

COMMUNICATION

Cite this: *Nanoscale*, 2025, **17**, 7008

Received 4th December 2024,

Accepted 17th February 2025

DOI: 10.1039/d4nr05111d

rsc.li/nanoscale

One-pot synthesis of long-range aligned nanochannels for Li-ion transfer pathways†

Zehan Chen,^a Isaac Alvarez Moises,^a Ruth Bruker,^b He Jia,^a Shanshan Yan,^a Yinghui Zhang,^a Zhenni He,^a Kejie Zhou,^c Sorin Melinte,^{id c} Laurent Rubatat,^{id d} Klaus Meerholz^{id b} and Jean-François Gohy^{id *a}

Limited ionic conductivity (σ) of solid polymer electrolytes (SPEs) is a bottleneck for their practical application. Constructing ordered ionic transfer highways is a prospective direction to promote σ . Here, we propose a straightforward one-pot synthesis strategy for the obtention of long-range aligned nanochannels, which is based on the evaporation of the solvent to induce the self-assembly of Pluronic® F127-resol micelles. To obtain SPEs, dicyandiamide (DCD) and LiClO₄ are uniformly dispersed in the F127-resol nanochannels. Compared to the random counterpart, the accordingly synthesized ordered SPE significantly improves room-temperature σ by 2 orders of magnitude reaching $1.65 \times 10^{-4} \text{ S cm}^{-1}$ at 20 °C. The FTIR spectra further demonstrate that the best performing sample possesses more Li⁺ ions coordinated to cyano groups from DCD and less coordinated to ether moieties from F127-resol, further decreasing the activation energy for Li⁺ mobility since cyano groups have lower binding energy to Li⁺ than ether ones. Both aligned nanostructures and beneficial coordinating groups synergistically accelerate the ionic transport, contributing to the formation of efficient Li-ion transfer pathways.

1 Introduction

With the ever-growing requirement for increased safety and high energy density, solid-state batteries (SSBs) are promising candidates for next-generation batteries.¹ More specifically, SSBs are based on solid-state electrolytes (SSEs) which should

be highly safe and capable to face with high-capacity Li anodes.^{2–4} SSEs include three main classes: inorganic solid electrolytes (ISEs), solid polymer electrolytes (SPEs) and their hybrids.⁵ Among them, SPEs composed of Li⁺-conducting polymers and Li salts have garnered great interest thanks to their high flexibility, good processability, light weight and low cost.^{6–8} Nevertheless, due to the high crystallinity of polymers, their limited room-temperature ionic conductivity (σ) is a main challenge.⁹

To date, considerable effort has been devoted to promote the σ of SPEs and constructing directional Li-ion transfer pathways.^{2,5,9} Through the introduction of fillers (e.g., nanoparticles,¹⁰ nanowires,^{9,11} nanochannels^{5,6,12–14}) into polymer matrixes, Li-ion transfer highways can be established along with the interfaces between polymers and fillers, efficiently promoting ionic conduction.¹⁵ The reason for the augmented Li-ion conductive behavior can be summarized by the three following aspects: (i) incorporated fillers substantially decrease or even suppress the crystallinity of polymers, and also boost the amorphous volume of the system, especially for the regions surrounding fillers; (ii) interactions between fillers and anions of Li salts are beneficial to disassociate Li salts, and meanwhile release more free Li⁺ ions to transfer; (iii) some modified surfaces of fillers allow Li⁺ ions to quickly coordinate/de-coordinate, consequently speeding up ionic transport, such as grafted groups with low binding energy,¹⁰ loaded ionic liquids,¹² and plasticizers.¹⁶

The shape and orientation of fillers deeply influence the enhancement effect of σ , since the formation of fast Li-ion transfer paths is accordingly affected.^{2,5,9} Fig. 1 illustrates fast conducting paths provided by fillers of various geometrical shapes and orientations. In the case of random nanoparticles, the fast ionic pathway is restricted due to the short-range, isolated interface, which is not conducive to continuous Li-ion transport. When the nanoparticles are interconnected, the interface tends to become continuous. For that, the enhancement on σ by nanowires is superior to that by nanoparticles, as the transfer routes provided by nanowires are long-range, relatively uninterrupted and beneficial for Li-ion migration. As far

^aInstitute of Condensed Matter and Nanosciences (IMCN), Bio- and Soft Matter (BSMA), Université catholique de Louvain, Place L. Pasteur, 1, 1348 Louvain-la-Neuve, Belgium. E-mail: jean-francois.gohy@uclouvain.be

^bInstitut für Physikalische Chemie, Department für Chemie, Universität zu Köln, Greinstraße 4-6, D-50939 Köln, Germany

^cInstitute of Information and Communication Technologies, Electro and Applied Mathematics (ICTEAM), Electrical Engineering (ELEN), Université catholique de Louvain, 1348 Louvain-la-Neuve, Belgium

^dUniversité de Pau et des Pays de l'Adour, E2S UPPA, CNRS, IPREM, Pau 64053, France

† Electronic supplementary information (ESI) available: Fig. S1–3, and Tables S1,

2. See DOI: <https://doi.org/10.1039/d4nr05111d>

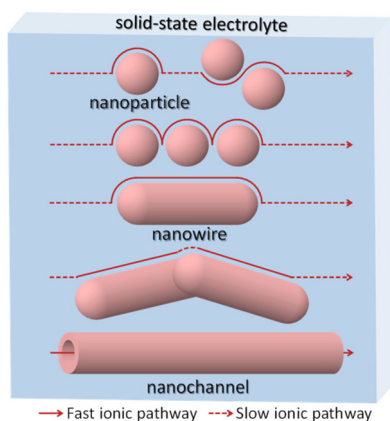


Fig. 1 Li-ion transfer paths for various geometrical structures in solid-state electrolytes.

as the orientation is concerned, randomly oriented fillers exhibit poorer Li^+ -conducting performance than the aligned ones, since the random orientation of fillers leads to the formation of tortuous and indirect Li-ion transfer pathways. Besides, the random stack of fillers inevitably generates crossing junctions. Conversely, the aligned structures can avoid the tortuosity and crossing junctions for ionic transfer pathways. Moreover, when the orientation of aligned channels is perpendicular to electrodes, the Li-ion conduction can be further promoted.^{2,5,9}

It has been reported that aligned nanochannels can be provided by preformed frameworks with ordered pores, such as porous inorganic² and polymeric⁵ membranes. However, their synthesis process is tedious, beginning with the preparation of a porous framework as a mold, followed by immersion in polymer solutions. Besides, in some cases of ionically insulating frameworks, the σ of bulk SSEs may significantly decrease as the inert content is excessive. To address those bottlenecks, a simple and straightforward synthesis method towards prolonged, aligned channels in SSEs is highly pursued.

