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Advanced High-Voltage Electrolyte Design Using Poly(ethylene Oxide) and High-Concentration Ionic Liquids for All-Solid-State Lithium-Metal Batteries / Zhang, Mingjie; Pal, Urbi; Makhlooghiazad, Faezeh; O'Dell, Luke; Kondou, Shinji; Elia, Giuseppe Antonio; Gerbaldi, Claudio; Forsyth, Maria. - In: ACS APPLIED MATERIALS & INTERFACES. - ISSN 1944-8244. - STAMPA. - 16:41(2024), pp. 56095-56105. [10.1021/acsami.4c11114]

*Availability:*

This version is available at: 11583/2991242 since: 2024-10-27T15:02:51Z

*Publisher:*

American Chemical Society (ACS)

*Published*

DOI:10.1021/acsami.4c11114

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# Advanced High-Voltage Electrolyte Design Using Poly(ethylene Oxide) and High-Concentration Ionic Liquids for All-Solid-State Lithium-Metal Batteries

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Cite This: *ACS Appl. Mater. Interfaces* 2024, 16, 56095–56105



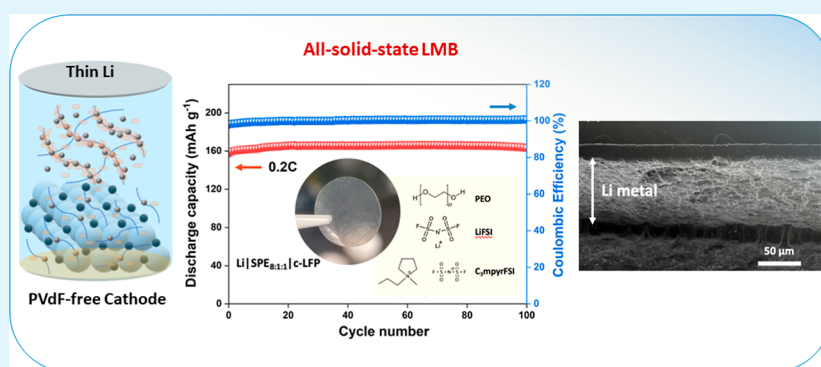
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**ABSTRACT:** Poly(ethylene oxide) (PEO)-based solid polymer electrolytes (SPEs) are among the most promising materials for solid-state lithium metal batteries (LMBs) due to their inherent safety advantages; however, they suffer from insufficient room-temperature ionic conductivity (up to  $10^{-6}$  S cm $^{-1}$ ) and limited oxidation stability ( $<4$  V). In this study, a novel “polymer-in-high-concentrated ionic liquid (IL)” (PiHCIL) electrolyte composed of PEO, *N*-propyl-*N*-methylpyrrolidinium bis(fluorosulfonyl) imide (C<sub>3</sub>mpyrFSI) IL, and LiFSI is designed. The EO/[Li/IL] ratio has been widely varied, and physical and electrochemical properties have been explored. The Li-coordination and solvation structure has been explored through Fourier-transform infrared spectroscopy and solid-state magic-angle spinning nuclear magnetic resonance. The newly designed electrolyte provides a promisingly high oxidative stability of 5.1 V and offers high ambient temperature ionic conductivity of  $5.6 \times 10^{-4}$  S cm $^{-1}$  at 30 °C. Li/Li symmetric cell cycling shows very stable and reversible cycling of Li metal over 100 cycles and a smooth dendrite-free deposition morphology. All-solid-state cells using a composite lithium iron phosphate cathode exhibit promising cycling with 99.2% capacity retention at a C/5 rate over 100 cycles. Therefore, the novel approach of PiHCIL enables a new pathway to design high-performing SPEs for high-energy-density all-solid-state LMBs.

**KEYWORDS:** electrolyte, PEO, ionic liquid, Li metal battery, all-solid-state battery

## 1. INTRODUCTION

Solid-state lithium metal batteries (LMBs) are recognized as the future of energy storage technology, offering unparalleled energy densities and safety that far exceed those of current lithium-ion batteries.<sup>1</sup> However, the widespread adoption of solid-state LMBs in sectors, such as electric vehicles, electric aviation, and energy storage, is hindered by significant challenges, particularly in the development of electrolyte materials. Among different types of solid electrolytes, solid polymer electrolytes (SPEs) stand out as promising candidates due to their inherent safety and processability advantages as well as the potential to facilitate high energy LMBs.<sup>2,3</sup> Unfortunately, the majority of SPEs require plasticization with a liquid solvent to improve their intrinsically low ionic conductivity and poor wettability, which not only compromises

the mechanical properties but also introduces safety concerns similar to those of liquid electrolytes, such as leakage and flammability.<sup>4–6</sup> Consequently, designing all-solid-state SPE systems that maintain both high ionic conductivity and mechanical integrity remains a significant challenge.

Poly(ethylene oxide) (PEO) has become the leading material for SPEs since the 1970s because of its exceptional

