

# Solid-state rigid-rod polymer composite electrolytes with nanocrystalline lithium ion pathways

*Ying Wang<sup>1</sup>, Curt J. Zanelotti<sup>1</sup>, Xiaoen Wang<sup>2</sup>, Robert Kerr<sup>2</sup>, Liyu Jin<sup>2</sup>, Wang Hay Kan<sup>3</sup>, Theo J. Dingemans<sup>4</sup>, Maria Forsyth<sup>2</sup>, and Louis A. Madsen<sup>1\*</sup>*

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6 1. Department of Chemistry and Macromolecules Innovation Institute  
7 Virginia Polytechnic Institute and State University  
8 Blacksburg, Virginia 24061, United States  
9 E-mail: lmadsen@vt.edu  
10 2. Institute for Frontier Materials and ARC Centre of Excellent for Electromaterials Science  
11 Deakin University  
12 Geelong, VIC 3216, Australia  
13 3. China Spallation Neutron Source  
14 Chinese Academy of Science  
15 Dongguan, Guangzhou 523803, China  
16 4. Department of Applied Physical Sciences  
17 University of North Carolina at Chapel Hill  
18 121 South Road, Chapel Hill, NC27599-3050, United States

20 **Abstract**

21 A critical challenge for next-generation lithium-based batteries lies in development of  
22 electrolytes that enable thermal safety along with use of high-energy-density electrodes. We  
23 describe molecular ionic composite (MIC) electrolytes based on an aligned liquid crystalline  
24 polymer combined with ionic liquids and concentrated Li salt. This high strength (200 MPa) and  
25 non-flammable solid electrolyte possesses outstanding  $\text{Li}^+$  conductivity ( $1 \text{ mS}\cdot\text{cm}^{-1}$  at  $25^\circ\text{C}$ ) and  
26 electrochemical stability (5.6 V vs  $\text{Li}|\text{Li}^+$ ) while suppressing dendrite growth and exhibiting low  
27 interfacial resistance ( $32 \Omega\cdot\text{cm}^2$ ) and overpotentials ( $\leq 120 \text{ mV}$  @  $1 \text{ mA}\cdot\text{cm}^{-2}$ ) during Li  
28 symmetric cell cycling. A heterogeneous salt doping process modifies a locally ordered polymer-  
29 ion assembly to incorporate an inter-grain network filled with defective LiFSI & LiBF<sub>4</sub>  
30 nanocrystals, strongly enhancing  $\text{Li}^+$  conduction. This modular material fabrication platform  
31 shows promise for safe and high-energy-density energy storage and conversion applications,  
32 incorporating the fast transport of ceramic-like conductors with the superior flexibility of  
33 polymer electrolytes.

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37 Solid-state polymer electrolytes (SPEs) have received great attention toward reviving high-  
38 energy-density Li-based batteries.<sup>1-4</sup> While Li-ion batteries play an important role in the energy  
39 storage landscape due to their relatively high specific energy and power density, they are  
40 approaching theoretical limits ( $\approx 400 \text{ Wh.kg}^{-1}$ ).<sup>5,6</sup> In order to increase capacity of Li-based  
41 batteries, researchers have largely focused on new electrode materials. Regarding cathodes, Li-  
42 air and Li-sulfur batteries represent leading frontier candidates.<sup>3,7-9</sup> At the anode, Li-metal can  
43 replace graphite to increase anode energy density by  $\sim 10$  fold.<sup>5-7</sup> However, electrode  
44 advancements require an enabling electrolyte to combat irreversible reactions and dendrite  
45 growth during long-term charge/discharge cycling.<sup>7,10</sup> To alleviate these issues, SPEs not only  
46 provide mechanical stiffness to block dendrites, but deliver safer (non-flammable) operation  
47 compared to liquid electrolytes.<sup>1,10-12</sup> Herein, we describe a solid-state ***molecular ionic***  
48 ***composite*** (MIC) electrolyte<sup>1,13-15</sup> based on an extremely rigid double helical sulfonated aromatic  
49 polyamide (similar to Kevlar®)<sup>16,17</sup> combined with an ionic liquid (IL) and a Li salt. We can  
50 adjust MIC properties widely by changing polymer content, IL type, and metal salt type and  
51 loading. Thus, MICs represent a modular material platform with potential to resolve a range of  
52 issues in electrolytic materials.

53 Previous researchers have developed a number of IL-based gel electrolytes (termed “ion gels”  
54 or “ionogels”) that combine the non-flammability of ILs with a mechanically supporting  
55 matrix.<sup>1,18-21</sup> These electrolytes consist of either a polymer matrix embedded with a large volume  
56 fraction of IL,<sup>1,22</sup> or an IL inside an inorganic matrix such as  $\text{SiO}_2$  and  $\text{TiO}_2$ .<sup>19,20,23</sup> Potential  
57 applications of these gels for high-energy-density Li batteries have been substantially  
58 explored.<sup>20,24,25</sup> However, these gels only show practical Li-metal cycling performance when  
59 doped with organic electrolytes,<sup>20,25</sup> which improve conductivity but introduce a volatile liquid

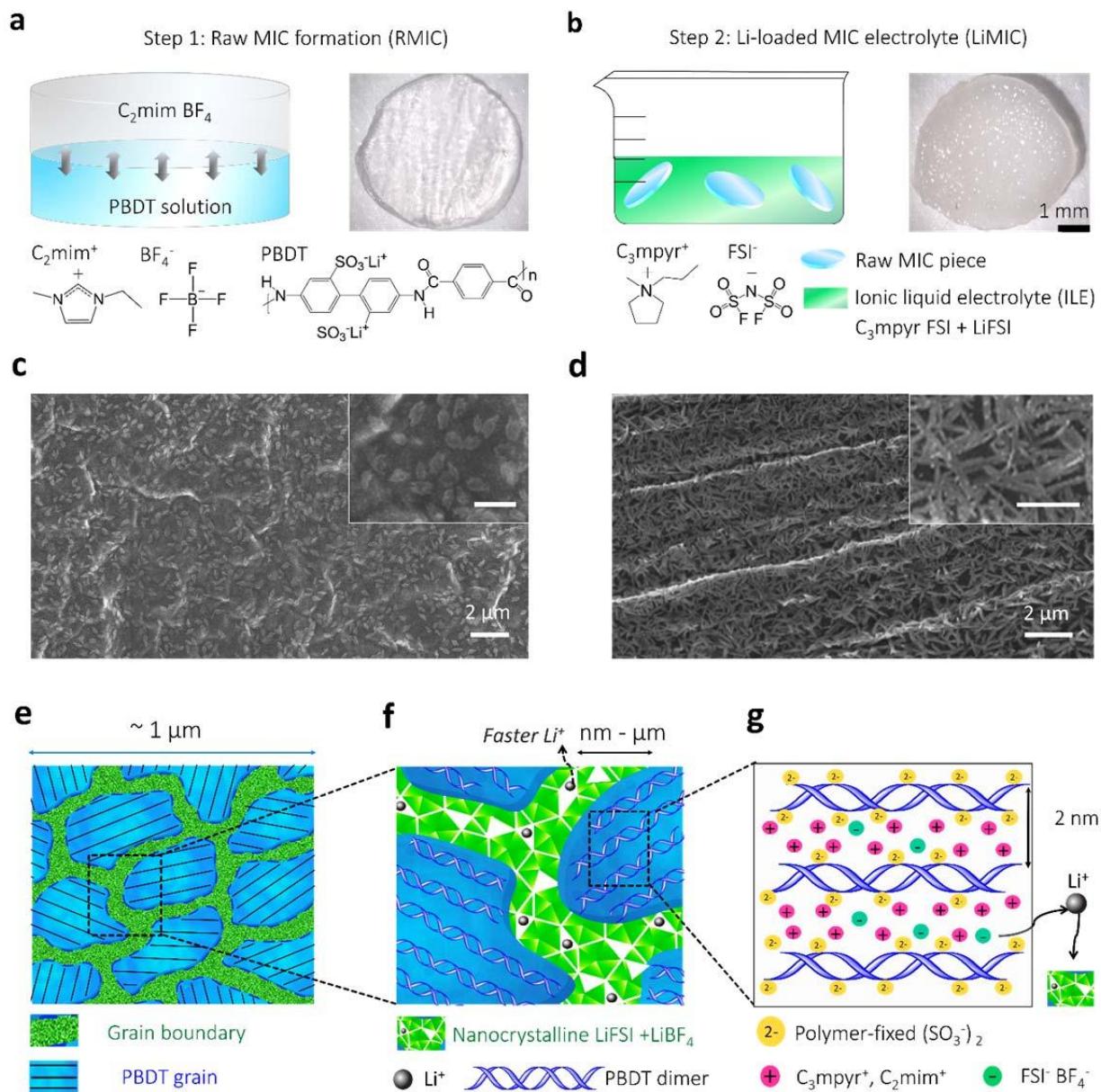
60 that diminishes safety against overheating and fire.<sup>5,6</sup> In this work, we describe solid-state MIC  
61 electrolytes that contain no volatile solvents but exhibit high ionic conductivity, beneficial  
62 electrode-electrolyte contact and high thermal stability, all while possessing sufficient modulus  
63 to serve as the separator in Li-metal batteries. Loading electrolytes with Li salts serves to  
64 increase Li-ion conductivity and supply Li<sup>+</sup> for reactions at the electrodes.<sup>2,26-28</sup> Maier et al. have  
65 demonstrated that heterogeneous doping and interfacially controlled materials can be used to  
66 increase Li<sup>+</sup> conductivity in electrolytes.<sup>10</sup> Christie et al. reported that the presence of the  
67 irregularly shaped bis(trifluoromethanesulfonyl)imide (TFSI) anion disrupts the electrostatic  
68 potential around Li<sup>+</sup> thereby enhancing ionic conductivity in a manner analogous to inorganic  
69 electrolytes such as AgBr<sub>1-x</sub>I<sub>x</sub>.<sup>2</sup> Recently, lithium bis(fluorosulfonyl)imide (LiFSI) has emerged  
70 as a promising electrolyte component.<sup>28-30</sup> Furthermore, the FSI<sup>-</sup> anion can decompose upon  
71 electroreduction to form a stable solid-electrolyte interphase (SEI) that enables reversible cycling  
72 with a graphitic anode.<sup>31</sup> In this project, we employ ionic liquid electrolytes (ILEs) containing *N*-  
73 propyl-*N*-methylpyrrolidinium (C<sub>3</sub>mpyr) FSI mixed with LiFSI ( $\leq 3.2$  mol/kg), which have  
74 previously shown Li-metal cycling at high rates.<sup>32,33</sup> By incorporating this ILE into a solid MIC,  
75 we demonstrate a highly lithium-dense solid-state electrolyte with potential to suppress Li  
76 dendrite growth on Li-metal anodes, enable fast Li<sup>+</sup> transport, and eliminate battery safety  
77 concerns.

78 The Li-loaded MIC (LiMIC) fabrication process requires two steps: (1) Initial polymer-IL  
79 network formation, followed by (2) ILE ion exchange to achieve high Li<sup>+</sup> loading. As shown in  
80 **Fig. 1a**, we obtain the raw MIC (RMIC), based on an interfacial ion-exchange process between a  
81 sulfonated aromatic polyamide, poly-2,2'-disulfonyl-4,4'-benzidine terephthalamide (Li-form  
82 PBDT) in H<sub>2</sub>O solution and an IL, C<sub>2</sub>mimBF<sub>4</sub> (1-ethyl-3-methylimidazolium tetrafluoroborate).<sup>1</sup>

83 PBDT is water-miscible and forms a highly ordered lyotropic nematic liquid crystal (LC) phase  
84 at concentrations > 2 wt%.<sup>16,17</sup> The local parallel packing of charged PBDT rods serves as the  
85 assembly template – not only offering mechanical integrity, but also endowing nanoscale  
86 structuring in the composite. RMICs are denoted with RMIC-5 and RMIC-15, in which the  
87 numbers denote PBDT weight percentage of 5% and 15%. In **Fig. 1b**, we immerse the rigorously  
88 dried RMICs in the desired ILE, i.e., C<sub>3</sub>mpyrFSI with 50 mol% LiFSI. This serves the dual  
89 purposes of lowering the concentration of BF<sub>4</sub><sup>-</sup> anions through ion-exchange while also  
90 introducing Li<sup>+</sup> ions into the polymer host matrix. By following this two-step fabrication method,  
91 we obtain a solid-state MIC electrolyte, denoted LiMIC-5 and LiMIC-15. The key to *Step 1* is  
92 that both the IL and LC polyelectrolyte dissolve in the same solvent. *Step 2* allows us to  
93 exchange a wide range of IL and Li salt mixtures into the MIC matrix and tailor properties of the  
94 product toward Li-metal batteries or other applications. The SEM images of RMICs (**Fig. 1c, d**)  
95 show locally aligned PBDT LC grains ( $\mu\text{m}$ -scale) interspersed with interconnected grain  
96 boundaries with a wide size distribution from nm -  $\mu\text{m}$ . This RMIC has mechanical cohesion  
97 propagated by a collective “electrostatic network,” which effectively arises from templating of  
98 the IL through the highly charged and rigid double helical PBDT rods.<sup>13,15</sup> The RMICs are  
99 macroscopically isotropic, but display local alignment originating from the rigid PBDT chains,  
100 which can be verified using polarized optical microscopy (**Supplementary Fig. 1**).<sup>1,17</sup>

101 **Fig. 1e-g** illustrates the concepts involved in multi-scale organization of the LiMICs. **Fig. 1e**  
102 shows the  $\mu\text{m}$ -scale structure of this solid electrolyte, incorporating aligned PBDT grains  
103 interleaved with a nanocrystalline ionic phase. These nanocrystalline grain boundaries serve as  
104 an additional conductive network providing fast Li<sup>+</sup> transport. As shown in **Fig. 1f**, we propose  
105 that after ion exchange with ILE, the interconnected boundaries separating the individual PBDT

106 grains allow for higher  $\text{Li}^+$  density and faster  $\text{Li}^+$  transport as compared to within the grains. **Fig.**  
 107 **1g** further illustrates the morphology and ion distribution in the internally aligned PBDT grains  
 108 and the nanocrystalline component formed at the grain boundaries. We will illustrate this model  
 109 in more detail in the following sections based on multi-modal material characterizations.



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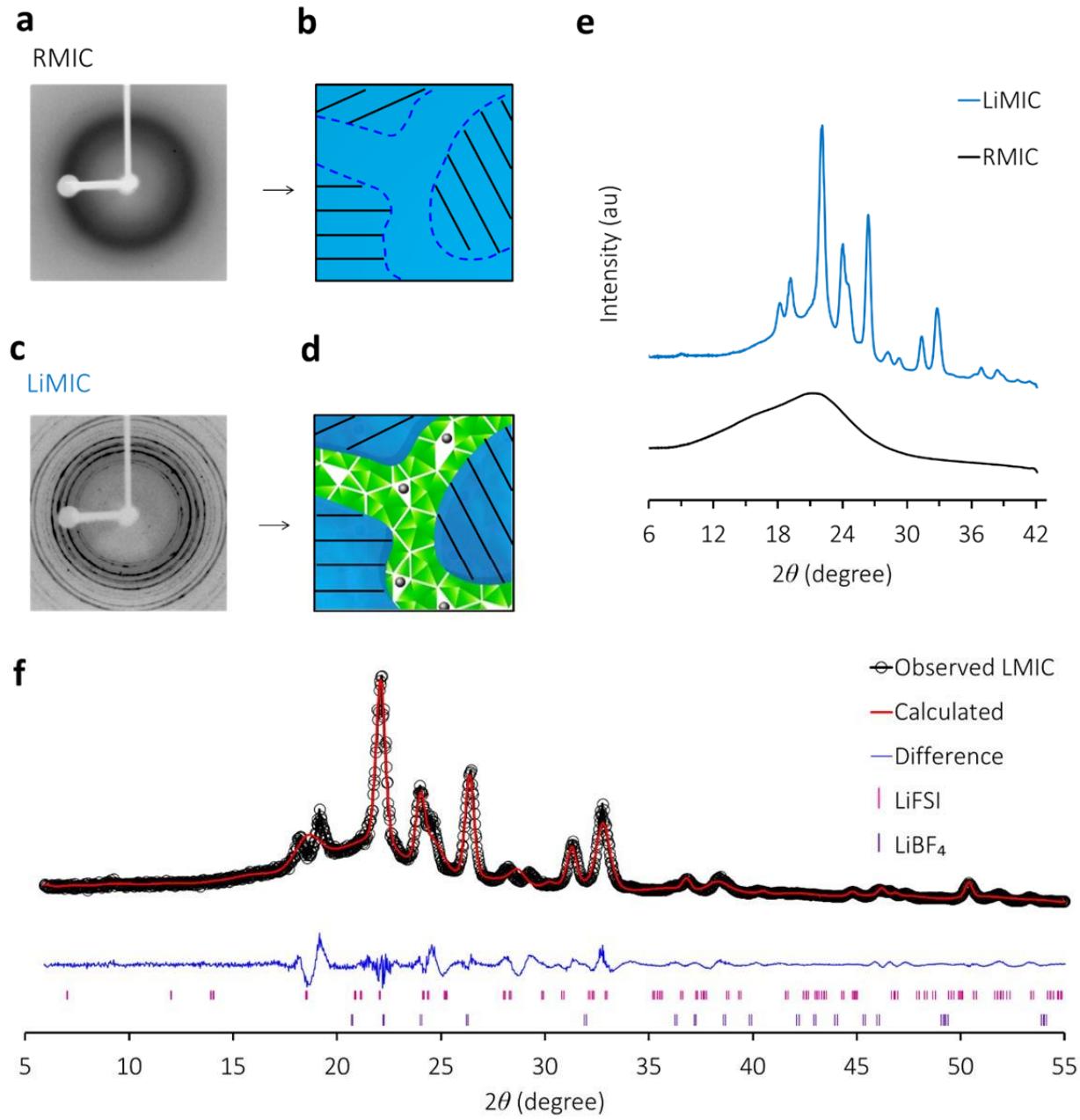
111 **Figure 1. Fabrication processes to form Li-loaded MIC electrolytes (LiMICs).** (a) **Step 1**  
 112 shows fabrication of the raw MIC (RMIC). Mechanical cohesion in this RMIC arises via