In the present work, we develop a novel approach towards the one-pot synthesis of long-range well-aligned nanochannels

in SPEs. Induced by the evaporation of ethanol solvent, prolonged ordered nanochannels based on Pluronic® F127 – resol micelles are gradually self-assembled with uniform dispersion of dicyandiamide (DCD) and LiClO_4 in the nanochannels. Due to the peculiar fabrication of aligned nanochannels containing an optimal amount of DCD additive, the accordingly synthesized SPE exhibits an outstanding σ of $1.65 \times 10^{-4} \text{ S cm}^{-1}$ at 20°C , which is improved by 2 orders of magnitude compared to the random-structure reference. Furthermore, we attempt to elucidate the mechanism of fast Li-ion migration from both composition and structure.

2 Results and discussion

Poly(propylene oxide) (PPO) blocks, and is characterized by a molar mass of $\sim 12\,000 \text{ g mol}^{-1}$ (Fig. S1†). In a polar solvent such as ethanol (EtOH), the hydrophilic PEO blocks tend to dissolve in the solvent while the hydrophobic PPO blocks perform oppositely, tending to repel the solvent molecules and favouring their aggregation. In the case of Pluronic® F127, this further results in the formation of spherical micellar structures with a PPO core and a PEO corona (Fig. 2). The evaporation of EtOH induces the ordered stacking of F127 micelles along the evaporation front, promoting nanosized channels vertically aligned to the surface of the substrate (*i.e.*, stainless steel spacer of coin cells). Moreover, non-covalent interactions formed among resol, DCD and PEO blocks are developing along the propagating evaporation front, therefore acting as a supplementary driving force towards the perpendicular orientation of the F127 micelles. This further promotes the formation of nanochannels containing resol and DCD molecules in interactions with PEO coronal chains from F127 micelles as depicted in Fig. 2 and previously demonstrated in a previous work by Xu *et al.*¹⁷ Because of the coordination (i) between Li^+ ions and EO groups and (ii) between Li^+ ions and cyano groups of DCD, Li^+ ions are distributed in the aligned nanochannels. After adequate drying, the F127-resol aligned nano-

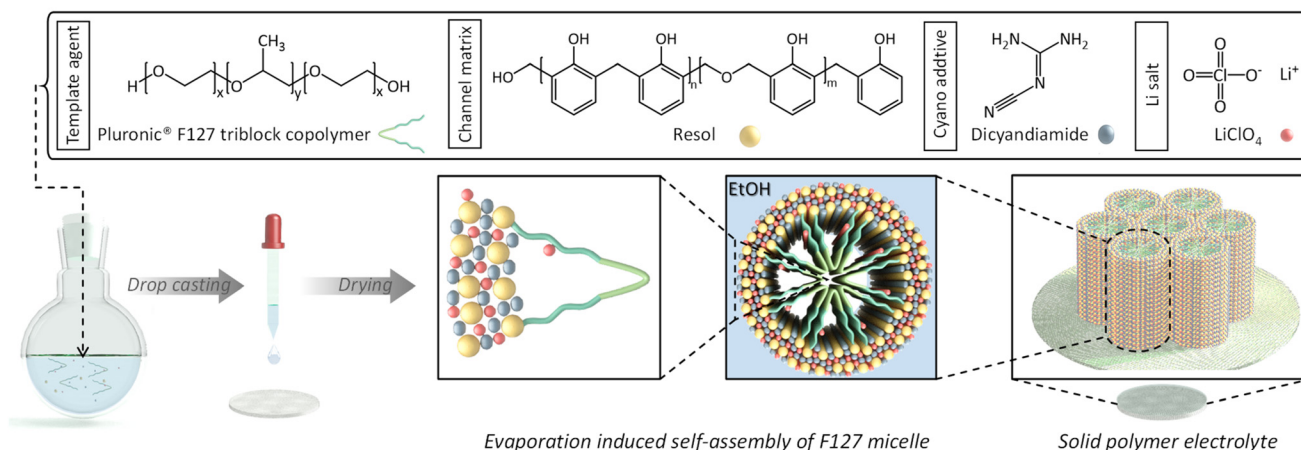


Fig. 2 Synthetic pathway towards SPEs consisting of long-range aligned nanochannels.

channels incorporating DCD and LiClO_4 are achieved, denoted as F127-channel-aligned-DCD- LiClO_4 , and further used as SPEs.