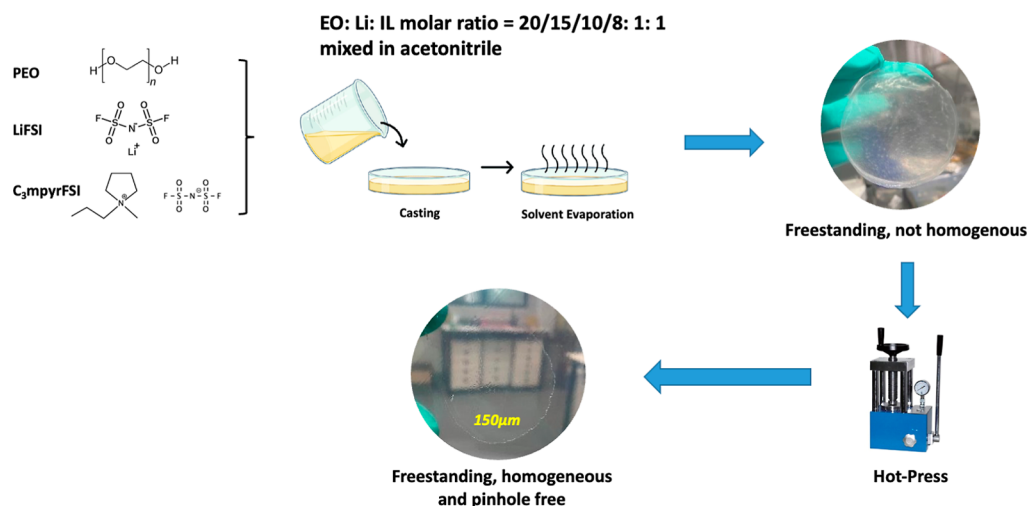
**Received:** July 8, 2024

**Revised:** September 21, 2024

**Accepted:** September 25, 2024

**Published:** October 6, 2024





**Figure 1.** Free-standing PiHCIL–SPE membrane preparation by solvent casting.

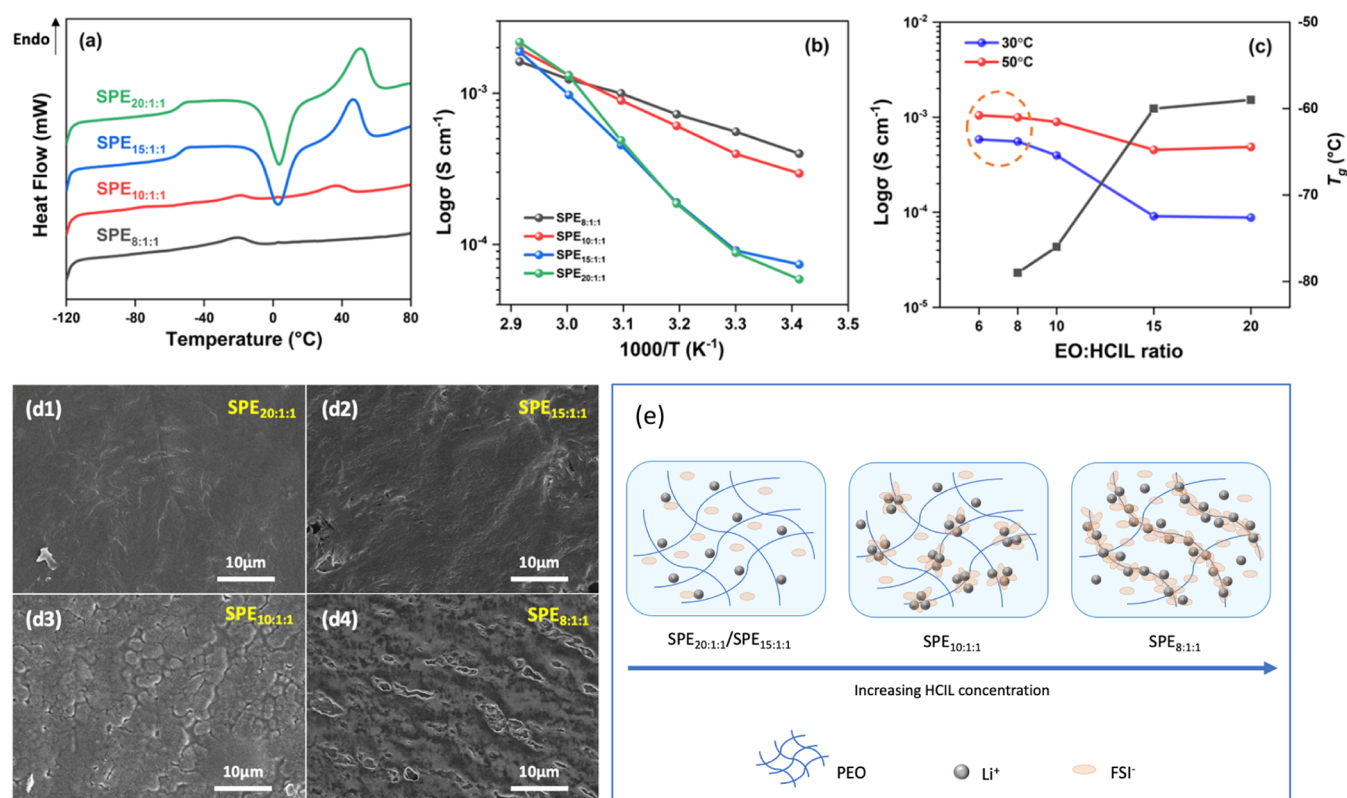
coordination and dissociation ability toward Li salt, excellent interfacial stability with Li metal, and high mechanical strength to form flexible membranes.<sup>7–9</sup> Specifically, high-molecular-weight PEO shows the advantages of preventing Li dendrites and improved cycling stability due to its prominent mechanical property compared to lower molecular weight PEO.<sup>10</sup> However, PEO-based SPEs are often criticized for their limited electrochemical stability window (ESW) primarily owing to the low oxidative stability of ether oxygen and limited room-temperature ionic conductivity (up to  $10^{-6}$  S cm<sup>-1</sup>) due to their crystallization tendency that restricts polymer segmental motion for ion transport.<sup>9</sup> These limitations significantly restrict their operational voltage range (<4 V) and fast cycling capability in solid-state LMBs. Intensive research has been centered on enhancing ionic conductivity<sup>11,12</sup> and interfacial stability of PEO-based SPEs,<sup>13,14</sup> such as applying inorganic fillers,<sup>15–17</sup> plasticizing ionic liquids,<sup>18</sup> designing complex polymer architectures and single-ion conducting polymers,<sup>19–22</sup> and introducing cross-linked networks.<sup>23,24</sup> Among these, IL-based electrolytes have received significant interest because of their good electrochemical and thermal stability, low vapor pressure, and nonflammability.<sup>25</sup> Early works from Howlett et al. and other researchers demonstrated promising physical and electrochemical properties of ILs as the electrolyte solvent for LMB applications.<sup>26–28</sup> Susan et al. have successfully incorporated ionic liquids with compatible polymers for the preparation of “ion gels”, showing increased thermal stability and high ambient temperature conductivity.<sup>29</sup> In recent years, enlightening from the idea of concentrated electrolytes,<sup>30–32</sup> research has identified a high-salt concentration IL electrolyte as a novel approach to effectively enhance Li-ion transport, electrochemical stability, and support fast charge–discharge.<sup>33,34</sup> Pal et al. and co-workers investigated an ether-aided super concentrated IL electrolyte that could effectively enhance ion transport and interfacial stability toward Li metal and high voltage materials.<sup>35–37</sup> With the ever-increasing attempt to boost the performance of SPEs, the use of highly concentrated salt-IL mixtures is predicted to improve both electrochemical stability and ion transport of PEO-based SPEs by altering the ion dynamics and creating more efficient Li transport pathways within the polymer matrix.

Although properties of binary IL electrolytes (i.e., either salt-IL or polymer-IL) have been extensively studied, the complex properties of “ternary systems” composed of a polymer and a high-concentration salt-IL mixture (HCIL) have been less explored. In this work, we report a novel PEO-in-high-salt concentrated ionic liquid system (PiHCIL–SPE)-based on LiFSI and C<sub>3</sub>mpyrFSI IL. We studied the effect of HCIL concentration on the physical and electrochemical properties of the composite electrolyte. By focusing on the enhancement of electrochemical window and ion transport, we seek to address a critical gap in the current understanding of PEO-based SPEs. Fourier-transform infrared spectroscopy (FTIR) and solid-state magic-angle spinning (MAS) NMR techniques are used to unravel the cation–polymer and cation–anion interactions and their impacts on ion dynamics within the designed SPEs. The optimal PiHCIL–SPE achieved high electrochemical stability and ambient temperature ionic conductivity. Stable and reversible cycling toward Li metal electrodes and favorable all-solid-state LMB performance were demonstrated. Based on the findings, an ion conduction network model consisting of interconnected ion clusters and pores is proposed to help understand the high ionic conductivity and promising battery performance of the designed PiHCIL–SPE. Thus, we believe the concept of incorporating high salt-concentrated IL into high-molecular-weight PEO to form a robust SPE represents a promising approach toward safer and high-performing all-solid-state LMBs.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** Poly(ethylene oxide) (PEO,  $M_w$  5,000,000, Sigma-Aldrich) was dried under a vacuum at 50 °C for 24 h before use. *N*-Propyl-*N*-methylpyrrolidinium bis(fluorosulfonyl) imide (C<sub>3</sub>mpyrFSI) (purity 99.5%) from Solvionic and lithium bis(fluorosulfonyl)imide (LiFSI) from Nippon Shokubai were dried under a vacuum at 50 °C for 48 h before use. The lithium iron phosphate (LFP) powder was purchased from Custom Cells, lithium manganese oxide (LMO) was supplied from Calix Ltd., and Super C65 carbon was purchased from Sigma. All materials were kept in an argon-filled glovebox for further SPE preparation.