113 electrostatic interactions,<sup>1,13,15</sup> and we obtain this material based on an interfacial ion exchange  
114 between a water-soluble IL (e.g., C<sub>2</sub>mimBF<sub>4</sub>) and an aqueous rigid-rod polyelectrolyte solution  
115 (Li-form PBDT in H<sub>2</sub>O). The photograph shows the sliced transparent RMIC sample. (b) **Step 2**  
116 shows the second ion exchange process wherein we immerse a sliced section of the RMIC into  
117 the ILE (C<sub>3</sub>mpyrFSI with 50 mol% LiFSI). During the infiltration process, the cation C<sub>3</sub>mpyr<sup>+</sup> in  
118 the ILE tends to segregate into the PBDT-rich phase,<sup>13,14</sup> as the FSI<sup>-</sup> and BF<sub>4</sub><sup>-</sup> anions  
119 preferentially associate with Li<sup>+</sup> and precipitate out to form a nanoscale heterogeneous structure  
120 in the grain boundaries. The photograph shows the sliced iridescent LiMIC sample. (c,d) SEM  
121 images for RMIC-5(c) and RMIC-15(d). Higher magnification images are shown in the upper  
122 right insets. The scale bar for the insets is 1  $\mu$ m. The interfaces between individual PBDT grains  
123 form the grain boundaries (darker regions). Both the aligned PBDT grains and the grain  
124 boundaries contain C<sub>2</sub>mimBF<sub>4</sub>. (e, f) After **Step 2**, the grain boundaries become predominantly  
125 the condensed salt phase, which consists of nanocrystalline grains that form a conductive  
126 network supporting fast Li<sup>+</sup> transport. (g) The morphology of an aligned LC grain contains  
127 PBDT double helical rods filled predominantly with mobile IL cations. The distance between  
128 PBDT rods is  $\sim$  2 nm.<sup>1,15</sup>

129  
130 To investigate the nanoscale morphology of these composites, we conducted powder X-ray  
131 diffraction (XRD) experiments on the RMIC and LiMIC. As shown in **Fig. 2a**, we observe an  
132 amorphous halo with scattering angle 2 $\theta$  from 12° to 30° for the RMIC, which we assign to the  
133 amorphous C<sub>2</sub>mimBF<sub>4</sub> in the RMIC. A schematic picture is shown in **Fig. 2b**, where the locally  
134 aligned PBDT rods serve as the assembly template for the amorphous IL. The diffraction peaks  
135 of the PBDT are overwhelmed by the large volume fraction of IL in the RMIC. By contrast, the  
136 XRD of the LiMIC (**Fig. 2c**) shows a heterogeneous structure based on coexistence of the weak  
137 amorphous halo and the sharp crystalline reflections. This pattern agrees with the schematic  
138 picture shown in **Fig. 2d**, depicting a highly defective nanocrystalline domain formed in-situ  
139 between the PBDT grains in the LiMICs. The extracted 1D spectra are shown in **Fig. 2e**. The

140 crystalline peaks (blue line), at first glance, appear to be superimposed diffraction patterns of  
141 LiFSI and LiBF<sub>4</sub>. We also notice that, compared to the amorphous phase, the crystalline phase is  
142 the dominant component in the LiMIC, which supports the solid-state NMR (SSNMR)  
143 integration results included in **Supplementary Table 1**, showing that ~ 80% anions (FSI<sup>-</sup> and  
144 BF<sub>4</sub><sup>-</sup>) in LiMIC are localized in the solid crystalline phase. We further use Le Bail refinement to  
145 determine the cell parameters for the two potential crystals.<sup>34</sup> **Fig. 2f** shows the fitting results  
146 with R-factor for the refinement  $R_p = 6.87\%$ , which indicates good alignment between the  
147 observed diffraction patterns and the simulated phases of LiFSI and LiBF<sub>4</sub>. The in-situ formed  
148 defective crystals of LiFSI and LiBF<sub>4</sub> possess preferred orientations, which contribute to the high  
149 density of vacancies that promote easier hopping of Li<sup>+</sup> between crystallites. We use the Scherrer  
150 equation<sup>35</sup> (**Supplementary Equation 1**) to determine the average crystallite size (19.4 nm)  
151 formed in the LiMIC grain boundary regions from the FWHM of the peak at  $2\theta = 26.363^\circ$  (012)  
152 from the LiBF<sub>4</sub> phase. **Table 1** summarizes the Le Bail refinement with cell parameters for the  
153 two defective crystals, and both belong to the trigonal crystal structure. These results provide  
154 evidence that these nanocrystals are localized in the grain boundaries instead of within PBDT  
155 grains, where the distance between PBDT chains is too small to accomodate the nanocrystals.<sup>1,15-</sup>

156 <sup>17</sup>



157

158 **Figure 2. X-ray diffraction patterns of RMIC and LiMIC.** (a) Powder XRD pattern for the

159 RMIC. (b) In the RMIC, PBDT LC grains and grain boundaries are filled with amorphous IL as

160 a result of **Step 1** of the fabrication process. (c) XRD pattern for the LiMIC. (d) In the LiMIC,

161 there exists an in-situ formed and highly defective nanocrystalline structure between PBDT LC

162 grains. (e) The extracted 1D spectra of the XRD images in (a) and (c). (f) Le Bail refinement

163 results for the LiMIC XRD pattern, which include the observed pattern, the calculated results and

164 the simulation of the in-situ formed nanocrystalline structure of LiFSI and LiBF<sub>4</sub>.

165

166 **Table 1. Li crystals formed in the LiMIC (R<sub>wp</sub> = 9.75%, R<sub>p</sub> = 6.87%)**

LiMIC-15	Phase1 (LiFSI)	Phase2 (LiBF <sub>4</sub> )
<b>Crystal structure</b>	<b>Trigonal</b>	<b>Trigonal</b>
<b>Space group</b>	P -3	P 31 2 1
<b>a (Å) (a)</b>	8.513 (90°)	4.9511(90°)
<b>b (Å) (β)</b>	8.513(90°)	4.9511(90°)
<b>c (Å) (γ)</b>	12.610 (120°)	11.112 (120°)
<b>Volume(Å<sup>3</sup>)</b>	779.76	228.02
<b>ICSD</b>	415618	171375

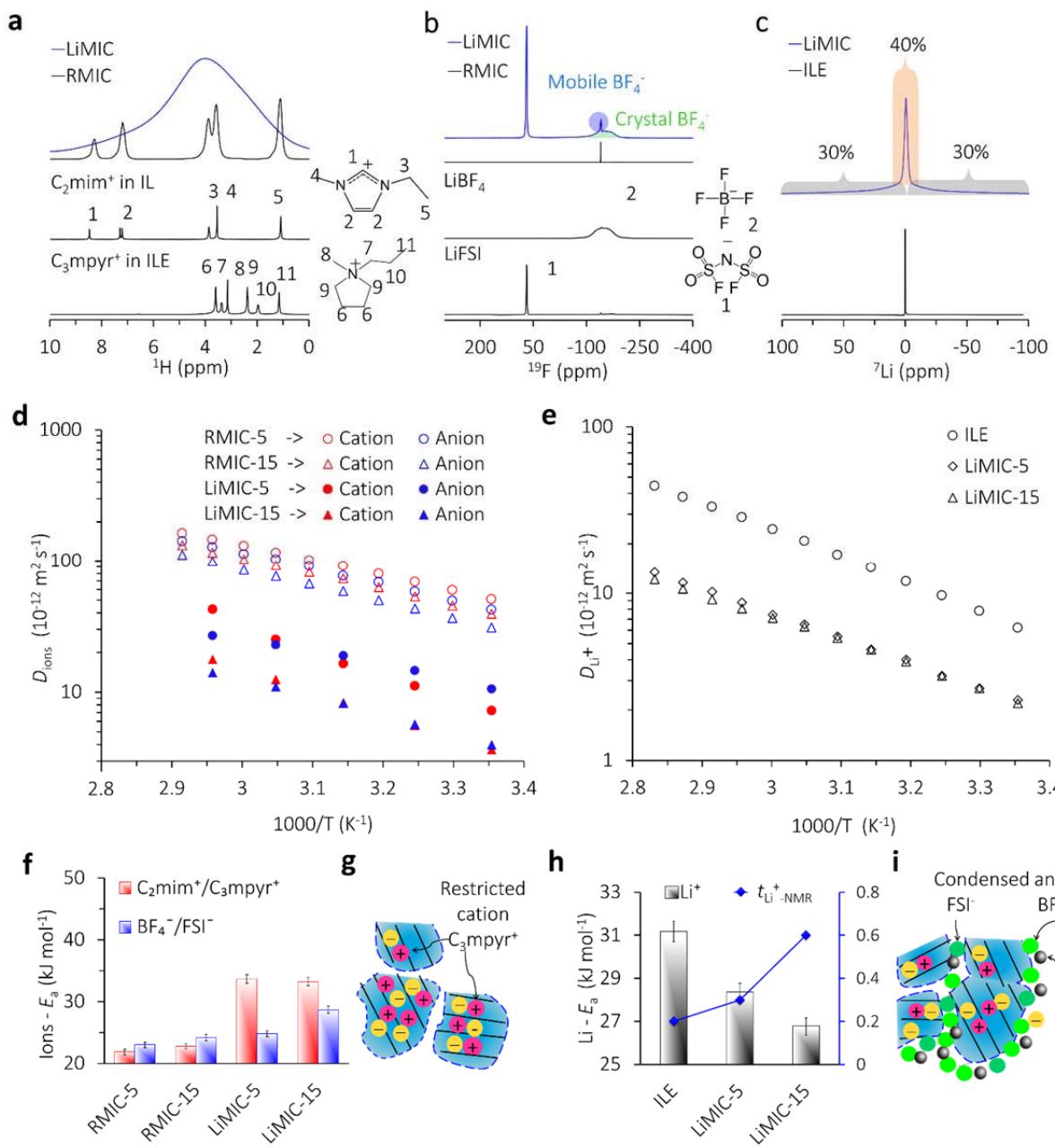
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168 To understand the ion transport and morphology in both RMIC and LiMIC, we first verify  
 169 the chemical composition of the products, qualitatively and quantitatively, based on <sup>1</sup>H, <sup>19</sup>F and  
 170 <sup>7</sup>Li NMR spectroscopy. **Fig. 3a, b, c** present key features of these NMR studies. **Fig. 3a** shows  
 171 <sup>1</sup>H spectra for C<sub>2</sub>mim<sup>+</sup> in neat IL and C<sub>3</sub>mpyr<sup>+</sup> in ILE (bottom two spectra), and compares <sup>1</sup>H  
 172 spectra in the RMIC to the LiMIC. The linewidth in the LiMIC (~ 1500 Hz) is much broader  
 173 compared to the RMIC (~ 100 Hz), which means a factor of ~ 15 faster *T*<sub>2</sub> spin-spin relaxation,  
 174 indicating slower motion of IL cations. **Supplementary Fig. 2** shows additional <sup>1</sup>H spectra for  
 175 RMIC-5 and RMIC-15. SSNMR offers promise for studying the same chemical species in  
 176 distinct phases, including the grain boundaries and the locally aligned PBDT grains in LiMICS.  
 177 **Fig. 3b** shows <sup>19</sup>F SSNMR spectra for LiMIC (blue line) along with spectra for the reference Li  
 178 salts (LiFSI and LiBF<sub>4</sub>). For the LiMIC, we observe a small percentage of mobile BF<sub>4</sub><sup>-</sup> with a  
 179 relatively narrow peak (light blue circle) at -150 ppm. The broad peak underneath (light green  
 180 semicircle) refers to BF<sub>4</sub><sup>-</sup> in the nanocrystalline grain boundaries. Due to its fast internal  
 181 dynamics, FSI<sup>-</sup> appears as only a singlet peak at 60 ppm, which we assign to the superposition of  
 182 mobile FSI<sup>-</sup> in aligned LC grains and solid FSI<sup>-</sup> in nanocrystalline grain boundaries. The  
 183 assignments, assumptions, and quantifications of different ionic species in the LiMICS are  
 184 summarized in **Supplementary Fig. 3** and **Supplementary Table 1**. **Fig. 3c** compares <sup>7</sup>Li

185 spectra between ILE and LiMIC. The widths and integration values of the peaks are displayed in  
186 **Supplementary Fig. 4**. This single-component 3:4:3 splitting pattern indicates that  $\text{Li}^+$  can only  
187 exist in either the crystalline grain boundaries or in the PBDT LC grains.<sup>36,37</sup> Based on the XRD,  
188 we observe that the  $\text{Li}^+$  mainly forms into crystalline phases of LiFSI and  $\text{LiBF}_4$  in the grain  
189 boundaries, thus demonstrating that  $\text{Li}^+$  is the dominant cation in the solid nanocrystals, instead  
190 of in PBDT LC grains.

191 Understanding and controlling ion transport, ion associations and  $\text{Li}^+$  transport mechanisms  
192 in electrolyte materials are critical for development of next-generation battery electrolytes. We  
193 can extract the diffusive activation energy ( $E_a$ ) of the ions present in RMIC and LiMIC  
194 electrolytes based on the temperature dependencies of  $D_{\text{Li}}^+$ ,  $D_{\text{cations}}$  and  $D_{\text{anions}}$  obtained from  
195 NMR diffusometry as shown in **Fig. 3d,e**.<sup>1,38-40</sup> As indicated from the faster  $T_2$  relaxation, we  
196 observe that  $D$  values for the mobile IL ions in LiMICs are an order of magnitude smaller than  
197 those in RMICs, as expected. **Fig. 3f** shows the extracted  $E_a$  values for cations and anions in  
198 RMICs and LiMICs via the Arrhenius equation. The  $E_a$  values for  $\text{C}_2\text{mim}^+$  and  $\text{BF}_4^-$  increase  
199 with polymer content in the RMICs. This suggests that the density of the PBDT matrix  
200 dominates the local energetic barriers that govern ion transport. In addition, compared to the  
201 RMICs, the  $E_a$  values for cations in the LiMICs almost doubles, whereas  $E_a$  for anions show only  
202 a slight increment with polymer content. This indicates that the PBDT matrix escalates the local  
203 energetic barriers for cation transport in LiMICs, primarily because of stronger associations  
204 between the  $\text{SO}_3^-$  on PBDT chains and  $\text{C}_3\text{mpyr}^+$ . Correspondingly, the schematic picture for the  
205 trapped cations within the aligned LC grain is shown in **Fig. 3g**. Conversely, the  $E_a$  values for  $\text{Li}^+$   
206 in the LiMIC (**Fig. 3h**) decrease with increasing polymer content, indicating smaller local  
207 energetic barriers for  $\text{Li}^+$  transport compared to the ILE.<sup>13,40</sup> This indicates that a different  $\text{Li}^+$

208 transport mechanism applies for LiMICs. As shown in **Supplementary Table 1**, the  
209 concentration of mobile cations ( $\text{C}_2\text{mim}^+$ ,  $\text{C}_3\text{mpyr}^+$ ) and anions ( $\text{FSI}^-$ ,  $\text{BF}_4^-$ ) in the LiMICs are ~  
210 6 times lower compared to the RMICs. Meanwhile, LiMICs show an order of magnitude slower  
211 diffusion coefficients for the same set of mobile cations and anions. Based on the Nernst–  
212 Einstein equation, we suggest that the unexpectedly high conductivity observed in this solid  
213 LiMIC electrolyte (see below, Fig. 4a) originates from a fast  $\text{Li}^+$  hopping ion transport  
214 mechanism in the solid nanocrystalline grain boundaries, as opposed to transport through a  
215 liquid-like mobile phase in the PBDT LC grains.<sup>39,41,42</sup> We further determine the  $\text{Li}^+$  transference  
216 number determined by diffusion ( $t_{\text{Li}^+ \text{-NMR}}$ ) in LiMICs based on the **Supplementary Equation 2**  
217 and include the results in **Supplementary Table 1**. **Fig. 3i** depicts the nanocrystalline anions  
218 located in the grain boundaries, which we propose give rise to atypically fast  $\text{Li}^+$  ion transport.



