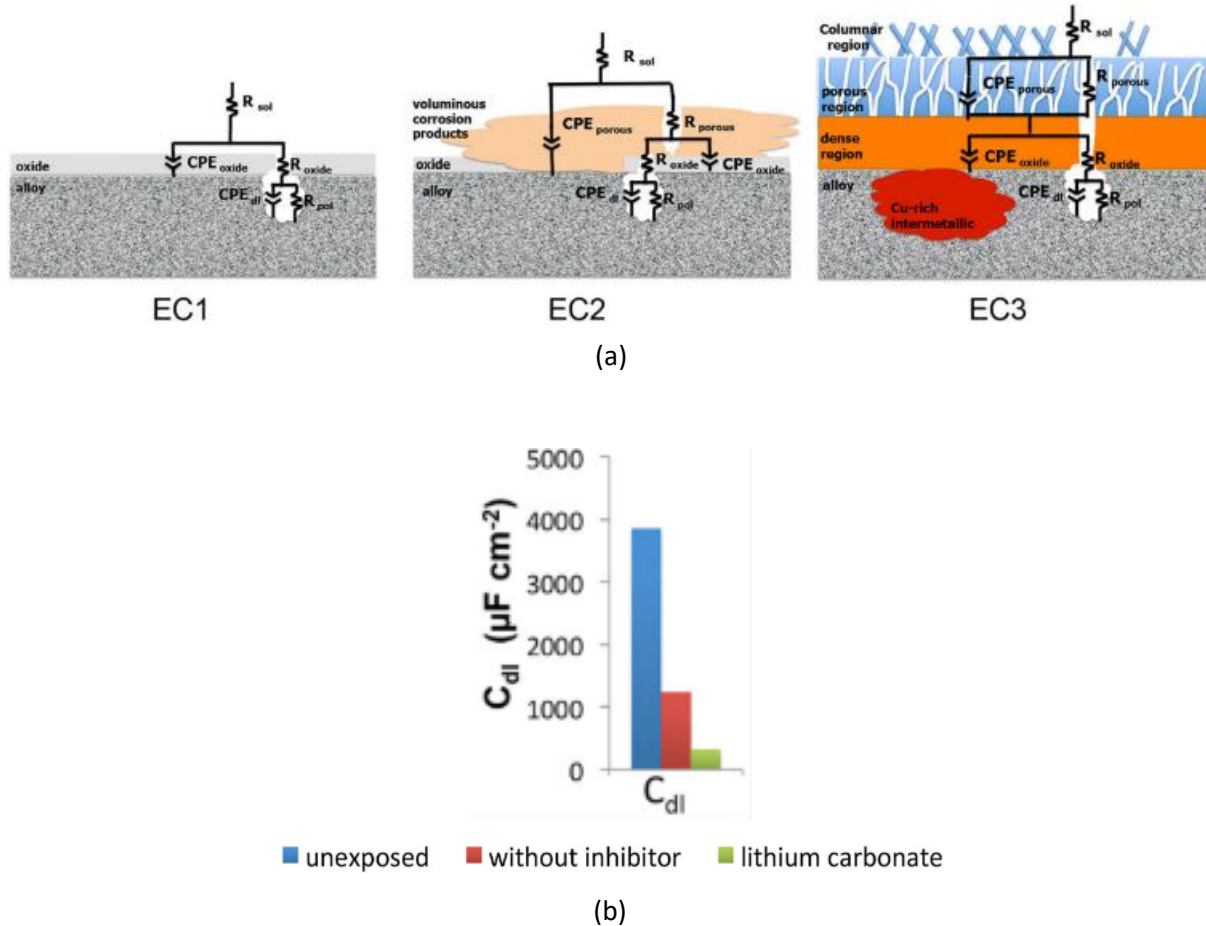


Figure 4.34 Equivalent circuits used to fit the EIS spectra: (EC1) unexposed defect areas and defect areas with few or no corrosion products; (EC2) defect areas with voluminous porous corrosion products; (EC3) defect areas with protective layer generated (a) and corresponding fitting results of AA2024 (b) [303].

4.6.4. Discussion about the fitting results

A typical EIS fitting result (before the normalization of the unit) is provided in Figure 4.35 to show the accuracy and the reproducibility of the fitting. First, the fitting plot should have a good agreement with the experimental plot in terms of both size and shape. Second, the error of each component needs to be as small as possible. Usually, as a rule of thumb, 10% or 20% is set as the maximum error for a cell in a liquid system. For the setup in this study, i.e., aluminium embedded in the cement paste, on the one hand, the two-phase cementitious system provides more error points in the experimental plot; on the other

hand, a more complicated circuit model is used, which increases the difficulty of finding parameter values all possessing acceptable errors. Therefore, while most component errors are controlled below 20%, a few others higher than 20% but lower than 100% are also tolerated. Finally, the better the fit is, the closer to 0 the Chi-squared value will be. And a Chi-squared value lower than 0.001 is normally thought to be acceptable. More fitting results are provided in Appendix A.4.

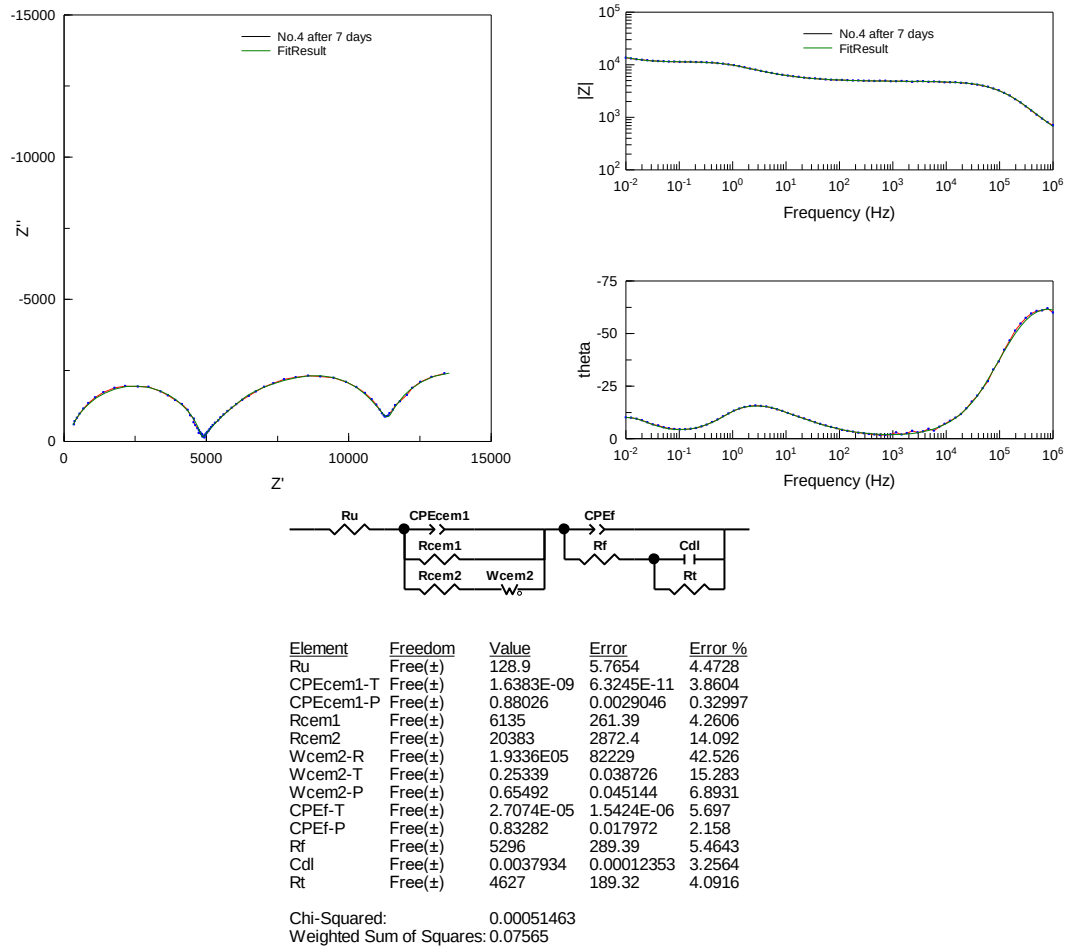


Figure 4.35 EIS fitting results of an OPC sample after 7 days in condition 1.

As addressed in Section 4.4, the parts corresponding to different time constants are likely to gradually overlap with each other in Nyquist and Bode plots as a function of time. Therefore, the fitting is easier at the beginning (because some parameter values can be directly obtained from Nyquist plots). Except in condition 1, when samples are immersed into limewater (after ~80 days), both the cement hydration and the corrosion variation are gradually varying processes, in which the shortening of the arc at the low frequency region is also a gradually changing process (an example is shown in Figure 5.1), thus the fitting results obtained at each time point are usually used as the starting values of the new fitting at the next time point. Even if the different arcs are not visibly separated in the Nyquist plots, the corresponding information is still included in the EIS results (the different kinds of information overlap in the plots instead of disappearing), an appropriate starting value selection in the fitting enables the separation of different

information. Besides, the changes of the cement hydration and the corrosion are both slow after the initial period, consequently the fitting values will not change significantly and this starting value selection benefits the fitting. The fitting results also need to be supported by other sources. The cement paste porosity determined by R_{cem1} was compared with the one obtained from MIP. The variation of R_f was studied to check whether the “air valley” effect of LDHs reported in the literature [153,154,156,171] can be found in the present study. SEM and GC were used to examine the reliability of the corrosion rates determined from R_t . When the fitting values of R_{cem1} , R_f , and R_t are confirmed by other sources (their values and variations were comparable to the ones obtained by other methods or reported in the literature) and the other parameters are all located in a reasonable range, the fitting results should have a higher reliability. Even if some works are performed to improve the reliability of the fitting results, the time constants overlap gradually increasing the difficulty of separating different information in the later fittings, thus more cautions are needed for the later results.

The comparisons between the results obtained from EIS fitting and the values from other sources are:

- The comparison of the cement paste porosity between the values determined by R_{cem1} and the values obtained from MIP. (Section 5.6)
- The comparison of R_f between the values obtained from EIS fitting and the values reported in the literature. (Section 4.8)
- The comparison of the corrosion rate between the values determined by R_t and the values obtained from GC and SEM. (Section 4.7.5)
- The comparison of CPE_{cem1} , CPE_f and C_d between the values obtained from EIS fitting and the values reported in the literature. (Section 4.6.2 and Section 4.6.3)

In conclusion, a significant effort has been made to ensure a physical justification of the selected equivalent circuit, choice of parameter ranges and fitting results. The parameter preselection has been supported by results from literature studies. Some fitting results i.e., R_{cem1} , R_f and R_t are specifically focused to examine the fitting reliability.

4.7. Corrosion rates

In this study, the corrosion rate is determined using three different techniques: EIS, GC and SEM. A series of parameters needed for the calculations are first discussed in the next sections.

4.7.1. Determination of R_t

R_t , as the charge transfer resistance, is determined from the impedance spectrum fitting. It is used to calculate the corrosion rate via Eq. (13) and (14), which provide an inversely proportional relationship

Chapter 4

between the R_t value and the corrosion rate. The R_t values obtained for the different samples, curing conditions and time are provided in Figure 4.36. The uncertainty of the results was also studied and graphs with error bars are given in Appendix A.6 (for a better readability, only the graphs without error bars are provided in this section).

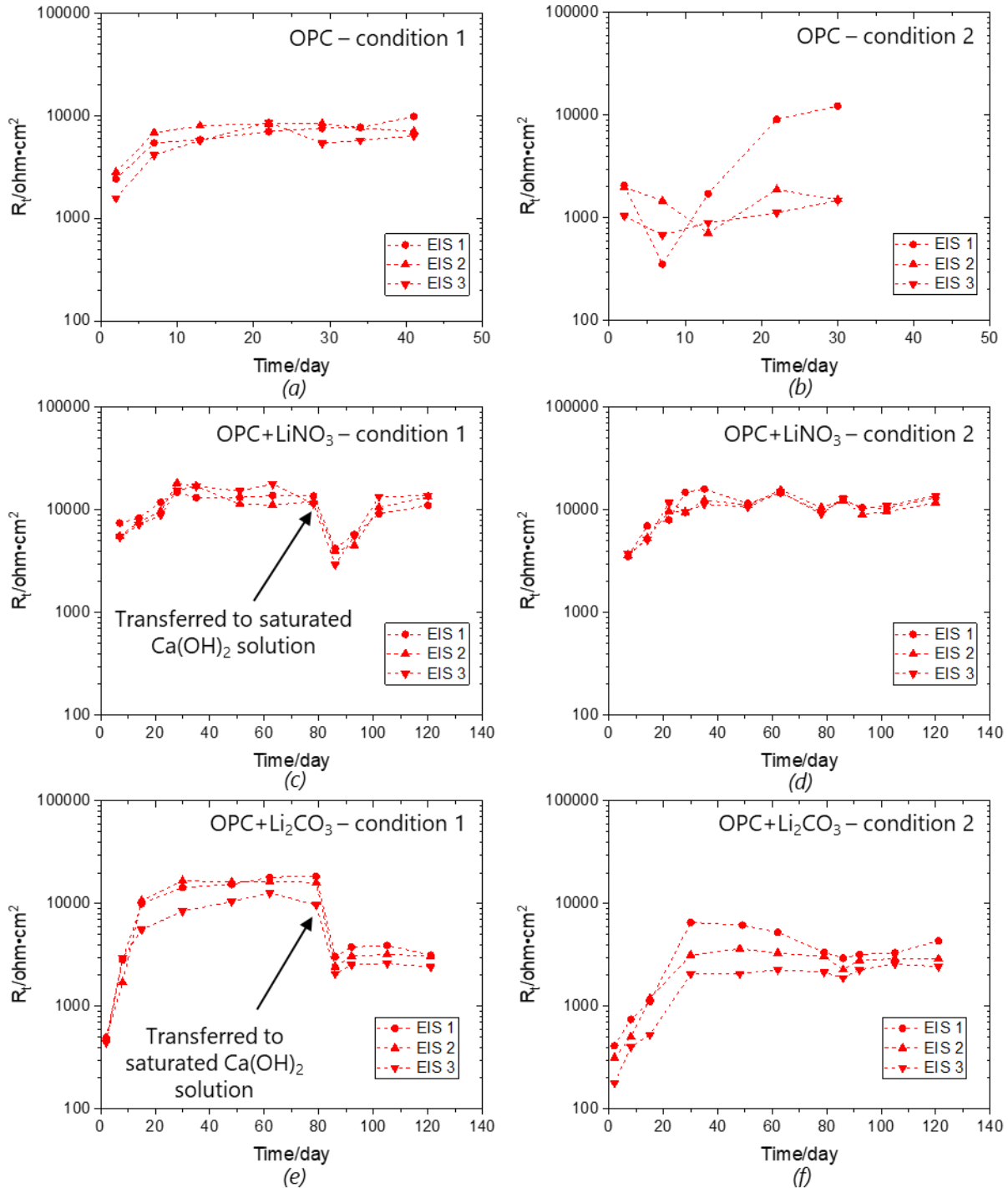


Figure 4.36 Evolution of R_t as a function of time of (a) OPC samples in condition 1, (b) OPC samples in condition 2, (c) OPC+LiNO₃ samples in condition 1, (d) OPC+LiNO₃ samples in condition 2, (e) OPC+Li₂CO₃ samples in condition 1, (f) OPC+Li₂CO₃ samples in condition.

The R_t results of pure OPC samples determined from EIS fitting are shown in Figure 4.36(a) and (b). Note that the measurements are only performed until 30 or 41 days because of the cracks leading to the difficulties of the EIS analysis. For samples in condition 1 (Figure 4.36(a)), the R_t values gradually increase until 13 days to reach a value around $7000 \text{ ohm}\cdot\text{cm}^2$, followed by a steady state. It represents that the corrosion rate decreases significantly at the beginning and then keeps almost stable. The triplicate samples (No.1, No.2 and No.3) show the good reproducibility of the measurements. For samples in condition 2, the R_t values are significantly influenced by the rapid propagation of cracks in the cement paste, leading to non-repetitive results, as shown in Figure 4.36(b).

Figure 4.36(c) and (d) provide the R_t results measured for OPC+LiNO₃ samples. In both conditions, R_t initially increases until reaching a steady state value around $10000 \text{ ohm}\cdot\text{cm}^2$. Note that in condition 1, a plunge in the graph can be observed after 80 days when the samples were transferred from the humid argon atmosphere into the limewater. However, R_t rapidly increases back to the steady state value observed before the transfer.

The R_t results, obtained for OPC+Li₂CO₃ are shown in Figure 4.36(e) and (f). In condition 1, R_t rapidly increases from $400 \text{ ohm}\cdot\text{cm}^2$ to about $10000 \text{ ohm}\cdot\text{cm}^2$, which corresponds to the sharp decrease of the corrosion rate. Afterwards, R_t remains stable until the immersion of the sample in Ca(OH)₂ solution after 80 days, which leads to a significant decrease of R_t . Afterwards, R_t remains constant. In condition 2, a rapid increase of R_t occurs in the first 28 day, followed by a steady state. In both conditions, the final value of R_t (around $2000\text{-}3000 \text{ ohm}\cdot\text{cm}^2$) are closely together.

The corrosion rate results determined from R_t are introduced in Section 4.7.5.

4.7.2. Determination of β_a and β_c

The other parameters entering equations (Eq. (13) and (14)) to evaluate the corrosion rate are obtained by extrapolation of the Tafel curves (see Section 3.2.2). The corresponding Tafel plots are shown in Figure 4.37.

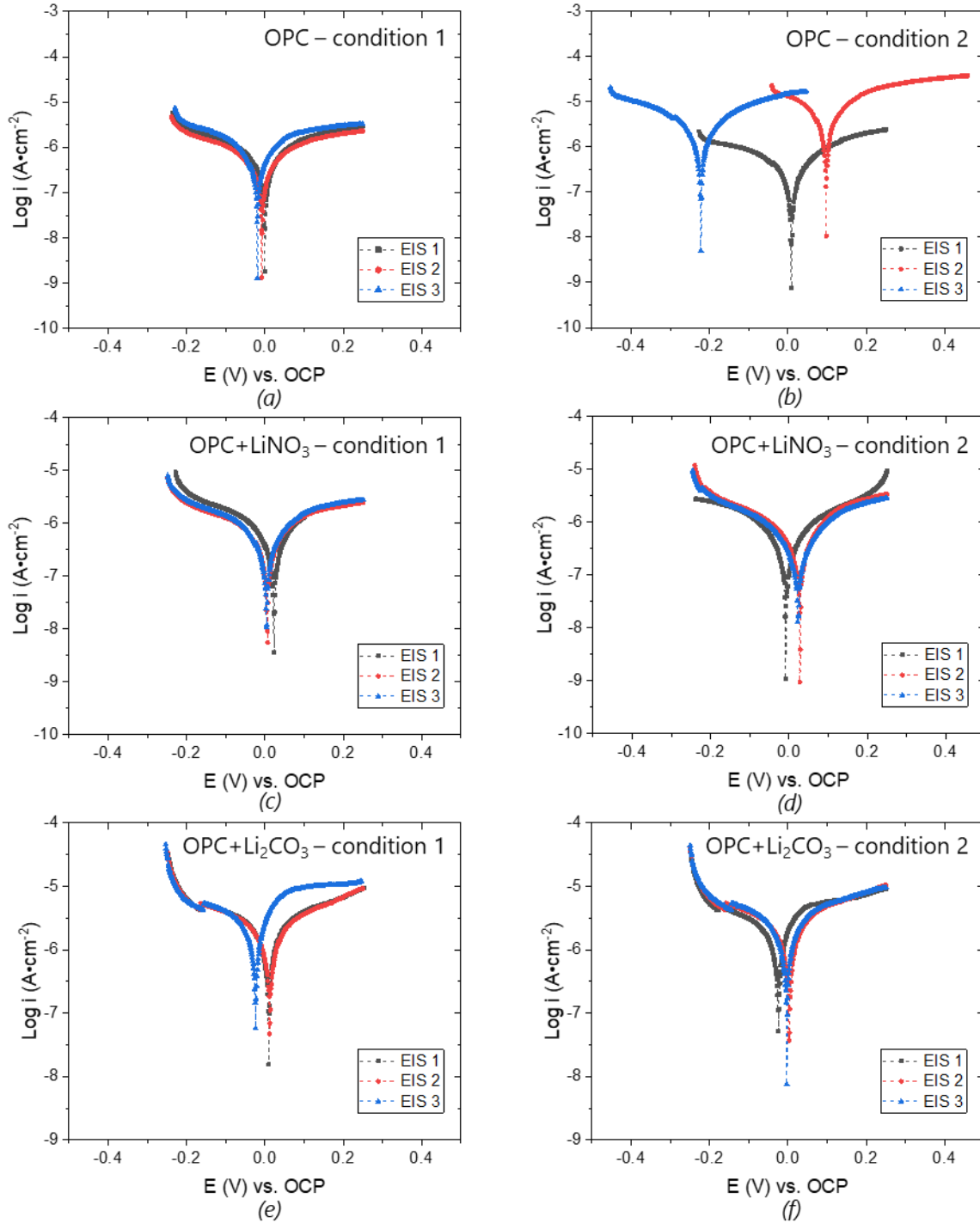
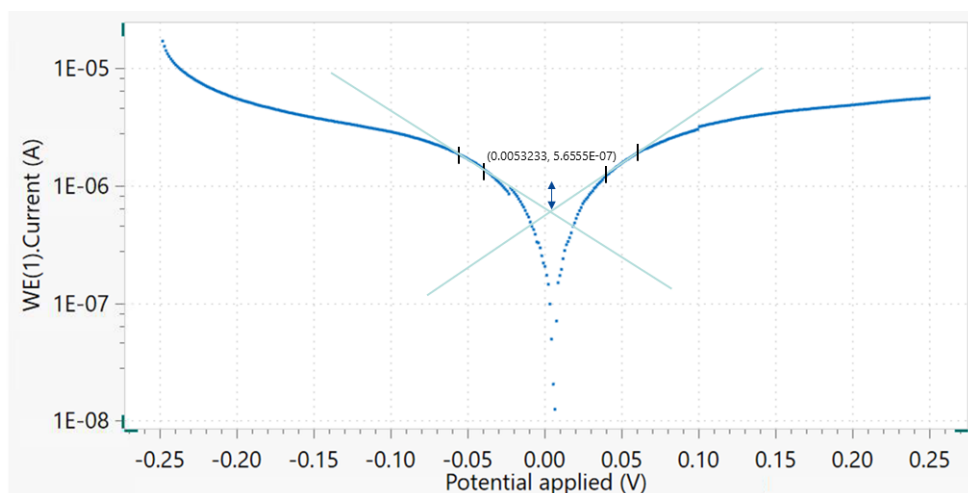


Figure 4.37 Tafel polarization plots of (a) OPC samples in condition 1, (b) OPC samples in condition 2, (c) OPC+LiNO₃ samples in condition 1, (d) OPC+LiNO₃ samples in condition 2, (e) OPC+Li₂CO₃ samples in condition 1, (f) OPC+Li₂CO₃ samples in condition 2.

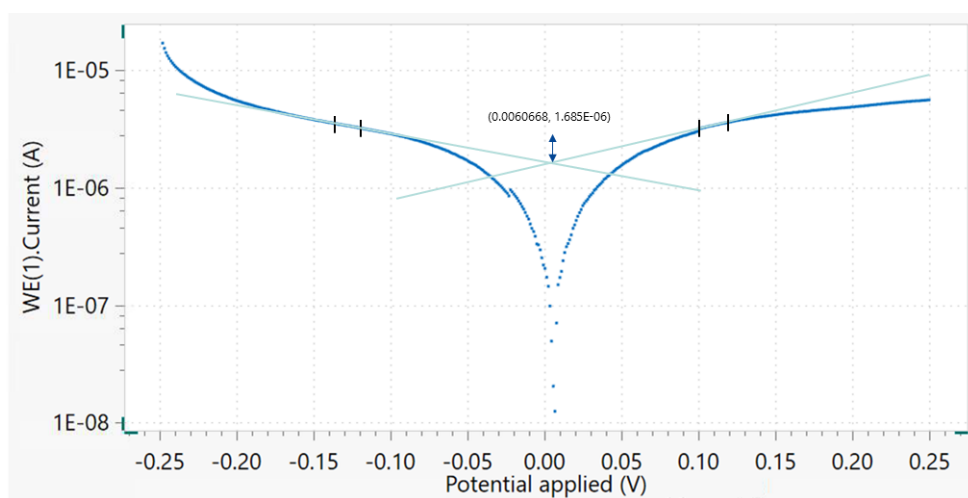
Chapter 4

In most cases, the triplicate samples (No.1, No.2 and No.3) show a good reproducibility of the measurements. Exceptionally, the corrosion potential values of OPC samples in condition 2 are different. The two identical electrodes in the cell have the same electrochemical responses, leading to a corrosion potential value around 0 V as shown in most samples. However, severe cracks occurred soon after the beginning of the measurements in OPC samples in condition 2 (see Section 4.7.5.1), which results in the potential difference between the two electrodes and correspondingly provides a corrosion potential value far from 0 V.

As addressed in Section 3.2.2, the Tafel region, with a linear relationship, is usually found in the range of ± 60 -120 mV to the E_{corr} according to the rule of thumb. However, the obtained polarization curves sometimes do not show a clear Tafel region with the linearity relationship. Different choices on the determination of the Tafel region are reported in the literature. Yan-qi et al. [304] mentioned that the Tafel curves, both the cathodic and the anodic branch, are close to linear from approximately 65 mV away from E_{corr} for Zn-Al alloys exposed in the saturated $\text{Ca}(\text{OH})_2$ solution. Cabot et al. [305] determined the anodic and cathodic Tafel slopes at potentials ± 70 mV around E_{corr} for aluminium in acid chloride solutions. Abdel-Gaber et al. [306] calculated the anodic and cathodic Tafel slopes as a slope of the points after corrosion potential (E_{corr}) by ± 50 mV for aluminium in $2 \text{ mol}\cdot\text{L}^{-1}$ NaOH solution containing different concentrations of lupine seed extract. Other studies chose higher potential ranges as the Tafel regions. For example, Tiancai et al. [307] chose the potential range of -100 mV to -120 mV vs OCP as the cathodic Tafel region for aluminum alloy. Ali et al. [308] also chose a high potential range (more than 100 mV) to determine the Tafel slopes of aluminium in $1 \text{ mol}\cdot\text{L}^{-1}$ NaOH in the absence and presence of aromatic carboxylic acids. In terms of this study, in which AA1100 is in contact with the cement paste, different strategies for the determination of Tafel slopes are tested. An example is provided in Figure 4.38. The determination of Tafel slopes in different potential ranges leads to distinct β_c , β_a values and B calculated using Eq. (13) is correspondingly different. The B value obtained by using the slopes at the points of about ± 50 mV away from E_{corr} (Figure 4.38(a)) is equal to 24 mV/dec, while the B value determined by using the slopes at the points of about ± 120 mV away from E_{corr} (Figure 4.38(a)) is 84 mV/dec. The B values are then used to calculate the corrosion rate. The different choices of the Tafel regions in Figure 4.38(a) and (b) give a corrosion rate equal to $19.39 \mu\text{m}\cdot\text{y}^{-1}$ and $67.89 \mu\text{m}\cdot\text{y}^{-1}$, respectively. Because SEM provides a corrosion rate equal to $8.70 \mu\text{m}\cdot\text{y}^{-1}$, the Tafel slopes are eventually chosen at the points of about ± 50 mV away from E_{corr} as shown in Figure 4.38(a). The same comparisons have been performed for other samples and gave similar results. Hence, the Tafel slopes are usually determined from potentials about ± 50 mV to E_{corr} . The β_c and β_a values together with the Stern Geary constant B , are provided in Table 11.



(a)



(b)

Figure 4.38 Example of the determination of Tafel slopes in different potential ranges for an OPC+LiNO₃ sample after 121 days in condition 1.

Table 11. Calculated β_c , β_a and B from Tafel polarization tests.

	Condition 1									
	No.1			No.2			No.3			
	β_a (mV/dec)	β_c (mV/dec)	B (mV)	β_a (mV/dec)	β_c (mV/dec)	B (mV)	β_a (mV/dec)	β_c (mV/dec)	B (mV)	Average B (mV)
OPC	114	136	27	136	149	31	143	148	32	30
OPC+LiNO ₃	97	121	23	104	115	24	106	126	25	24
OPC+Li ₂ CO ₃	119	130	27	136	146	31	113	219	32	30
	Condition 2									
	No.1			No.2			No.3			
	β_a (mV/dec)	β_c (mV/dec)	B (mV)	β_a (mV/dec)	β_c (mV/dec)	B (mV)	β_a (mV/dec)	β_c (mV/dec)	B (mV)	Average B (mV)
OPC	112	135	27	109	113	24	113	109	24	25
OPC+LiNO ₃	93	106	22	77	95	19	86	99	20	20
OPC+Li ₂ CO ₃	118	152	29	122	157	30	121	147	29	29

4.7.3. Determination of the produced hydrogen volume

The concentration variation of H₂ gas is measured from GC tests and hence the corresponding corrosion rate (V_{corr}) is calculated according to the relationship between the H₂ generated and the Al consumed (Eq. (16) and (17)). The H₂ concentration results are shown in Figure 4.39.

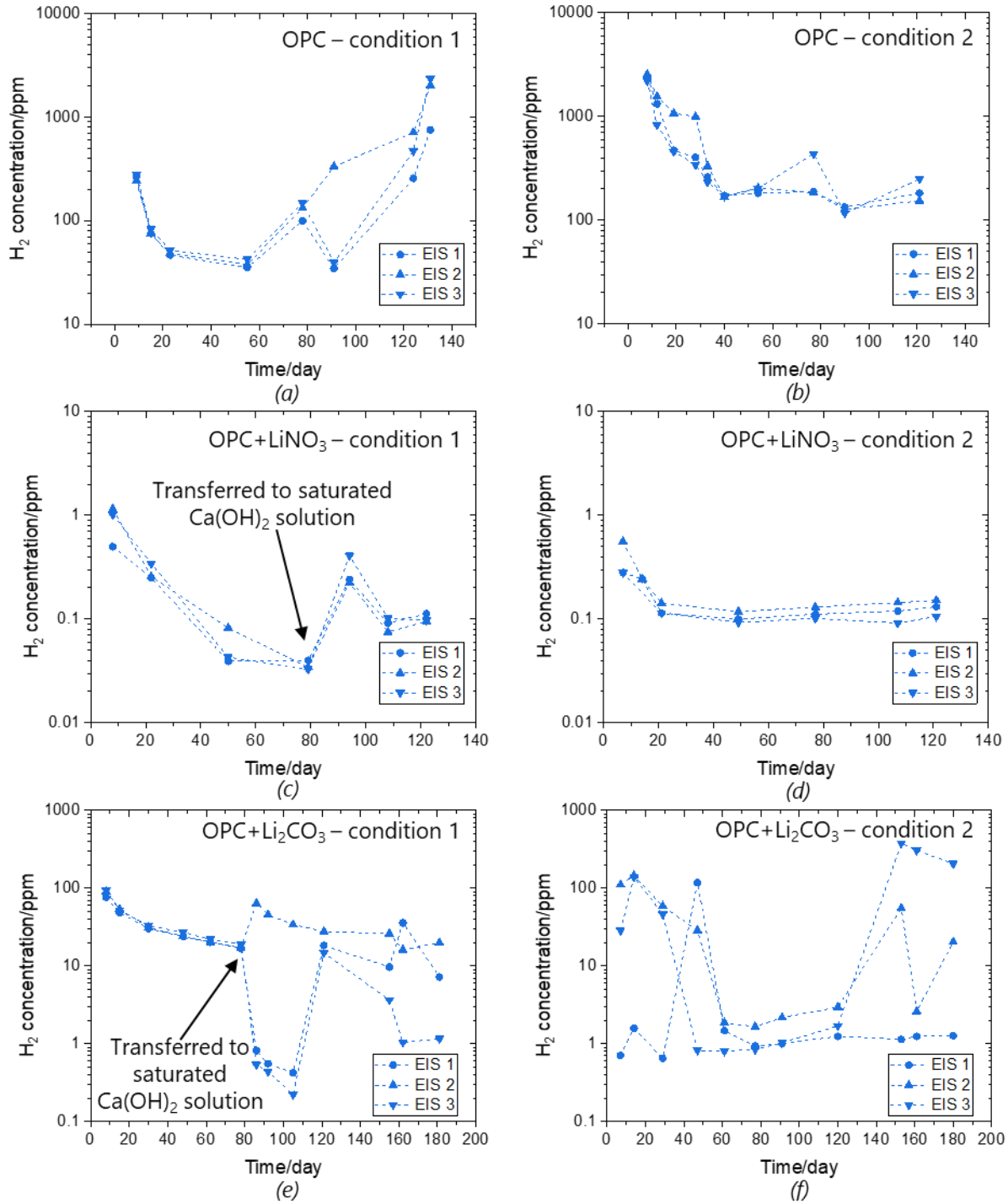


Figure 4.39 Evolution of H_2 concentration measured from GC as a function of time of (a) OPC samples in condition 1, (b) OPC samples in condition 2, (c) OPC+LiNO₃ samples in condition 1, (d) OPC+LiNO₃ samples in condition 2, (e) OPC+Li₂CO₃ samples in condition 1, (f) OPC+Li₂CO₃ samples in condition 2.

The H_2 concentration results of pure OPC samples determined from EIS fitting are shown in Figure 4.39(a) and (b). For samples in condition 1 (see Figure 4.39(a)), the H_2 concentration values plunge

at the beginning to reach a value around 50 ppm, followed by a relatively steady state. After about 50 days, the H_2 concentration values increase significantly because of the development of cracks in the cement paste. For samples in condition 2, the H_2 concentration descends rapidly in the first 40 days, followed by a relatively steady state.

Figure 4.39(c) and (d) provide the H_2 concentration results measured for OPC+LiNO₃ samples. In both conditions, the H_2 concentration values are abnormally low (less than 1 ppm) during the entire measuring period. However, the variation trends of the H_2 concentration seem to be of meaning. For example, the H_2 concentration value increases rapidly after the immersion of samples in saturated Ca(OH)₂ solution and then decreases until a steady state is reached, which complies with the corrosion rate trend provided by other techniques (see Section 4.7.5.2).

The results, obtained for OPC+Li₂CO₃ are shown in Figure 4.39(e) and (f). In condition 1, the H_2 concentration gradually decreases at the beginning. After the immersion of samples in saturated Ca(OH)₂ solution, the triplicate GC samples begin to show significant discrepancies and the H_2 concentration irregularly fluctuates in the range of 0.1 - 100 ppm. In condition 2, the triplicate GC samples provide completely different results.

4.7.4. Determination of the corrosion product layer thickness

The thickness of corrosion product film is measured from SEM and hence the corresponding corrosion rate (V_{corr}) is calculated according to the growth rate of the film (Equation. (18)). All the results are provided in Figure 4.40 except the ones of pure OPC samples. The SEM characterization applied to pure OPC samples failed to provide trustworthy film thickness results. The presence of holes and cracks led to the wide discrepancy of the film thickness results at different locations. Besides, it was difficult to identify the boundary between the cement paste and the corrosion product film in some samples. The thickness value of all kinds of samples increases monotonically, representing that the rapid dissolution of the corrosion product film does not exist.

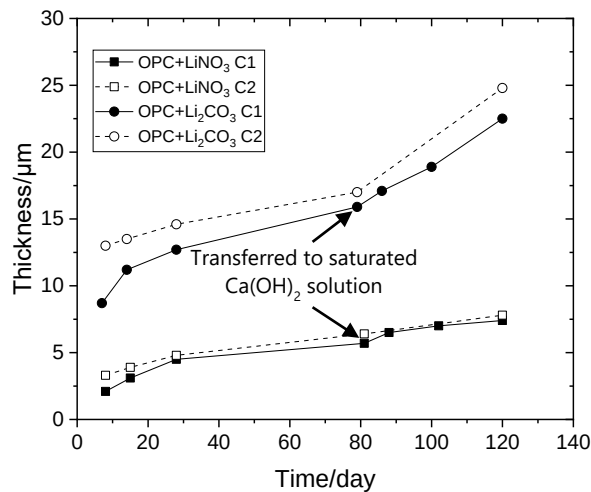


Figure 4.40 Variation of the film thickness as a function of time for OPC+LiNO₃ and OPC+Li₂CO₃ samples from SEM characterisation.

Then, the corrosion rates determined by EIS, GC and SEM are compared. The corresponding corrosion rate results are shown in the next sections.

4.7.5. Comparison of the corrosion rate obtained by EIS, GC and SEM

This section provides the corrosion rates obtained by EIS, GC and SEM. The corrosion rate was determined via Eq. (13) and Eq. (14) for the EIS data (Section 3.2), via Eq. (17) for the GC data (Section 3.3) and via Eq. (18) for the SEM data (Section 3.4). The variation of the corrosion rate of each sample is summarized and analysed. And the results determined from different techniques are compared. Finally, the effectiveness of LiNO₃ and Li₂CO₃ as corrosion inhibitors is discussed.

4.7.5.1. 0.36 w/c OPC

A comparison of the corrosion rates, measured with EIS and GC, of pure OPC samples tested in condition 1 is given in Figure 4.41(a). As mentioned earlier, the SEM characterization applied to pure OPC samples failed to provide trustworthy film thickness results. Firstly, the presence of holes and cracks led to the wide discrepancy of the film thickness results at different locations (see Section 4.9); secondly, it was difficult to identify the boundary between the cement paste and the corrosion product film in some samples. Therefore, no corrosion rate calculated from SEM data for pure OPC samples is reported in Figure 4.41.

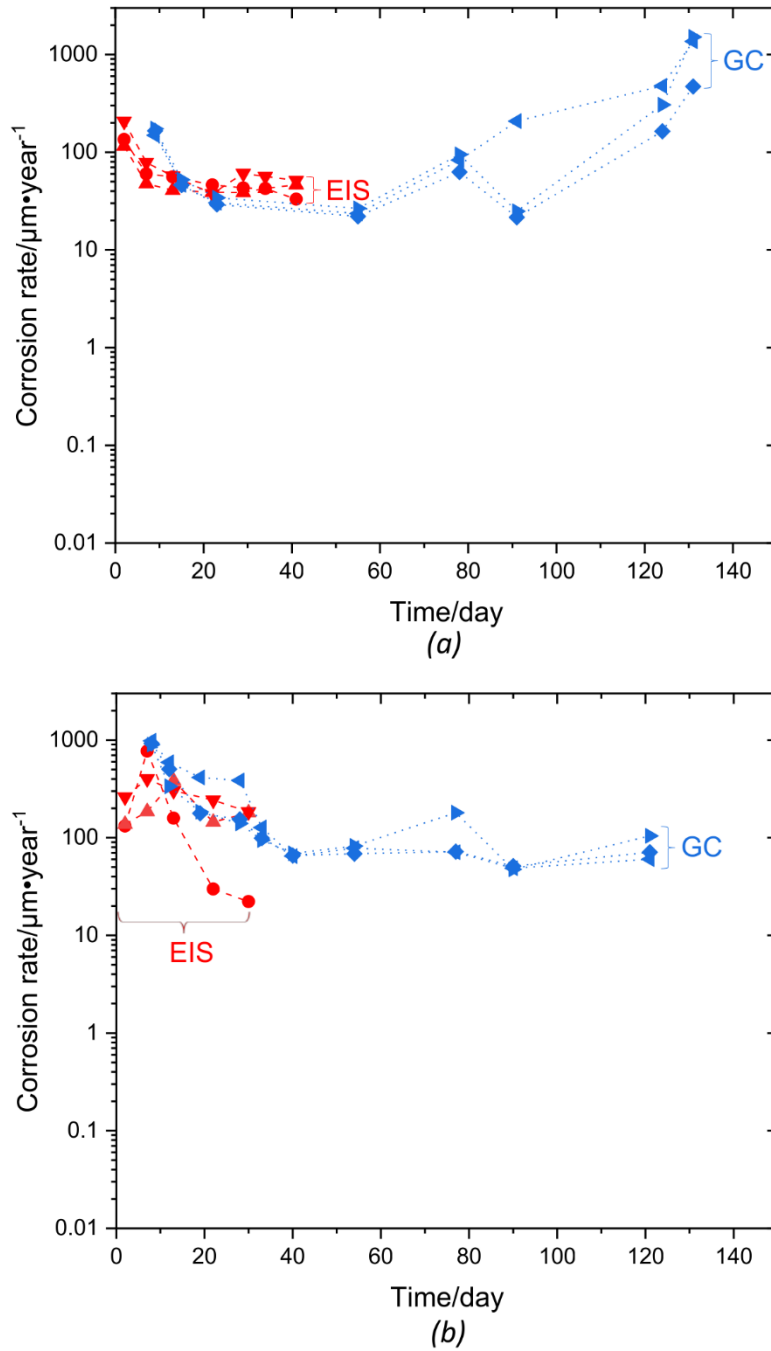


Figure 4.41 Variation of the corrosion rates as a function of time of
(a) OPC samples in condition 1, (b) OPC samples in condition 2.

The corrosion rates from both techniques (EIS and GC) show a decreasing trend as a function of time. Initially, the corrosion rate reached $\sim 200 \mu\text{m}\cdot\text{y}^{-1}$ and decreased to $\sim 30 \mu\text{m}\cdot\text{y}^{-1}$ after a few tens of days. This obvious decrease can be linked to the hydration of the cement paste and the accumulation of the corrosion products. The water content in the cement paste declines as a function of the hydration degree and hence induces a decrease of the corrosion rate. Besides, the accumulation of corrosion products forms a thicker physical barrier, which is also able to inhibit the corrosion rate. The main difference between EIS and GC is that the variation of the corrosion rate from GC is behind that from EIS in terms of time. In other words,

Chapter 4

the corrosion rate from GC can be obtained via the rightward shift of that from EIS as shown in Figure 4.41(a) (e.g., the decrease of the corrosion rate from GC occurs later than that from EIS). This can be explained by the different characteristics of the two methods. The corrosion rate from GC is actually the average corrosion rate over the period before the time point, while the rate from EIS is the real-time value. Therefore, a delay shift can occur in GC results. Besides, the different configurations are likely to cause discrepancies because of the differences in the exposed areas and positions in the bulk of the cement paste that can affect the diffusion process of reactants and products. In general, except the difference on time, the rate results obtained from two techniques are comparable. After 40 days, the EIS tests were stopped because longer time might lead to the generation of cracks, which interferes with the next tests. It can also be seen that the corrosion rate determined by GC goes up rapidly after 50 days of testing. This increase can be attributed to the development of cracks in the cement paste, which eventually led to the complete split of the cement paste into two parts (see Figure 4.42(a)).

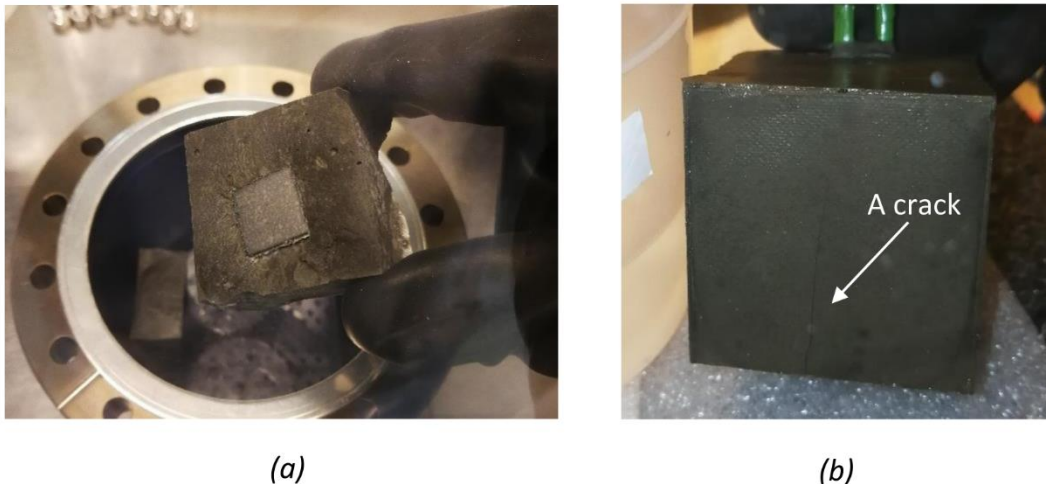


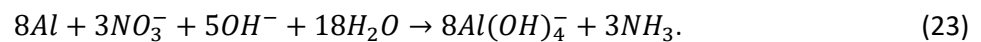
Figure 4.42 Pictures showing (a) the breach of a GC sample in condition 1 after 133 days and (b) a crack in an EIS sample appeared in condition 2 generated after 8 days.

In condition 2, visible cracks can be observed in EIS samples after 8 days (see Figure 4.42(b)). These cracks propagated with time, leading to a significant spread of the results in Figure 4.41(b). Spasova et al. [62] and Zhou et al. [63] reported similar cracking phenomena regarding the corrosion of Al embedded in BFS/OPC cement system. This is attributed to the increasing internal stress generated by the production of H_2 gas and by the accumulation of the corrosion products involving volume changes compared to the pure Al phase. On the contrary, GC samples did not show any visible cracks, which could probably be attributed to the smaller size (15x15x1mm) of GC samples compared to the larger EIS samples (30x30x1mm). Besides, the steady corrosion rate in condition 2 is slightly higher than that in condition 1, which can be explained by the fact that the complete saturation of the cement paste provided more water for the corrosion reaction in condition 2.

4.7.5.2. 0.36 w/c OPC+3 wt.% LiNO₃

Figure 4.43 provides the corrosion rates measured for OPC+LiNO₃ samples. The magnitude and variation of the corrosion rates with time from EIS and SEM techniques are comparable in both conditions. Initially, the corrosion rate decreases until reaching a steady state value around 10-20 $\mu\text{m}\cdot\text{y}^{-1}$. Note that in condition 1, a bump in the graph can be observed after 80 days when the samples were transferred from the humid argon atmosphere into the limewater. However, the corrosion rate decreases back fast to the steady state value observed before the transfer. This decrease could be due to the fast growth of the corrosion product film associated to a high corrosion rate. Later, the thicker film retards the corrosion rate. Compared to pure OPC samples, the OPC+LiNO₃ samples exhibited a lower corrosion rate while no visible cracks were observed, which indicates that the formation of the Li-Al LDH film improved the corrosion protection performance [141].

The results also show that although the corrosion rates measured with GC follow the same trend as those obtained from EIS and SEM (including the peak in the corrosion rate when the sample was transferred to saturated Ca(OH)₂), the values of the corrosion rate obtained from GC are about 2 orders of magnitude lower than those from EIS and SEM. This matches the findings of Matsuo et al. [124,125] and Delpech et al. [126], which showed that the corrosion rate obtained from GC is several orders of magnitude smaller than the one obtained from impedance spectroscopy [126] and could be as low as a few micrometers per year [124]. A possible reason for the discrepancy between the corrosion rate values determined by EIS/SEM and GC could be the fact that in the presence of nitrate, the corrosion of aluminium mainly produces aluminates and ammonia, instead of hydrogen [178], as follow:



Because the calculation of the corrosion rate is merely based on the generation of H₂ (Eq. (16)), an underestimation of the gas production results in the abnormally low corrosion rate from GC.

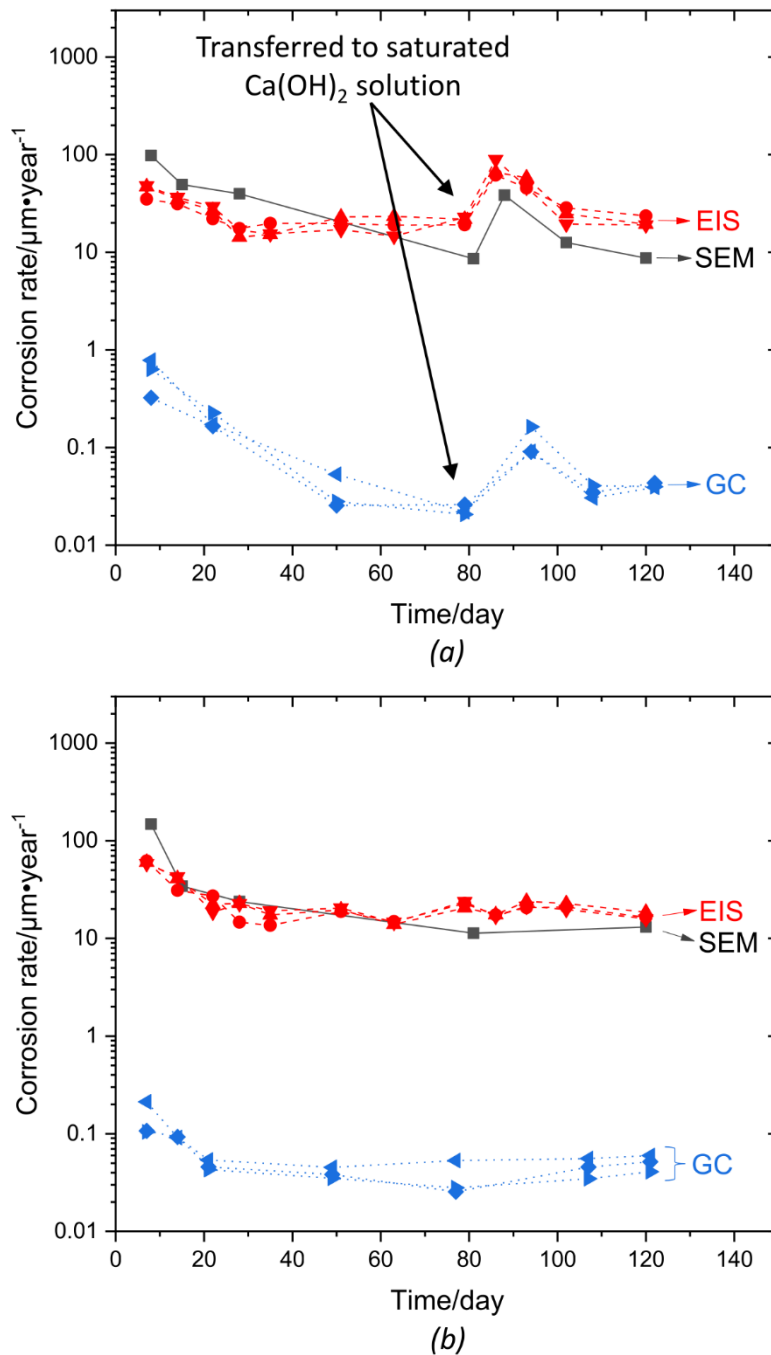


Figure 4.43 Variation of the corrosion rates as a function of time of (a) OPC+LiNO₃ samples in condition 1, (b) OPC+LiNO₃ samples in condition 2.

4.7.5.3. 0.50 w/c OPC+1.607 wt.% Li₂CO₃

For OPC+Li₂CO₃ samples in condition 1 (see Figure 4.44(a)), the corrosion rates gathered from the three different techniques are in good agreement until the immersion of the samples in limewater (after 80 days). The corrosion rate of the samples decreased from around 600 $\mu\text{m}\cdot\text{y}^{-1}$ to around 20 $\mu\text{m}\cdot\text{y}^{-1}$ after 80 days.

Chapter 4

This decline is sharper at the beginning and slowed down afterwards. This trend could be attributed to two possible mechanisms: (1) the accumulation of the protective corrosion product film decreases the corrosion rate; (2) the lower water content and porosity of the cement paste, as a function of its hydration process, decreases the corrosion rate. After 80 days, when the samples were immersed in saturated Ca(OH)_2 solution, the corrosion rate determined by EIS and SEM increased rapidly until reaching a plateau at $70\text{--}100\ \mu\text{m}\cdot\text{y}^{-1}$, which should be attributed to the fact that the corrosion product film loses effectiveness after the immersion. However, when looking at the data obtained from GC measurements, triplicate GC samples begin to show significant discrepancies and the corrosion rates irregularly fluctuate in the range of $0.1\ \mu\text{m}\cdot\text{y}^{-1}$ to $20\ \mu\text{m}\cdot\text{y}^{-1}$. For condition 2, both EIS and SEM show a sharp decrease of the corrosion rate in the first days before slightly rising back to reach values around $70\text{--}90\ \mu\text{m}\cdot\text{y}^{-1}$ after ~ 120 days. These corrosion rates are equivalent to the one observed in condition 1 after the immersion in Ca(OH)_2 solution. Note that the corrosion rate decreases more and for a longer period when it is extracted from SEM micrographs compared to EIS before to reach comparable values. A possible explanation for this difference can be the influence of a delamination of the corrosion product film. Indeed, a delamination phenomenon was found by SEM characterisation in parts of the corrosion product film after 30 days and became more severe with time. The different delamination states (when and where the delamination occurred, how fast they developed, etc.) in distinctive samples can therefore lead to the different corrosion rates that have been measured in this study. More information about this delamination process is provided in Section 4.9. Regarding the triplicate GC samples, they provided different corrosion rates without a clear varying trend. It seems that the immersion of the samples in saturated Ca(OH)_2 solution induces a change in the corrosion mechanism resulting in perturbation in the hydrogen production and therefore, to the determination of the corrosion rate by GC in both curing conditions. It is still difficult to understand the detailed mechanisms behind the erratic GC results and further research is needed to better understand the phenomenon encountered. For example, aluminium is reported to be able to reduce carbonates [309], which might be the real reason.

