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## **Anisotropic Mass Transport Using Ionic Liquid Crystalline Electrolyte to Suppress Lithium Dendrite Growth**

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### **Abstract**

Lithium metal as anode has been widely accepted due to its higher negative electrochemical potential and theoretical capacity. Nevertheless, the existing safety and cyclability issues limits the lithium metal anodes from practical use in high-energy density batteries. The repeated Li deposition and dissolution processes upon cycling lead to the formation of dendrites at the interface which results in reduced Li availability for the electrochemical reactions, disruption in Li transport through the interface and increased safety concerns due to short circuiting. Here, we demonstrate a novel strategy using Ionic Liquid Crystals (ILCs) as electrolyte cum pseudo-separator to detain the dendrite growth with their anisotropic properties controlling the Li-ion mass transport. The thermotropic ILC with two-dimensional Li-ion conducting pathways was synthesized and characterized. Microscopic and spectroscopic analysis elucidate that the ILC formed with smectic A phase, which can be utilized for wide temperature window operation. The results of electrochemical studies corroborate the efficacy of ILC electrolytes in mitigating dendrites formation even after 850 hours and it is further substantiated by numerical simulation and deduced the mechanism involved in dendritic suppression.

Keywords: Ionic liquid crystals, Anisotropy, 2D ionic conduction, Li dendrites, Modeling.

## Introduction

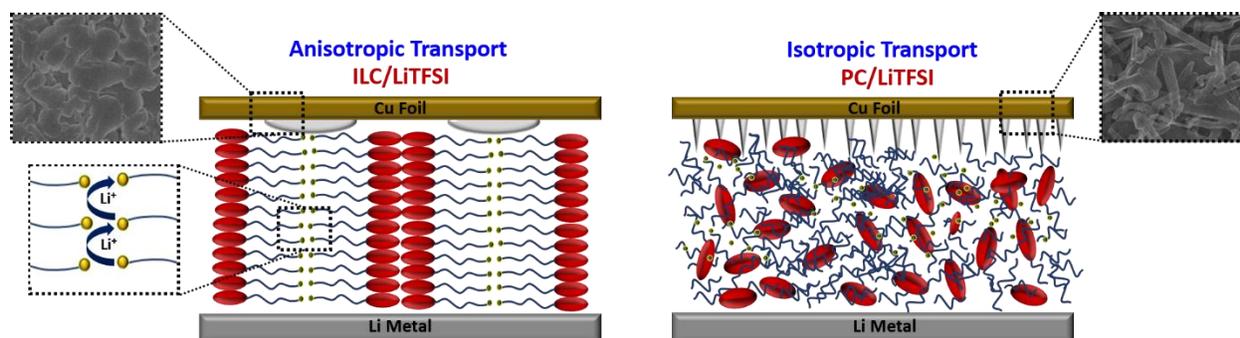
Research on rechargeable Li metal-based batteries has been amplified as Li metal can deliver a specific capacity of  $\sim 3862 \text{ mAh g}^{-1}$ , which positions it as a promising component in portable energy devices, electric vehicle systems, robotics, and other grid storage technologies.<sup>1-4</sup> However, the demand for portable energy storage devices with high energy density remains a challenge. In this scenario, Li-O<sub>2</sub> and Li-S batteries are capable of delivering ultra-high energy densities and are considered as next generation energy storage systems.<sup>5</sup> Unfortunately, the intrinsic issues instigated by electrode/electrolyte interactions causing problems in terms of safety and cyclability in these batteries hinder their practical implementation in certain applications.<sup>6,7</sup> In particular, the heterogeneous anode materials can lead to the formation of dendrites on their surface, which has a longstanding negative affect on the Li battery (LiB) performance in terms of safety and cycle life.<sup>8,9</sup> The effects on the stability of battery cycling by the dendrite growth can be due to the increased interfacial resistance and poor Coulombic efficiencies which lead to cell short-circuiting, cell failure, and explosion.<sup>8,10</sup> Hence, prevention of dendrite formation is necessary to employ Li metal as an anode in batteries.

At the Li metal/electrolyte interface, Li-ions react with electrons during the charging process and electrochemically get reduced and deposited onto the Li metal anode.<sup>11, 12</sup> Impurities and protrusions on the anode surface cause the nucleation of dendritic Li structures with faster kinetics and inconsistent deposition.<sup>13</sup> Li mass transport is the main factor for the dendrite growth, which depends on many physical processes such as advection, ion migration and reactions at the electrode / electrolyte interface.<sup>14,15</sup> Large variations in the Li<sup>+</sup> ion concentration gradient across the surface of the anode also appear to encourage the deposition and Li dendrite formation. Researchers have

taken tremendous efforts to suppress dendrite growth through various techniques such as electrode modification, controlling the Li morphology, designing different cell configurations by introducing protective layers and conducting scaffolds, implementing different kinds of electrolytes including solid-state, gel electrolytes, and more.<sup>9, 10, 16</sup> The limited success of these strategies call for a better approach towards dendrite suppression.

Recent theoretical studies based on liquid crystals suggest that the anisotropic properties of the electrolyte can control the Li-ion mass transport and paves way for the suppression of dendrite growth.<sup>12</sup> Also, modelling and simulation studies indicate that the electrolyte which enables high ionic conductivity and lithium transference number ( $t_{Li^+}$ ) near to unity at the reaction sites can reduce the concentration gradient and thereby the dendrite growth.<sup>17, 18</sup> Among the several electrolytes explored, ionic liquid crystals (ILCs) are promising due to their exceptionally efficient 1D, 2D and 3D anisotropic ion-conduction pathways and have the capability to form robust solid electrolyte interfaces (SEI) with reduced resistance because of their liquid-like mobility.<sup>19-24</sup> Recently, rod like ILCs consisting of cyclic carbonate derivative moiety and lithium bis (trifluoromethylsulfonyl)imide (LiTFSI) have been studied in Li-ion batteries.<sup>25</sup> However, till date, there are no reports on how anisotropic properties of ILC could influence dendrite growth on Li anode.

Here, we developed a novel imidazolium based thermotropic ILC material from a long-alkylated phenol, 3-pentadecyl phenol (3 PDP). The characterization of ILC revealed bent core structure with self-assembled molecules exhibiting high ionic conductivity at both RT and elevated temperatures. We report that these ILCs with their anisotropic properties can act as a pseudo separator-cum-electrolyte and control the Li ion concentration gradient at the electrolyte-anode interface, which helps in controlling Li ion mass transportation and thereby suppressing dendrite



Scheme 1. Schematic representation of the working of anisotropic transport when compared to the isotropic transport.

growth, as shown in Scheme 1. To complement the experimental results, numerical simulations were performed to explore the mechanism of dendrite suppression based on the properties of the ILC electrolyte.

