

A pH Buffer Additive for Aqueous Processing of Spinel and Layered Li-Ion Positive Electrodes

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Aqueous processing of cathodes offers a lower-cost, greener alternative to poly(vinylidene fluoride)/N-methyl-2-pyrrolidone routes, but contact with water elevates slurry pH and drives metal leaching, causing Al current-collector corrosion and electrode voids. Strong acids (e.g., H_3PO_4) can curb corrosion yet often disrupt rheology, increase leaching, and weaken adhesion. Herein, lithium dihydrogen phosphate (LiH_2PO_4) is introduced as a lithium-containing pH buffer ($\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ near-neutral pH) for water-based processing of $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (NMC622) and $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{1.45}\text{Al}_{0.05}]\text{O}_4$ (LNMO). Slurry pH evolution and

transition-metal dissolution under H_3PO_4 versus LiH_2PO_4 dosing are quantified and showing that LiH_2PO_4 more effectively stabilizes pH and suppresses leaching. Electrodes cast with LiH_2PO_4 additives display reduced Al pitting, crack-free coatings with good adhesion, and improved cycling stability. X-ray photoelectron spectroscopy detects surface phosphorus species consistent with a thin phosphate passivation layer. These results establish LiH_2PO_4 as a simple, scalable additive that enables robust aqueous processing of high-voltage cathodes without the side effects associated with strong acids.

1. Introduction

Efforts to increase the energy density of lithium-ion batteries (LIBs) are accelerating across academia and industry. LIB positive electrodes are composite films comprising active material, conductive carbon, and a polymeric binder; within this architecture, the cathode (positive electrode) plays a central role in delivering high performance. Accordingly, substantial research targets materials that simultaneously provide high power, safety, long cycle life, and cost-effectiveness.^[1–4] Among layered oxides, $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (NMC622) has attracted particular interest because it combines high-voltage operation (>4.3 V vs. Li/Li^+), specific capacity > 180 mAh g^{-1} , good cycling stability, favorable Li-ion diffusivity with weak temperature dependence, comparatively low cost, and a good safety profile.^[5–11] In parallel, the

high-voltage spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) is emerging as a compelling positive electrode for next-generation, high-energy LIBs owing to its very high working potential of 4.7 V versus Li/Li^+ , 147 mAh g^{-1} theoretical capacity, rapid Li-ion diffusion, excellent thermal stability, and cobalt-free composition.^[12–14]

Although the binder is not an electrochemically active component, it critically governs the mechanical integrity, adhesion, porosity, and even the electrochemical response of composite electrodes. Poly(vinylidene fluoride) (PVDF) remains the most widely used binder.^[15–20] It is applied in both anodes and cathodes owing to its broad electrochemical stability and strong adhesion to active materials and current collectors.^[15,18,19,21,22] However, PVDF processing involves dissolution in N-methyl-2-pyrrolidone (NMP); this polar organic solvent is effective for processing but raises safety, environmental, and cost concerns.^[17,20,23,24] These considerations have intensified efforts to adopt nontoxic binders and aqueous processing routes.

Water processing route, however, introduces its own challenges. Upon contact with water, many cathode materials generate surface hydroxide species and drive an increase in the slurry pH.^[15,25–27] Elevated pH accelerates aluminum current-collector corrosion with H_2 evolution, promotes electrode detachment, and leads to unwanted surface impurities or voids in the coating.^[20,28] A common mitigation strategy is acidification, with for example phosphoric acid (PA) being widely used, to lower pH and suppress corrosion.^[20,25,29] However, strong-acid dosing can disrupt slurry rheology, decrease electrode conductivity, increase Li and transition-metal leaching, and weaken adhesion.^[25,29] These trade-offs motivate the use of lithium-containing pH buffers that moderate slurry chemistry without the adverse side effects associated with strong acids.

In this study, we examine aqueous processing of LNMO and NMC622 cathodes. First, we assess the stability of the

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active-material powders in water by tracking pH evolution over time and metals leaching. Then, we modulate the slurry chemistry using PA (H_3PO_4) and lithium dihydrogen phosphate (LiH_2PO_4) for also comparative analysis. To our knowledge, this is the first use of LiH_2PO_4 as an additive for water-based cathode processing. Leveraging the $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ couple near-neutral pH (with Li^+ as the counter-ion), LiH_2PO_4 provides a better pH control and reduced metal dissolution compared with H_3PO_4 . We then process aqueous LNMO and NMC622 electrodes with and without LiH_2PO_4 and evaluate coating morphology, adhesion, Al corrosion, and electrochemical performance. The use of LiH_2PO_4 additive proves beneficial for NMC622, delivering improved film integrity and cycling stability, whereas it is found to be partially detrimental for LNMO, leading to degraded electrochemical performance; these contrasting outcomes are analyzed and discussed.

2. Experimental Section

2.1. Electrode Fabrication

Aqueous cathodes, prepared with and without additives, used Al-doped $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (Johnson Matthey, referred to as LNMO), and $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (NMC622; Xiamen TOB New Energy Technology) as the active material. All powders were stored in an argon-filled glovebox (MBraun; <0.1 ppm O_2 and H_2O) prior to use. Dispersions were prepared with deionized water purified to $18\text{ M}\Omega\text{ cm}^{-1}$ (Milli-Q Direct 8). This approach maintains strict control over moisture and ionic contamination during handling while ensuring consistent water quality for slurry preparation.