The morphology, structure, and thermal properties of F127-channel-aligned-1/16DCD-1/20 LiClO_4 have been investigated. Besides, a reference sample, denoted as F127-random-structure-1/16DCD-1/20 LiClO_4 , has also been studied for the sake of comparison. This reference sample has the same composition as the channel-aligned sample but in a random arrangement. The primary distinction between their synthesis processes lies in the evaporation conditions (see 4.3 Sample synthesis). In the case of the F127-channel-aligned-1/16DCD-1/20 LiClO_4 sample, the orientation of the channels has been controlled by the propagating evaporation front of the solvent while for the

F127-random-structure-1/16DCD-1/20 LiClO_4 sample, fast evaporation has been employed without control over the orientation. The morphology of both samples has been observed by SEM. It should be noted that samples for SEM characterization have been calcined under an inert atmosphere before observation. This process allows the formation of a hollow channel structure observable by SEM, since polymeric and organic matters have been transformed into stable carbonaceous material. The calcined F127-channel-aligned-1/16DCD-1/20 LiClO_4 sample exhibits prolonged and straight stripe-like nanochannels with diameters of ~ 10 nm. Moreover, most of them are aligned (Fig. 3A and S2†). Intriguingly, the apical and the lateral cross sections are observed in two detail views from different angles, revealing the complete structure of the nano-

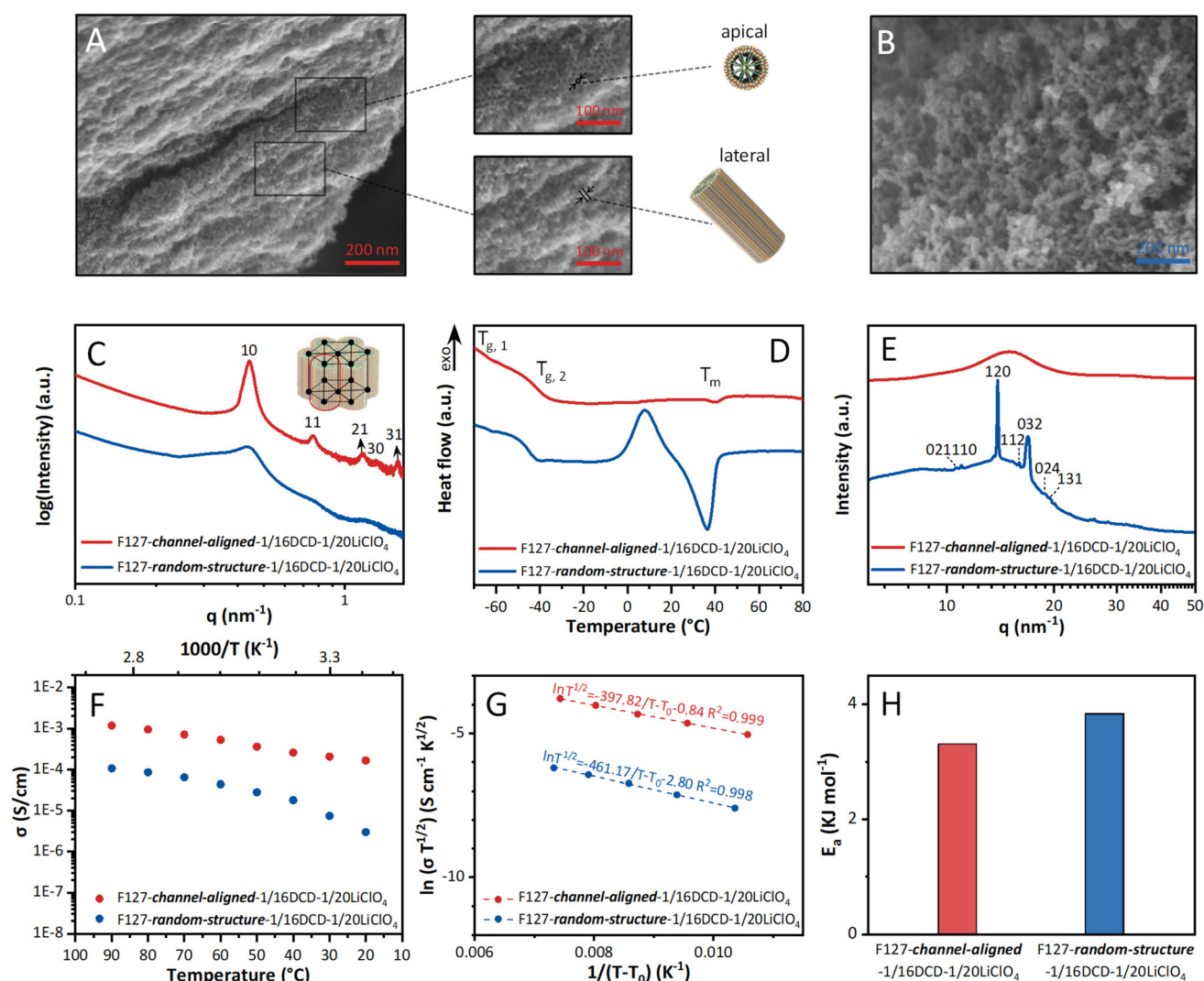


Fig. 3 Comparison of samples with channel-aligned and random structures. SEM images of (A) calcined F127-channel-aligned-1/16DCD-1/20 LiClO_4 sample (with detail views and corresponding structure diagrams) and (B) calcined F127-random-structure-1/16DCD-1/20 LiClO_4 sample. SAXS patterns (C), DSC curves (D), and WAXS patterns (E) of F127-channel-aligned-1/16DCD-1/20 LiClO_4 and F127-random-structure-1/16DCD-1/20 LiClO_4 samples. Temperature-dependent σ (F) of F127-channel-aligned-1/16DCD-1/20 LiClO_4 and F127-random-structure-1/16DCD-1/20 LiClO_4 samples. VFT fitting plots (G) for the σ and E_a diagram (H) of F127-channel-aligned-1/16DCD-1/20 LiClO_4 and F127-random-structure-1/16DCD-1/20 LiClO_4 samples.