219  
220 **Figure 3. Chemical identification, diffusion coefficients, activation energies and transport**  
221 **mechanism in RMICs and LiMICs.** (a)  $^1\text{H}$  NMR spectra of cations in neat IL ( $\text{C}_2\text{mimBF}_4$ ), ILE  
222 ( $\text{C}_3\text{mpyrFSI}$  with 50 mol% LiFSI), RMIC and LiMIC. The peak in the LiMIC shows overlapping  
223  $\text{C}_3\text{mpyr}^+$  and  $\text{C}_2\text{mim}^+$  signals. (b)  $^{19}\text{F}$  NMR spectra of solid LiFSI, solid  $\text{LiBF}_4$ , RMIC and  
224 LiMIC. (c)  $^7\text{Li}$  spectra of liquid ILE and LiMIC. LiMIC shows single anisotropic environment  
225 with relative integration values of each broad satellite component being 30% and the narrow

226 central component being 40% due to the quadrupole splitting of Li. (d) Temperature-dependent  
227  $D_{\text{cations}}$  and  $D_{\text{anions}}$  in the RMICs and LiMIC. For LiMICs,  $D_{\text{cations}}$  represents the average value for  
228  $\text{C}_3\text{mpyr}^+$  and  $\text{C}_2\text{mim}^+$ . The  $D_{\text{anions}}$  is the average value for mobile  $\text{FSI}^-$  and  $\text{BF}_4^-$ .  $D_{\text{anions}}$  is the  
229 computed weighted average value for the anions based on the mole ratio of mobile  $\text{FSI}^-$  and  $\text{BF}_4^-$   
230 as quantified by  $^{19}\text{F}$  NMR shown in **Supplementary Fig. 3** and **Supplementary Table 1**. (e)  
231 Temperature-dependent  $D_{\text{Li}^+}$  in ILE and LiMICs. (f)  $E_a$  values for cations and anions obtained  
232 from Arrhenius fitting of diffusion results. Uncertainties in diffusion are smaller than the marker  
233 and uncertainties in  $E_a$  are  $\approx \pm 0.5$  kJ/mol. (g) Schematic showing  $\text{C}_3\text{mpyr}^+$  separations into  
234 locally aligned LC grains. (h)  $E_a$  values for  $\text{Li}^+$  obtained from Arrhenius fitting. The blue line  
235 compares the measured  $t_{\text{Li}^+ \text{-NMR}}$  in ILE to that in LiMICs. (i) Schematic of the electrolyte  
236 structure showing the formation mechanism of nanocrystalline  $\text{LiBF}_4$  and  $\text{LiFSI}$  in the grain  
237 boundaries.

238

239 Building on the RMIC morphology,<sup>1</sup> we propose that the formation mechanism for the  
240 heterogeneous structure in LiMICs lies in preferential associations and co-crystallization of  
241 specific ions.  $\text{SO}_3^-$  and  $\text{C}_3\text{mpyr}^+$  ions should have the weakest associations with other ions due to  
242 their size and local charge distributions. Based on XRD and SSNMR results, we expect that  $\text{FSI}^-$   
243 and  $\text{BF}_4^-$  have a strong affinity with  $\text{Li}^+$  to form a thermodynamically favorable crystalline phase.  
244 These nanocrystals (20 nm) form within the grain boundaries when the concentration locally  
245 exceeds the saturation point of  $\text{LiBF}_4$  and  $\text{LiFSI}$  in the ILE. This leaves the exchanged  $\text{C}_3\text{mpyr}^+$   
246 and residual  $\text{C}_2\text{mim}^+$  cations to neutralize predominantly the polymer-fixed  $\text{SO}_3^-$  anions within  
247 the PBDT LC grains. The Li-rich nanocrystalline phase serves as a highly ion-conductive  
248 network that can transport  $\text{Li}^+$ . In these grain boundaries, the space-charge zone and nano-size  
249 effects among the polycrystalline  $\text{LiBF}_4$ ,  $\text{LiFSI}$  and aligned crystalline PBDT grains should  
250 enhance the vacancy density and conductivity of  $\text{Li}^+$ , which is consistent with the decreasing  $E_a$   
251 of  $\text{Li}^+$  obtained from NMR diffusometry. We also note that this nanocrystalline phase likely  
252 exhibits features of plastic crystal behavior.<sup>39,43-45</sup> Further investigation of transport mechanisms,

253 grain boundary heterogeneities, space-charge effects and ion interactions in this heterogeneous  
254 structure will provide deeper understanding of these solid electrolytes for future materials design.

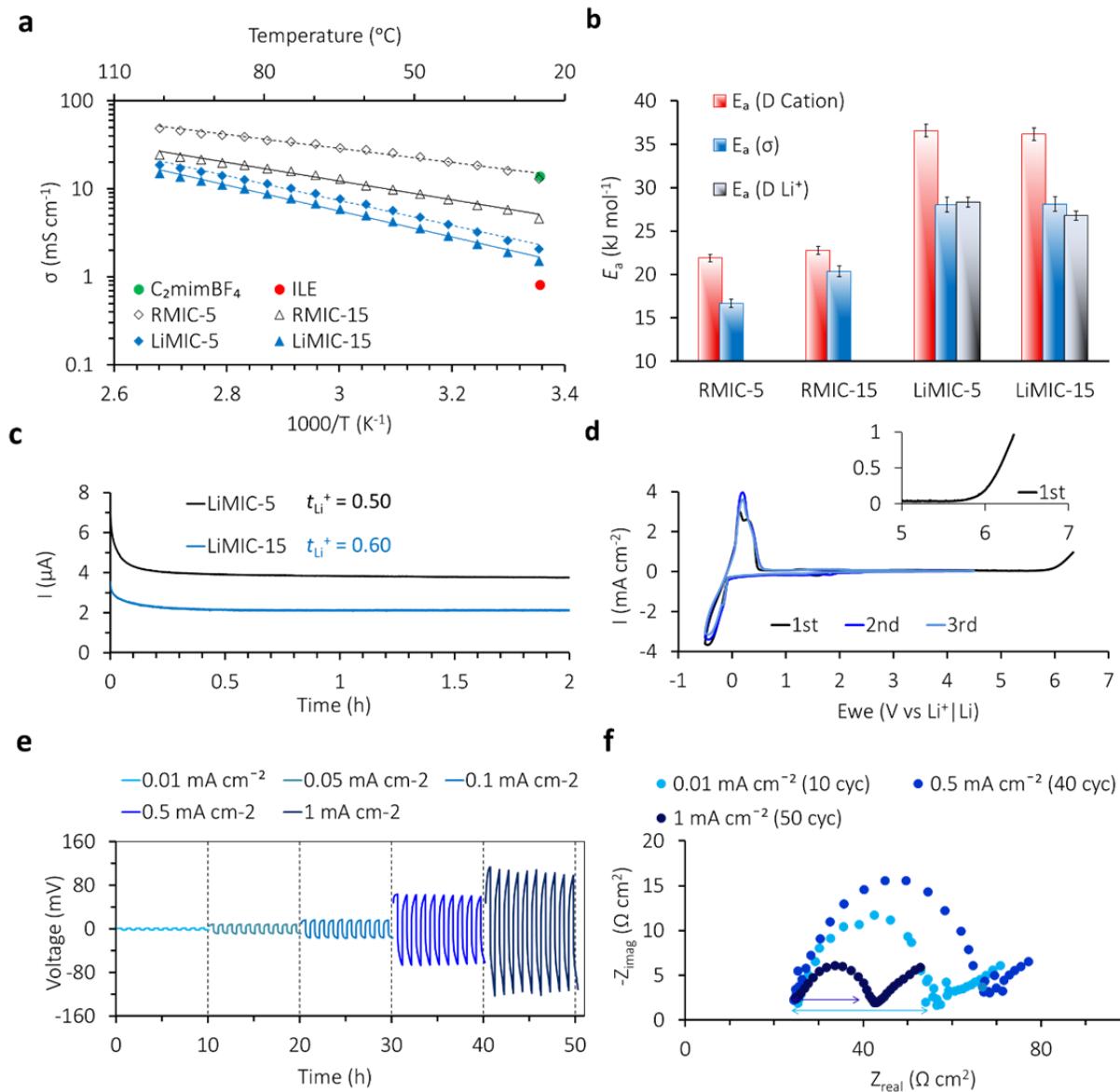
255 **Fig. 4a** shows ionic conductivities of LiMICs and RMICs as a function of temperature. The  
256 exceedingly high  $\sigma$  of LiMIC-5 ( $2.1 \text{ mS}\cdot\text{cm}^{-1}$ ) and LiMIC-15 ( $1.5 \text{ mS}\cdot\text{cm}^{-1}$ ) at  $25^\circ\text{C}$  surpasses  
257 that of state-of-the-art SPEs and even the liquid ILE ( $0.82 \text{ mS}\cdot\text{cm}^{-1}$ ) we used for ion exchange in  
258 *Step 2*.<sup>24,32</sup> In terms of transport energy barriers, LiMICs show higher  $E_a(\sigma)$  values compared to  
259 RMICs (**Fig. 4b**), which again indicates a distinct transport mechanism in LiMICs. We notice  
260 that  $E_a$  ( $\text{Li}^+$ -NMR) in LiMIC is close to the  $E_a(\sigma)$  obtained from conductivity. This further  
261 indicates that the unexpectedly high conductivity in LiMICs originates from the nanocrystalline  
262 conductive network with an ionic alloy ( $\text{LiBF}_4$  and  $\text{LiFSI}$ ) that forms at the boundaries between  
263 individual grains. To supplement this demonstration, we determined the  $t_{\text{Li}}^+$  based on the steady-  
264 state current of the Li symmetric cell assembled with LiMICs as electrolyte and separator in **Fig.**  
265 **4c**. The corresponding impedance spectra of the cells before polarization are shown in  
266 **Supplementary Fig. 5**. The calculation details are included in **Supplementary Table 2** and  
267 **Equation S3**. The determined  $t_{\text{Li}}^+$  in LiMIC-15 (0.60) is much higher compared to the ILE ( $t_{\text{Li}}^+ =$   
268  $0.18$ ).<sup>32</sup> One can then determine the fraction of conductivity due to  $\text{Li}^+$  ( $\sigma_{\text{Li}}^+ = 1 \text{ mS cm}^{-1}$ ) in  
269 LiMICs by multiplying the overall conductivity by  $t_{\text{Li}}^+$ .

270 We also performed cyclic voltammetry to evaluate the Li plating (negative scan) and  
271 stripping (positive scan) behavior in LiMICs. As shown in the 1<sup>st</sup> cycle in **Fig. 4d**, upon scanning  
272 in the positive direction, the electrolyte shows no significant sign of electrochemical  
273 decomposition up to  $5.6 \text{ V}$  vs  $\text{Li}|\text{Li}^+$ . In addition, this electrolyte displays excellent cathodic  
274 stability for Li-metal cycling in the following cycles (2<sup>nd</sup> and 3<sup>rd</sup> cycles). In **Supplementary Fig.**  
275 **6**, we observe that the columbic efficiency of LiMICs increases with cycle number, whereas the

276 ILE shows diminished performance, indicating more effective SEI formation on Li-metal anode  
277 when using LiMICs.

278 Next, we prepared Li|Li symmetric cells and recorded the voltage response for stepped  
279 current densities ranging from  $0.01 \text{ mA}\cdot\text{cm}^{-2}$  to  $1 \text{ mA}\cdot\text{cm}^{-2}$ . **Fig. 4e** shows the voltage response  
280 for LiMIC-15 electrolytes. We observe that LiMIC-15 exhibits stable cycling and can withstand  
281 a current density ( $J$ ) to  $1 \text{ mA}\cdot\text{cm}^{-2}$ . This represents state-of-the art performance for SPEs or IL-  
282 based electrolyte materials.<sup>5,20</sup> Overpotential is proportional to applied  $J$  (**Supplementary Fig. 7**),  
283 which follows the Butler-Volmer equation, thus avoiding the possibility of soft shorts.<sup>5,33</sup>

284 The LMIC electrolyte prepared with the ILE containing the highest concentration of LiFSI  
285 ( $3.2 \text{ mol kg}^{-1}$ ) shows the most stable cycling performance (**Supplementary Fig. 8** and  
286 **Supplementary Table 3**).<sup>32,33</sup> EIS spectra shown in **Fig. 4f** indicate that the SEI resistance  
287 increases over the first 40 cycles, then decreases upon further cycling and reduces below that of  
288 the initial state at 50 cycles. This is generally associated with an improving SEI layer that forms  
289 upon cycling and is commonly observed when cycling Li-metal in this ILE with high salt  
290 concentration. Notably, the interfacial resistance for this LiMIC-15 is unusually small, both  
291 before ( $32 \Omega\cdot\text{cm}^{-2}$ ) and after ( $17 \Omega\cdot\text{cm}^{-2}$ ) cycling, compared to other solid-state ion conductors,  
292 thereby overcoming the poor electrolyte-electrode contact between Li-metal anode and solid-ion  
293 conductor typically observed for, e.g.,  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ .<sup>46</sup>



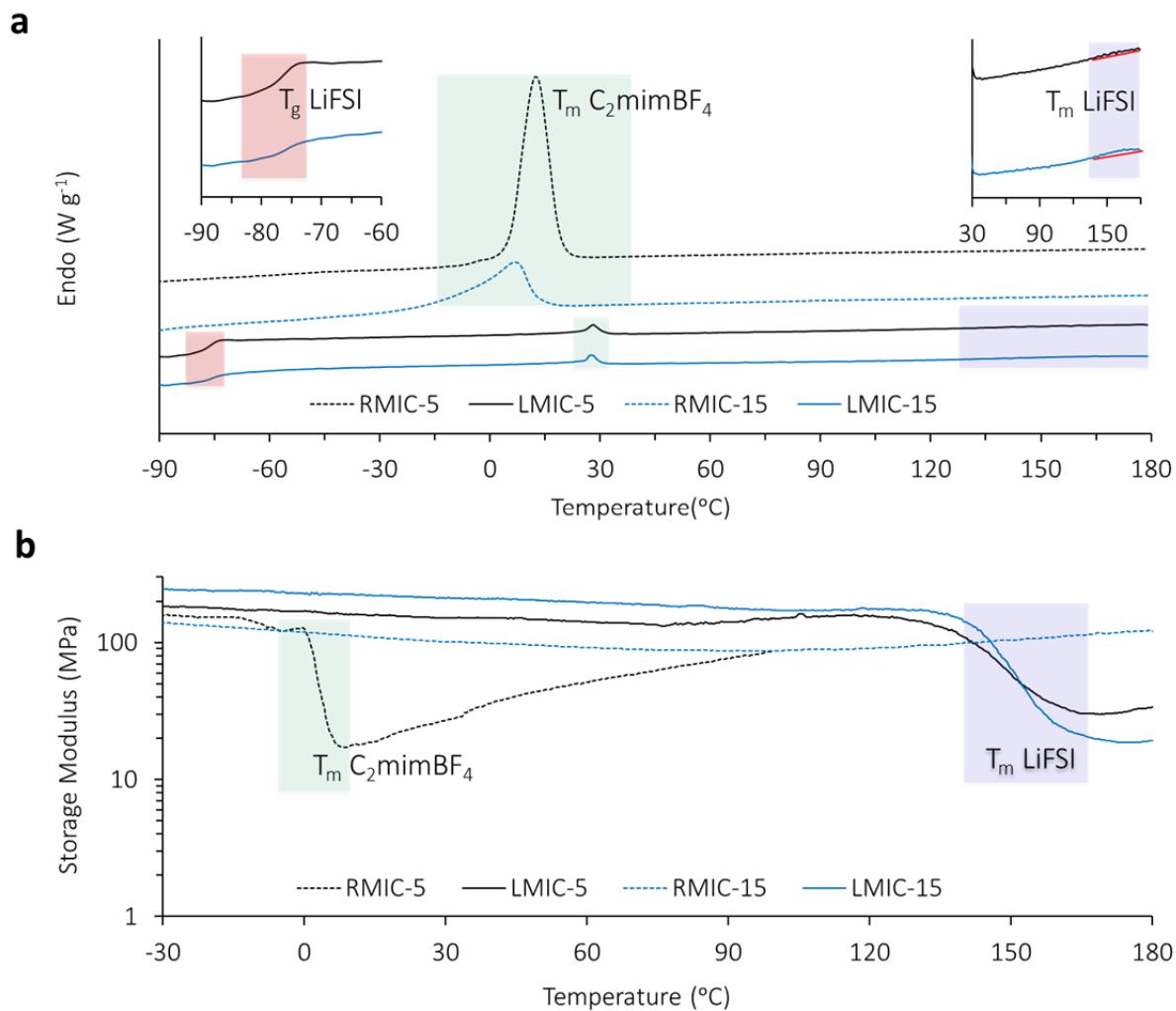
294  
295 **Figure 4. Ionic conductivity, activation energy,  $\text{Li}^+$  transference number, electrochemical**  
296 **window, Li symmetric cell cycling performance, and interfacial charge-transfer resistance**  
297 **in MICs.** (a) Arrhenius plot used to extract activation energies ( $E_a$ ) for ionic conductivity within  
298 RMICs and LiMICs. The green dot shows the conductivity ( $\sigma$ ) of  $\text{C}_2\text{mimBF}_4$  ( $25^\circ\text{C}$ ), used for  
299 developing RMICs. The ionic conductivity value in ILE is indicated with red dots. (b) Comparison of  $E_a$  values obtained from the conductivity results to  $E_a$  values of cations and  $\text{Li}^+$  based on Arrhenius fitting of NMR diffusometry. (c) Steady-state current in symmetric  $\text{Li}|\text{Li}$  cell using LiMICs under  $10 \text{ mV}$  polarization. (d) Cyclic voltammetry curves for Li plating and stripping in LiMIC-15 at a sweep rate of  $5 \text{ mV s}^{-1}$ . Inset plot shows the enlarged view of the 1st cycle in the high voltage range. (e) Cell voltage versus time for a symmetric  $\text{Li}|\text{Li}$  cell using

305 LiMIC-15 at current densities ( $J$ ) from 0.01 to 1  $\text{mA} \cdot \text{cm}^{-2}$  (each cycle lasts 1 h) with changes in  $J$   
306 every 10 cycles. (f) Corresponding impedance spectra scanned before variation of  $J$  (10 cycles)  
307 for the LiMIC-15. The frequency range used is 1Hz – 1MHz.