For slurry preparation protocol without additive (Figure 1A), a 1.6 wt% sodium carboxymethyl cellulose (CMC) (Nippon Paper

Chemicals) solution was first prepared by dissolving CMC in Milli-Q water using low-energy ball milling. The active material (LNMO or NMC622) and carbon black SC45 (Imerys) were then incorporated into the binder solution and mixed by low-energy ball milling; additional Milli-Q water was added as needed to adjust viscosity and ensure uniform dispersion. Finally, a TRD202A aqueous dispersion (JSR) was introduced and mixing continued for 2 h. The dried-electrode composition was 90 wt% active material (LNMO or NMC622), 5 wt% SC45, 4 wt% TRD202A, and 1 wt% CMC. For slurries prepared with additive (Figure 1B), the same protocol was followed except that 1 wt% LiH_2PO_4 (Sigma-Aldrich) was added at the start of slurry preparation, before CMC. The corresponding dried-electrode composition was 89 wt% active material (LNMO or NMC622), 5 wt% SC45, 4 wt% TRD202A, 1 wt% CMC, and 1 wt% LiH_2PO_4 . All slurries were doctor-bladed onto aluminum current collectors using a $300\text{ }\mu\text{m}$ gap, dried at room temperature for 1 h and then at $110\text{ }^\circ\text{C}$ for 12 h. The typical mass loading was $\approx 20\text{ mg cm}^{-2}$. Before electrochemical testing, electrodes were pressed at 3 t for 2 min and vacuum-dried at $110\text{ }^\circ\text{C}$ for 12 h.

2.2. Cell Assembly

Electrochemical tests used two-electrode CR2032 cells (SS316 hardware) with lithium metal as counter/pseudo-reference, a single glass-fiber separator (Whatman GF/D), and 1.2 M LiPF_6 in ethylene carbonate/diethyl carbonate (EC/EMC) as electrolyte. Cells were cycled at constant current (C/10) between 3.0 and 4.9 V for LNMO and 2.8–4.4 V for NMC622, where C is the theoretical capacity of the cathode material (147 and 180 mAh g^{-1} for LNMO and NMC622, respectively).

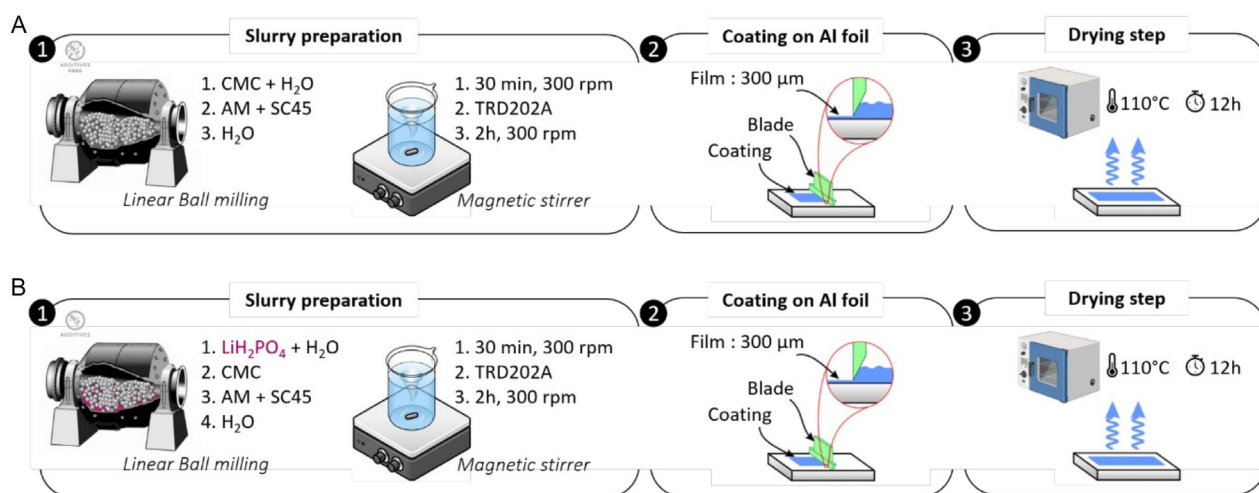


Figure 1. Water-based cathode processing workflow. A) Processing without additive: a 1.6 wt% CMC solution in Milli-Q water (low-energy ball milling) is first prepared, followed by the dispersion of active material (LNMO or NMC622) and carbon black (SC45), adjusting viscosity with water, and finally addition of TRD202A and mixing for another 2 h. B) With additive: identical sequence but with 1 wt% LiH_2PO_4 added at the beginning, prior to CMC. Slurries were blade-coated on Al foil with a $300\text{ }\mu\text{m}$ gap and dried at room temperature for 1 h followed by drying at $110\text{ }^\circ\text{C}$ for 12 h. Dried-electrode compositions: without additive 90:5:4:1 (AM:SC45:TRD202A:CMC); with additive 89:5:4:1:1 (AM:SC45:TRD202A:CMC: LiH_2PO_4).

2.3. pH and Leaching Experiments and Analysis

Dilute dispersions of LNMO and NMC were prepared with and without additives—PA (Acros Organics) or LiH_2PO_4 —at 1 g AM/1.5 mL H_2O /0.1 g additive. Dispersions were stirred in Milli-Q water at 300 rpm (magnetic stirring), and pH was recorded at regular intervals using a Fisherbrand accumet AE150 benchtop pH meter.

Leaching samples were prepared identically and left in water for 24 h. Solutions were first filtered through 0.4 and then 0.2 μm PTFE syringe filters, followed by centrifugation to separate solid and liquid phases. The supernatant was filtered again through a 0.2 μm PTFE filter and analyzed by inductively coupled plasma - optical emission spectroscopy (ICP-OES) (Avio 220 Max, Scott/Cross-Flow configuration) to determine Li, Ni, Mn, Al, and Co concentrations.