channels (Fig. 3A detail views and the corresponding structure diagrams). Oppositely, in the calcined F127-random-structure-1/16DCD-1/20LiClO₄ sample, a randomly stacked and even locally aggregated structure is observed, without continuous channels (Fig. 3B). The small angle X-ray scattering (SAXS) pattern (Fig. 3C) of the F127-channel-aligned-1/16DCD-1/20LiClO₄ sample reveals five scattering peaks with q -values of 0.44, 0.76, 1.16, 1.32 and 1.58 nm⁻¹. The q -value ratios of those peaks correspond precisely to 1 : $\sqrt{3}$: $\sqrt{7}$: $\sqrt{9}$: $\sqrt{13}$ and can be indexed to the 10, 11, 21, 30 and 31 planes of a 2D hexagonal array.¹⁸ This SAXS signature evidences a long-range ordering of hexagonal packed cylinders. The unit cell parameter is calculated to be about 16.5 nm, which is slightly larger than the SEM result. This difference is reasonable because the sample used for SEM is calcined, resulting in framework shrinkage.¹⁸ In sharp contrast, the SAXS pattern of the F127-random-structure-1/16DCD-1/20LiClO₄ sample displays a broad structural peak at 0.43 nm⁻¹, comparable to the previous sample, with weak higher orders. This reflects a poorly ordered nanostructure. Differential scanning calorimetry (DSC) has been conducted to survey thermal transitions of the investigated samples (Fig. 3D and Table 1). The F127-random-structure-DCD-LiClO₄ sample shows glass transition temperatures (T_g) of -64.8 °C and -44.2 °C, corresponding to PPO blocks and PEO blocks respectively. The presence of a melting temperature (T_m) at 36.2 °C is attributed to the crystallization of polymer coronal chains from the F127 micelles and the degree of crystallization χ_c is calculated to be as high as 75.2%. Compared to the random structure counterpart, the $T_{g,1}$ value of F127-channel-aligned-1/16DCD-1/20LiClO₄ remains similar, however, $T_{g,2}$ and T_m values increase and the χ_c dramatically decreases to 2.0%. DSC results suggest that the structure of the aligned channels has a great influence on the crystallization behavior of samples, which is further proved by the wide-angle X-ray scattering (WAXS) experiments (Fig. 3E). The WAXS pattern of the F127-random-structure-DCD-LiClO₄ sample displays a series of peaks located at 10.64, 10.98, 13.89, 15.97, 16.89, 18.84, and 19.36 nm⁻¹, corresponding to (021), (110), (120), (112), (032), (024), and (131) of crystalline PEO domains, respectively.¹⁹ As a comparison, there is not any

intense peak of crystalline PEO, but only a broad peak in the WAXS pattern of the channel-aligned sample (Fig. 3E). In sum, the PEO coronal chains in randomly stacked F127 micelles show tendency to crystallize while, in the channel-aligned sample, the conformation adopted by PEO coronal blocks obviously does not favor crystallization.

The Li⁺-conducting performances of the F127-channel-aligned-1/16DCD-1/20LiClO₄ sample as a SPE have been subsequently investigated. The electrochemical impedance spectroscopy (EIS) plots measured in the temperature range of 90 to 20 °C are presented in Fig. S3†. The resulting temperature-dependent σ is presented in Fig. 3F. Noticeably, the F127-channel-aligned-1/16DCD-1/20LiClO₄ sample achieves a σ as high as 1.65×10^{-4} S cm⁻¹ at 20 °C, corresponding to almost two orders of magnitude amelioration compared to the random-structure control sample (2.99×10^{-6} S cm⁻¹ at 20 °C). Such excellent performance at RT also outperforms most of previously reported SSEs equipped with ionic transfer pathways (see Table S1†). The temperature-dependent σ data have been further simulated by the Vogel-Fulcher-Tammann (VFT) equation corresponding to segmental motion of polymer chains allowing Li⁺ ions to transfer between coordination sites.^{20–22} The fitting results and the accordingly calculated activation energies (E_a) are displayed in Fig. 3G and H. The E_a of the F127-channel-aligned-1/16DCD-1/20LiClO₄ (3.31 kJ mol⁻¹) is smaller than that of the random-structure sample (3.83 kJ mol⁻¹). Compared to the random-structure counterpart, the channel-aligned sample exhibits increased σ and minimal E_a , suggesting that the channel-aligned structure is promoting Li-ion migration. It is hypothesized that those long-range aligned channels can be considered as Li-ion transfer routes and are substantially decreasing the number of crossing junctions during transport.

In addition to the structural analysis, the influence of different compositions on Li⁺-conducting performances has been investigated (EIS plots detailed in Fig. S4† and temperature-dependent σ in Fig. 4A). Firstly, the influence of Li salt concentration on σ has been probed by varying the Li⁺/EO molar ratio of samples from 1/25 to 1/8. With the increase of Li-ion concentration, the σ increases and then decreases, and this trend is observed at each temperature within the studied range. This trend is frequently observed in SPEs and is attributed to an increased amount of charge carriers as the concentration of added salt is increased until it reaches a critical threshold where the excessive formation of immobilized ion pairs of salt results in a decreased Li-ion migration, in agreement with previously reported results.¹⁵ Among the investigated samples, the best performing one is F127-channel-aligned-1/16DCD-1/20LiClO₄, suggesting that 1/20 is the optimal Li⁺/EO molar ratio (Fig. 4A). This sample has been further explored by FTIR spectroscopy (Fig. 4B). Note that the coordination between Li⁺ and ether leads to a red shift of the band corresponding to the stretching vibration of C–O–C. The C–O–C band experiences a larger red shift when the Li⁺/EO molar ratio increases from 1/25 to 1/8 (except for 1/20). To clarify, an increase in the Li⁺/EO ratio means a decrease in the weight percentage of ether groups.