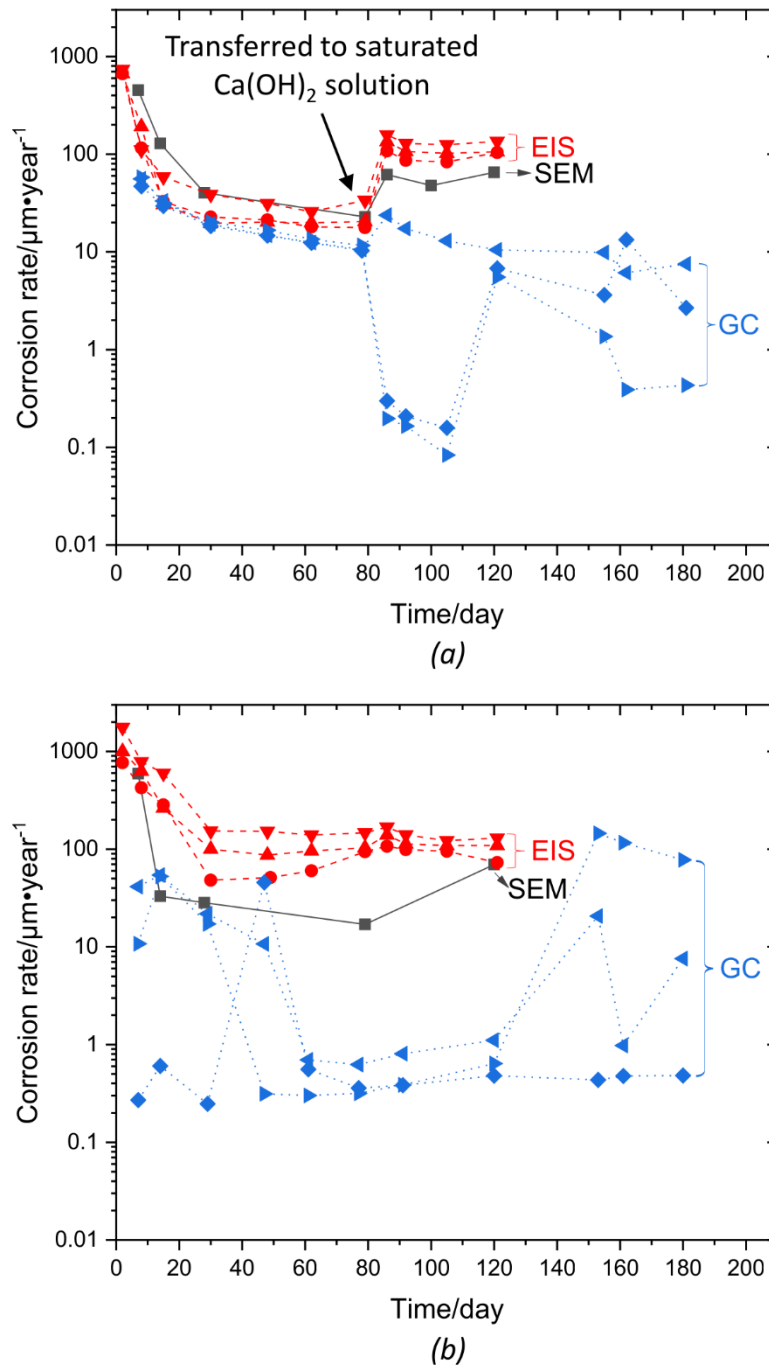


Figure 4.44 Variation of the corrosion rates as a function of time of (a) OPC+Li₂CO₃ samples in condition 1, (b) OPC+Li₂CO₃ samples in condition 2.

4.7.5.4. Discussion about the efficiency of LiNO₃ and Li₂CO₃

Generally, OPC+Li₂CO₃ samples exhibit a higher corrosion rate compared to OPC+LiNO₃ samples in both curing conditions. For example, the corrosion rate of OPC+Li₂CO₃ samples is up to 1000 $\mu\text{m}\cdot\text{y}^{-1}$ much larger than that of OPC+LiNO₃ samples (around 100 $\mu\text{m}\cdot\text{y}^{-1}$) in the first week. However, it is difficult to compare the efficiency of Li₂CO₃ and LiNO₃ in cement pastes directly, because the higher water content (0.5) in

OPC+Li₂CO₃ samples also influences the corrosion rate. In terms of the influence of anions on corrosion inhibition, NO₃⁻ is theoretically favoured. Indeed, considering the ion exchange equilibrium constant in LDH based films, the value decreases in the following order: CO₃²⁻ > SO₄²⁻ > OH⁻ > F⁻ > Cl⁻ > Br⁻ > NO₃⁻ > I⁻ [173]. Therefore, compared to CO₃²⁻, NO₃⁻ ions in LDH films are easier exchanged with outer aggressive species such as Cl⁻, F⁻, Br⁻ and SO₄²⁻, which can have a beneficial effect on the corrosion protection by entrapping the harmful anions in the film [141,153,154]. For pure OPC samples, the formation of cracks can lead to a high corrosion rate up to 1000 μm·y⁻¹ as shown in Figure 4.41(b).

4.8. Resistance of the corrosion product film (R_f)

R_f is the resistance of the corrosion product film determined from the fitting. In general, R_f is proportional to the film thickness, i.e. the R_f value will become higher as the film thickens. Furthermore, due to the porous structure of the LDH films, intrusion of outer solution could significantly decrease the R_f value by filling the pores [153-156]. Therefore, although R_f is not the only decisive factor, it reveals the protection ability of the corrosion product film to some extent, and studying its variation with time gives important information in relation with the corrosion mechanism of AA1100 in contact with cement pastes.

The R_f results of pure OPC samples gathered from EIS fitting are shown in Figure 4.45(a) and (b). For samples in condition 1 (Figure 4.45(a)), the R_f values slightly increase in the first 7 days to reach a value around 5000 ohm·cm², which is attributed to the increase of the thickness of the film. Afterwards, R_f drops to about 1000 ohm·cm² and remains constant. A possible explanation for the decrease of R_f is that the corrosion products contain more and more solution in the film pores. This increasing water content can be caused by several factors such as (1) a reduction of the amount of water consumed in the corrosion reactions (due to a decrease of the corrosion rate), or (2) an additional supply of water due to the high humidity of the outer atmosphere. As explained earlier, the R_f values of the film in condition 2 are significantly influenced by the rapid propagation of cracks in the cement paste (see Figure 4.42), leading to non-repetitive results, as shown in Figure 4.45(b).

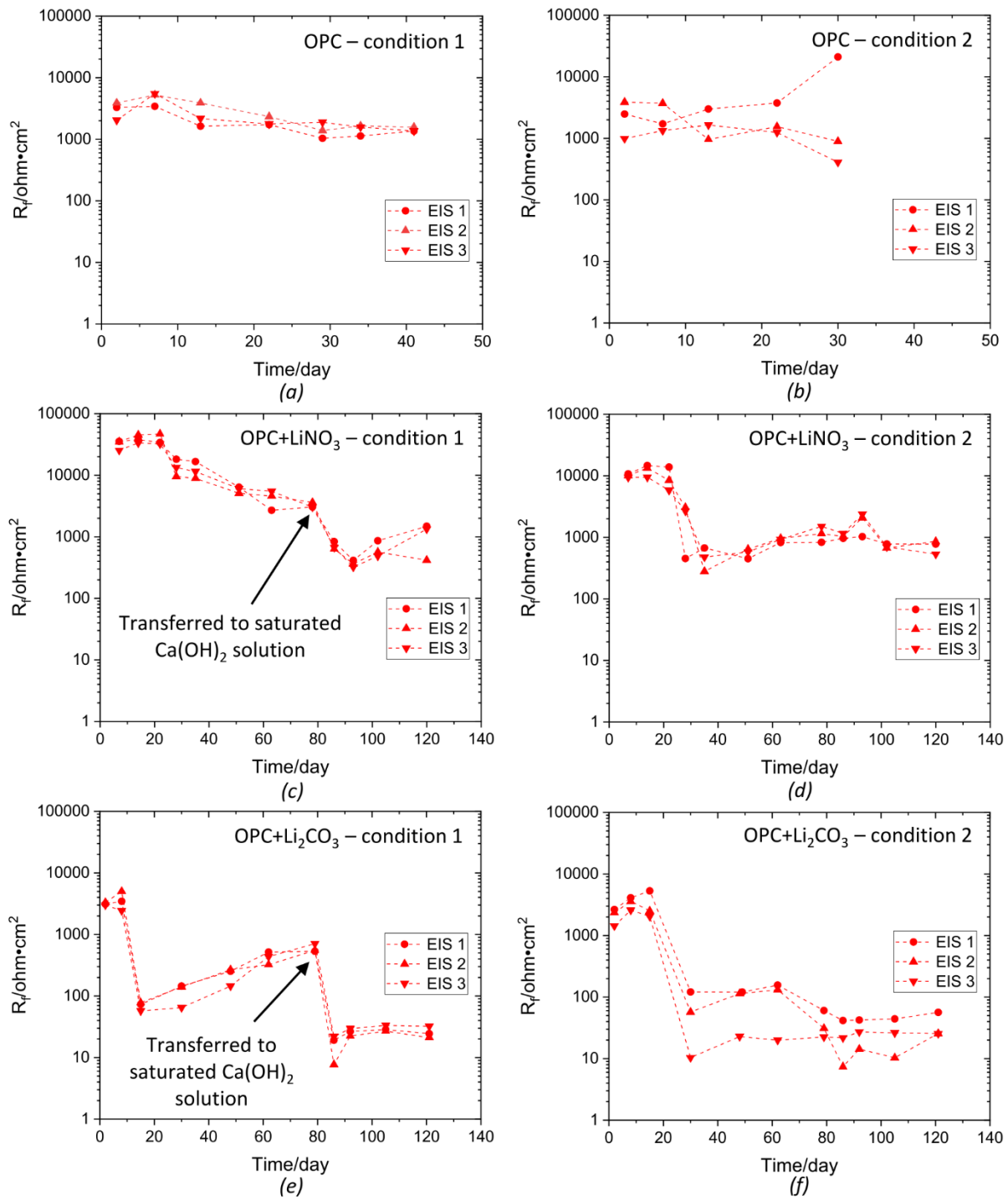


Figure 4.45 Evolution of R_f as a function of time of (a) OPC samples in condition 1, (b) OPC samples in condition 2, (c) OPC+LiNO₃ samples in condition 1, (d) OPC+LiNO₃ samples in condition 2, (e) OPC+Li₂CO₃ samples in condition 1, (f) OPC+Li₂CO₃ samples in condition 2.

Figure 4.45(c) and (d) show the variation of R_f values of the OPC+LiNO₃ samples. For condition 1 (Figure 4.45(c)), R_f gradually decreases from ~40000 ohm·cm² to about 2000 ohm·cm² over an 80-days period. After 80 days of testing, the cement sample was immersed in saturated Ca(OH)₂ solution. Within

Chapter 4

the first 14 days after immersing the sample in saturated Ca(OH)_2 , an apparent drop of R_f to $\sim 300 \text{ ohm}\cdot\text{cm}^2$ occurred. This drop is believed to be attributed to the fact that the LDH film got gradually saturated with Ca(OH)_2 solution, leading to a decrease of its resistance. After this drop, R_f increases again because of the accelerated corrosion of the Al causing a thickening of the corrosion product film, which inevitably leads to an increase of the resistance of the corrosion product film. In condition 2, R_f drops down significantly during the first days of the tests, which is assumed to be caused by the increasing amount of solution in the film, and reaches a fairly constant value afterwards. It was also observed that the steady-state value of R_f , measured at the end of the testing period, was similar for both conditions, i.e. around $1000 \text{ ohm}\cdot\text{cm}^2$.

The R_f results, obtained for $\text{OPC}+\text{Li}_2\text{CO}_3$ are shown in Figure 4.45(e) and (f). In condition 1, R_f rapidly decreases from $3000 \text{ ohm}\cdot\text{cm}^2$ to about $100 \text{ ohm}\cdot\text{cm}^2$ during the first 14 days. This sharp decrease is likely due to the ingress of solution into the film. Afterwards, the growth of the film raises R_f until the immersion of the sample in Ca(OH)_2 solution after 80 days, which leads to a significant decrease of R_f . After this drop, R_f remains fairly constant at a value of about $20\text{-}40 \text{ ohm}\cdot\text{cm}^2$. This final steady state is in contradiction with SEM characterisation, which shows a continuous increase of the film thickness. Meanwhile, a delamination of the corrosion product film occurs after the immersion. Therefore, it is assumed that this R_f drop after the immersion is dominated by delamination. In condition 2, after an initial increase, R_f rapidly decreases between the 20th and 28th day from $\sim 3000 \text{ ohm}\cdot\text{cm}^2$ to values between 10 and $100 \text{ ohm}\cdot\text{cm}^2$. This sudden drop in R_f is believed to be caused by the delamination that was observed by SEM after 28 days (see Section 4.9). After this drop, R_f remains fairly constant (with a slight decrease in two of triplicate samples after 60 days). The end value for R_f is similar ($\sim 30\text{-}40 \text{ ohm}\cdot\text{cm}^2$) in both conditions for the $\text{OPC}+\text{Li}_2\text{CO}_3$ samples, whereas R_f is significantly higher ($\sim 1000 \text{ ohm}\cdot\text{cm}^2$) for the other cement pastes (OPC, $\text{OPC}+\text{LiNO}_3$). This can be explained by the delamination: after delamination, only the resistance of the thin newly born film on the Al surface counted as R_f in the EIS fitting.

The variation of R_f results agrees with the ones reported in the literature. The R_f values presented in Figure 4.45 decrease after the initial period or after the immersion in Ca(OH)_2 solution. The same decrease is found in the impedance study of different Al based LDH films immersed in solutions [153-156]. This decrease is believed to be caused by the ingress of the electrolyte, replacing the trapped air in the porous structure of the LDH film. This intrusion process of the electrolyte decreases the film resistance. Iqbal et al. reported that an impedance decrease by at least one order of magnitude occurred within 7 days after the immersion in NaCl solution in the impedance study of CaAl-LDH films [153] and MgAl-LDH [154]. Cao et al. [156] found that the impedance of ZnAl-LDH films remained stable up to 21 days in NaCl solution and decreased dramatically after 28 days. In conclusion, the R_f can not be used to evaluate the corrosion rate directly since it changes as a function of multiple factors e.g. the film thickness, the film composition and the environmental humidity. However, it helps understanding the corrosion process.

4.9. Characterization of the Al/corrosion product film/cement paste interface by SEM

SEM characterisation was performed to determine the thickness of the corrosion product film, which is used to calculate the corrosion rate as introduced in Section 3.4. Figure 4.40 provides the film thickness values as a function of time for OPC+LiNO₃ and OPC+Li₂CO₃ samples (the thickness determination of pure OPC samples was interfered by cracks and holes). The film thickness monotonically increases in all cases, even after the immersion of Ca(OH)₂ solution in condition 1. This can be attributed to two possible mechanisms: (i) the corrosion product film cannot dissolve even when immersing the samples in Ca(OH)₂ solutions or (ii) the film can dissolve, but the accumulation of the corrosion product is always faster than the dissolution of the film. On the contrary, the thickness of the corrosion product film has an obvious instantaneous increase after the immersion, which is attributed to the increase of corrosion rate when more solution is available.

The morphology of the cement paste/corrosion product film/Al interface has also been studied by SEM. SEM images of the OPC, OPC+LiNO₃ and OPC+Li₂CO₃ samples after 28 and about 80 days of testing in condition 2 are shown in Figure 4.46. Figure 4.47 summarizes the SEM images of these three types of samples after 28 and about 80 days of testing in condition 1.

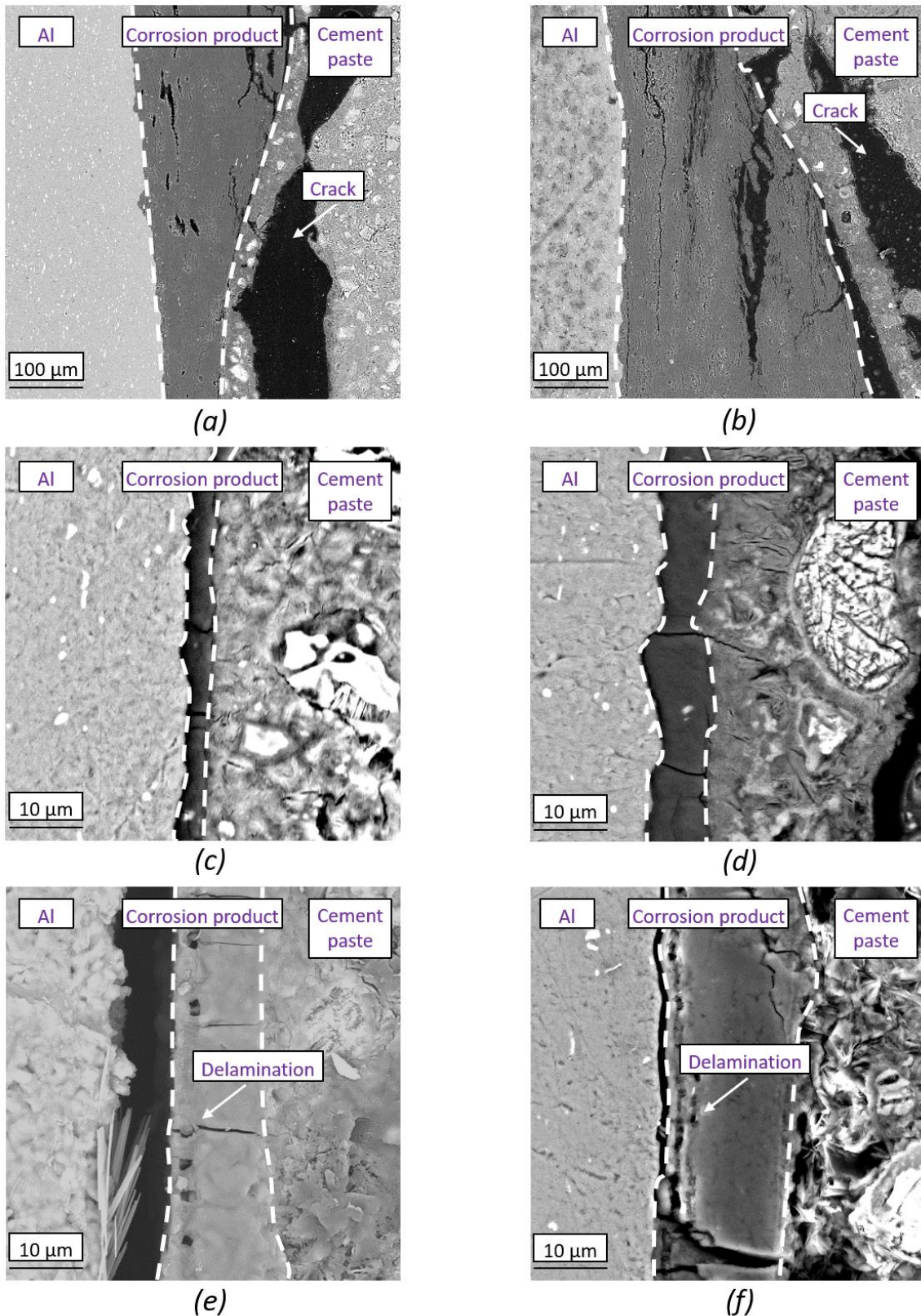


Figure 4.46 SEM micrographs of (a) the pure OPC sample after 28 days, (b) the pure OPC sample after 79 days, (c) the OPC+LiNO₃ sample after 28 days, (d) the OPC+LiNO₃ sample after 81 days, (e) the OPC+Li₂CO₃ sample after 28 days, (f) the OPC+Li₂CO₃ sample after 79 days. All samples were aged in condition 2.

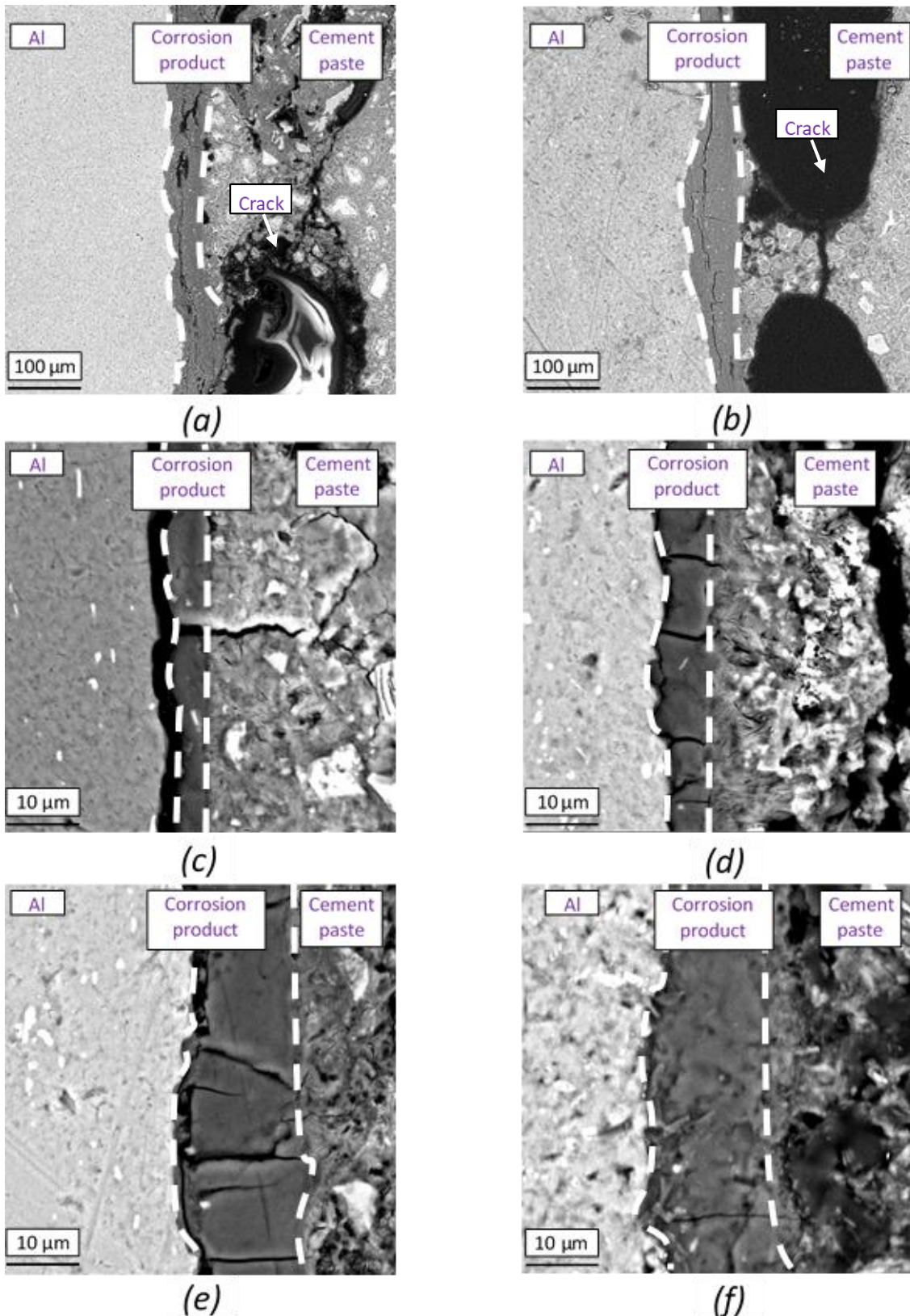


Figure 4.47 SEM micrographs of (a) the pure OPC sample after 28 days, (b) the pure OPC sample after 79 days, (c) the OPC+LiNO₃ sample after 28 days, (d) the OPC+LiNO₃ sample after 81 days, (e) the OPC+Li₂CO₃ sample after 28 days, (f) the OPC+Li₂CO₃ sample after 79 days. All samples were aged in condition 1.

Chapter 4

In terms of pure OPC samples in condition 2, it can be clearly seen in Figure 4.46(a) and (b) that cracks or holes formed in the cement paste near the interface. Meanwhile, the thickness of the corrosion product film varied significantly, leading to difficulties in the determination of the average thickness value. The same phenomenon can be seen in OPC samples in condition 1 (Figure 4.47(a) and (b)).

Figure 4.46(c) and (d) provide SEM micrographs of OPC+LiNO₃ samples in condition 2. In these samples, the corrosion product film is thin and dense. Figure 4.47(c) and (d) indicate that OPC+LiNO₃ samples in condition 1 have similar results.

Figure 4.48 shows a line-scan EDX result of the elemental distributions of four different elements (Al, O, Ca and Si) in the cross-section of the OPC+LiNO₃ sample after 81 days in humid Ar atmosphere in condition 1. The distributions of Al and O indicate the boundaries of the different phases (Al/corrosion product film/cement paste), while Ca and Si are typical elements present in the cement paste, which tend to diffuse from the cement paste towards the corrosion product film. The Al content dramatically decreases on the aluminium/corrosion product film boundary, while the O content significantly increases. The content of Al (about 30%) and O (about 60%) remains constant in the corrosion product film. This Al:O ratio (1:2) is higher than the ones of standard LDH films (hydrates lead to a high oxygen content). This can be explained by two possible mechanisms. First, the corrosion product film is a complex mixture with other constituents such as Al₂O₃ and hydroxoaluminates decreasing the overall Al:O ratio. Second, EDX is a semi-quantitative technique, leading to some uncertainty on the elemental concentration. Ca and Si diffuse from the cement paste (the high concentration region) to the corrosion product film (the low concentration region). It is worth mentioning that the O concentration is even higher than the one in the cement paste. The Ca concentration dramatically decreases at the interface between the cement paste and the corrosion product film, followed by a relatively steady state at a low level. The Si content shows an obvious diffusion gradient in the corrosion product film.

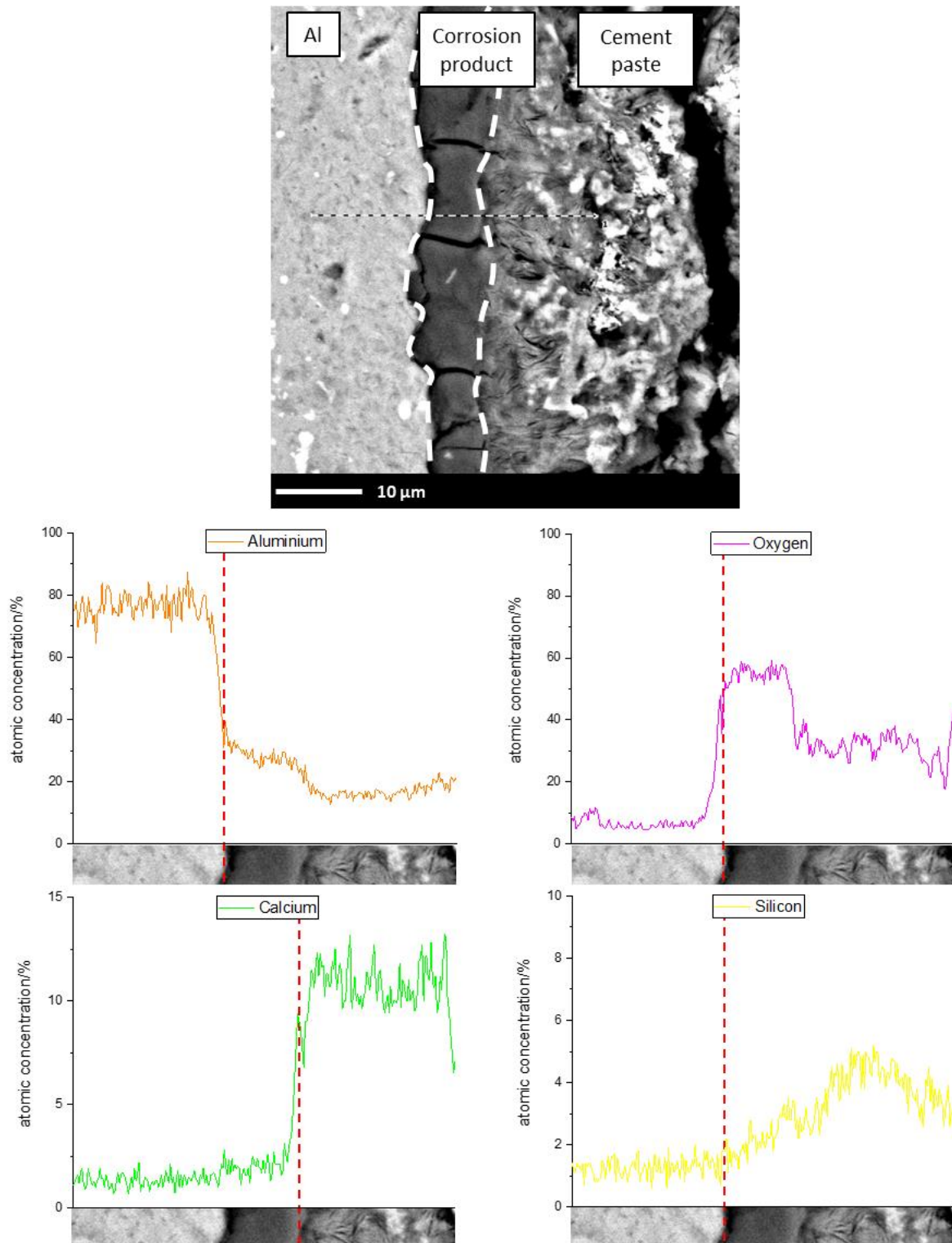


Figure 4.48 EDX line scan results (Al, O, Ca and Si) of the cross-section of an OPC+LiNO₃ sample after exposure in humid Ar atmosphere (condition 1) for 81 days.

As introduced before, delamination has been observed in some OPC+Li₂CO₃ samples. In condition 1, delamination is found only after immersion in Ca(OH)₂ solution. In condition 2, delamination is firstly observed after 28 days and proceeds further as a function of time (see Figure 4.46(e) and (f)). In

Chapter 4

OPC+Li₂CO₃ samples, the main component of the corrosion product film is assumed to be Li-Al layered double hydroxide. According to SEM characterization, it seems that the Li-Al LDH film is prone to delaminate and form a newly born film when the thickness of the old film reaches a certain value.

In order to further understand the mechanism, a line-scan analysis was performed by EDX to gain information on the evolution of the elemental concentration inside the corrosion product layer. Figure 4.49 shows the content distributions of four different elements (Al, O, Ca and Si) of the cross-section of the OPC+Li₂CO₃ sample after 79d in condition 2. Similar to the results of the OPC+LiNO₃ sample in Figure 4.48, the Al content significantly decreases on the aluminium/corrosion product film boundary, while the O content dramatically rises. The sharp changes in Al and O content are localized in a small zone near the boundary, the other part of the corrosion product film has almost fixed contents of Al (about 30%) and O (about 60%). Moreover, the Ca concentration sharply decreases at the interface between the cement paste and the corrosion product film. Afterwards, the Ca concentration is gradually decreasing until reaching the surface of AA1100. The evolution of the Si concentration is similar to the one of Ca. Its content declines from the cement paste to the corrosion product film. However, unlike the Ca concentration, the Si concentration reaches zero near the delamination surface (the boundary between the old film and the newly born film) and not on the surface of AA1100. This could be explained by the fact that Si diffusion is hindered by delamination. Additional EDX results (Figure 4.50 and Figure 4.51) provide more evidences that Si diffusion follows different rules on the two sides of the delamination inside the corrosion product film since the Si concentration is zero in the newly born film in these EDX observations. One possible explanation is that the delamination creates a new interface and hence interferes the Si diffusion.

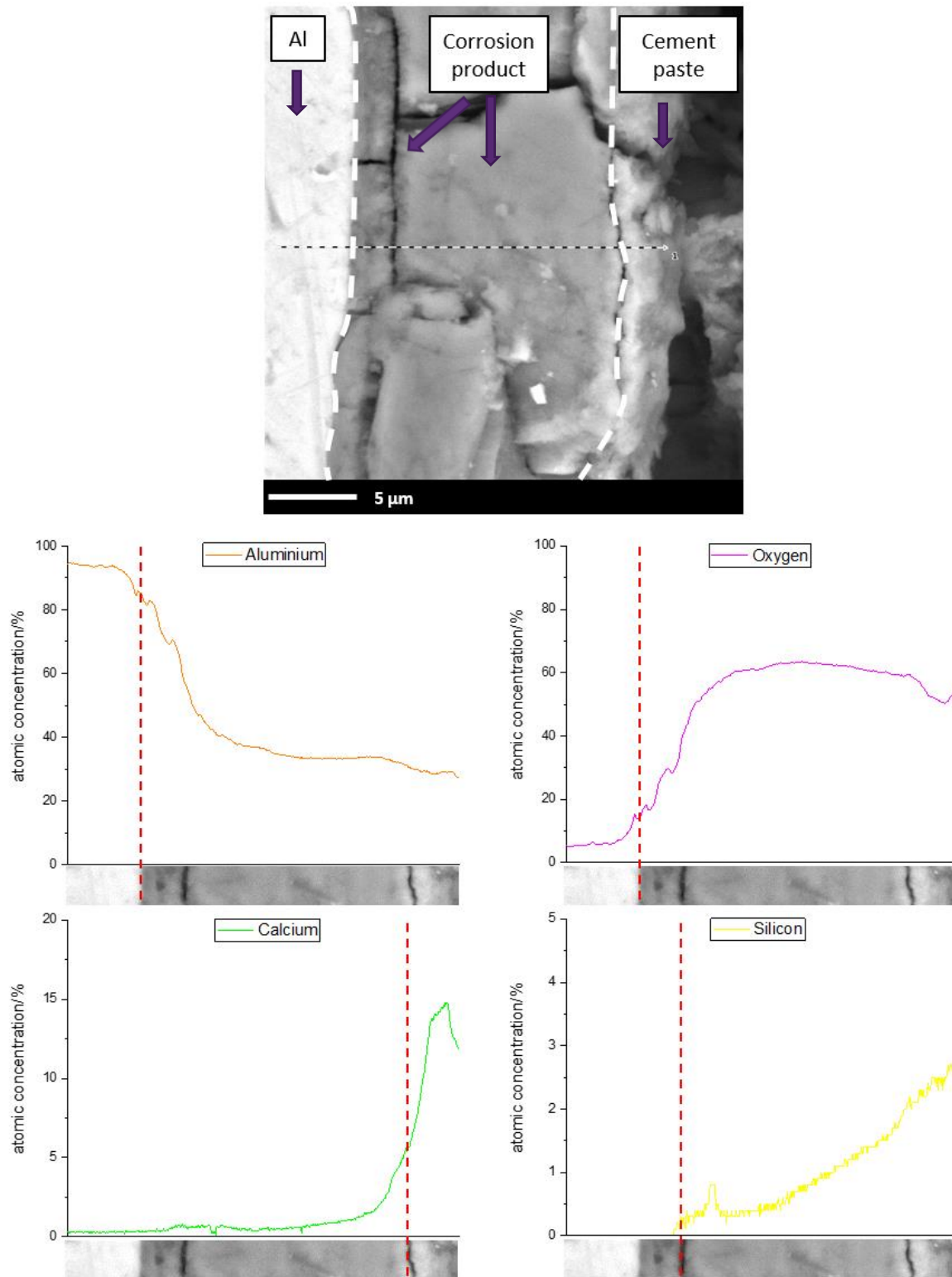


Figure 4.49 EDX line scan results (Al, O, Ca and Si) of the cross-section of a OPC+Li₂CO₃ sample after exposure to saturated Ca(OH)₂ (condition 2) for 79 days.

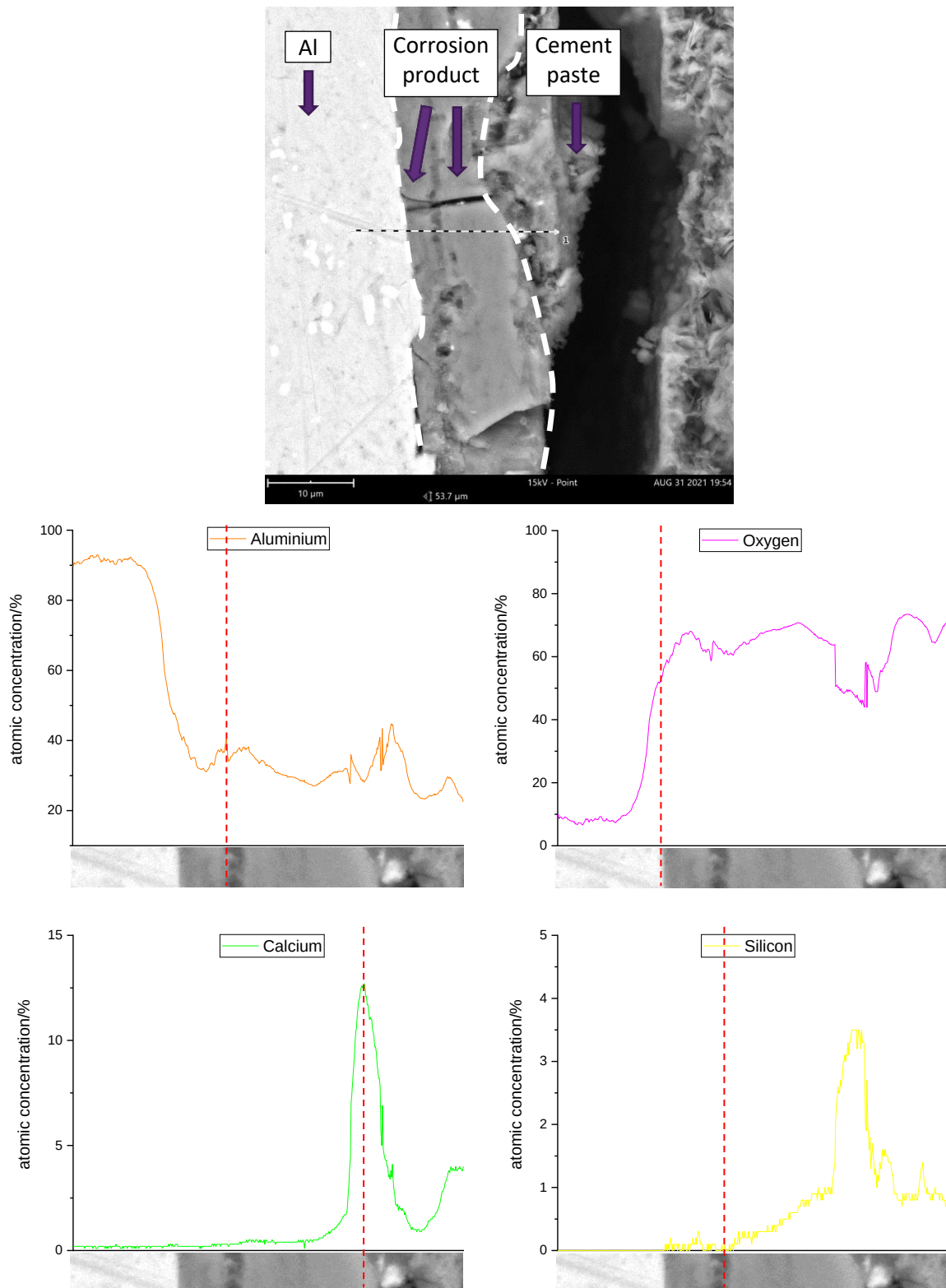


Figure 4.50 Example of EDX line scan results (Al, O, Ca and Si) of the cross-section of a OPC+Li₂CO₃ sample after exposure to saturated Ca(OH)₂ (condition 2) for 79 days.

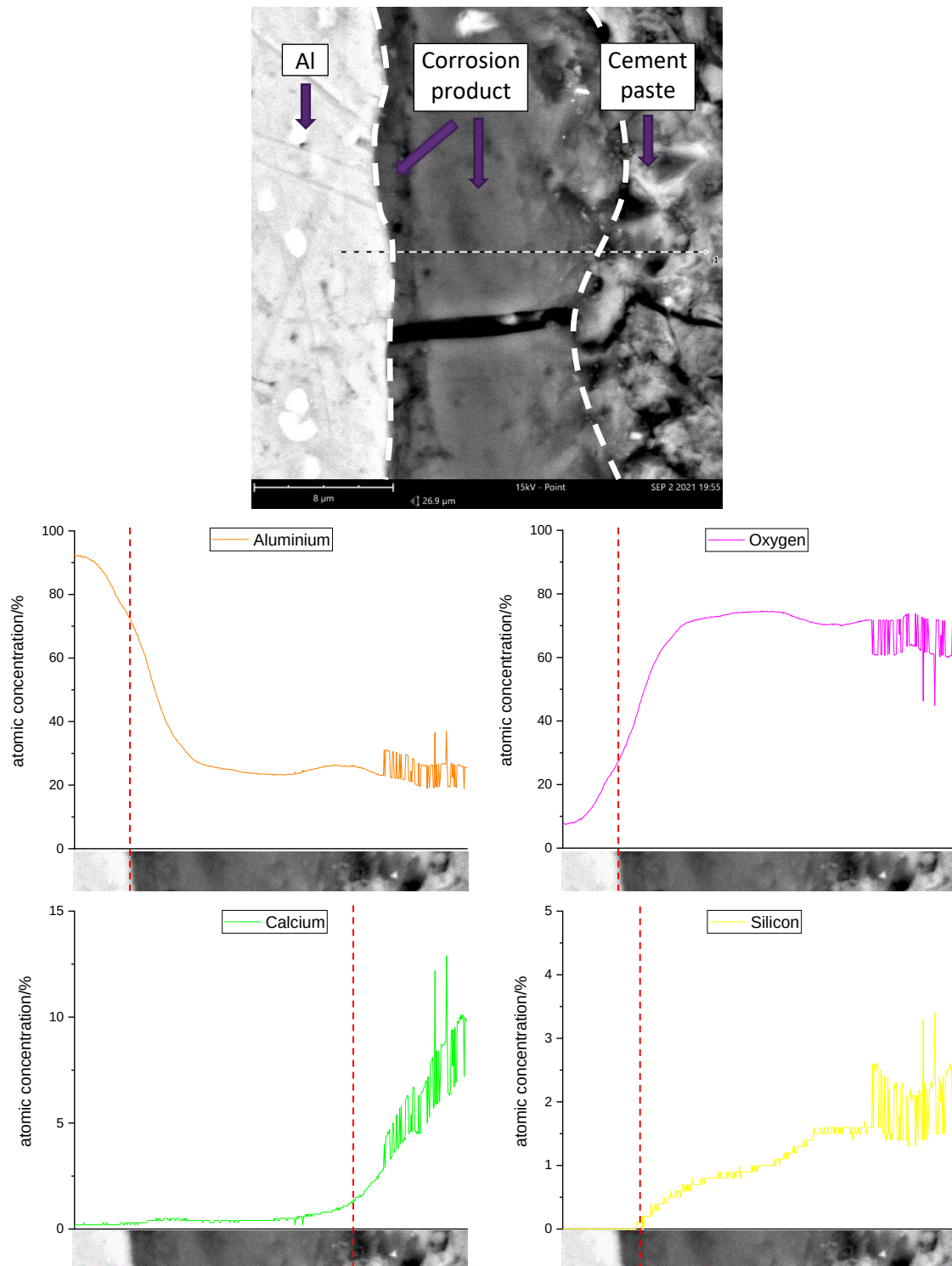


Figure 4.51 Example of EDX line scan results (Al, O, Ca and Si) of the cross-section of a $\text{OPC}+\text{Li}_2\text{CO}_3$ sample after exposure to saturated $\text{Ca}(\text{OH})_2$ (condition 2) for 79 days.

4.10. Mechanisms of formation of corrosion product film

Based on the results presented before and information reported in the literature [310,311], the mechanisms controlling the corrosion process of pure OPC samples can be hypothesized as shown in Figure 4.52. After the air-formed oxide layer is consumed, the corrosion of aluminium initiates with the formation of aluminium hydroxide gel and hydrogen gas. Aluminium hydroxide immediately reacts with hydroxyl ion to form Al(OH)_4^- in the highly alkaline pore solution of the cement paste [310]. Considering the microstructure of the cement paste, the generated Al(OH)_4^- ions are difficult to be thoroughly dissolved in the pore solution (insufficient amount of pore solution at the interface) or completely diffuse into the cement paste matrix (the constrained diffusion path). Therefore, Al(OH)_4^- ions are most likely to precipitate as hydroxoaluminate salts at the interface to form the corrosion product film. The ions present in the cement paste (such as e.g. Ca^{2+} , Mg^{2+} , Zn^{2+} , etc.) could also lead to the formation of LDH films [153-157]. For example, in the literature it is reported that Al can react with $\text{Ca(NO}_3)_2$ solution in alkaline condition (pH 10) to form Ca-Al layered double hydrates $[\text{CaAl}_2(\text{OH})_6]_n^{2+} \cdot 2X^{n-} \cdot y\text{H}_2\text{O}$, where X^{n-} can be NO_3^- , CO_3^{2-} or other anions) [153]. Unlike an Li LDH film that is easily formed on aluminium alloys at room temperature by simply immersing the alloy in an alkaline lithium salt solution [122], the formation and the growth of Ca, Mg, Zn based LDH films and their corrosion protection properties are usually highly related to temperature and time [153-157]. Iqbal et al. [154] reported that both the film thickness and the corrosion resistance of an Mg-Al LDH film increase as a function of reaction time and temperature. Liang et al. [155] also reported that the Mg-Al LDH film becomes more compact with the increase of the reaction temperature according to the characterization of morphology. The cement paste environment is difficult to satisfy all the conditions of forming a fully developed LDH film, e.g., the high reaction temperature and the long reaction time, bringing uncertainties on the corrosion protection properties of these LDH films. Therefore, this corrosion product film could be a mixture of hydroxoaluminate salts and layered double hydrates, which does not show good corrosion-resistant ability. Meanwhile, the diffusion direction of Al ions is from the interface to the cement paste, which leads to the formation of Strätlingite in the cement paste [310]. The corrosion products such as H_2 gas raise the internal stress and consequently induce cracks in the cement paste matrix.

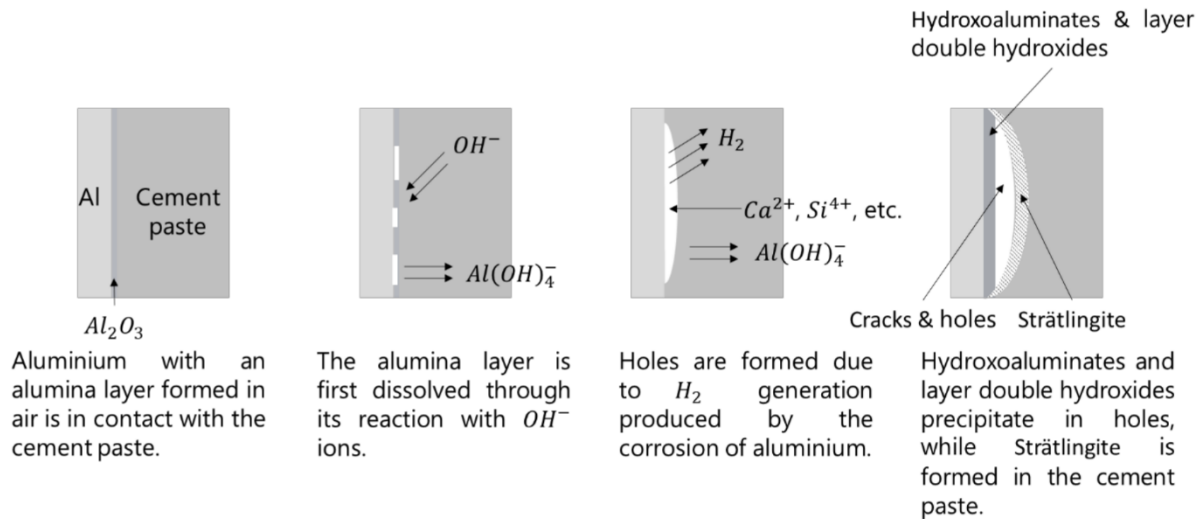


Figure 4.52 Proposed scenario for the corrosion process of Al in the pure OPC paste.

The corrosion process of OPC+LiNO₃ samples and OPC+ Li₂CO₃ samples can be hypothesized as shown in Figure 4.53. With the consumption of the preceding air-formed oxide layer, the aluminium hydroxide gel is formed and immediately reacts with Li⁺, Ca²⁺, Mg²⁺ and other ions to form an LDH film in the highly alkaline pore solution of the cement paste. Afterwards, the LDH film grows slowly with the corrosion of aluminium. Moreover, this LDH film is prone to delaminate and form a newly born film when the thickness of the old film reaches a certain value. Note that because of the introduction of CO₃²⁻, NO₃⁻ ions into the complex chemical system, the gaseous corrosion product could be H₂, NH₃ or other products. For example, NH₃ is probably formed as introduced in Section 4.7.5.2. In general, with the addition of lithium salts, no holes or cracks would be observed in the cement paste.

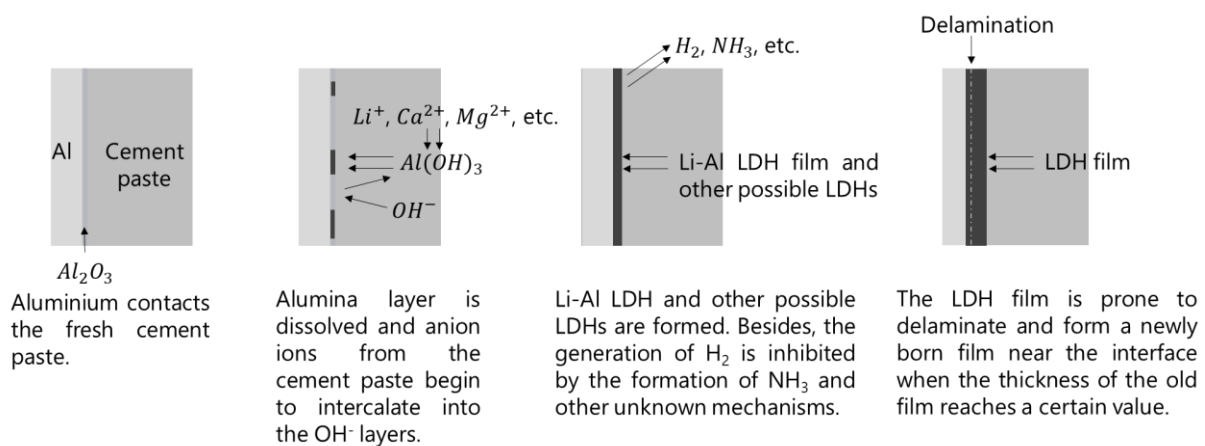


Figure 4.53 Proposed scenario for the corrosion process of Al in the OPC paste with the addition of LiNO₃ or Li₂CO₃.

Chapter 4

The formation of $\text{Al}(\text{OH})_4^-$ ions include two steps. First, Al^{3+} ions react with OH^- ions to form $\text{Al}(\text{OH})_3$. Afterwards, if more OH^- ions can be provided such as in the pure OPC paste, $\text{Al}(\text{OH})_3$ can further react with OH^- to form $\text{Al}(\text{OH})_4^-$, which is the case in Figure 4.52.