2.4. Physicochemical Characterization

Scanning electron microscopy (SEM) was used to examine the morphology of electrodes and pristine powders. Images were acquired on a Zeiss Auriga FIB-SEM. Samples for X-ray photoelectron spectroscopy (XPS) were prepared in an argon-filled glovebox and transferred in a sealed vessel directly docked to the ultrahigh-vacuum system to avoid air exposure. XPS was performed on a PHI 5000 VersaProbe II using an Al $K\alpha$ source ($h\nu = 1486.6$ eV). Spectra were calibrated by setting the low-binding-energy component of C 1s to 284.8 eV. Peak fitting and quantification were carried out in CasaXPS using Doniach–Sunjic line shapes convoluted with a Gaussian/Lorentzian distribution and a Shirley background.

3. Results and Discussion

3.1. pH and Metal Leaching Control

Cathode materials based on transition-metal oxides react with water, exchanging Li^+ for H^+ and forming surface hydroxide species,^[15,25–27] with the resulting alkaline medium corroding the aluminum current collector.^[17] In contrast, under acidic conditions Li and transition-metal dissolution is favored.^[30] It is therefore essential to assess the water stability of the pristine active material. Figure 2A shows a rapid rise in slurry pH immediately after adding LNMO or NMC622, followed by plateaus at 10.8 and 12.3, respectively, after about 90 min of exposure. This alkalization stems from heterogeneous Li^+/H^+ exchange at the particle surface: consumption of H^+ generates OH^- , which combines with Li^+ to form dissolved LiOH ; subsequent reaction of LiOH with atmospheric CO_2 yielding Li_2CO_3 .^[30] The high steady-state pH highlights the need for controlled buffering to limit Al corrosion and maintain reproducible aqueous processing.

The attained pH values in this work are similar to those reported by Bauer and al.,^[25] who obtained pH values of 10.3 and 12.3 for aqueous dispersions of LNMO and NMC622, respectively. Moreover, these results are in argument with Wood et al.,^[30] and Hawley et al.,^[31] who demonstrated that cathode active materials such as LiCoO_2 (LCO), LiFePO_4 (LFP), LiMn_2O_4 (LMO), $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA), and $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ (NMC532), dispersed in Milli-Q water exhibit alkaline pH value.^[30,31] We then quantified metal leaching in the supernatant after 24 h exposure of the powders to water (Figure 2B). Substantial Li was detected for both type of materials,

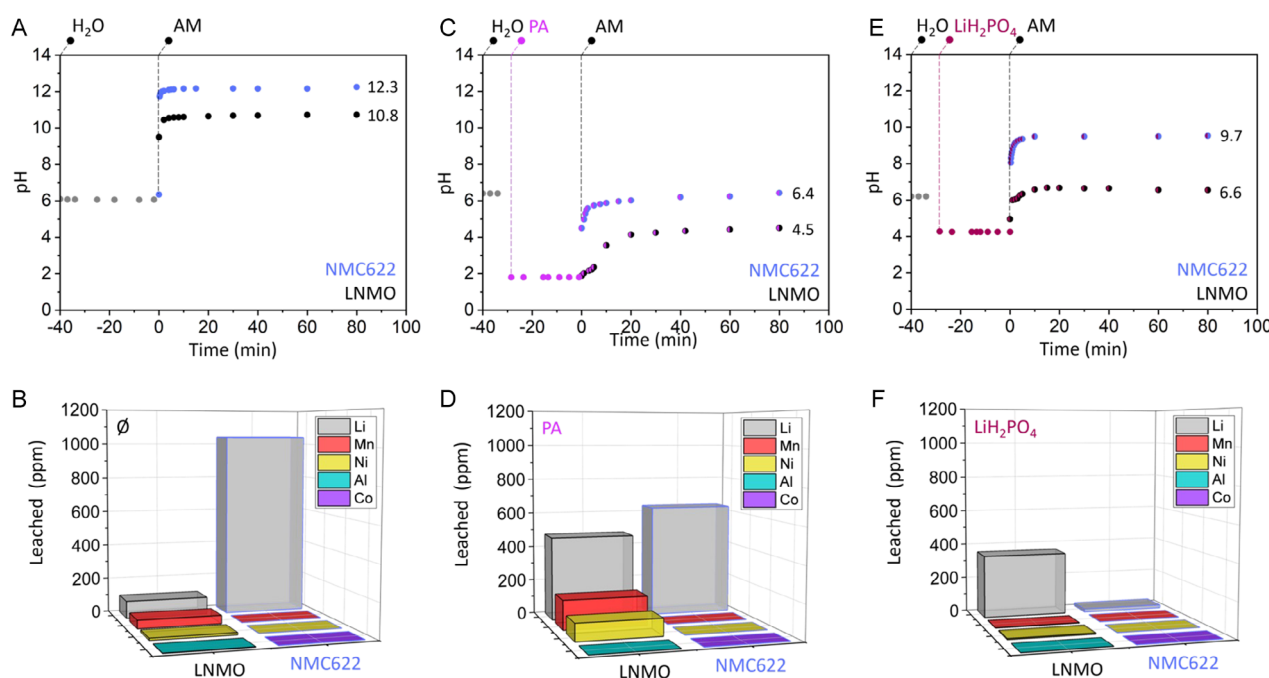


Figure 2. pH evolution and metal leaching in aqueous dispersions of LNMO and NMC622. A) pH versus time in Milli-Q water without additive; C) with phosphoric acid (H_3PO_4 , PA); E) with lithium dihydrogen phosphate (LiH_2PO_4). B,D,F) ICP-OES analysis of Li, Ni, Mn, Co, and Al in the supernatant after 24 h exposure for the corresponding conditions.

100 ppm for LNMO and 1041 ppm for NMC622, confirming spontaneous lithium release in water. For LNMO, additional transition metals were present (Mn 48 ppm, Ni 12 ppm, Al 2 ppm). In contrast, for NMC622, Mn, Ni, and Co were not detected. These data indicate distinct water–solid interactions: LNMO exhibits transition-metal dissolution alongside Li leaching, whereas NMC622 predominantly releases Li.