## Experimental Section

**2.1 Characterization of ILC electrolytes:** ILC electrolytes were characterized for their ionic conductivity and anisotropic nature using electrochemical impedance spectroscopy (EIS) and differential scanning calorimetry (DSC) analysis.  $^1\text{H}$  NMR was carried out to confirm the formation of targeted LC. Further, wide angle X-ray diffraction (WAXD), small angle X-ray scattering (SAXS) and polarizing optical microscopy (PLOM) studies were used to determine the crystal data and orientation of the additive containing LC.

**2.2 Anisotropy conductivity measurements:** Anisotropic ionic conductivity was measured in both directions parallel and perpendicular to the self-assembled layers using the alternating current impedance technique. Anisotropy in ionic conductivity of LCs was analyzed by a pair of comb shaped gold electrodes (Cell A) and a pair of Indium tin oxide (ITO) plates (Cell B). First, gold was sputtered onto a glass plate in a comb shape by leaving a 1 mm distance between the teeth and a sidewise width of approximately 0.3 mm. The thickness of the sputtered gold was about 0.8  $\mu\text{m}$ . The compound mixtures were filled in both the cells and their orientation were confirmed by a

polarizing microscope. Ionic conductivity parallel to the oriented layer was measured using cell A, and the one perpendicular to the oriented layer was obtained by using cell B. In Cell B, a pair of indium tin oxide (ITO) electrodes were separated with a thickness of 30  $\mu\text{m}$  using a Teflon spacer. In both cases, homeotropic alignment of sample mixtures were observed.

**2.3 Interfacial Mesoscale Modeling:** The numerical simulations use a multiphase reactive transport model based on smoothed particle hydrodynamics (SPH) which is a Lagrangian particle-based method. SPH was first developed for astrophysical problems and it has been adapted to solve fluid dynamics, multiphase flows, and reactive transport by discretizing the continuity equations.<sup>12, 26-28</sup> The model used for the studies presented in this work is based on previous modeling of dendrite growth.<sup>12, 29, 30</sup> The details of the model equations and implementation can be found in Tan et al.<sup>12</sup> This model was developed using an open-source software called Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS).<sup>31</sup>

#### **2.4. Electrochemical measurement:**

The electrodeposition of Li in the LC based electrolytes using galvanostatic cycling of Li| LiTFSI-LC| Li symmetric lithium cells in which lithium striping process was carried out under constant current which resembles conventional Lithium metal battery. The symmetric cells were fabricated using CR2032 cells with Li electrodes of 10 mm in size on both sides of the separator made of Teflon with a hole of 1.6 mm diameter at the center facilitating the ionic mobility between the Li electrodes and preventing any other side reactions. The prepared novel ILC electrolyte with optimized amount of LiTFSI was filled in the hole of separator. Symmetric cell cycling from -1 to 1 V was conducted on Arbin electrochemical workstation with a current density of 0.1  $\text{mAcm}^{-2}$  at 60 °C. The charging and discharge times were restricted to 3 hours. The control experiment with electrolyte containing LiTFSI and PC were also carried out for comparison studies.

Electrochemical impedance spectroscopic (EIS) studies were conducted in the frequency range 1 Hz to 1 MHz using a bio-logic electrochemical workstation. Li|Au cells for the electrochemical stability measurement were fabricated by using Au (blocking electrode) as working electrode and Li as reference and counter. Gold sputtered stainless steel was used as the blocking electrode for this experiment.

## Results and discussion

Details pertaining to the synthesis of 3-(12-(3-pentadecylphenoxy) dodecyl)-1-methylimidazole\_3-3ium hexafluoro-phosphate (PDDMHP) is explained and provided in the supporting information. Formation of the targeted compound is schematically represented in scheme S1 and it is confirmed by proton nuclear magnetic resonance ( $^1\text{H}$  NMR) analysis. In the NMR spectrum (Figure. S1) of PDDMHP, the triplet at a  $\delta$  value of 0.9 ppm is corresponding to the terminal methyl protons of the pentadecyl chain. Peaks in between 1 and 3 ppm are ascribed to the methylenic protons present in the pentadecyl side chain and dodecyl spacer chain. Methylenic protons present adjacent to the electronegative  $\text{O}^-$  and  $\text{N}^-$  atoms give characteristic triplets at 3.9 and 4.2 ppm, respectively. A sharp singlet at 3.8 ppm is due to the protons of the methyl groups attached directly to the imidazolium ring. Aromatic protons in the phenyl ring give characteristic peaks in between 6.8 and 7.2 ppm, whereas the protons in the imidazole ring produce peaks at 7.8 and 9.2 ppm. Thus,  $^1\text{H}$ NMR analysis clearly confirmed the formation of an imidazolium based ionic liquid crystal.

Further, Fourier transform infrared spectrometer (FT-IR) analysis was carried out to confirm the functional group present in the as synthesized compound and the corresponding spectra is shown in Figure S2. The presence of an alkyl chain having symmetric and asymmetric C-H stretching vibrations can be observed as multiple peaks in the range of  $2800 - 3000 \text{ cm}^{-1}$ . The peaks from