With the presence of lithium ions, the final product is Li-Al LDH instead of $\text{Al}(\text{OH})_4^-$. It is still unclear whether it is $\text{Al}(\text{OH})_4^-$ or $\text{Al}(\text{OH})_3$, which reacts with lithium ions to form Li-Al LDH. Some literature [140,149] indicated that lithium ions are incorporated into the $\text{Al}(\text{OH})_3$ structure by the substitution of aluminium ions with lithium ions in the formation of Li-Al LDH, while the other researchers [159,170] thought that lithium ions react with $\text{Al}(\text{OH})_4^-$ to form Li-Al LDH.

According to the study of Gareth and Dermot [140], either neutral lithium salts (LiCl , LiNO_3 , etc.) or strongly alkaline LiOH directly reacts with $\text{Al}(\text{OH})_3$ to form Li-Al LDH without the formation of $\text{Al}(\text{OH})_4^-$ ions. Therefore, it was assumed in Figure 4.53 that the formation of $\text{Al}(\text{OH})_4^-$ is replaced with the formation of Li-Al LDH coming from the reaction between $\text{Al}(\text{OH})_3$ and lithium ions.

Because of the difficulty of directly measuring the presence of lithium ions in the corrosion product film, the constituents of the corrosion product film are just deduced according to literature (see Section 2.6). Hence, more experimental characterizations of the corrosion product film in order to study the chemical constituents could be the research direction of future studies.

4.11. Conclusions

In this chapter, the corrosion of AA1100 in contact with cement pastes were primarily investigated using EIS and Tafel polarization tests. Information about the properties of the cell system such as the variation of the corrosion behaviours has been directly identified from the EIS spectra. Then, an equivalent circuit model was constructed with in depth justification of the choices of the elements for EIS fitting to quantitatively understand the EIS results. R_t , determined by EIS fitting, was used together with Stern Geary constant (B), obtained from Tafel polarization, to determine the corrosion rate. The results were compared with the SEM and GC data. The R_f value, which reveals the protection ability of the corrosion product film to some extent, was also analysed and compared with the results reported in the literature. Besides, the morphology and the chemical composition of the aluminium/corrosion product film/cement paste interface was studied by SEM and EDX. A model for the corrosion process was proposed according to the results obtained by experiments and the mechanisms proposed in literature. The main findings of the study are the following:

1. In general, the corrosion rates determined by different techniques i.e. EIS, SEM and GC, support each other, enhancing the reliability of the data. For OPC samples, the EIS results agree with the results determined by GC. For $\text{OPC}+\text{LiNO}_3$ and $\text{OPC}+\text{Li}_2\text{CO}_3$ samples, the EIS results are closer to the results measured by SEM, while the application of GC for measuring the corrosion rate is problematic. The use of hydrogen production determined by GC for studying the corrosion rate

Chapter 4

possibly provides misleading results. For example, in the presence of LiNO_3 , the corrosion mechanism differs and NH_3 is produced instead of H_2 , leading to an underestimation of the corrosion rates of samples with LiNO_3 addition. For samples with an addition of Li_2CO_3 , GC gives irregular results, for which no satisfactory explanation has been found yet.

2. Both LiNO_3 and Li_2CO_3 are effective corrosion inhibitors for Al in cement pastes. OPC+ LiNO_3 and OPC+ Li_2CO_3 samples have a lower corrosion rate and a thinner corrosion product layer compared to pure OPC. This leads to lower mechanical stress as revealed by the absence of cracks of the cement paste when adding LiNO_3 or Li_2CO_3 . LiNO_3 is more suitable for the encapsulation of Al in the cement paste, as the combination of 0.36 water/cement ratio and 3 wt.% LiNO_3 provides the lowest corrosion rates without any curing problems. The low and predictable level of hydrogen production of OPC+ LiNO_3 samples is also beneficial to the long-term encapsulation.
3. The ingress of saturated $\text{Ca}(\text{OH})_2$ solution significantly increases the corrosion rate of Al in cement pastes, which can be seen in the corrosion rate results of OPC+ LiNO_3 and OPC+ Li_2CO_3 samples. This increase can be attributed to the fact that more water is provided for the corrosion process after immersing the cement paste samples and this change could be either temporary (for OPC+ LiNO_3 samples) or irreversible (for OPC+ Li_2CO_3 samples) according to the corrosion product film properties.
4. The variation of the resistance of the corrosion product film (R_f) is associated to the thickness, the film composition, the water content of the film, etc. A higher R_f value is usually beneficial for the corrosion protection because the R_f value reveals the corrosion protection ability of the film to some extent. This is, however, not always true since R_f depends on numerous different factors. With the ingress of the electrolyte into the film, the R_f value decreases gradually, which normally occurs at the beginning of tests or after immersing the samples in saturated $\text{Ca}(\text{OH})_2$ solution.
5. Delamination of the corrosion product film is observed in samples with Li_2CO_3 addition when the thickness of the corrosion product film reaches a critical value (about 10 μm). This phenomenon can have a significant impact on the corrosion rate. For examples, after immersing the OPC+ Li_2CO_3 samples in saturated $\text{Ca}(\text{OH})_2$ solution in condition 1, the corrosion rate increases significantly to remain constant at about 70-100 $\mu\text{m}\cdot\text{y}^{-1}$, while the R_f value rapidly drops to $\sim 20 \text{ ohm}\cdot\text{cm}^2$ to remain constant afterwards. Meanwhile, the delamination phenomenon begins to occur. Hence, the variation of the corrosion rate and R_f changes can be explained by the occurrence of delamination. EDX results indicate that the delamination seems to be related to elements' diffusion. Further research is needed for detailed mechanisms.

5

Analysis of the cement paste porosity using EIS coupled with GEM

The innovative methodology for determining the porosity results is organized in a paper, which will be submitted later.

Preamble: This chapter works on the determination of the cement paste porosity by innovatively combining EIS and GEM.

Chapter 5. Analysis of the cement paste porosity using EIS coupled with GEM

5.1. Introduction

The mechanical and transport properties of cement pastes depend on their porosity. As a result, the corrosion processes of aluminium embedded in cement paste is also strongly influenced by the porous framework. Hence, the porosity of the cement paste is also investigated in this research. An innovative methodology is thus proposed to quantitatively characterize the capillary porosity of cement pastes by combining an equivalent circuit model constructed to analyse the electrochemical impedance spectroscopy (EIS) response with a two-phase model derived from the general effective media theory (GEM).

First, the impedance spectra determined from EIS also contain the electrochemical responses from the cement paste between the two electrodes. Therefore, some information can be directly identified from the analysis of spectra. Then, the EIS fitting is performed to extract the key parameters for a quantitative analysis.

The equivalent circuit model shown in Figure 4.6 is also suitable for the study of the cement paste. This model provides the resistance of connected capillary pores (R_{cem1}) between the two electrodes. As introduced in Chapter 3, R_{cem1} is then used to determine σ_{eff} , which is needed in the GEM.

Except R_{cem1} , another parameter, which still needs to be known, is the conductivity of capillary pore phase σ_p . Because the pore phase is always filled with the pore solution, the conductivity of the pore solution is measured following the method introduced in Chapter 3 and used as σ_p . The pH values of the pore solutions are also measured incidently, because a higher pH accelerates the corrosion process of aluminium and the addition of Li_2CO_3 is reported to enhance pH [118].

After collecting all parameters needed in the GEM model, the porosity values of different cement pastes are determined. On the one hand, the porosity results determined by the new methodology are compared with the ones obtained with MIP to examine the reliability of the methodology; on the other hand, the influence of the curing conditions on the porosity results determined by this methodology is analysed. Finally, the relationship between the corrosion rate variation of aluminium and the porosity variation of cement pastes is explored.

5.2. Methods

This porosity study combines EIS and GEM to determine the porosity of cement pastes. In this study, the equivalent circuit model constructed to analyse the electrochemical impedance spectroscopy (EIS) response is theoretically linked to a two-phase model derived from the general effective media theory (GEM). Then, the resistance of connected capillary pores as provided by the EIS analysis is used to approximate the effective resistance of the cement paste entering the GEM. Other input parameters needed in the GEM theory, i.e. the percolation threshold (ϕ_c), the tortuosity (t) and the conductivity of the solid-gel phase (σ_s), are collected from the literature, while the conductivity of the capillary pores (σ_p) uses the pore solution conductivity experimentally measured. Then, the porosity of the cement paste can be determined using Equation (19) provided in Section 3.5:

$$\phi = \frac{\left[\left(\frac{\sigma_p}{\sigma_{eff}} \right)^{\frac{1}{t}} + \left(\frac{1-\phi_c}{\phi_c} \right) \right] \times \left[\left(\frac{\sigma_s}{\sigma_{eff}} \right)^{\frac{1}{t}} - 1 \right]}{\left[\left(\frac{\sigma_p}{\sigma_{eff}} \right)^{\frac{1}{t}} + \left(\frac{1-\phi_c}{\phi_c} \right) \right] \times \left[\left(\frac{\sigma_s}{\sigma_{eff}} \right)^{\frac{1}{t}} - 1 \right] - \left[\left(\frac{\sigma_p}{\sigma_{eff}} \right)^{\frac{1}{t}} - 1 \right] \times \left[\left(\frac{\sigma_s}{\sigma_{eff}} \right)^{\frac{1}{t}} + \left(\frac{1-\phi_c}{\phi_c} \right) \right]}. \quad (19)$$

MIP tests are performed to examine the reliability of this new method. The influence of the curing conditions is also analysed to extract the impact on the porosity. Last but not least, the cracks and holes in the cement paste caused by the corrosion process are observed by SEM and the mass transfer in the cement paste can be measured by EDX. The characteristics of the main methods used to determine the porosity are summarized in Table 12.

Table 12. Methods for the porosity study.

EIS	GEM	MIP
The resistance of connected capillary pores of the cement paste (R_{cem1})	The conductivity of overall cement paste (σ_{eff})	The volume of mercury entering the cement paste
Porosity determined from the volume of the pore solution occupying the pores		Porosity determined from the volume of mercury occupying the pores

5.3. Impedance spectrum results

As mentioned in the introduction of this chapter, the impedance spectra also contain the electrochemical responses coming from the cement paste between two electrodes. Hence, some important information including the variation of the cement paste in some samples can be directly identified by the simple observation of the spectrum results, which is introduced in this section.

Three time constants can be distinguished in the impedance spectra of pure OPC samples in Figure 5.1. The three time constants are also found when measuring samples with the addition of LiNO_3 or Li_2CO_3 : (i) in the high-frequency domain, (ii) around the 1~10 Hz domain and (iii) in the low-frequency domain, respectively. Exceptionally, for one OPC+ Li_2CO_3 sample, a fourth time constant in the range of 1 to ~10 kHz is occasionally observed at the early stages of the tests. Generally, the responses of the cement paste part are mainly revealed in the higher frequency regions, while the lower frequencies reveal the responses of the interface between the aluminium and cement paste, including a corrosion product film. Some explanations about the time constants can be found in literature regarding the impedance plots in cementitious systems [214,261], but a direct comparison might bring errors because of the influential differences in the cement paste composition, the experimental set-up, the curing environment, etc. The water content of the cement paste decreases with ongoing cement hydration process. This leads to the following results: (i) the number of the capillary pores decreases with ongoing cement hydration, (ii) the thickness of the corrosion product film has a monotonically increasing trend and the corrosion rate of Al reduces fast at the beginning. Some of these changes are revealed in the impedance spectra [312]. For example, the diameter of the first semicircle in the high-frequency domain, which is related to the resistance of the disconnected pores, increases drastically until 13 days to reach a steady state value. It implies that the number of the disconnected pores decreases rapidly at the beginning of the cement hydration. The diameter of the intermediate semicircle in the 1~10 Hz region reveals the resistance of the connected pore path of the cement paste, which is important for the study of the cement paste porosity. The diameter of this semicircle increases monotonically as a function of time. In the first 28 days, it increases fast because of the fast hydration process of the cement paste at the beginning and afterwards it increases with a lower rate. The arc in the low-frequency domain, which corresponds to the interfacial response, gradually overlaps with the intermediate semicircle. This is attributed to the overlapping of the time constants, which are situated in the same frequency region. In terms of the impedance plots of other samples (LiNO_3 and Li_2CO_3 samples), the same problem of overlapping time constants brings difficulties to analyse impedance results only by visual observation of the Nyquist and Bode plots as already addressed in Section 4.4.

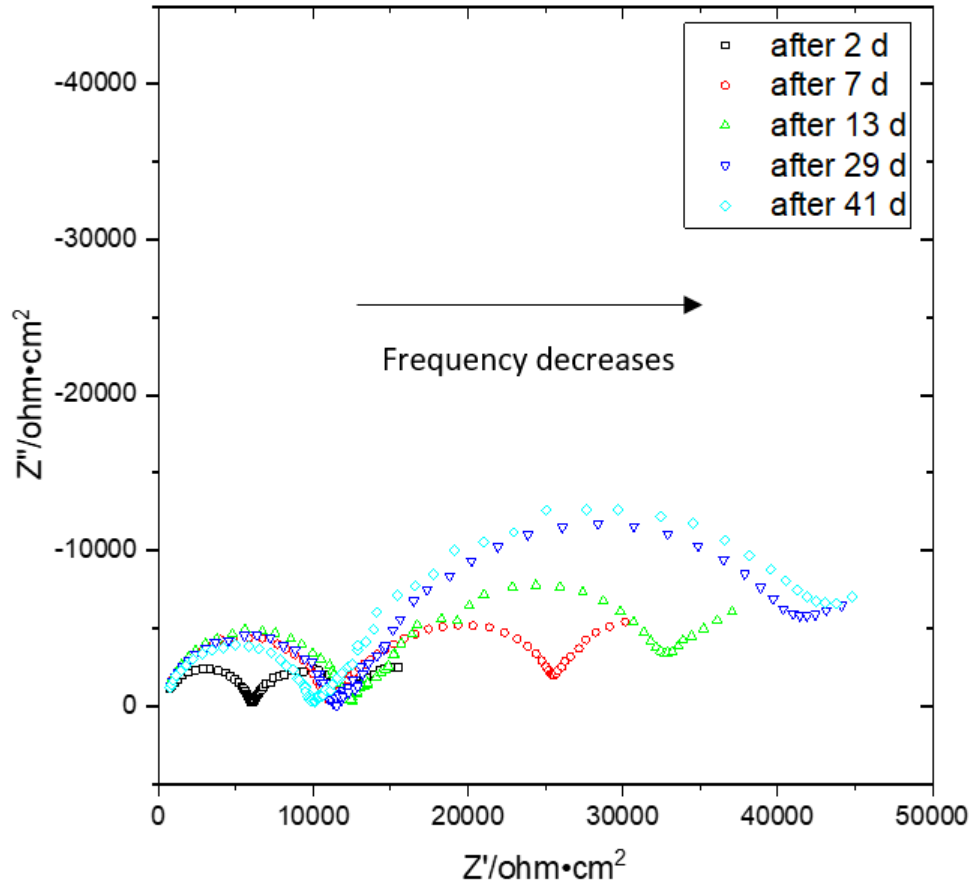


Figure 5.1 Variation of Nyquist plots of AA1100 with time in pure OPC paste under condition 1.

5.4. Equivalent circuit model

The EIS spectrum was fitted using the EEC presented in Figure 5.2 (the same as in Figure 4.6), in order to quantitatively analyse the electrochemical impedance results. As already explained in the previous chapter, the EEC consists of 3 parts and it is constructed based on the physical structure of the cell. Regarding the cement paste study, the second part of the EEC composed of three branches corresponding to the electrochemical properties of the cement paste between two electrodes is of interest. The resistance of the connected capillary pores (R_{cem1}) is used to approximate the effective resistance of the cement paste (R_{eff}) as addressed in Section 5 of Chapter 3. The parameter values obtained for the different samples, curing conditions and time are provided in Figure 5.3. For OPC samples, the R_{cem1} values in condition 1 increase rapidly until 22 days to reach a value around 18000 ohm and then keep constant, while the values

Chapter 5

in condition 2 are completely irregular because of the early occurrence of cracks as addressed in Section 4.7.5.1 and are not used for the porosity determination. The R_{cem1} values of OPC+LiNO₃ samples in condition 1 increase until 28 days followed by a relatively steady period. Two weeks after the immersion of samples in saturated Ca(OH)₂ solution, the R_{cem1} values suddenly plummet. In general, the R_{cem1} values of OPC+ LiNO₃ samples in condition 2 rise gradually during the entire period of the test. In terms of OPC+Li₂CO₃ samples, the R_{cem1} values in both conditions increase until 30 days and then remain constant at a relatively low level, i.e. 2000-3000 ohm. Although R_{cem1} reveals the porosity of the cement paste to some extent, it is not the only decisive factor that determines the porosity value. For example, even if the R_{cem1} evolution of OPC samples in condition 1 is very similar to the one of OPC+LiNO₃ samples in condition 1 (Figure 5.3(a) and (c)), their porosity values can be different because of the different pore solution conductivities, which will be introduced in the next section.

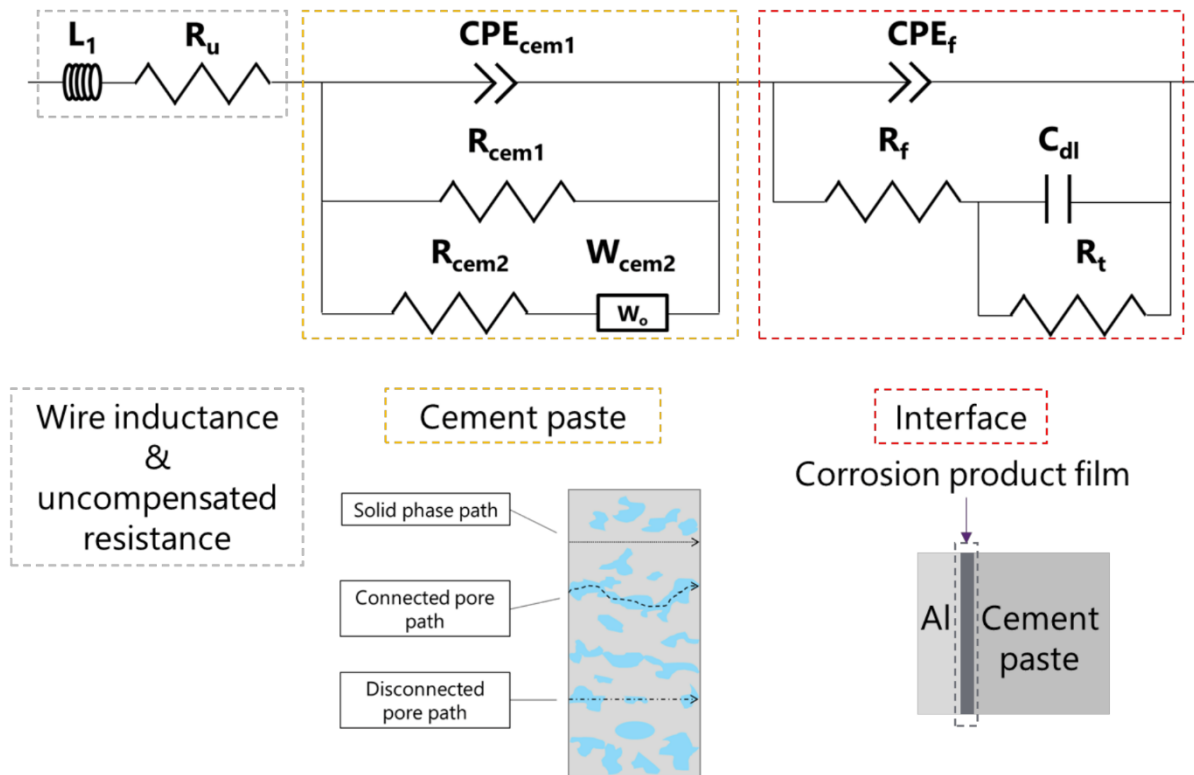


Figure 5.2 Electrical equivalent circuit employed to fit EIS spectra for the corrosion of Al plate in cement pastes.

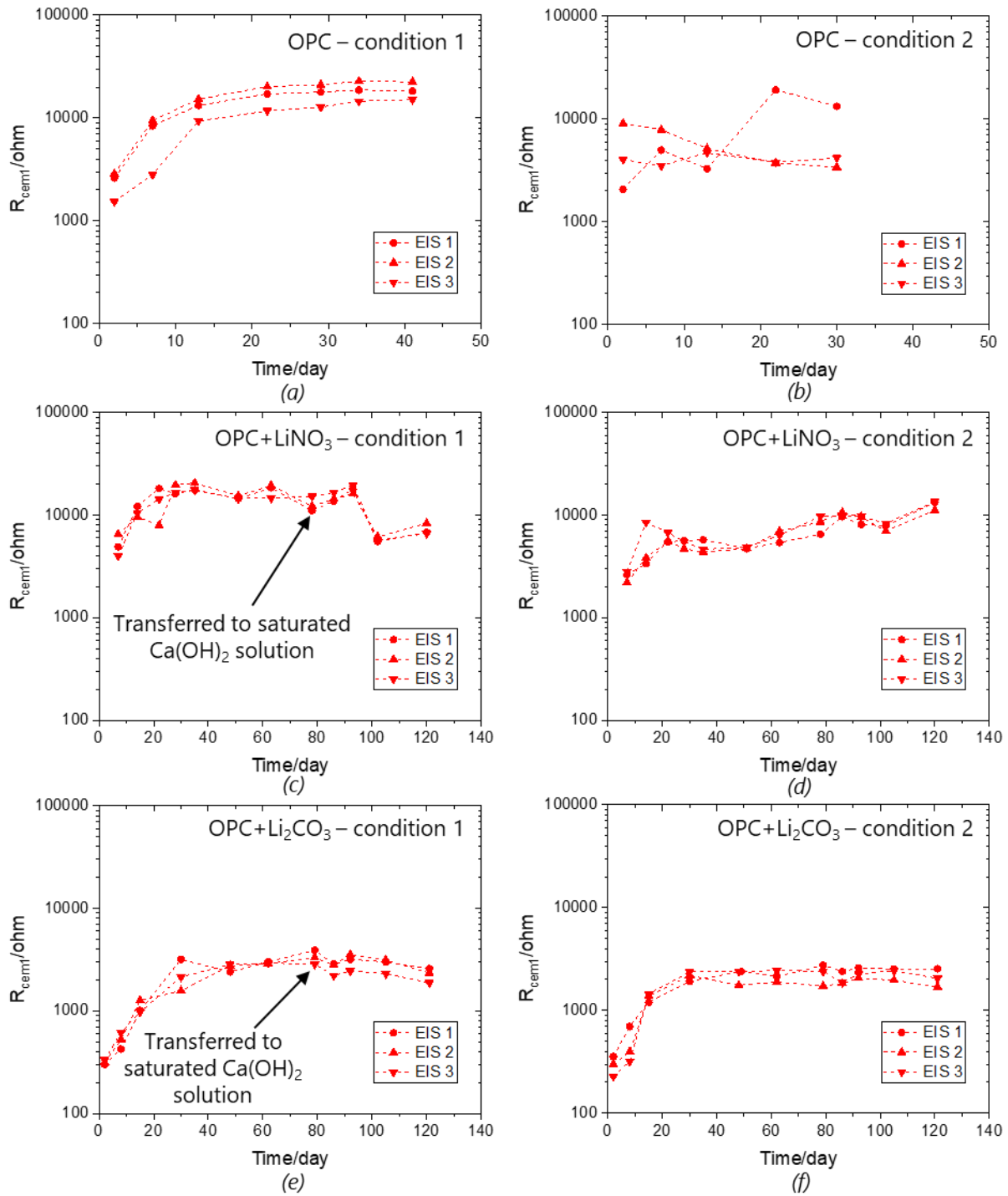


Figure 5.3 Evolution of R_{cem1} as a function of time of (a) OPC samples in condition 1, (b) OPC samples in condition 2, (c) OPC+LiNO₃ samples in condition 1, (d) OPC+LiNO₃ samples in condition 2, (e) OPC+Li₂CO₃ samples in condition 1, (f) OPC+Li₂CO₃ samples in condition.

5.5. Conductivity and pH of pore solution

After obtaining the R_{cem1} , another parameter needed in the GEM is the conductivity of the cement pore solution. Therefore, the cement pore solution was collected by the squeezing method (see Section 3.6), to analyse the conductivity and pH values. This was measured by conductivity and pH meters, respectively. Note that one cement pore solution was collected for each type of cement paste at each time point. The results of the conductivity measurements of the squeezed cement pore solutions are given in Figure 5.4. Generally, the pore solution conductivity of each cement paste is almost constant in a specific curing condition. For samples cured in condition 1, the conductivity values are almost stable (16 S/m for OPC+LiNO₃ and 14 S/m for OPC+Li₂CO₃), except a small increase at the beginning, until they significantly decrease towards values close to those measured for samples cured in condition 2 (12 S/m for OPC+LiNO₃ and 9 S/m for OPC+Li₂CO₃) after the immersion of samples in saturated Ca(OH)₂ solution. Note that the data for the 0.36 w/c OPC cement paste specimens, tested in condition 1 and without the addition of lithium salts, are missing after 4 days because no pore solution could be collected out of the specimens. It might be due to the fact that the low water/cement ratio caused the lack of residual water inside the cement paste. However, no problem occurred for OPC+LiNO₃ samples with the same w/c ratio. Some studies [286-291] reported that the Li ions can be incorporated into the C–S–H at the early stages of the hydration through the occupation of calcium sites in the C–S–H-like structure. This absorption may contribute to a decrease of the interlayer water or of the physically adsorbed water in C–S–H and hence can rise the water level in capillary pores. Further research is needed to confirm this hypothesis. The conductivity values of pore solution for all samples in condition 2 remain relatively constant over time and the conductivity of OPC, OPC+LiNO₃ and OPC+Li₂CO₃ samples fluctuates at around 7 S/m, 12 S/m, 9 S/m respectively. Besides, it can be clearly seen that the addition of lithium salts increases the conductivity. The conductivity decreases in the following order: [OPC+LiNO₃] > [OPC+Li₂CO₃] > OPC. This trend is found for both conditions. Furthermore, the conductivity in condition 1 is higher than that in condition 2. This is probably caused by the higher availability of water in condition 2 (compared to condition 1) resulting in a stronger dilution of the ion concentrations and consequently in a reduction of the conductivity. The conductivity value for each cement paste in a specific curing condition is regarded as a constant (see Table 13) and is used for the value of σ_p in the GEM model.

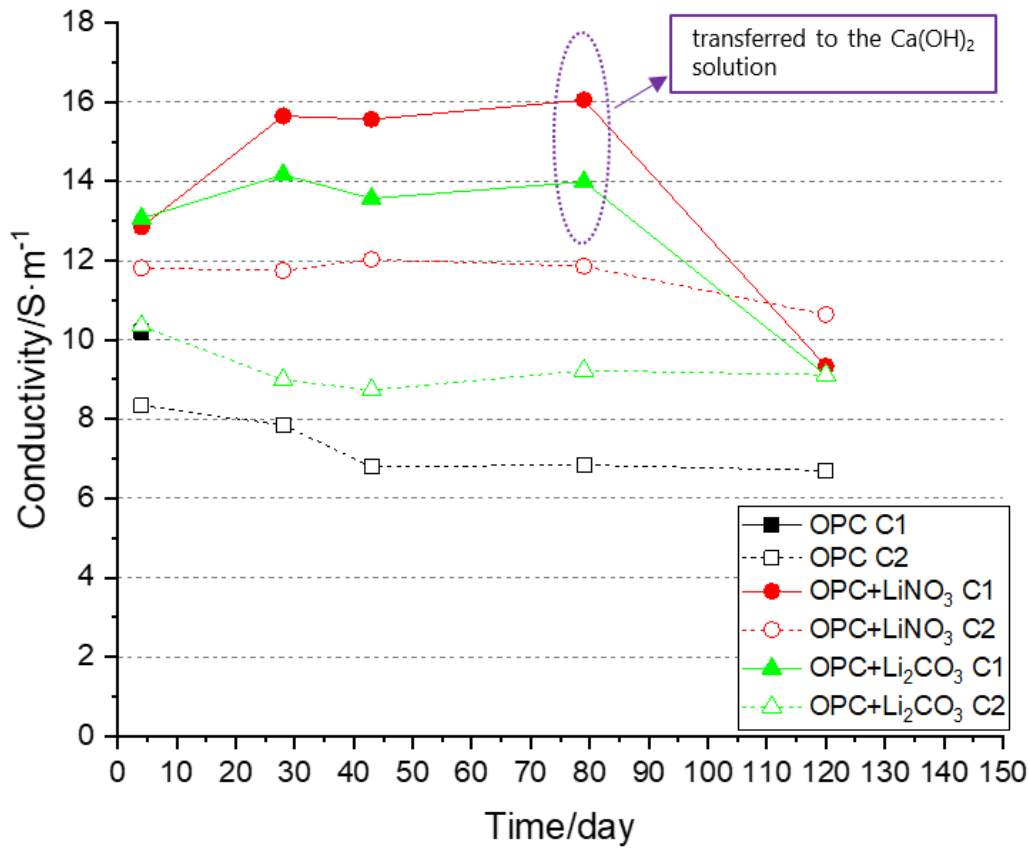


Figure 5.4 Variation of the conductivity of cement pore solution as a function time for different conditions with or without inhibitors.

Table 13. Pore solution conductivities (S/m) used in the GEM for each cement paste system.

Pore solution conductivities (S/m)	Condition 1		Condition 2
	Humid Ar	Ca(OH) ₂ solution	Ca(OH) ₂ solution
0.36 OPC	10		7
0.36 OPC+3% LiNO ₃	16	9	12
0.50 OPC+1.607% Li ₂ CO ₃	14	9	9

Figure 5.5 illustrates the variation of pH of the pore solution with time. The enhanced pH reported by Diamond [118] when adding Li₂CO₃ is not observed in our results. By contrast, the addition of LiNO₃ and Li₂CO₃ seems to decrease the pH in comparison to pure OPC systems without any lithium addition, which is probably attributed to the increased water content diluting the concentration of OH⁻ ions. In general, all samples showed a high pH, above 12.

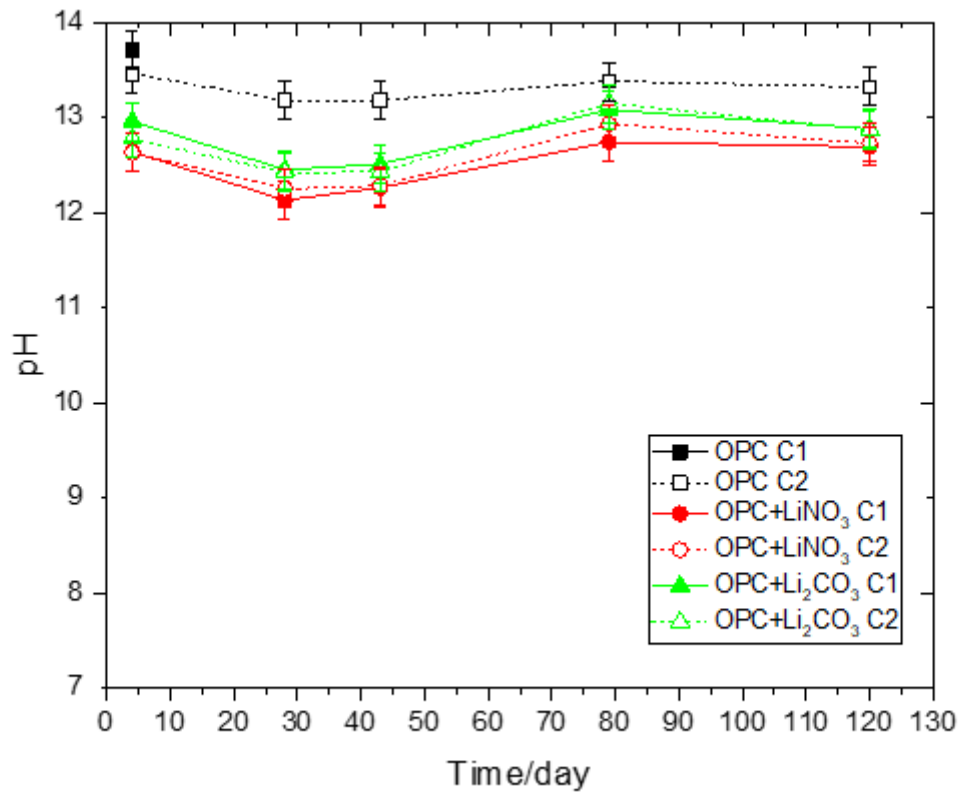


Figure 5.5 Variation of the pH of cement paste pore solutions as a function of time.

5.6. Cement paste porosity

After having obtained/measured all parameters needed in the GEM model (see Section 3.5 and Section 5.5), the determination of the porosity was performed by using Equation (19) (see Section 3.5). The porosity evolution of three types of cement pastes (Portland cement pastes with a 0.36 water/cement ratio with/without the addition of 3 wt.% LiNO₃ and Portland cement paste with a 0.50 water/cement ratio with 1.607 wt.% Li₂CO₃) cured in two types of conditions (in humid Ar and in saturated Ca(OH)₂ solution) was studied. These three different pastes and two conditions were studied to examine the reliability of the proposed methodology.

A comparison of the porosity results obtained from EIS and MIP measurements is shown in Figure 5.6. For the 0.36 OPC specimens in condition 1 (Figure 5.6(a)), the tests were stopped after 40 days because scatter in impedance plots increased as a function of time [312], consequently leading to the difficulties of obtaining reliable fitting results and to the failure of porosity determination after 40 days. This should be attributed to the accumulation of corrosion products at the interface of aluminium/cement paste and the generation of H₂ caused by the fast corrosion of Al leading to cracks and holes inside the cement paste.

Chapter 5

These cracks and holes were observed by SEM already after 28 days (Figure 5.7) and also at the surface of the blocks after 133 days (see Figure 5.8).

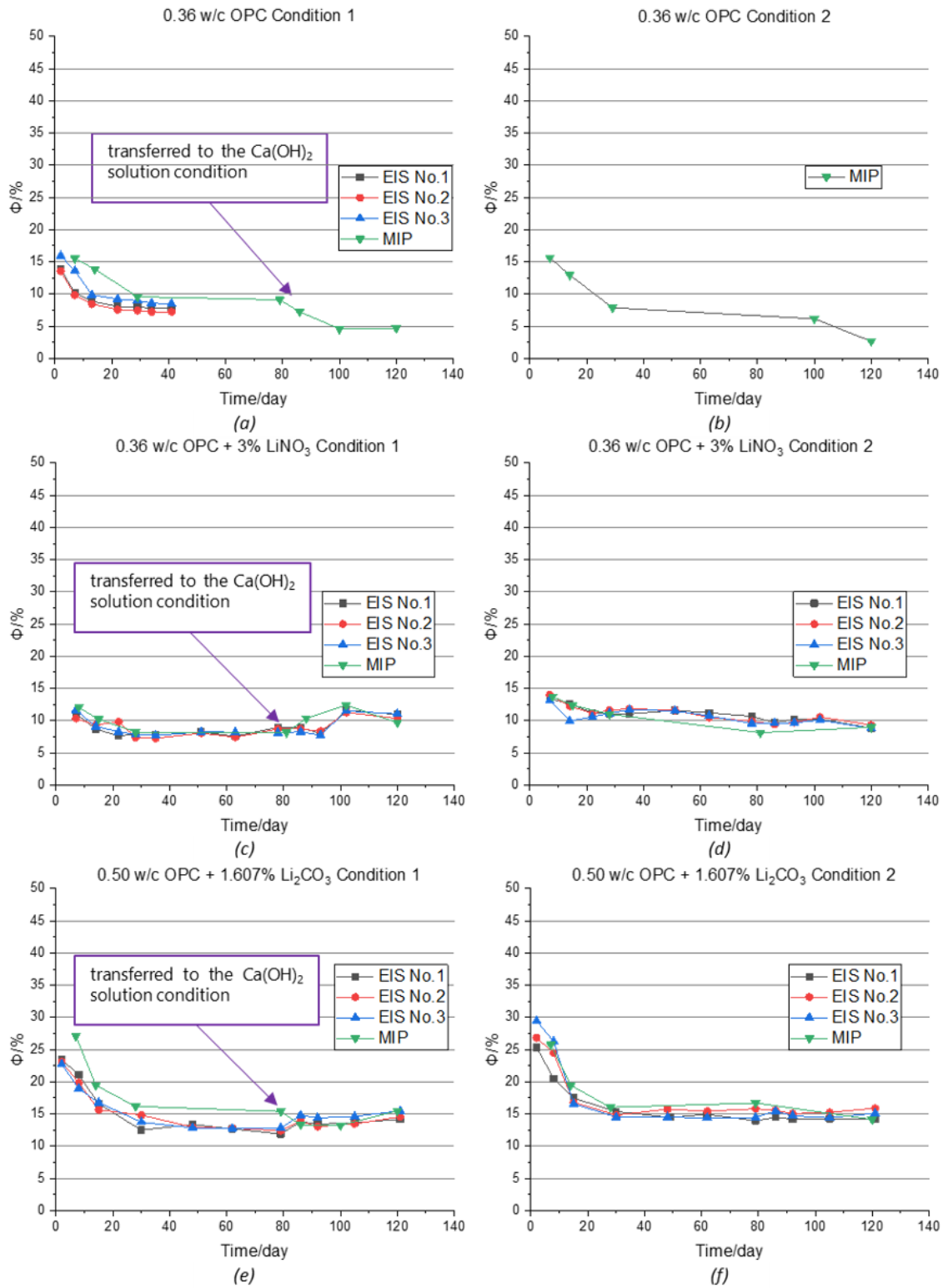


Figure 5.6 Variation of the porosity as a function of time measured by EIS and MIP of (a) 0.36 OPC samples in condition 1, (b) OPC samples in condition 2, (c) OPC+ LiNO_3 samples in condition 1, (d) OPC+ LiNO_3 samples in condition 2, (e) OPC+ Li_2CO_3 samples in condition 1, (f) OPC+ Li_2CO_3 samples in condition 2.

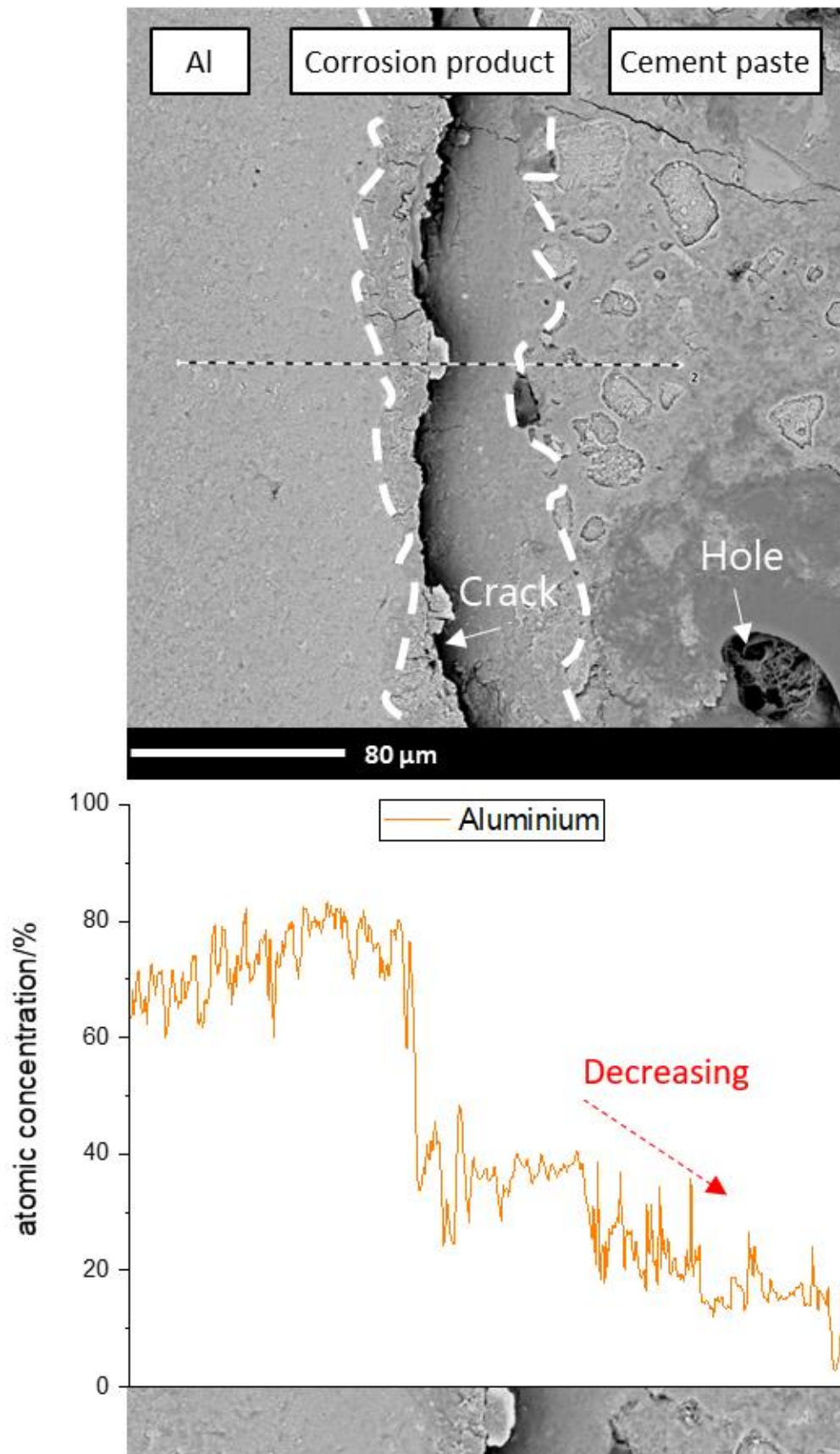


Figure 5.7 SEM and EDX line scan results of the Al element of the cross-section of an OPC sample in condition 1 for 28 days.

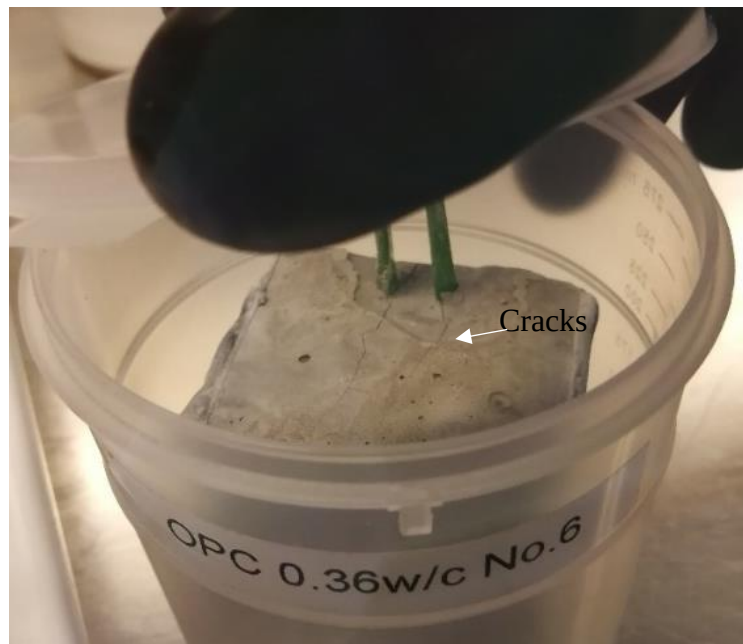


Figure 5.8 Tiny cracks appeared in one of the three replicate 0.36 OPC samples after 133 days in condition 1.

In Figure 5.6(a), the porosity measured with EIS decreases from about 15% to around 8% over the first 15 days and remains constant afterwards. The porosity extracted from the MIP measurements also declines during the first 30 days, then remains constant and finally decreases after 80 days. This second decrease is likely linked to the immersion of the cement paste specimen in saturated $\text{Ca}(\text{OH})_2$ solution after 80 days of testing with the probable precipitation of $\text{Ca}(\text{OH})_2$ occluding the connected pores. From Figure 5.6(a), it is also apparent that the porosity values obtained from EIS are slightly lower than the values measured with MIP. This might be caused by the characteristics of the EIS method. First, the porosity measured by EIS represents the porosity of the cement paste in the centre part of the specimen between the two electrodes. This part of the cement paste is contaminated by the corrosion product, which may occlude the cement pores thereby decreasing the porosity. While the MIP analysis was performed using cement paste particles that were not in a direct contact with aluminium electrodes (see Section 3), this difference might lead to the discrepancy. Indeed, the distribution of the aluminium (Figure 5.7), which mainly comes from the corrosion products, indicates that the corrosion products have the tendency of diffusing towards the cement paste matrix as the Al content decreases with increasing distance from the interface. This occlusion could be especially severe when there is no formation of a dense corrosion product film in these 0.36 OPC samples (without the addition of lithium, the corrosion product film of Al in cement pastes is porous and hence cannot prevent the proceeding of corrosion process into the Al matrix, which results in a fast generation of corrosion products on the surface). Another possible explanation is that the porosity measured by EIS is related to the amount of cement paste pore

Chapter 5

solution. In this research, the conductivity of the pore solution was measured and was used as the conductivity of capillary pore phase σ_p in the GEM theory, which is only appropriate when the capillary pores are entirely filled with pore solution as shown in Figure 3.14(a). When the capillary pores are only partly filled with pore solution (Figure 3.14(b)), this approximation leads to an underestimation of the porosity. According to literature [314-316], the amount of pore solution is determined by many factors, such as humidity and initial water/cement ratio. Larger capillary pores are prone to lose water first, followed by the small capillary pores and finally the gel pores. In the hydration process, the rapid consumption of the pore solution could possibly lead to a lack of pore solution for filling in all capillary pores. Besides, the extra water consumption caused by the corrosion process probably intensifies this solution deficiency. Hence, this pore solution deficiency could be the reason for the slightly different porosity percentage obtained from EIS and MIP.

Regarding the porosity of OPC samples in condition 2 (Figure 5.6(b)), only MIP results are shown because it was not possible to obtain valuable information from the EIS measurements since all samples breached soon after the start of the tests (as mentioned in Figure 4.42(b)). No repetitive results were obtained from these EIS samples because of the cell geometry change caused by cracks. Cui et al. [199] reported that the porosity values for OPC pastes of 0.3 and 0.4 water/cement ratios are 5.9% and 9.1% respectively after a long hydration period (210 days), which is similar to the results obtained by MIP in this study.

Figure 5.6(c) and (d) provides the porosity results of 0.36 OPC+3% LiNO₃ samples obtained from EIS and MIP measurements. The percentage of porosity measured by EIS and MIP are similar in both curing conditions. This probably means that 0.36 OPC+3% LiNO₃ samples contain enough pore solution to fill all the capillary pores even in a humid Ar atmosphere at the beginning of the tests done in condition 1. This is consistent with the fact that more pore solution could be extracted from the 0.36 OPC+3% LiNO₃ samples compared to the 0.36 OPC samples (as already explained in Section 5.5). In condition 1, the porosity value of the 0.36 OPC+3% LiNO₃ samples slightly decreases during the first 20 days and then keeps stable at around 10% until immersion of the cement paste samples in saturated Ca(OH)₂ solution. After the immersion, MIP shows that the porosity increases instantly, which can be attributed to the fast leaching of salts, i.e. LiNO₃, inside the cement paste into the solution, while it takes a longer time to observe the same increase using EIS technique (observed after 93 days). This retardation in EIS can be explained by the longer diffusion path of salts in EIS samples. In condition 2, the porosity slightly decreases to about 10% at the beginning followed by a long steady state measured until the end of the test. In the steady state after the initial hydration i.e. from 28th day to 80th day, the porosity in condition 2 (normally above 10%) is a bit higher than that in condition 1 (around 7.5%). This is probably attributed to the dissolution of LiNO₃ into saturated Ca(OH)₂ solution in condition 2.

Chapter 5

A comparison of the porosity results obtained from EIS and MIP measurements for 0.50 OPC+1.607% Li_2CO_3 are shown in Figure 5.6(e) and (f). In condition 1, the porosity values measured from EIS and MIP follow the same trend initially. However, the absolute values obtained from EIS are clearly lower than that from MIP. Similar to the situation of 0.36 OPC samples in condition 1, this might be caused by a lack of pore solution. After 80 days, the cement paste samples were immersed into saturated $\text{Ca}(\text{OH})_2$ solution. Correspondingly, the porosity from EIS increases slightly and then remains fairly the same as those obtained from MIP. This increase is likely due to the fact that immersion of the cement paste samples in saturated $\text{Ca}(\text{OH})_2$ solution provided enough water to fill all the pores in the cement paste, and hence higher porosity values were measured. In condition 2, the results from EIS and MIP are identical on the whole period of test, showing that data obtained by EIS can be efficiently used for the determination of the cement porosity in these conditions. In both conditions, the porosity obtained from MIP drops from above 25% after 7 days to about 15% after 28 days. Boel et al. [317] studied the porosity variation of OPC pastes and reported a porosity decrease from about 22% after 14 days to about 16% after 3 months for the cement paste of 0.50 water/cement ratio. Hence, the addition of 1.607% Li_2CO_3 has little impact on the porosity variation.

Considering the corrosion rate variation reported in Chapter 4, it can be concluded that the porosity decrease at the beginning of cement hydration is usually accompanied with the decrease of the corrosion rate. The decrease of the porosity increases the difficulty of the mass transfer leading to a lack of corrosion reactants and an accumulation of products on the aluminium surface, which should be one of the reasons that the corrosion rates decrease.

5.7. Conclusion

Electrochemical impedance spectroscopy (EIS) is a common technique used to study the corrosion of metals in solutions as well as in cementitious matrices. In parallel to that, this chapter describes the possibility to gain quantitative and in situ information on the porosity of cement paste by combining EIS with the General Effective Media (GEM) theory. The effective resistance (R_{eff}) entering the GEM theory is approximated by the resistance of connected capillary pores given by R_{cem1} from the fitting of the EIS curve. This approximation is valid because the capillary pore solution of cement pastes is highly conductive compared with the solid phase. Therefore, the contribution of the solid phase is almost negligible. Other input parameters needed in the GEM theory, such as the percolation threshold (ϕ_c), the tortuosity (t) and the conductivity of the solid-gel phase (σ_s), were collected from the literature, while the conductivity of the capillary pores (σ_p) uses the pore solution conductivity experimentally measured. The porosity results determined from EIS are then compared with the ones obtained from mercury intrusion porosimetry (MIP).

The whole procedure followed in this chapter to determine the cement paste porosity is illustrated in Figure 5.9.

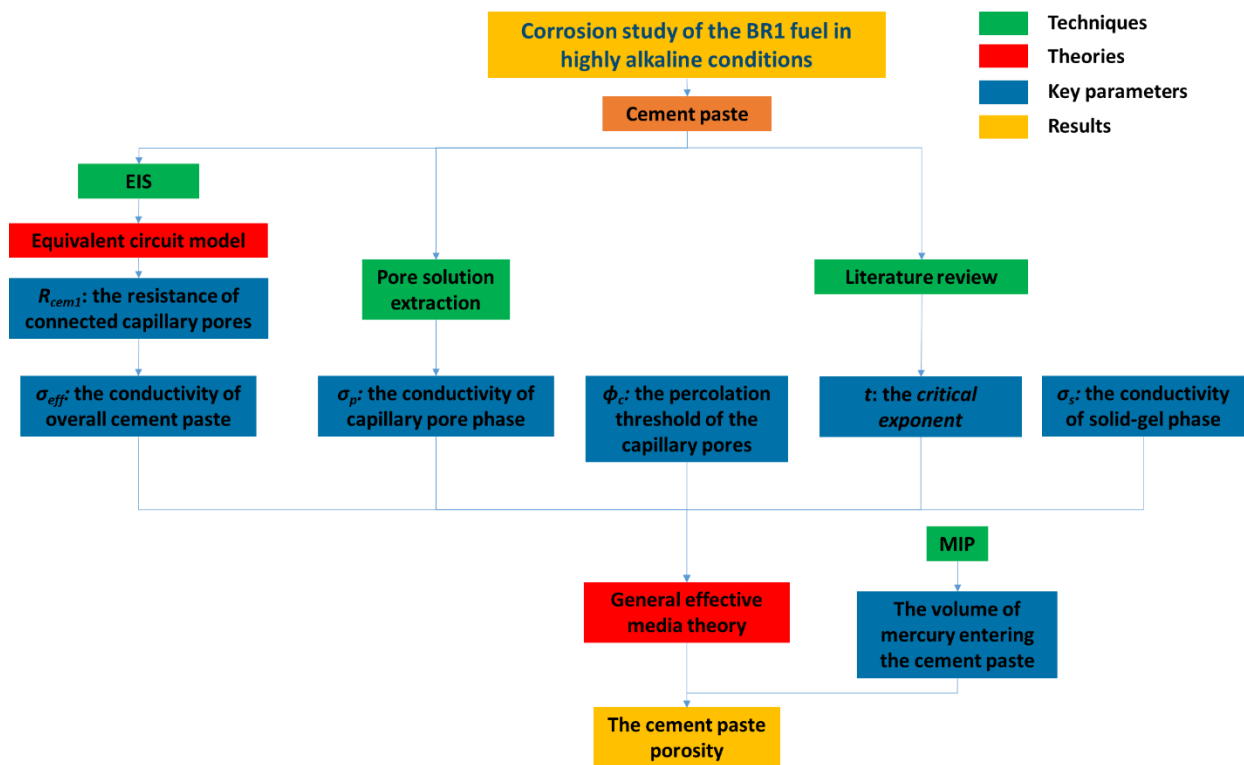


Figure 5.9 Methodology for the study the cement paste porosity using a combination of EIS and GEM.