Hamam et al.^[32] investigated LiNiO_2 (LNO), $\text{LiNi}_{0.83}\text{Co}_{0.15}\text{Al}_{0.02}\text{O}_2$ (NCA), and $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ (NMC532) in acidic, neutral, and basic aqueous media and identified two pH-dependent reaction regimes. At high pH, Li^+/H^+ ion-exchange dominates: protons from solution intercalate while Li^+ deintercalates from the host lattice, with minor or no solid dissolution. At lower pH, ion exchange is minor but delithiation is accompanied by substantial transition-metal dissolution. The pH boundary between these regimes was found to depend on Ni content and particle morphology. Considering our data (Figure 2B), we infer that LNMO follows the delithiation–dissolution regime (presence of Mn and Ni in solution), whereas NMC622 undergoes predominantly Li^+/H^+ exchange with negligible transition-metal dissolution.

Recent studies have shown that slurry pH can be adjusted by adding acids, with primary purpose of mitigating aluminum corrosion.^[20,25,32–36] We therefore examined the effect of PA on pH (Figure 2C). The water pH decreased by ≈ 1.9 units upon PA addition; subsequent introduction of the active material led to stable pH values of 4.5 for LNMO and 6.4 for NMC622, indicating that PA curtails the pH rise observed in water alone. To evaluate whether PA is an appropriate additive, we next quantified metal leaching after 24 h (Figure 2D). For LNMO, Li 475, Mn 166, and Ni 98 ppm were detected. Relative to the no-additive case (Figure 2B; Li 100, Mn 48, Ni 12, Al 2 ppm), two features stand out: i) Al from the LNMO lattice was no longer detected, and ii) Li, Mn, and Ni leaching increased markedly upon PA addition. These trends suggest that, while PA suppresses Al release, it shifts LNMO toward the delithiation–dissolution regime at lower pH.^[32]

Building on the pH-control results in Figure 2C and the LNMO leaching trends in Figure 2D, we compared our observations with prior reports to place the PA effect in context. Bichon et al.^[37] showed that immersing NMC532 in H_2O –PA yields higher dissolved metal contents than immersion in pure water, while Loeffler et al.^[20] found that adding PA increases Li release from NMC333. These studies are consistent with the notion that acidification shifts layered oxides toward a delithiation–dissolution regime,^[32] even as it suppresses aluminum corrosion in slurry processing. For NMC622, however, our data reveal a distinct response: after 24 h in H_2O –PA system, only Li (623 ppm) was detected, with Mn, Ni, and Co remaining below our detection limits (Figure 2D). Moreover, Li content decreased relative to the additive-free case (Figure 2B, 1041 ppm). Thus, while delithiation remains operative, PA does not promote transition-metal dissolution in NMC622 and in fact reduces Li release under studied conditions. This contrasts with the trends reported for NMC333^[20] and NMC532.^[37]

To probe whether composition governs this divergence, we examined NMC111 and NMC811 (Figure S1, Supporting Information): PA increased Li in solution for NMC111, whereas,

analogous to NMC622 case, it decreased Li for NMC811. Taken together, these results indicate a compositional dependence in the PA response that correlates with Ni content (but also potentially surface impurities, or quality of NMC materials), consistent with the pH-dependent regime boundary mapped by Hamam et al.^[32] A plausible interpretation is that Ni-rich phases, under the mildly acidic conditions set by PA, remain largely in the Li^+/H^+ exchange window (limited transition-metal dissolution) and may form stabilizing surface phosphate species more rapidly, whereas Ni-poor compositions more readily cross into delithiation–dissolution regime. Further mechanistic work would be valuable, but the present trends are robust across the compositions tested and align with the literature framework.

We next evaluated LiH_2PO_4 as the alternative additive designed to both moderate slurry chemistry and compensate early-cycle Li loss. Beyond delaying the pH rise via the $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ buffer pair (near-neutral range), LiH_2PO_4 supplies Li^+ , which can offset initial consumption at the SEI/CEI. Adding LiH_2PO_4 to water set the initial pH at about 4.2; introducing the active material then led to stable values of 6.6 for LNMO and 9.7 for NMC622 (Figure 2E). Thus, predosing with LiH_2PO_4 buffers the slurry, curbing the strong alkalization observed without additives and providing milder conditions than those attained with PA during processing. Elemental analyses with iH_2PO_4 (Figure 2F) were corrected by subtracting the Li background from LiH_2PO_4 content in water (408 ppm measured after 24 h). For LNMO, the corrected filtrates contained Li 355, Mn 1, and Ni 6 ppm, with Al below the detection limit, mirroring the absence of Al observed with PA (Figure 2D) while markedly suppressing transition-metal release. The lower Li relative to both LNMO in water (Figure 2B) and LNMO in PA (Figure 2D) indicates that, with LiH_2PO_4 , LNMO predominantly follows the delithiation-only regime.^[32] For NMC622, only Li 18 ppm was detected, the smallest among the three conditions (compare Figure 2B,D), pointing to minimal dissolution pathways under buffered, Li-containing conditions. In contrast to PA, therefore, LiH_2PO_4 achieves pH control without driving substantial metal leaching, supporting its use as a practical additive for water-based cathode processing.