Table 1 Thermal properties characterized by DSC for F127-channel-aligned-1/16DCD-1/20LiClO₄ and F127-random-structure-1/16DCD-1/20LiClO₄ samples

Samples	T_g (°C)		T_m (°C)	χ_c^a
	$T_{g,1}$	$T_{g,2}$		
F127-channel-aligned-1/16DCD-1/20LiClO ₄	-64.7	-39.2	40.2	2.0%
F127-random-structure-1/16DCD-1/20LiClO ₄	-64.8	-44.2	36.2	75.2%

^a The degree of crystallization χ_c is calculated by $\chi_c = (\Delta H_m)/(\omega \times \Delta H_0)$, wherein ΔH_m (J g⁻¹) represents the specific heat of fusion, obtained from the integration of the T_m peak from the DSC curve; ω is the mass fraction of the PEO blocks in the composite material; ΔH_0 (J g⁻¹) is the enthalpy of fusion of 100% crystalline PEO, namely 205 J g⁻¹.¹⁵

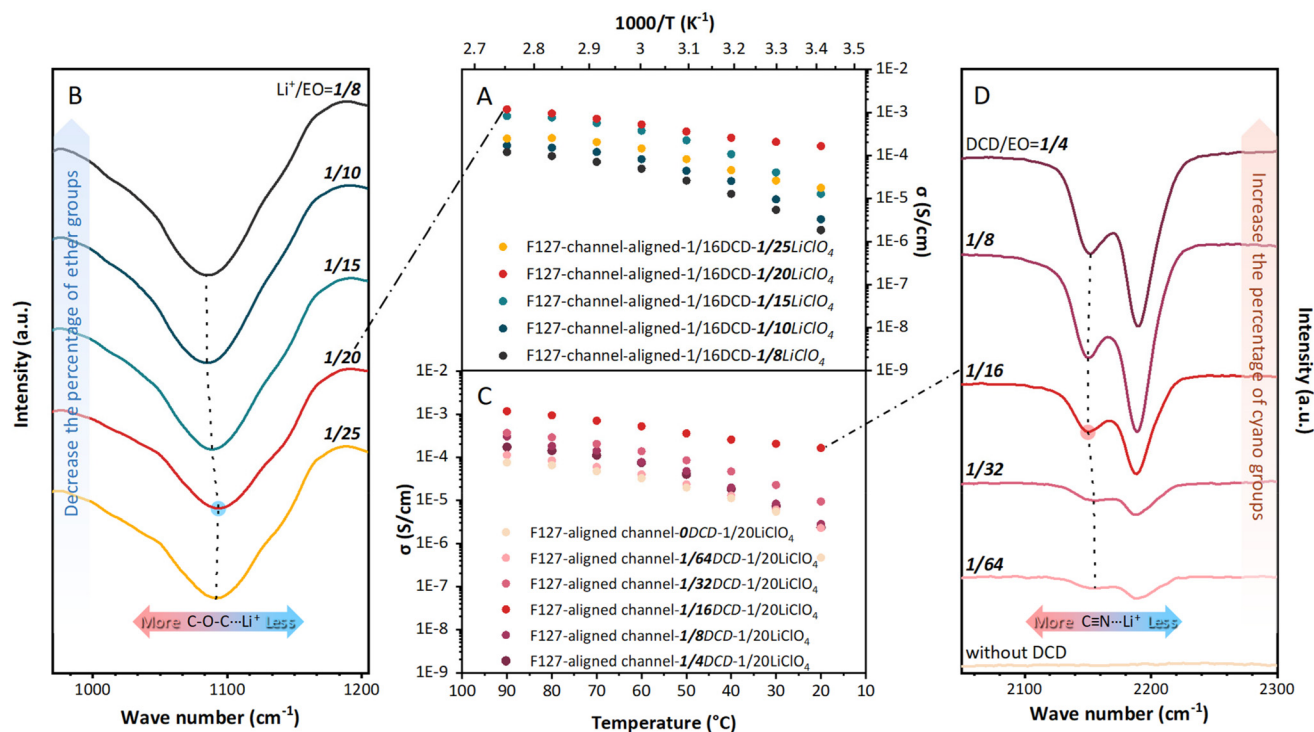


Fig. 4 Ionic conductivity and FTIR characterizations of F127-channel-aligned-DCD-LiClO₄ SPEs. Temperature-dependent σ (A) and FTIR spectra (B) of F127-channel-aligned-1/16DCD-LiClO₄ SPEs with various Li⁺/EO molar ratios in the range of 1/25–1/8. Temperature-dependent σ (A) and FTIR spectra (B) of F127-channel-aligned-1/16DCD-LiClO₄ SPEs with various Li⁺/EO molar ratios in the range of 1/25–1/8. Temperature-dependent σ (C) and FTIR spectra (D) of F127-channel-aligned-DCD-1/20LiClO₄ SPEs with various DCD/EO molar ratios in the range of 0–1/4.

Interestingly, an opposite shift trend is only observed for the sample with the 1/20 Li⁺/EO molar ratio, indicating that the ether groups in this sample have a decreased coordination with Li⁺ ions compared to the other investigated samples.

The impact of the DCD component on σ has been evaluated by measuring samples with various DCD concentrations in which the DCD/EO molar ratio changes from 0 to 1/4 (temperature-dependent σ in Fig. 4C and EIS plots in Fig. S5†). Fig. 4C demonstrates that σ increases until reaching an optimal DCD/EO molar ratio of 1/16, and then decreases. In the case of the absence of DCD, the σ is inferior at each temperature compared to DCD-containing samples. Note that there is a dramatic drop of σ beginning at 30 °C. This plunge may be related to a thermal transition in the sample, caused by the crystallization of the polymer component (see thermal properties in Fig. S3 and Table S2†). This result sheds light on the important role of the DCD component in dramatically decreasing polymer crystallinity. The coordination between DCD and Li⁺ was analyzed by FTIR spectroscopy (Fig. 4D). In DCD-containing samples, a characteristic band of cyano groups locates at ~ 2158 cm⁻¹, which experiences a red shift when coordinating with Li⁺. Among all investigated samples, the sample with the 1/16 DCD/EO molar ratio exhibits the largest red shift, indicating the highest degree of C≡N...Li⁺ coordination.