**2.2. SPE Membrane Preparation.** The PiHCIL–SPEs were prepared using solvent casting within an argon-filled glovebox, as shown in Figure 1. First, LiFSI and C<sub>3</sub>mpyrFSI (LiFSI/IL molar ratio equal to 1:1) were mixed and fully dissolved. The obtained solution



**Figure 2.** (a) Phase behavior of different PiHCIL–SPE systems obtained from DSC measurements. (b) Ionic conductivities of different PiHCIL–SPE systems in the temperature range 20–70 °C. (c) Ionic conductivities of the PiHCIL–SPEs at 30 and 50 °C and their  $T_g$  as a function of EO/HCIL ratio. (d) SEM revealing the surface morphology of different PiHCIL–SPEs. (e) Schematic morphology model of different PiHCIL–SPE systems.

was then mixed with various amounts of PEO in acetonitrile to form SPEs with EO/Li/IL molar ratios equal to 8:1:1, 10:1:1, 15:1:1, and 20:1:1. The obtained mixtures were then cast into silicon molds inside a glovebox (MBraun UNILab, H<sub>2</sub>O and O<sub>2</sub> content <1 ppm) and rested for 48 h to ensure slow solvent evaporation. The obtained solid membranes were then put between two Mylar sheets and hot pressed (70 °C, 2 MPa, 10 min) to obtain a homogeneous, free-standing, and pinhole-free SPE with a thickness of  $120 \pm 10 \mu\text{m}$ . The membranes were transferred to a Buchi oven and vacuum dried at 50 °C for another 24 h before further characterization and cell assembly. The SPEs are named PiHCIL–SPE<sub>x:1:1</sub>, where  $x$  is the polymer content.

**2.3. Characterization Techniques.** Differential scanning calorimetry (DSC) (Mettler Toledo DSC1) was used to investigate the phase behavior of the prepared PiHCIL–SPEs in the temperature range of –120 to 80 °C. A 10 °C min<sup>-1</sup> heating and 20 °C min<sup>-1</sup> cooling rate was used and the sample loading was about 15 mg.

Electrochemical impedance spectroscopy (EIS) analysis (MTZ-35 impedance analyzer, Biologic) was used to measure ionic conductivity ( $\sigma$ ) of the PiHCIL–SPEs. The measurements were conducted over a temperature range of 20–70 °C with a frequency from 0.1 Hz to 1 MHz. A SS|PiHCIL–SPEs|SS (stainless-steel) coin cell configuration was used. The bulk resistance was calculated from the impedance curve at high frequencies, and the ionic conductivity was calculated based on the following equation

$$\sigma = \frac{l}{R_b \cdot A}$$

where  $\sigma$  is the ionic conductivity (S cm<sup>-1</sup>),  $R_b$  is the bulk resistance (derived from the impedance curve),  $l$  is the membrane thickness, and  $A$  is the area.

FTIR spectra were obtained at room temperature in an argon atmosphere using a PerkinElmer Spectrum 400. Thirty-two scans from 650 to 4000 cm<sup>-1</sup> were accumulated per sample.

Thermal gravimetric analysis (TGA) was performed by using a Mettler Toledo TGA STAR instrument to understand the thermal decomposition of the membranes with a sample loading of 10 mg. Mass loss was recorded over 30–600 °C with a 10 °C min<sup>-1</sup> heating rate under constant N<sub>2</sub> flow.

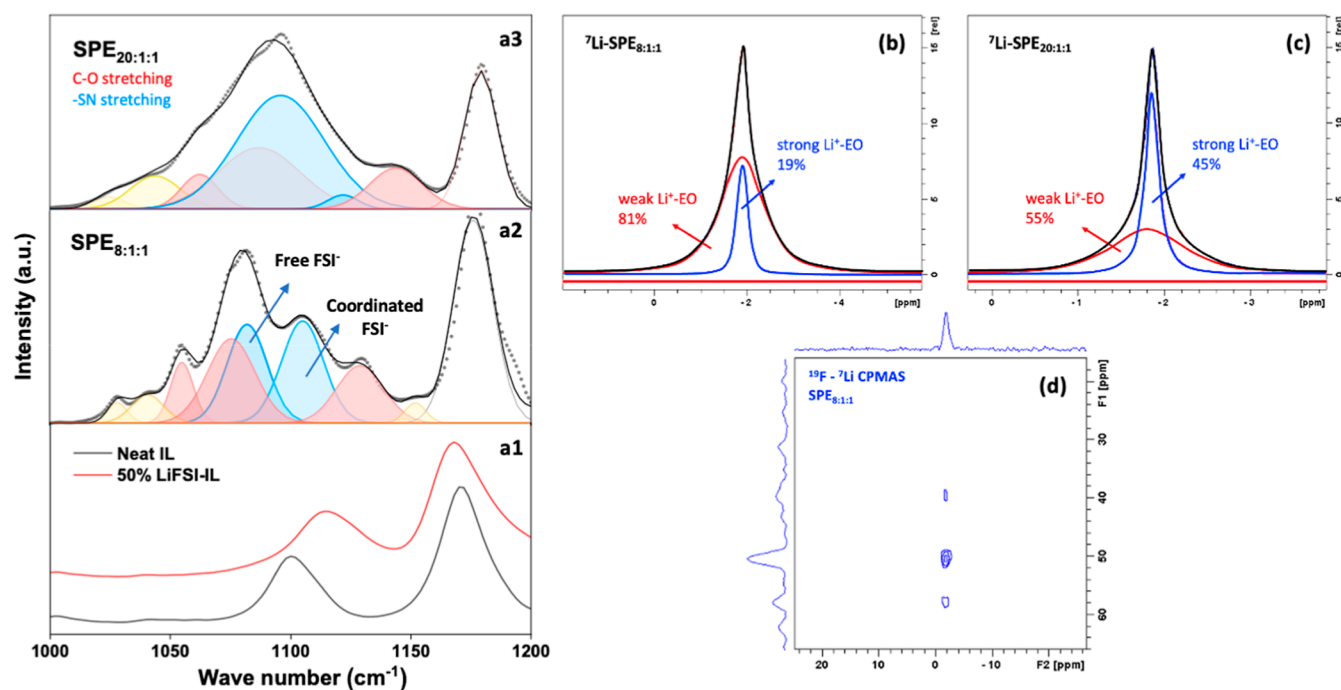
Scanning electron microscopy (SEM) analysis was carried out for the pristine PiHCIL–SPEs as well as cycled cells. A coin cell disassembly unit (Hohsen) was used inside a glovebox to disassemble the cycled cells. A JSM-IT300 SEM instrument from JEOL (Japan) was used to study the surface and cross-section morphology with a 10 kV acceleration voltage.

A solid-state MAS NMR spectroscopy technique was used to probe the cation–polymer and cation–anion interactions. Zirconia MAS rotors (2.5 mm diameter) were used to pack the samples inside an argon glovebox. A Bruker 2.5 mm HXY probe spinning at 25 kHz under a 11.7 T magnetic field (500 MHz <sup>1</sup>H frequency) was used to perform the experiment. One-dimensional <sup>7</sup>Li and <sup>19</sup>F spectra were obtained by a single-pulse experiment. Additionally, a two-dimensional <sup>19</sup>F–<sup>7</sup>Li heteronuclear correlation (HETCOR) spectrum was acquired.