3.2. Aluminum Current Collector Corrosion

To establish a baseline prior to introducing LiH_2PO_4 , we first prepared water-processed LNMO and NMC622 electrodes without additives. SEM reveals a homogeneous, crack-free surface for LNMO (Figure 3A), whereas the NMC622 coating exhibits cracks and voids (Figure 3B). During casting of the NMC622 slurry, significant gassing was also observed (Figure S2, Supporting Information), consistent with alkaline corrosion of aluminum under the high-pH conditions as discussed earlier. To isolate the role of the current collector, we compared pristine Al foil with Al recovered after removing the dried coatings (LNMO-SC45-CMC—TRD202A and NMC622-SC45-CMC—TRD202A). The coatings were softened by soaking in Milli-Q water for several days and gently rubbed off with water. Residual binder domains remain on the surface (Figure 3C), but the Al recovered from LNMO electrodes closely resembles the reference foil, with no obvious corrosion

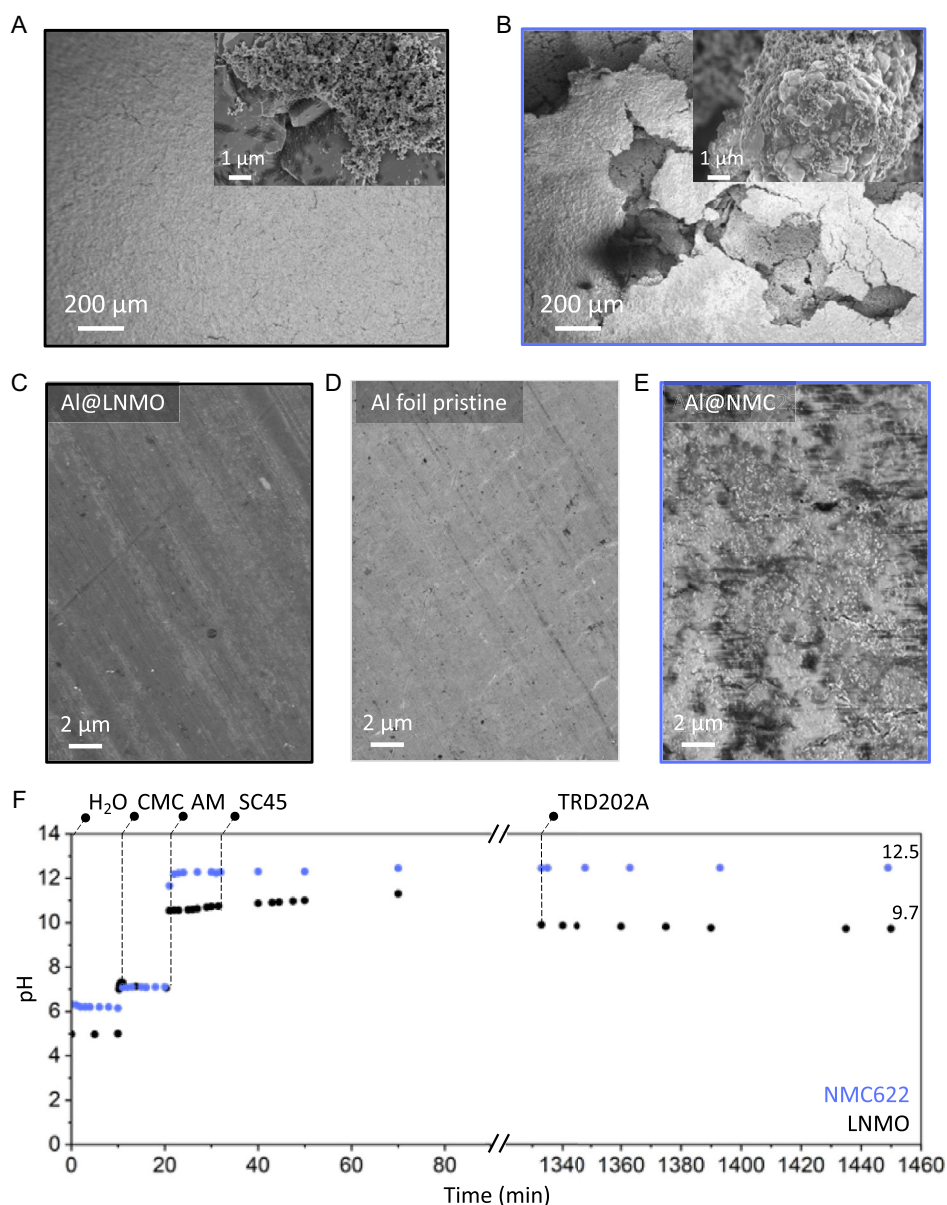


Figure 3. A) SEM images of water-based LNMO, and B) water-based NMC622 processed electrodes. Insets display high magnification snapshots of LNMO and NMC622 particles. Surface state analysis of Al foil after removing: C) the LNMO coating, D) pristine Al foil, and E) NMC622 coating. F) pH variation during the electrode preparation.

features (Figure 3D). In contrast, Al recovered from NMC622 electrodes displays distinct corrosion pits (Figure 3E; see also Figure S2C, Supporting Information). These morphological differences are consistent with the slurry pH evolution during electrode preparation (Figure 3F): under used conditions the pH of the final LNMO slurry remained below the threshold that yielded observable Al corrosion, whereas the pH of the NMC622 slurry increased to strongly alkaline values that promote pitting. This motivated the use of controlled buffering as discussed next.