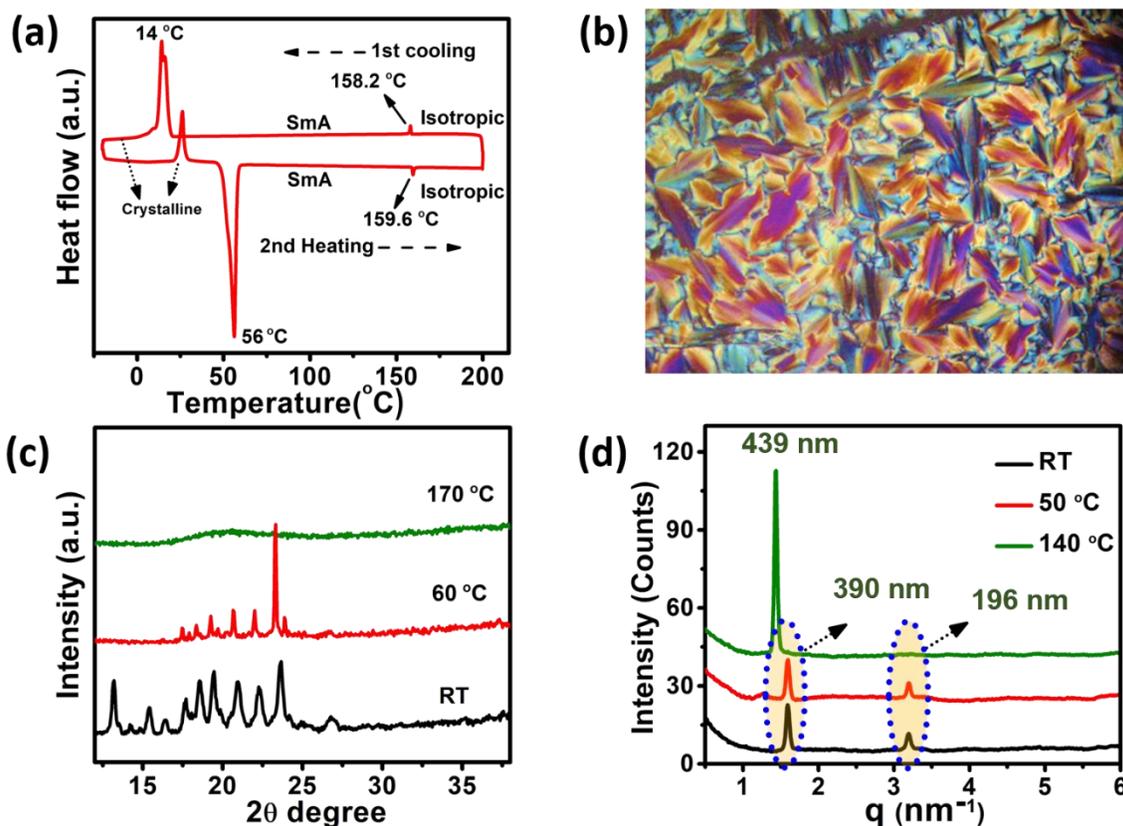


Figure 1: (a) DSC heating and cooling scans of PDDMHP showing thermotropic behavior. (b) PLOM images showing the SmA phase of the PDDMHP. (c) WAXD patterns of PDDMHP at different temperature (d) SAXS pattern of PDDMHP.

3000 to 3200  $\text{cm}^{-1}$  correspond to C-H vibration modes of aromatic rings. C-C stretching, and C-N bending vibrations can be observed from the peaks in the range of 1600 – 1585  $\text{cm}^{-1}$ . The peak at 1455  $\text{cm}^{-1}$  contributes to the C-H alkyl deformation, where a peak at 1189  $\text{cm}^{-1}$  indicates the C-N stretching vibration. C-O-C stretching of alkyl aryl ether is visible with the presence of a peak at 1158  $\text{cm}^{-1}$ . Finally, P-F stretching vibrations of  $\text{PF}_6^-$  anion is observed at 820  $\text{cm}^{-1}$ . To validate the fact that synthesized imidazolium based ILCs exhibited a thermotropic mesophase, we performed differential scanning calorimetry (DSC) thermograms measurements. To analyze the thermotropic phase transition of the synthesized compound, the sample was heated and cooled from 200 to -20 °C. On a heating ramp, PDDMHP displays a transition from crystalline to liquid crystalline phase, i.e. Smectic A (SmA) at a temperature of 55 °C and an isotropic phase at 165 °C (Figure 1a). On

cooling from the isotropic melt, PDDMHP transforms to smectic A phase again at 165 °C and returns to its crystalline nature at 25°C. These features can be observed clearly in the DSC spectrum shown in Figure 1a. The phase transition temperatures and enthalpy changes of PDDMHP are derived from DSC traces and are listed in Table S1.

Though the precise phase cannot be identified using DSC, the level of enthalpy change involved at the phase transition gives an estimate of the type of phase involved.<sup>32,33</sup> The structural changes, which occur during the temperature variation, reflect the enthalpy changes. The enthalpy changes of liquid crystalline to an isotropic liquid transition indicate that the LC phase is smectic A (SmA).<sup>34</sup> Furthermore, the type of mesophase that the compound exhibits is confirmed by using

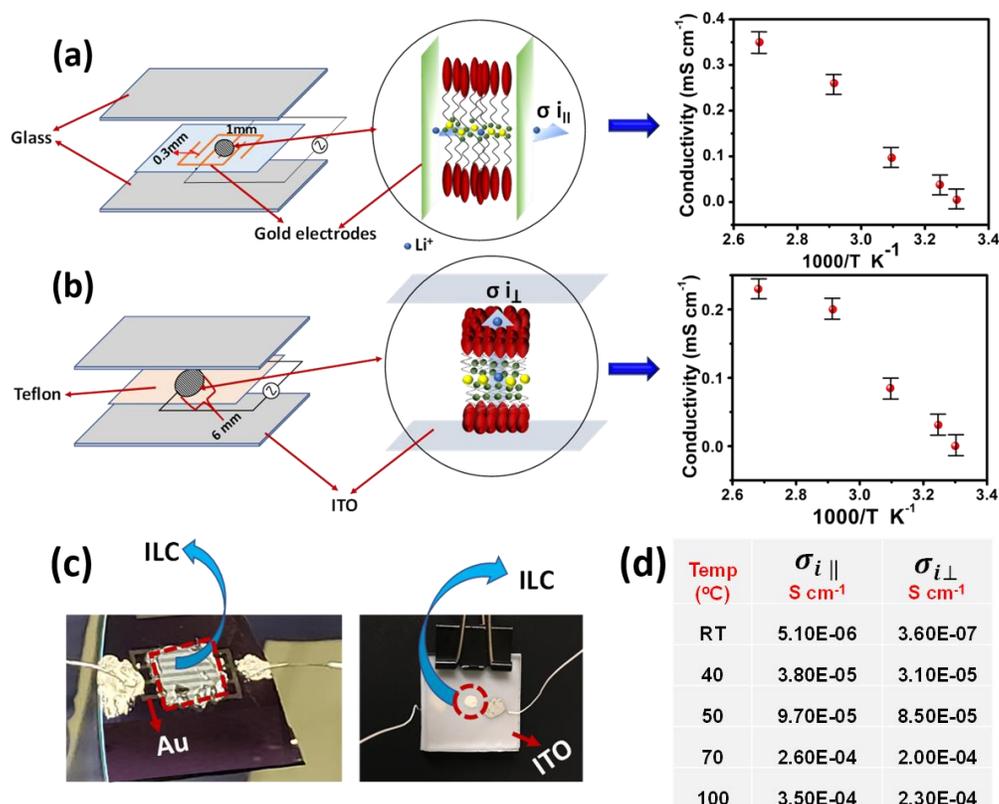


Figure 2: Anisotropic ionic conductivity measurements. (a) Structure of comb shaped gold electrode cell for horizontal ionic conductivity analysis of PDDMHP, (b) Structure of ITO electrode cell for perpendicular ion conductivity analysis, (c) gold electrode cell and ITO electrode cell, and (d) Table with parallel and perpendicular ionic conductivity in PDDMHP at different temperatures varying from RT, 40, 50, 70 and 100 °C.