The main findings of the cement paste porosity study are the following:

1. The pore solution conductivity of each cement paste is almost constant in a specific curing condition. The conductivity values of samples tested in condition 1 are almost stable (16 S/m for OPC+LiNO₃ and 14 S/m for OPC+Li₂CO₃) except a negligible increase at the beginning. Then, they plunge towards values close to the ones measured in condition 2 (12 S/m for OPC+LiNO₃ and 9 S/m for OPC+Li₂CO₃) after the immersion of samples in saturated Ca(OH)₂ solution. The results of OPC samples tested in condition 1 are missing after 4 days because no pore solution could be successfully collected.
2. The porosity results obtained from EIS and MIP are in good agreement in general. For OPC and OPC+Li₂CO₃ samples in condition 1, the porosity values determined by EIS in the humid Ar atmosphere are a bit lower than the ones determined by MIP, which can be attributed to the fact

Chapter 5

that the partly saturated pores lead to an underestimation of the total porosity. After the immersion of OPC+Li₂CO₃ samples in saturated Ca(OH)₂ solution, the porosity values determined by EIS and MIP become close, which means that all pores become saturated. In terms of OPC+LiNO₃ samples in condition 1, the porosity values measured by EIS and MIP are similar all the time. This can be explained by the fact that the addition of LiNO₃ probably results in an increase of the pore solution amount, which is also revealed in the extraction process of the pore solution. In condition 2, the EIS measurements of OPC samples failed to provide reliable results because of the occurrence of cracks, while the results of OPC+LiNO₃ samples and OPC+Li₂CO₃ samples determined by EIS and MIP are in good agreement.

3. The porosity decrease at the beginning of cement hydration is probably one of the reasons of the decrease of the corrosion rate. As introduced in Section 4.7.5, a decrease of the corrosion rate at the beginning of cement hydration is observed in all kinds of samples. On the one hand, this decrease is attribute to the depletion of water available for the corrosion process because of the rapid consumption by the cement hydration and the corrosion reaction; on the other hand, the decrease of the porosity can limit the mass transfer of corrosion products, leading to the decrease of the corrosion rate.

These results indicate, in the context of the analysis of the corrosion rate of aluminium alloy 1100 in contact with Portland cement pastes, that it is also possible to gather in situ porosity information from the cement paste matrix via a non-destructive EIS method.

6

Conclusions

Chapter 6. Conclusions

The reactor BR1 has been working for more than 70 years and the dismantling works of BR1 need to be considered. The disposal of BR1 fuel, which uses a uranium core coated by a series of outer layers and finally encapsulated in an aluminium cladding, is challengeable. Different methods are available for the final disposal of the BR1 fuel, such as the pre-treatment and the direct encapsulation of the fuel. The thesis focused on the route of geological disposal, where the BR1 fuel is directly encapsulated in a cementitious material, because of the technical convenience and the economic feasibility. In this disposal strategy, the aluminium cladding as the outermost layer of BR1 fuels is in direct contact with the cementitious environment. Because of its amphoteric character, aluminium exhibits a high corrosion resistance in both acidic ($\text{pH} < 3.8$) and alkaline ($\text{pH} > 8.6$) environments. Portland cement is the most widely used cement type and a candidate for the waste encapsulation. However, the pore solution pH of Portland cementitious materials is usually above 12.5, which results in a high corrosion rate of aluminium. The high corrosion rate leads to the rapid production of H_2 gas (under anoxic conditions) and the fast accumulation of solid corrosion products, resulting in volume changes compared to the metallic aluminium. The volume changes cause an increase in residual stress and consequently induce cracks in the cementitious matrix. Furthermore, after breaching of the outermost aluminium cladding caused by the fast corrosion reaction, the corrosion of the inner components, i.e. the AlSi bonding layer, the $\text{U}(\text{Al},\text{Si})_3$ anti-diffusion layer and the uranium core, would occur in sequence leading to the leakage of radionuclides into the environment. The application of lithium salts, i.e., LiNO_3 and Li_2CO_3 , is a way to inhibit the corrosion of AA1100 embedded in OPC pastes, owing to the formation of a protective layered double hydroxide film on the aluminium surface.

The objective of the thesis is to investigate the corrosion of AA1100 embedded in OPC pastes and the porosity variation of OPC pastes. For this purpose, we followed the methodology shown in Figure 6.1. It indicates that the aluminium corrosion process and the cement paste porosity variation can be studied by EIS simultaneously and quantitatively. The fitting of the equivalent circuit determines R_t and R_{cem1} from EIS spectra. Afterwards, the two parameters are used to determine the corrosion rate (Chapter 4) and the cement paste porosity (Chapter 5), respectively. The results of the corrosion rate and the cement paste porosity were confirmed by the application of other techniques, such as SEM and GC for the corrosion rate and MIP for the cement paste porosity.

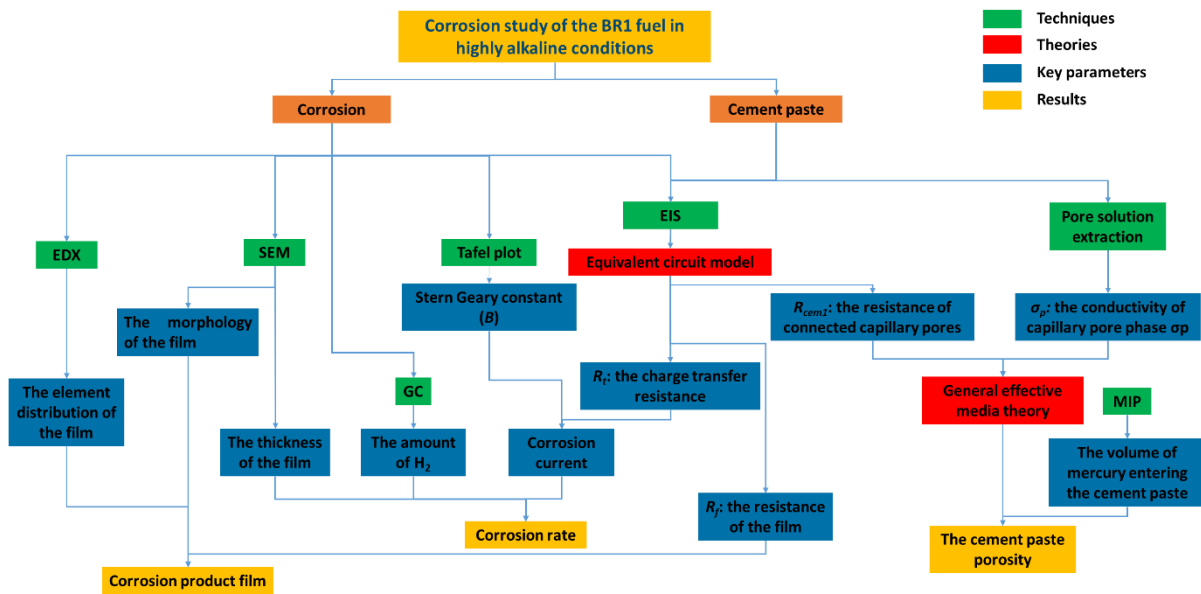


Figure 6.1 Summary of the methods used in the thesis.

The primary task was to study the corrosion behaviour of AA1100 embedded in OPC pastes involving the inhibition efficiency of lithium salts, the influence of the curing conditions and the corrosion mechanisms of different samples. This corrosion study focused on two parts: (1) corrosion rate measurements and (2) characteristics (thickness, morphology, composition, etc.) of the corrosion product film. The corrosion rate of aluminium embedded in OPC pastes with/without lithium addition was studied by a combination of different methods. For EIS, an equivalent circuit model was constructed to quantitatively study the impedance spectra obtained by EIS measurements. Afterwards, a combination of EIS and Tafel was used to determine the corrosion current density and later the corrosion rate of the different studied systems. The corrosion product film thickness determined by SEM and the hydrogen gas produced during the corrosion reaction measured by GC were also used to calculate the corrosion rates to compare with the results obtained from EIS. Furthermore, the resistance of the corrosion product film (R_f), which reveals the protection ability of the film to some extent and which is derived from EIS fitting, was determined and compared to data reported in the literature. The morphology and the chemical composition of the aluminium/corrosion product film/cement paste interface were also studied by SEM and EDX, respectively. Finally, the corrosion mechanisms of different samples were hypothesized according to the results of the corrosion rate and the corrosion product film.

To better understand the influence of cement paste pores on the corrosion process, the porosity of cement pastes was also studied by an innovative methodology combining an equivalent circuit model, constructed to analyse the EIS response, with a two-phase model, derived from the GEM. The equivalent circuit can separate the different information from aluminium, the corrosion product film and the cement

paste, giving the resistance of connected capillary pores of the cement paste. Then, the resistance of connected capillary pores was innovatively used to approximate the overall resistance of the cement paste. Several input parameters entering the GEM theory, such as the percolation threshold (ϕ_c), the tortuosity (t) and the conductivity of the solid-gel phase (σ_s), were collected from the literature. The conductivity of the capillary pores (σ_p) was determined experimentally from pore solution conductivity measurements. Finally, the capillary porosity of Portland cement pastes was calculated after collecting all the parameters needed in the GEM model. In order to examine the reliability of this innovative methodology, MIP measurements were performed as a comparison.

The most important findings corresponding to the objectives are listed below:

1. The corrosion rates of aluminium were determined by EIS/Tafel, GC and SEM in order to evaluate the corrosion inhibition effect of LiNO_3 and Li_2CO_3 on AA1100 embedded in OPC pastes. The experimental results clearly show that both LiNO_3 and Li_2CO_3 are effective corrosion inhibitors for Al embedded in cement pastes. The addition of lithium salts effectively decreases the corrosion rate of Al on the one hand and prevented the generation of cracks in the cement paste matrix on the other hand (severe cracks were observed in pure OPC samples as shown in Figure 4.42). For example, corrosion rate values for Al embedded in OPC+ LiNO_3 as low as $10\text{--}20\ \mu\text{m}\cdot\text{y}^{-1}$ were measured at the end of a 4 month testing period, whereas the experiments with OPC (without addition of Li) had to be interrupted prematurely because of the generation of cracks. The corrosion rates determined by different techniques i.e., EIS, SEM and GC, agree with each other, enhancing the reliability of the data.
2. For samples without lithium addition, this corrosion product film is likely to be a mixture of hydroxoaluminate salts and layered double hydrates, which does not show good corrosion-resistant ability. Hence, due to the fast accumulation of corrosion products such as H_2 gas, the internal stress levels increase and consequently cracks are induced in the cement paste matrix. For samples with the addition of LiNO_3 or Li_2CO_3 , the corrosion inhibition is attributed to the formation of a protective Li-Al LDH film on the surface of the aluminium substrate. This film works as a physical barrier against water and ion migration. Also, the main gaseous corrosion product in OPC+ LiNO_3 samples becomes ammonia instead of H_2 .
3. Compared with Li_2CO_3 , LiNO_3 is more suitable for the encapsulation of Al in the cement paste, because the combination of 0.36 water/cement ratio and 3 wt.% LiNO_3 provides the lowest corrosion rates ($10\text{--}20\ \mu\text{m}\cdot\text{y}^{-1}$ after the first 28 days) without any curing problems. The combination of 0.50 water/cement ratio and 1.607 wt.% Li_2CO_3 gives a relatively higher corrosion rate up to $100\ \mu\text{m}\cdot\text{y}^{-1}$ after the initial period. Furthermore, the addition of Li_2CO_3 increases the viscosity of the cement paste leading to a problem of workability of this cement paste. Last but not least, the low and predictable level of hydrogen production in OPC+ LiNO_3 samples is also beneficial to the long-term encapsulation. Therefore, LiNO_3 seems to be the best inhibitor of the corrosion of aluminium in OPC paste.

Chapter 6

4. In both curing conditions (i.e. condition 1 and condition 2), the ingress of saturated Ca(OH)_2 solution significantly increases the corrosion rate of Al in cement pastes either temporarily (LiNO_3 samples) or irreversibly (Li_2CO_3 samples). Moreover, the corrosion rates of the samples with the addition of lithium salts in condition 1 and condition 2 are comparable at the end of the measurements since samples in both conditions are immersed in saturated Ca(OH)_2 solution at last. The curing conditions also affect the pore solution of cement pastes. For example, the pore solution conductivity of cement pastes in a humid Ar atmosphere is always larger than the one in a saturated Ca(OH)_2 solution, which can be attributed to the dilution of the pore solution.
5. By innovatively combining GEM and EIS, a new methodology has been created to determine the cement paste porosity. MIP measurements were also performed to examine the reliability of this new methodology. The porosity results obtained from EIS and MIP are in good agreement. Note that if the cement paste does not contain enough pore solution, the partly saturated pores lead to an underestimation of the total porosity in the new methodology. In both curing conditions, the samples with a 0.36 water/cement ratio have a porosity around 10% after 28 days, while the samples with a 0.50 water/cement ratio have a porosity at 15%. It seems that curing conditions have little influence.
6. The porosity decreases at the beginning of cement hydration (normally within the first 28 days) is usually accompanied with a decrease of the corrosion rate. The decrease of the porosity increases the difficulty of the mass transfer leading to a lack of corrosion reactants (such as the localized depletion of OH^-) and an accumulation of products on the aluminium surface, which should be one of the reasons for the corrosion rates to descend.

7

Perspectives

Chapter 7. Perspectives

This thesis focused on the corrosion and the cement paste studies of AA1100 embedded in Portland cement pastes and explored a feasible solution for the geological disposal of BR1 fuel. Even if some questions were answered during this thesis, further studies are needed based on the findings of this thesis. Here are some perspectives.

In terms of the corrosion research, the constituents of the protective layer formed by lithium salts should be further characterized. Although a morphology similar to that of LDHs reported in the literature was observed, the real composition of the protective layer is much more complex in the cementitious environment. The ions present in the cement paste pore solution (Ca^{2+} , Mg^{2+} , etc.) in addition to Li^+ possibly lead to the formation of other types of LDHs. Because the synthesis conditions are different for distinct LDHs (see Section 2.6.1), the influence of the complex cementitious condition (e.g. the ion diffusion in the pores, the heat release and the water reduction due to the cement hydration) is difficult to be determined without further research.

Other types of corrosion inhibitors should be tested. For example, similar experiments could be performed on lithium oxalate ($\text{Li}_2\text{C}_2\text{O}_4$), which is reported in the literature [318] to be an effective corrosion inhibitor for aluminium. Moreover, other methods for the preparation of Li-Al LDH films could be studied. Unlike the natural growth of the LDH film in our works, researchers [153-156] reported that LDH films could be artificially prepared on the aluminium substrates. Hence, the thickness and the quality of the LDH films should be controlled to provide a better corrosion protection.

Alternative cement-based materials, e.g., MKPC and MSH as addressed in Section 2.4, having a lower pH pore solution, or mortars and concretes containing a lower amount of pore solution, could be investigated as an alternative of the Portland cement paste used in this work. Both the lower pH environment and the lower water content are beneficial to the corrosion protection of aluminium.

Besides, different cell configurations such as the three-electrode cell and the four-electrode cell can be used for the same EIS measurements to compare the results obtained from different configurations.

Finally, the processes after breaching of the aluminium cladding need to be understood. As mentioned in Section 1.2, the BR1 fuel is composed of several layers. After failure of the protection of the outermost aluminium cladding, the corrosion of the inner components, i.e. the AlSi bonding layer, the $\text{U}(\text{Al},\text{Si})_3$ anti-diffusion layer and the uranium core, would happen in sequence. Meanwhile, galvanic corrosion between different materials is likely to occur. Hence, a systematic research needs to be performed to understand the mechanisms.

For the cement paste porosity study, mechanical tests analysing mechanical properties such as compressive strength should be performed to evaluate whether the cement pastes are qualified for the

Chapter 7

application of geological disposal. More investigations could focus on the methodology used for determining the porosity of cement pastes. Because it is a novel method that combines EIS and GEM, more experiments involving different cement pastes and different electrode materials could be performed to further examine its reliability. For example, similar experiments can be conducted on cement pastes with different water/cement ratio to check whether this methodology is still effective in a broader range of conditions. Also, some parameter values, such as the conductivity of the solid-gel phase (σ_s) used in this method, taken from literature, should be experimentally confirmed. Other cement paste components of the equivalent circuit model such as the capacitance of the solid phase in the cement paste (CPE_{cem1}) can be investigated to check whether it reveals the actual variation of the cement hydration. Moreover, an in-depth analysis whether this novel methodology could be used in other research areas could be considered. Because it is an easy method for determining the porosity of cement pastes, it could be considered either in the lab as a powerful research tool or industrial application for in situ monitoring. For example, one major challenge for the long-term safety of a bridge is the carbonation of the cementitious materials. This methodology shows the possibility of real-time monitoring of the inner porosity variation of cementitious materials, evaluating the influence of the carbonation.

Finally, other technical routes for the disposal of BR1 fuel, such as the removal of the active outer layers, the oxidation of the metal before disposal or the recycling of the fuel can be alternatively explored.

Appendix

Appendix

A.1. The electrochemical cell setup

EIS is a powerful technique for characterizing the electrical behaviour of cement-based materials and interfaces. The choice of the electrochemical cell setup plays an important role in the measurements. Therefore, at the start of this study, the effect of the different setups of the electrochemical cell was investigated.

This doctoral research aims at simultaneously studying the corrosion of AA1100 in OPC pastes and the porosity variation of OPC pastes by EIS. Usually, a cell setup is designed either for studying the corrosion processes or for obtaining valuable information on the cementitious material. First, a literature review involving possible cell setups for the study of cementitious materials was performed. As addressed in Section 2.7, the cell setups for the electrochemical measurements of cementitious materials can be categorized into the direct contact method, the indirect contact method and the non-contact method depending on the type of media present in between the electrode surface and the sample surface. Compared to the indirect contact method and the non-contact method, the direct contact method with a direct contact between the electrodes and the cementitious material provides the simplest setup and thus is the most convenient. Besides, the direct contact provides a cementitious environment for the electrodes and consequently the electrochemical responses of the electrodes in a corrosive cementitious environment are included in the EIS results. Hence, the direct contact is obligatory when the corrosion behaviour of electrodes needs to be studied.

In this study, the direct contact method is adopted, and aluminium plates are used as the electrodes. Therefore, the EIS results include information coming from two different parts of the cell. The first source of the information is the aluminium/corrosion product film/cement paste interface, which can be used for studying the corrosion of AA1100 encapsulated in OPC pastes. The second source is the cement paste providing the information of the cement paste porosity. By the analysis of the result (mainly indicating the EIS fitting using the electrical equivalent circuit), the two kinds of information can be separated and used for two studies, respectively.

Another problem involving the cell setup is the number of electrodes. In terms of the electrochemical cell used for the study of cementitious materials, literature [213,263,319,320] reported three types of configurations i.e. two-electrode configuration, three-electrode configuration and four-electrode configuration as shown in Figure A.1. Theoretically, these electrode configurations should give the same results. However, this does not seem to be always true for the study of cementitious materials. Mason et al. [263] reported that in the EIS study of the cementitious materials, not only the impedance spectra of

Appendix

different electrode configurations can be distinct, but also the 'forward' and 'reverse' four-electrode spectra are completely different from one another. They attributed these phenomena to the introduction of the reference electrode impedance and hence recommended the application of the two-electrode configuration when high frequencies are used for the study of cementitious materials. Xie et al. [319] also found that the impedance spectra from three-electrode or four-electrode measurements are strongly influenced by the contact areas between the specimen and reference electrodes. An example of the different impedance spectra caused by the introduction of the reference electrode in their study is shown in Figure A.2. Ford et al. [320] thought that even if reliable results can be obtained using multi-electrode configuration (three-electrode configuration and four-electrode configuration), the corresponding microstructure models used for studying cement paste should be reconstructed compared with that for the two-electrode measurement. Wang et al. [213] compared two-electrode and four-electrode systems and mentioned that the contact impedance between the electrodes and the cement-based materials needs to be known or evaluated in a four-electrode measurement. Hsieh et al. [321] studied the effects of the reference electrode in three-electrode EIS measurements and indicated that the application of the reference electrode probably leads to distortions, especially in systems with low conductivity electrolytes. These studies explained the popularity of the two-electrode configuration for EIS measurements of cementitious materials. In this doctoral study, the introduction of the reference electrodes also interferes with the current flow in the circuit and consequently affects the cell constant K (see Section 3.5.5) used for determining the cement paste porosity. Moreover, the absolute potential provided by the reference electrodes is not obligatory in this corrosion study. As shown in Chapter 4, neither the calculation of the corrosion rate nor the analysis of the corrosion product film involves the potential data. By contrast, the introduction of the reference electrodes increases the complexity of the measurements. Therefore, the two-electrode configuration was adopted in this study.

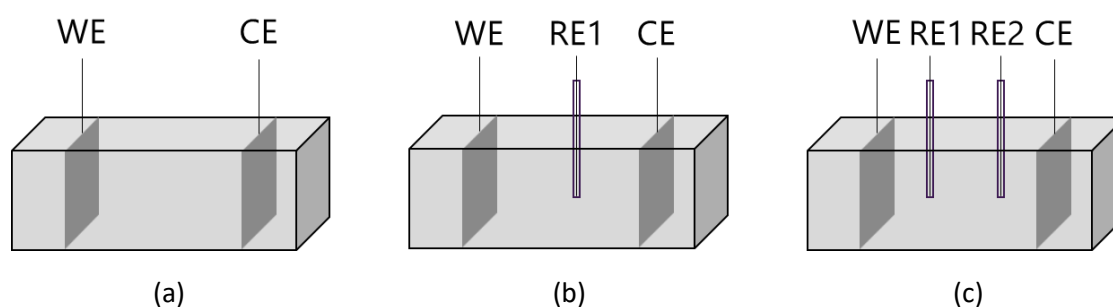


Figure A.1 Schematic of (a) two-electrode, (b) three-electrode, and (c) four-electrode cell configurations (WE is the working electrode, CE is the counter electrode, RE1 and RE2 are the reference electrodes).

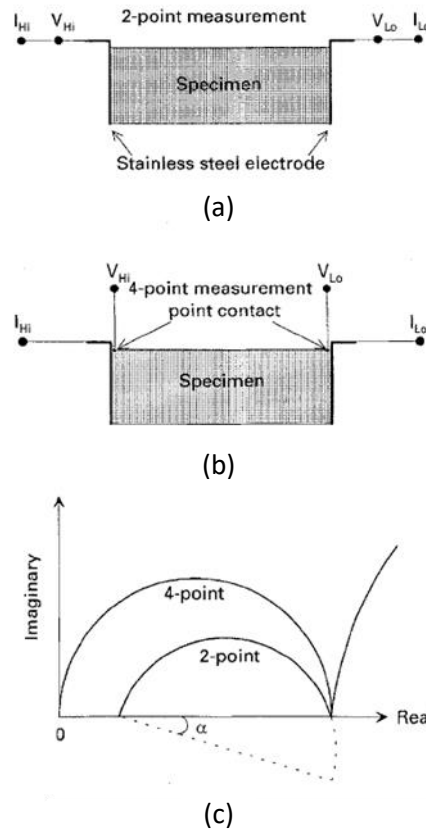


Figure A.2 Schematic of (a) two-electrode and (b) four-electrode cell configurations and (c) the corresponding impedance spectra in the literature [319].

Another question involving the setup is about the application of two identical aluminium electrodes. First, the configuration using two identical electrodes as the working electrode and the counter electrode is widely reported in many papers [213,214,217,319,320,322] in the study of cementitious materials, because such a symmetrical configuration benefits when analysing the EIS results. For example, Wang et al. [213] assumed that the impedances of two identical steel electrodes are the same and consequently can be simply merged into one bigger impedance as twice as the one of each electrode, when counting the electrical contribution of the electrodes. In their two-electrode cell configuration (see Figure A.3), the measured impedance (Z_{t2}) can be expressed as:

$$Z_{t2} = Z_m + Z_{2c}, \quad (24)$$

where Z_m is the impedance of the sample and Z_{2c} is the sum of the contact impedances between the electrodes and the sample. If the two electrodes are different (size, material, shape, etc.), the electrical contributions of the electrodes are different and cannot be easily merged. Hence, the setup of two identical electrodes prevails in the EIS study of cementitious materials.

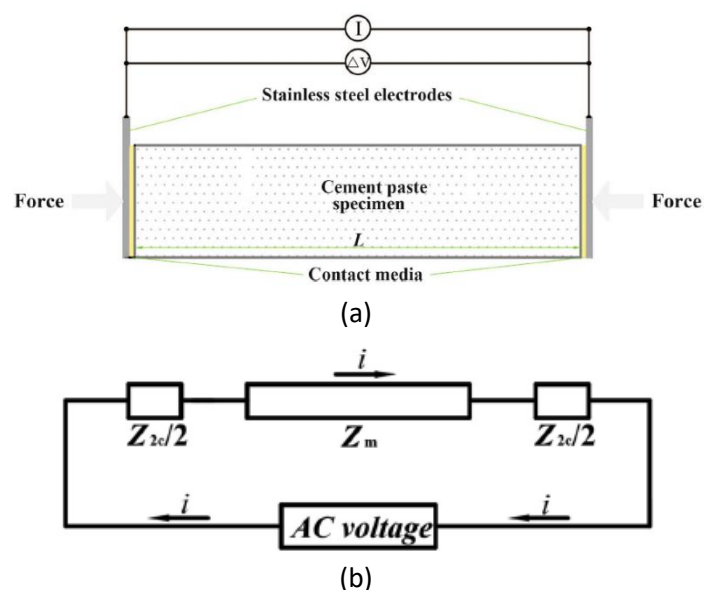


Figure A.3 Schematic of the two-electrode cell configuration and the corresponding equivalent circuit [213].

However, inert materials such as graphite, stainless steel, etc. are usually used as electrodes for studying cementitious materials [212]. Compared with these materials, the biggest problem with aluminium is that the surface state of the aluminium electrodes changes relatively faster because of the high corrosion rate.

A literature review on this problem was performed. Many papers [323-329] involving corrosion studies reported that electrochemical noise analysis measurements usually adopt a symmetrical cell setup (see Figure A.4 [323]), in which a pair of identical corroding electrodes is used and both electrodes are regarded as the working electrodes. Consequently, the electrochemical responses are actually the sum of the responses coming from both electrodes. For example, a symmetrical cell has been used for the electrochemical noise study on mild steel corrosion in 1 M HCl solution [325].

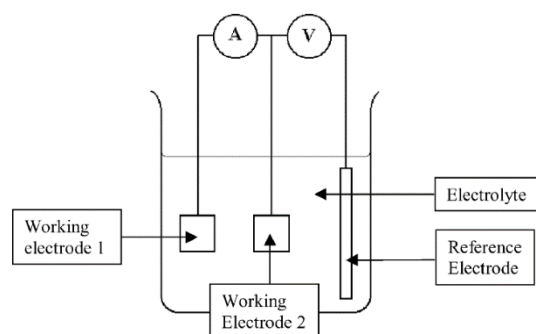


Figure A.4 Schematic of electrochemical noise analysis setup of two identical corroding electrodes [323].

Appendix

A symmetrical cell setup is also used in other types of electrochemical measurements such as polarization measurements and EIS measurements. Danielson [330] and Bandy [331] studied the application of a pair of identical corroding electrodes for polarization measurements. Nagiub and Mansfeld [332] studied microbiologically influenced corrosion of AA2024, mild steel and brass in artificial seawater solution by EIS measurements using a symmetrical cell. Wu et al. [333] used two identical electrodes to study the corrosion of carbon steel in 3.5% NaCl solution by EIS measurements and compared the results with the ones obtained from other setups. Curioni et al. [334] evaluated the corrosion behaviour of magnesium in 3.5% NaCl solutions using EIS measurements. They reported that the values of the resistances estimated from EIS results have a good correlation with the corrosion currents calculated from the hydrogen production. Besides, the corrosion currents in their study are usually up to several $\text{mA}\cdot\text{cm}^{-2}$, which are hundreds/thousands of times larger than the ones in our research, proving the feasibility of using active electrodes in a symmetrical cell setup.

In terms of the corrosion of AA1100 in this doctoral study, if the change of the surface state is too fast, it leads to the failure of the EIS measurements, because the system being measured must be at a steady state throughout the time required to measure the EIS spectrum. The occurrence of this kind of failure only depends on the nature of AA1100 in the cementitious materials, instead of the cell setup. In other words, if the fast corrosion process of aluminium results in the failure of EIS measurements, it just represents that EIS is not suitable for the study of aluminium encapsulated in the cement pastes, changes on the cell configuration e.g. changing the counter electrode material or using a three-electrode configuration do not help. In order to know whether our system is steady during EIS measurements, the EIS data was first examined experimentally by running the measurement first in the descending frequency step direction, followed by the measurement in the ascending direction, i.e. from low to high. Besides, K-K transforms of the EIS data was performed after the measurement. Both results proved that the system is at a steady state during the EIS measurements (Section 4.3). Moreover, the application of EIS for the study of aluminium alloys in the cementitious materials has already been reported in literature [126,335,336], in which the EIS measurements did not fail because of the change of the steady state during the measurements.

Another concern is that the two identical aluminium electrodes gradually become different because of significantly different corrosion behaviour. If this case occurs, the two electrodes have very different electrochemical responses and the execution of simply merging their electrical contributions when constructing the equivalent circuit (see the explanation for Figure A.3) will have high errors. The surface state revealed by the equivalent circuit is the “averaged” value of two electrodes and is different from the real surface state on each electrode. However, because the preparation method of both electrodes is identical and both electrodes are exposed to the same experimental conditions, a similar surface state of the two electrodes can be expected.

Appendix

The two working electrodes (the exposed area of each electrode is about 2.26 cm^2 in this study) are mathematically equal to a big working electrode (the exposed area is 4.52 cm^2), which is twice larger than each electrode. This can be attributed to the fact that the response of the two working electrode configuration is the sum of the responses coming from two electrodes (such as C and D as shown in Figure A.5(b)), while the response of the one working electrode configuration can be regarded as the sum of the responses coming from different parts of the electrode (A and B as shown in Figure A.5(a)). Consequently, the difference between the two electrodes could be mathematically regarded as the difference between two parts of the big virtual electrode when considering the electrochemical responses. If the two parts of the big electrode (A and B) can be assumed to have the same surface state (severe corrosion occurring at preferential sites does not exist), it should also apply to two individual electrodes (C and D). This can be intuitively understood as follows: for the same alloy in the same corrosive condition, the surface states should always be comparable regardless of whether the corrosion rate is high or low, except severe corrosion occurs at preferential sites because of the inhomogeneity of the alloy or the corrosive condition. If the differences between the two electrodes are indeed too big to perform the measurements because of severe corrosion occurring at preferential sites, it just represents that no reproducible results can be obtained for this kind of sample regardless of the experimental setup, because even if just one big working electrode is used, the measurements can fail since the severe corrosion occurring at preferential sites leads to differences between different parts of the same electrode.

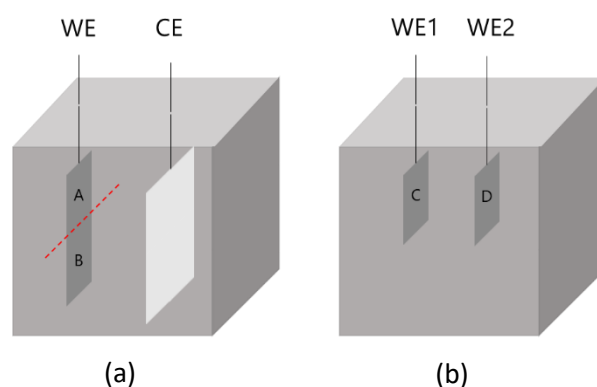


Figure A.5 Schematic of one big electrode (a) and two electrodes (b) in cement paste (A, B, C and D have the same area).

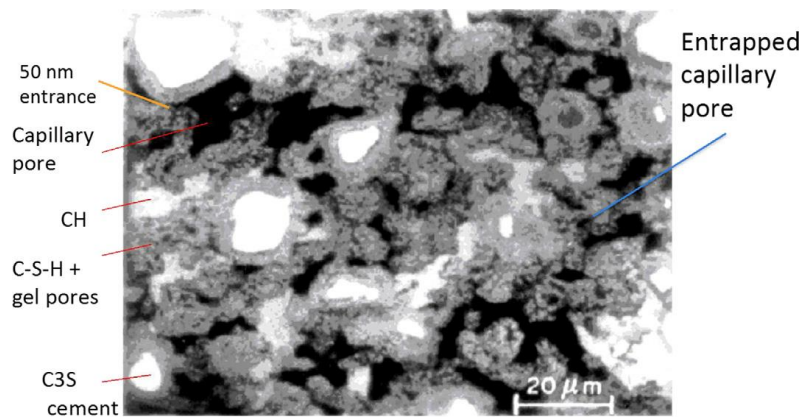
In practice, the difference between the two electrodes can be experimentally examined by the measurements of the open circuit potential. Danielson [330] mentioned that when there is no difference in corrosion potential, the two-electrode method works as well as the three-electrode method and provides a corrosion rate of an error as low as a few %. In this doctoral study, the open circuit potential of such a cell is usually close to 0 (see Figure 4.37), which represents that the two electrodes possess close

electrochemical potentials (Note that two perfectly identical electrodes are a theoretical ideal that can never be achieved in practice). The only exception is the pure OPC samples in condition 2, in which severe cracks result in the differences of the two electrodes and hence give distinct open circuit potentials as shown in Figure 4.37(b). However, the occurrence of the cracks also belongs to the nature of AA1100 encapsulated in the cement pastes, which cannot be simply avoided or influenced by the design of the cell setup.

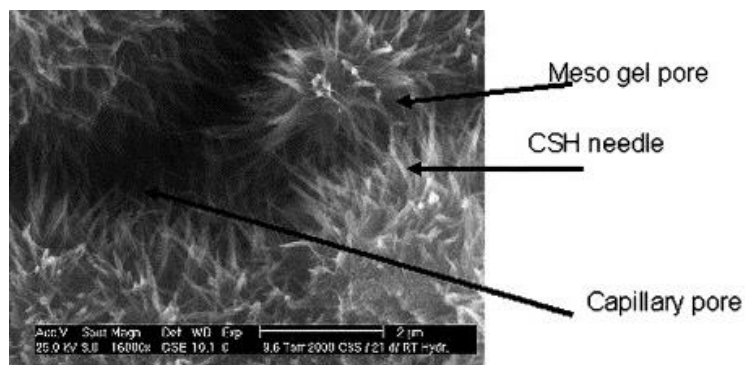
Therefore, it is assumed that the two AA1100 electrodes in the two-electrode configuration are identical and at a steady state during the time of the EIS measurement, the same as the two-electrode configuration using other electrode materials. The only difference is that in this study, not only the electrochemical responses coming from the cementitious matrix were studied, but also the information coming from the interface between the electrode and the cementitious matrix (i.e. Al/corrosion product film/cement paste interface) was analysed instead of being regarded as an interference of the cement study. In conclusion, the two-electrode configuration using two identical aluminium electrodes does not seem to be problematic for the EIS measurements.

A.2. Preselection of the model for cement paste

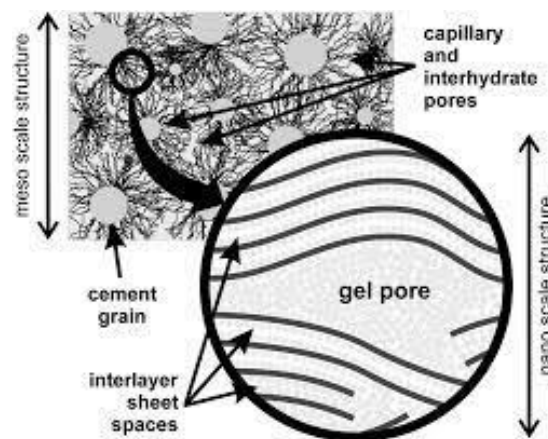
The equivalent circuit model for the cement paste has been preselected. First, because the equivalent circuit model must have physical meanings, the physical structure of the Portland cement paste is first reviewed (see Section 2.4 and 2.7). The main constituent of the hydrated Portland cement paste is C-S-H (Calcium-silicate-hydrate). Other minor constituents include the hydration products, i.e. $\text{Ca}(\text{OH})_2$, ettringite, aluminoferrite monosulphate, hydrogarnet and unhydrated cement particles. Moreover, the hydrated cement paste contains a large number of pores, which are normally categorized as the capillary pores between C-S-H globules and the gel pores inside the C-S-H gel (the gel pores will be discussed later). The microstructure of the cement paste is illustrated in Figure A.6 [337-339].



(a)



(b)



(c)

Figure A.6 BSE image of the Portland cement paste sample milled by FIB [337] (a), the hydrated cement particle after 21 days curing time, C-S-H needles with diameter approx. 5 nm [338] (b) and the schematic structure of the calcium-silicate-hydrate (C-S-H) paste on the meso- and nano-scale (white cement paste) [339] (c).

If only the capillary pores are considered and the gel pores are regarded as part of the solid phase (mainly C-S-H), the microstructure of the cement paste can be simplified as shown in Figure A.7. The similar simplification of the microstructure is reported in literature [265, 340].

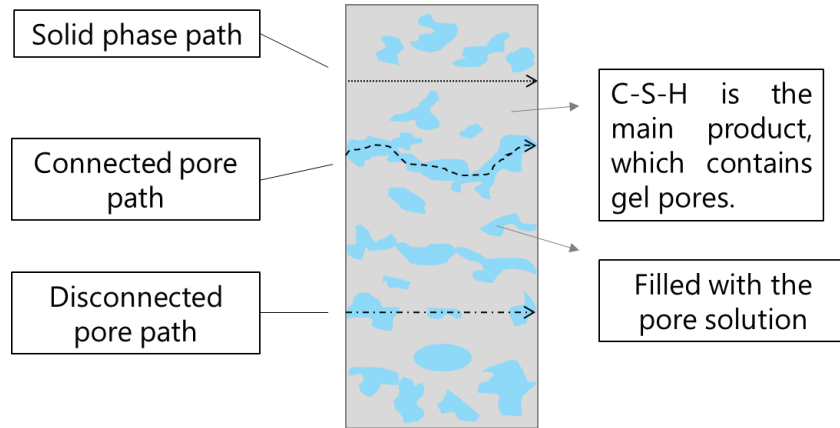


Figure A.7 Schematic illustration of pore network in the cementitious system.

Then, according to the cement paste microstructure, various equivalent circuit models are reported as Hu et al. classified in the literature [270]. On this basis, a series of models were preliminarily tested. The models as shown in Figure A.8 were first excluded because of bad fitting results and some others were directly rejected due to lack of physical meanings.

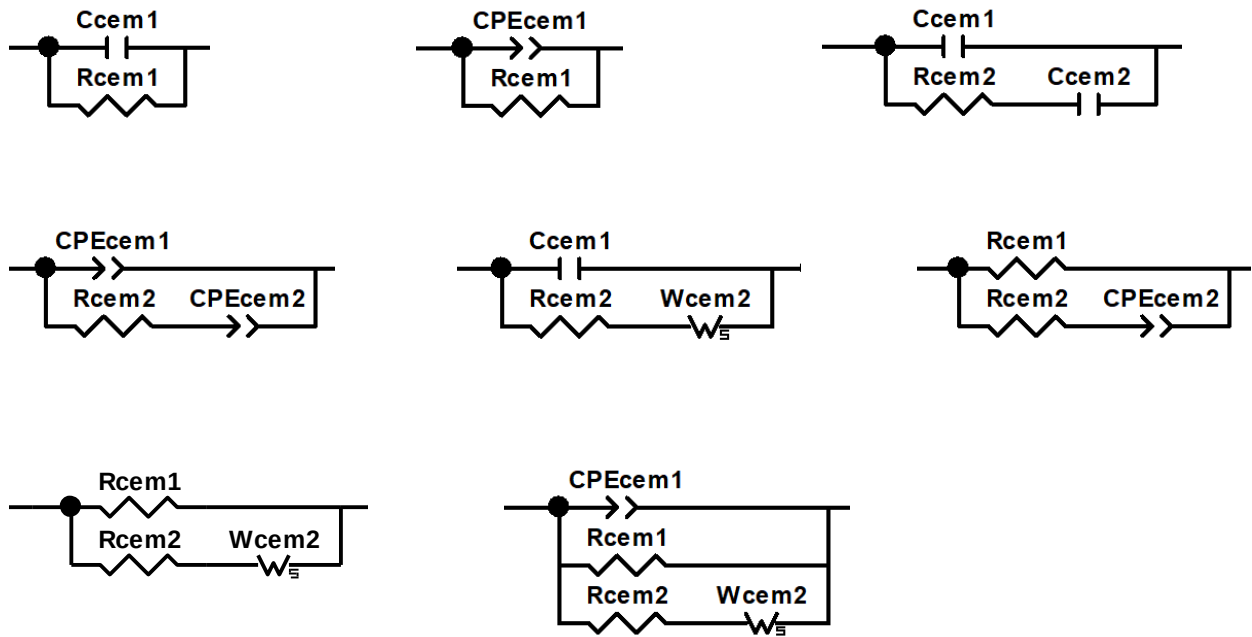


Figure A.8 Excluded models because of bad fitting.

A.3. The comparison of W_{cem2} and CPE_{cem2}

As discussed in the Section 4.5.2, two possible elements (CPE_{cem2} and W_{cem2}) were considered for describing the electrochemical responses of the solid phase between disconnected pores. The model in Figure 4.22(b) used the CPE_{cem2} element to describe the electrochemical responses of the solid phase between disconnected pores, while the model in Figure 4.22(c) used W_{cem2} . If a CPE element is selected, the solid phase between disconnected pores is regarded to be non-conductive and to behave closer to a capacitor with surface toughness. However, a W element was used in this doctoral study, in which the solid phase between disconnected pores contributes an electrical conductivity by the ions' diffusion. The reason of the application of a W element is discussed in this section.

(i) The ion diffusion in the gel pores of C-S-H.

The primary key to make the selection is to understand whether the solid phase involves the ion diffusion (if not, the use of Warburg element is not appropriate). Many papers reported ionic diffusion in the solid phase of the cement pastes. The gel pores of C-S-H (the main constituent of the solid phase) are filled with the solution containing hydroxyl ions, calcium ions, etc. Nagao et al. [277] measured experimentally (both by DC and AC methods) the conductivity of C-S-H, which ranges from 10^{-4} to 10^{-3} S/cm in humidified air at temperatures between 60 and 100 °C (Figure A.9). They indicated that the hydroxide ion is the major charge carrier in C-S-H. Patel et al. [278] reported that the inter-layer of C-S-H does not contribute to the diffusion in C-S-H, while all gel pores contribute to the ion diffusivity in terms of electric resistivity measurements. Yogarajah et al. [279] studied the influence of the gel porosity and of the tortuosity on the ion diffusion in C-S-H. Hence, the ion diffusion in the solid phase of the cementitious materials is a fact and accounts for the conductivity of the solid phase.

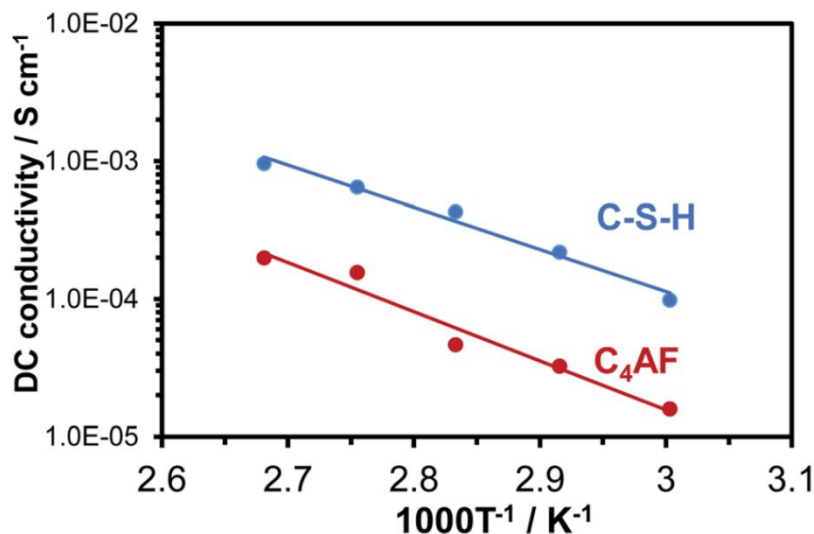


Figure A.9 Temperature dependence of DC conductivity for C-S-H and C₄AF [277].

Appendix

(ii) The microstructure of the gel pores providing the Warburg element with a reflective boundary.

Second, W_{cem2} used here is the Warburg element with a reflective boundary i.e. W_o (the Warburg element with a transmissive boundary does not provide good fitting, e.g. leading to an error more than 100%), which is typically associated with diffusion where one of the boundaries is blocking, such as in a porous electrode. W_o is more complex than the conventional Warburg element ($Z = \sigma \cdot \sqrt{\omega} \cdot (1 - j)$) and can be written as:

$$Z = \frac{W_o - R \cdot \coth((j \cdot W_o - T \cdot \omega)^{W_o - P})}{(j \cdot W_o - T \cdot \omega)^{W_o - P}}, \quad (25)$$

where $W_o - R$ is related to the resistance, $W_o - T = \frac{L^2}{D}$ (L is the effective diffusion thickness and D is the effective diffusion coefficient of the particle), $W_o - P$ ranges from 0 to 1. A typical impedance spectrum of a Warburg element with a reflective boundary is provided in Figure A.10(a). Cooper et al. [280] simulated the impedance spectra of diffusion in porous microstructure and reported the results as shown in Figure A.10(b) for the closed-end systems. Figure A.10(a) and (b) clearly show that the application of a Warburg element with a reflective boundary for the diffusion in closed-end pores is appropriate. Indeed, the physical microstructure of C-S-H has a corresponding geometry i.e. closed-end pores. For example, in the hydration of the cement grain, the C-S-H phase is first formed on the outer surface of the cement grain while the inner part of the cement grain remains unhydrated as shown in Figure A.10 (c) [281,282]. On one hand, the gel pores (the inter-C-S-H pores in Figure A.10(c)) on the surface are in contact with the capillary pores; on the other hand, the gel pores are closed by the unhydrated cement grain or by the C-S-H needles. Hence, the microstructure of C-S-H can be correlated with W_o .

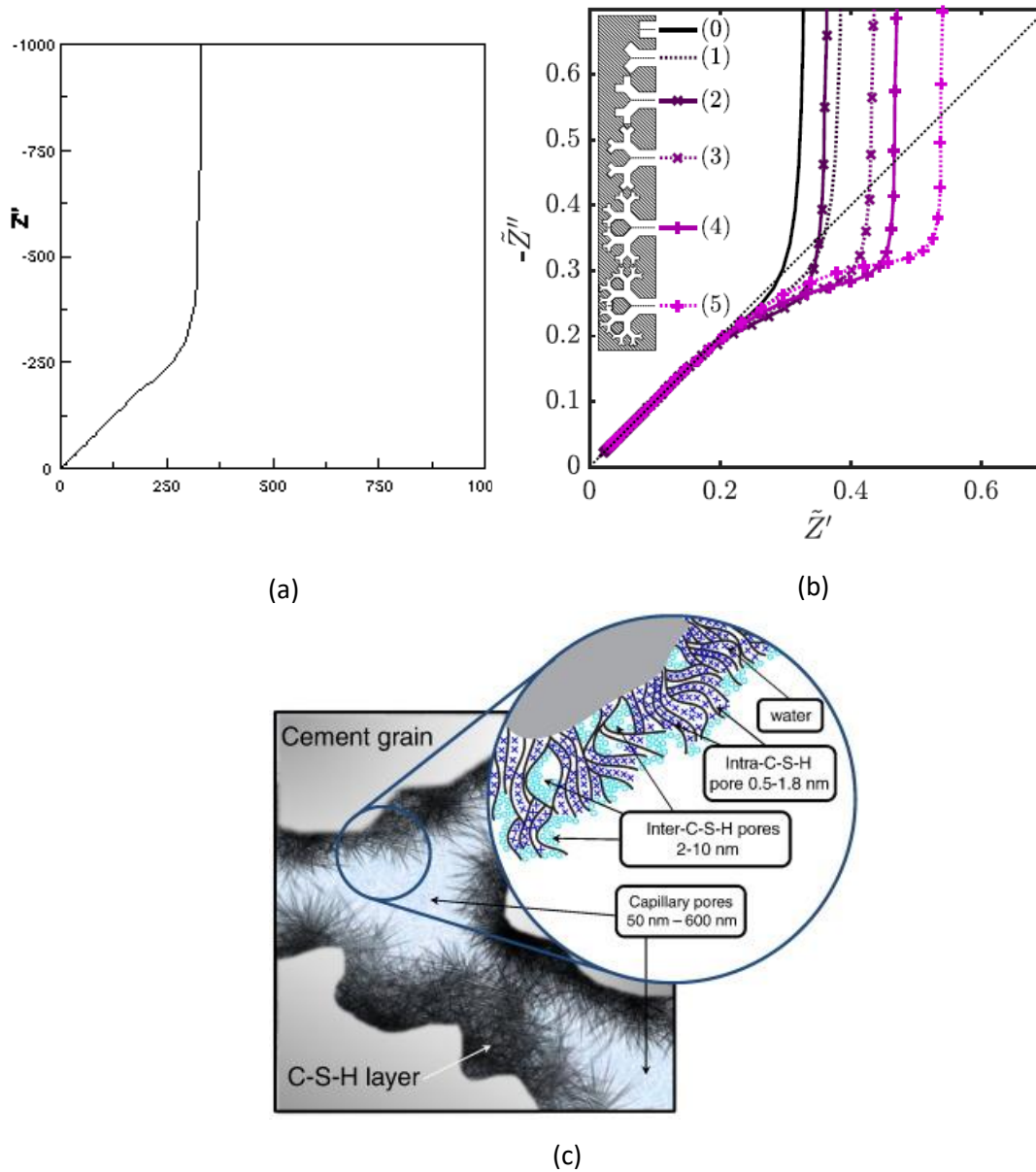


Figure A.10 Typical impedance spectrum of a Warburg element with a reflective boundary i.e. W_o (a), simulated impedance spectra of porous microstructures with closed ends [280] (b) and the porous microstructure of C-S-H on the surface of the cement grains [281,282] (c).

(iii) How to understand the use of a Warburg element from the point of view of the current flow?

The presence of the Warburg element can also be understood from the point of view of the current flow. The electrical current should be the same everywhere in a circuit. For the current to flow in the capillary pores, there must be enough ions as charge carriers. The solution space accounting for the ion transport path is constrained along the interface between the capillary pores and the gel pores (see Figure A.11). The gel pores do not contain enough ions as the charge carriers and the current becomes diffusion controlled. A similar phenomenon is commonly reported in different researches on porous

Appendix

materials. For example, Steinhauer et al. [337] reported that the lithium ion diffusion behaviour in micron particles of a lithium-ion battery can be represented by a Warburg element as shown in Figure A.12.