The stepwise pH monitoring during slurry preparation (Figure 3F) shows a systematic increase in alkalinity as CMC, active material, and SC45 are added. After the main components are incorporated, the pH reached 11.3 for LNMO and 12.5 for

NMC622. Introducing TRD202A at the final mixing step lowered the LNMO slurry to pH 9.7, whereas the NMC622 slurry remained at pH 12.5. These values rationalize the morphological observations: the strongly alkaline NMC622 slurry promotes aluminum attack during coating and drying, consistent with gassing during casting (Figure S2, Supporting Information) and the corrosion pits on Al recovered from NMC622 electrodes (Figure 3E); while the LNMO slurry, though still basic, appears sufficiently moderated to avoid Al damage over the processing time. Prior reports of accelerated Al corrosion at elevated pH are in agreement with this behavior.^[20,28]

Consequently, to mitigate the aluminum corrosion observed for NMC622 without additive (Figure 3BE; and Figure S2,

Supporting Information), we prepared aqueous LNMO and NMC622 electrodes incorporating LiH_2PO_4 (Figure 1). **Figure 4** shows homogeneous coatings for both type of materials. For LNMO, the morphology is essentially unchanged relative to the additive-free case (Figure 4A vs. Figure 3A). For NMC622 however, LiH_2PO_4 suppressed the cracks and voids characteristic of the unbuffered slurry (Figure 4B; cf. Figure 3B). This improvement is consistent with the buffered pH achieved during slurry preparation (Figure 2E), which maintains the mixture below the corrosion regime identified earlier (Figure 3F). Surface inspections of the current-collector corroborate this: pristine Al (Figure 4C) and Al recovered after removing the NMC622– LiH_2PO_4 coating (Figure 4D) are comparable and free of obvious pitting, in sharp contrast to the Al recovered from additive-free NMC622 coatings (Figure 3E). Together, these results confirm that LiH_2PO_4 prevents Al corrosion during aqueous processing and enables uniform, well-adhered NMC622 films.

3.3. Electrode Morphology Changes Induced by LiH_2PO_4

Having established that LiH_2PO_4 additive suppresses macroscopic cracking and Al corrosion (Figure 3 and 4) and buffers slurry pH (Figure 2E), we next examined the coating microstructure at higher magnification as a function of LiH_2PO_4 loading (**Figure 5**). Relative to the additive-free films, introducing LiH_2PO_4 produces dispersed spherical surface domains for both types of electrode materials, with larger and more numerous features found in NMC622 as compared to in LNMO. The spherical particles on LNMO appear smoother, whereas those on NMC622 are rougher and more faceted. The different slurry pH values achieved with LiH_2PO_4 (Figure 2E) likely contribute to these contrasts: the NMC622 slurry remains more basic than the LNMO slurry during

processing. Control micrographs of pristine LiH_2PO_4 and CMC (Figure S3, Supporting Information) do not match these morphologies exactly, consistent with particle modification under the slurry's pH history and ball milling; the features are therefore tentatively assigned to phosphate-/binder-rich agglomerates formed during mixing and drying.

To probe how LiH_2PO_4 alters interfacial chemistry, we performed complementary XPS analysis on solids recovered after controlled exposures. LNMO and NMC622 powders were dispersed i) in water, ii) in full slurries without additive, and iii) in slurries containing LiH_2PO_4 ; with in parallel, pristine powders analyzed as references. Each dispersion was stirred for 24 h, then centrifuged to separate the solid (active material with any adsorbed species and, for slurry samples, binder/conductive carbon) from the liquid. The solids were rinsed, dried, and analyzed by XPS. Figure S4–S7, Supporting Information compile Ni 2p and P 2p spectra for the four conditions.

With LiH_2PO_4 , clear P 2p doublets appear for both chemistries, whereas no P is detected in the other conditions. The P 2p binding energies (ca. 133–135 eV) are consistent with surface phosphate species (PO_4^{3-}), indicative of a thin, largely inorganic phosphate layer forming on the active-material surface. This observation aligns with the buffering action of $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ and the reduced metal leaching measured in Figure 2F. The Ni 2p envelopes evolve differently for the two materials. For LNMO, immersion in water and subsequent slurry processing leave the average Ni oxidation state essentially unchanged; upon adding LiH_2PO_4 , a modest shift consistent with increased Ni^{3+} character is observed, in agreement with the higher Li detected in solution for LNMO under LiH_2PO_4 (Figure 2F) and supporting a delithiation-dominated regime without significant transition-metal dissolution. In contrast, for NMC622 the addition of LiH_2PO_4 produces a slight shift toward

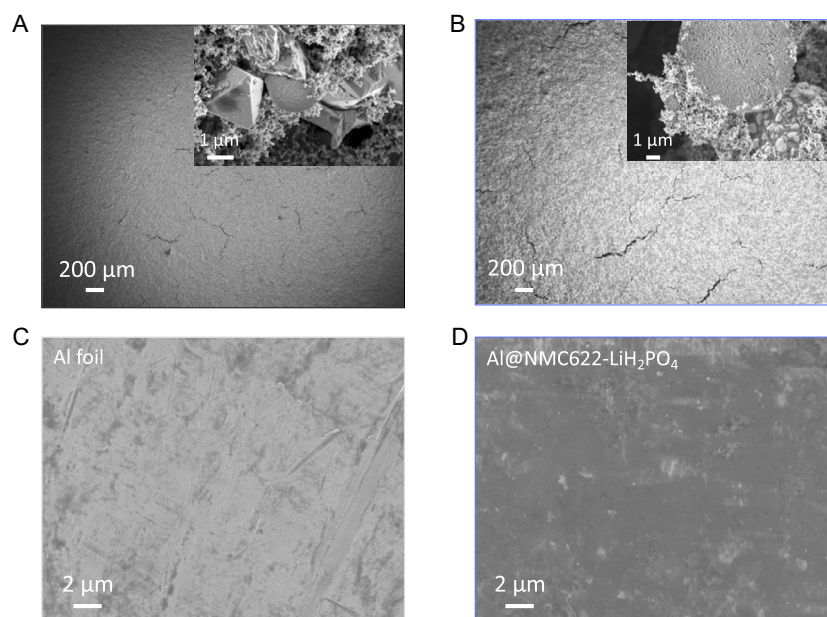


Figure 4. Effect of LiH_2PO_4 additive on coating morphology and aluminum current-collector surface state. SEM images of aqueous A) LNMO and B) NMC622 electrodes prepared with LiH_2PO_4 . Insets display high magnification snapshots of LNMO and NMC622 particles. Surface inspection of C) pristine aluminum foil, as compared to D) aluminum foil after removal of the NMC622– LiH_2PO_4 coating.