**2.4. Electrode Preparation, Cell Assembly, and Electrochemical Measurements.** The composite LFP (c-LFP) and LMO (c-LMO) electrodes were prepared by mixing LFP or LMO powder, Super C65, and our prepared SPE<sub>20:1:1</sub> as the binder in 80:10:10 wt % in acetonitrile. The slurry was mixed until smooth and cast using a doctor-blade on carbon-coated aluminum foil. The obtained c-LFP and c-LMO electrodes have average cathode mass loading of 2.5 and 3 mg cm<sup>-2</sup> and areal capacity of 0.46 and 0.45 mAh cm<sup>-2</sup>, respectively. The composite cathodes were then cut into 8 mm diameter discs and vacuum-dried at 50 °C for 24 h prior to cell assembly.

For all the cell measurements, lithium metal (100 μm, Gelon) was used as the anode material and current collector. The all-solid-state battery cells were then assembled using a Li metal anode, a free-





**Figure 3.** (a) FTIR spectra of SPE<sub>8:1:1</sub> and SPE<sub>20:1:1</sub>. Neat IL and 50 mol % LiFSI–IL were measured for references. (b,c) Deconvoluted <sup>7</sup>Li solid-state MAS NMR spectra of SPE<sub>8:1:1</sub> and SPE<sub>20:1:1</sub>. (d) <sup>19</sup>F–<sup>7</sup>Li HETCOR spectrum of SPE<sub>8:1:1</sub>.

standing SPE<sub>8:1:1</sub> membrane, and the prepared composite cathodes (c-LFP and c-LMO).

A multichannel potentiostat VMP3 (BioLogic) was used to conduct the electrochemical measurements. Li transference number (*t*<sub>Li<sup>+</sup></sub>) was measured using a Li/Li symmetric cell at 70 °C and calculated using the Bruce–Vincent equation

$$t_{\text{Li}^+} = \frac{I_s (\Delta V - I_0 R_0)}{I_0 \Delta V - I_s R_s}$$

where  $\Delta V$  is the applied voltage (10 mV polarization),  $R_0$  and  $R_s$  are the charge-transfer resistances of the initial and steady-state phases, respectively, and  $I_0$  and  $I_s$  are currents in initial and steady-state stages, respectively.

The galvanostatic cycling for Li||Li, Li||LFP/c-LFP, and Li||LMO/c-LMO cells was also carried out. All electrochemical measurements were conducted by using CR2032 coin cells (Hohsen Corp.). Cell cycling was carried out at 50 °C with voltage limits of 2.5 to 4 V for Li/c-LFP cells and 3 to 4.3 V for Li/c-LMO cells. Two formation cycles at C/20 were used before long-term cycling, unless mentioned otherwise. The reproducibility of the results was checked by multiple tests.

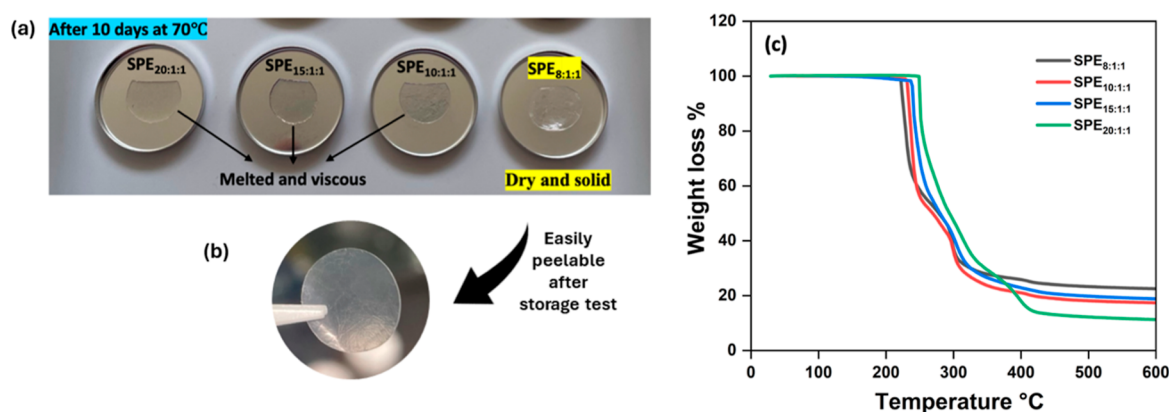
### 3. RESULTS AND DISCUSSION

**3.1. Phase Behavior, Ionic Conductivity, and Microstructure.** Figure 2 provides an overview of PiHCIL–SPEs, where the relative ratio of PEO and high salt content ionic liquids (HCIL), influences the phase behavior, ionic conductivity, and morphology. It is established that PEO is a semicrystalline polymer with a melting transition at 65 °C.<sup>7</sup> As shown in Figure 2a, the addition of HCIL to PEO in a 20:1:1 molar ratio reduces the melting transition temperature to 50 °C and introduces *T*<sub>g</sub> at −55 °C, indicating the coexistence of amorphous and crystalline phases in SPE<sub>20:1:1</sub>. Increasing the HCIL ratio to 10:1:1 further lowers the melting transition in both the temperature and enthalpy, accompanied by a significant reduction in *T*<sub>g</sub> (−76 °C). This notable decrease in *T*<sub>g</sub> in SPE<sub>10:1:1</sub> compared to SPE<sub>20:1:1</sub> or SPE<sub>15:1:1</sub> likely

results from altered interactions between the polymer chains and the Li<sup>+</sup> ions in the presence of FSI<sup>−</sup> anions, which will be further discussed. At an even higher HCIL ratio of 8:1:1, the melting peak disappears and the *T*<sub>g</sub> drops further to −79 °C, suggesting a highly amorphous phase. Notably, in samples with higher HCIL ratios (SPE<sub>8:1:1</sub> and SPE<sub>10:1:1</sub>), a small peak at approximately −20 °C appears, which is attributed to a phase transition in the C<sub>3</sub>mpyrFSI/LiFSI IL, indicating the solubility limit of the IL in PEO and potential phase separation.<sup>34,38</sup>

The impact of HCIL on the ionic conductivity of the prepared SPEs is shown in Figure 2b,c. There is a clear dependency of conductivity on the HCIL concentration. The conductivity values for SPE<sub>20:1:1</sub> and SPE<sub>15:1:1</sub> are remarkably similar, aligning with their comparable melting transitions and *T*<sub>g</sub> values (Figure 2a). They exhibit a sharp increase in ionic conductivity from the order of 10<sup>−5</sup> S cm<sup>−1</sup> at 30 °C to 10<sup>−3</sup> S cm<sup>−1</sup> at 70 °C, which is consistent with the DSC data showing a melting transition from 35 °C (onset) to 65 °C (end). Furthermore, there is a significant rise in ionic conductivity from SPE<sub>15:1:1</sub> (9.1 × 10<sup>−5</sup> S cm<sup>−1</sup> at 30 °C) to SPE<sub>10:1:1</sub> (4 × 10<sup>−4</sup> S cm<sup>−1</sup> at 30 °C) and SPE<sub>8:1:1</sub> (5.56 × 10<sup>−4</sup> S cm<sup>−1</sup> at 30 °C), suggesting that HCIL enhances overall ionic mobility. This is confirmed by DSC data, where the crystallization peak diminishes for SPE<sub>10:1:1</sub> and disappears for SPE<sub>8:1:1</sub>. No gain in ionic conductivity is observed above a 8:1:1 ratio (Figures 2c and S1) and excess IL starts to exude from the polymer matrix in SPE<sub>6:1:1</sub> (Figure S2), indicating a potential HCIL solubility limit in the PEO matrix.<sup>39</sup> Therefore, we speculate that SPE<sub>8:1:1</sub> represents an optimal EO/Li/IL ratio, favoring high ambient temperature ionic conductivity, which is closely approximating that of HCIL liquid electrolytes.<sup>35</sup>