optical polarizing microscopy in conjunction with DSC analysis. The images (Figure 1b) were taken while cooling from the isotropic phase starting at 165 °C. During cooling, the randomly aligned or disordered ionic liquid crystal molecules are aligned together to form supramolecular organized liquid crystalline phases by several noncovalent interactions such as electrostatic, ionic assembling and Van der Waal's interactions, helping to form a mesophase in the compound with different extents of order. The images show that the liquid crystals are in the smectic A phase at temperatures ranging from 55 to 165 °C and are shown in Figure 1b. Wide angle X-ray diffraction (WAXD) was carried out at different temperatures to examine the phase transformation of the synthesized compound and is shown in Figure 1c. At room temperature, PDDMHP was highly crystalline due to the strong ionic interactions between the charged counterparts and long alkyl chains. PDDMHP was heated to form amorphous phases without any characteristic peaks, showing a complete transformation to the isotropic phase above 170 °C. On cooling from the melt, the quasi-crystalline nature reappeared with a few of the reflections at a temperature below 100 °C, confirming the recrystallization of the melt to an anisotropic liquid crystalline phase. The high intensity peaks at the LC and crystalline phases are attributed to the stacking of imidazolium cations. The emergence of moderately crystalline peaks when the isotropic melt is cooled below 100 °C could be corroborated to the formation of the anisotropic LC phase. This observation is in well agreement with the DSC analysis.

Thermotropic liquid crystalline phase formation of the compound is followed with Small-angle X-ray scattering (SAXS) analysis (Figure 1d). At room temperature, the SAXS pattern of PDMHP displays two peaks with d-spacing values of 39 Å and 19.6 Å owing to the crystalline order of the ionic liquid crystal. Increasing the temperature to 50 °C, the liquid crystalline phase begins to emerge, and in addition to the peaks mentioned before, a shoulder initiates at a lower scattering

vector. SAXS analysis of the compound at 140 °C clearly illustrates the formation of a liquid crystalline phase as the crystalline peaks completely disappear and a sharp self-assembly peak with a d-spacing of 43.9 Å persists. This sharp peak corresponds to the self-assembly of PDDMHP by means of non-covalent interactions such as alkyl chain interdigitation, van der Waal's interactions and ion-lone pair interactions. The expected layered 2D conduction pathways allow ion transportation in both parallel and perpendicular directions. This is confirmed by carrying out anisotropic ILC measurements in both directions for ILCs at varying temperature. The ionic conductivity value of each cell (gold electrode and Indium tin oxide (ITO) based electrode) is different at each temperature (SmA phase), explaining the anisotropic nature of these ILCs (Figure 2a and 2b). Both gold and ITO electrode cell configurations are shown in figure 2c. The ionic conductivity (IC) between the gold teeth (parallel to the smectic layer) is found to be higher when compared to that between ITO plates perpendicular to the layer. The IC values at various temperatures in both directions are summarized in the Figure 2d.

### Electrochemical Studies:

Composition	$\sigma$ (S cm <sup>-2</sup> )
LC/LiTFSI, 1:1	$1.37 * 10^{-4}$
LC/LiTFSI, 3:1	$1.72 * 10^{-4}$
LC/LiTFSI, 9:1	$1.85 * 10^{-4}$

Table 1: Ionic conductivities of different lithium composites containing PDDMHP and LiTFSI at different ratios of 9:1, 3:1 and 1:1, respectively.

To further use LCs as an electrolyte for LiBs, the synthesized compounds were mixed with an optimized amount of lithium bis (trifluoromethyl sulfonyl) imide (LiTFSI) salt. This was to form 2D ion conducting pathways through ion – dipole interactions between the imidazole group and

Li ions in the salt.<sup>25, 35</sup> It is expected that the concentration of salt has an impact on liquid-crystalline behavior, along with its viscosity and ionic conductivity. To verify, lithium composites of different ratios of 9:1, 3:1 and 1:1 were prepared by solvent evaporation of a corresponding solution in tetrahydrofuran. Ionic conductivities of these electrolytes were measured repeatedly in ambient atmosphere by AC impedance spectroscopy over a frequency range of 1 Hz to 1 MHz at 60°C with amplitude 10 mV to ensure the reproducibility. Figure 3a shows the resultant electrochemical impedance Nyquist plot and the corresponding equivalent circuit and the magnified portion is shown in Figure 3b. The solution resistance from the fitted impedance spectra is measured and the ionic conductivity is mathematically calculated and plotted against temperature (1000/T) (Figure 4a).<sup>36, 37</sup>

The expression for ionic conductivity calculation is  $\sigma = (l / R_s) (l / a)$  where  $l$  is the thickness of the samples and  $a$  is the area of the electrode. The measured ionic conductivities in the order of  $10^{-4} \text{ S cm}^{-1}$  are obtained in the SmA phase and are shown in Table 1. There is an increase in ionic conductivity as the temperature is increased and when the material transforms to the liquid crystalline phase, SmA phase which can be due to the oriented conductive pathways creation. The higher conductivities at elevated temperatures, at SmA phases (<60°C) are due to the lower viscosity and broader 2D conducting pathways<sup>38</sup>. These 2D arrangements of the ion conducting groups can provide opportunities for lithium ions to travel in both X and Y-directions, overcoming the defects confronted throughout the pathways while continuing directional movement. Among the different compositions of LC and Li salt, 9:1 ratio shows high ionic conductivity. The optimized amount of LiTFSI was found to be 9 equimolar (the molar ratio of PDMHP to LiTFSI was 9:1) and this mixture was selected as electrolyte for further electrochemical measurements.

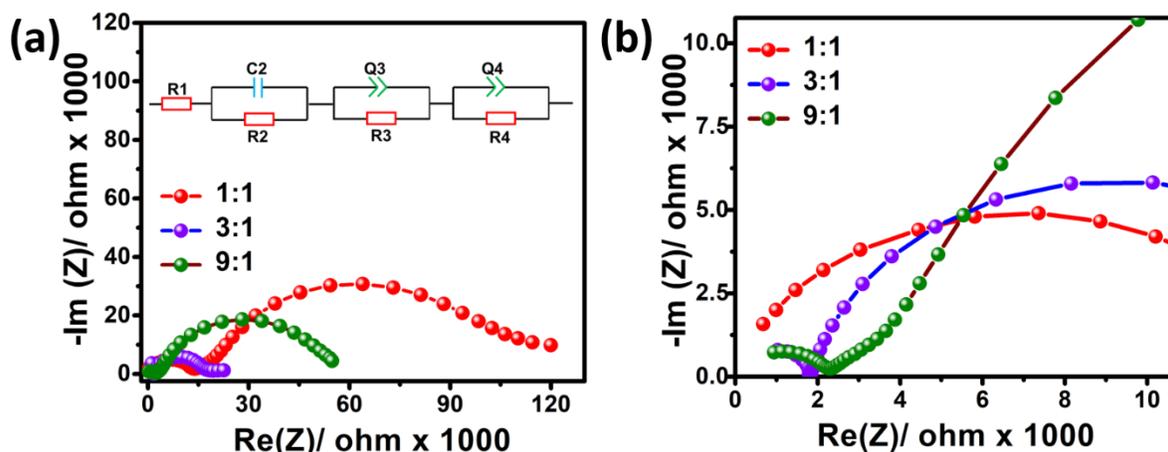


Figure 3: (a) Nyquist plot of different composition of PDDMHP with LiTFSI and corresponding equivalent circuit, and (b) magnified plot.