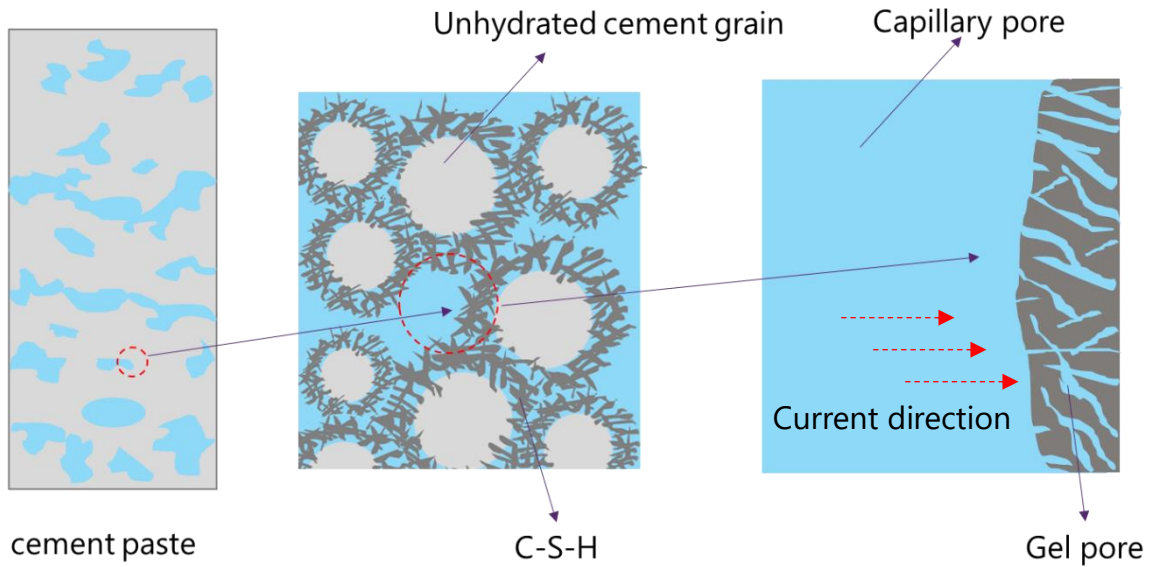


Figure A.11 Current flow on the capillary/gel interface.

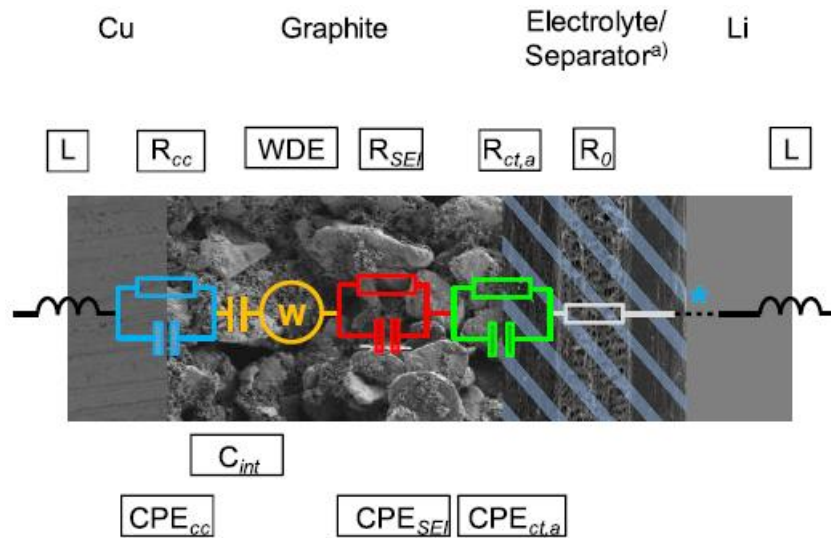


Figure A.12 Equivalent circuit model used for a lithium-ion battery [337].

(iv) Literature reported some cases of the application of the Warburg element in comparable systems.

Finally, the same selection has been reported in the literature by Marriaga et al. [283]. They first used the equivalent circuit model (see Figure A.13(a)), which is the same as the model shown in Figure 4.22(b), for the EIS fitting of OPC mortars. The n value (a in their paper) of the CPE in the non-conductive paths is close to 0.5 (Figure A.13(b)). Correspondingly, they proposed to replace the CPE element with the Warburg element defining the diffusion behaviour of the non-conductive paths. The only difference between Marriaga et al. and the present work in terms of the Warburg element is that they justify the use of the

Appendix

Warburg element from the mass transport in the Interfacial Transition Zone (ITZ) (the surface of the aggregate), while in this work, it is assumed that it is derived from the ion diffusion in the gel pores of C-S-H (the surface of the cement grain). Like the gel pore structure in C-S-H, the ITZ has also a porous structure as shown in Figure A.14 [284-285].

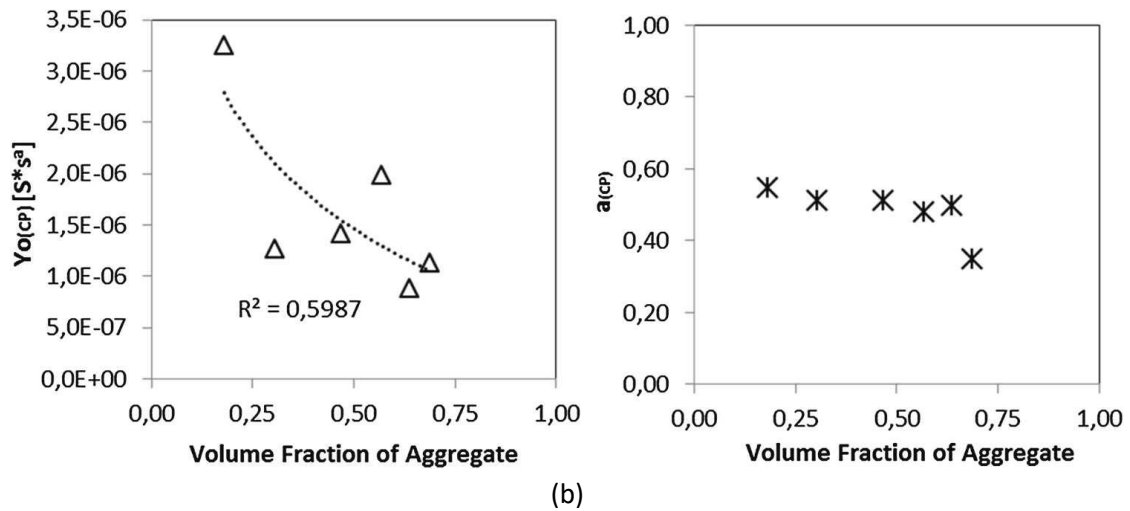
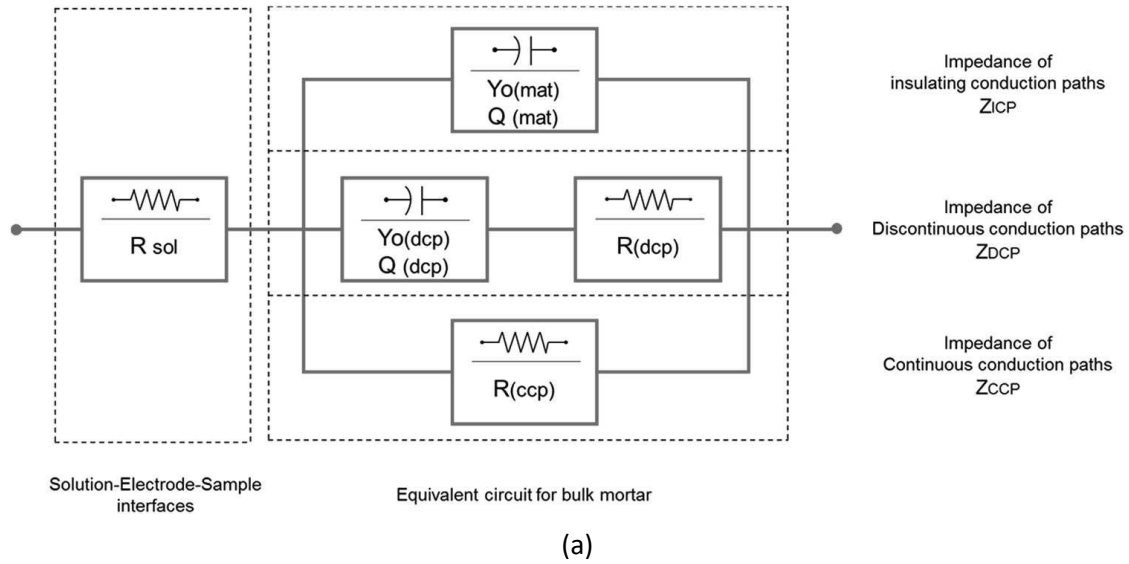
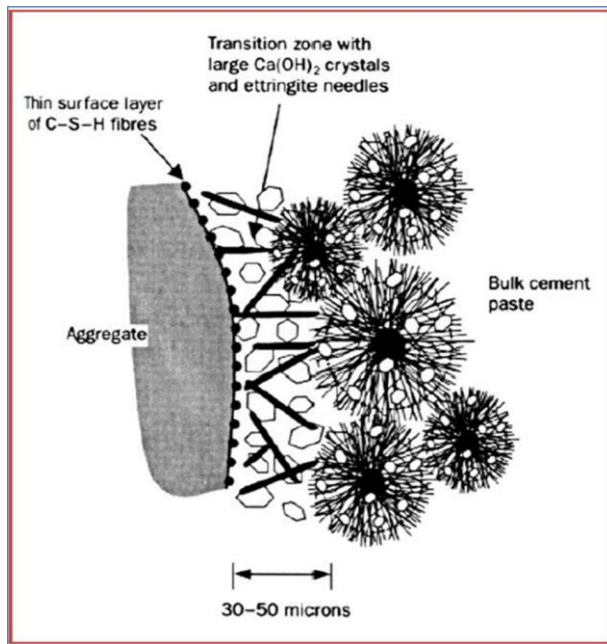
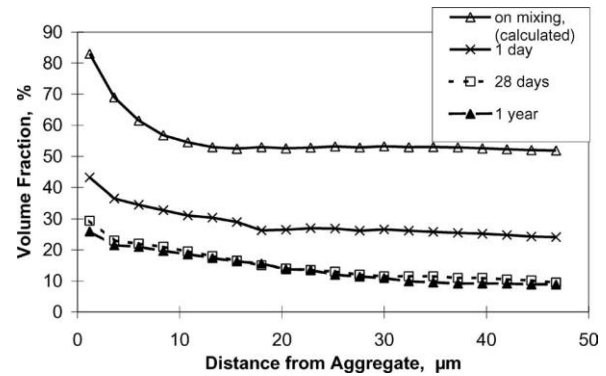


Figure A.13 Equivalent circuit model used for the fitting of the mortars reported by Marriaga et al. and the corresponding electrical behaviour of non-conductive pore capacitance [283].



(a)



(b)

Figure A.14 Schematic diagram of ITZ (a) [284] and average porosity in ITZ at various age (b) [285].

The application of a Warburg element in the equivalent circuit to describe the ionic conductor can be found in other studies. Huang et al. [342] reported that when the n value of the CPE defining the capacitance of a porous geopolymer is close to 0.5, the CPE should be replaced with a Warburg element describing the diffusion process (note that Huang et al. used geopolymer instead of OPC-based materials and their equivalent circuit model is different from ours). Jamnik et al. [343] reported that when the ionic conductor is mixed with an electron conductor, the Warburg diffusion of ions in the ionic conductor corresponding to R_{ion} needs to be considered in the equivalent circuit (see Figure A.15). Boadu et al. [344] and Rocha et al. [345] proposed an equivalent circuit for soils, in which a Warburg impedance element of the form $A(i\omega)^{-c}$ is used to describe the ion diffusion in the blocked pore fluid. This Warburg element is related to the nature of the rough surfaces described by the interfaces between the pore fluid and the clay particles (Figure A.16).

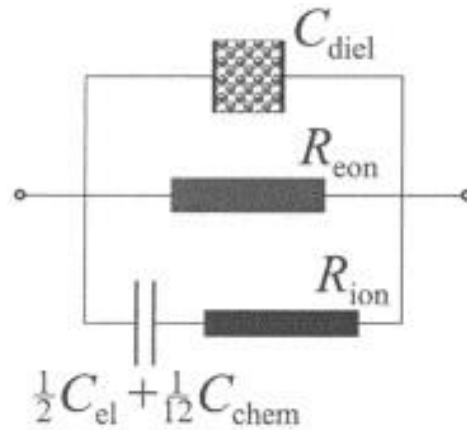


Figure A.15 Simplification of the equivalent circuit of a mixed conductor which applies for low frequencies [343].

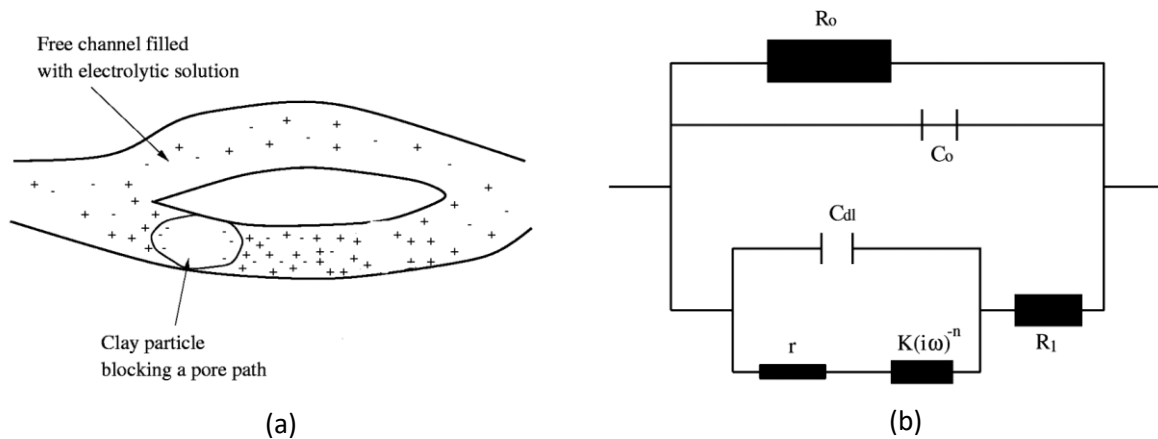


Figure A.16 Schematic of the electrical conduction in soils (a) and the corresponding equivalent circuit of soils (b) [344].

The application of a Warburg element in the disconnected pore path brings some questions:

(i) First, if the solid phase between the disconnected pores behaves as a Warburg element, how about the solid phase in the solid phase path? Adding a Warburg element in the solid phase path did not work. The diffusion occurring in C-S-H is assumed to have a reflective boundary, i.e. closed ends, which means that the diffusion process in the gel pores of C-S-H may be considerable between the capillary pores but is difficult to account for the charge transport over large distances (the Warburg element with a reflective boundary behaves like a capacitor at low frequencies and has a very large impedance). This matches the fact that each cement grain (either hydrated or unhydrated) is regarded to be relatively independent. Moreover, if a Warburg element is added to describe the diffusion in the solid phase path, the equivalent circuit would be as shown in Figure A.17. However, because the ion transport in the connected capillary pores is much easier than that in the half-closed gel pores. It implies that the R_{cem1} is expected to be much lower than W_{cem1} over the whole frequency region. Hence, the W_{cem1} would be short-circuited by R_{cem1} (A

similar explanation is given by Song [265]) and hence the addition of W_{cem1} is meaningless. Please note that even if ignoring of W_{cem1} is thought to be acceptable in most cases, it is still likely to negatively affect the fitting i.e. bringing more uncertainties on other elements such as CPE_{cem1} .

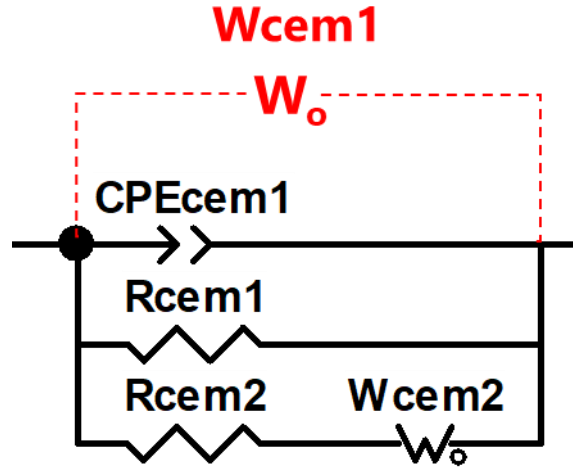


Figure A.17 Equivalent circuit with a Warburg element describing the diffusion in the solid phase path.

(ii) If a CPE with the n value close to 1 fits well, could we still use W_o to describe the electrochemical responses of the solid phase (C-S-H)? For a Warburg element with a reflective boundary, its electrochemical responses can be roughly separated into two frequency domains. The typical impedance spectrum is shown in Figure A.18. In the high frequency domain, the phase angle of W_o is fixed at -45° , which corresponds to the diffusion controlled process. In the low frequency domain, the phase angle of W_o is fixed at -90° , indicating that it behaves like a capacitor. The impedance spectra of porous microstructures with closed ends (Figure A.10) are expected to have such electrochemical responses. In terms of the gel pores in C-S-H, the physical meaning of two frequency domains is that the ion transport in the gel pores follows different rules under different frequencies. In the high frequency region, the ion transport direction alternates fast and the process of ion migration towards one direction is short, then it is a diffusion controlled process because of the geometry constraint. By contrast, in the low frequency region, the long duration associated with ion migration towards one direction, leads to the accumulation of anions/cations on the surface of the closed end in the gel pores, which works like an electrical double layer. Between the two frequency domains, there is a transition zone. In terms of the gel pores of C-S-H, there are many influential factors e.g., the cement hydration, the humidity and the temperature. Even the addition of lithium salts is reported to change the C-S-H structure [286-291]. Therefore, the gel pores of C-S-H can have different pore sizes, pore shapes, ion concentrations, etc., corresponding to distinct ion diffusion behaviours. Considering the replacement of W_o with a CPE , if the diffusion controlled process of W_o with a phase angle at -45° (the high frequency part) is predominant in the measured frequency range,

Appendix

the n value of a CPE is 0.5; if the capacitor behaviour of W_o with a phase angle at -90° (the low frequency part) is predominant in the measured frequency range, the n value of a CPE is 1. However, when both domains cannot be neglected in fitting the electrochemical responses of C-S-H, the replacement of W_o with a CPE leads to the failure of good fitting in the entire frequency range. By contrast, W_o always works regardless of the variation of C-S-H. Even if the electrochemical responses of C-S-H show a capacitor behaviour, W_o can fit appropriately by behaving like a CPE with an n value higher than 0.5 (this also explains why sometimes the n value of W_o in the fitting is higher than 0.5). An example is provided in Figure A.19. Note that the small deviation from a standard CPE in the low frequency region can be avoided by adjusting the values of W_o .

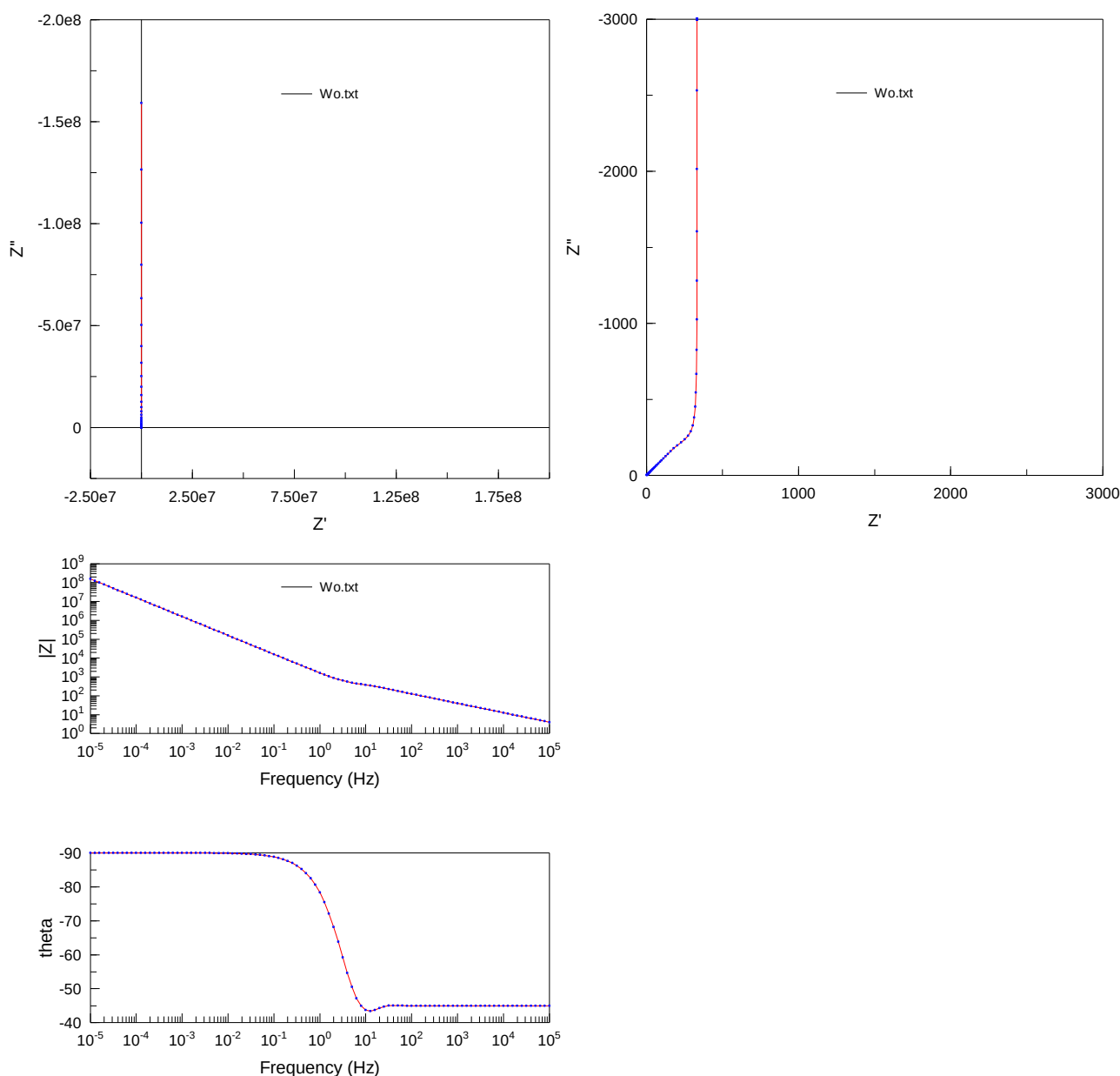


Figure A.18 Typical impedance spectra of a Warburg element with a reflective boundary produced with: $W_o-R = 1000$; $W_o-T = 0.1$; $W_o-P = 0.5$.

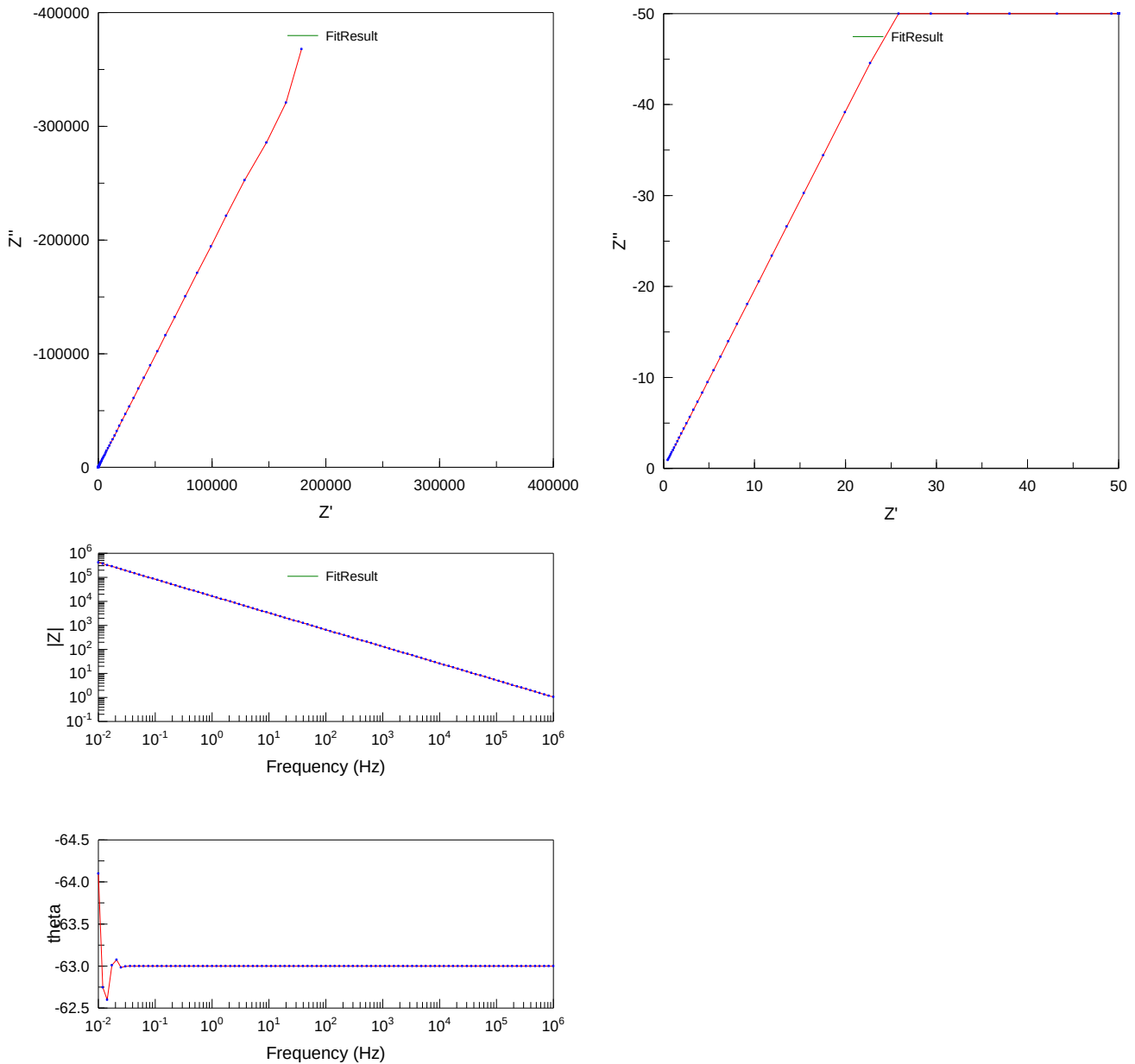


Figure A.19 Impedance spectra of a Warburg element with a reflective boundary produced with: $W_o-R = 2.0 \times 10^6$; $W_o-T = 150$; $W_o-P = 0.7$.

(iii) What is the difference of the fitting results between using a W_o and using a CPE ? The use of the two kinds of elements is compared. For some data, using a W_o or using a CPE for the fitting has little difference (see Figure A.20), especially for the three important parameters, i.e. R_{cem1} , R_f and R_t . For some other samples, the difference might be a bit larger as shown in Figure A.21. Besides, in terms of a few samples, the application of a CPE provides doubtful fitting results, which are intuitively contradictory to the physical variation of the cement paste. For example, the fitting results using a CPE before and after the immersion

of the samples into limewater are provided in Figure A.22 and Figure A.23. Results show that R_{cem1} , which indicates the resistance of connected pores in the cement paste, increases after the immersion of the samples into limewater. However, because more outer solution can enter the connected pores after the limewater immersion, R_{cem1} is expected to decrease (such a decrease is indeed observed in the fitting of the model using a W_o). The same problem also occurs in R_t . After the immersion, the corrosion rate of aluminium should significantly rise, which indicates a plunge of R_t . According to SEM results, the corrosion rate is at least doubled after the immersion (R_t reduces by half at least), which is revealed in the fitting results of the model using a W_o . Nevertheless, this decrease is not obvious in Figure A.23 in the model using a CPE . Compared with the model using a CPE , the model using a W_o better describes the physical variation of the cement paste (see Section 4.7, Section 4.8 and Section 5.6).

Appendix

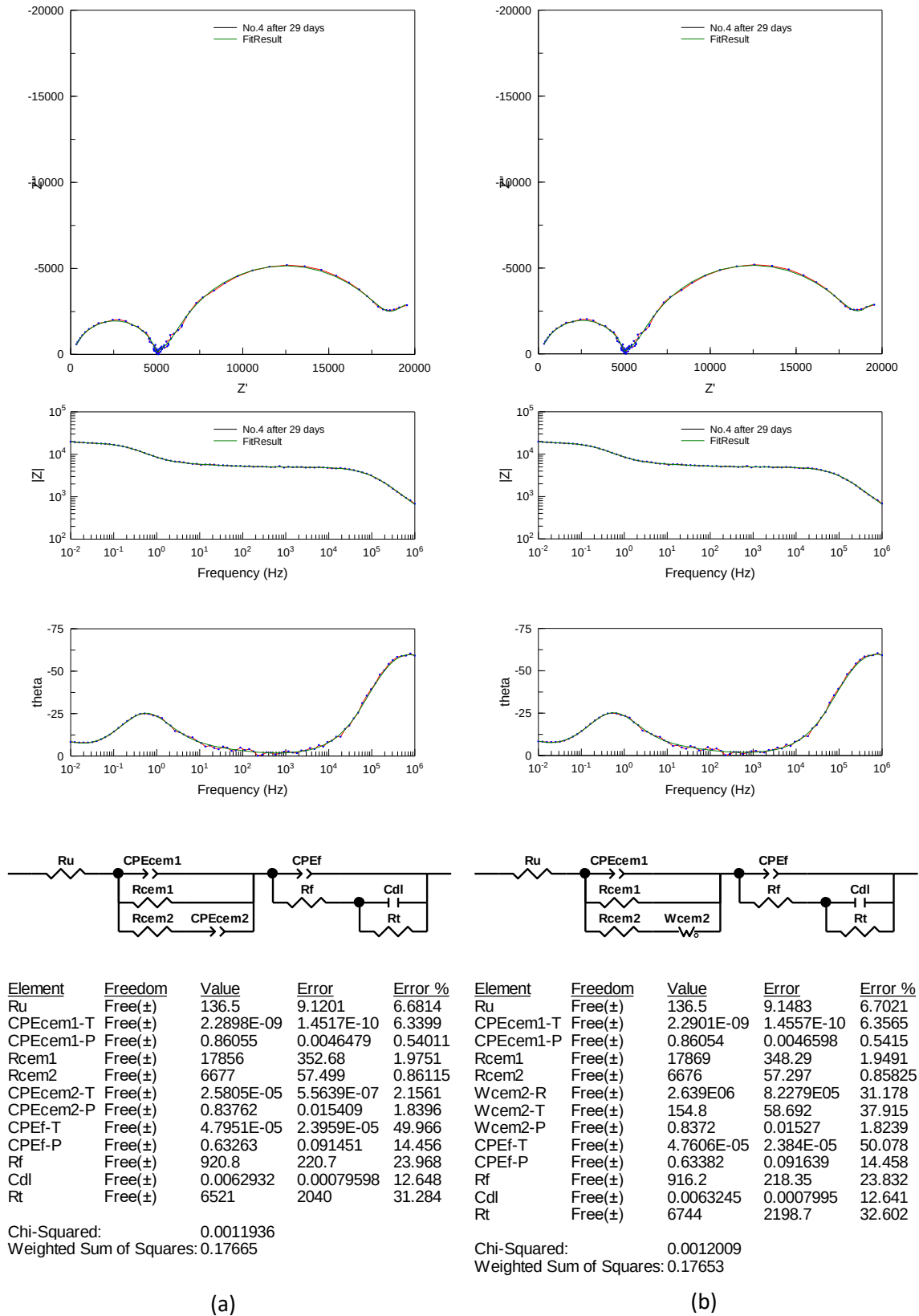


Figure A.20 EIS fitting results using a CPE (a) and using a W_o (b) of an OPC sample after 29 days in condition 1.

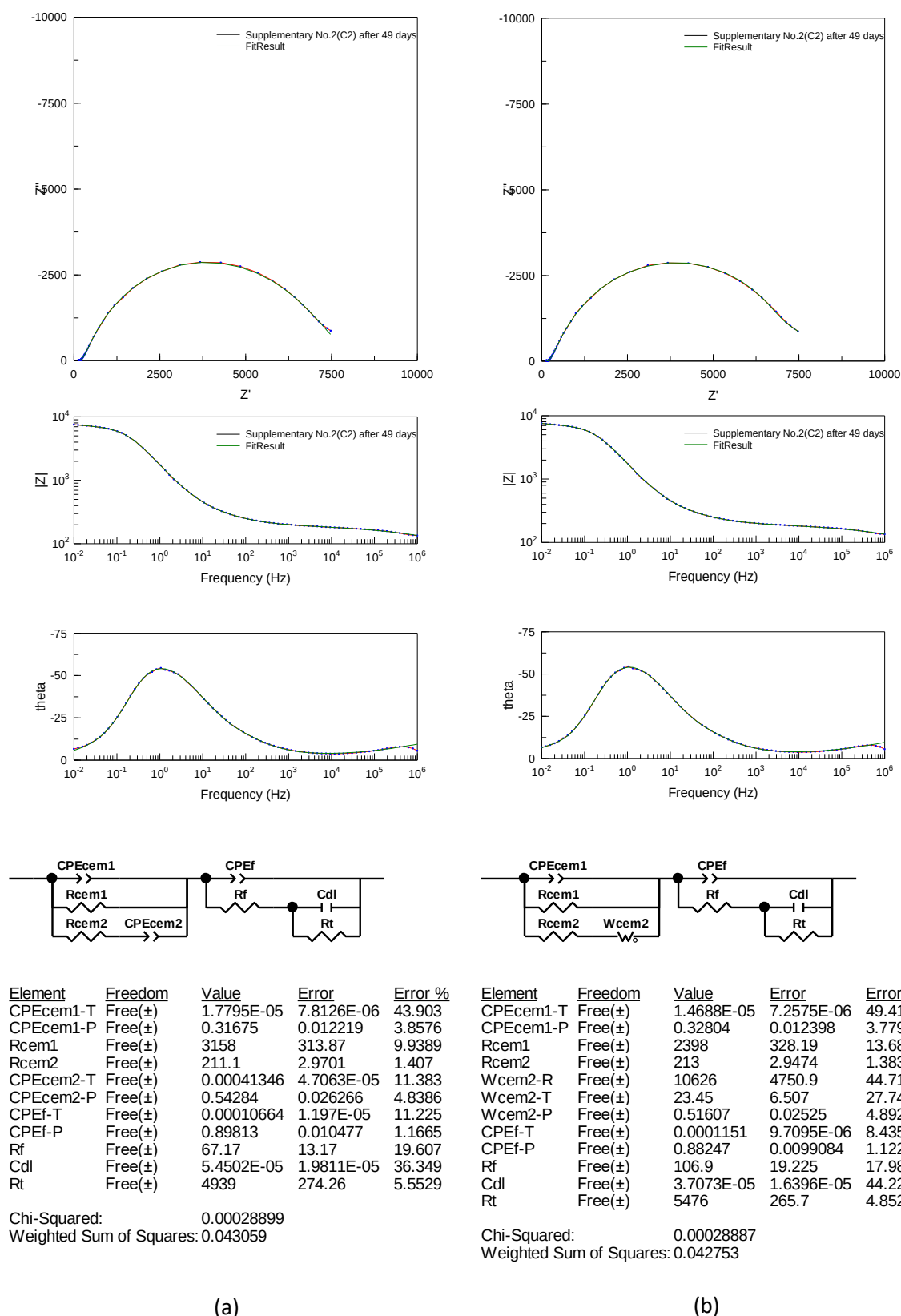
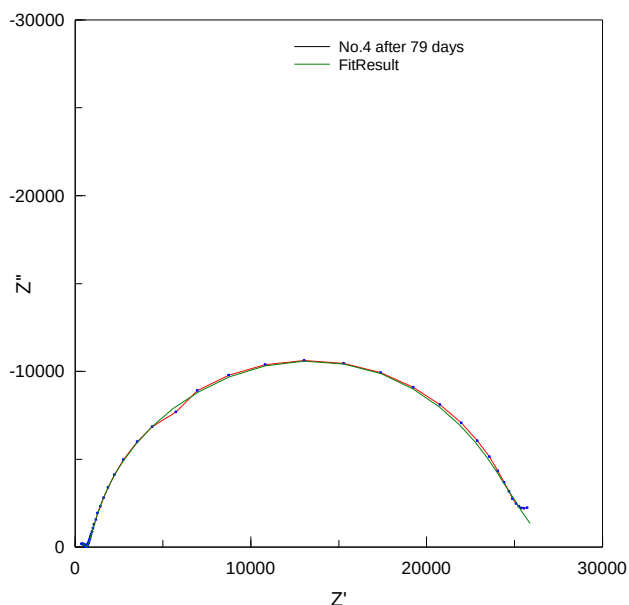
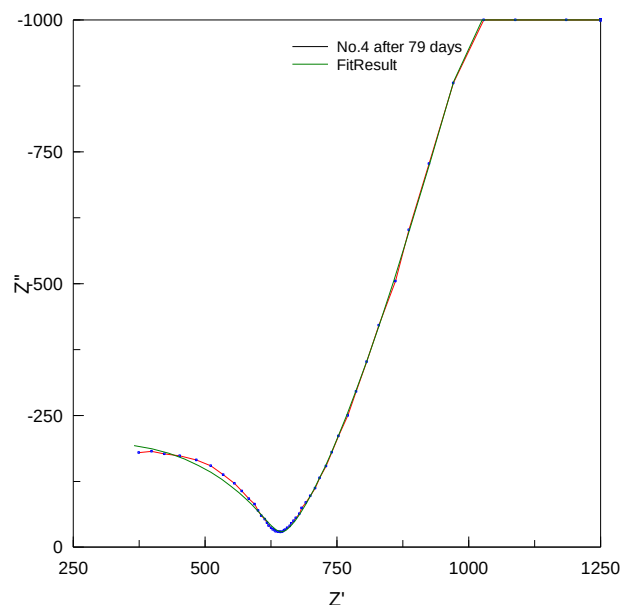


Figure A.21 EIS fitting results using a CPE (a) and using a W_0 (b) of an OPC+Li₂CO₃ sample after 49 days in condition 2.

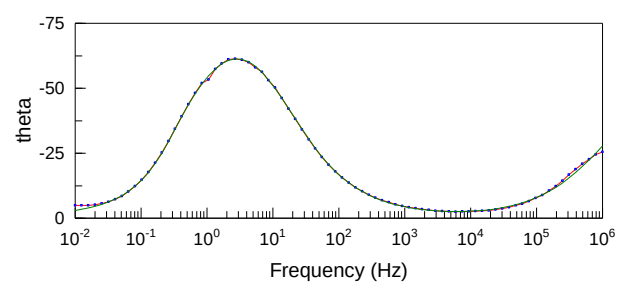
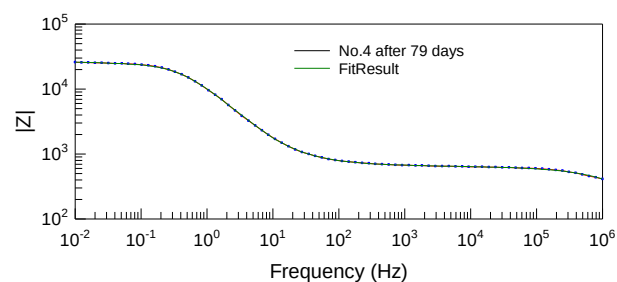
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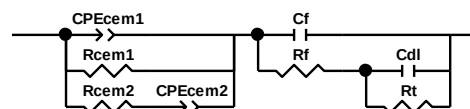
(a)



(b)



(c)



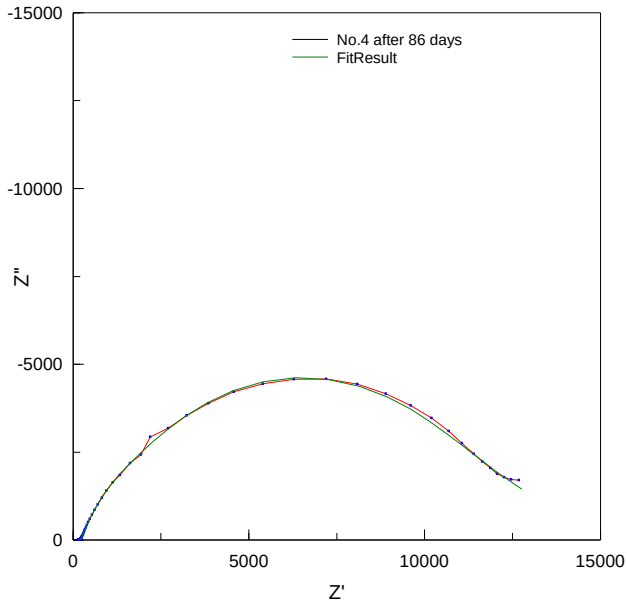
Element	Freedom	Value	Error	Error %
CPEc1-T	Free(±)	2.3315E-08	2.0399E-09	8.7493
CPEc1-P	Free(±)	0.69662	0.0055328	0.79424
Rcem1	Free(±)	7203	274.41	3.8097
Rcem2	Free(±)	703.1	2.823	0.40151
CPEc2-T	Free(±)	0.00014151	9.0578E-06	6.4008
CPEc2-P	Free(±)	0.53947	0.010155	1.8824
Cf	Free(±)	1.6164E-05	2.5838E-07	1.5985
Rf	Free(±)	15321	299.62	1.9556
Cdl	Free(±)	5.7192E-05	7.6054E-06	13.298
Rt	Free(±)	4456	386.49	8.6735

Chi-Squared: 0.0003272
Weighted Sum of Squares: 0.04908

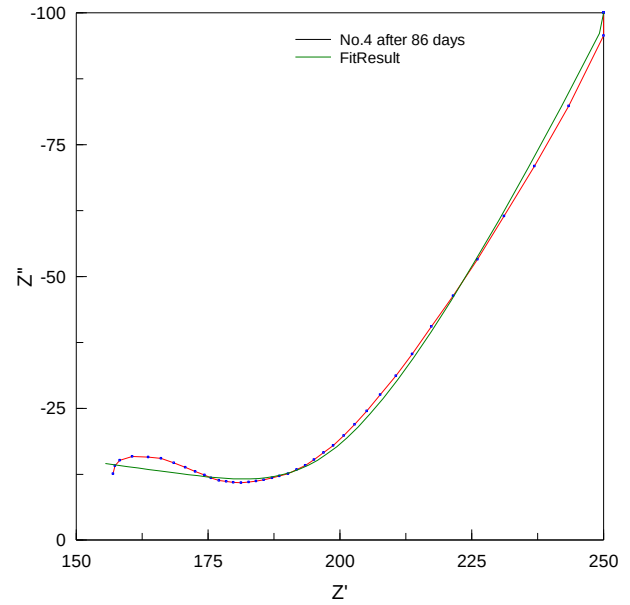
(d)

Figure A.22 EIS fitting results using a CPE (Nyquist (a), (b), Bode (c) plots and the fitting parameters (d)) of an OPC+LiNO₃ sample after 79 days in condition 1.

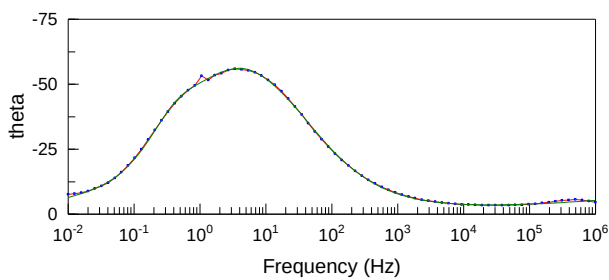
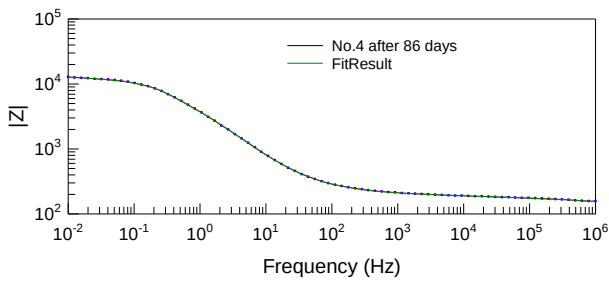
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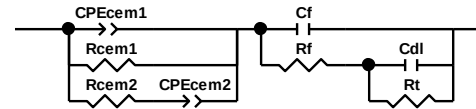
(a)



(b)



(c)



Element	Freedom	Value	Error	Error %
CPEcem1-T	Free(±)	6.818E-05	1.4687E-05	21.542
CPEcem1-P	Free(±)	0.20975	0.010945	5.2181
Rcem1	Free(±)	9011	649.39	7.2066
Rcem2	Free(±)	219.9	2.9217	1.3286
CPEcem2-T	Free(±)	0.00014086	9.1532E-06	6.4981
CPEcem2-P	Free(±)	0.62459	0.0090611	1.4507
Cf	Free(±)	5.232E-05	1.7372E-06	3.3203
Rf	Free(±)	3167	81.453	2.5719
Cdl	Free(±)	9.5008E-05	3.8908E-06	4.0952
Rt	Free(±)	3649	115.13	3.1551

Chi-Squared: 0.00025061
Weighted Sum of Squares: 0.037592

(d)

Figure A.23 EIS fitting results using a CPE (Nyquist (a), (b), Bode (c) plots and the fitting parameters (d)) of an OPC+LiNO₃ sample after 86 days in condition 1.

(iv) Why only W_{cem2} is used to replace CPE_{cem2} when the n values of other CPE elements such as CPE_f are low occasionally? An important reason is that the determination of the cement paste porosity in the second half of study relies on GEM theory, in which the solid phase of the cement paste is regarded as a

low-conductive ionic conductor (see Section 3.5.4) and possesses a certain number of conductivity (i.e. the ion diffusion in the solid phase is considered in GEM). To keep the same assumption in one study, the diffusion in the solid phase of the cement paste also needs to be considered when constructing the equivalent circuit model. Hence, the application of a Warburg element describing the electrical contribution of the solid phase in the disconnected pore path appears more appropriate.

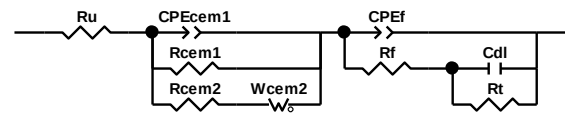
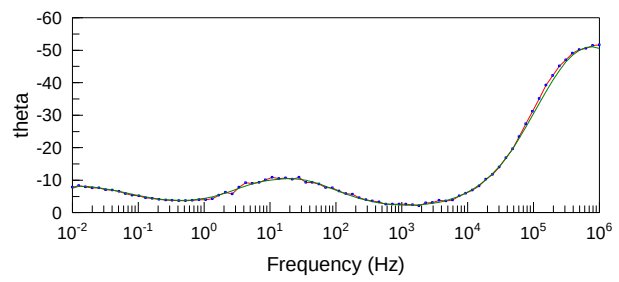
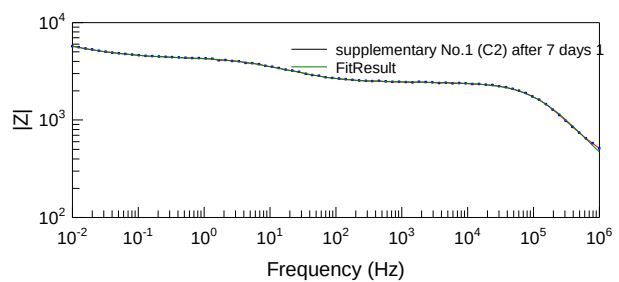
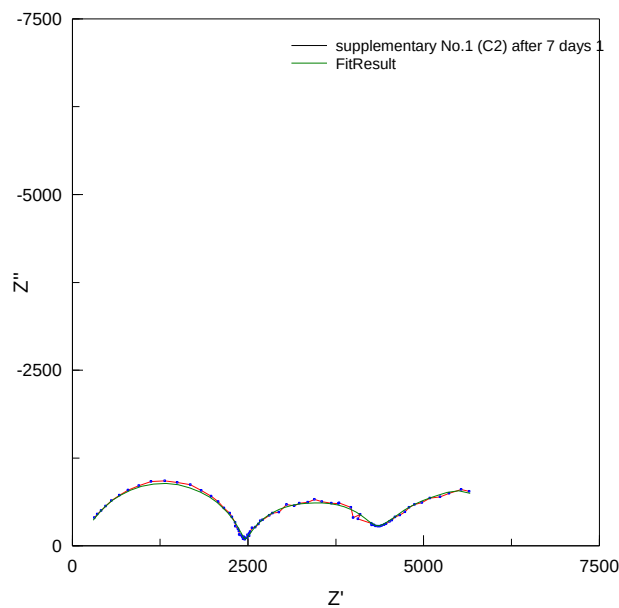
A.4. Fitting results

Some EIS fitting results are provided below. The picture number of each sample is shown in Table A1. For each test, three repetitive samples (1st, 2nd and 3rd) were tested.

Table A1. Part of the EIS fitting results.

OPC	Condition 1	Condition 2
7 d		Figure A.24
13 d	Figure A.25	Figure A.26
29 d	Figure A.27	
30 d		Figure A.28
41 d	Figure A.29	
OPC+LiNO ₃	Condition 1	Condition 2
7 d	Figure A.30	Figure A.31
28 d	Figure A.32	Figure A.33
79 d	Figure A.34	
120 d	Figure A.35	Figure A.36
OPC+Li ₂ CO ₃	Condition 1	Condition 2
8 d	Figure A.37	Figure A.38
30 d	Figure A.39	Figure A.40
79 d	Figure A.41	
121 d	Figure A.42	Figure A.43

Appendix

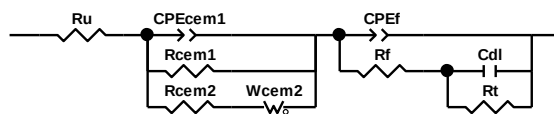
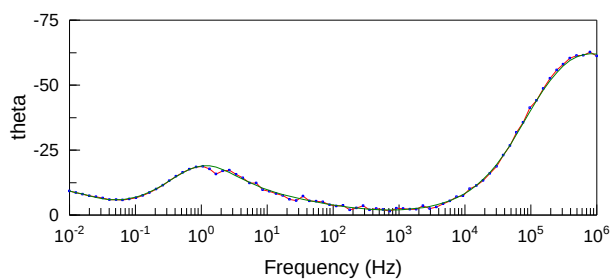
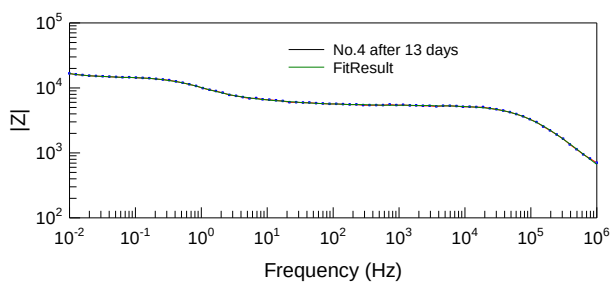
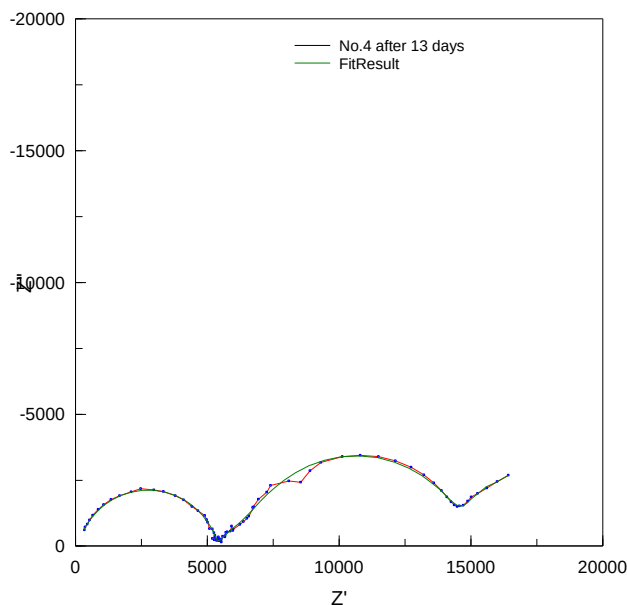


Element	Freedom	Value	Error	Error %
Ru	Free(±)	130	6.5146	5.0112
CPEcem1-T	Free(±)	5.4147E-09	3.6465E-10	6.7344
CPEcem1-P	Free(±)	0.82915	0.004864	0.58662
Rcem1	Free(±)	5000	443.28	8.8656
Rcem2	Free(±)	4358	333.55	7.6537
Wcem2-R	Free(±)	31317	11448	36.555
Wcem2-T	Free(±)	100.8	25.294	25.093
Wcem2-P	Free(±)	0.66346	0.055827	8.4145
CPEf-T	Free(±)	1.4482E-05	3.0962E-06	21.38
CPEf-P	Free(±)	0.79643	0.035407	4.4457
Rf	Free(±)	1519	162.27	10.683
Cdl	Free(±)	7.363E-05	3.1813E-05	43.207
Rt	Free(±)	313.8	125.52	40

Chi-Squared: 0.0011107
Weighted Sum of Squares: 0.16328

Data File: C:\Users\xlii\Desktop\Experimental data h
Circuit Model File: C:\Users\xlii\Desktop\Experimental data h
Mode: Run Fitting / Freq. Range (0.01 - 1000000)
Maximum Iterations: 100
Optimization Iterations: 10
Type of Fitting: Complex
Type of Weighting: Calc-Modulus

Figure A.24 EIS fitting results of an OPC sample after 7 days in condition 2.