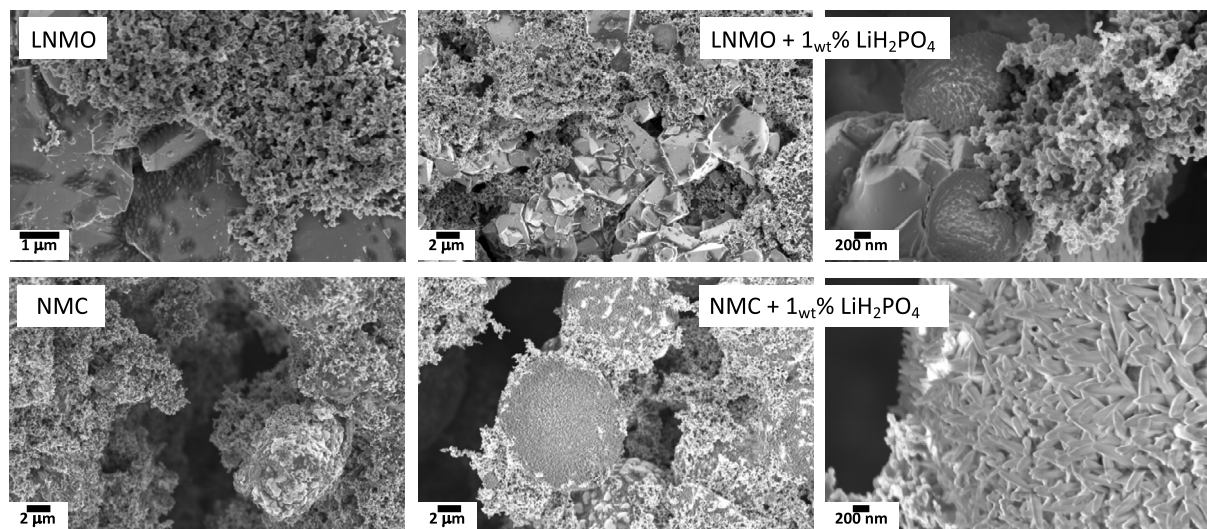


Figure 5. SEM images of LNMO and NMC622 water-processed electrodes prepared without and with 1 wt% amount of LiH_2PO_4 additive.

lower average Ni oxidation state, consistent with the strong suppression of Li loss (Figure 2F) in the more alkaline, buffered slurry environment. Taken together, these XPS results provide indirect yet coherent evidence that pH regulation by LiH_2PO_4 modifies the surface chemistry of both powders, forming phosphate species while steering LNMO and NMC622 along distinct leaching/delithiation pathways that mirror the trends in Figure 2E,F.

3.4. LiH_2PO_4 Additive Impact on the Electrochemical Performance

The effect of LiH_2PO_4 on electrochemical performance was evaluated in half-cell coin cells (Figure 6). For LNMO, first-cycle voltage profiles with and without 1 wt% additive are essentially identical (Figure 6A): a faint plateau near 4.1 V associated with the $\text{Mn}^{3+}/\text{Mn}^{4+}$ couple, followed by two dominant plateaus at about 4.7

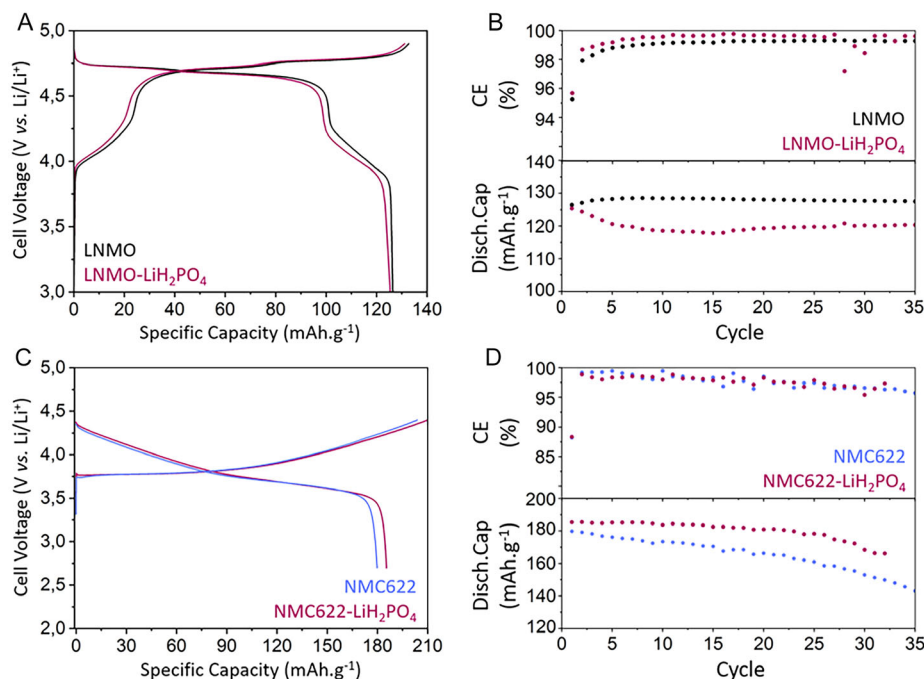


Figure 6. Electrochemical performance of aqueous-processed LNMO and NMC622 electrodes with and without LiH_2PO_4 additive. First-cycle charge/discharge profiles of A) LNMO and C) NMC622 electrodes. B,D) Respective specific discharge capacity and coulombic efficiency versus cycle number. Two-electrode CR2032 half-cell configuration was used, cells cycled at C/10 within 3.0–4.9 V (LNMO) and 2.8–4.4 V (NMC622), with electrolyte: 1.2 M LiPF_6 in EC/EMC (3:7 w/w).