Ion conductivity measurements are followed by lithium transference number ( $t_{\text{Li}^+}$ ) studies to find the suitability of these electrolytes for better Li-ion battery performance. The Li transference number ( $t_{\text{Li}^+}$ ) is calculated at RT and 60 °C via electrochemical impedance spectroscopy (EIS) before and after the chronoamperometric technique (CA) test. In Figure 4b, chronoamperometry and EIS results of both the cells with and without LC are shown. At room temperature (Figure S3 and S4),  $t_{\text{Li}^+}$  is found to be 0.062 whereas at elevated temperature (100 °C), it increases to 0.32. It is well known that the coulombic interaction between cation and anion dominantly plays a major role in the transference and mobility of  $\text{Li}^+$  ions. Although conventional liquid electrolytes exhibit high ionic conductivity, the transference number used to be low. This is certainly due to the strong preferential solvation of  $\text{Li}^+$  by anion and strong coulombic interaction between them, resulting in a bulky solvation shell around  $\text{Li}^+$  compared to that of typical anions<sup>39</sup>. However, in our case, as cation is bigger, the Coulombic interaction between the larger cation and anion will become lower which tends to increase mobility of cations over anions<sup>40</sup>. As per previous reports, it is expected that with a higher  $t_{\text{Li}^+}$  value, the concentration gradient will be reduced by removing the anion depletion induced electric fields near the electrode/ electrolyte interface, which limits the

nucleation of Li dendrites.<sup>41</sup> According to Monroe and Newman's simulation studies, when  $t_{Li^+}$  approaches unity, the ion concentration gradient near the Li anode is suppressed by extending the stands time i.e. stopping or delaying the dendrite growth.<sup>41,42</sup> The synergistic effect of higher ionic conductivity and appropriate  $t_{Li^+}$  values for parallel Li-ion conduction thus controls the

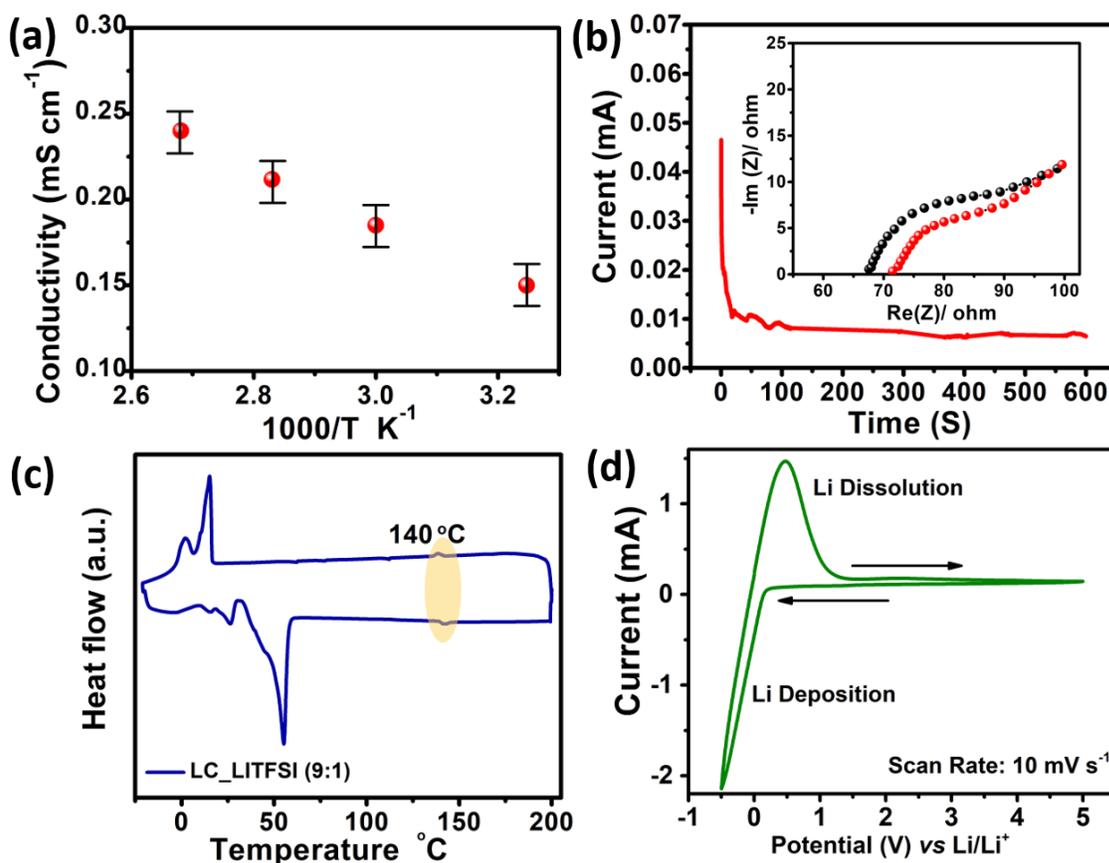


Figure 4: (a) Ionic conductivity of optimized LiTFSI/PDDMHP, (b) Li transference number measurement: Chronoamperometry profile for PDDMHP as electrolyte in symmetric Li/ (LiTFSI/PDDMHP) / Li cell with an applied voltage of 10mV, Nyquist plot for symmetric Li/ (LiTFSI/PDDMHP) / Li cell before and after polarization, (c) DSC measurements of optimized LiTFSI/PDDMHP, and (d) Electrochemical stability of formulated ILC based electrolyte.

concentration gradient near the electrode surface through effectively regulating Li ion mass transfer, which eventually inhibits the dendrite formation and its growth. This is further evidenced by both the experimental and the interfacial computational simulations as given below.