308

309 In addition to the high  $\text{Li}^+$  conductivity achieved by LiMICs, we also performed DSC and  
310 DMA to better understand their thermal and mechanical stability. As shown in **Fig. 5a**, DSC  
311 curves show that  $\text{C}_2\text{mimBF}_4$  has been mostly exchanged or replaced in LiMICs after *Step 2* of  
312 ion exchange. In addition, we observe a glass transition ( $T_g = -75^\circ\text{C}$ ) for LiFSI, which originates  
313 from the LiFSI phase, as reported in this ILE previously.<sup>32,33</sup> The enlarged view on the right  
314 displays a broad melting transition ( $T_m$ ) of LiFSI in LiMICs, consistent with the XRD results  
315 showing that there exists a highly defective LiFSI crystalline phase in LiMICs. However, the  $T_m$   
316 is not obvious, possibly originating from an endothermic melting process that has been offset by  
317 the exothermic degradation of LiFSI, as reported previously.<sup>47</sup> Meanwhile, we employed DMA  
318 to investigate the mechanical properties of RMICs and LiMICs between  $-50^\circ\text{C}$  to  $180^\circ\text{C}$ , as  
319 shown in **Fig. 5b**. We observe that LiMIC-15 maintains high storage modulus (200 MPa)  
320 between  $-50$  to  $140^\circ\text{C}$ , which then drops above  $140^\circ\text{C}$ , near the  $T_m$  of LiFSI as well as the  
321 degradation temperature for FSI.<sup>47</sup> During the heating process, the LiMIC modulus surpasses all  
322 previous state-of-the-art SPEs, which usually show poor mechanical strength at temperatures  
323 beyond the polymer  $T_g$  or  $T_m$ .<sup>48</sup> Flammability caused by formation of lithium dendrites represents  
324 another key obstacle to safe operation of Li-metal batteries. We included flammability testing  
325 results for RMIC in **Supplementary Fig. 9** and observe that RMICs are stable and cannot be  
326 ignited under a methane/ $\text{O}_2$  flame. Additionally, we carried out nanoindentation experiments to  
327 study the microscopic modulus of the MIC materials (**Supplementary Fig. 10**), where we  
328 observe a large distribution of modulus values, reflecting the heterogeneous structure in LiMICs.

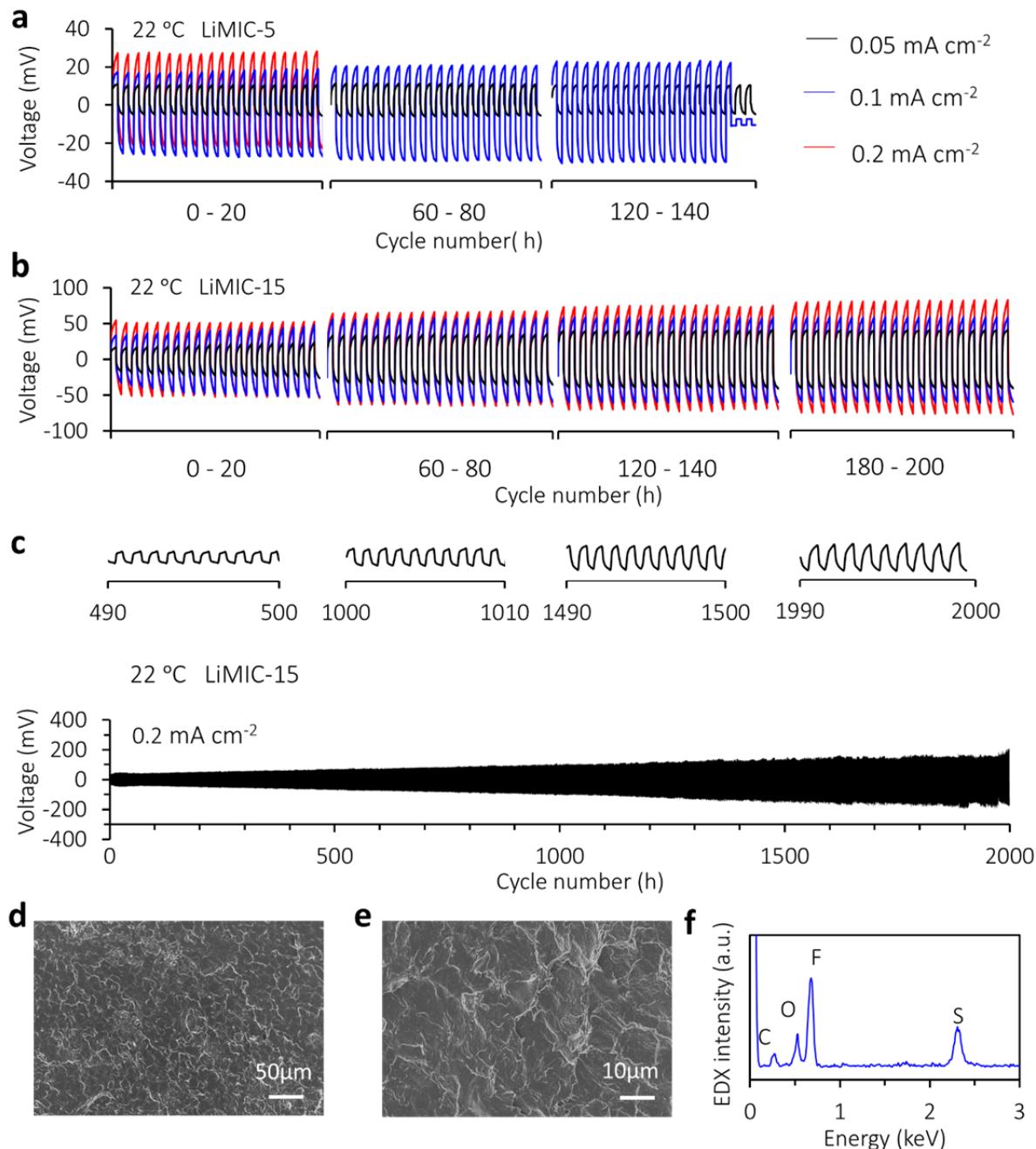
329 The median values shown in the boxplots indicate high consistency with macroscopic DMA  
 330 results.



331  
 332 **Figure 5. Thermal and mechanical properties of RMICs and LiMICS.** (a) DSC shows  
 333 apparent differences between LiMICS and RMICs. RMICs display the melting ( $T_m$ ) of IL  
 334  $\text{C}_2\text{mimBF}_4$  at 17  $^{\circ}\text{C}$ , whereas we only see a slight  $T_m$  peak for  $\text{C}_2\text{mimBF}_4$  in LiMICS in  
 335 agreement with the fact that  $\text{C}_2\text{mimBF}_4$  has been largely exchanged out. According to peak  
 336 integration analysis, only < 3% of  $\text{C}_2\text{mimBF}_4$  remains in the LiMICS. Notably, we do not  
 337 observe any apparent melting peaks belonging to  $\text{C}_3\text{mpyrFSI}$  or  $\text{C}_3\text{mpyrBF}_4$ . The enlarged inset  
 338 on the left shows the glass transition ( $T_g$ ) at -75  $^{\circ}\text{C}$ , which originates from the in-situ formed and  
 339 defective LiFSI phase. The enlarged inset on the right displays the broad melting transition ( $T_m$ )  
 340 of LiFSI in LiMICS. The  $T_m$  peak is not obvious, likely because of the opposing thermal  
 341 transition processes of melting and degradation of LiFSI. (b) DMA shows the mechanical

342 properties of RMICs and LiMICs from -30 °C to 180 °C. RMIC-5 shows a melting drop around  
343 the  $T_m$  of  $C_2mimBF_4$ . LiMICs maintain high modulus (200 MPa) between -50 to 140 °C then  
344 start dropping at 140 °C, which is near both the melting and degradation temperatures of LiFSI  
345 (140 °C).<sup>47</sup>

346 In addition to the cycling results in Fig. 4e, **Fig. 6a-b** shows long-term cycling performance  
347 of the LiMICs as a function of polymer content and current density ( $J$ ). Based on comparison  
348 between LMIC-5 and LiMIC-15 at increasing  $J$ , (0.05, 0.1, 0.2  $mA \cdot cm^{-2}$ ), we observe that  
349 LiMIC-15 (higher polymer content) shows longer cycling stability at all current densities. This  
350 suggests that Li dendrite growth is better suppressed by increasing the rigid polymer content.  
351 The discussion of short circuit behavior observed for LiMIC-5 is included in Note 10 of  
352 supplementary information. **Fig. 6c** demonstrates the cycling stability of LiMIC-15 at  $J = 0.2$   
353  $mA \cdot cm^{-2}$ . Here, we observe that the cell can cycle without short circuit for > 2000 cycles, which  
354 corresponds to 2000 h cycling time and thus removal (and re-plating) of an accumulated total of  
355 1 mm thickness from each Li-metal electrode. Based on the falciform (curved) potential  
356 observed in the charging and discharging processes shown in the selected cycles across the long  
357 period, we do not observe the unstable voltage profile that typically exists in organic electrolytes  
358 at high rates.<sup>32,33</sup> Though overpotential is increasing, we can expect changes to the SEI layer  
359 formed on Li-metal during cycling, which is stable enough to suppress Li dendrite growth and  
360 prevent short-circuit. Post-cycling SEM of the Li-metal electrode surface (**Fig. 6d, e**) shows a  
361 smooth surface devoid of significant dendrites or ‘mossy’ lithium seen in typical organic  
362 electrolyte systems. Peaks from the breakdown products of the  $FSI^-$  anion can be seen in the  
363 EDX spectra (**Fig. 6f**), which are known to aid in chemically suppressing Li dendrites.<sup>31</sup>



364

365 **Figure 6. Voltage-time profiles for Li|Li symmetric cells incorporating LiMICs at ambient**  
 366 **temperature.** 1 cycle = 1 h, or 30 min for each charge and discharge. (a) 0.05 mA·cm<sup>-2</sup>, 0.1  
 367 mA·cm<sup>-2</sup>, 0.2 mA·cm<sup>-2</sup> for LiMIC-5, (b) for LiMIC-15. (c) Long-term cycling of LiMIC-15 at  
 368 current density of 0.2 mA·cm<sup>-2</sup> with 1 h charge/discharge, insets are profiles for selected cycle  
 369 numbers in the cycling period. (d, e) SEM images with different magnifications for the  
 370 disassembled Li-metal electrode after 2000 h long-term cycling in (c) using LiMIC-15 as both  
 371 electrolyte and separator. (f) EDX spectra of Li-metal surface after long-term cycling.

372 We have described materials development, mechanisms for ion transport, morphological  
373 self-assembly, as well as thermal, mechanical, and electrochemical properties of a new Li-loaded  
374 solid-state electrolyte. This inorganic/organic composite material shows immense potential to  
375 serve as a next-generation electrolyte for a range of electrochemical devices, suited for frontier  
376 battery technologies such as Li-metal, Li-S, or Na-based systems. The fabrication method  
377 described enables generation of non-flammable and highly conductive electrolytes with tunable  
378 modulus and with selectable metal ion type and varying concentrations. In addition to the initial  
379 component IL ( $C_2mimBF_4$ ) described here, we can also fabricate MICs based on different  
380 combinations of ILs and PBDT. **Supplementary Table 4** summarizes the currently accessible  
381 MIC fabrication parameter space. Beyond batteries, MICs represent a modular material platform  
382 into which we can incorporate a wide range of ionic fluids and salts with an adjustable  
383 concentration of the highly charged and rigid double helical PBDT polymer. Such compositional  
384 freedom enables the fabrication of MICs with dramatic variations in chemical, mechanical,  
385 conductive, electrolytic, and thermal properties to enable applications in the next generation of  
386 safe and high-energy-density energy storage devices and beyond.

387 **Methods**

388 *Materials:* Poly 2,2'-disulfonyl-4,4'-benzidine terephthalamide (PBDT) was synthesized by  
389 interfacial condensation polymerization as described previously.<sup>17,49</sup> 1-ethyl-3-methyl  
390 imidazolium tetrafluoroborate ( $C_2mimBF_4$ , purity > 99%) was purchased from Solvent  
391 Innovation GmbH (Cologne, Germany). N-propyl-N-methylpyrrolidinium  
392 bis(fluorosulfonyl)imide ( $C_3mpyrFSI$ , purity > 99.9%) was purchased from Solvionic. Lithium  
393 bis(fluorosulfonyl)imide (LiFSI, purity > 99.5%) was sourced from Suzhou Fluolyte Co., Ltd.,  
394 China. Lithium metal was sourced from China Energy Lithium Co. Ltd. (purity > 99.9%). IL

395 electrolytes (ILEs) in this paper were prepared by adding the prescribed amount of LiFSI to  
396 C<sub>3</sub>mpyrFSI IL at room temperature in an Ar-filled glove box (< 0 ppm O<sub>2</sub> and < 10 ppm H<sub>2</sub>O).

397 *Preparation of the RMIC:* C<sub>2</sub>mimBF<sub>4</sub> with the same volume as the (Li-counterion) PBDT  
398 seed aqueous solution was slowly pipetted on top of each solution. After 24 hours ion exchange,  
399 the hydrated MIC gel was formed in the bottom polymer solution phase and the residual water/IL  
400 supernatant was poured off. After vacuum drying the initially hydrated RMIC at 80 °C for more  
401 than 24 hours, we obtained the RMIC electrolytes.

402 *Preparation of the Li-loaded MIC:* The RMICs were sliced by hand using a scalpel as thin as  
403 possible, to obtain a thickness of 250 µm with a standard deviation of 20%. Performance results  
404 will improve as we decrease/optimize the thickness of the electrolytes in future investigations.  
405 The sliced RMICs were then immersed in the ILEs for > 24 h at room temperature. These  
406 operations were completed in an Ar-filled glove box.

407 *<sup>1</sup>H, <sup>19</sup>F and <sup>7</sup>Li NMR spectroscopy and pulsed-field-gradient (PFG) NMR diffusometry:* A  
408 Bruker Avance III widebore 400 MHz (9.4 T) NMR was equipped with a diff60 pulsed-field-  
409 gradient diffusion probe having a maximum gradient value of 2000 G/cm (at 33 A) along the Z  
410 axis and 5 mm <sup>7</sup>Li and 8 mm <sup>1</sup>H/<sup>19</sup>F rf coils. The PGSTE sequence used a  $\pi/2$  pulse, gradient  
411 pulse duration  $\delta$  of 1 - 2 ms, diffusion times  $\Delta$  of 10 - 50 ms and the number of scans for each  
412 step was adjusted from 16 - 1024 to ensure good signal-to-noise ratio (SNR). 16 gradient steps  
413 were applied for each diffusion experiment. All parameters for the NMR diffusometry  
414 experiments have been calibrated and optimized as reported earlier.<sup>50</sup> Solid-state NMR analysis  
415 was performed for chemical identification of various samples. The LiMIC samples were  
416 prepared in glove box and flame sealed without breaking vacuum in a 5 mm NMR tube to a  
417 length of 3 cm filling the coil region of the probe completely. Water content of the samples were

418 examined using  $^1\text{H}$  NMR to ensure the samples were dry as shown in **Supplementary Fig. 11**.  
419 For solid-state NMR, a Bruker Avance III widebore 400 MHz (9.4 T) NMR was equipped with a  
420 static High Power HX SSNMR Probe to allow for short high-power excitation pluses to ensure a  
421 wide spectral excitation bandwidth. For  $^{19}\text{F}$  spectra a single pulse with a  $1.1\ \mu\text{s}$  duration at 200  
422 W was used to achieve a tilt angle of  $50^\circ$ .  $^{19}\text{F}$  spectra were collected using an acquisition time of  
423 0.0204 s, relaxation delay of 4 s, pre-scan delay of  $10\ \mu\text{s}$ , and 64 scans. For the  $^7\text{Li}$  spectra a  
424 single pulse with a  $2.8\ \mu\text{s}$  duration at 200 W was used to achieve a tilt angle of  $90^\circ$ .  $^7\text{Li}$  spectra  
425 were collected using an acquisition time of 0.0198 s, relaxation delay of 10 s, pre-scan delay of  
426  $10\ \mu\text{s}$ , and 128 scans. All parameters for the solid-state experiments have been calibrated and  
427 optimized to ensure integration values of all spectra are precise. All solid-state NMR spectra  
428 were conducted at  $25^\circ\text{C}$ .

429 *X-ray diffraction (XRD):* XRD experiments were carried out on a Rigaku Oxford Diffraction  
430 Xcalibur Nova Single-Crystal Diffractometer equipped with an Onyx CCD detector and a Cu  
431 microsource operating at 49.5 kV and 80 mA at room temperature. The RMIC was sliced to a  
432 thickness  $\sim 1$  mm and mounted on the edge of a steel pin, such that the gel extended above the  
433 steel pin and into the X-ray beam. The sample-to-detector distance was 50 mm, giving data at  
434 scattering angle  $2\theta$  from  $5^\circ$  to  $42^\circ$ . The sample was rotated  $2^\circ$  along the  $\phi$  direction. For each  
435 sample, a total of 6 images each with 30 s exposure time was collected and summed to increase  
436 signal-to-noise ratio. The software CrysAlisPro (v1.171.37.35, Rigaku Oxford Diffraction, 2015,  
437 Rigaku Corporation, Oxford, UK) was used for data collection and analysis.

438 *Cyclic voltammetry:* A stainless steel working electrode and a Li-metal foil counter electrode  
439 were employed for cyclic voltammetry. The CV measurements were performed against  $\text{Li}|\text{Li}^+$   
440 redox potential.<sup>33</sup> All scans were performed at  $25^\circ\text{C}$  with  $5\ \text{mV s}^{-1}$  scan rate using a Biologic SP-

441 200 controlled by EC-Lab (ver. 10.40) software.

442 *Symmetric lithium metal coin cells*: The coin cells were prepared with CR2032 cases with  
443 two 3.2 mm (1/8 inch) diameter lithium electrodes in an Ar-filled glove box. The coin cells were  
444 used for impedance spectroscopy and cycling measurements. A VMP3 (BioLogic) system and a  
445 Neware system were used for battery testing.