and 4.75 V assigned to $\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Ni}^{3+}/\text{Ni}^{4+}$, respectively.^[38,39] The impact of the additive becomes evident in the cycling metrics (Figure 6B). Additive-free LNMO delivers a slightly higher initial discharge capacity (≈ 130 vs $\approx 120 \text{ mAh g}^{-1}$), whereas LiH_2PO_4 -processed LNMO exhibits consistently higher coulombic efficiency ($\approx 99.6\%$ vs $\approx 99.1\%$ on average). The modest capacity penalty is consistent with the chemical analyses: in the presence of LiH_2PO_4 the LNMO slurry remains only mildly buffered (Figure 2E) yet releases more Li into solution than the water-only case (Figure 2F), reducing the cyclable Li inventor.^[31] In parallel, SEM analysis reveals phosphate/binder-rich surface domains when LiH_2PO_4 is used (Figure 5), which may increase interfacial impedance during early cycles. Conversely, the higher Coulombic efficiency likely reflects formation of a thin phosphate-containing cathode–electrolyte interphase detected by XPS (Figure S4–S5, Supporting Information), which suppresses parasitic reactions even if the available Li is slightly diminished. Taken together, these results indicate that, for LNMO, LiH_2PO_4 trades a small amount of initial capacity for improved reversibility, in line with the distinct leaching/buffering behavior established in Section 3.1 (Figure 2E,F).

Turning to NMC622, the first-cycle voltage profiles are also very similar with and without 1 wt% LiH_2PO_4 (Figure 6B). As noted earlier, the additive-free coatings however required careful handling because of cracking and gas evolution during casting (thus, impractical - Figure 3B and S2, Supporting Information), whereas LiH_2PO_4 yielded uniform films (Figure 4B,D). A small feature near 3.75 V on the first charge appears for both conditions and was found to vanish on subsequent cycles (Figure S8, Supporting Information), consistent with the removal of surface hydroxide/carbonate species rather than a bulk redox event. In contrast to the nearly identical profiles, the cycling metrics diverge (Figure 6D): the additive-free NMC622 shows a progressive loss of discharge capacity, while NMC622– LiH_2PO_4 maintains a markedly flatter capacity retention profile. The coulombic efficiencies are comparable on average, indicating that the principal benefit of LiH_2PO_4 is sustained capacity retention rather than a large change in CE.

These electrochemical trends correlate with the chemical and morphological evidence. Elemental analyses show that Li leaching is strongly reduced for NMC622 in the presence of LiH_2PO_4 (Figure 2F), while the buffered slurry suppresses Al pitting and macroscopic cracking (Figure 3E and 4B,D) and produces homogeneous microstructures. Together, reduced loss of cyclable lithium and improved interfacial/mechanical integrity plausibly underlie the superior stability of the LiH_2PO_4 -processed NMC622.^[31] Finally, we note that in both cases capacity fade accelerates after about 40–45 cycles, accompanied by signs of cell dry-out. We ascribe this limitation to the $\text{LiPF}_6/\text{EC-EMC}$ electrolyte in contact with Li metal and to the relatively high cathode loading used here ($\approx 20 \text{ mg cm}^{-2}$), which constrain lifetime in the two-electrode half-cell configuration rather than reflecting an intrinsic failure of the cathode coating.

4. Conclusion

In this study, we examined aqueous processing of high-voltage LNMO and NMC622 cathodes with attention to slurry chemistry, aluminum current-collector compatibility, and the impact of a lithium dihydrogen phosphate (LiH_2PO_4) additive. Without additive, LNMO slurries reached a moderately basic pH (≈ 9.7) and yielded uniform, crack-free coatings, whereas NMC622 slurries became strongly alkaline (≈ 12.5), leading to gas evolution during casting, cracking in the dried films, and pitting of the Al foil. These behaviors are consistent with Li^+/H^+ exchange driving alkalization and, at sufficiently high pH, promoting Al corrosion. Elemental analyses further showed composition-dependent leaching in water and under PA, aligning with a transition between ion-exchange and delithiation–dissolution regimes.

Introducing LiH_2PO_4 lowered and buffered slurry pH and reduced metal leaching relative to PA. For NMC622, LiH_2PO_4 suppressed Al pitting and macroscopic cracking, produced homogeneous coatings, and improved cycling stability. XPS detected phosphorus species consistent with a thin phosphate layer on the active-material surface, which, together with the moderated slurry chemistry, likely contributes to the enhanced electrochemical behavior. For LNMO, LiH_2PO_4 maintained uniform coatings but was associated with modestly lower initial discharge capacity, consistent with the higher Li detected in solution. However, coulombic efficiency improved, suggesting formation of a stabilizing phosphate-containing interphase. SEM analysis revealed fine, secondary surface domains in LiH_2PO_4 -processed films; their appearance varied with loading and is plausibly linked to phosphate/binder agglomeration under the slurry's pH history and mixing conditions. Overall, LiH_2PO_4 emerges as a practical pH-buffering, lithium-compatible additive for aqueous processing of high-voltage cathodes, particularly effective for NMC622 where strong alkalinity otherwise compromises the current collector and coating integrity. Continued studies into the mechanistic role of such additives, their interactions with active materials and binders, and their influence on long-term cycling stability are essential to further optimize this approach and enable scalable, sustainable electrode manufacturing.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: aqueous electrode processing · aluminum corrosion · pH buffer additives · metal leaching · water-based slurry formulation

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