To corroborate the ILC property after adding LiTFSI salts, we performed DSC measurement on the LC-LiTFSI (9:1) mixture, as shown in Figure 4c. These thermotropic ILCs have a wide liquid crystalline window that provides the potential of utilizing their anisotropic nature over a wide range of temperatures. DSC measurements confirmed that the mixture was still in the LC phase, with small changes in its anisotropy or mesophase window (Figure 4c). With the incorporation of Li salt (LiTFSI) to this ILC, there was a slight decrease in the anisotropic window, although it still extended up to 140 °C. The smectic A phase transitions underwent small changes with the incorporation of LiTFSI. This is attributed to the fact that the in-plane packing of mesogens within the smectic layer is disturbed by the addition of bulky LiTFSI salts. Also, the LC electrolyte is expected to show higher ionic conductivity and is chosen as an electrolyte for electrochemical measurements. The isotropization temperature decreases for the mixture containing ILC and LiTFSI in a 9:1 molar ratio, although the SmA phase is still present over a wide temperature range. The SmA phase with higher molecular motion exhibited higher molecular conductivity as expected at an elevated liquid crystalline temperature, making them preferable for using as electrolytes in LiBs. As previously mentioned, the ionic conductivity is satisfactorily enhanced to  $1.85 \times 10^{-4}$  at a temperature of 60 °C due to the lower viscosity and highly efficient oriented ion conducting pathways of the SmA phase. Thus, the ILC: LiTFSI mixture in a 9:1 molar ratio, can act as an electrolyte with its persisting anisotropic nature enabling controlled Li ion mass transport.

Electrochemical stability of the ILC- LiTFSI composite based electrolyte was evaluated using cyclic voltammetry using Li|Au blocking electrode cell at an elevated temperature of 60 °C where the SmA – anisotropic phase was observed (Figure 4d). The measurement was conducted in a potential range from 0 to 5 V versus Li/Li<sup>+</sup> at a scan rate of 10 mVs<sup>-1</sup> and the voltammogram is shown in Figure 4d. There is an increase and decrease in current near the 0 V versus Li/Li<sup>+</sup> during

the anodic and cathodic sweep is due to the Li deposition and dissolution on the gold sputtered stainless steel substrate. The absence of any peak over the Li deposition and dissolution region indicates that there is no significant electrolyte decomposition at higher voltage, which suggests stable Li transportation, and electrochemical reactions at the electrodes in the presence of an ILC electrolyte in a wide potential window. Thus, the electrolyte mixture with an optimized molar ratio of ILC and LiTFSI shows a higher electrochemical stability without any decomposition at a higher

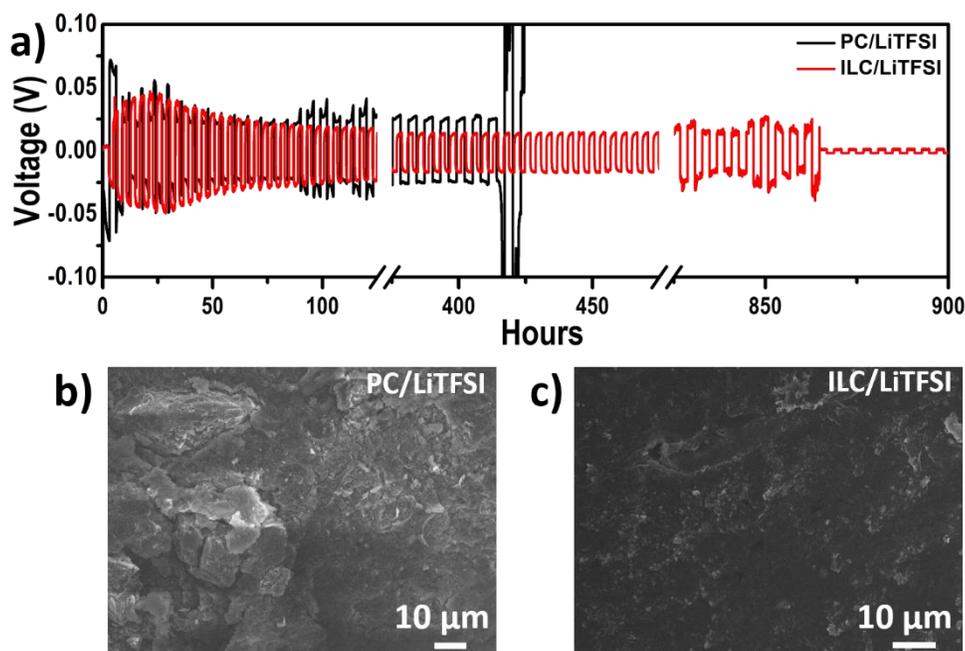


Figure 5. (a) Electrochemical Li plating/stripping of symmetric Li|ILC/LiTFSI|Li and Li|PC/LiTFSI|Li cells with a current density of  $0.1 \text{ mA cm}^{-2}$ , postmortem analysis (FE-SEM) of the cycled Li electrode of b) PC/LiTFSI and c) ILC/LiTFSI cells.

voltage range, indicating the efficient transport of Li ions between the electrodes without undergoing any electrochemical reactions. This can be attributed to the presence of mesogens acting as an ion conducting moiety.

Electrochemical cycling performance: After formulating the electrolyte, dendrite suppression studies were carried out where the anisotropic nature of the ILC is believed to regulate the ion concentration gradient at the interface. The electrodeposition of Li in the ILC based electrolytes

was investigated using galvanostatic cycling of Li| LC-LiTFSI| Li symmetric lithium cells in which the lithium stripping process is carried out under constant current 0.032 mA. The symmetric cells contain Li counter/ reference and working electrode on both sides of a hollow teflon spacer filled with ILC electrolyte. Symmetrical Li/Li cells with and without ILC as electrolyte were tested at a current density of 0.1 mA cm<sup>-2</sup> and a temperature of 60 °C to evaluate the long-term electrochemical cycling stability of the Li electrodes. Li/ILC-LiTFSI/Li showed a stable Li plating/stripping behavior in the presence of an anisotropic electrolyte with a gradual increase in polarization, which can be clearly seen in the voltage hysteresis. The difference between Li stripping and plating voltages represents the voltage hysteresis and is principally determined from the applied current density, electrode/ electrolyte interfacial properties and charge transfer resistance. A symmetrical Li/Li cell containing LiTFSI/propylene carbonate (PC) as an electrolyte shows a stable voltage hysteresis without any irregular oscillations when compared with the cell having ILC; however, a dendrite induced internal short circuit is seen after 400 hours as shown in Figure 5a. In contrast, the cell with the ILC electrolyte is able to cycle stably for more than 850 hours as the anisotropic electrolyte medium can improve the Li<sup>+</sup> mass transport between the major dendrite growth sites, and thereby form dendrites in a uniform and compact way. The Li metal after cycling was removed from the cycled cells and was analyzed using FE-SEM, as shown in Figure 5b, c. The cycled Li from the PC/LiTFSI cell showed a very rough surface with uneven chunks of Li metal, which can be attributed to the repeated uneven Li plating/stripping from the surface. On the other hand, the cycled Li from the ILC/LiTFSI cell was relatively much smoother with very small corrugations. The relatively smoother Li indicates stable cycling of the cell with minimal loss in the Li during the formation of the SEI, which is due to the relatively lower surface area. This is also one of the reasons for the lower polarization of the cell.