446 *Ionic conductivity*: The ionic conductivity was measured via dielectric response over a 1 Hz –  
447 1 MHz frequency range (to emphasize the electrode-electrolyte interfacial resistance) at an  
448 amplitude of 20 mV. A temperature scan range 20 °C to 100 °C was selected, and the  
449 temperature was controlled by a Eurotherm 2204 temperature controller. Conductivity of the  
450 LiMIC was extracted using a value of electrical resistance obtained by fitting the data to an  
451 equivalent circuit model using EC-Lab (ver. 10.40) software®. Two heating scans with 10 °C  
452 intervals were conducted, and the data shown in this study were extracted from the second  
453 heating scan.

454 *Li Transference Number ( $t_{\text{Li}}^+$ )*: The transference number was electrochemically determined  
455 by direct current (DC) polarization. An AC impedance test was firstly performed over a 0.1 Hz  
456 to 1 MHz range to obtain a total resistance  $R_{\text{cell}}$ . Then the polarization was carried out to obtain a  
457 stable current. Cells were polarized at ambient temperature with a constant potential of 10 mV  
458 for 2 h.

459 *Dynamic Mechanical Analysis (DMA)*: The mechanical properties of the composites were  
460 investigated at 1Hz frequency using a DMA 8000 (PerkinElmer) from -50 to 200 °C. The sample  
461 preparation was finished in a N<sub>2</sub>-filled glovebox (H<sub>2</sub>O < 100 ppm). The compression mode was  
462 used to determine the storage modulus and loss modules of each electrolyte. The test sample was  
463 first cooled to -50 °C and then heated to 200 °C at a heating rate of 2 °C/min.

464        *Differential scanning calorimetry (DSC):* A Netzsch DSC (214 polyma), calibrated with  
465        cyclohexane, was used to investigate the thermal behaviour of the MICs. The heating and  
466        cooling rate were 10 °C min<sup>-1</sup>. Samples were cooled to -100 °C and then three heating scans  
467        were followed.

468        *Nanoindentation* results were measured at room temperature using a hysitron triboindenter.

469        *Scanning electron microscopy* was performed using a JSM IT 300 series microscope and  
470        energy dispersive X-ray spectroscopy was measured with an Oxford X-Max 50 mm<sup>2</sup> EDX  
471        detector.

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609 **Data availability**

610 All data generated and analyzed in this study are included in this published article and its  
611 supplementary information file and are also available from the corresponding author on  
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618 **Author contributions**

619 YW designed and executed all major experiments and composed and edited article drafts. XW,

620 RK, LJ, and MF performed and assisted with electrochemistry and impedance experiments and  
621 contributed written sections and editing to the article. CJZ performed solid-state NMR  
622 experiments and contributed written sections and editing to the article. WHK analyzed the XRD  
623 data and contributed written sections to the article. TJD modified and supplied polymer,  
624 conceived experiments and contributed written sections and editing to the article. LAM  
625 conceived ideas, oversaw experiments, and composed and edited the article.

# Solid-state rigid-rod polymer composite electrolytes with nanocrystalline lithium ion pathways

*Ying Wang<sup>1</sup>, Curt J. Zanelotti<sup>1</sup>, Xiaoen Wang<sup>2</sup>, Robert Kerr<sup>2</sup>, Liyu Jin<sup>2</sup>, Wang Hay Kan<sup>3</sup>, Theo J. Dingemans<sup>4</sup>, Maria Forsyth<sup>2</sup>, and Louis A. Madsen<sup>1\*</sup>*

1. Department of Chemistry and Macromolecules Innovation Institute  
Virginia Polytechnic Institute and State University  
Blacksburg, Virginia 24061, United States  
E-mail: lmadsen@vt.edu
2. Institute for Frontier Materials and ARC Centre of Excellent for Electromaterials Science  
Deakin University  
Geelong, VIC 3216, Australia
3. China Spallation Neutron Source  
Chinese Academy of Science  
Dongguan, Guangzhou 523803, China
4. Department of Applied Physical Sciences  
University of North Carolina at Chapel Hill  
121 South Road, Chapel Hill, NC27599-3050, United States

20 **Abstract**

21 A critical challenge for next-generation lithium-based batteries lies in development of  
22 electrolytes that enable thermal safety along with use of high-energy-density electrodes. We  
23 describe molecular ionic composite (MIC) electrolytes based on an aligned liquid crystalline  
24 polymer combined with ionic liquids and concentrated Li salt. This high strength (200 MPa) and  
25 non-flammable solid electrolyte possesses outstanding  $\text{Li}^+$  conductivity ( $1 \text{ mS}\cdot\text{cm}^{-1}$  at  $25^\circ\text{C}$ ) and  
26 electrochemical stability (5.6 V vs  $\text{Li}|\text{Li}^+$ ) while suppressing dendrite growth and exhibiting low  
27 interfacial resistance ( $32 \Omega\cdot\text{cm}^2$ ) and overpotentials ( $\leq 120 \text{ mV} @ 1 \text{ mA}\cdot\text{cm}^{-2}$ ) during Li symmetric  
28 cell cycling. A heterogeneous salt doping process modifies a locally ordered polymer-ion assembly  
29 to incorporate an inter-grain network filled with defective  $\text{LiFSI} \& \text{LiBF}_4$  nanocrystals, strongly  
30 enhancing  $\text{Li}^+$  conduction. This modular material fabrication platform shows promise for safe and  
31 high-energy-density energy storage and conversion applications, incorporating the fast transport  
32 of ceramic-like conductors with the superior flexibility of polymer electrolytes.

33

34

35

36 Solid-state polymer electrolytes (SPEs) have received great attention toward reviving high-  
37 energy-density Li-based batteries.<sup>1-4</sup> While Li-ion batteries play an important role in the energy  
38 storage landscape due to their relatively high specific energy and power density, they are  
39 approaching theoretical limits ( $\approx 400$  Wh.kg<sup>-1</sup>).<sup>5,6</sup> In order to increase capacity of Li-based  
40 batteries, researchers have largely focused on new electrode materials. Regarding cathodes, Li-air  
41 and Li-sulfur batteries represent leading frontier candidates.<sup>3,7-9</sup> At the anode, Li-metal can replace  
42 graphite to increase anode energy density by  $\sim 10$  fold.<sup>5-7</sup> However, electrode advancements  
43 require an enabling electrolyte to combat irreversible reactions and dendrite growth during long-  
44 term charge/discharge cycling.<sup>7,10</sup> To alleviate these issues, SPEs not only provide mechanical  
45 stiffness to block dendrites, but deliver safer (non-flammable) operation compared to liquid  
46 electrolytes.<sup>1,10-12</sup> Herein, we describe a solid-state ***molecular ionic composite*** (MIC)  
47 electrolyte<sup>1,13-15</sup> based on an extremely rigid double helical sulfonated aromatic polyamide (similar  
48 to Kevlar®)<sup>16,17</sup> combined with an ionic liquid (IL) and a Li salt. We can adjust MIC properties  
49 widely by changing polymer content, IL type, and metal salt type and loading. Thus, MICs  
50 represent a modular material platform with potential to resolve a range of issues in electrolytic  
51 materials.

52 Previous researchers have developed a number of IL-based gel electrolytes (termed “ion gels”  
53 or “ionogels”) that combine the non-flammability of ILs with a mechanically supporting  
54 matrix.<sup>1,18-21</sup> These electrolytes consist of either a polymer matrix embedded with a large volume  
55 fraction of IL,<sup>1,22</sup> or an IL inside an inorganic matrix such as SiO<sub>2</sub> and TiO<sub>2</sub>.<sup>19,20,23</sup> Potential  
56 applications of these gels for high-energy-density Li batteries have been substantially  
57 explored.<sup>20,24,25</sup> However, these gels only show practical Li-metal cycling performance when  
58 doped with organic electrolytes,<sup>20,25</sup> which improve conductivity but introduce a volatile liquid

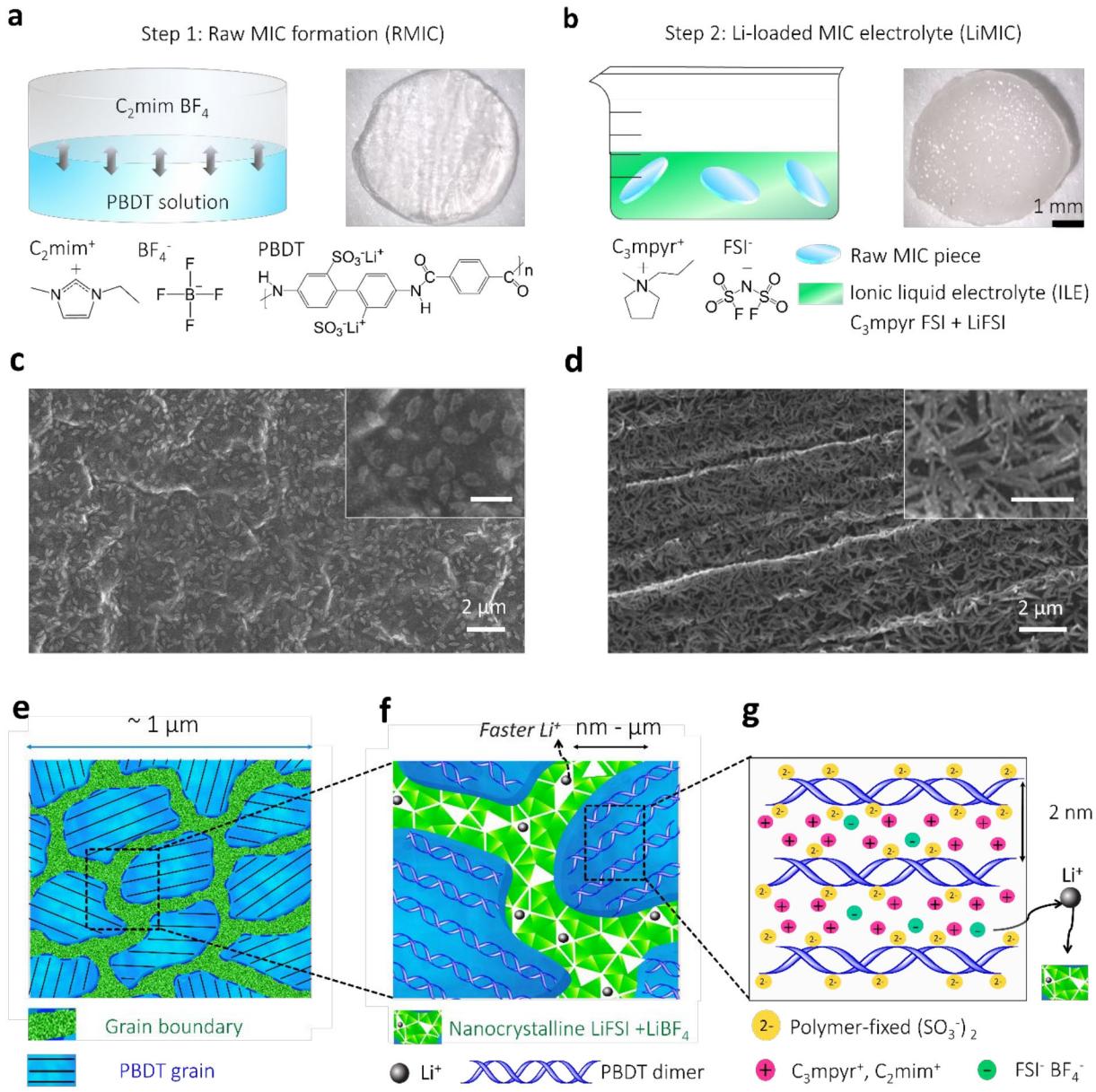
59 that diminishes safety against overheating and fire.<sup>5,6</sup> In this work, we describe solid-state MIC  
60 electrolytes that contain no volatile solvents but exhibit high ionic conductivity, beneficial  
61 electrode-electrolyte contact and high thermal stability, all while possessing sufficient modulus to  
62 serve as the separator in Li-metal batteries. Loading electrolytes with Li salts serves to increase  
63 Li-ion conductivity and supply Li<sup>+</sup> for reactions at the electrodes.<sup>2,26-28</sup> Maier et al. have  
64 demonstrated that heterogeneous doping and interfacially controlled materials can be used to  
65 increase Li<sup>+</sup> conductivity in electrolytes.<sup>10</sup> Christie et al. reported that the presence of the  
66 irregularly shaped bis(trifluoromethanesulfonyl)imide (TFSI<sup>-</sup>) anion disrupts the electrostatic  
67 potential around Li<sup>+</sup> thereby enhancing ionic conductivity in a manner analogous to inorganic  
68 electrolytes such as AgBr<sub>1-x</sub>I<sub>x</sub>.<sup>2</sup> Recently, lithium bis(fluorosulfonyl)imide (LiFSI) has emerged as  
69 a promising electrolyte component.<sup>28-30</sup> Furthermore, the FSI<sup>-</sup> anion can decompose upon  
70 electroreduction to form a stable solid-electrolyte interphase (SEI) that enables reversible cycling  
71 with a graphitic anode.<sup>31</sup> In this project, we employ ionic liquid electrolytes (ILEs) containing *N*-  
72 propyl-*N*-methylpyrrolidinium (C<sub>3</sub>mpyr) FSI mixed with LiFSI ( $\leq 3.2$  mol/kg), which have  
73 previously shown Li-metal cycling at high rates.<sup>32,33</sup> By incorporating this ILE into a solid MIC,  
74 we demonstrate a highly lithium-dense solid-state electrolyte with potential to suppress Li dendrite  
75 growth on Li-metal anodes, enable fast Li<sup>+</sup> transport, and eliminate battery safety concerns.

76 The Li-loaded MIC (LiMIC) fabrication process requires two steps: (1) Initial polymer-IL  
77 network formation, followed by (2) ILE ion exchange to achieve high Li<sup>+</sup> loading. As shown in  
78 **Fig. 1a**, we obtain the raw MIC (RMIC), based on an interfacial ion-exchange process between a  
79 sulfonated aromatic polyamide, poly-2,2'-disulfonyl-4,4'-benzidine terephthalamide (Li-form  
80 PBDT) in H<sub>2</sub>O solution and an IL, C<sub>2</sub>mimBF<sub>4</sub> (1-ethyl-3-methylimidazolium tetrafluoroborate).<sup>1</sup>  
81 PBDT is water-miscible and forms a highly ordered lyotropic nematic liquid crystal (LC) phase at

82 concentrations > 2 wt%.<sup>16,17</sup> The local parallel packing of charged PBDT rods serves as the  
83 assembly template – not only offering mechanical integrity, but also endowing nanoscale  
84 structuring in the composite. RMICs are denoted with RMIC-5 and RMIC-15, in which the  
85 numbers denote PBDT weight percentage of 5% and 15%. In **Fig. 1b**, we immerse the rigorously  
86 dried RMICs in the desired ILE, i.e., C<sub>3</sub>mpyrFSI with 50 mol% LiFSI. This serves the dual  
87 purposes of lowering the concentration of BF<sub>4</sub><sup>-</sup> anions through ion-exchange while also  
88 introducing Li<sup>+</sup> ions into the polymer host matrix. By following this two-step fabrication method,  
89 we obtain a solid-state MIC electrolyte, denoted LiMIC-5 and LiMIC-15. The key to *Step 1* is that  
90 both the IL and LC polyelectrolyte dissolve in the same solvent. *Step 2* allows us to exchange a  
91 wide range of IL and Li salt mixtures into the MIC matrix and tailor properties of the product  
92 toward Li-metal batteries or other applications. The SEM images of RMICs (**Fig. 1c, d**) show  
93 locally aligned PBDT LC grains (μm-scale) interspersed with interconnected grain boundaries  
94 with a wide size distribution from nm - μm. This RMIC has mechanical cohesion propagated by a  
95 collective “electrostatic network,” which effectively arises from templating of the IL through the  
96 highly charged and rigid double helical PBDT rods.<sup>13,15</sup> The RMICs are macroscopically isotropic,  
97 but display local alignment originating from the rigid PBDT chains, which can be verified using  
98 polarized optical microscopy (**Supplementary Fig. 1**).<sup>1,17</sup>

99 **Fig. 1e-g** illustrates the concepts involved in multi-scale organization of the LiMICs. **Fig. 1e**  
100 shows the μm-scale structure of this solid electrolyte, incorporating aligned PBDT grains  
101 interleaved with a nanocrystalline ionic phase. These nanocrystalline grain boundaries serve as an  
102 additional conductive network providing fast Li<sup>+</sup> transport. As shown in **Fig. 1f**, we propose that  
103 after ion exchange with ILE, the interconnected boundaries separating the individual PBDT grains  
104 allow for higher Li<sup>+</sup> density and faster Li<sup>+</sup> transport as compared to within the grains. **Fig. 1g**

105 further illustrates the morphology and ion distribution in the internally aligned PBDT grains and  
 106 the nanocrystalline component formed at the grain boundaries. We will illustrate this model in  
 107 more detail in the following sections based on multi-modal material characterizations.