The surface morphology of the prepared PiHCIL–SPEs was characterized by SEM and is shown in Figure 2d. With high PEO content and low HCIL amount (i.e., SPE<sub>20:1:1</sub> and SPE<sub>15:1:1</sub>), the SPEs show a relatively dense and smooth surface (Figure 2d1,d2), highlighting the good miscibility of PEO and



**Figure 4.** (a,b) Thermal storage experiment and (c) thermal stability of the prepared PiHCIL–SPEs.

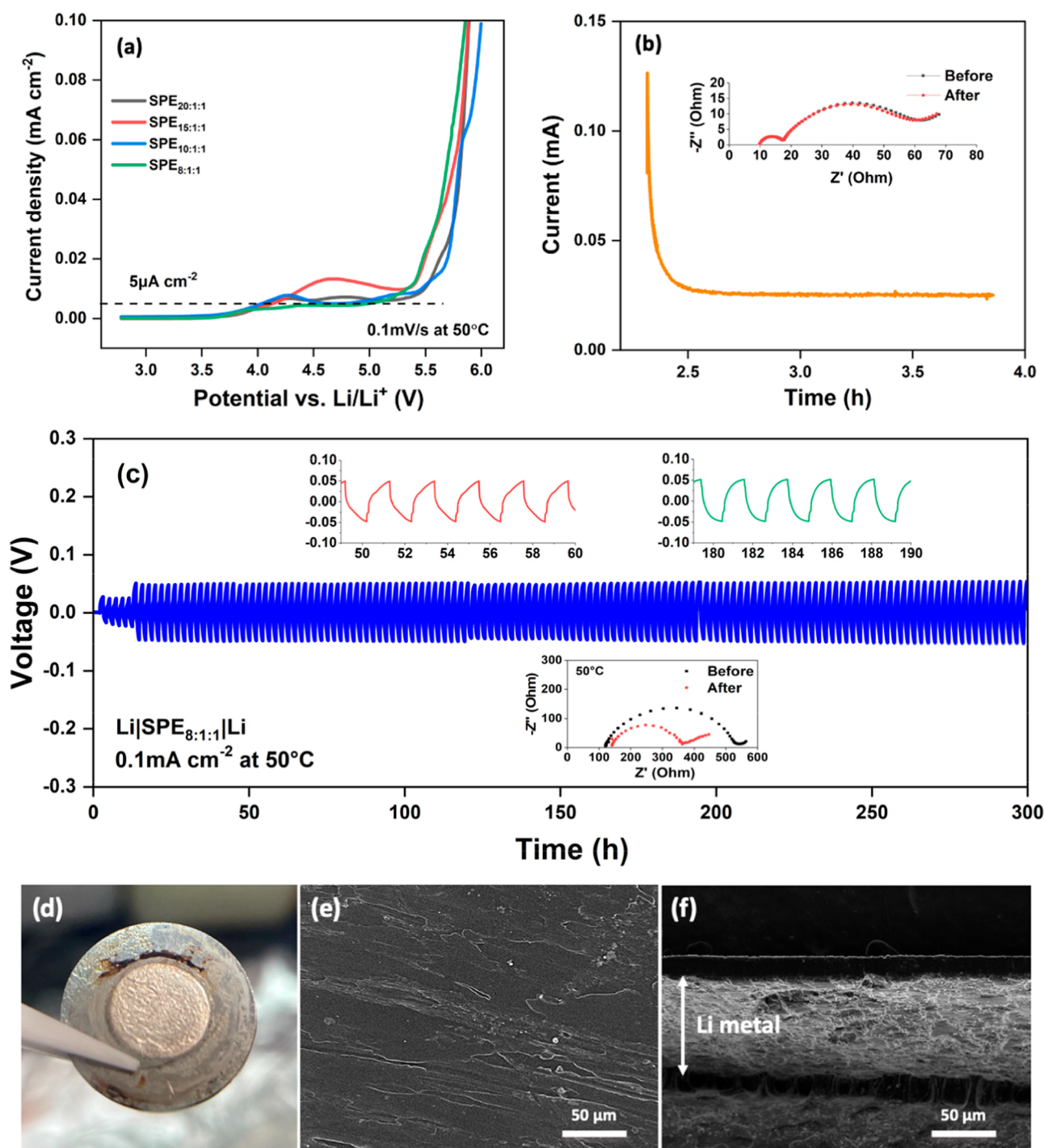
HCIL. With decreasing PEO content, a heterogeneous microstructure is observed (Figure 2d3), indicating the formation of separated phases, most likely approaching the miscibility limit of HCIL into the polymer. When the ratio reaches 8:1:1, a porous, interconnected, and locally aligned ion conducting network is formed (Figure 2d4). It can be proposed that at a high polymer content most LiFSI can be dissociated by the PEO backbone and most FSI<sup>−</sup> anions exist as free ions. Li<sup>+</sup> ions mainly transfer via chain segmental motion.<sup>40</sup> Therefore, ionic conductivity increases slowly with increasing HCIL content due to increased charge carrier amounts; whereas at a low polymer content and high HCIL content, a considerable amount of LiFSI cannot be dissociated, and together with the anions from the IL they can form aggregated ion clusters, resulting in phase separation and pores in the system. The ion conduction behavior in this case can be explained by a “polymer-in-salt” percolation model, where high salt content favors the formation of an ion conductive network composed of interconnected ion clusters that provide percolation pathways for fast ion transport.<sup>41,42</sup> Consistent with the polymer-in-salt system,<sup>40</sup> in SPE<sub>8:1:1</sub>, the excessive FSI<sup>−</sup> anions from both LiFSI and C<sub>3</sub>mpyrFSI form interconnected cluster networks and pores, as shown in Figure 2d4. Interestingly, these connected ion clusters and pores also happen to be locally aligned, which can provide direct pathways for Li<sup>+</sup> transport, reducing the tortuosity. This can lead to more efficient ion transport and higher conductivity. The pores may help accommodate volume change during cell cycling, potentially enhancing mechanical stability and longevity of the SPE. Figure 2e shows a proposed morphology model to help in understanding the structural change and ion dynamics in the prepared PiHCIL–SPEs.