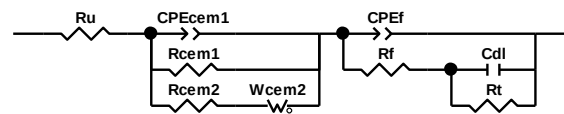
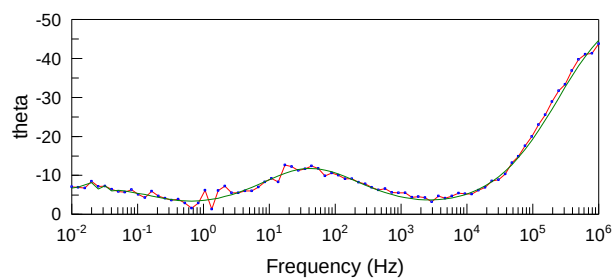
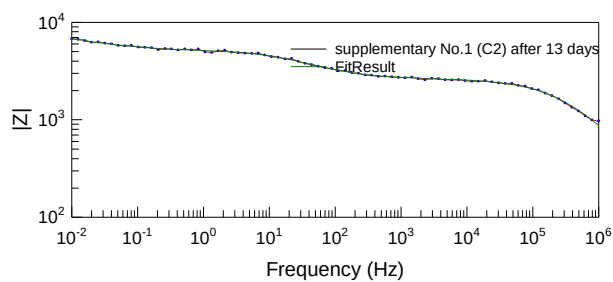
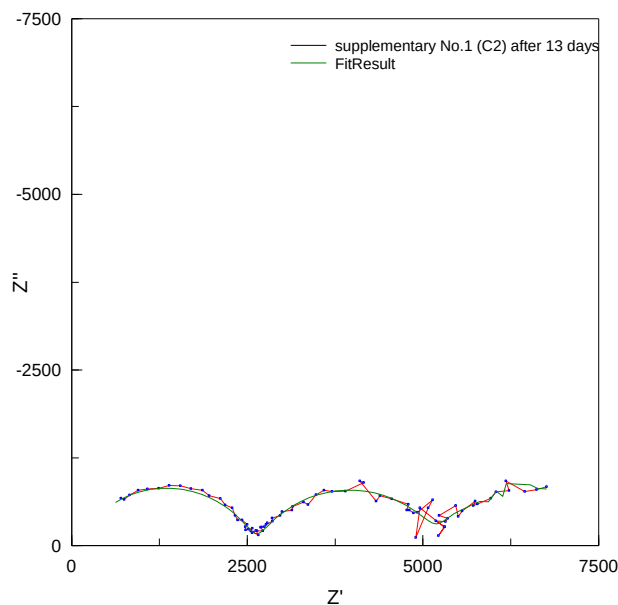


Element	Freedom	Value	Error	Error %
Ru	Free(±)	112.1	7.6974	6.8665
CPEcem1-T	Free(±)	2.112E-09	1.0755E-10	5.0923
CPEcem1-P	Free(±)	0.86344	0.0037465	0.4339
Rcem1	Free(±)	13248	416.49	3.1438
Rcem2	Free(±)	8746	158.46	1.8118
Wcem2-R	Free(±)	4.3451E06	8.9075E05	20.5
Wcem2-T	Free(±)	102.1	24.379	23.878
Wcem2-P	Free(±)	0.86878	0.021309	2.4527
CPEf-T	Free(±)	3.2911E-05	1.1885E-05	36.113
CPEf-P	Free(±)	0.65749	0.063659	9.6821
Rf	Free(±)	1444	379.77	26.3
Cdl	Free(±)	0.0042083	0.00027896	6.6288
Rt	Free(±)	5186	460.24	8.8747

Chi-Squared: 0.00087702
Weighted Sum of Squares: 0.12892

Data File: C:\Users\xlii\Desktop\Experimental data h
Circuit Model File: C:\Users\xlii\Desktop\Experimental data h
Mode: Run Fitting / Freq. Range (0.01 - 1000000)
Maximum Iterations: 100
Optimization Iterations: 10
Type of Fitting: Complex
Type of Weighting: Calc-Modulus

Figure A.25 EIS fitting results of an OPC sample after 13 days in condition 1.



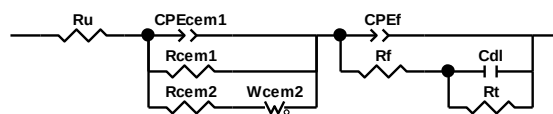
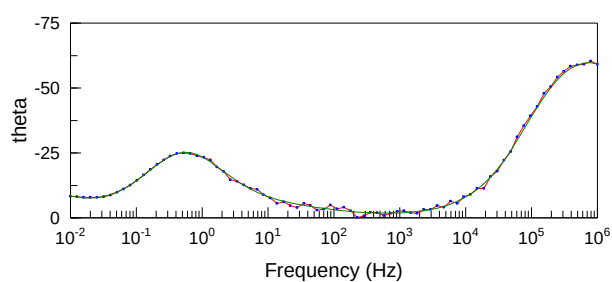
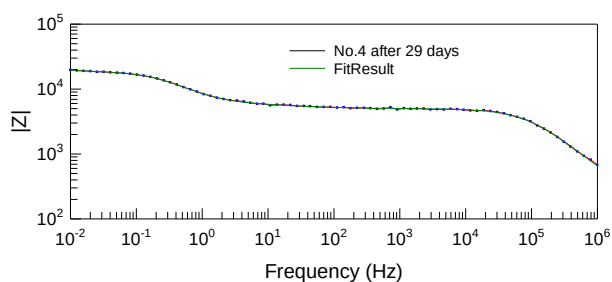
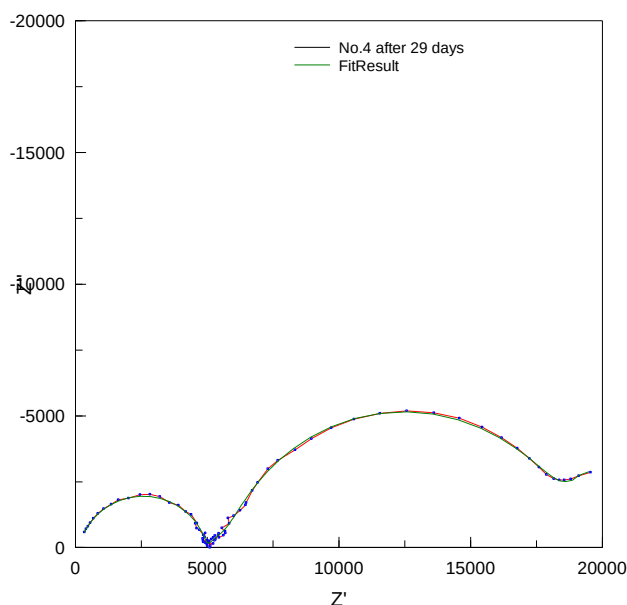
Element	Freedom	Value	Error	Error %
Ru	Free(±)	70.63	32.619	46.183
CPEcem1-T	Free(±)	1.1846E-08	1.8262E-09	15.416
CPEcem1-P	Free(±)	0.72392	0.012269	1.6948
Rcem1	Free(±)	3288	200.07	6.0849
Rcem2	Free(±)	11462	2387.3	20.828
Wcem2-R	Free(±)	2.7666E05	1.4211E05	51.366
Wcem2-T	Free(±)	44.36	4.4878	10.117
Wcem2-P	Free(±)	0.91167	0.042494	4.6611
CPEf-T	Free(±)	1.1934E-05	1.067E-06	8.9408
CPEf-P	Free(±)	0.68115	0.016519	2.4252
Rf	Free(±)	2652	52.473	1.9786
Cdl	Free(±)	0.0095767	0.0027301	28.508
Rt	Free(±)	1524	165.89	10.885

Chi-Squared: 0.0025246
Weighted Sum of Squares: 0.37112

Data File: C:\Users\xlii\Desktop\Experimental data h
Circuit Model File: C:\Users\xlii\Desktop\Experimental data h
Mode: Run Fitting / Freq. Range (0.01 - 1000000)
Maximum Iterations: 100
Optimization Iterations: 10
Type of Fitting: Complex
Type of Weighting: Calc-Modulus

Figure A.26 EIS fitting results of an OPC sample after 13 days in condition 2.

Appendix

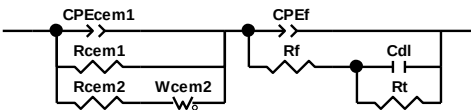
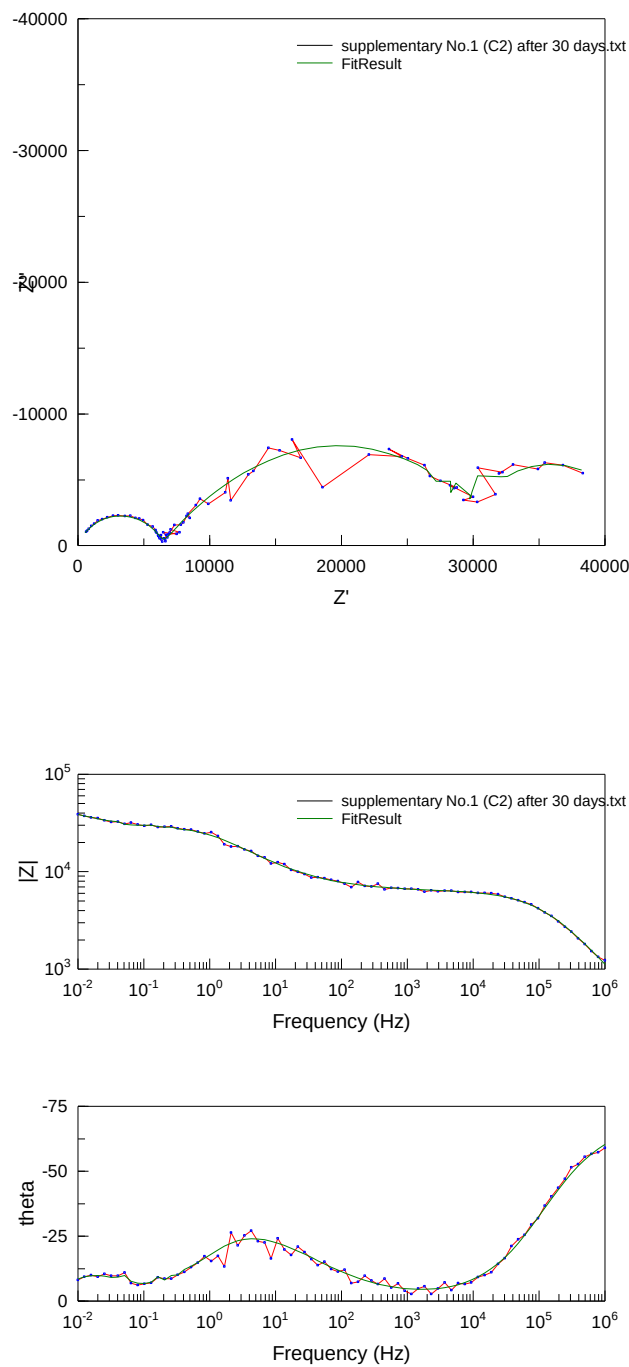


Element	Freedom	Value	Error	Error %
Ru	Free(±)	136.5	9.1483	6.7021
CPEcem1-T	Free(±)	2.2901E-09	1.4557E-10	6.3565
CPEcem1-P	Free(±)	0.86054	0.0046598	0.5415
Rcem1	Free(±)	17869	348.29	1.9491
Rcem2	Free(±)	6676	57.297	0.85825
Wcem2-R	Free(±)	2.639E06	8.2279E05	31.178
Wcem2-T	Free(±)	154.8	58.692	37.915
Wcem2-P	Free(±)	0.8372	0.01527	1.8239
CPEf-T	Free(±)	4.7606E-05	2.384E-05	50.078
CPEf-P	Free(±)	0.63382	0.091639	14.458
Rf	Free(±)	916.2	218.35	23.832
Cdl	Free(±)	0.0063245	0.0007995	12.641
Rt	Free(±)	6744	2198.7	32.602

Chi-Squared: 0.0012009
Weighted Sum of Squares: 0.17653

Data File: C:\Users\xlj\Desktop\Experimental data h
Circuit Model File: C:\Users\xlj\Desktop\Experimental data h
Mode: Run Fitting / Freq. Range (0.01 - 1000000)
Maximum Iterations: 100
Optimization Iterations: 10
Type of Fitting: Complex
Type of Weighting: Calc-Modulus

Figure A.27 EIS fitting results of an OPC sample after 29 days in condition 1.

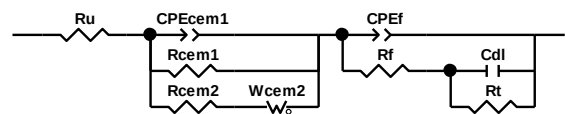
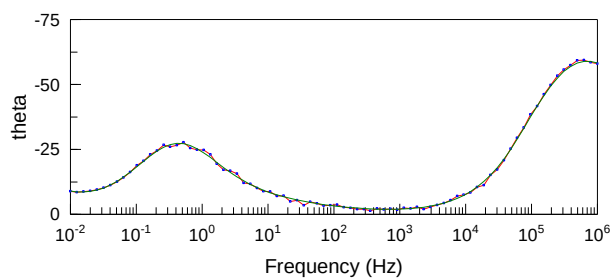
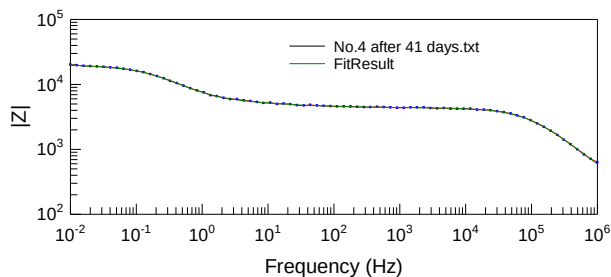
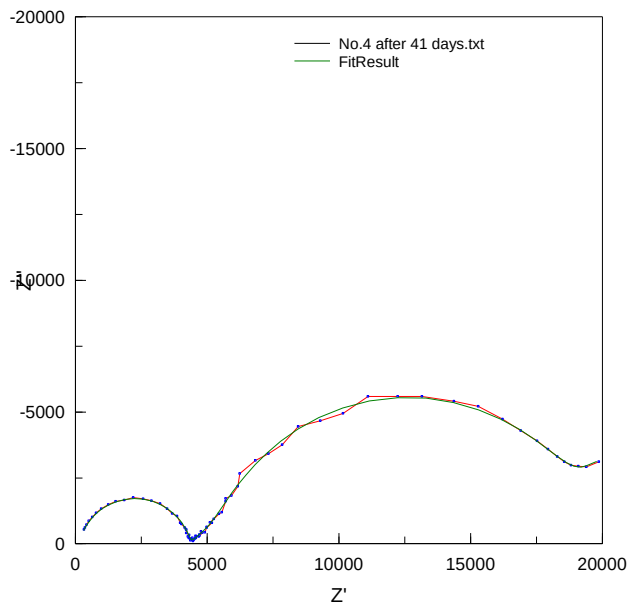


Element	Freedom	Value	Error	Error %
CPEcem1-T	Free(±)	4.4026E-09	4.7555E-10	10.802
CPEcem1-P	Free(±)	0.77587	0.0073962	0.95328
Rcem1	Free(±)	13310	2435	18.295
Rcem2	Free(±)	12315	2159.5	17.536
Wcem2-R	Free(±)	8.9135E05	2.1961E05	24.638
Wcem2-T	Free(±)	5.296	0.49474	9.3418
Wcem2-P	Free(±)	0.91235	0.043372	4.7539
CPEf-T	Free(±)	1.1687E-05	2.1922E-06	18.758
CPEf-P	Free(±)	0.58549	0.031658	5.4071
Rf	Free(±)	18615	2900.7	15.583
Cdl	Free(±)	0.00094725	0.00012744	13.454
Rt	Free(±)	10888	1167.1	10.719

Chi-Squared: 0.0046716
Weighted Sum of Squares: 0.6914

Data File: C:\Users\xlii\Desktop\Experimental data h
Circuit Model File: C:\Users\xlii\Desktop\Experimental data h
Mode: Run Fitting / Freq. Range (0.01 - 1000000)
Maximum Iterations: 100
Optimization Iterations: 10
Type of Fitting: Complex
Type of Weighting: Calc-Modulus

Figure A.28 EIS fitting results of an OPC sample after 30 days in condition 2.



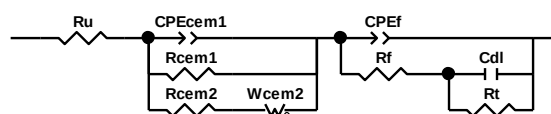
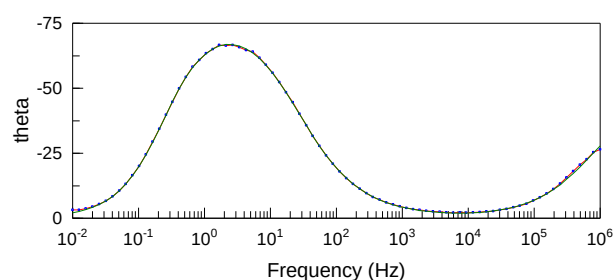
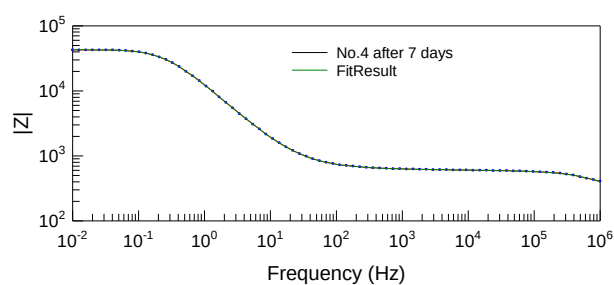
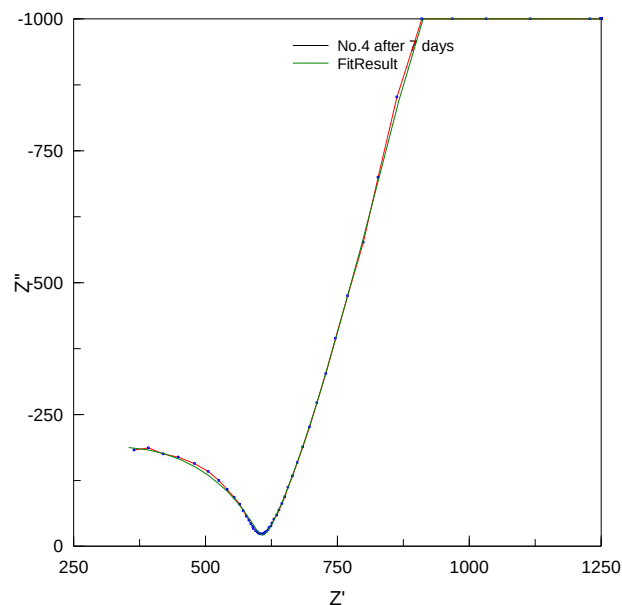
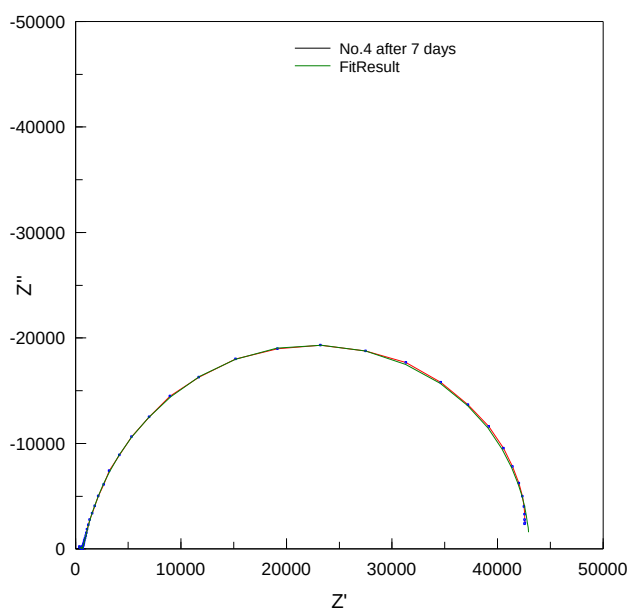
Element	Freedom	Value	Error	Error %
Ru	Free(±)	136.2	6.5599	4.8164
CPEcem1-T	Free(±)	2.3537E-09	1.2612E-10	5.3584
CPEcem1-P	Free(±)	0.86562	0.0039582	0.45727
Rcem1	Free(±)	18320	442.28	2.4142
Rcem2	Free(±)	5495	41.617	0.75736
Wcem2-R	Free(±)	1.9932E06	5.3047E05	26.614
Wcem2-T	Free(±)	170.8	54.855	32.117
Wcem2-P	Free(±)	0.82839	0.014336	1.7306
CPEf-T	Free(±)	8.9726E-05	3.4277E-05	38.202
CPEf-P	Free(±)	0.53584	0.066552	12.42
Rf	Free(±)	1205	347.92	28.873
Cdl	Free(±)	0.0069486	0.00092773	13.351
Rt	Free(±)	8765	4248.7	48.473

Chi-Squared: 0.00071818
Weighted Sum of Squares: 0.10557

Data File: C:\Users\xlii\Desktop\Experimental data h
Circuit Model File: C:\Users\xlii\Desktop\Experimental data h
Mode: Run Fitting / Freq. Range (0.01 - 1000000)
Maximum Iterations: 100
Optimization Iterations: 10
Type of Fitting: Complex
Type of Weighting: Calc-Modulus

Figure A.29 EIS fitting results of an OPC sample after 41 days in condition 1.

Appendix



Element	Freedom	Value	Error	Error %
Ru	Free(±)	77.02	9.3842	12.184
CPEcem1-T	Free(±)	7.9231E-09	6.6718E-10	8.4207
CPEcem1-P	Free(±)	0.78676	0.0076998	0.97867
Rcem1	Free(±)	4898	1217.5	24.857
Rcem2	Free(±)	590.9	22.406	3.7918
Wcem2-R	Free(±)	7882	3237	41.068
Wcem2-T	Free(±)	1.162	0.53281	45.853
Wcem2-P	Free(±)	0.5704	0.012489	2.1895
CPEf-T	Free(±)	1.409E-05	3.9188E-07	2.7813
CPEf-P	Free(±)	0.96777	0.010181	1.052
Rf	Free(±)	31449	2619.5	8.3294
Cdl	Free(±)	1.9444E-05	8.1445E-06	41.887
Rt	Free(±)	6618	2604.9	39.361

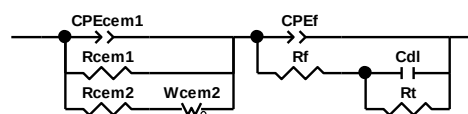
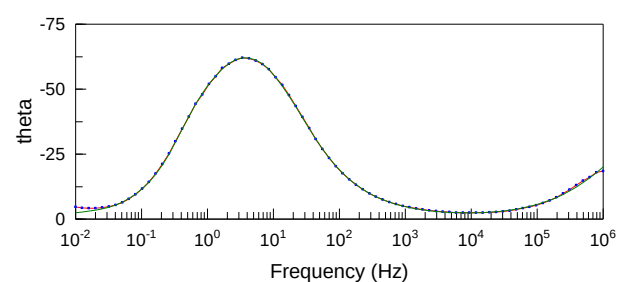
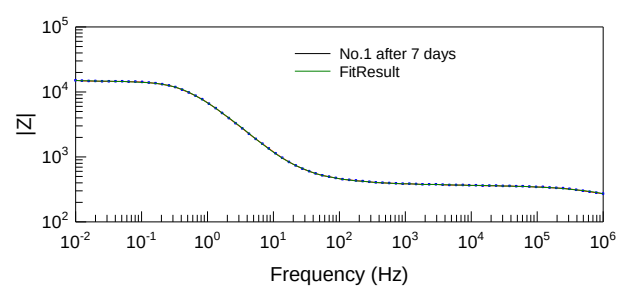
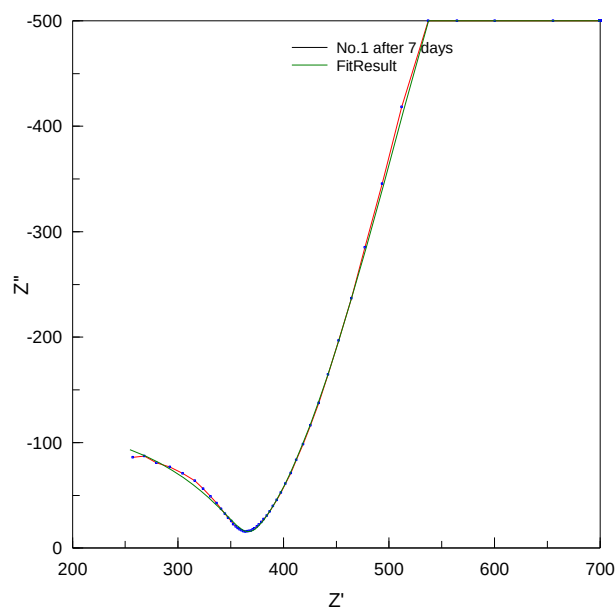
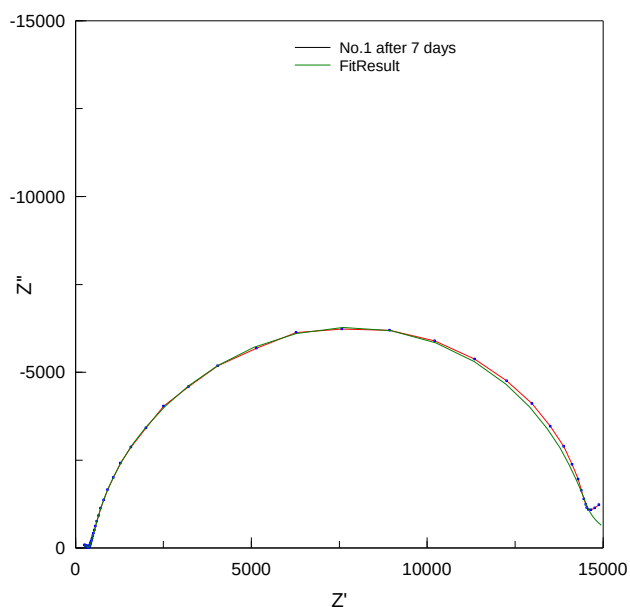
Chi-Squared: 0.00013721

Weighted Sum of Squares: 0.02017

Data File: C:\Users\xlii\Desktop\Experimental data h
 Circuit Model File: C:\Users\xlii\Desktop\Experimental data h
 Mode: Run Fitting / Freq. Range (0.01 - 1000000)
 Maximum Iterations: 100
 Optimization Iterations: 10
 Type of Fitting: Complex
 Type of Weighting: Calc-Modulus

Figure A.30 EIS fitting results of an OPC+LiNO₃ sample after 7 days in condition 1.

Appendix



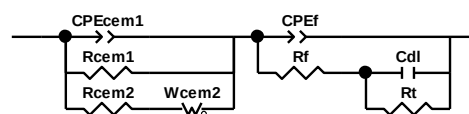
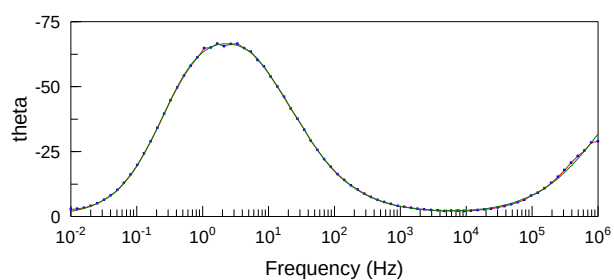
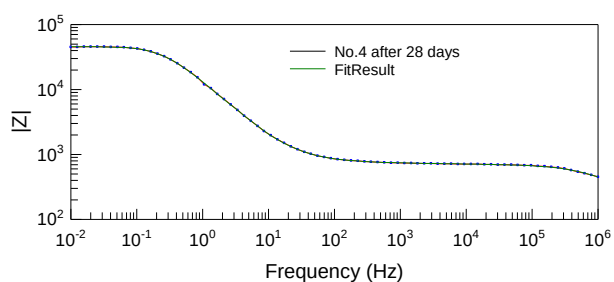
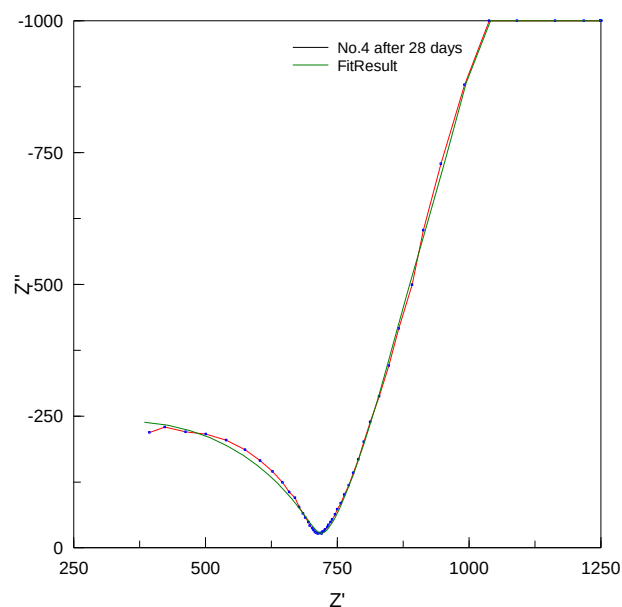
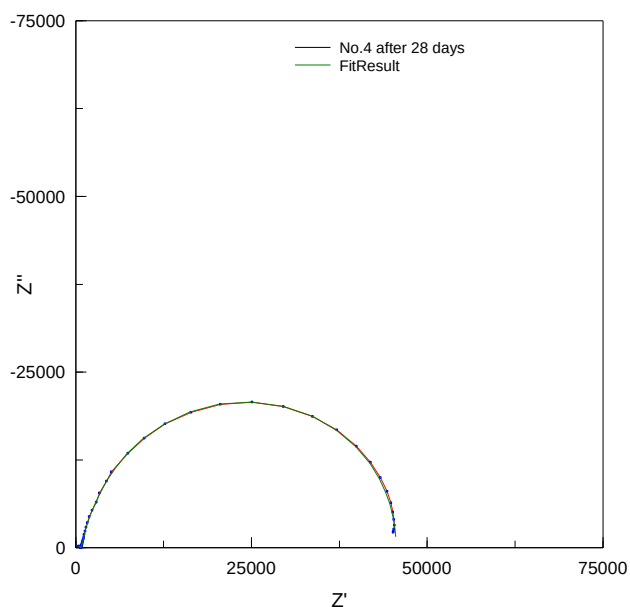
Element	Freedom	Value	Error	Error %
CPEc1-T	Free(±)	4.0419E-08	5.2664E-09	13.03
CPEc1-P	Free(±)	0.67017	0.013321	1.9877
Rcem1	Free(±)	2632	328.54	12.483
Rcem2	Free(±)	421.9	21.981	5.21
Wcem2-R	Free(±)	16376	863.58	5.2734
Wcem2-T	Free(±)	25.58	1.7242	6.7404
Wcem2-P	Free(±)	0.49519	0.039553	7.9874
CPEf-T	Free(±)	2.083E-05	8.3141E-07	3.9914
CPEf-P	Free(±)	0.98425	0.012638	1.284
Rf	Free(±)	9516	1367.2	14.367
Cdl	Free(±)	5.7473E-05	1.8444E-05	32.092
Rt	Free(±)	3124	1002.6	32.093

Chi-Squared: 0.00041548
Weighted Sum of Squares: 0.061491

Data File: C:\Users\xlii\Desktop\Experimental data h
Circuit Model File: C:\Users\xlii\Desktop\Experimental data h
Mode: Run Fitting / Freq. Range (0.01 - 100000)
Maximum Iterations: 100
Optimization Iterations: 10
Type of Fitting: Complex
Type of Weighting: Calc-Modulus

Figure A.31 EIS fitting results of an OPC+LiNO₃ sample after 7 days in condition 2.

Appendix



Element	Freedom	Value	Error	Error %
CPEc1-T	Free(±)	1.0117E-08	8.5702E-10	8.4711
CPEc1-P	Free(±)	0.74948	0.0054386	0.72565
Rcem1	Free(±)	16203	1943.7	11.996
Rcem2	Free(±)	747.8	5.0056	0.66938
Wcem2-R	Free(±)	1015	138.61	13.656
Wcem2-T	Free(±)	0.057383	0.0094012	16.383
Wcem2-P	Free(±)	0.52573	0.0065363	1.2433
CPEf-T	Free(±)	1.2696E-05	6.5867E-07	5.188
CPEf-P	Free(±)	0.96604	0.015979	1.6541
Rf	Free(±)	16143	2348.9	14.551
Cdl	Free(±)	1.1447E-05	1.2571E-06	10.982
Rt	Free(±)	13220	1144.2	8.6551

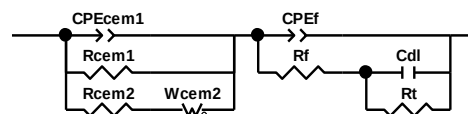
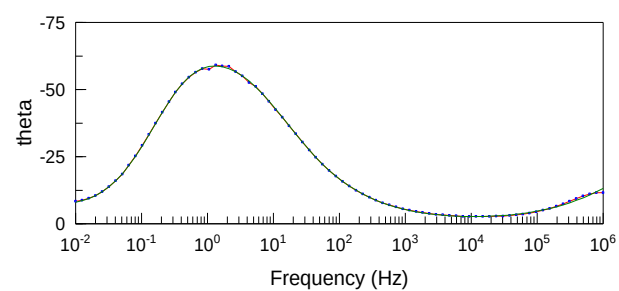
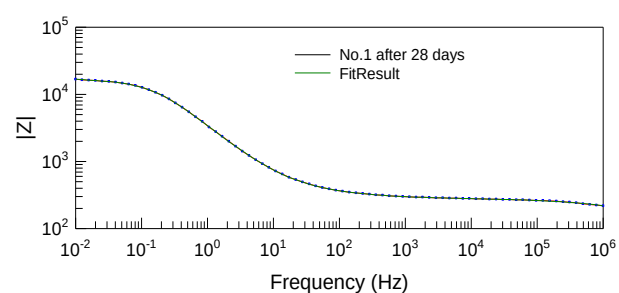
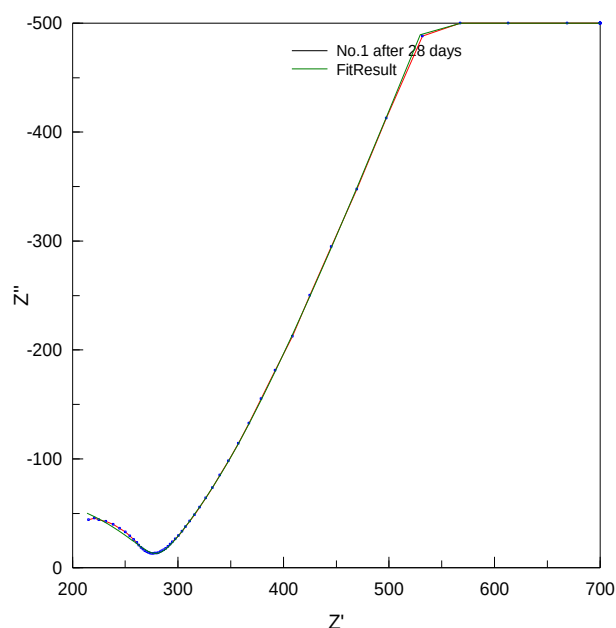
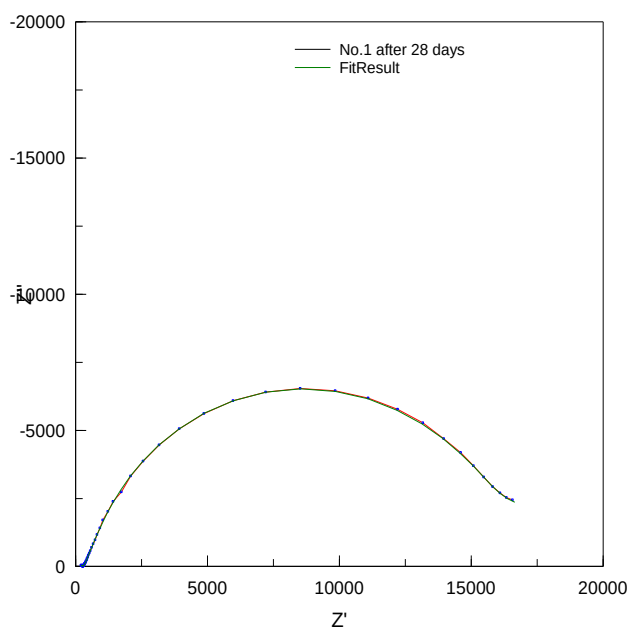
Chi-Squared: 0.00040927

Weighted Sum of Squares: 0.060572

Data File: C:\Users\xlii\Desktop\Experimental data h;
 Circuit Model File: C:\Users\xlii\Desktop\Experimental data h;
 Mode: Run Fitting / Freq. Range (0.01 - 1000000)
 Maximum Iterations: 100
 Optimization Iterations: 10
 Type of Fitting: Complex
 Type of Weighting: Calc-Modulus

Figure A.32 EIS fitting results of an OPC+LiNO₃ sample after 28 days in condition 1.

Appendix



Element	Freedom	Value	Error	Error %
CPEcem1-T	Free(±)	2.0836E-07	3.3388E-08	16.024
CPEcem1-P	Free(±)	0.56017	0.008627	1.5401
Rcem1	Free(±)	5643	452.59	8.0204
Rcem2	Free(±)	292.9	1.4668	0.50079
Wcem2-R	Free(±)	12885	2830.2	21.965
Wcem2-T	Free(±)	40.42	6.9147	17.107
Wcem2-P	Free(±)	0.48063	0.017169	3.5722
CPEf-T	Free(±)	6.6082E-05	1.7911E-06	2.7104
CPEf-P	Free(±)	0.88539	0.0043227	0.48823
Rf	Free(±)	401.7	235.27	58.569
Cdl	Free(±)	3.4067E-06	2.7328E-06	80.218
Rt	Free(±)	13198	236.67	1.7932

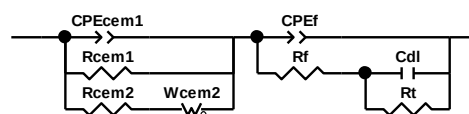
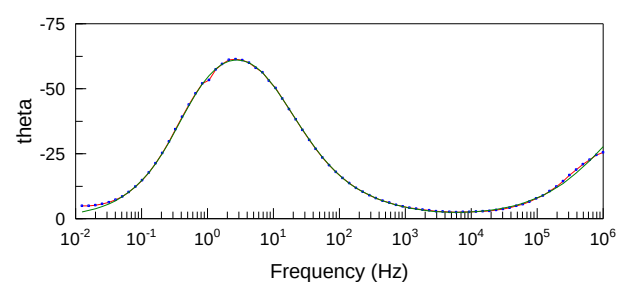
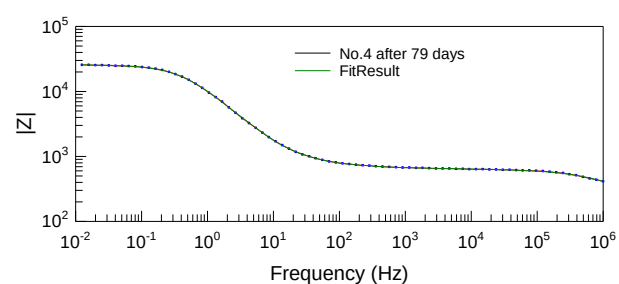
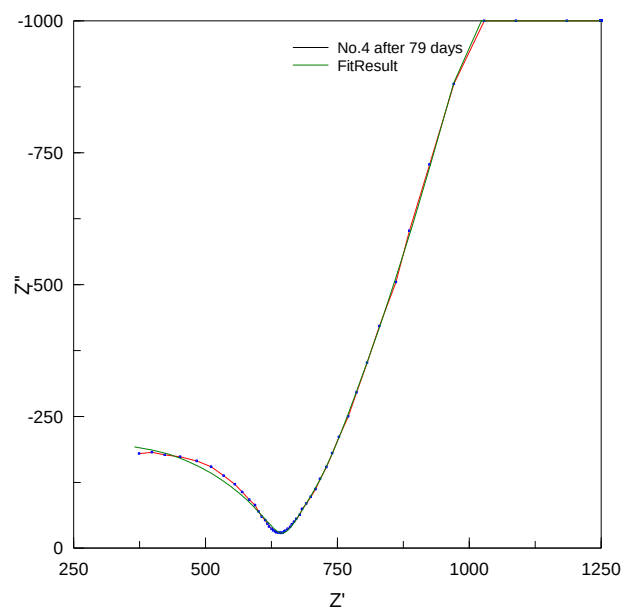
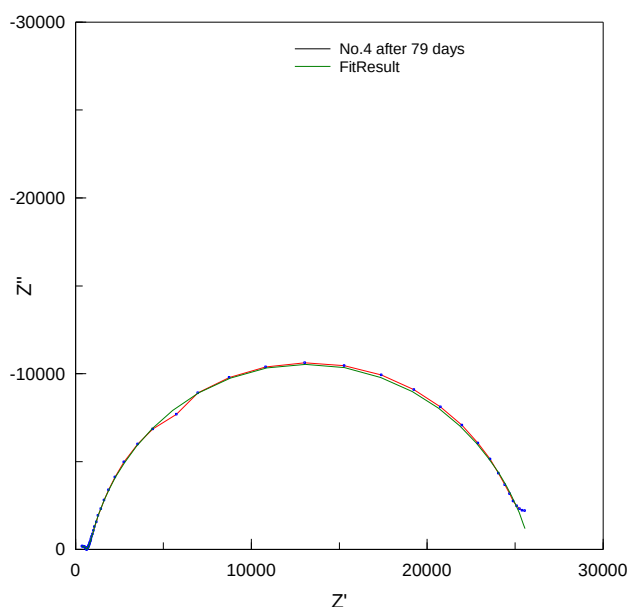
Chi-Squared: 0.0001148

Weighted Sum of Squares: 0.016991

Data File: C:\Users\xlii\Desktop\Experimental data h;
 Circuit Model File: C:\Users\xlii\Desktop\Experimental data h;
 Mode: Run Fitting / Freq. Range (0.01 - 1000000)
 Maximum Iterations: 100
 Optimization Iterations: 10
 Type of Fitting: Complex
 Type of Weighting: Calc-Modulus

Figure A.33 EIS fitting results of an OPC+LiNO₃ sample after 28 days in condition 2.

Appendix



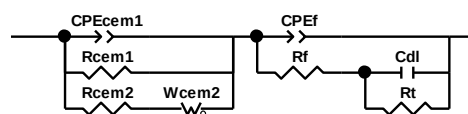
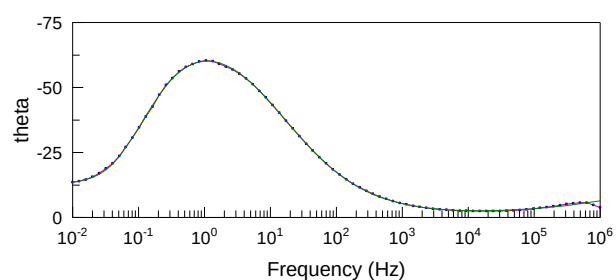
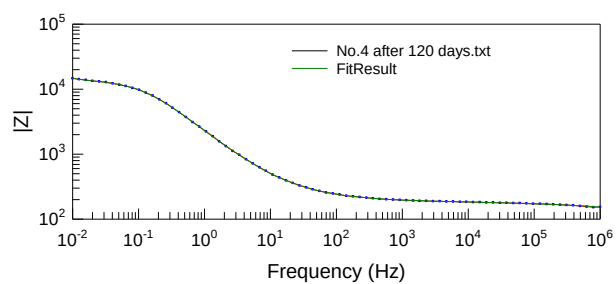
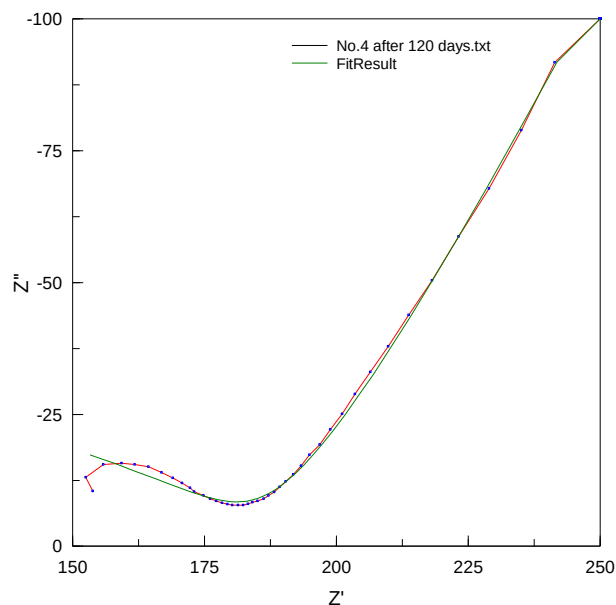
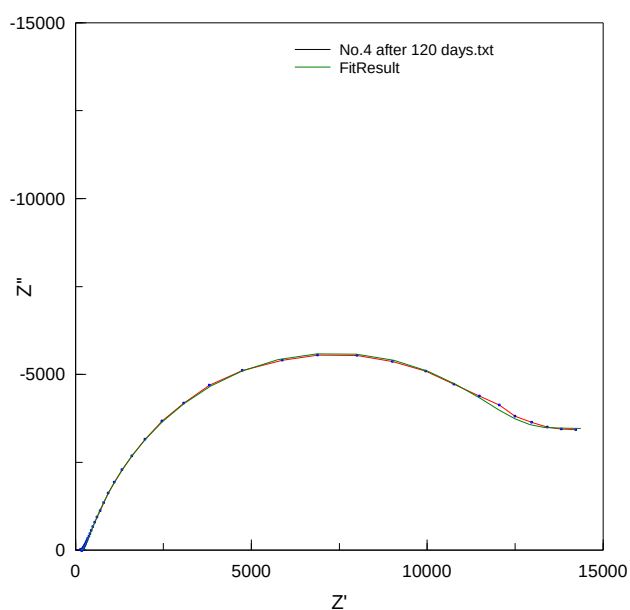
Element	Freedom	Value	Error	Error %
CPEc1-T	Free(±)	2.5302E-08	2.5558E-09	10.101
CPEc1-P	Free(±)	0.69147	0.0062754	0.90754
Rcem1	Free(±)	11070	1774.3	16.028
Rcem2	Free(±)	682.5	7.6363	1.1189
Wcem2-R	Free(±)	184.8	43.67	23.631
Wcem2-T	Free(±)	0.0052341	0.0015704	30.003
Wcem2-P	Free(±)	0.49069	0.0080801	1.6467
CPEf-T	Free(±)	3.1121E-05	5.6029E-06	18.004
CPEf-P	Free(±)	0.79899	0.024711	3.0928
Rf	Free(±)	2709	626.42	23.124
Cdl	Free(±)	3.5356E-06	8.0499E-07	22.768
Rt	Free(±)	12136	1448.1	11.932

Chi-Squared: 0.0003808
Weighted Sum of Squares: 0.055597

Data File: C:\Users\xlii\Desktop\Experimental data h:
Circuit Model File: C:\Users\xlii\Desktop\Experimental data h:
Mode: Run Fitting / Freq. Range (0.01 - 1000000)
Maximum Iterations: 100
Optimization Iterations: 10
Type of Fitting: Complex
Type of Weighting: Calc-Modulus

Figure A.34 EIS fitting results of an OPC+LiNO₃ sample after 79 days in condition 1.

Appendix



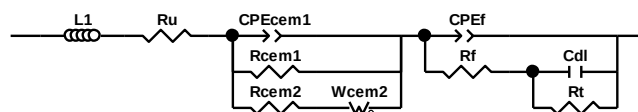
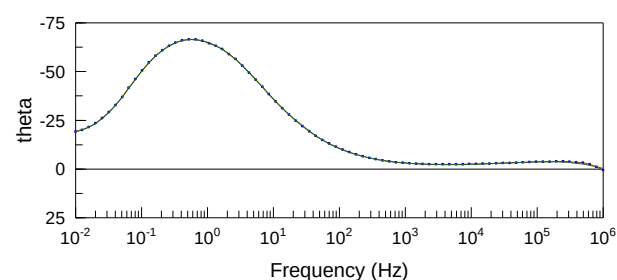
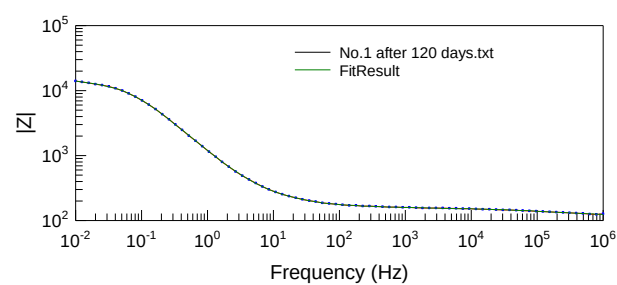
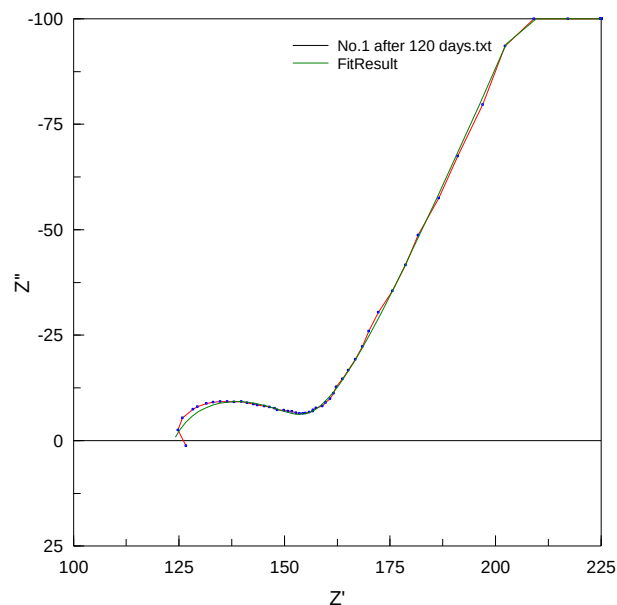
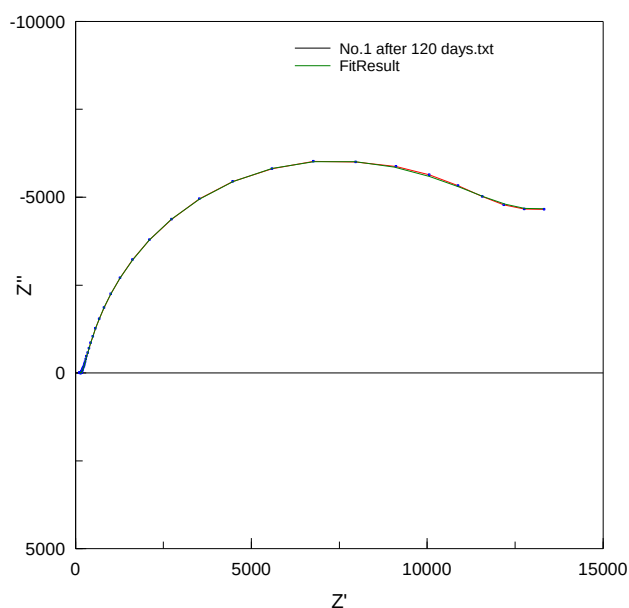
Element	Freedom	Value	Error	Error %
CPEc1-T	Free(±)	4.664E-06	1.4897E-06	31.94
CPEc1-P	Free(±)	0.36149	0.014968	4.1406
Rcem1	Free(±)	6796	278.74	4.1015
Rcem2	Free(±)	193.2	1.3993	0.72428
Wcem2-R	Free(±)	7887	1258.7	15.959
Wcem2-T	Free(±)	18.95	1.4259	7.5245
Wcem2-P	Free(±)	0.5181	0.013706	2.6454
CPEf-T	Free(±)	0.00010469	2.2953E-06	2.1925
CPEf-P	Free(±)	0.88516	0.0056611	0.63956
Rf	Free(±)	1316	596.27	45.309
Cdl	Free(±)	6.4167E-06	1.5439E-06	24.061
Rt	Free(±)	9836	520.36	5.2904

Chi-Squared: 0.0001979
Weighted Sum of Squares: 0.029289

Data File: C:\Users\xlii\Desktop\Experimental data h;
Circuit Model File: C:\Users\xlii\Desktop\Experimental data h;
Mode: Run Fitting / Freq. Range (0.01 - 1000000)
Maximum Iterations: 100
Optimization Iterations: 10
Type of Fitting: Complex
Type of Weighting: Calc-Modulus

Figure A.35 EIS fitting results of an OPC+LiNO₃ sample after 120 days in condition 1.