As reported elsewhere, ether groups have relatively high affinity to Li⁺ ions while cyano groups possessing weak binding energy to Li⁺ are promising alternatives to lower the

energy barrier during transport.²³ Based on the above FTIR analysis, the F127-channel-aligned-1/16DCD-1/20LiClO₄ sample shows less C–O–C...Li⁺ and more C≡N...Li⁺ coordinated species compared to the other investigated samples. This further confirms that the Li⁺ ions in this sample are prone to coordinate with cyano groups, suppressing the stronger interaction between ether and Li⁺, and diminishing the coordination/de-coordination energy, which is beneficial for fast and smooth Li-ion migration.¹⁰ It is worth mentioning that C≡N...Li⁺ is efficiently utilized in the channel-aligned structure, as demonstrated by the comparison between the aligned and random structures (Fig. 3F–H). Indeed, for the same composition, the random structure without any continuous channels leads to worse σ , compared to the channel-aligned sample. In a word, the highly efficient Li-ion transport is realized by the collaborative contributions from the continuous channel-aligned structure and the low-binding-energy coordinating sites from the DCD component.

On the basis of the above characterization findings and ionic conductivity performances, and drawing insights from previously reported literature,^{2,9,12,13,16} the Li⁺ ion migration mechanism in the F127-channel aligned-DCD-LiClO₄ SPE is understood as follows (Fig. 5). Some Li⁺ ions, derived from LiClO₄ salt, coordinate with ether groups of F127 copolymers and migrate among the coordination sites assisted by segmental polymer chain motions (blue arrow in Fig. 5). Meanwhile, other Li⁺ ions coordinate to cyano groups of DCD with whom

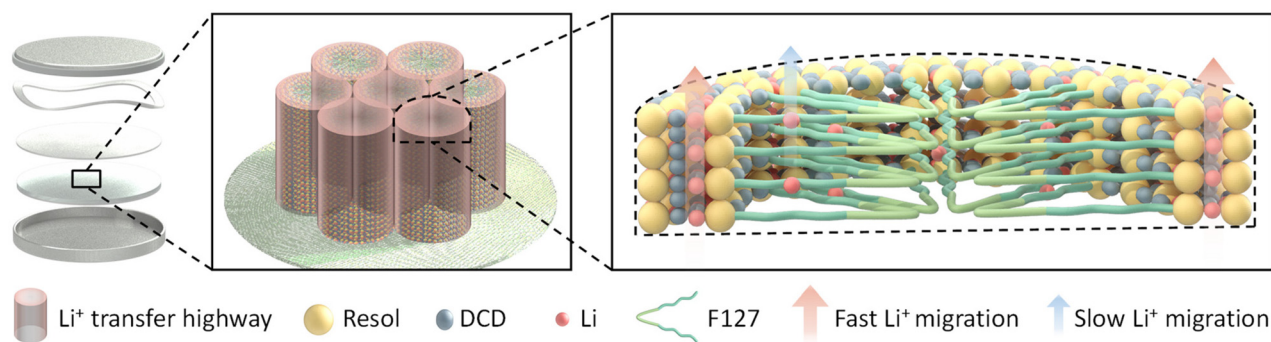


Fig. 5 Illustration of Li-ion migration in long-range aligned nanochannels of F127-channel-aligned-DCD-LiClO₄ SPEs.

the binding energy is relatively low.²³ More importantly, DCD is distributed in the aligned-channels framework. Hence, DCD attracts Li⁺ ions to the locations of nanochannels and allows them to smoothly and quickly transport across the SPE (red arrows in Fig. 5). Both of the peculiar structure and optimal composition synergistically establish the Li-ion transfer pathways.

3 Conclusions

The long-range aligned sample F127-channel-aligned-DCD-LiClO₄ has been fabricated by a straightforward one-pot strategy. The construction of nanochannels is induced by the EtOH solvent evaporation and the self-assembly of the F127-based micelles. The accordingly synthesized samples achieve continuous and aligned nanochannels with the reduced crystallinity of polymers. When investigated as a SPE, the channel-aligned sample exhibits the striking σ of $1.65 \times 10^{-4} \text{ S cm}^{-1}$ at 20 °C and decreased E_a of 3.31 kJ mol^{-1} , reflecting the structural benefit for Li-ion migration. The compositional analysis by FTIR demonstrates that the optimal sample possesses more Li⁺ ions coordinated to cyano groups and less Li⁺ ions coordinated to ether groups, in comparison to other investigated samples. Thanks to the relatively low binding energy of cyano to Li⁺, the SPE mitigates the stronger interaction between Li⁺ and ether, diminishing the energy of coordination/dissociation. The beneficial coordinating groups and directional nanochannels both synergistically enable Li⁺ to rapidly and smoothly transport across SPEs. Those results pave the way towards the utilization of our SPEs with aligned channels in SSBs prototypes.

4 Experimental section

4.1 Materials

Phenol was supplied by Acros Organics. Formaldehyde (37 wt%) was supplied by TCI. Dicyandiamide (DCD) was supplied by Thermo Scientific. Pluronic® F127 was supplied by BASF. Ethanol (EtOH), hydrochloric acid (HCl, 37%), sodium hydroxide (NaOH), dimethylformamide (DMF) were supplied

by VWR. Ammonium hexafluorophosphate (NH₄PF₆) was supplied by Sigma-Aldrich. Lithium perchlorate (LiClO₄, anhydrous, 99.5%) was supplied by Alfa Aesar. All chemicals were used as received without any further treatment. Milli-Q water was used.

4.2 Characterizations

Fourier transform infrared (FTIR) spectra were collected on a Nicolet iN10 IR microscope from Thermo Fisher Scientific using a diamond attenuated total reflection (ATR) technique. Differential scanning calorimetry (DSC) was conducted using a Mettler Toledo DSC1 equipped with STARE software. Samples were placed in 40 μL sealed aluminum pans. The temperature was swept from -80 to 100 °C at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. Scanning electron microscopy (SEM) images were collected by a Zeiss Auriga FIB-SEM. Samples for SEM measurements were scraped from the substrate and calcined in a tube furnace (Nabertherm R 50/250/13 with Controller C450) under argon atmosphere, to make the nanochannel structure hollow and detectable in the SEM. Molar masses of polymers were measured on a Polymer Standards Service size exclusion chromatography (SEC) system calibrated with poly(ethylene oxide) (PEO) standards. A NH₄PF₆ solution (2.5 mM in DMF) was used for elution. Small angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) experiments were performed at BL11-NCD beamline at ALBA (Barcelona, Spain). The sample-to-detector distance and the X-ray wavelength were 6.68 m and 1 Å respectively. The scattering intensities are plotted *versus* the norm of the scattering vector, q , defined as $q = 4\pi/\lambda \sin(\theta/2)$ with θ the scattering angle. Samples for SAXS and WAXS measurements were scraped from their substrates.