The morphology of the Li deposition was analyzed using Cu/Li cells, where Cu was the working electrode and Li was the reference and the counter. Li deposition onto the Cu foil was carried out at a current density of  $0.25 \text{ mA cm}^{-2}$  for 4 hours, after which the coin cells were disassembled to obtain the Cu foil for analysis using FE-SEM. Figure 6 and S5 shows the morphology of the Li deposition using PC/LiTFSI and ILC/LiTFSI electrolytes. In agreement with the previous

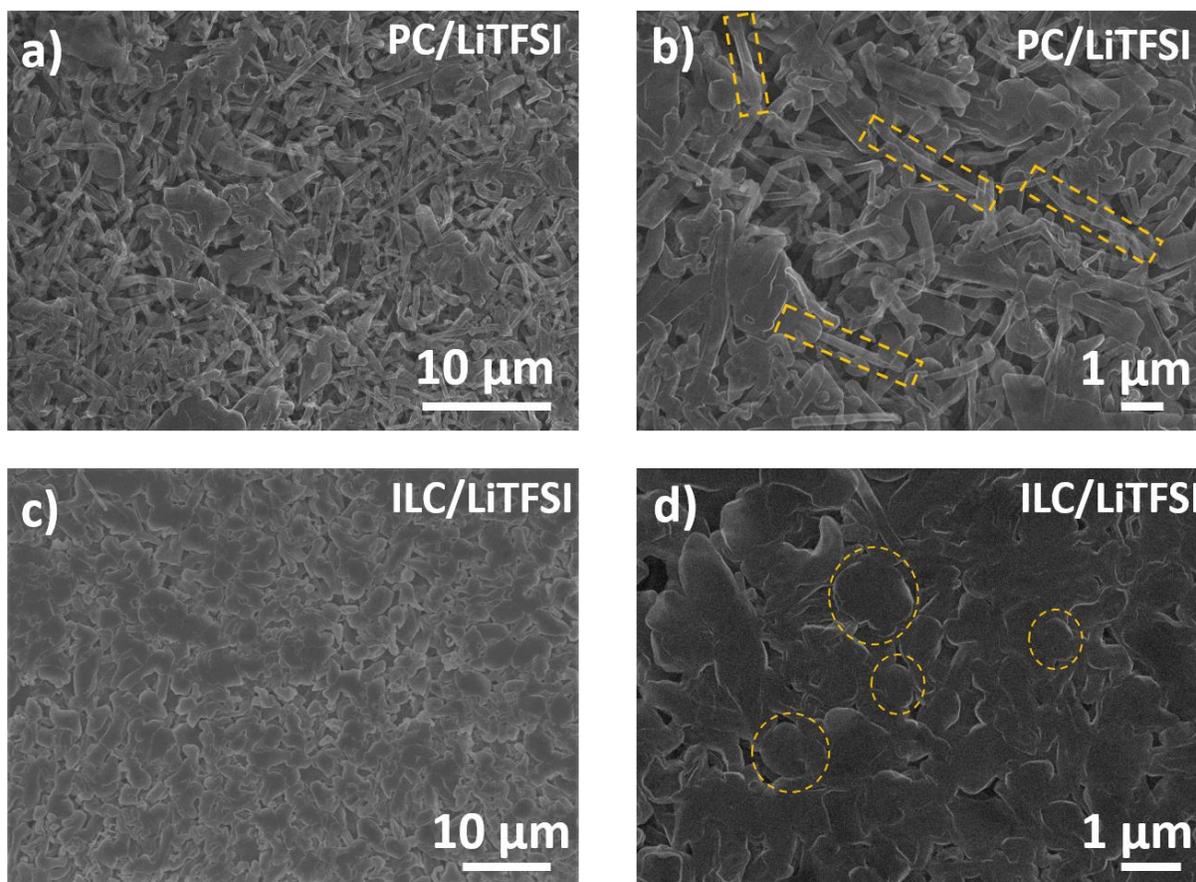


Figure 6. FE-SEM Li deposition morphological studies of a, b) PC/LiTFSI, and c, d) ILC/LiTFSI.

reports<sup>43,44</sup>, the Li plating using PC/LiTFSI resulted in sharp nodule like deposits, as seen in Figure 6a, b, and S5a. The diameter of the needle like structure was found to be in the range between 400 nm and  $0.2 \mu\text{m}$ , which can easily penetrate through any separator easily that can lead to the short circuiting of the cell. Such formation of dendritic Li structures is reported in several other popular electrolytes affecting the cyclability of Li metal batteries<sup>45,46</sup>. In contrast, the ILC/LiTFSI deposits

showed no such needle like morphology that correspond to the formation of Li dendrites. The morphology was spherical in shape with a diameter of 0.5 to 1.2  $\mu\text{m}$ , as shown in Figure 6c, d. It is difficult for such bigger sized morphology with curved edges to penetrate any separator. Also, the surface area is also drastically reduced as it is a well-known fact that a sphere possesses the lowest surface area compared to any other morphology, which increases the efficiency of the Li deposition process by reducing the amount of Li that is consumed in the formation of SEI. Further, the Li deposit using ILC/LiTFSI was found to be uniform and compact (Figure S5b, c), which can be ascribed to the horizontal growth in the y-direction due to the anisotropic type of mass transport occurring in the electrolyte.

**Simulation of the Interfacial Reactive Transport:** To understand the local transport mechanisms that lead to dendrite suppression in the ILC electrolyte, a numerical model is developed to study the reactive transport near the electrode-electrolyte interface. A Lagrangian particle-based modeling method known as smoothed particle hydrodynamics (SPH) is used to investigate how changes in local ion transport properties affect the growth of dendrites. To approximate the ILC electrolyte, a pseudo-separator like structure is simulated. Based on the experimental characterization of the ILC electrolyte, it is assumed ILC supra molecules in the electrolyte have a semi-ordered structure that can be approximated as a separator of rod-like particles. Rod-like particles on the order of a few microns in length are dispersed throughout the electrolyte in different orientations. The effects of particle orientation are varied from completely parallel to the anode surface, to randomly oriented (Figure 7a). Simulations are used to elucidate how the ILCs effect local transport and dendrite growth. Dendrite growth increases as the supramolecules align perpendicular to the anode surface. While a random orientation or alignment favoring the direction

parallel to the anode reduces the dendrite growth, as seen in Figure 7a. This can also be seen in the contour plots of local mass flux in Figure 7b and the growth rate of Figure 7c.