Appendix



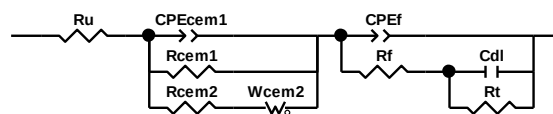
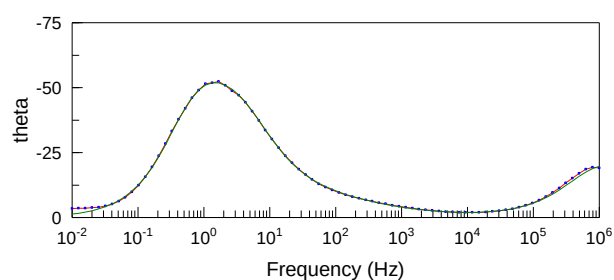
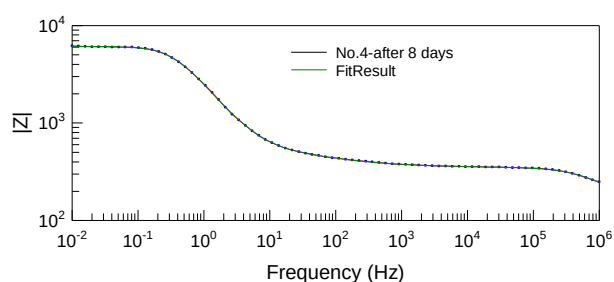
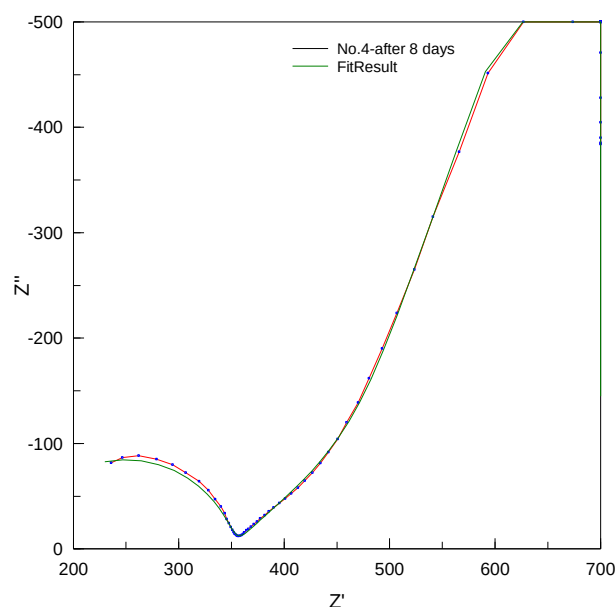
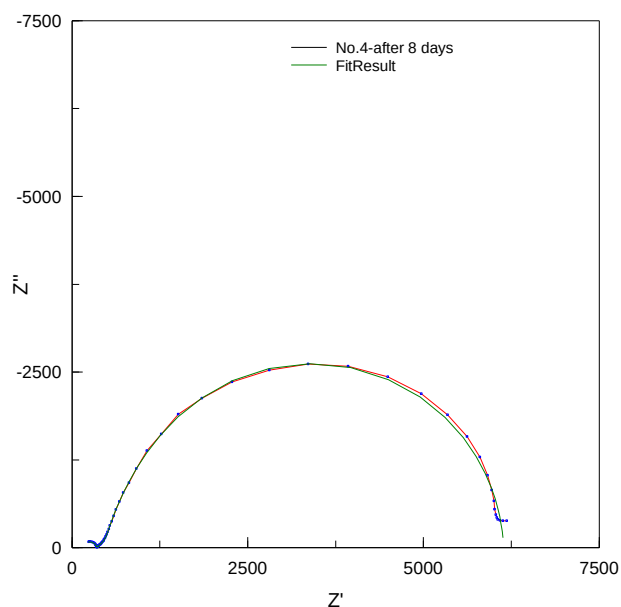
Element	Freedom	Value	Error	Error %
L1	Free(±)	1.0568E-06	9.0611E-08	8.5741
Ru	Free(±)	115.2	1.4784	1.2833
CPEcem1-T	Free(±)	5.6742E-06	1.3064E-06	23.024
CPEcem1-P	Free(±)	0.60035	0.02247	3.7428
Rcem1	Free(±)	13273	1737.5	13.09
Rcem2	Free(±)	38.83	1.8747	4.828
Wcem2-R	Free(±)	456.6	59.716	13.078
Wcem2-T	Free(±)	1.652	0.27839	16.852
Wcem2-P	Free(±)	0.43095	0.0078031	1.8107
CPEf-T	Free(±)	0.00016224	1.5837E-06	0.97615
CPEf-P	Free(±)	0.90258	0.003235	0.35842
Rf	Free(±)	689.9	65.306	9.466
Cdl	Free(±)	2.0044E-05	1.3706E-06	6.838
Rt	Free(±)	11748	109.51	0.93216

Chi-Squared: 7.8673E-05
Weighted Sum of Squares: 0.011486

Data File: C:\Users\xlii\Desktop\Experimental data handli
Circuit Model File: C:\Users\xlii\Desktop\Experimental data handli
Mode: Run Fitting / Freq. Range (0.01 - 1000000)
Maximum Iterations: 100
Optimization Iterations: 10
Type of Fitting: Complex
Type of Weighting: Calc-Modulus

Figure A.36 EIS fitting results of an OPC+LiNO₃ sample after 120 days in condition 2.

Appendix



Element	Freedom	Value	Error	Error %
Ru	Free(±)	146.8	5.4052	3.682
CPEc1-T	Free(±)	6.8217E-09	1.3129E-09	19.246
CPEc1-P	Free(±)	0.87575	0.016774	1.9154
Rcem1	Free(±)	425.2	24.264	5.7065
Rcem2	Free(±)	396.7	47.851	12.062
Wcem2-R	Free(±)	6522	2795.1	42.856
Wcem2-T	Free(±)	0.19172	0.11025	57.506
Wcem2-P	Free(±)	0.54252	0.032746	6.0359
CPEf-T	Free(±)	5.9377E-05	2.0398E-06	3.4353
CPEf-P	Free(±)	0.97114	0.006885	0.70896
Rf	Free(±)	3059	543.67	17.773
Cdl	Free(±)	5.0671E-05	8.5343E-06	16.843
Rt	Free(±)	2508	568.69	22.675

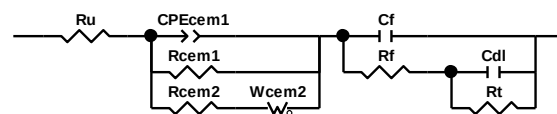
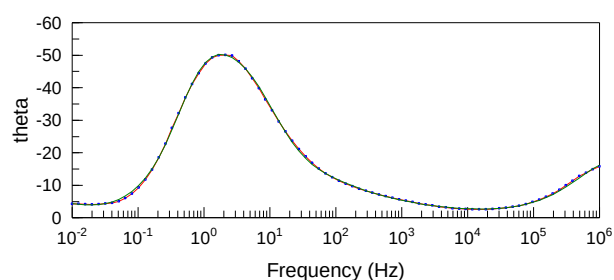
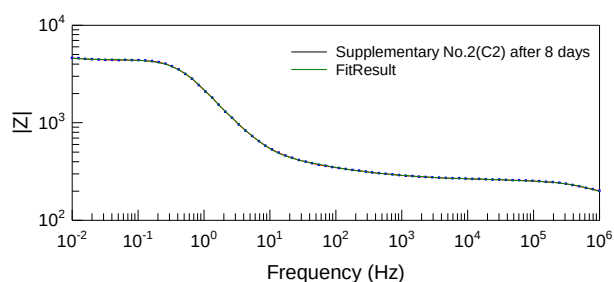
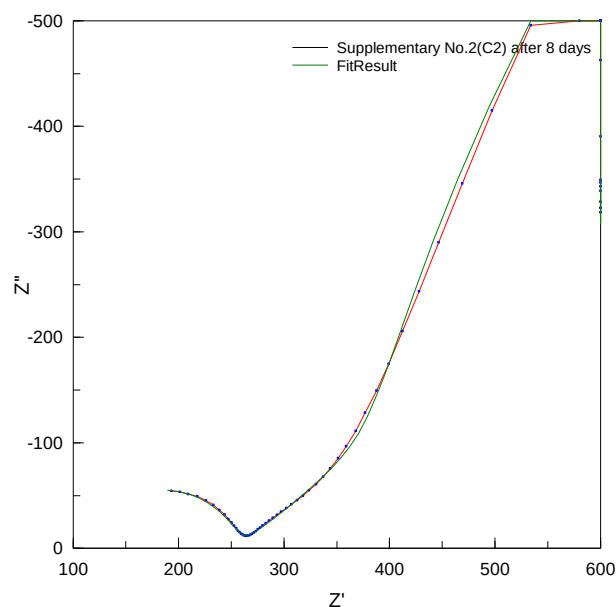
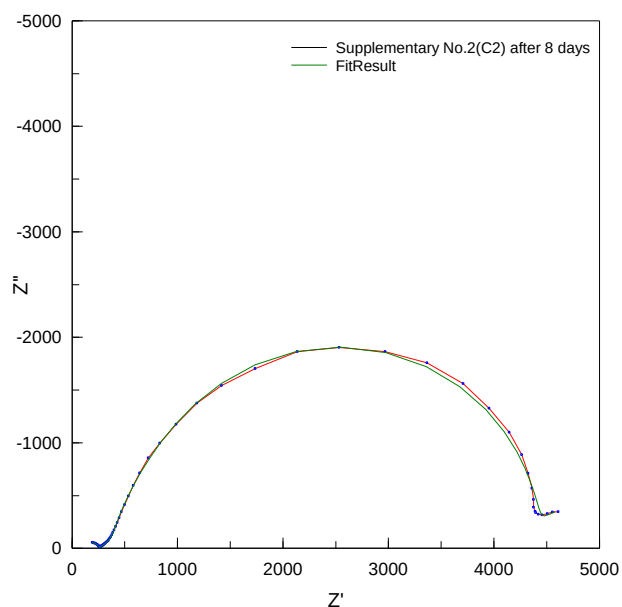
Chi-Squared: 0.00040355

Weighted Sum of Squares: 0.059321

Data File: C:\Users\xlii\Desktop\Experimental data h
 Circuit Model File: C:\Users\xlii\Desktop\Experimental data h
 Mode: Run Fitting / Freq. Range (0.01 - 1000000)
 Maximum Iterations: 100
 Optimization Iterations: 10
 Type of Fitting: Complex
 Type of Weighting: Calc-Modulus

Figure A.37 EIS fitting results of an OPC+Li₂CO₃ sample after 8 days in condition 1.

Appendix



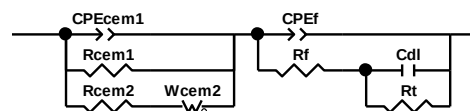
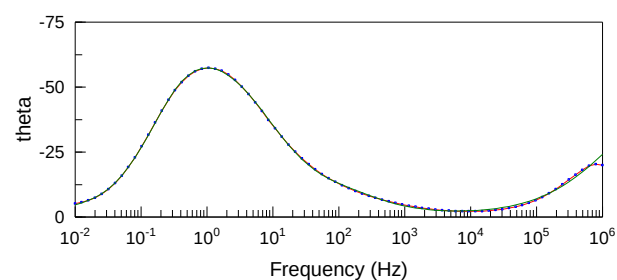
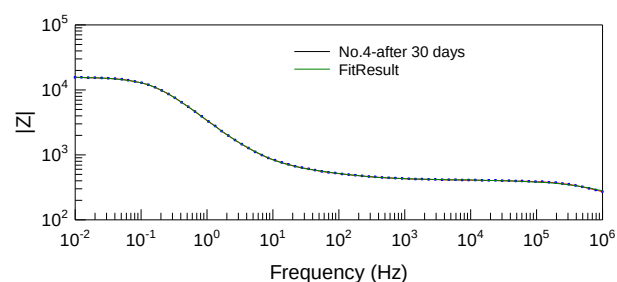
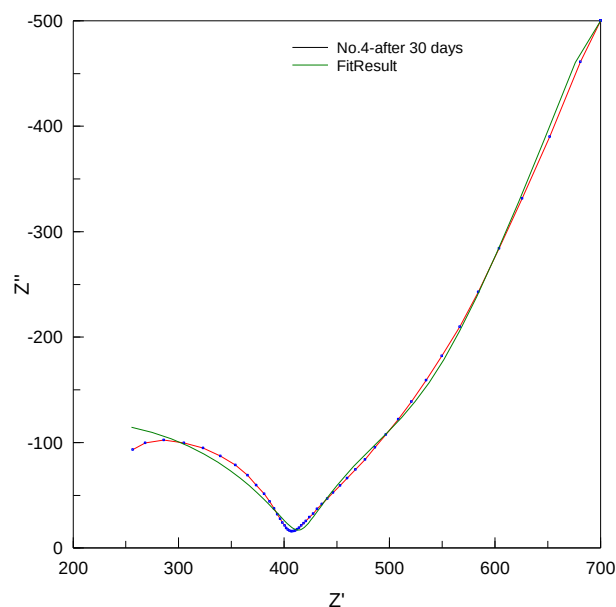
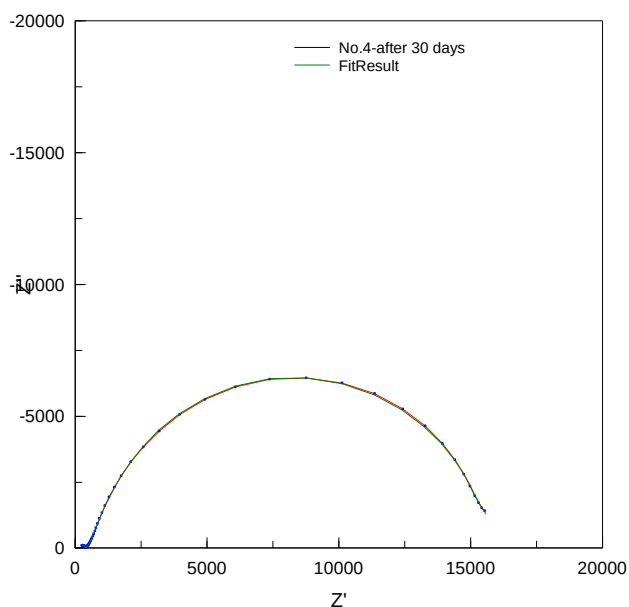
Element	Freedom	Value	Error	Error %
Ru	Free(±)	114.8	5.0021	4.3572
CPEcem1-T	Free(±)	1.3074E-08	2.5908E-09	19.816
CPEcem1-P	Free(±)	0.83848	0.017212	2.0528
Rcem1	Free(±)	697.3	32.441	4.6524
Rcem2	Free(±)	175.7	9.1544	5.2102
Wcem2-R	Free(±)	697.1	37.044	5.314
Wcem2-T	Free(±)	0.032535	0.0011632	3.5752
Wcem2-P	Free(±)	0.43237	0.0074234	1.7169
Cf	Free(±)	8.5012E-05	1.2902E-06	1.5177
Rf	Free(±)	3643	30.703	0.84279
Cdl	Free(±)	0.047109	0.0027972	5.9377
Rt	Free(±)	661.2	102.27	15.467

Chi-Squared: 0.00020022
Weighted Sum of Squares: 0.029633

Data File: C:\Users\xlii\Desktop\Experimental data h
Circuit Model File: C:\Users\xlii\Desktop\Experimental data h
Mode: Run Fitting / Freq. Range (0.01 - 1000000)
Maximum Iterations: 100
Optimization Iterations: 10
Type of Fitting: Complex
Type of Weighting: Calc-Modulus

Figure A.38 EIS fitting results of an OPC+Li₂CO₃ sample after 8 days in condition 2.

Appendix



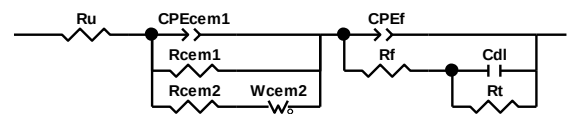
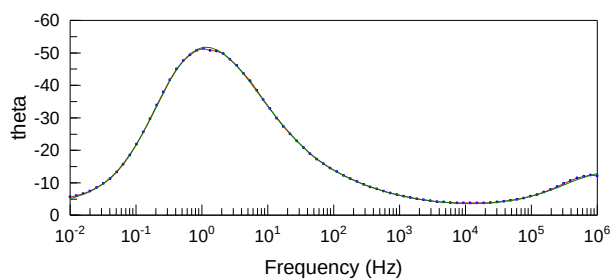
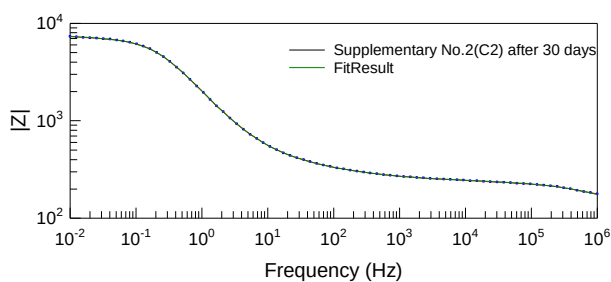
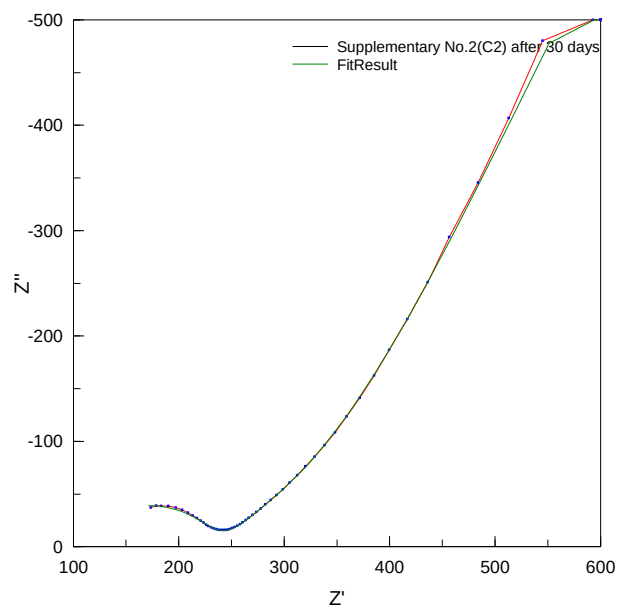
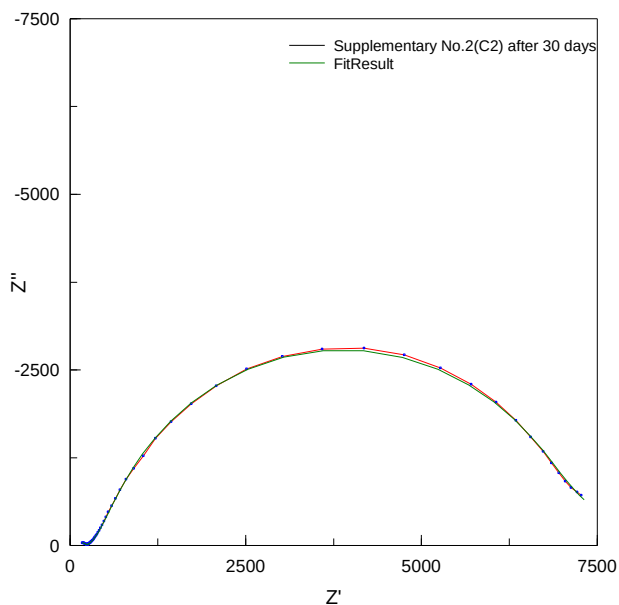
Element	Freedom	Value	Error	Error %
CPEcem1-T	Free(±)	4.9834E-08	7.8555E-09	15.763
CPEcem1-P	Free(±)	0.66635	0.0081876	1.2287
Rcem1	Free(±)	3175	973.38	30.658
Rcem2	Free(±)	475.7	17.615	3.703
Wcem2-R	Free(±)	33401	11373	34.05
Wcem2-T	Free(±)	34.57	14.252	41.226
Wcem2-P	Free(±)	0.57277	0.029171	5.093
CPEf-T	Free(±)	3.5811E-05	3.4844E-06	9.73
CPEf-P	Free(±)	0.87099	0.010968	1.2593
Rf	Free(±)	128.1	16.555	12.923
Cdl	Free(±)	3.5411E-05	6.9022E-06	19.492
Rt	Free(±)	12772	811.31	6.3523

Chi-Squared: 0.00050108

Weighted Sum of Squares: 0.07416

Data File: C:\Users\xlii\Desktop\Experimental data h
 Circuit Model File: C:\Users\xlii\Desktop\Experimental data h
 Mode: Run Fitting / Freq. Range (0.01 - 1000000)
 Maximum Iterations: 100
 Optimization Iterations: 10
 Type of Fitting: Complex
 Type of Weighting: Calc-Modulus

Figure A.39 EIS fitting results of an OPC+Li₂CO₃ sample after 30 days in condition 1.



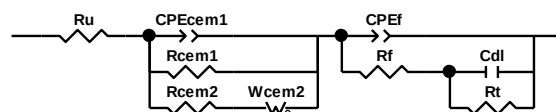
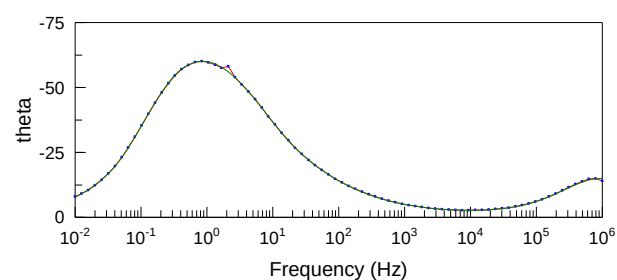
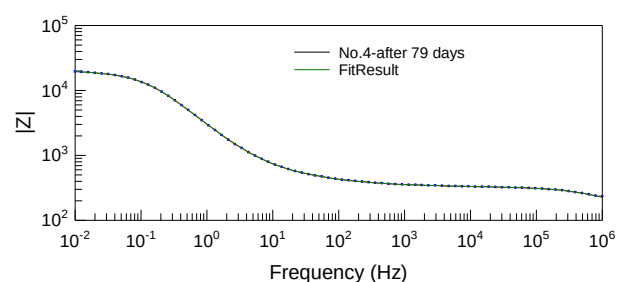
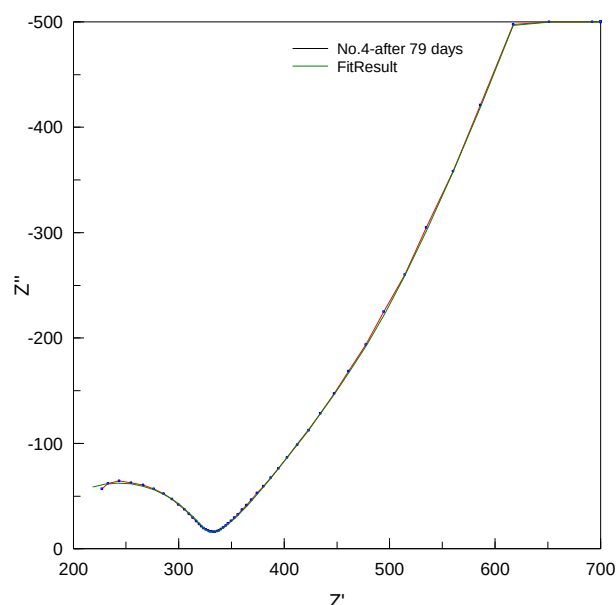
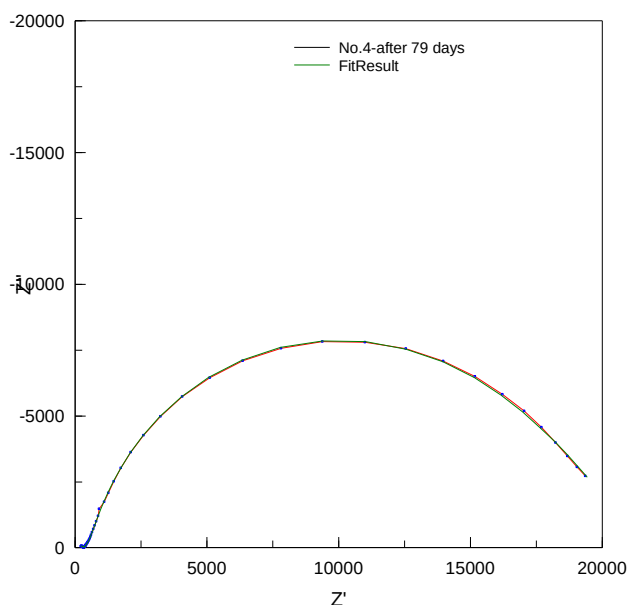
Element	Freedom	Value	Error	Error %
Ru	Free(±)	108.3	3.8852	3.5874
CPEcem1-T	Free(±)	1.5635E-07	3.1529E-08	20.166
CPEcem1-P	Free(±)	0.69225	0.017746	2.5635
Rcem1	Free(±)	1916	279.5	14.588
Rcem2	Free(±)	133.8	5.7062	4.2647
Wcem2-R	Free(±)	6120	1550.3	25.332
Wcem2-T	Free(±)	45.68	32.251	70.602
Wcem2-P	Free(±)	0.38232	0.0087151	2.2795
CPEf-T	Free(±)	0.00010637	4.8608E-06	4.5697
CPEf-P	Free(±)	0.8878	0.0058161	0.65511
Rf	Free(±)	107.3	73.667	68.655
Cdl	Free(±)	1.2189E-05	5.5402E-06	45.452
Rt	Free(±)	5824	98.663	1.6941

Chi-Squared: 7.3678E-05
Weighted Sum of Squares: 0.010831

Data File: C:\Users\xlii\Desktop\Experimental data h
Circuit Model File: C:\Users\xlii\Desktop\Experimental data h
Mode: Run Fitting / Freq. Range (0.01 - 1000000)
Maximum Iterations: 100
Optimization Iterations: 10
Type of Fitting: Complex
Type of Weighting: Calc-Modulus

Figure A.40 EIS fitting results of an OPC+Li₂CO₃ sample after 30 days in condition 2.

Appendix



Element	Freedom	Value	Error	Error %
Ru	Free(±)	160.2	3.4839	2.1747
CPEcem1-T	Free(±)	2.1511E-08	5.0236E-09	23.354
CPEcem1-P	Free(±)	0.82591	0.013441	1.6274
Rcem1	Free(±)	3910	214.09	5.4754
Rcem2	Free(±)	168.9	4.6908	2.7773
Wcem2-R	Free(±)	3500	602.42	17.212
Wcem2-T	Free(±)	6.288	2.8328	45.051
Wcem2-P	Free(±)	0.41122	0.0096651	2.3503
CPEf-T	Free(±)	6.5179E-05	1.0504E-06	1.6116
CPEf-P	Free(±)	0.8972	0.0057372	0.63946
Rf	Free(±)	471.7	90.836	19.257
Cdl	Free(±)	1.0401E-05	1.1295E-06	10.86
Rt	Free(±)	16343	287.05	1.7564

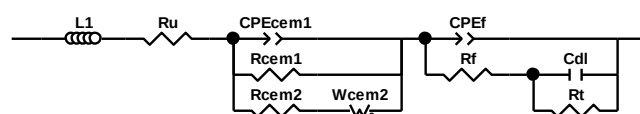
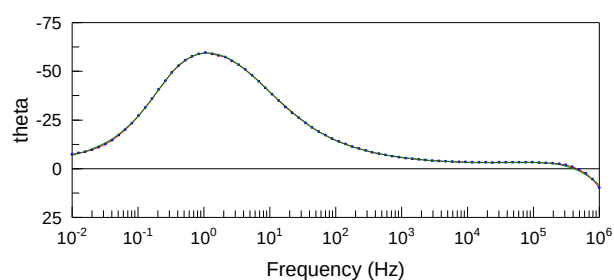
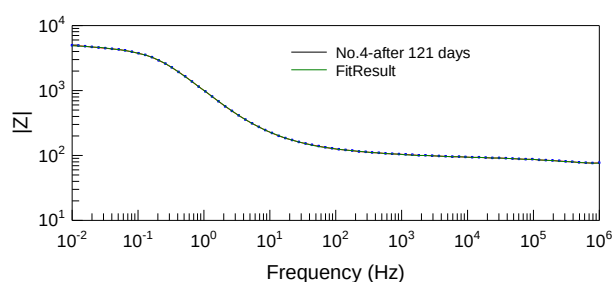
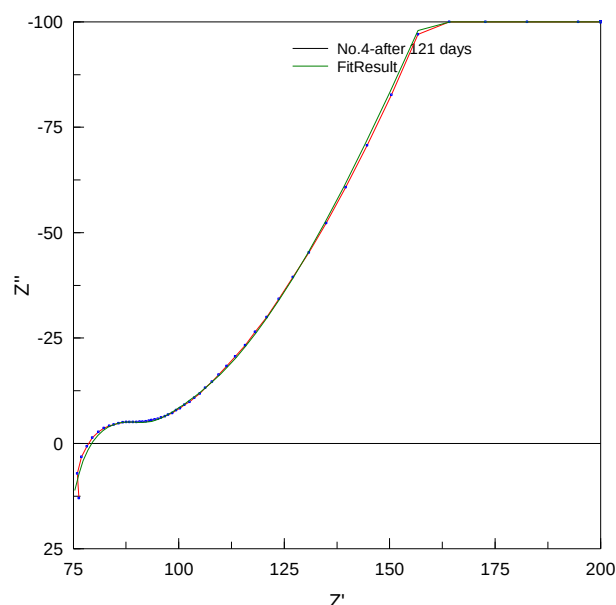
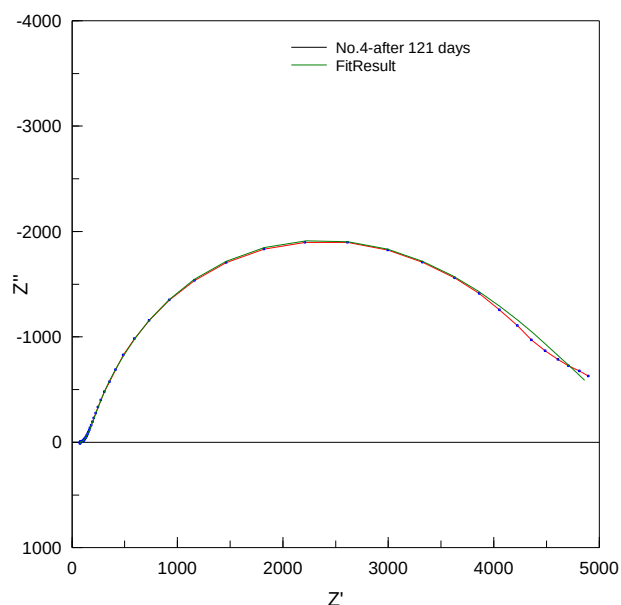
Chi-Squared: 0.00012143

Weighted Sum of Squares: 0.017851

Data File: C:\Users\xlii\Desktop\Experimental data h
 Circuit Model File: C:\Users\xlii\Desktop\Experimental data h
 Mode: Run Fitting / Freq. Range (0.01 - 100000)
 Maximum Iterations: 100
 Optimization Iterations: 10
 Type of Fitting: Complex
 Type of Weighting: Calc-Modulus

Figure A.41 EIS fitting results of an OPC+Li₂CO₃ sample after 79 days in condition 1.

Appendix



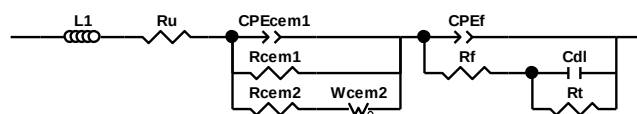
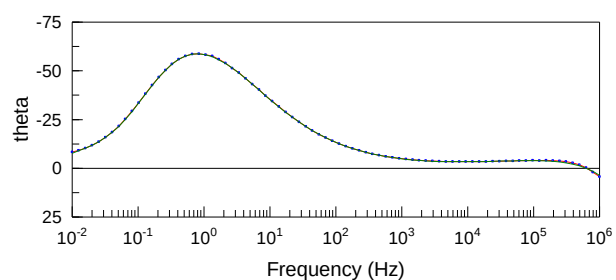
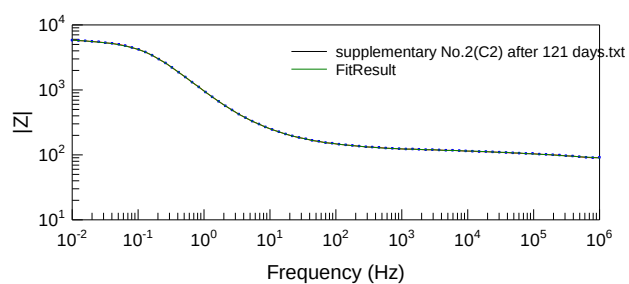
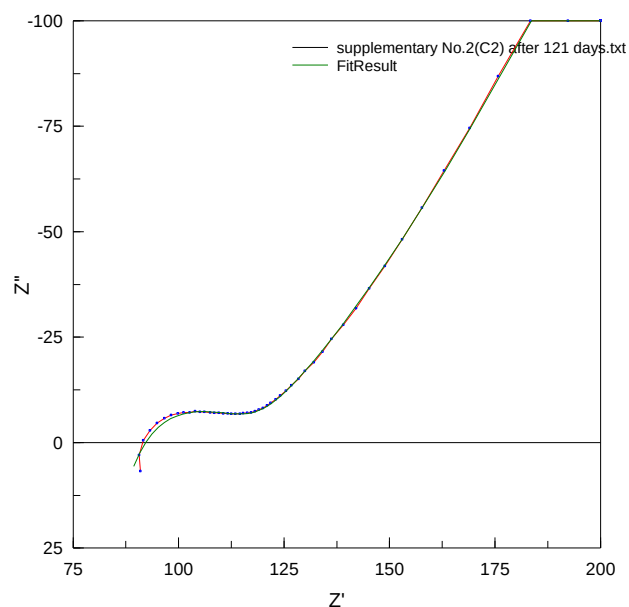
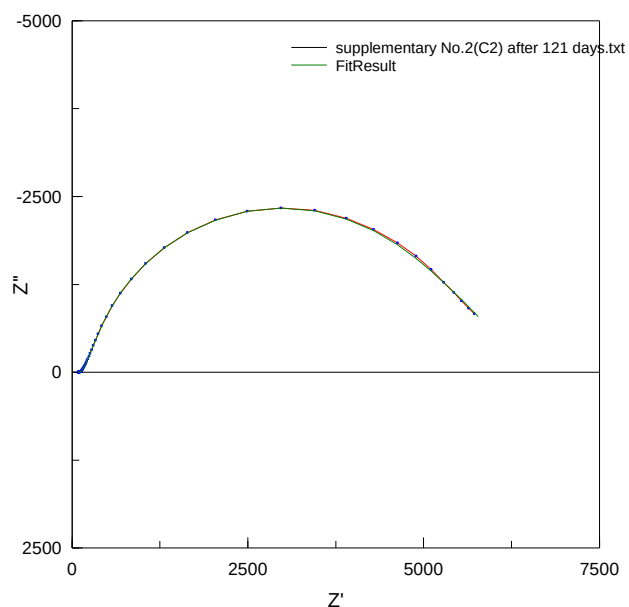
Element	Freedom	Value	Error	Error %
L1	Free(±)	2.6494E-06	9.1878E-08	3.4679
Ru	Free(±)	69.6	1.47	2.1121
CPEcem1-T	Free(±)	0.00056246	2.5089E-05	4.4606
CPEcem1-P	Free(±)	0.5149	0.0092908	1.8044
Rcem1	Free(±)	2582	45.159	1.749
Rcem2	Free(±)	54.3	5.3521	9.8565
Wcem2-R	Free(±)	2423	249.73	10.307
Wcem2-T	Free(±)	0.92251	0.069098	7.4902
Wcem2-P	Free(±)	0.57641	0.008455	1.4668
CPEf-T	Free(+)	2.7202E-06	7.6018E-07	27.946
CPEf-P	Free(±)	0.67533	0.045583	6.7497
Rf	Free(±)	21.64	2.1453	9.9136
Cdl	Free(±)	0.00023426	1.4043E-06	0.59946
Rt	Free(±)	2793	32.435	1.1613

Chi-Squared: 0.00012504
Weighted Sum of Squares: 0.018257

Data File: C:\Users\xlii\Desktop\Experimental data handli
Circuit Model File: C:\Users\xlii\Desktop\Experimental data handli
Mode: Run Fitting / Freq. Range (0.01 - 1000000)
Maximum Iterations: 100
Optimization Iterations: 10
Type of Fitting: Complex
Type of Weighting: Calc-Modulus

Figure A.42 EIS fitting results of an OPC+Li₂CO₃ sample after 121 days in condition 1.

Appendix



Element	Freedom	Value	Error	Error %
L1	Free(±)	2.2941E-06	8.1208E-08	3.5399
Ru	Free(±)	69.45	3.2251	4.6438
CPEcm1-T	Free(±)	0.00071055	2.1779E-05	3.0651
CPEcm1-P	Free(±)	0.55679	0.0034347	0.61688
Rcem1	Free(±)	2545	89.276	3.5079
Rcem2	Free(±)	883.1	213.29	24.152
Wcem2-R	Free(±)	16312	4386.4	26.891
Wcem2-T	Free(±)	1.831	0.13765	7.5177
Wcem2-P	Free(±)	0.66751	0.032961	4.9379
CPEf-T	Free(±)	3.0216E-05	3.6657E-06	12.132
CPEf-P	Free(±)	0.43895	0.018546	4.2251
Rf	Free(±)	50.03	3.5589	7.1135
Cdl	Free(±)	0.000271	4.0479E-06	1.4937
Rt	Free(±)	3855	86.627	2.2471

Chi-Squared: 6.6624E-05
Weighted Sum of Squares: 0.0097271

Data File: C:\Users\xlii\Desktop\Experimental data handli
Circuit Model File: C:\Users\xlii\Desktop\Experimental data handli
Mode: Run Fitting / Freq. Range (0.01 - 1000000)
Maximum Iterations: 100
Optimization Iterations: 10
Type of Fitting: Complex
Type of Weighting: Calc-Modulus

Figure A.43 EIS fitting results of an OPC+Li₂CO₃ sample after 121 days in condition 2.

A.5. The link between the microstructures and the spectra

To what extent the impedance spectra can be linked to the microstructures described in the equivalent circuit is evaluated by testing the influences of parameters on the spectra. First, the EIS results are fitted using the selected equivalent circuit. As an example, the EIS fitting results of an OPC specimen after 22 days in condition 1 is shown in Figure A.44.

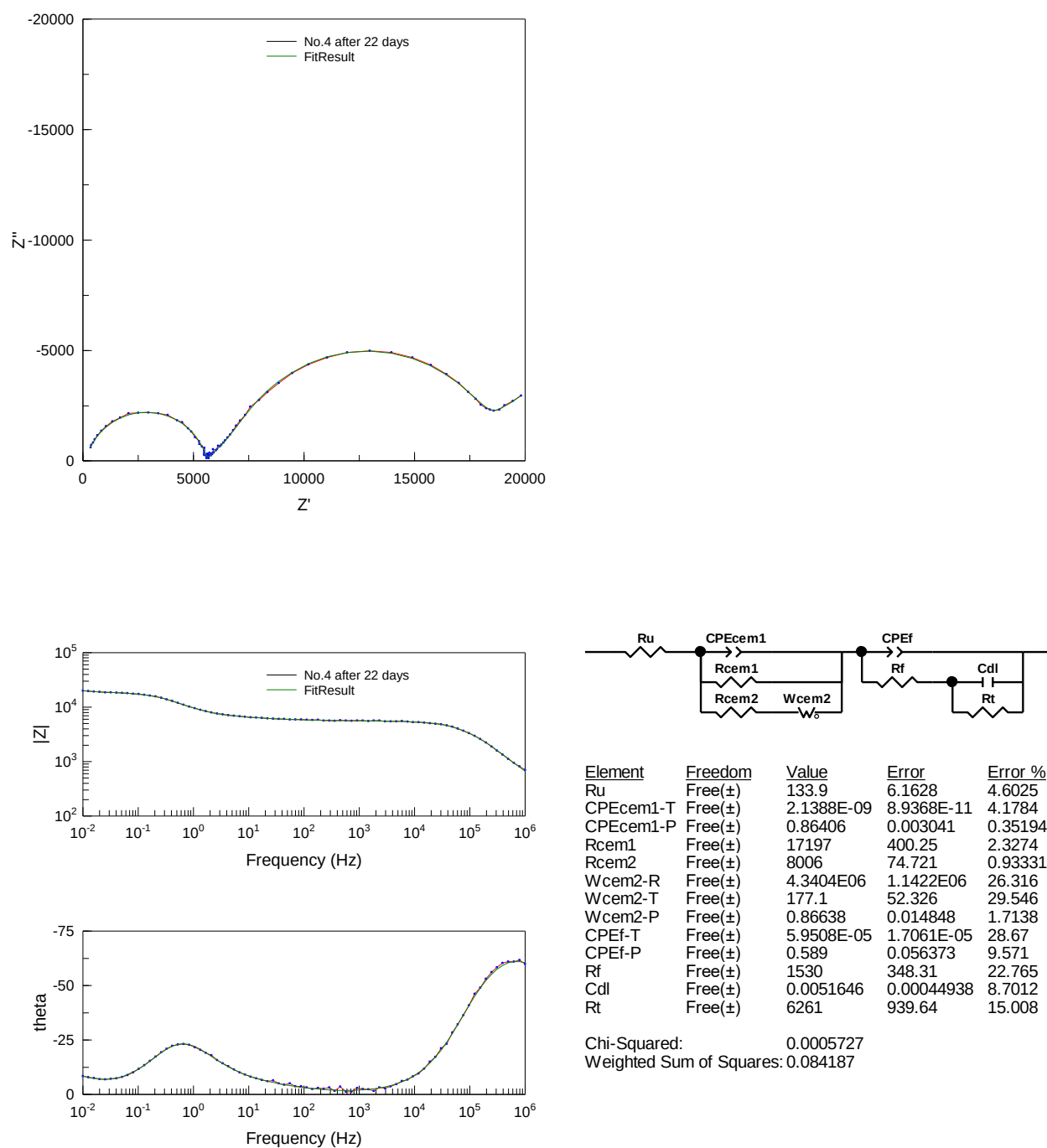
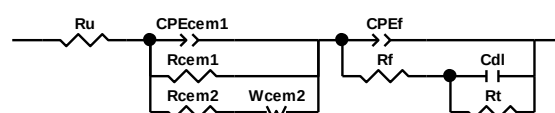
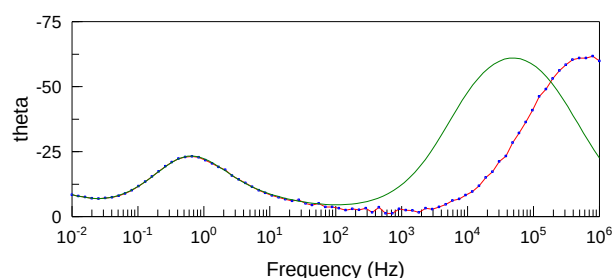
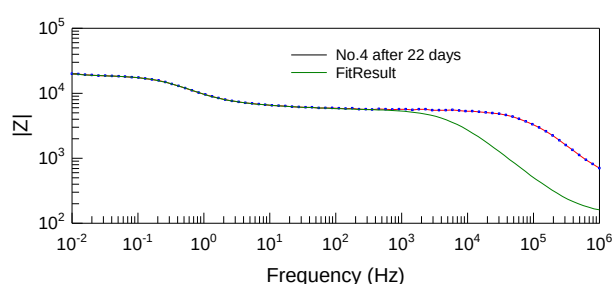
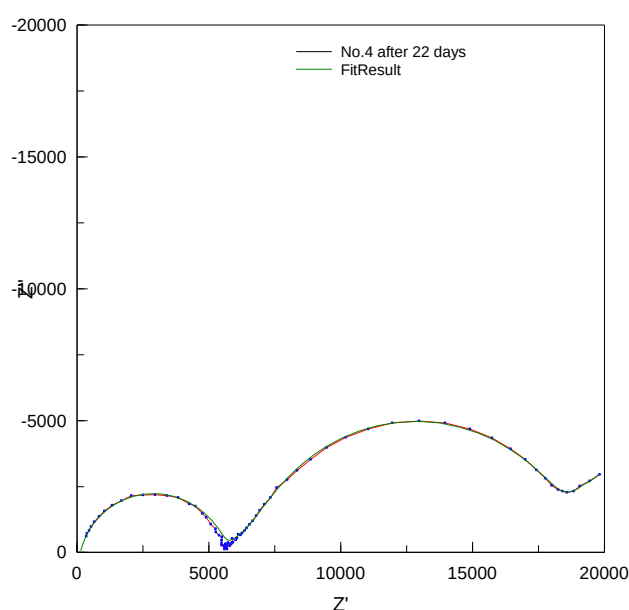


Figure A.44 EIS fitting results of an OPC sample after 22 days in condition 1.

Appendix

Afterwards, a simulation is performed with one parameter changed and other parameters fixed, the corresponding spectra are compared with the previous fitting spectra.

The change of CPE_{cem1} mainly affects the the first semicircle in the high frequency domain. When the $CPE_{cem1}-T$ decreases by ten times, the corresponding peak of the phase angle in the Bode plot shift left by about an order of magnitude (See Figure A.45).

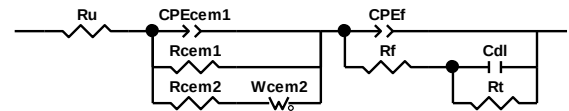
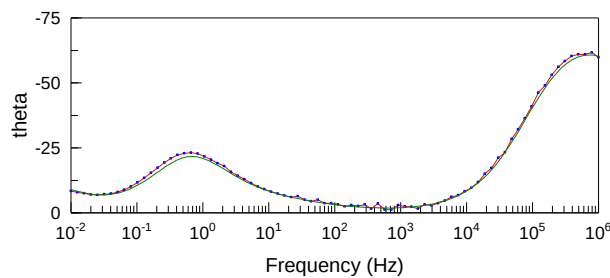
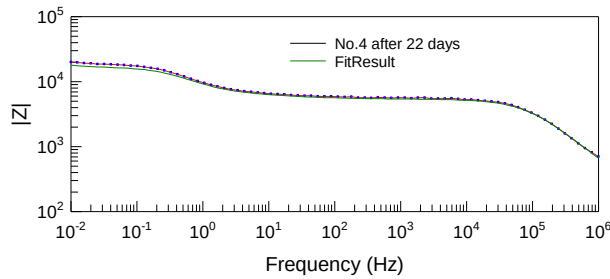
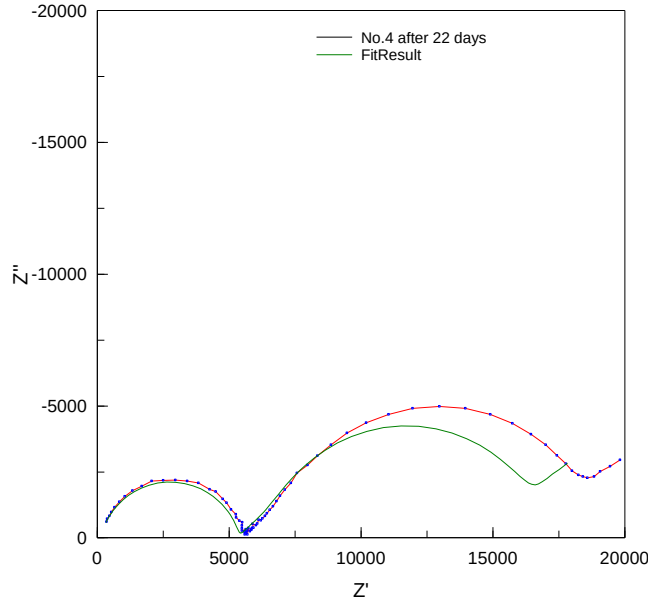


Element	Freedom	Value	Error	Error %
Ru	Free(±)	133.9	N/A	N/A
$CPE_{cem1}-T$	Free(±)	2.139E-08	N/A	N/A
$CPE_{cem1}-P$	Free(±)	0.86406	N/A	N/A
Rcem1	Free(±)	17197	N/A	N/A
Rcem2	Free(±)	8006	N/A	N/A
Wcem2-R	Free(±)	4.3404E06	N/A	N/A
Wcem2-T	Free(±)	177.1	N/A	N/A
Wcem2-P	Free(±)	0.86638	N/A	N/A
CPEf-T	Free(±)	5.9509E-05	N/A	N/A
CPEf-P	Free(±)	0.589	N/A	N/A
Rf	Free(±)	1530	N/A	N/A
Cdl	Free(±)	0.0051646	N/A	N/A
Rt	Free(±)	6261	N/A	N/A

Figure A.45 The simulation of EIS results of an OPC sample after 22 days in condition 1 with $CPE_{cem1}-T$ decreasing by ten times.

Appendix

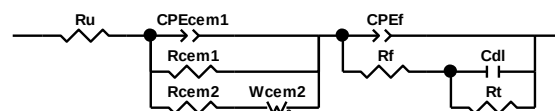
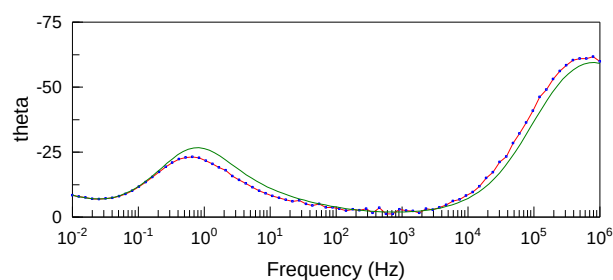
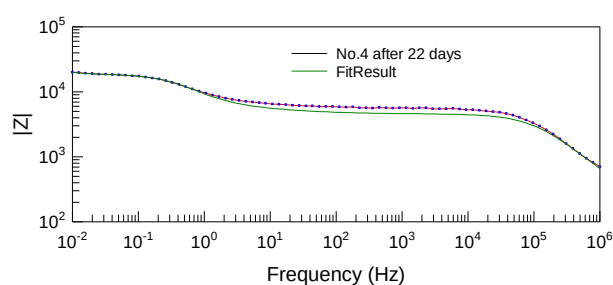
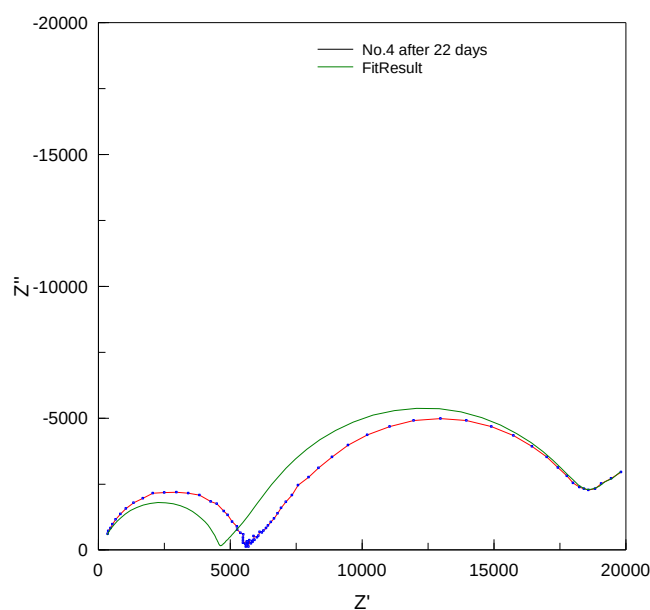
The simulation with a decrease of R_{cem1} by 2000Ω is provided in Figure A.46. The diameter of the intermediate semicircle in the ~ 1 Hz region decreases by about 2000Ω , indicating the link between the intermediate semicircle and R_{cem1} .