4.3 Sample synthesis

4.3.1 Synthesis of resol. Resol, also known as phenolic resin, with low molecular weight was prepared from phenol and formaldehyde assisted by a base catalyst.^{17,24} For a typical synthesis of resol, phenol (8.0 g) was melted in a flask at 45 °C. A NaOH aqueous solution (0.279 ml, 20 wt%) was mixed into the melted phenol and stirred for 10 min. Then formaldehyde (4.805 ml, 37 wt%) was dropwise added into the

above mixture. Successively, the whole mixture was heated in an oil bath at 70 °C for 1 h. After cooling to RT, the pH value of the mixture was adjusted to ~7 by a HCl solution (2 M). The remaining water of the mixture was further removed by rotary evaporator at 40 °C. The resulting product, namely resol, was dissolved in EtOH at the weight ratio of 20 wt%, for further use.

4.3.2 Synthesis of F127-channel-aligned-DCD-LiClO₄. In a typical process for a F127-channel-aligned-DCD-LiClO₄ sample, predetermined amounts of DCD and LiClO₄ were dissolved in EtOH (2 ml) at room temperature (RT) and mixed at 40 °C. Then a resol solution (0.5 g, 20 wt% in EtOH) was added into the above mixture drop by drop. Besides, Pluronic® F127 (0.1 g) was dissolved in EtOH (1 ml) at 40 °C and then added into the above mixture. After stirring for 30 min at 40 °C, the liquid mixture was dropwise casted on stainless-steel (SS) spacers of coin cells. After evaporating the EtOH at RT overnight, these samples were further heated at 100 °C for 24 h in a vacuum oven. The dry membrane was finally obtained as a F127-channel-aligned-xDCD-yLiClO₄ sample, where *x* refers to the molar ratio of DCD to ethylene oxide (EO) in the sample, ranging from 0, 1/64, 1/32, 1/16, 1/8 to 1/4; *y* stands for the molar ratio of Li⁺ to EO in the sample, ranging from 1/25, 1/20, 1/15, 1/10 to 1/8.

4.3.3 Synthesis of F127-random-structure-DCD-LiClO₄. A mixture of DCD (0.1 mmol) and LiClO₄ (0.08 mmol) was dissolved in EtOH (2 ml) at RT. Then a resol solution (0.615 ml, 20 wt% in EtOH) was added into the above mixture drop by drop. Besides, Pluronic® F127 (0.1 g) was dissolved in EtOH (1 ml) at 40 °C and then added into the above mixture. After stirring for 30 min, the liquid mixture was dropwise casted on SS spacers of coin cells. After evaporating the EtOH at RT under intensive ventilation, these samples were further heated at 100 °C for 24 h in a vacuum oven. The dry membrane was finally obtained as a F127-random-structure-1/16DCD-1/20LiClO₄ sample.

4.4 Electrochemical measurements

Electrochemical impedance spectroscopy (EIS) was conducted on a SPE assembled into a symmetric SS configuration for measuring the ionic conductivity. EIS was measured in the frequency range from 7 MHz to 100 mHz and in the temperature range from 90 to 20 °C on a Bio-Logic VMP-300 instrument. Temperature was controlled by a climate chamber with a ramp rate of 0.33 °C min⁻¹, besides a period of 30 min was applied for each 10 °C as an equilibration time for measurement.

5 Calculation section

5.1 Ionic conductivity calculated by electrochemical impedance spectroscopy

The σ of a SPE was determined from the resistance measured by EIS in a cell configuration of SS symmetric electrodes from 20 °C to 90 °C using eqn (1):

$$\sigma = \frac{l}{RA} \quad (1)$$

where σ (S cm⁻¹) is the ionic conductivity of the SPE sample, *l* (cm) is the thickness of the membrane-like SPE sample, *R* (Ω) is the bulk resistance measured by EIS, and *A* (cm²) is the contact area between the SPE and SS.²⁵

5.2 Activation energy fitted by the Vogel–Fulcher–Tammann equation

Above the melting temperature *T_m*, the segmental movement of polymer chains helps Li⁺ ions transfer among the coordination sites. The Li-ion transfer mechanism is suitable to be simulated by the Vogel–Fulcher–Tammann (VFT) equation. The relationship between temperature and σ is interpreted as eqn (2):

$$\sigma = A_{\text{VFT}} T^{-\frac{1}{2}} \times e^{-\frac{E_a}{R(T-T_0)}} \quad (2)$$

where σ (S cm⁻¹) is the ionic conductivity of samples, *A_{VFT}* (S cm⁻¹ K^{0.5}) is the VFT pre-exponential factor, *T* (K) is the absolute temperature, *E_a* (J mol⁻¹) is the activation energy, *R* (J mol⁻¹ K⁻¹) is the gas constant, and *T₀* (K) is the reference temperature, related to the glass transition temperature *T_g* of a sample.²⁰

Eqn (2) is transformed into eqn (3):

$$\ln(\sigma T^{\frac{1}{2}}) = \frac{E_a}{R(T - T_0)} \quad (3)$$

By plotting $\ln(\sigma T^{\frac{1}{2}})$ vs. $(T - T_0)^{-1}$, *E_a* can be related to the slope. *T₀* better meet VFT simulation conditions and to improve the fitting accuracy, the temperature-dependent σ data from 50 °C to 90 °C are chosen to be simulated.