**3.2. Coordination Environment through FTIR and MAS Solid-State NMR.** FTIR was used to investigate the changes of cation–polymer and cation–anion interactions in the prepared PiHCIL–SPEs, as shown in Figure 3a (the full spectrum is given in Figure S3, Supporting Information). In the region between 1000 and 1200 cm<sup>−1</sup>, a vibrational peak at 1100 cm<sup>−1</sup> from the neat IL (Figure 3a1) is assigned to the –SNS symmetric stretching from the FSI<sup>−</sup> anions.<sup>43</sup> Our previous work showed that adding 50 mol % LiFSI salt to the neat IL shifted this peak to 1115 cm<sup>−1</sup>, which was attributed to the increased coordination between Li<sup>+</sup> and FSI<sup>−</sup> anions.<sup>35</sup> After PEO was added (Figure 3a2), the –SNS stretching peak shifts to lower wavenumbers and splits into free FSI<sup>−</sup> and coordinated FSI<sup>−</sup> (blue), indicating a coordination

environment change of the FSI<sup>−</sup> anions that may be due to the introduced Li<sup>+</sup>–EO coordination in SPE<sub>8:1:1</sub>. As PEO content increases, the coordinated FSI<sup>−</sup> peak dramatically decreased leaving mainly free FSI<sup>−</sup> in the SPE<sub>20:1:1</sub> (Figure 3a3). Additionally, three –CO stretching peaks (red) from PEO shifted to higher wavenumbers, suggesting a coordination environment change of the –CO groups, which may be due to increased Li<sup>+</sup>–EO coordination and this is consistent with PEO–salt systems.<sup>44,45</sup> Therefore, summarily, it can be stated that increasing HCIL concentration in the PEO matrix results in more coordinated FSI<sup>−</sup> anions, leading to the formation of a connected anion-rich ion conducting phase that can be further supported by the microstructure analysis in Figure 2d. These separated phases might also decrease the crystalline regions of PEO, leading to higher chain mobility, improving the ionic conductivity, and thus accounting for faster Li<sup>+</sup> transport.

To further illustrate the Li<sup>+</sup> coordination environment in PiHCIL–SPEs, solid-state MAS NMR experiments were performed. Analysis of the asymmetric <sup>7</sup>Li signals (Figure S4a) shows two Li<sup>+</sup> environments (Figure 3b,c). Consistent with Greenbaum’s work,<sup>46</sup> the right peak (45% of total integral) in SPE<sub>20:1:1</sub> is assigned to the Li<sup>+</sup> ions closely bound to the EO units, which can be considered as solvated Li<sup>+</sup>. The left peak (55% of total integral) represents Li<sup>+</sup> ions that have weakened Li<sup>+</sup>–EO interactions, which are less restricted and behave more as in ionic states. As the HCIL concentration increases, SPE<sub>8:1:1</sub> shows 81% weakly coordinated Li<sup>+</sup> and only 19% strongly bonded Li<sup>+</sup>, indicating that more Li<sup>+</sup> ions escape from strong Li<sup>+</sup>–EO interactions to the disordered environment, where they possess a higher degree of freedom. Thus, the addition of HCIL can mitigate the affinity between EO and Li<sup>+</sup> interactions, which is consistent with FTIR results. Previous research has shown that Li<sup>+</sup> ions are more mobile in disordered environments, promoting faster ion transport.<sup>47</sup> This is consistent with our EIS analysis, where SPE<sub>8:1:1</sub> shows the highest ionic conductivity. The close interactions between Li<sup>+</sup> and FSI<sup>−</sup> anions are established in the <sup>19</sup>F–<sup>7</sup>Li HETCOR spectrum, as shown in Figure 3d, where <sup>19</sup>F shows strong cross peaks with the <sup>7</sup>Li signal. Taken together, solid-state NMR results confirm the important role of the Li<sup>+</sup> environment in the overall ionic conductivity. The favorable Li<sup>+</sup>-ion environment of SPE<sub>8:1:1</sub> promotes its superior room-temperature ionic conductivity among the prepared PiHCIL–SPEs.

**3.3. Dimensional and Thermal Stability.** As Li<sup>+</sup> conduction in SPEs mainly relies on chain segmental motion within the polymer’s amorphous regions, a high salt

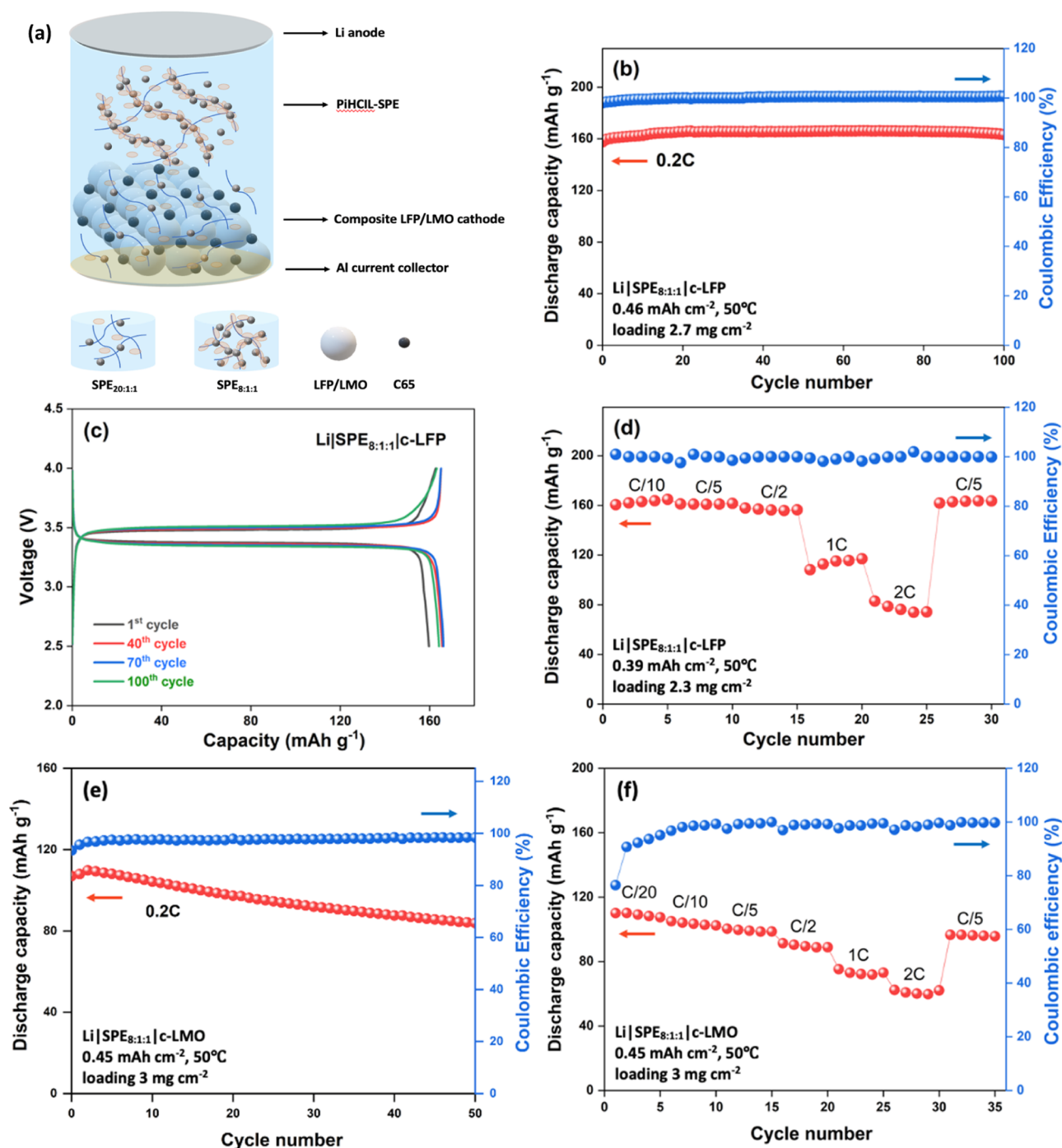


**Figure 5.** (a) Electrochemical stability of the prepared PiHCIL-SPEs. (b) Change of current and impedance with time in the symmetric  $\text{Li|SPE}_{8:1:1}|\text{Li}$  cell under polarization at  $10 \text{ mV}$  and  $70^\circ\text{C}$ . (c)  $\text{Li}||\text{Li}$  symmetric cell cycling of  $\text{SPE}_{8:1:1}$ . (d–f) Surface image, surface morphology, and cross-section SEM images of Li metal electrode (plated) after 150 cycles.