Element	Freedom	Value	Error	Error %
Ru	Free(±)	133.9	N/A	N/A
CPEcem1-T	Free(±)	2.1388E-09	N/A	N/A
CPEcem1-P	Free(±)	0.86406	N/A	N/A
Rcem1	Free(±)	15197	N/A	N/A
Rcem2	Free(±)	8006	N/A	N/A
Wcem2-R	Free(±)	4.3404E06	N/A	N/A
Wcem2-T	Free(±)	177.1	N/A	N/A
Wcem2-P	Free(±)	0.86638	N/A	N/A
CPEf-T	Free(±)	5.9509E-05	N/A	N/A
CPEf-P	Free(±)	0.589	N/A	N/A
Rf	Free(±)	1530	N/A	N/A
Cdl	Free(±)	0.0051646	N/A	N/A
Rt	Free(±)	6261	N/A	N/A

Figure A.46 Simulation of EIS results of an OPC sample after 22 days in condition 1 with R_{cem1} decreasing by 2000Ω .

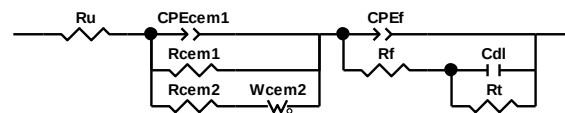
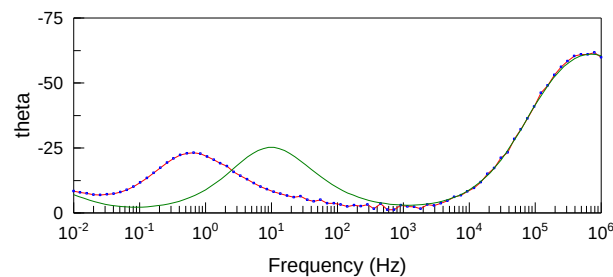
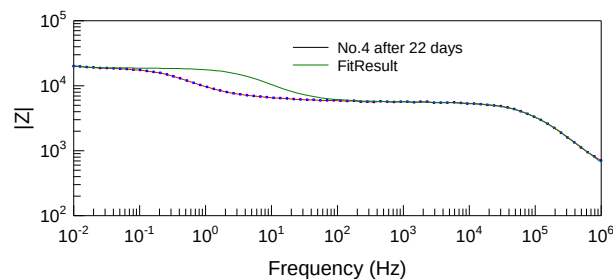
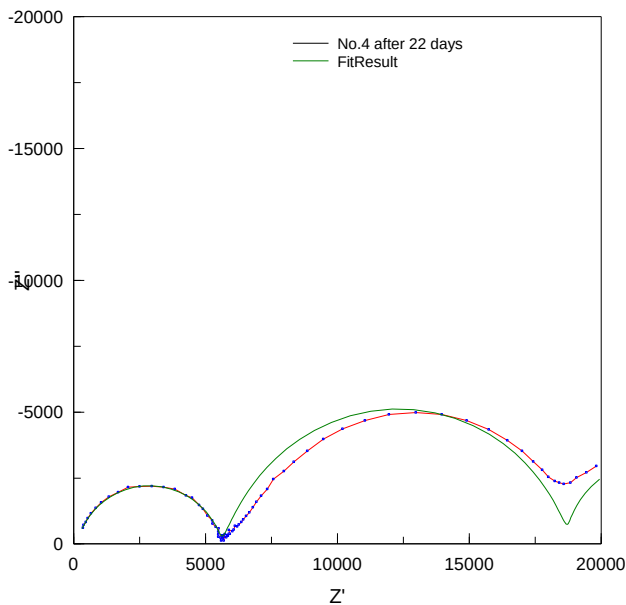
The change of R_{cem2} brings about the variations of the first semicircle in the high frequency domain and the intermediate semicircle. As Figure A.47 shows, a decrease of R_{cem2} by 2000Ω leads to the decrease of the first semicircle by 1000Ω and the increase of the intermediate semicircle.



Element	Freedom	Value	Error	Error %
Ru	Free(±)	133.9	N/A	N/A
CPEcem1-T	Free(±)	2.1388E-09	N/A	N/A
CPEcem1-P	Free(±)	0.86406	N/A	N/A
Rcem1	Free(±)	17197	N/A	N/A
Rcem2	Free(±)	6006	N/A	N/A
Wcem2-R	Free(±)	4.3404E06	N/A	N/A
Wcem2-T	Free(±)	177.1	N/A	N/A
Wcem2-P	Free(±)	0.86638	N/A	N/A
CPEf-T	Free(±)	5.9509E-05	N/A	N/A
CPEf-P	Free(±)	0.589	N/A	N/A
Rf	Free(±)	1530	N/A	N/A
Cdl	Free(±)	0.0051646	N/A	N/A
Rt	Free(±)	6261	N/A	N/A

Figure A.47 Simulation of EIS results of an OPC sample after 22 days in condition 1 with R_{cem2} decreasing by 2000 Ω .

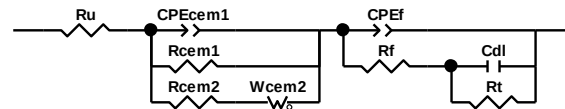
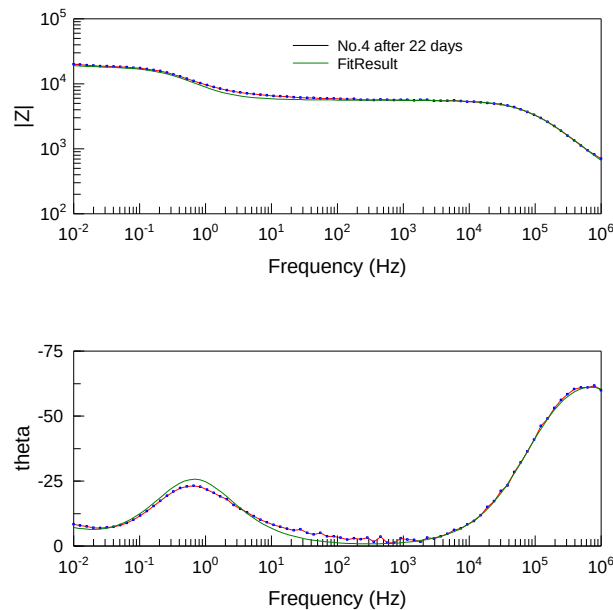
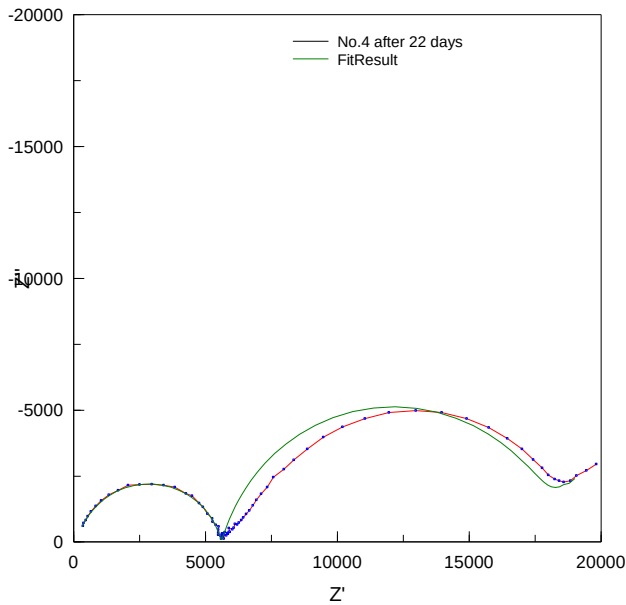
The electrochemical responses of W_{cem2} are related to the intermediate semicircle. For example, if the W_{cem2} -R increases by ten times, the corresponding peak of the phase angle in the Bode plot moves right by one order of magnitude as shown in Figure A.48.



Element	Freedom	Value	Error	Error %
Ru	Free(±)	133.9	N/A	N/A
CPEcem1-T	Free(±)	2.139E-09	N/A	N/A
CPEcem1-P	Free(±)	0.86406	N/A	N/A
Rcem1	Free(±)	17197	N/A	N/A
Rcem2	Free(±)	8006	N/A	N/A
Wcem2-R	Free(±)	4.3404E07	N/A	N/A
Wcem2-T	Free(±)	177.1	N/A	N/A
Wcem2-P	Free(±)	0.86638	N/A	N/A
CPEf-T	Free(±)	5.9509E-05	N/A	N/A
CPEf-P	Free(±)	0.589	N/A	N/A
Rf	Free(±)	1530	N/A	N/A
Cdl	Free(±)	0.0051646	N/A	N/A
Rt	Free(±)	6261	N/A	N/A

Figure A.48 Simulation of EIS results of an OPC sample after 22 days in condition 1 with W_{cem2-R} increasing by an order of magnitude.

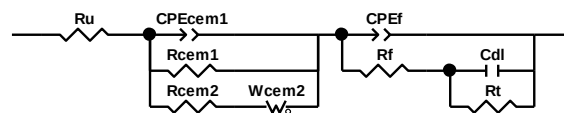
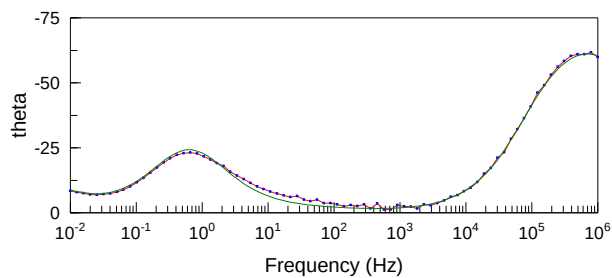
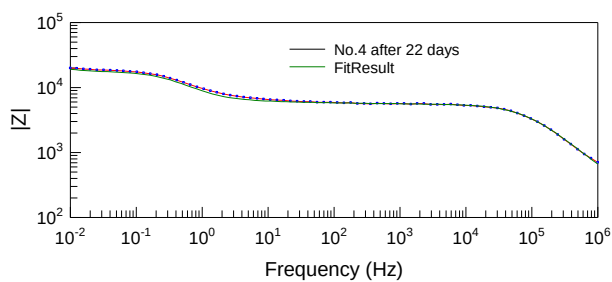
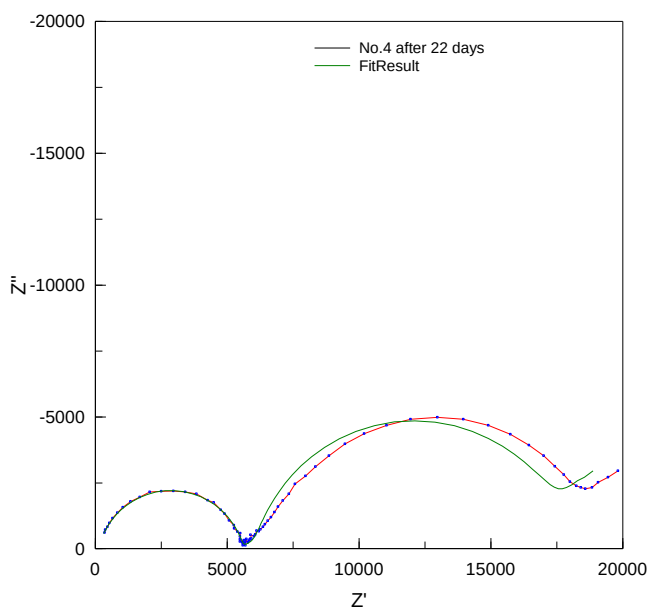
The variation of CPE_f is also associated with the intermediate semicircle. An example is provided in Figure A.49, in which the parts representing the intermediate semicircle change significantly in the Nyquist and Bode plots, when CPE_f-T increases by an order of magnitude.



Element	Freedom	Value	Error	Error %
Ru	Free(±)	133.9	N/A	N/A
CPEcem1-T	Free(±)	2.139E-09	N/A	N/A
CPEcem1-P	Free(±)	0.86406	N/A	N/A
Rcem1	Free(±)	17197	N/A	N/A
Rcem2	Free(±)	8006	N/A	N/A
Wcem2-R	Free(±)	4.3404E06	N/A	N/A
Wcem2-T	Free(±)	177.1	N/A	N/A
Wcem2-P	Free(±)	0.86638	N/A	N/A
CPEf-T	Free(±)	0.00059509	N/A	N/A
CPEf-P	Free(±)	0.589	N/A	N/A
Rf	Free(±)	1530	N/A	N/A
Cdl	Free(±)	0.0051646	N/A	N/A
Rt	Free(±)	6261	N/A	N/A

Figure A.49 Simulation of EIS results of an OPC sample after 22 days in condition 1 with CPE_{f-T} increasing by an order of magnitude.

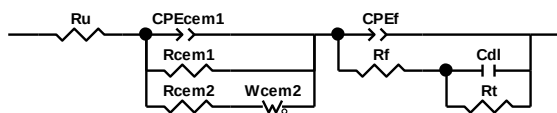
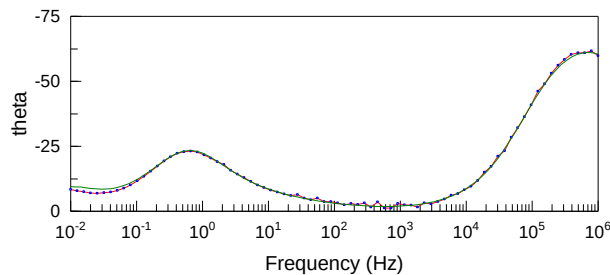
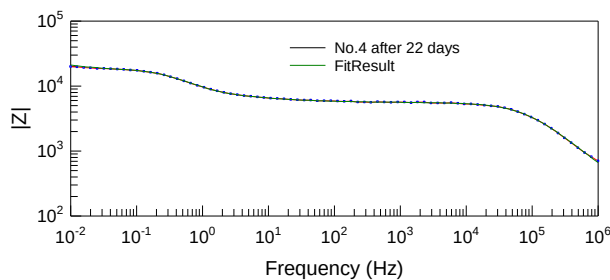
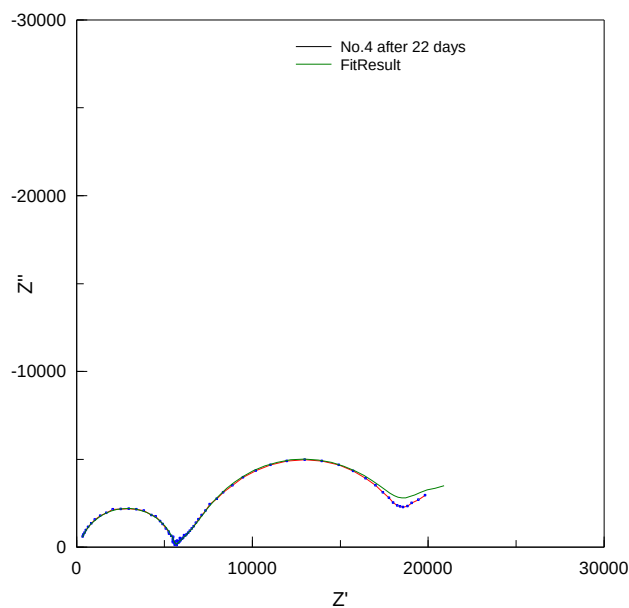
Figure A.50 indicates that the diameter of the intermediate semicircle decreases by about 1000 Ω, when R_f decreases by 1000 Ω.



Element	Freedom	Value	Error	Error %
Ru	Free(±)	133.9	N/A	N/A
CPEc1-T	Free(±)	2.1388E-09	N/A	N/A
CPEc1-P	Free(±)	0.86406	N/A	N/A
Rcem1	Free(±)	17197	N/A	N/A
Rcem2	Free(±)	8006	N/A	N/A
Wc2-R	Free(±)	4.3404E06	N/A	N/A
Wc2-T	Free(±)	177.1	N/A	N/A
Wc2-P	Free(±)	0.86638	N/A	N/A
CPEf-T	Free(±)	5.9509E-05	N/A	N/A
CPEf-P	Free(±)	0.589	N/A	N/A
Rf	Free(±)	530	N/A	N/A
Cdl	Free(±)	0.0051646	N/A	N/A
Rt	Free(±)	6261	N/A	N/A

Figure A.50 Simulation of EIS results of an OPC sample after 22 days in condition 1 with R_f decreasing by 1000 Ω .

The change of C_{dl} mainly affects the the arc at the low-frequency limit. When C_{dl} decreases by 0.002, the arc at the low-frequency limit changes (see Figure A.51).



Element	Freedom	Value	Error	Error %
Ru	Free(±)	133.9	N/A	N/A
CPEcem1-T	Free(±)	2.139E-09	N/A	N/A
CPEcem1-P	Free(±)	0.86406	N/A	N/A
Rcem1	Free(±)	17197	N/A	N/A
Rcem2	Free(±)	8006	N/A	N/A
Wcem2-R	Free(±)	4.3404E06	N/A	N/A
Wcem2-T	Free(±)	177.1	N/A	N/A
Wcem2-P	Free(±)	0.86638	N/A	N/A
CPEf-T	Free(±)	5.9509E-05	N/A	N/A
CPEf-P	Free(±)	0.589	N/A	N/A
Rf	Free(±)	1530	N/A	N/A
Cdl	Free(±)	0.0031646	N/A	N/A
Rt	Free(±)	6261	N/A	N/A

Figure A.51 Simulation of EIS results of an OPC sample after 22 days in condition 1 with C_{dl} decreasing by 0.002.

When R_t decreases by 2000 Ω , the diameter of the arc at the low-frequency limit seems to decreases as shown in Figure A.52.

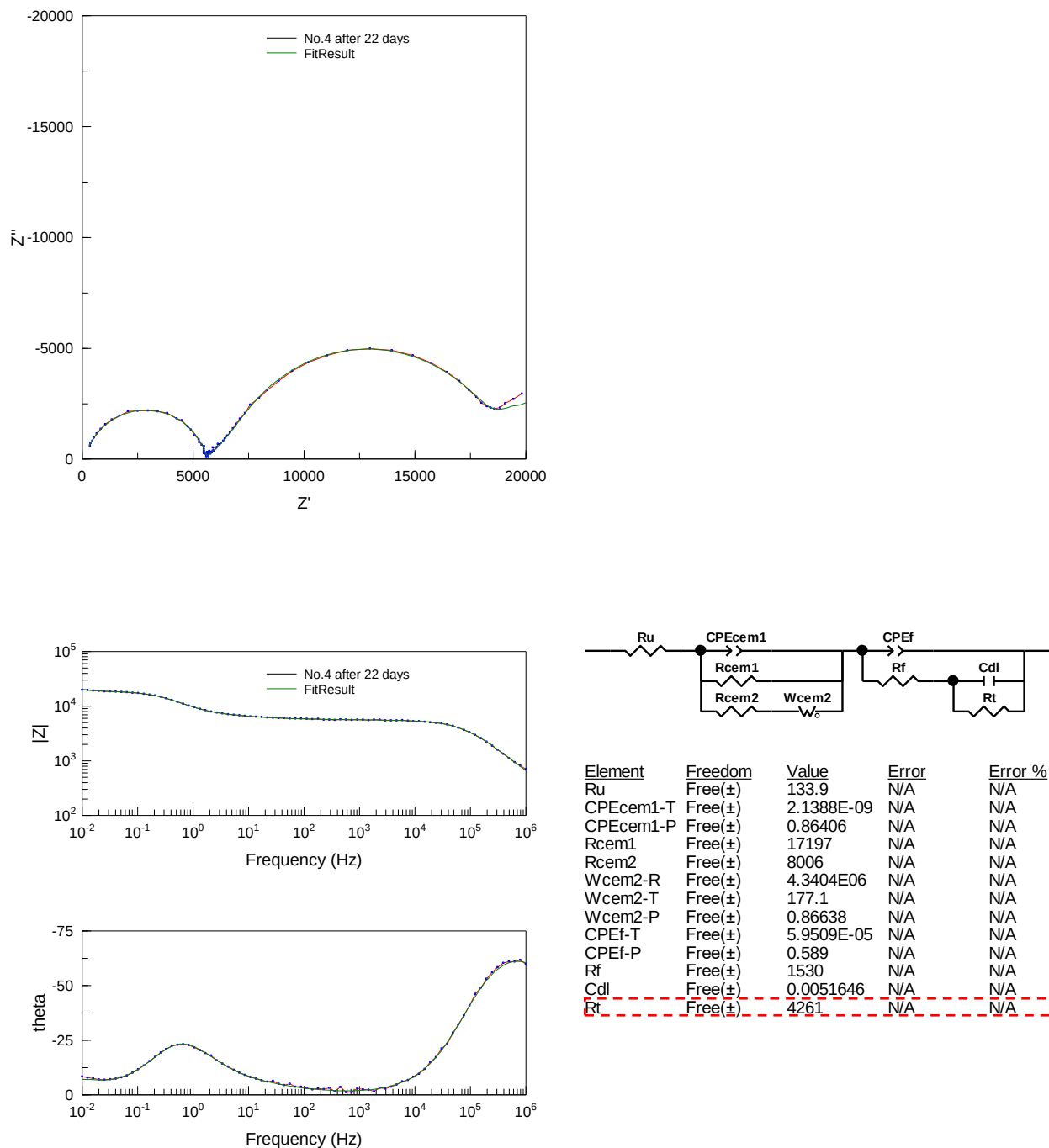


Figure A.52 Simulation of EIS results of an OPC sample after 22 days in condition 1 with R_t decreasing by 2000 Ω .

The other samples all have similar simulation results. In conclusion, due to the complexity of the system and the degradation of time constants, one arc or semicircle in the Nyquist plot probably corresponds to different parts of the system simultaneously. Generally, the responses of the cement paste part are mainly revealed in the higher frequency regions, while the responses of the interface are represented in the lower frequencies.

A.6. Uncertainty of the measurements

The average values and the error bars of data are added into some key figures to reveal the uncertainty of the measurements. Note that the error bars used here represent the standard deviation of data.

The R_t values obtained for the different samples, curing conditions and time are provided in Figure A.53 with the addition of the average values and the error bars, which are calculated from the triplicate samples. It should be noted that the Y-axis uses the logarithmic scale in order to clearly reveal all the variations (because the values vary in a wide range, a linear scale possibly cannot show some tiny changes). Nevertheless, for OPC samples in condition 2, because of the generation of cracks in these samples, the triplicate samples show significant discrepancies and consequently lead to errors that can be larger than the value itself (for example $R_t = 1000 \pm 1200 \text{ ohm}\cdot\text{cm}^{-2}$) and they go until the X-axis (Figure A.53(b)). The same phenomenon also appears in the results of H_2 concentration obtained from GC (see in Figure A.54), when the three parallel samples have significantly different results. The thickness of corrosion product film measured from SEM is provided in Figure A.55, in which the average value and the error bars of each point are calculated from 12 thickness values obtained from different locations of the corrosion product film.

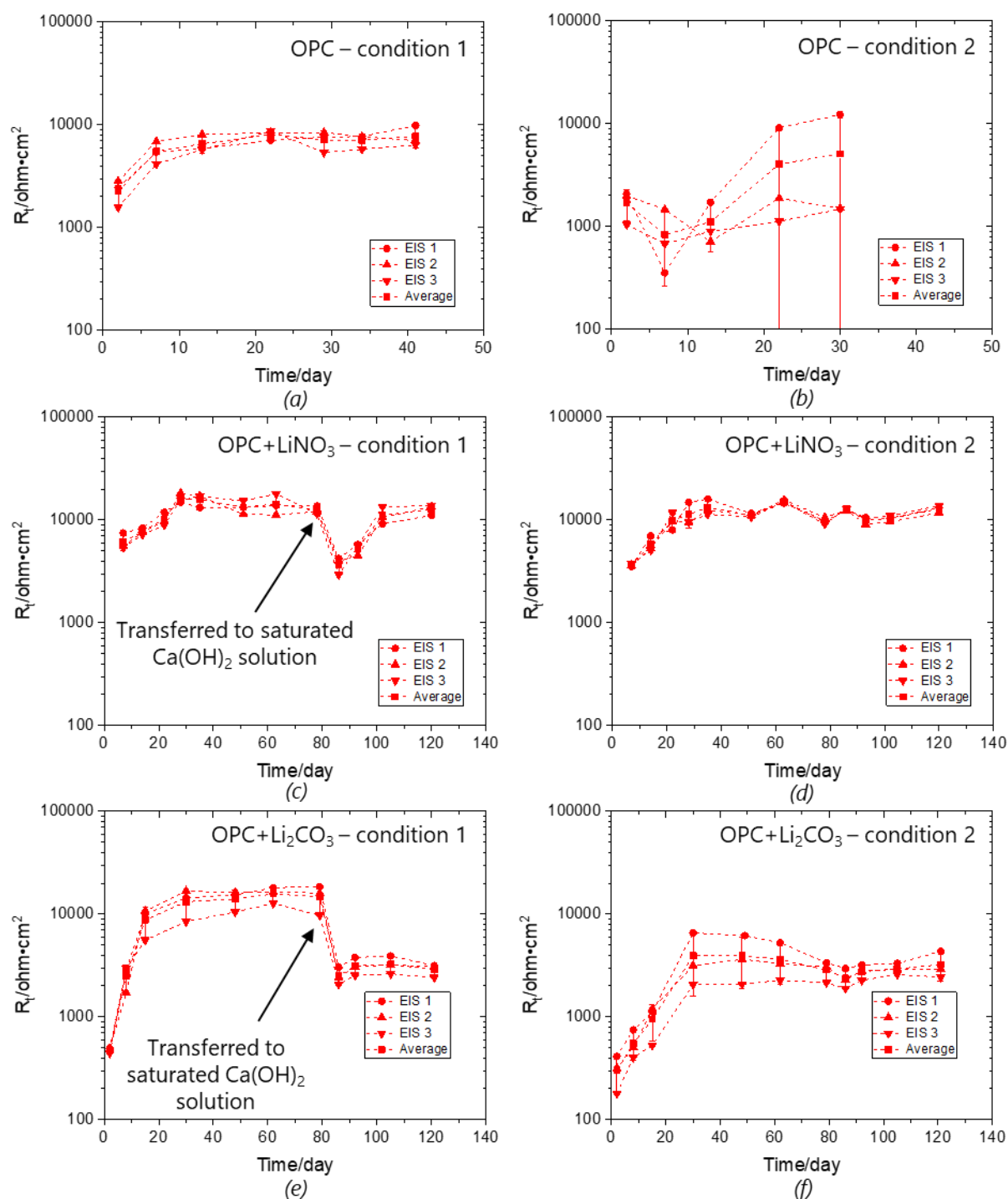


Figure A.53 Evolution of R_t (with the average values and the error bars) as a function of time of (a) OPC samples in condition 1, (b) OPC samples in condition 2, (c) OPC+LiNO₃ samples in condition 1, (d) OPC+LiNO₃ samples in condition 2, (e) OPC+Li₂CO₃ samples in condition 1, (f) OPC+Li₂CO₃ samples in condition 2.

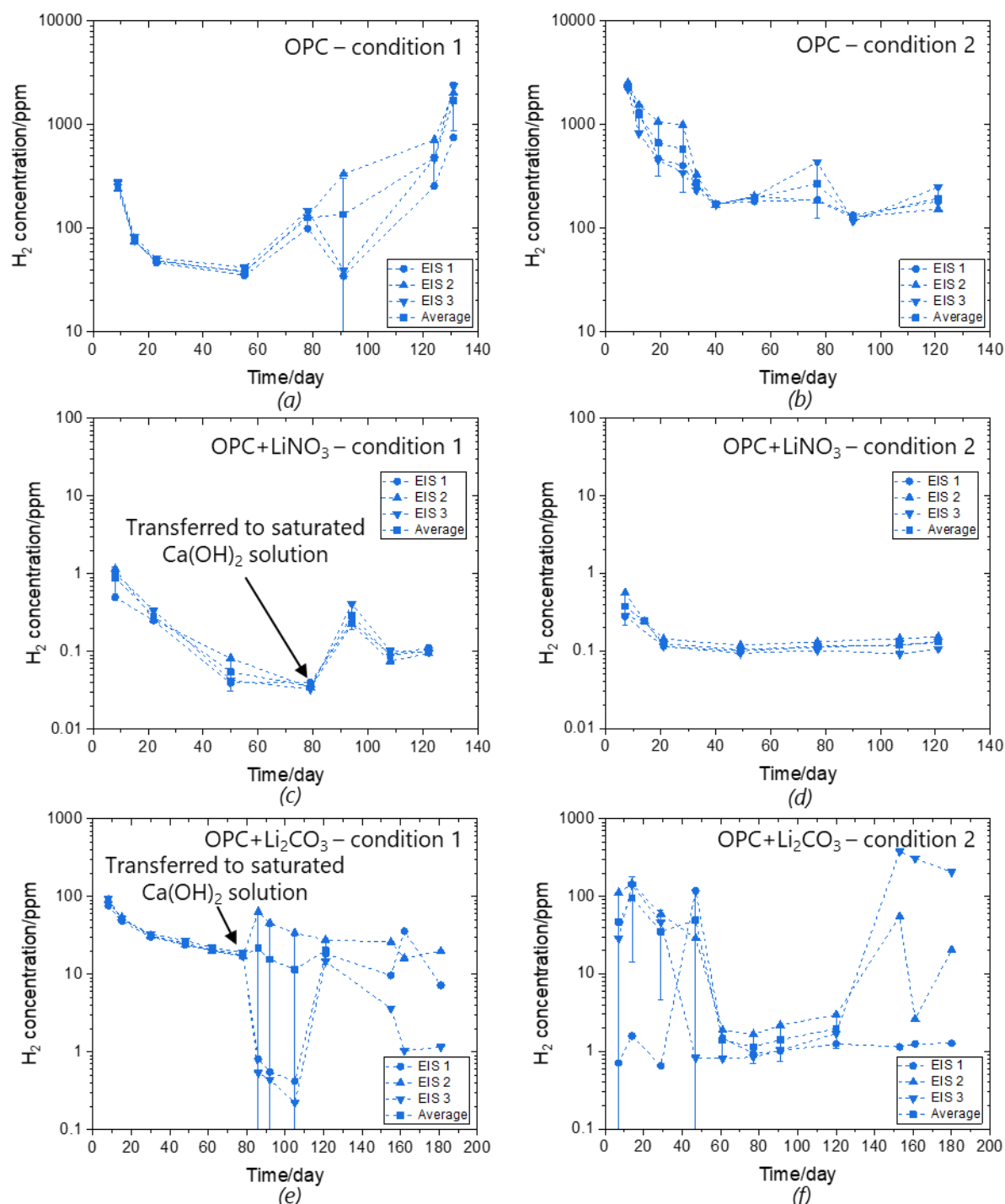


Figure A.54 Evolution of H_2 concentration (with the average values and the error bars) as a function of time of (a) OPC samples in condition 1, (b) OPC samples in condition 2, (c) OPC+LiNO₃ samples in condition 1, (d) OPC+LiNO₃ samples in condition 2, (e) OPC+Li₂CO₃ samples in condition 1, (f) OPC+Li₂CO₃ samples in condition 2.

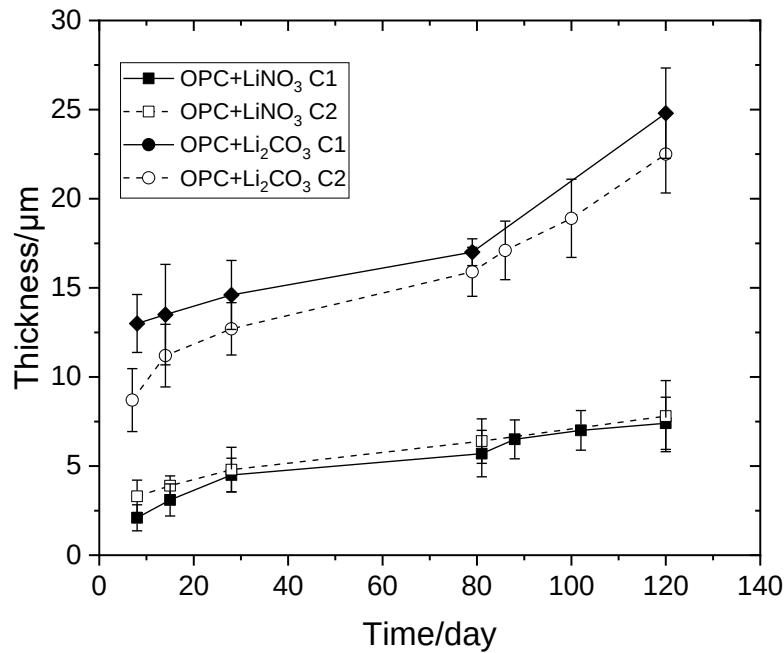


Figure A.55 Variation of the film thickness (with the average values and the error bars) as a function of time for OPC+LiNO₃ and OPC+Li₂CO₃ samples from SEM characterisation.

The average values and the error bars of the corrosion rates are shown in Figure A.56. For the results obtained from EIS and GC, the average values and the error bars determined from the triplication samples. For the results obtained from SEM, the average values and the error bars are calculated from 12 thickness values obtained from different locations of the corrosion product film. Some error bars of the corrosion rates obtained by SEM have values less than 0 and they go until the X-axis. Indeed, the thickness of the corrosion product film just shows a tiny error (see Figure A.55), the big errors of the corrosion rates obtained by SEM mainly come from the calculation process (the corrosion rate calculation uses Eq. (18) in Section 3.4). The standard deviation after the addition/subtraction operation of two random variables (the film thickness values at two times are regarded as two variables) is associated with their individual standard deviations and the covariance between them:

$$\sigma(X \pm Y) = \sqrt{\text{var}(X) + \text{var}(Y) \pm 2\text{cov}(X, Y)}, \quad (26)$$

where $\text{var}(X)$ and $\text{var}(Y)$ are the variances of the two variables, $\text{cov}(X, Y)$ is the covariance between them. As shown by the equation, the standard deviation after the operation could be larger than that of each variable. Besides, 12 parallel data are used for the calculation of the film thickness (variable) in order to obtain the representative average result. However, the large number of data also lead to the big variances and covariances, increasing the final standard deviation.

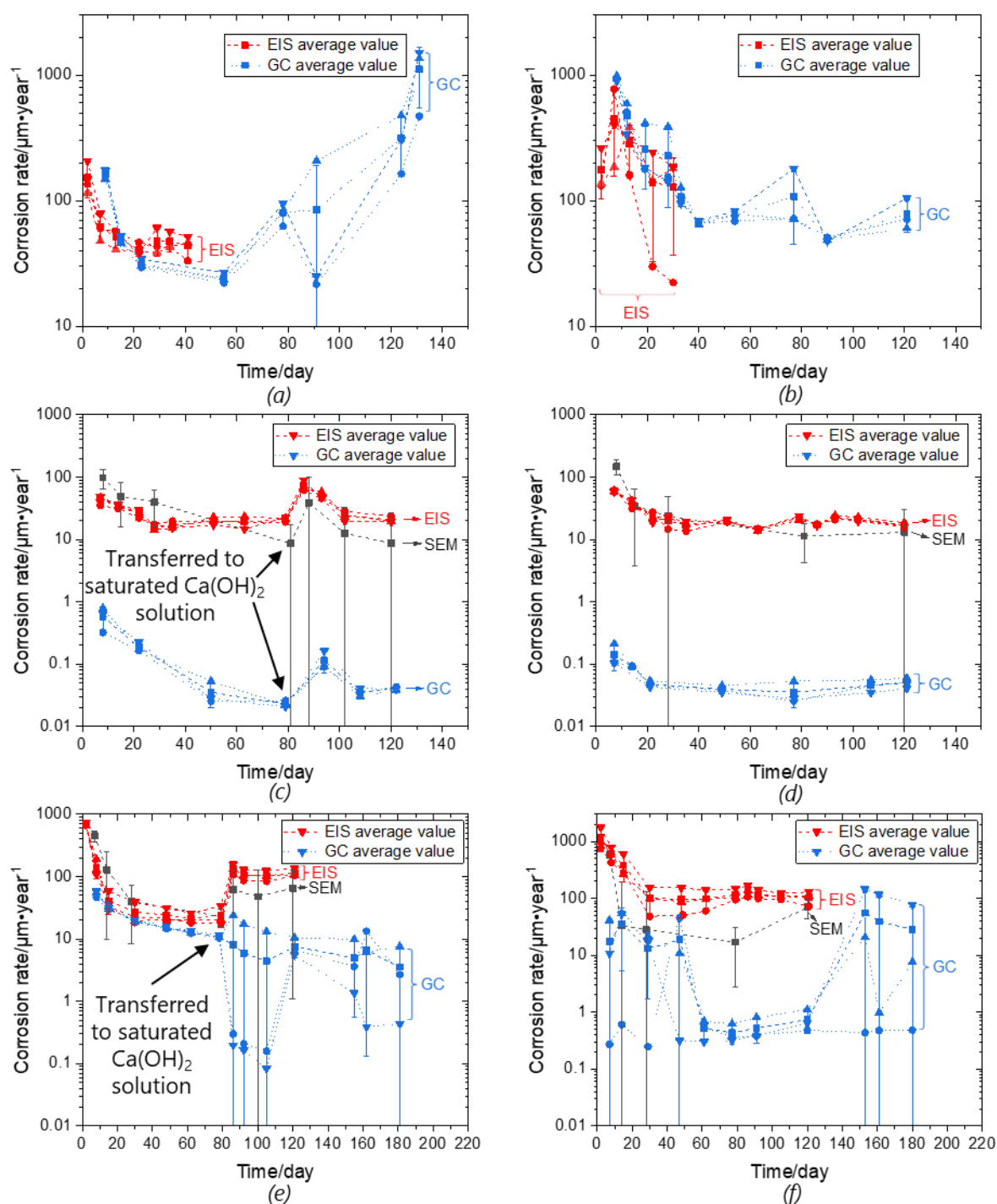


Figure A.56 Evolution of corrosion rates (with the average values and the error bars) as a function of time of (a) OPC samples in condition 1, (b) OPC samples in condition 2, (c) OPC+LiNO₃ samples in condition 1, (d) OPC+LiNO₃ samples in condition 2, (e) OPC+Li₂CO₃ samples in condition 1, (f) OPC+Li₂CO₃ samples in condition 2.

Appendix

The R_f values obtained for the different samples, curing conditions and time are provided in Figure A.57 with the addition of the average values and the error bars, which are calculated from the triplicate samples. Like the R_t results, the average values comply with the ones of the triplicate samples and the error bars are small, except the OPC samples in condition 2.

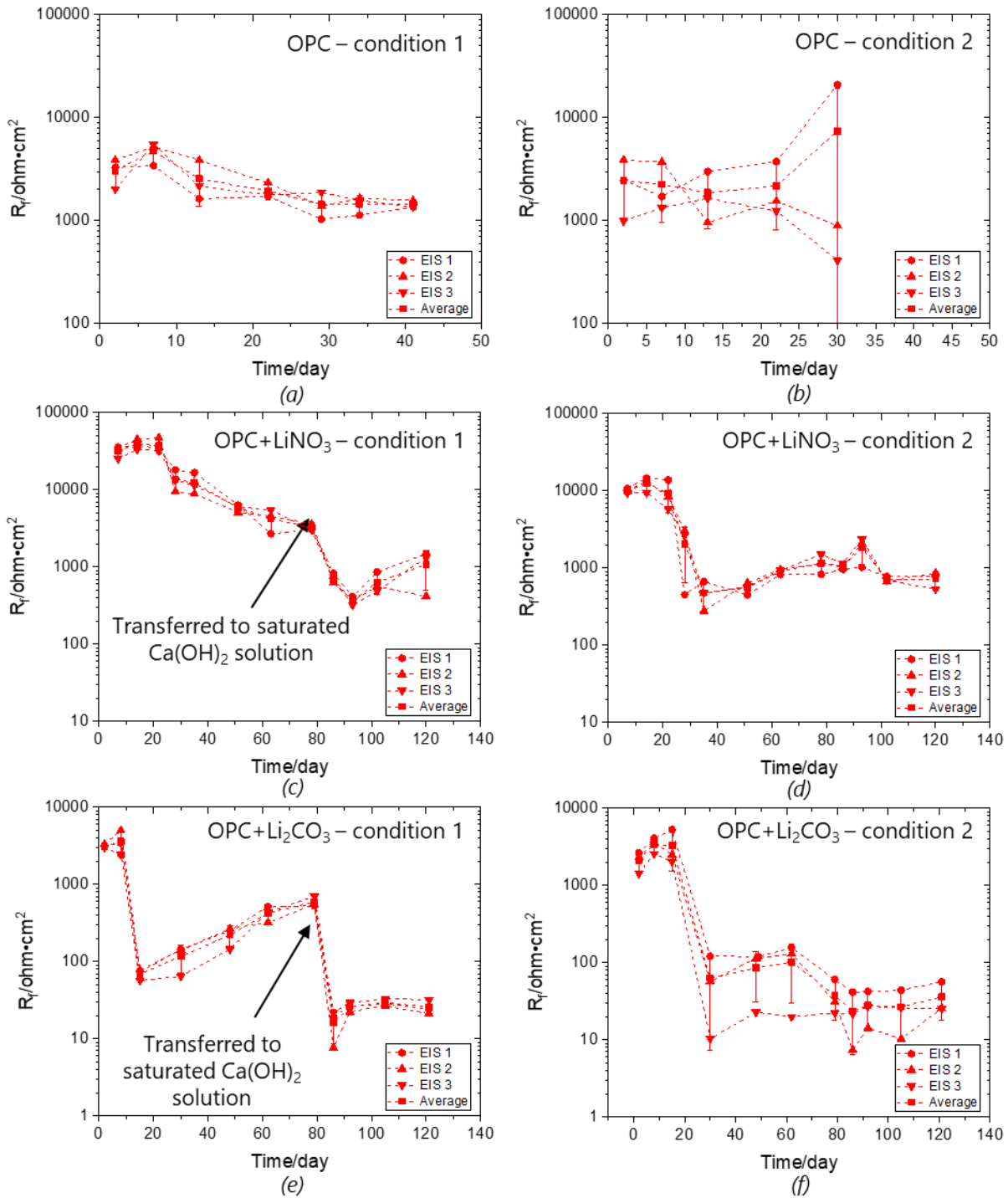


Figure A.57 Evolution of R_f (with the average values and the error bars) as a function of time of (a) OPC samples in condition 1, (b) OPC samples in condition 2, (c) OPC+LiNO₃ samples in condition 1, (d) OPC+LiNO₃ samples in condition 2, (e) OPC+Li₂CO₃ samples in condition 1, (f) OPC+Li₂CO₃ samples in condition 2.

Appendix

The R_{cem1} values obtained for the different samples, curing conditions and time are provided in Figure A.58 with the addition of the average values and the error bars, which are calculated from the triplicate samples. The average values comply with the ones of the triplicate samples and the error bars are small, except the OPC samples in condition 2.

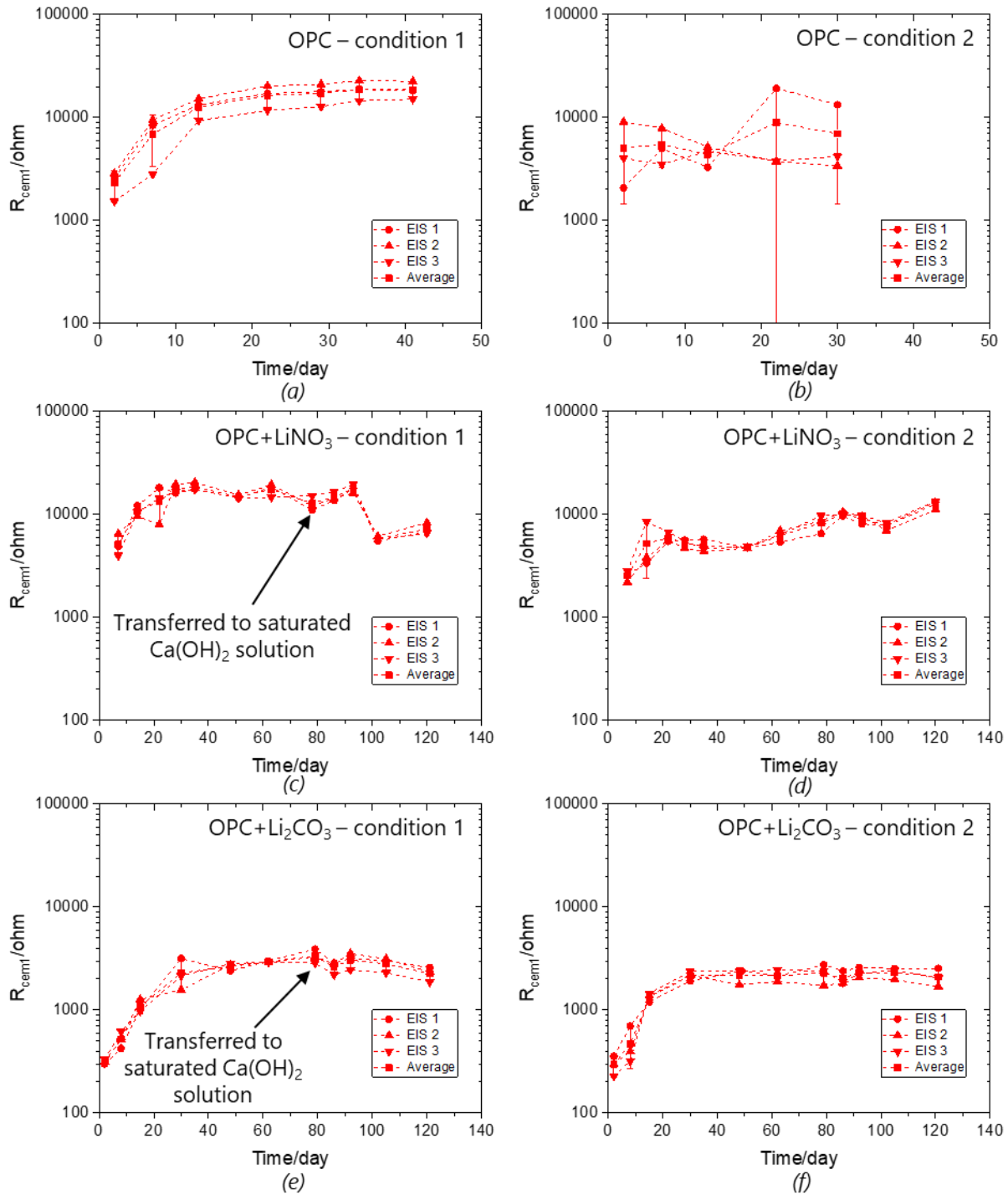


Figure A.58 Evolution of R_{cem1} (with the average values and the error bars) as a function of time of (a) OPC samples in condition 1, (b) OPC samples in condition 2, (c) OPC+LiNO₃ samples in condition 1, (d) OPC+LiNO₃ samples in condition 2, (e) OPC+Li₂CO₃ samples in condition 1, (f) OPC+Li₂CO₃ samples in condition 2.

Appendix

The average porosity values and the error bars are added into the porosity results as shown in Figure A.59. For the results determined from EIS, the average values and the error bars are calculated from the triplicate samples. For the results determined from MIP, because only one sample is used for each measurement, 12.5% is adopted as the standard deviation for all the results. According to Rubner et al. [346], the standard deviation of porosity measurements on cementitious mortars using MIP ranges from 7.5% to 23.75%, providing an average value of about 12.5%.

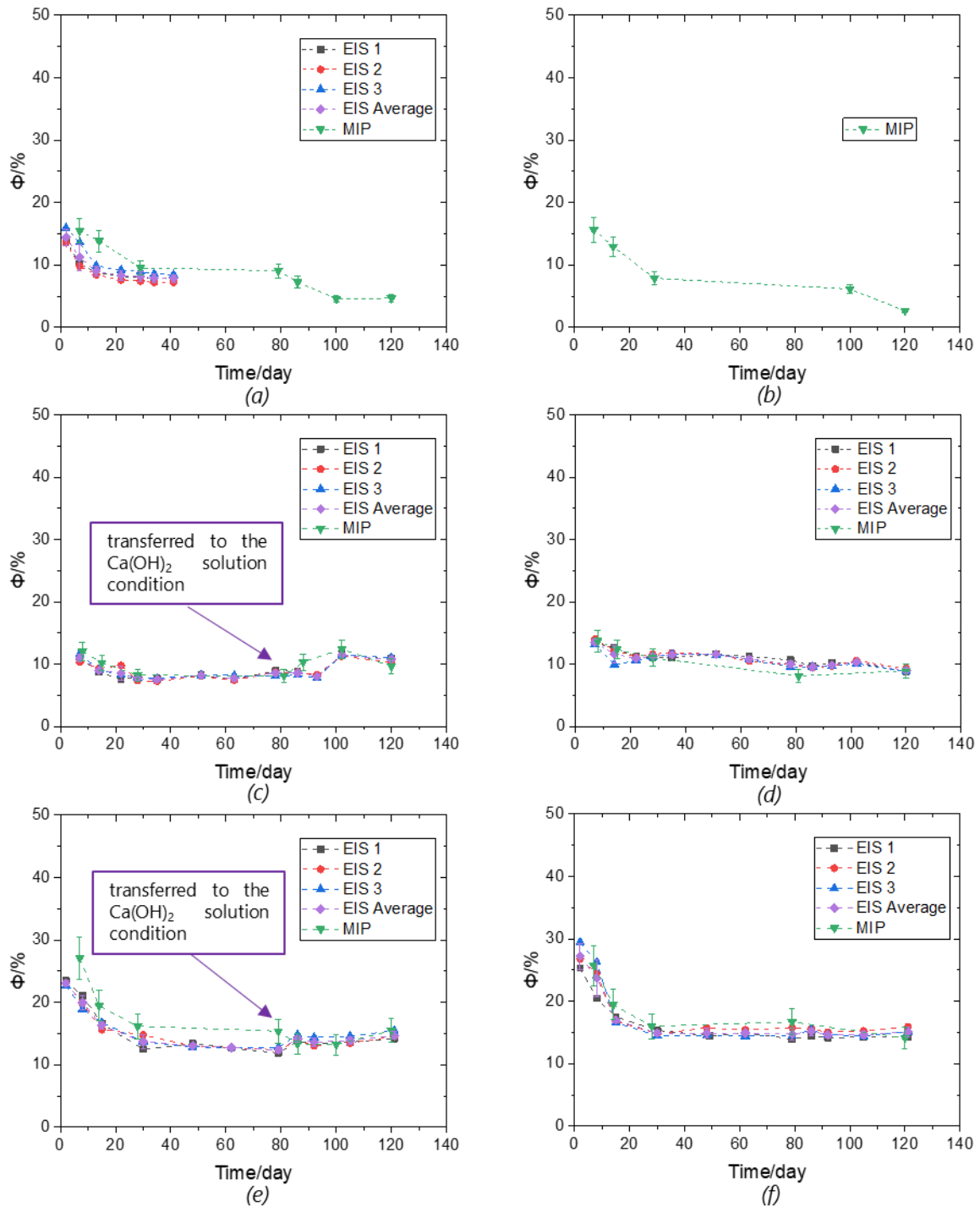


Figure A.59 Variation of the porosity (with the average values and the error bars) as a function of time measured by EIS and MIP of (a) 0.36 OPC samples in condition 1, (b) OPC samples in condition 2, (c) OPC+LiNO₃ samples in condition 1, (d) OPC+LiNO₃ samples in condition 2, (e) OPC+Li₂CO₃ samples in condition 1, (f) OPC+Li₂CO₃ samples in condition 2.

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