Author contributions

Z. C.: data curation; formal analysis; investigation; methodology; validation; visualization; writing – original draft. I. A. M., R. B., H. J., S. Y., Y. Z., Z. H., and K. Z.: data curation; formal analysis; investigation. S. M., L. R., and K. M.: formal analysis; investigation; review. J.-F. G.: conceptualization; funding acquisition; methodology; project administration; resources; supervision; writing – original draft; writing – review & editing.

Data availability

The data supporting the findings of this study are available within the article and the ESI.† Any other data can be provided upon request.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Z. C., S. Y., and Z. H. acknowledge the China Scholarship Council. J.-F. G. is grateful to Service Public de Wallonie (Win4Excellence BATFACTORY 310153 project) for financial support.

References

- 1 M. Arrese-Igor, M. Martinez-Ibañez, E. Pavlenko, M. Forsyth, H. Zhu, M. Armand, F. Aguesse and P. López-Aranguren, *ACS Energy Lett.*, 2022, **7**, 1473–1480.
- 2 X. Zhang, J. Xie, F. Shi, D. Lin, Y. Liu, W. Liu, A. Pei, Y. Gong, H. Wang, K. Liu, Y. Xiang and Y. Cui, *Nano Lett.*, 2018, **18**, 3829–3838.
- 3 H. Wu, Y. Lin, Z. Wang, K. Shi, J. Li, J. Pan, J. Ren, X. Li, Y. Min, M. Wu and Q. Liu, *Chem. Eng. J.*, 2024, **486**, 150343.
- 4 S. Yan, H. Jia, Y. Li, Z. Chen, R. Lyons, Z. He, Y. Zhang, C. Liu, C.-A. Fustin and J.-F. Gohy, *Chem. Eng. J.*, 2024, **495**, 153874.
- 5 J. Wan, J. Xie, X. Kong, Z. Liu, K. Liu, F. Shi, A. Pei, H. Chen, W. Chen, J. Chen, X. Zhang, L. Zong, J. Wang, L.-Q. Chen, J. Qin and Y. Cui, *Nat. Nanotechnol.*, 2019, **14**, 705–711.
- 6 Y. Cui, J. Wan, Y. Ye, K. Liu, L.-Y. Chou and Y. Cui, *Nano Lett.*, 2020, **20**, 1686–1692.
- 7 D. Lin, W. Liu, Y. Liu, H. R. Lee, P.-C. Hsu, K. Liu and Y. Cui, *Nano Lett.*, 2016, **16**, 459–465.
- 8 S. Liu, H. Shan, S. Xia, J. Yan, J. Yu and B. Ding, *ACS Appl. Mater. Interfaces*, 2020, **12**, 31439–31447.
- 9 W. Liu, S. W. Lee, D. Lin, F. Shi, S. Wang, A. D. Sendek and Y. Cui, *Nat. Energy*, 2017, **2**, 17035.
- 10 X. Cai, J. Ding, Z. Chi, W. Wang, D. Wang and G. Wang, *ACS Nano*, 2021, **15**, 20489–20503.
- 11 L. Zhang, H. Gao, S. Xiao, J. Li, T. Ma, Q. Wang, W. Liu and S. Wang, *ACS Mater. Lett.*, 2022, **4**, 1297–1305.
- 12 Y. Liang, N. Chen, W. Qu, C. Yang, L. Li, F. Wu and R. Chen, *ACS Appl. Mater. Interfaces*, 2021, **13**, 42957–42965.
- 13 S. Hu, L. Du, G. Zhang, W. Zou, Z. Zhu, L. Xu and L. Mai, *ACS Appl. Mater. Interfaces*, 2021, **13**, 13183–13190.
- 14 Y. Xu, S. Zhang, T. Liang, Z. Yao, X. Wang, C. Gu, X. Xia and J. Tu, *ACS Appl. Mater. Interfaces*, 2021, **13**, 11018–11025.
- 15 Z. Chen, H. Jia, S. Yan and J.-F. Gohy, *Nano Energy*, 2023, **114**, 108637.
- 16 W. Lyu, G. He and T. Liu, *ChemistryOpen*, 2020, **9**, 713–718.
- 17 H. Xu, H. Xu, Z. Chen, X. Ran, J. Fan, W. Luo, Z. Bian, W. Zhang and J. Yang, *ACS Appl. Mater. Interfaces*, 2019, **11**, 3861–3868.
- 18 Y. Meng, D. Gu, F. Zhang, Y. Shi, L. Cheng, D. Feng, Z. Wu, Z. Chen, Y. Wan, A. Stein and D. Zhao, *Chem. Mater.*, 2006, **18**, 4447–4464.
- 19 G. Zardalidis, J. Mars, J. Allgaier, M. Mezger, D. Richter and G. Floudas, *Soft Matter*, 2016, **12**, 8124–8134.
- 20 K. M. Diederichsen, H. G. Buss and B. D. McCloskey, *Macromolecules*, 2017, **50**, 3831–3840.
- 21 S. Srivastava, J. L. Schaefer, Z. Yang, Z. Tu and L. A. Archer, *Adv. Mater.*, 2014, **26**, 201–234.
- 22 Y. He, S. Chen, L. Nie, Z. Sun, X. Wu and W. Liu, *Nano Lett.*, 2020, **20**, 7136–7143.
- 23 Y. Zhao, L. Wang, Y. Zhou, Z. Liang, N. Tavajohi, B. Li and T. Li, *Adv. Sci.*, 2021, **8**, 2003675.
- 24 W. Teng, Z. Wu, J. Fan, H. Chen, D. Feng, Y. Lv, J. Wang, A. M. Asiri and D. Zhao, *Energy Environ. Sci.*, 2013, **6**, 2765.
- 25 L. Bai, S. Ghiassinejad, J. Brassinne, Y. Fu, J. Wang, H. Yang, A. Vlad, A. Minoia, R. Lazzaroni and J.-F. Gohy, *ACS Appl. Mater. Interfaces*, 2021, **13**, 44844–44859.