concentration that leads to increased amorphous domains therefore facilitates faster ion transport, owing to its plasticizing effect.<sup>48</sup> However, this increase in ion conductivity often comes at the expense of mechanical robustness due to reduced crystallinity and increased segmental motion. This dynamic shifts with our PiHCIL-SPEs, where membrane robustness is not solely reliant on the crystalline domains. Conducting a simple storage experiment at  $70^\circ\text{C}$  provides valuable insights into the mechanical stability, as depicted in Figure 4a. After 10 days of storage at  $70^\circ\text{C}$ , all SPEs above the  $8:1:1$  ratio lost

their dimensional integrity to some extent because of the existence of crystalline domains, as shown in the DSC results in Figure 2a, whereas  $\text{SPE}_{8:1:1}$  remained in its original shape and integrity in Figure 4b. Hence, despite the absence of crystalline regions,  $\text{SPE}_{8:1:1}$  shows high structural stability under elevated temperatures, pointing to sufficient mechanical robustness to prevent thermal deformation and potential Li dendrite penetration. Furthermore, thermal stability of SPEs is important for safe battery operation. Figure 4c presents the TGA results of the PiHCIL-SPEs. The negligible weight loss





**Figure 6.** (a) Schematic illustration of the assembled all-solid-state  $\text{Li|SPE}_{8:1:1}|$ c-LFP/c-LMO cell. (b) Cycling performance of  $\text{Li|SPE}_{8:1:1}|$ c-LFP ( $2.7 \text{ mg cm}^{-2}$ ) cell cycled at  $\text{C}/5$  rate (or  $0.2\text{C}$ ) between 2.5–4.0 V for 100 cycles. (c) Charge–discharge profiles of different cycle numbers at  $\text{C}/5$  rate. (d) Rate performances of  $\text{Li|SPE}_{8:1:1}|$ c-LFP cell ( $2.3 \text{ mg cm}^{-2}$ ) at different C rates. (e) Cycling performance of  $\text{Li|SPE}_{8:1:1}|$ c-LMO ( $3 \text{ mg cm}^{-2}$ ) cell cycled at  $\text{C}/5$  rate between 3–4.3 V for 50 cycles. (f) Rate performances of  $\text{Li|SPE}_{8:1:1}|$ c-LMO cell ( $3 \text{ mg cm}^{-2}$ ) at different C rates.

below  $150^\circ\text{C}$  is ascribed to trapped moisture. The weight loss between  $150$  and  $220^\circ\text{C}$  is due to the initial breakdown of LiFSI.<sup>49</sup> Extensive decomposition of the SPE started at above  $220^\circ\text{C}$ . Adding LiFSI salt sped up the thermal breakdown of PiHCIL-SPEs.<sup>50</sup> Nevertheless, the PiHCIL-SPEs are still stable enough for safe use in solid-state LMBs.

**3.4. Electrochemical Stability.** The ESW of the PiHCIL-SPEs was obtained by the LSV measurement of a  $\text{Li||SS}$  cell, scanning from open-circuit voltage to 6 V against  $\text{Li}^+/\text{Li}$  at a rate of  $0.1 \text{ mV s}^{-1}$ , as shown in Figure 5a. Apart

from  $\text{SPE}_{8:1:1}$ , all the other SPEs experienced oxidative degradation below 4 V, which is commonly seen in PEO-based SPEs,<sup>9</sup> whereas  $\text{SPE}_{8:1:1}$  showed a high electrochemical stability of 5.1 V ( $5 \mu\text{A cm}^{-2}$  current density was used as the cutoff current<sup>51</sup>), indicating its excellent oxidation stability and potential to work with high-voltage materials. The excellent electrochemical stability of  $\text{SPE}_{8:1:1}$  can be attributed to a high concentration of HCIL, promoting the polymer chains to strongly interact with  $\text{Li}^+$  ions and  $\text{FSI}^-$  anion clusters.<sup>52</sup> The coordinated ions and surrounded ion clusters act like a shield,



protecting EO from oxidation and reducing the highest occupied molecular orbital level of the PiHCIL–SPE,<sup>30,53</sup> all of which contribute to its improved oxidation stability. Thereby SPE<sub>8:1:1</sub> has been chosen as the best candidate among others and be investigated for the advanced electrochemical testing that will be discussed below.

Li transference number ( $t_{\text{Li}^+}$ ) of the SPE<sub>8:1:1</sub> was measured using a Li|Li symmetric cell at 70 °C. Figure 5b displays the current profile following a 10 mV polarization, and the inset shows the impedances of the initial state and steady state. The  $t_{\text{Li}^+}$  of SPE<sub>8:1:1</sub> was calculated to be 0.2, which is consistent with the typical PEO system and the HCIL electrolyte.<sup>27</sup> Ionic conduction in PEO-based SPEs is attributed to the chain segmental motion,<sup>54,55</sup> where Li<sup>+</sup> ion coordinates with the ether oxygen on the PEO backbone, leading to Li dissociation.<sup>56</sup> However, Li<sup>+</sup> movements are restricted by the strong Li<sup>+</sup>–EO coordination, which results in relatively low ionic conductivity and low  $t_{\text{Li}^+}$  (around 0.2–0.3).<sup>57,58</sup> Thereby, the transference number achieved by the SPE<sub>8:1:1</sub> falls within the well-accepted region, supporting the previous literature reports.

The interface compatibility between Li metal and the optimum SPE<sub>8:1:1</sub> was evaluated by a Li plating–stripping cycling test. The symmetric Li|SPE<sub>8:1:1</sub>|Li cell was cycled at constant current density of 0.1 mA cm<sup>−2</sup> for 1 h polarization at each step at 50 °C. As shown in Figure 5c, the long-term cycling of the Li|SPE<sub>8:1:1</sub>|Li cell showed very stable performance with an overpotential of 50 mV over 150 cycles at 50 °C, and there was no sign of short circuit, indicating that SPE<sub>8:1:1</sub> has good compatibility with the Li metal anode. The interfacial resistance decreased after 150 cycles (inset in Figure 5c), indicating that the SPE<sub>8:1:1</sub> continually adjusted to enhance its contact with the lithium surface. The surface image and morphology of Li metal after 150 cycles are shown in Figure 5d–f. A smooth and dense Li metal surface was observed with no signs of Li dendrites or dead Li, indicating a uniform Li deposition process and the formation of a stable SEI layer. The cross-sectional SEM of the plated side displayed a uniform and dense interface, which confirmed the excellent mechanical and electrochemical properties of SPE<sub>8:1:1</sub> that allow it to accommodate volume changes of the Li anode, thereby sustaining facile and reversible Li plating–stripping.