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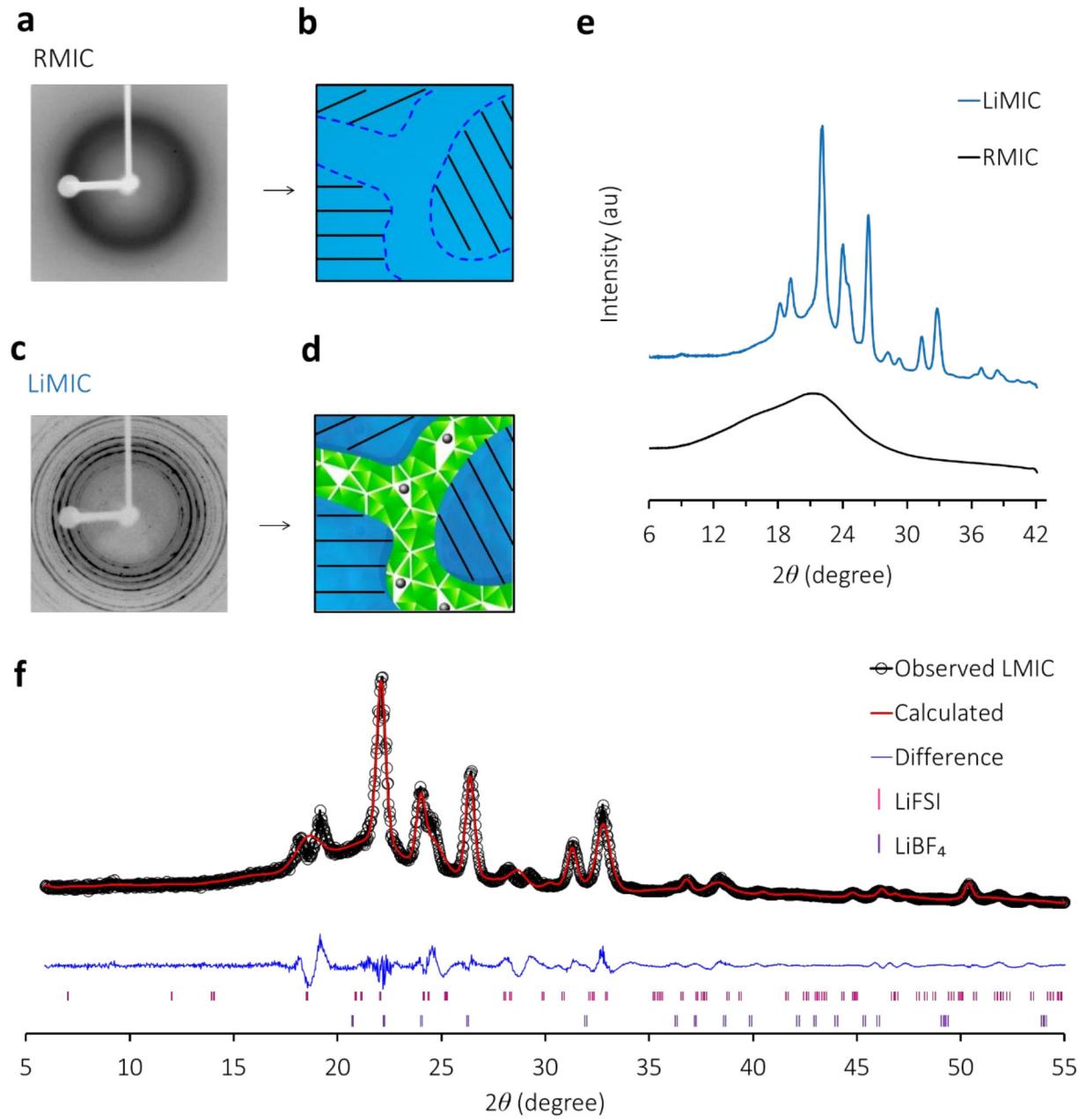
109 **Figure 1. Fabrication processes to form Li-loaded MIC electrolytes (LiMICs).** (a) *Step 1*  
 110 shows fabrication of the raw MIC (RMIC). Mechanical cohesion in this RMIC arises via  
 111 electrostatic interactions,<sup>1,13,15</sup> and we obtain this material based on an interfacial ion exchange  
 112 between a water-soluble IL (e.g.,  $C_2mimBF_4$ ) and an aqueous rigid-rod polyelectrolyte solution

113 (Li-form PBDT in H<sub>2</sub>O). The photograph shows the sliced transparent RMIC sample. (b) **Step 2**  
114 shows the second ion exchange process wherein we immerse a sliced section of the RMIC into the  
115 ILE (C<sub>3</sub>mpyrFSI with 50 mol% LiFSI). During the infiltration process, the cation C<sub>3</sub>mpyr<sup>+</sup> in the  
116 ILE tends to segregate into the PBDT-rich phase,<sup>13,14</sup> as the FSI<sup>-</sup> and BF<sub>4</sub><sup>-</sup> anions preferentially  
117 associate with Li<sup>+</sup> and precipitate out to form a nanoscale heterogeneous structure in the grain  
118 boundaries. The photograph shows the sliced iridescent LiMIC sample. (c,d) SEM images for  
119 RMIC-5(c) and RMIC-15(d). Higher magnification images are shown in the upper right insets.  
120 The scale bar for the insets is 1  $\mu$ m. The interfaces between individual PBDT grains form the grain  
121 boundaries (darker regions). Both the aligned PBDT grains and the grain boundaries contain  
122 C<sub>2</sub>mimBF<sub>4</sub>. (e, f) After **Step 2**, the grain boundaries become predominantly the condensed salt  
123 phase, which consists of nanocrystalline grains that form a conductive network supporting fast Li<sup>+</sup>  
124 transport. (g) The morphology of an aligned LC grain contains PBDT double helical rods filled  
125 predominantly with mobile IL cations. The distance between PBDT rods is  $\sim$  2 nm.<sup>1,15</sup>

126

127 To investigate the nanoscale morphology of these composites, we conducted powder X-ray  
128 diffraction (XRD) experiments on the RMIC and LiMIC. As shown in **Fig. 2a**, we observe an  
129 amorphous halo with scattering angle 2 $\theta$  from 12° to 30° for the RMIC, which we assign to the  
130 amorphous C<sub>2</sub>mimBF<sub>4</sub> in the RMIC. A schematic picture is shown in **Fig. 2b**, where the locally  
131 aligned PBDT rods serve as the assembly template for the amorphous IL. The diffraction peaks of  
132 the PBDT are overwhelmed by the large volume fraction of IL in the RMIC. By contrast, the XRD  
133 of the LiMIC (**Fig. 2c**) shows a heterogeneous structure based on coexistence of the weak  
134 amorphous halo and the sharp crystalline reflections. This pattern agrees with the schematic picture  
135 shown in **Fig. 2d**, depicting a highly defective nanocrystalline domain formed in-situ between the  
136 PBDT grains in the LiMICs. The extracted 1D spectra are shown in **Fig. 2e**. The crystalline peaks  
137 (blue line), at first glance, appear to be superimposed diffraction patterns of LiFSI and LiBF<sub>4</sub>. We  
138 also notice that, compared to the amorphous phase, the crystalline phase is the dominant  
139 component in the LiMIC, which supports the solid-state NMR (SSNMR) integration results

140 included in **Supplementary Table 1**, showing that  $\sim 80\%$  anions ( $\text{FSI}^-$  and  $\text{BF}_4^-$ ) in LiMIC are  
141 localized in the solid crystalline phase. We further use Le Bail refinement to determine the cell  
142 parameters for the two potential crystals.<sup>34</sup> **Fig. 2f** shows the fitting results with R-factor for the  
143 refinement  $R_p = 6.87\%$ , which indicates good alignment between the observed diffraction patterns  
144 and the simulated phases of LiFSI and LiBF<sub>4</sub>. The in-situ formed defective crystals of LiFSI and  
145 LiBF<sub>4</sub> possess preferred orientations, which contribute to the high density of vacancies that  
146 promote easier hopping of  $\text{Li}^+$  between crystallites. We use the Scherrer equation<sup>35</sup>  
147 (**Supplementary Equation 1**) to determine the average crystallite size (19.4 nm) formed in the  
148 LiMIC grain boundary regions from the FWHM of the peak at  $2\theta = 26.363^\circ$  (012) from the LiBF<sub>4</sub>  
149 phase. **Table 1** summarizes the Le Bail refinement with cell parameters for the two defective  
150 crystals, and both belong to the trigonal crystal structure. These results provide evidence that these  
151 nanocrystals are localized in the grain boundaries instead of within PBDT grains, where the  
152 distance between PBDT chains is too small to accomodate the nanocrystals.<sup>1,15-17</sup>



153 **Figure 2. X-ray diffraction patterns of RMIC and LiMIC.** (a) Powder XRD pattern for the  
154 RMIC. (b) In the RMIC, PBDT LC grains and grain boundaries are filled with amorphous IL as a  
155 result of **Step 1** of the fabrication process. (c) XRD pattern for the LiMIC. (d) In the LiMIC, there  
156 exists an in-situ formed and highly defective nanocrystalline structure between PBDT LC grains.  
157 (e) The extracted 1D spectra of the XRD images in (a) and (c). (f) Le Bail refinement results for  
158 the LiMIC XRD pattern, which include the observed pattern, the calculated results and the  
159 simulation of the in-situ formed nanocrystalline structure of LiFSI and LiBF<sub>4</sub>.  
160

161

162 **Table 1. Li crystals formed in the LiMIC (R<sub>wp</sub> = 9.75%, R<sub>p</sub> = 6.87%)**

LiMIC-15	Phase1 (LiFSI)	Phase2 (LiBF <sub>4</sub> )
<b>Crystal structure</b>	<b>Trigonal</b>	<b>Trigonal</b>
<b>Space group</b>	P -3	P 31 2 1
<b>a (Å) (a)</b>	8.513 (90°)	4.9511(90°)
<b>b (Å) (β)</b>	8.513(90°)	4.9511(90°)
<b>c (Å) (γ)</b>	12.610 (120°)	11.112 (120°)
<b>Volume(Å<sup>3</sup>)</b>	779.76	228.02
<b>ICSD</b>	415618	171375

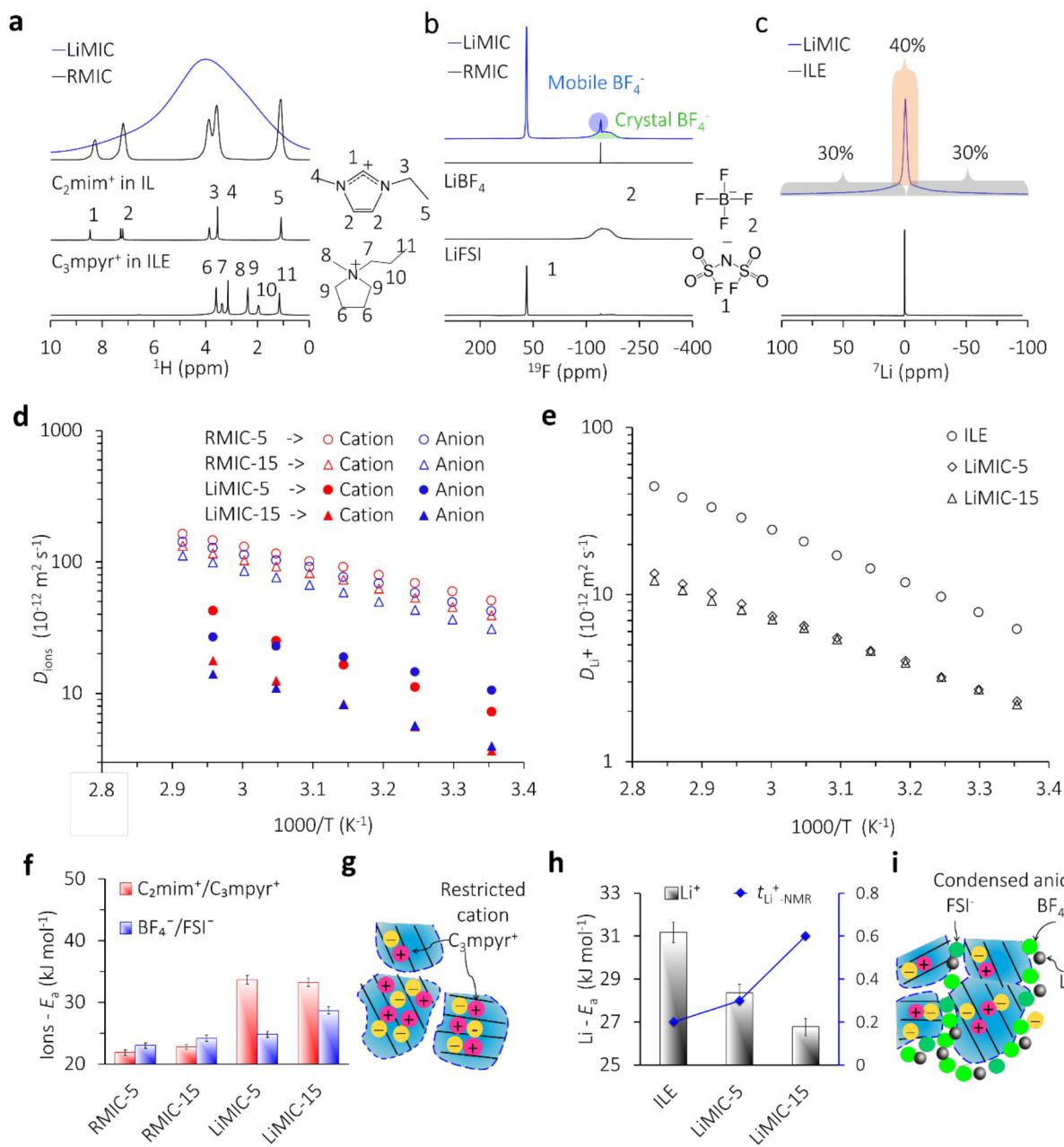
163

164 To understand the ion transport and morphology in both RMIC and LiMIC, we first verify the  
 165 chemical composition of the products, qualitatively and quantitatively, based on <sup>1</sup>H, <sup>19</sup>F and <sup>7</sup>Li  
 166 NMR spectroscopy. **Fig. 3a, b, c** present key features of these NMR studies. **Fig. 3a** shows <sup>1</sup>H  
 167 spectra for C<sub>2</sub>mim<sup>+</sup> in neat IL and C<sub>3</sub>mpyr<sup>+</sup> in ILE (bottom two spectra), and compares <sup>1</sup>H spectra  
 168 in the RMIC to the LiMIC. The linewidth in the LiMIC (~ 1500 Hz) is much broader compared to  
 169 the RMIC (~ 100 Hz), which means a factor of ~ 15 faster *T*<sub>2</sub> spin-spin relaxation, indicating slower  
 170 motion of IL cations. **Supplementary Fig. 2** shows additional <sup>1</sup>H spectra for RMIC-5 and RMIC-  
 171 15. SSNMR offers promise for studying the same chemical species in distinct phases, including  
 172 the grain boundaries and the locally aligned PBDT grains in LiMICS. **Fig. 3b** shows <sup>19</sup>F SSNMR  
 173 spectra for LiMIC (blue line) along with spectra for the reference Li salts (LiFSI and LiBF<sub>4</sub>). For  
 174 the LiMIC, we observe a small percentage of mobile BF<sub>4</sub><sup>-</sup> with a relatively narrow peak (light blue  
 175 circle) at -150 ppm. The broad peak underneath (light green semicircle) refers to BF<sub>4</sub><sup>-</sup> in the  
 176 nanocrystalline grain boundaries. Due to its fast internal dynamics, FSI<sup>-</sup> appears as only a singlet  
 177 peak at 60 ppm, which we assign to the superposition of mobile FSI<sup>-</sup> in aligned LC grains and solid  
 178 FSI<sup>-</sup> in nanocrystalline grain boundaries. The assignments, assumptions, and quantifications of  
 179 different ionic species in the LiMICS are summarized in **Supplementary Fig. 3** and  
 180 **Supplementary Table 1**. **Fig. 3c** compares <sup>7</sup>Li spectra between ILE and LiMIC. The widths and

181 integration values of the peaks are displayed in **Supplementary Fig. 4**. This single-component  
182 3:4:3 splitting pattern indicates that  $\text{Li}^+$  can only exist in either the crystalline grain boundaries or  
183 in the PBDT LC grains.<sup>36,37</sup> Based on the XRD, we observe that the  $\text{Li}^+$  mainly forms into  
184 crystalline phases of LiFSI and  $\text{LiBF}_4$  in the grain boundaries, thus demonstrating that  $\text{Li}^+$  is the  
185 dominant cation in the solid nanocrystals, instead of in PBDT LC grains.

186 Understanding and controlling ion transport, ion associations and  $\text{Li}^+$  transport mechanisms in  
187 electrolyte materials are critical for development of next-generation battery electrolytes. We can  
188 extract the diffusive activation energy ( $E_a$ ) of the ions present in RMIC and LiMIC electrolytes  
189 based on the temperature dependencies of  $D_{\text{Li}^+}$ ,  $D_{\text{cations}}$  and  $D_{\text{anions}}$  obtained from NMR  
190 diffusometry as shown in **Fig. 3d,e**.<sup>1,38-40</sup> As indicated from the faster  $T_2$  relaxation, we observe  
191 that  $D$  values for the mobile IL ions in LiMICs are an order of magnitude smaller than those in  
192 RMICs, as expected. **Fig. 3f** shows the extracted  $E_a$  values for cations and anions in RMICs and  
193 LiMICs via the Arrhenius equation. The  $E_a$  values for  $\text{C}_2\text{mim}^+$  and  $\text{BF}_4^-$  increase with polymer  
194 content in the RMICs. This suggests that the density of the PBDT matrix dominates the local  
195 energetic barriers that govern ion transport. In addition, compared to the RMICs, the  $E_a$  values for  
196 cations in the LiMICs almost doubles, whereas  $E_a$  for anions show only a slight increment with  
197 polymer content. This indicates that the PBDT matrix escalates the local energetic barriers for  
198 cation transport in LiMICs, primarily because of stronger associations between the  $\text{SO}_3^-$  on PBDT  
199 chains and  $\text{C}_3\text{mpyr}^+$ . Correspondingly, the schematic picture for the trapped cations within the  
200 aligned LC grain is shown in **Fig. 3g**. Conversely, the  $E_a$  values for  $\text{Li}^+$  in the LiMIC (**Fig. 3h**)  
201 decrease with increasing polymer content, indicating smaller local energetic barriers for  $\text{Li}^+$   
202 transport compared to the ILE.<sup>13,40</sup> This indicates that a different  $\text{Li}^+$  transport mechanism applies  
203 for LiMICs. As shown in **Supplementary Table 1**, the concentration of mobile cations ( $\text{C}_2\text{mim}^+$ ,

204  $\text{C}_3\text{mpyr}^+$ ) and anions ( $\text{FSI}^-$ ,  $\text{BF}_4^-$ ) in the LiMICs are  $\sim 6$  times lower compared to the RMICs.  
205 Meanwhile, LiMICs show an order of magnitude slower diffusion coefficients for the same set of  
206 mobile cations and anions. Based on the Nernst–Einstein equation, we suggest that the  
207 unexpectedly high conductivity observed in this solid LiMIC electrolyte (see below, Fig. 4a)  
208 originates from a fast  $\text{Li}^+$  hopping ion transport mechanism in the solid nanocrystalline grain  
209 boundaries, as opposed to transport through a liquid-like mobile phase in the PBDT LC  
210 grains.<sup>39,41,42</sup> We further determine the  $\text{Li}^+$  transference number determined by diffusion ( $t_{\text{Li}^+\text{-NMR}}$ )  
211 in LiMICs based on the **Supplementary Equation 2** and include the results in **Supplementary**  
212 **Table 1.** **Fig. 3i** depicts the nanocrystalline anions located in the grain boundaries, which we  
213 propose give rise to atypically fast  $\text{Li}^+$  ion transport.