The anisotropic mass transport effect is proposed as a novel concept towards dendrite growth suppression in Li batteries and the corresponding schematic is shown in Figure 7d. The

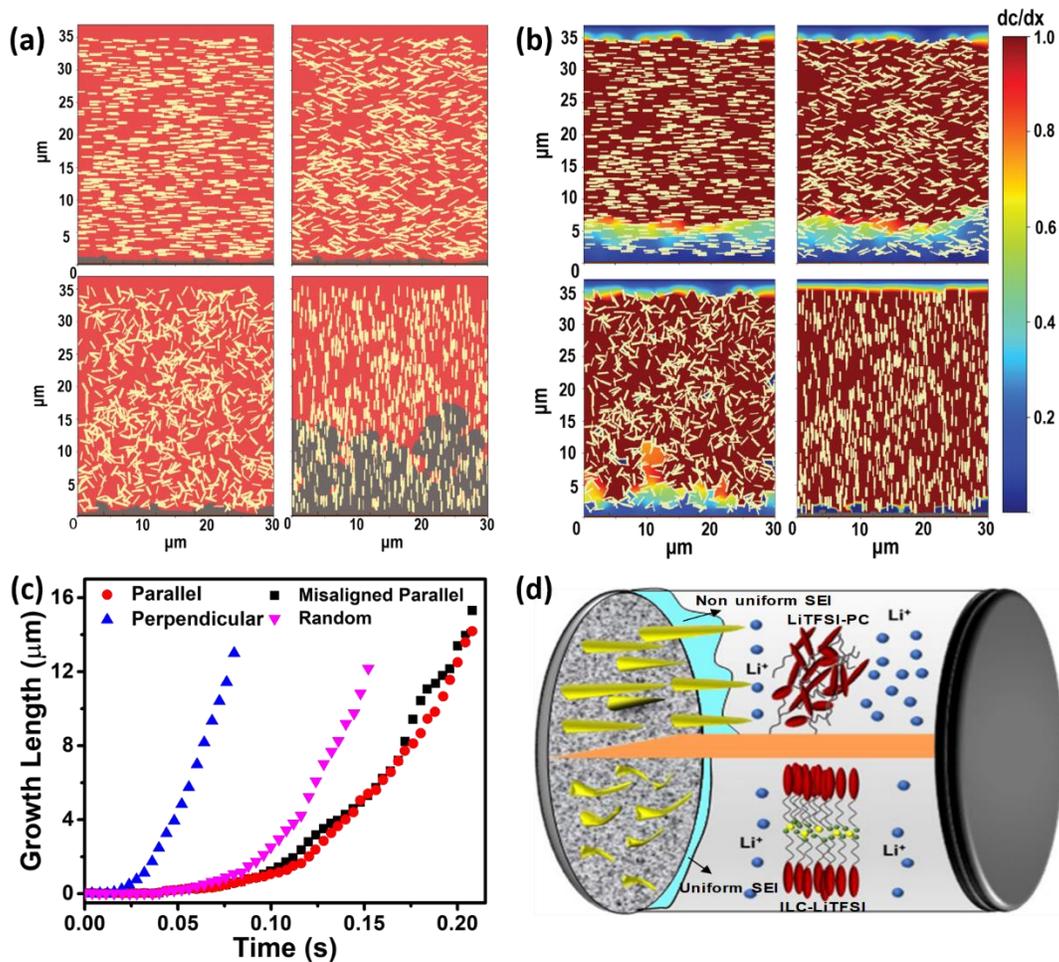


Figure 7. (a) Simulations domains for structures parallel, misaligned parallel, random, and perpendicular to the anode. (b) Local mass flux through the separators as dendrite grow into the separator from the anode (at  $y=0$ ). (c) Growth rate of dendrites over time for each separator structure. (d) Graphical representation of the proposed mechanism.

concentration gradient near the anode-electrolyte interface can be controlled by inducing these directional properties in Li ion batteries with the help of anisotropic ILCs.<sup>47</sup> From the numerical models of Figure 7b, the ILC supramolecules restrict local mass transport near the electrode interface. This leads to slower dendrite growth. The parallelly aligned liquid crystalline molecules

with their layered structure control the Li ion mass transfer, which in turn affects the Li ion concentration in the vicinity of the electrode. The Li ion concentration gradient near the electrode/electrode interface is the major reason for dendrite growth after nucleation. This lesser ion concentration gradient is reflected in the uniform SEI formation, which controls the dendrite growth rate.

The effects of local transport mechanisms on dendrite growth are also seen in the numerical models of the interface as seen in Figures 7b. The concentration gradients drive the transport of Li near the interface. Along the surface of the anode (bottom of Figure 7a, b), the gradient goes toward zero in the cases of parallel, random, and misaligned parallel structures. This is due to the high tortuosity through these structures. In the case of the perpendicular structure the tortuosity is roughly one and the separator has little effect on the local mass flux. The lower mass flux along the anode leads to the suppression of dendrite growth and longer battery lifetime. The low mass flux indicates an even distribution of Li concentration across the anode surface, which leads to a more even Li deposition. This allows for slower and more uniform growth, resulting in less harmful dendrites. In the presence of an anisotropic electrolyte medium, major dendrites form at the interspace between the initial dendritic nucleation sites, while the already formed dendrites are suppressed. This is supported by the numerical models as seen in the parallel and random cases of Figure 5b. In the anisotropic case, the Li ion diffusion to the major dendrite growth region decreases and hinders the replenishment of Li<sup>+</sup> ions in that region, prompting Li<sup>+</sup> ions to deposit in the adjacent dendrite free regions and thus leads to the formation of more compact and flat dendrites. Thus, these thermotropic ILC electrolytes with their ability to orient themselves in different directions to control Li mass transport and thereby dendrite growth can act as pseudo separator.

## Conclusions

In summary, we have shown that the synthesis of anisotropic liquid crystalline electrolytes and their efficacy in the mitigation of dendrite growth characteristics by reducing the Li ion concentration near the dendrite tip. The numerical models have demonstrated the mechanism of ILC electrolytes in dendrite suppression and for better Li diffusion control. This anisotropic mass transport effect can suppress the dendrite growth without sacrificing the battery performance. New thermotropic ILC with SmA phase for a wide temperature window containing 2D ion conducting pathways has been prepared and well characterized using various microscopic and spectroscopic techniques. The anisotropic ion conductivity was probed by conducting EIS measurements using both gold electrodes and ITO electrodes in both parallel and perpendicular directions consecutively. The PDDMHP: LiTFSI in the 9:1 molar ratio was tested for dendrite studies and it showed that highly ionic conducting pathways and near unity  $t_{Li^+}$  can greatly reduce the Li ion concentration at the anode surface and retard the dendrite formation and growth. This is further exemplified through continuous lithium plating/stripping around 850 hrs. with negligible changes polarization at extended cycling, suggesting the compact and robustness of an anisotropic ILC electrolyte mitigating dendrites formation. The demonstrated results reveal that the anisotropic ILCs are promising LIB electrolytes for long cell cycle life while ensuring safety by controlling dendritic parasitic reactions in the cells.

## Conflicts of interest

The authors declare no competing financial interest.

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