**3.5. All Solid-State LMB Full Cell Cycling.** The prepared all-solid-state Li|SPE<sub>8:1:1</sub>|c-LFP/c-LMO cell is sketched in Figure 6a. Figure 6b presents the cycling performance of the Li|SPE<sub>8:1:1</sub>|c-LFP cell, which was cycled at a rate of C/5 at 50 °C between 2.5 and 4 V. The c-LFP cathode was prepared using the designed SPE as the binder to maintain the Li percolation within the cathode structure (more details are mentioned in the experimental section). Thereby, the LMB constructed here is all-solid-state, avoiding any trace of liquid wetting, and the cell delivered 160 mAh g<sup>−1</sup> initial discharge capacity. The performance then increased to 165 mAh g<sup>−1</sup> after 20 cycles and stabilized, demonstrating the self-adaptability of the SPE<sub>8:1:1</sub> membrane over cycling. After 100 cycles, the cell maintained an exceptional capacity retention of 99.2% and achieved nearly 100% Coulombic efficiency throughout cycling. Other works are summarized in Table S1, which clearly outlines the novelty of our PiHCIL–SPE<sub>8:1:1</sub> membrane and thereby suggesting an impressive performance in comparison with the existing literature using a similar cathode active loading and applied current density. Charge–discharge profiles at various cycle numbers are displayed in Figure 6c.

The polarization remains low (180 mV) after 100 cycles, demonstrating the high stability of SPE<sub>8:1:1</sub>. AC impedance profiles (Figure S5a) showed an initial increase due to SEI formation, and after 40 cycles, the impedance slowly increased due to interface stability. A rate capability test was conducted at C/10, C/5, C/2, 1C, 2C, and C/5 current rates (1C is 0.4 mA cm<sup>−2</sup>), as shown in Figure 6d. The Li|SPE<sub>8:1:1</sub>|c-LFP cell showed 162, 159, and 155 mAh g<sup>−1</sup> discharge capacities under C/10, C/5, and C/2 rate, respectively. It can maintain 47.3% discharge capacity when the current density is increased 20 fold from C/10 to 2C, indicating that the all-solid-state Li|SPE<sub>8:1:1</sub>|c-LFP cell has an excellent tolerance to high current rate. The charge–discharge profiles at different C-rates are shown in Figure S6a. The excellent rate performance indicated that SPE<sub>8:1:1</sub> has close contact with both Li and LFP electrodes to facilitate effective Li<sup>+</sup> transport and low interfacial resistance between the SPE<sub>8:1:1</sub> and cathode.<sup>59</sup>

To assess the potential for wider applications of the prepared PiHCIL–SPEs working with high voltage materials, we assembled Li||c-LMO cells with a cathode loading of 3 mg cm<sup>−2</sup> with SPE<sub>8:1:1</sub>. Figure 6e illustrates the cycling performance of the Li|SPE<sub>8:1:1</sub>|c-LMO cell at 0.2C in the voltage range between 3 and 4.3 V. The Li|SPE<sub>8:1:1</sub>|c-LMO cell maintains 80% discharge capacity after 50 cycles and interfacial resistance (Figure S5b) slowly increases through cycling. Figure S6b presents the charge–discharge profiles at different cycle numbers. The capacity decay may be due to the dissolution of unstable manganese in LMO, which is a common issue of high manganese active materials. The cell was further subjected to a rate capability test at various rates from C/20 to 2C, as shown in Figure 6f. The SPE shows a satisfactory discharge capacity retention of 55% from C/20 to 2C, demonstrating superior tolerance to high current rate. The exceptional rate performance and cycling stability of the Li|SPE<sub>8:1:1</sub>|c-LMO cell confirm the potential of the designed SPE to work with high voltage cathodes and further applications to high energy storage systems.

## 4. CONCLUSIONS

In this study, we report the first use of a “high salt concentration IL” electrolyte with high-molecular-weight PEO to form high-performance SPEs and their application in all-solid-state LMBs. These designed electrolytes are featured with unique interconnected and locally aligned ion clusters and pores that provide extra Li<sup>+</sup>-ion transport pathways, leading to both high room-temperature ionic conductivity and wide ESW. Benefiting from the organized structure change and increased ion dynamics by adding concentrated IL, an ionic conductivity of  $5.6 \times 10^{-4}$  S cm<sup>−1</sup> at 30 °C is achieved with the optimal composition. Further, FTIR and solid-state MAS NMR investigations confirm that these promising behaviors can be ascribed to a Li<sup>+</sup> environment change including increased Li<sup>+</sup>–FSI<sup>−</sup> interactions and weakened Li<sup>+</sup>–EO interactions, leading to the formation of interconnected ion clusters as a distinct phase. The coordinated ions and surrounding ion clusters protect EO from oxidation, leading to improved oxidation stability (5.1 V). The novel PiHCIL–SPE provides stable Li symmetric cycling and promising electrochemical performance with a composite LFP cathode using the designed PiHCIL–SPE as the binder material, reflecting the superiority of the “PEO-in-HCIL” strategy. The implications of this research bring a new understanding of PEO-based SPEs, promising not only to advance the field of all-solid-state LMBs but also to

contribute to the broader pursuit of sustainable and high-performance energy storage solutions.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.4c11114>.

Ionic conductivities of different PiHCIL–SPE systems in the temperature range 20–70 °C, different PiHCIL–SPE systems prepared by solvent casting, FTIR spectra of prepared PiHCIL–SPEs in the range of 650–4000  $\text{cm}^{-1}$ , solid-state MAS NMR spectra of  $^7\text{Li}$  and  $^{19}\text{F}$ , impedance profiles of  $\text{Li|SPE}_{8:1:1}\text{|c-LFP}$  cell and  $\text{Li|SPE}_{8:1:1}\text{|c-LMO}$  cell at different cycles at 0.2 C, charge–discharge profiles of  $\text{Li|SPE}_{8:1:1}\text{|c-LFP}$  cell at different C-rates and of  $\text{Li|SPE}_{8:1:1}\text{|c-LMO}$  cell at different cycles at 0.2 C, and literature survey on performance of PEO-based SPEs (PDF)

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### Author Contributions

Mingjie Zhang carried out the experiments, analyzed the data, and wrote the original manuscript. Urbi Pal conceived and mentored the research and revised the manuscript. Faezeh Makhlooghiazad mentored and revised the manuscript. Shinji

Kondou helped in IR data analysis. Luke A. O'Dell helped to carry out the NMR measurements. Claudio Gerbaldi coconceived the project and revised the manuscript. Maria Forsyth coconceived and supervised the research and revised the manuscript. All the authors discussed the test results and put forward comments on the manuscript.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The authors would like to acknowledge the financial support of the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie Grant agreement (grant no 860403) and the Australian Research Council for providing funding through the Industry Transformation Training Centre for Future Energy Technologies (storEnergy). The authors thank Deakin University's SEM facility, Dr. Meisam Hasanpoor and Dr. Anthony Somers for their help with the SEM training. Deakin University's Advanced Characterisation Facility is acknowledged for use of the NMR facility. The authors also thank the Battery Technology Research and Innovation Hub (BatTRI-Hub) at Deakin University for their battery prototyping facilities.

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