221 being 40% due to the quadrupole splitting of Li. (d) Temperature-dependent  $D_{\text{cations}}$  and  $D_{\text{anions}}$  in  
222 the RMICs and LiMIC. For LiMICs,  $D_{\text{cations}}$  represents the average value for  $\text{C}_3\text{mpyr}^+$  and  $\text{C}_2\text{mim}^+$ .  
223 The  $D_{\text{anions}}$  is the average value for mobile  $\text{FSI}^-$  and  $\text{BF}_4^-$ .  $D_{\text{anions}}$  is the computed weighted average  
224 value for the anions based on the mole ratio of mobile  $\text{FSI}^-$  and  $\text{BF}_4^-$  as quantified by  $^{19}\text{F}$  NMR  
225 shown in **Supplementary Fig. 3** and **Supplementary Table 1**. (e) Temperature-dependent  $D_{\text{Li}^+}$   
226 in ILE and LiMICs. (f)  $E_a$  values for cations and anions obtained from Arrhenius fitting of diffusion  
227 results. Uncertainties in diffusion are smaller than the marker and uncertainties in  $E_a$  are  $\approx \pm 0.5$   
228 kJ/mol. (g) Schematic showing  $\text{C}_3\text{mpyr}^+$  separations into locally aligned LC grains. (h)  $E_a$  values  
229 for  $\text{Li}^+$  obtained from Arrhenius fitting. The blue line compares the measured  $t_{\text{Li}^+}\text{-NMR}$  in ILE to  
230 that in LiMICs. (i) Schematic of the electrolyte structure showing the formation mechanism of  
231 nanocrystalline  $\text{LiBF}_4$  and  $\text{LiFSI}$  in the grain boundaries.

232

233 Building on the RMIC morphology,<sup>1</sup> we propose that the formation mechanism for the  
234 heterogeneous structure in LiMICs lies in preferential associations and co-crystallization of  
235 specific ions.  $\text{SO}_3^-$  and  $\text{C}_3\text{mpyr}^+$  ions should have the weakest associations with other ions due to  
236 their size and local charge distributions. Based on XRD and SSNMR results, we expect that  $\text{FSI}^-$   
237 and  $\text{BF}_4^-$  have a strong affinity with  $\text{Li}^+$  to form a thermodynamically favorable crystalline phase.  
238 These nanocrystals (20 nm) form within the grain boundaries when the concentration locally  
239 exceeds the saturation point of  $\text{LiBF}_4$  and  $\text{LiFSI}$  in the ILE. This leaves the exchanged  $\text{C}_3\text{mpyr}^+$   
240 and residual  $\text{C}_2\text{mim}^+$  cations to neutralize predominantly the polymer-fixed  $\text{SO}_3^-$  anions within the  
241 PBDT LC grains. The Li-rich nanocrystalline phase serves as a highly ion-conductive network that  
242 can transport  $\text{Li}^+$ . In these grain boundaries, the space-charge zone and nano-size effects among  
243 the polycrystalline  $\text{LiBF}_4$ ,  $\text{LiFSI}$  and aligned crystalline PBDT grains should enhance the vacancy  
244 density and conductivity of  $\text{Li}^+$ , which is consistent with the decreasing  $E_a$  of  $\text{Li}^+$  obtained from  
245 NMR diffusometry. We also note that this nanocrystalline phase likely exhibits features of plastic  
246 crystal behavior.<sup>39,43-45</sup> Further investigation of transport mechanisms, grain boundary

247 heterogeneities, space-charge effects and ion interactions in this heterogeneous structure will  
248 provide deeper understanding of these solid electrolytes for future materials design.

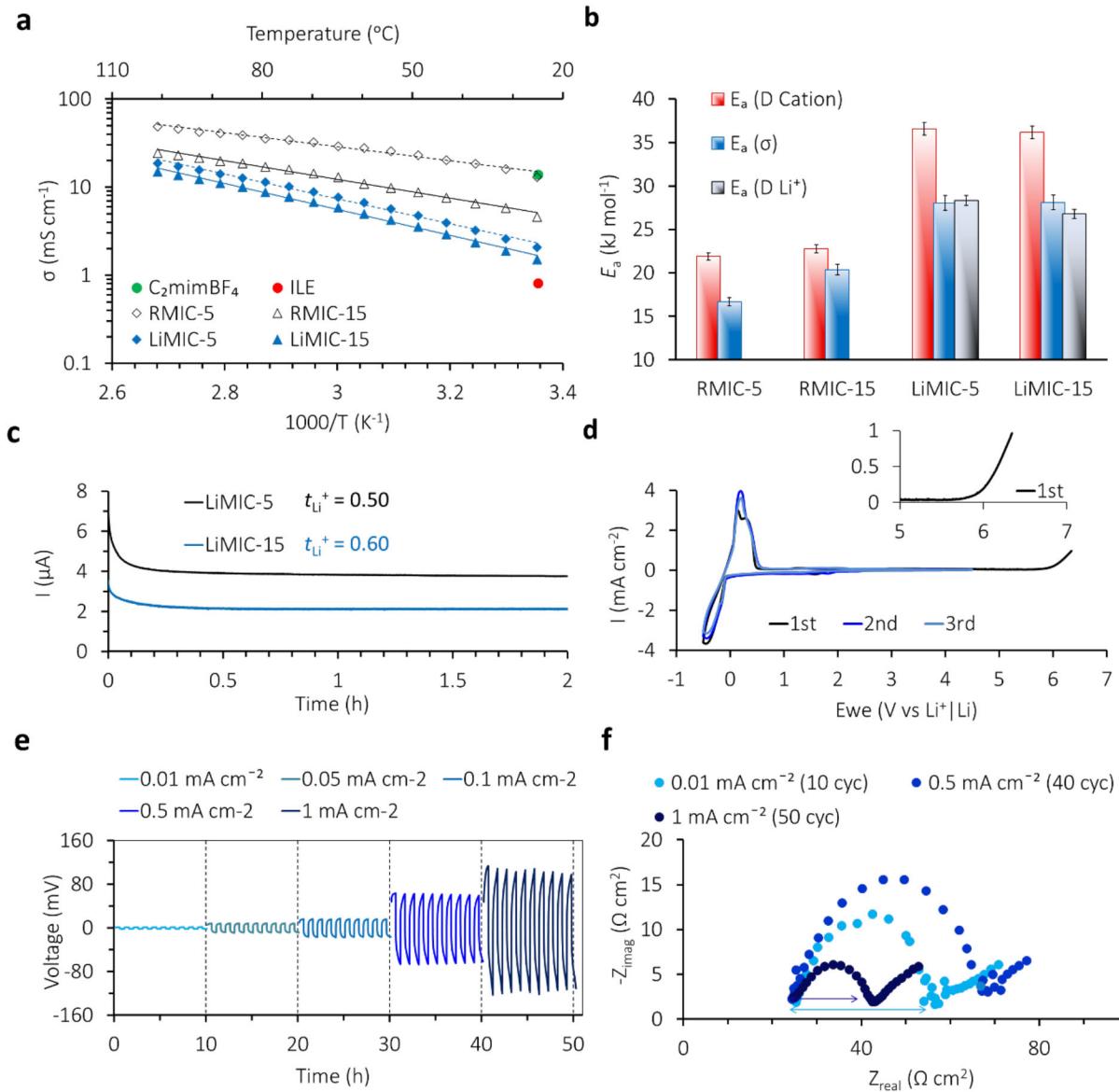
249 **Fig. 4a** shows ionic conductivities of LiMICs and RMICs as a function of temperature. The  
250 exceedingly high  $\sigma$  of LiMIC-5 ( $2.1 \text{ mS} \cdot \text{cm}^{-1}$ ) and LiMIC-15 ( $1.5 \text{ mS} \cdot \text{cm}^{-1}$ ) at  $25^\circ\text{C}$  surpasses that  
251 of state-of-the-art SPEs and even the liquid ILE ( $0.82 \text{ mS} \cdot \text{cm}^{-1}$ ) we used for ion exchange in *Step*  
252 2.<sup>24,32</sup> In terms of transport energy barriers, LiMICs show higher  $E_a(\sigma)$  values compared to RMICs  
253 (**Fig. 4b**), which again indicates a distinct transport mechanism in LiMICs. We notice that  $E_a(\text{Li}^+$ -  
254 NMR) in LiMIC is close to the  $E_a(\sigma)$  obtained from conductivity. This further indicates that the  
255 unexpectedly high conductivity in LiMICs originates from the nanocrystalline conductive network  
256 with an ionic alloy (LiBF<sub>4</sub> and LiFSI) that forms at the boundaries between individual grains. To  
257 supplement this demonstration, we determined the  $t_{\text{Li}^+}$  based on the steady-state current of the Li  
258 symmetric cell assembled with LiMICs as electrolyte and separator in **Fig. 4c**. The corresponding  
259 impedance spectra of the cells before polarization are shown in **Supplementary Fig. 5**. The  
260 calculation details are included in **Supplementary Table 2** and **Equation S3**. The determined  $t_{\text{Li}^+}$   
261 in LiMIC-15 (0.60) is much higher compared to the ILE ( $t_{\text{Li}^+} = 0.18$ ).<sup>32</sup> One can then determine  
262 the fraction of conductivity due to  $\text{Li}^+$  ( $\sigma_{\text{Li}^+} = 1 \text{ mS cm}^{-1}$ ) in LiMICs by multiplying the overall  
263 conductivity by  $t_{\text{Li}^+}$ .

264 We also performed cyclic voltammetry to evaluate the Li plating (negative scan) and stripping  
265 (positive scan) behavior in LiMICs. As shown in the 1<sup>st</sup> cycle in **Fig. 4d**, upon scanning in the  
266 positive direction, the electrolyte shows no significant sign of electrochemical decomposition up  
267 to 5.6 V vs Li|Li<sup>+</sup>. In addition, this electrolyte displays excellent cathodic stability for Li-metal  
268 cycling in the following cycles (2<sup>nd</sup> and 3<sup>rd</sup> cycles). In **Supplementary Fig. 6**, we observe that the

269 columbic efficiency of LiMICs increases with cycle number, whereas the ILE shows diminished  
270 performance, indicating more effective SEI formation on Li-metal anode when using LiMICs.

271 Next, we prepared Li|Li symmetric cells and recorded the voltage response for stepped current  
272 densities ranging from  $0.01 \text{ mA} \cdot \text{cm}^{-2}$  to  $1 \text{ mA} \cdot \text{cm}^{-2}$ . **Fig. 4e** shows the voltage response for LiMIC-  
273 15 electrolytes. We observe that LiMIC-15 exhibits stable cycling and can withstand a current  
274 density ( $J$ ) to  $1 \text{ mA} \cdot \text{cm}^{-2}$ . This represents state-of-the art performance for SPEs or IL-based  
275 electrolyte materials.<sup>5,20</sup> Overpotential is proportional to applied  $J$  (**Supplementary Fig. 7**), which  
276 follows the Butler-Volmer equation, thus avoiding the possibility of soft shorts.<sup>5,33</sup>

277 The LMIC electrolyte prepared with the ILE containing the highest concentration of LiFSI ( $3.2 \text{ mol kg}^{-1}$ ) shows the most stable cycling performance (**Supplementary Fig. 8** and **Supplementary**  
278 **Table 3**).<sup>32,33</sup> EIS spectra shown in **Fig. 4f** indicate that the SEI resistance increases over the first  
279 40 cycles, then decreases upon further cycling and reduces below that of the initial state at 50  
280 cycles. This is generally associated with an improving SEI layer that forms upon cycling and is  
281 commonly observed when cycling Li-metal in this ILE with high salt concentration. Notably, the  
282 interfacial resistance for this LiMIC-15 is unusually small, both before ( $32 \Omega \cdot \text{cm}^{-2}$ ) and after ( $17 \Omega \cdot \text{cm}^{-2}$ )  
283 cycling, compared to other solid-state ion conductors, thereby overcoming the poor  
284 electrolyte-electrode contact between Li-metal anode and solid-ion conductor typically observed  
285 for, e.g.,  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ .<sup>46</sup>



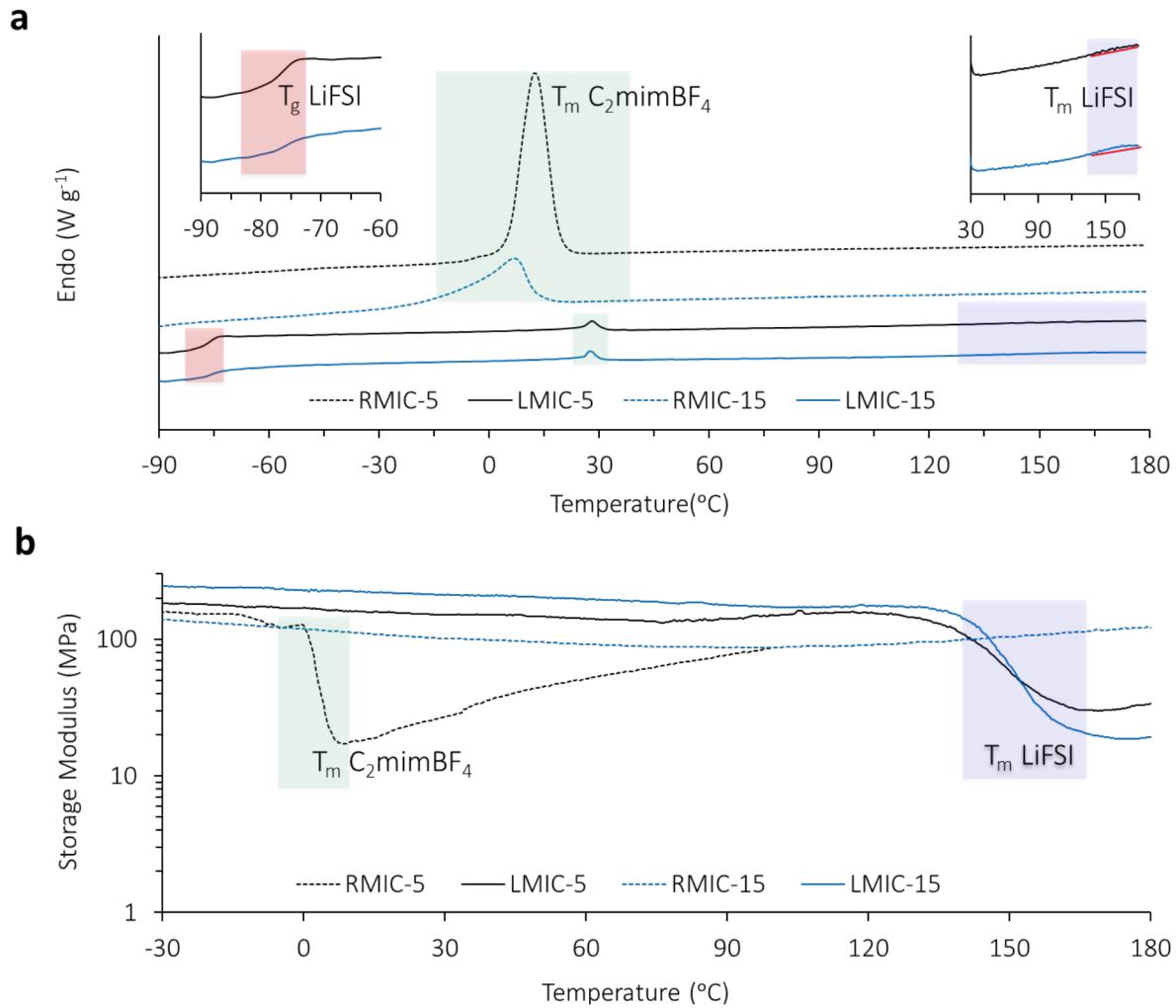
287  
288 **Figure 4. Ionic conductivity, activation energy,  $\text{Li}^+$  transference number, electrochemical**  
289 **window, Li symmetric cell cycling performance, and interfacial charge-transfer resistance**  
290 **in MICs.** (a) Arrhenius plot used to extract activation energies ( $E_a$ ) for ionic conductivity within  
291 RMICs and LiMICs. The green dot shows the conductivity ( $\sigma$ ) of  $\text{C}_2\text{mimBF}_4$  ( $25^\circ\text{C}$ ), used for  
292 developing RMICs. The ionic conductivity value in ILE is indicated with red dots. (b) Comparison  
293 of  $E_a$  values obtained from the conductivity results to  $E_a$  values of cations and  $\text{Li}^+$  based on  
294 Arrhenius fitting of NMR diffusometry. (c) Steady-state current in symmetric  $\text{Li}|\text{Li}$  cell using  
295 LiMICs under  $10 \text{ mV}$  polarization. (d) Cyclic voltammetry curves for Li plating and stripping in  
296 LiMIC-15 at a sweep rate of  $5 \text{ mV s}^{-1}$ . Inset plot shows the enlarged view of the 1st cycle in the  
297 high voltage range. (e) Cell voltage versus time for a symmetric  $\text{Li}|\text{Li}$  cell using LiMIC-15 at

298 current densities ( $J$ ) from 0.01 to 1  $\text{mA}\cdot\text{cm}^{-2}$  (each cycle lasts 1 h) with changes in  $J$  every 10  
299 cycles. (f) Corresponding impedance spectra scanned before variation of  $J$  (10 cycles) for the  
300 LiMIC-15. The frequency range used is 1Hz – 1MHz.

301

302 In addition to the high  $\text{Li}^+$  conductivity achieved by LiMICs, we also performed DSC and  
303 DMA to better understand their thermal and mechanical stability. As shown in **Fig. 5a**, DSC curves  
304 show that  $\text{C}_2\text{mimBF}_4$  has been mostly exchanged or replaced in LiMICs after *Step 2* of ion  
305 exchange. In addition, we observe a glass transition ( $T_g = -75^\circ\text{C}$ ) for LiFSI, which originates from  
306 the LiFSI phase, as reported in this ILE previously.<sup>32,33</sup> The enlarged view on the right displays a  
307 broad melting transition ( $T_m$ ) of LiFSI in LiMICs, consistent with the XRD results showing that  
308 there exists a highly defective LiFSI crystalline phase in LiMICs. However, the  $T_m$  is not obvious,  
309 possibly originating from an endothermic melting process that has been offset by the exothermic  
310 degradation of LiFSI, as reported previously.<sup>47</sup> Meanwhile, we employed DMA to investigate the  
311 mechanical properties of RMICs and LiMICs between  $-50^\circ\text{C}$  to  $180^\circ\text{C}$ , as shown in **Fig. 5b**. We  
312 observe that LiMIC-15 maintains high storage modulus (200 MPa) between  $-50$  to  $140^\circ\text{C}$ , which  
313 then drops above  $140^\circ\text{C}$ , near the  $T_m$  of LiFSI as well as the degradation temperature for FSI.<sup>47</sup>  
314 During the heating process, the LiMIC modulus surpasses all previous state-of-the-art SPEs, which  
315 usually show poor mechanical strength at temperatures beyond the polymer  $T_g$  or  $T_m$ .<sup>48</sup>  
316 Flammability caused by formation of lithium dendrites represents another key obstacle to safe  
317 operation of Li-metal batteries. We included flammability testing results for RMIC in  
318 **Supplementary Fig. 9** and observe that RMICs are stable and cannot be ignited under a  
319 methane/ $\text{O}_2$  flame. Additionally, we carried out nanoindentation experiments to study the  
320 microscopic modulus of the MIC materials (**Supplementary Fig. 10**), where we observe a large

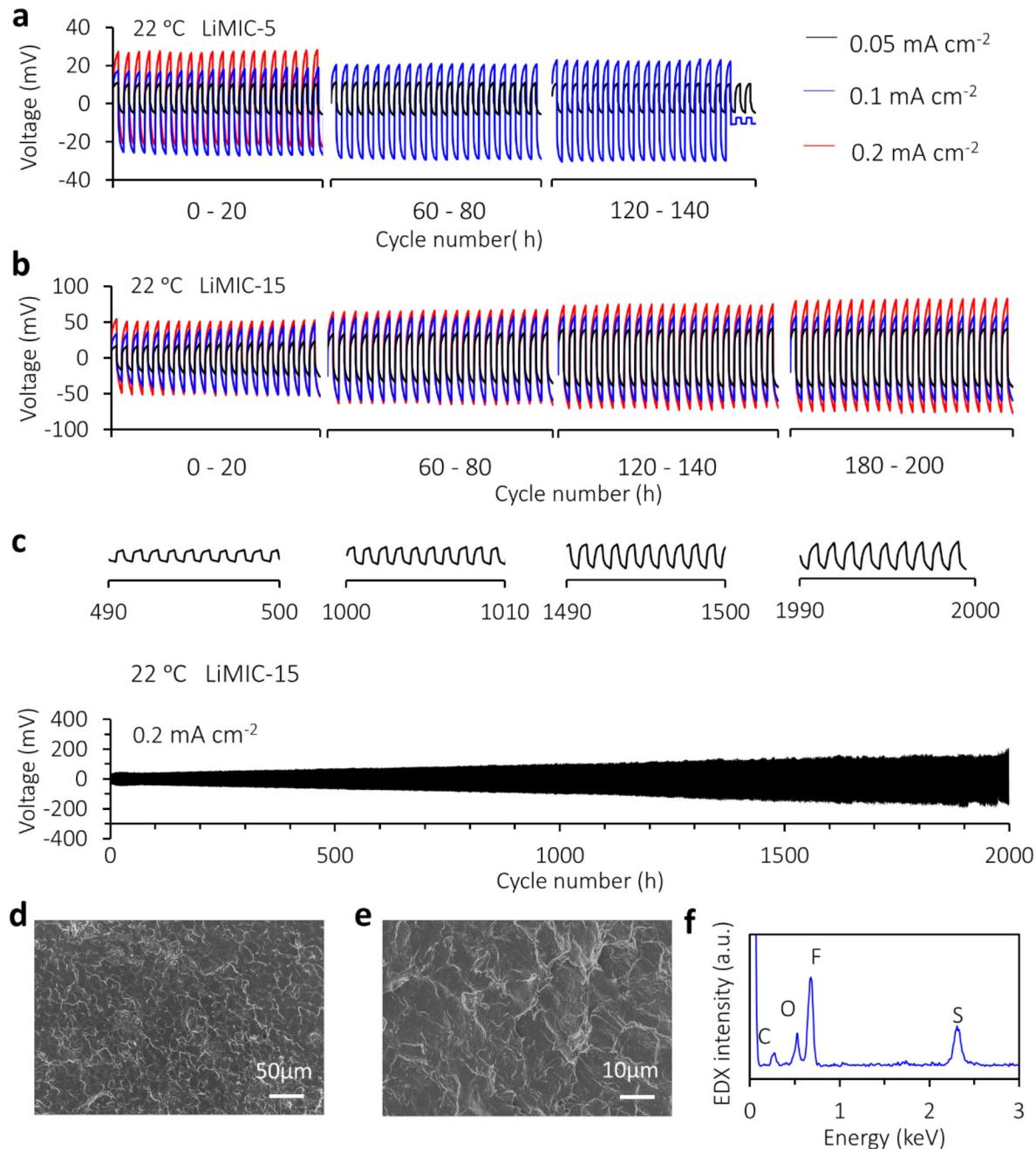
321 distribution of modulus values, reflecting the heterogeneous structure in LiMICs. The median  
 322 values shown in the boxplots indicate high consistency with macroscopic DMA results.



323  
 324 **Figure 5. Thermal and mechanical properties of RMICs and LiMICs.** (a) DSC shows apparent  
 325 differences between LiMICs and RMICs. RMICs display the melting ( $T_m$ ) of IL  $C_2mimBF_4$  at 17  
 326 °C, whereas we only see a slight  $T_m$  peak for  $C_2mimBF_4$  in LiMICs in agreement with the fact that  
 327  $C_2mimBF_4$  has been largely exchanged out. According to peak integration analysis, only < 3% of  
 328  $C_2mimBF_4$  remains in the LiMICs. Notably, we do not observe any apparent melting peaks  
 329 belonging to  $C_3mpyrFSI$  or  $C_3mpyrBF_4$ . The enlarged inset on the left shows the glass transition  
 330 ( $T_g$ ) at -75 °C, which originates from the in-situ formed and defective LiFSI phase. The enlarged  
 331 inset on the right displays the broad melting transition ( $T_m$ ) of LiFSI in LiMICs. The  $T_m$  peak is  
 332 not obvious, likely because of the opposing thermal transition processes of melting and  
 333 degradation of LiFSI. (b) DMA shows the mechanical properties of RMICs and LiMICs from -30

334      °C to 180 °C. RMIC-5 shows a melting drop around the  $T_m$  of C<sub>2</sub>mimBF<sub>4</sub>. LiMICs maintain high  
335      modulus (200 MPa) between -50 to 140 °C then start dropping at 140 °C, which is near both the  
336      melting and degradation temperatures of LiFSI (140 °C).<sup>47</sup>

337      In addition to the cycling results in Fig. 4e, **Fig. 6a-b** shows long-term cycling performance of  
338      the LiMICs as a function of polymer content and current density ( $J$ ). Based on comparison between  
339      LMIC-5 and LiMIC-15 at increasing  $J$ , (0.05, 0.1, 0.2 mA·cm<sup>-2</sup>), we observe that LiMIC-15  
340      (higher polymer content) shows longer cycling stability at all current densities. This suggests that  
341      Li dendrite growth is better suppressed by increasing the rigid polymer content. The discussion of  
342      short circuit behavior observed for LiMIC-5 is included in Note 10 of supplementary information.  
343      **Fig. 6c** demonstrates the cycling stability of LiMIC-15 at  $J = 0.2$  mA·cm<sup>-2</sup>. Here, we observe that  
344      the cell can cycle without short circuit for > 2000 cycles, which corresponds to 2000 h cycling  
345      time and thus removal (and re-plating) of an accumulated total of 1 mm thickness from each Li-  
346      metal electrode. Based on the falciform (curved) potential observed in the charging and  
347      discharging processes shown in the selected cycles across the long period, we do not observe the  
348      unstable voltage profile that typically exists in organic electrolytes at high rates.<sup>32,33</sup> Though  
349      overpotential is increasing, we can expect changes to the SEI layer formed on Li-metal during  
350      cycling, which is stable enough to suppress Li dendrite growth and prevent short-circuit. Post-  
351      cycling SEM of the Li-metal electrode surface (**Fig. 6d, e**) shows a smooth surface devoid of  
352      significant dendrites or ‘mossy’ lithium seen in typical organic electrolyte systems. Peaks from the  
353      breakdown products of the FSI<sup>-</sup> anion can be seen in the EDX spectra (**Fig. 6f**), which are known  
354      to aid in chemically suppressing Li dendrites.<sup>31</sup>



355

356 **Figure 6. Voltage-time profiles for Li|Li symmetric cells incorporating LiMICs at ambient**

357 **temperature.** 1 cycle = 1 h, or 30 min for each charge and discharge. (a) 0.05 mA·cm<sup>-2</sup>, 0.1

358 mA·cm<sup>-2</sup>, 0.2 mA·cm<sup>-2</sup> for LiMIC-5, (b) for LiMIC-15. (c) Long-term cycling of LiMIC-15 at

359 current density of 0.2 mA·cm<sup>-2</sup> with 1 h charge/discharge, insets are profiles for selected cycle

360 numbers in the cycling period. (d, e) SEM images with different magnifications for the

361 disassembled Li-metal electrode after 2000 h long-term cycling in (c) using LiMIC-15 as both

362 electrolyte and separator. (f) EDX spectra of Li-metal surface after long-term cycling.

363 We have described materials development, mechanisms for ion transport, morphological  
364 self-assembly, as well as thermal, mechanical, and electrochemical properties of a new Li-loaded  
365 solid-state electrolyte. This inorganic/organic composite material shows immense potential to  
366 serve as a next-generation electrolyte for a range of electrochemical devices, suited for frontier  
367 battery technologies such as Li-metal, Li-S, or Na-based systems. The fabrication method  
368 described enables generation of non-flammable and highly conductive electrolytes with tunable  
369 modulus and with selectable metal ion type and varying concentrations. In addition to the initial  
370 component IL ( $C_2mimBF_4$ ) described here, we can also fabricate MICs based on different  
371 combinations of ILs and PBDT. **Supplementary Table 4** summarizes the currently accessible  
372 MIC fabrication parameter space. Beyond batteries, MICs represent a modular material platform  
373 into which we can incorporate a wide range of ionic fluids and salts with an adjustable  
374 concentration of the highly charged and rigid double helical PBDT polymer. Such compositional  
375 freedom enables the fabrication of MICs with dramatic variations in chemical, mechanical,  
376 conductive, electrolytic, and thermal properties to enable applications in the next generation of  
377 safe and high-energy-density energy storage devices and beyond.

378 **Methods**

379 *Materials:* Poly 2,2'-disulfonyl-4,4'-benzidine terephthalamide (PBDT) was synthesized by  
380 interfacial condensation polymerization as described previously.<sup>17,49</sup> 1-ethyl-3-methyl  
381 imidazolium tetrafluoroborate ( $C_2mimBF_4$ , purity > 99%) was purchased from Solvent Innovation  
382 GmbH (Cologne, Germany). N-propyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide  
383 ( $C_3mpyrFSI$ , purity > 99.9%) was purchased from Solvionic. Lithium bis(fluorosulfonyl)imide  
384 (LiFSI, purity >99.5%) was sourced from Suzhou Fluolyte Co., Ltd., China. Lithium metal was  
385 sourced from China Energy Lithium Co. Ltd. (purity > 99.9%). IL electrolytes (ILEs) in this paper

386 were prepared by adding the prescribed amount of LiFSI to C<sub>3</sub>mpyrFSI IL at room temperature in  
387 an Ar-filled glove box (< 0 ppm O<sub>2</sub> and < 10 ppm H<sub>2</sub>O).

388 *Preparation of the RMIC:* C<sub>2</sub>mimBF<sub>4</sub> with the same volume as the (Li-counterion) PBDT seed  
389 aqueous solution was slowly pipetted on top of each solution. After 24 hours ion exchange, the  
390 hydrated MIC gel was formed in the bottom polymer solution phase and the residual water/IL  
391 supernatant was poured off. After vacuum drying the initially hydrated RMIC at 80 °C for more  
392 than 24 hours, we obtained the RMIC electrolytes.

393 *Preparation of the Li-loaded MIC:* The RMICs were sliced by hand using a scalpel as thin as  
394 possible, to obtain a thickness of 250  $\mu$ m with a standard deviation of 20%. Performance results  
395 will improve as we decrease/optimize the thickness of the electrolytes in future investigations. The  
396 sliced RMICs were then immersed in the ILEs for > 24 h at room temperature. These operations  
397 were completed in an Ar-filled glove box.

398 *<sup>1</sup>H, <sup>19</sup>F and <sup>7</sup>Li NMR spectroscopy and pulsed-field-gradient (PFG) NMR diffusometry:* A  
399 Bruker Avance III widebore 400 MHz (9.4 T) NMR was equipped with a diff60 pulsed-field-  
400 gradient diffusion probe having a maximum gradient value of 2000 G/cm (at 33 A) along the Z  
401 axis and 5 mm <sup>7</sup>Li and 8 mm <sup>1</sup>H/<sup>19</sup>F rf coils. The PGSTE sequence used a  $\pi/2$  pulse, gradient pulse  
402 duration  $\delta$  of 1 - 2 ms, diffusion times  $\Delta$  of 10 - 50 ms and the number of scans for each step was  
403 adjusted from 16 - 1024 to ensure good signal-to-noise ratio (SNR). 16 gradient steps were applied  
404 for each diffusion experiment. All parameters for the NMR diffusometry experiments have been  
405 calibrated and optimized as reported earlier.<sup>50</sup> Solid-state NMR analysis was performed for  
406 chemical identification of various samples. The LiMIC samples were prepared in glove box and  
407 flame sealed without breaking vacuum in a 5 mm NMR tube to a length of 3 cm filling the coil  
408 region of the probe completely. Water content of the samples were examined using <sup>1</sup>H NMR to

409 ensure the samples were dry as shown in **Supplementary Fig. 11**. For solid-state NMR, a Bruker  
410 Avance III widebore 400 MHz (9.4 T) NMR was equipped with a static High Power HX SSNMR  
411 Probe to allow for short high-power excitation pluses to ensure a wide spectral excitation  
412 bandwidth. For <sup>19</sup>F spectra a single pulse with a 1.1  $\mu$ s duration at 200 W was used to achieve a  
413 tilt angle of 50°. <sup>19</sup>F spectra were collected using an acquisition time of 0.0204 s, relaxation delay  
414 of 4 s, pre-scan delay of 10  $\mu$ s, and 64 scans. For the <sup>7</sup>Li spectra a single pulse with a 2.8  $\mu$ s  
415 duration at 200 W was used to achieve a tilt angle of 90°. <sup>7</sup>Li spectra were collected using an  
416 acquisition time of 0.0198 s, relaxation delay of 10 s, pre-scan delay of 10  $\mu$ s, and 128 scans. All  
417 parameters for the solid-state experiments have been calibrated and optimized to ensure integration  
418 values of all spectra are precise. All solid-state NMR spectra were conducted at 25 °C.

419 *X-ray diffraction (XRD)*: XRD experiments were carried out on a Rigaku Oxford Diffraction  
420 Xcalibur Nova Single-Crystal Diffractometer equipped with an Onyx CCD detector and a Cu  
421 microsource operating at 49.5 kV and 80 mA at room temperature. The RMIC was sliced to a  
422 thickness ~ 1 mm and mounted on the edge of a steel pin, such that the gel extended above the  
423 steel pin and into the X-ray beam. The sample-to-detector distance was 50 mm, giving data at  
424 scattering angle  $2\theta$  from 5° to 42°. The sample was rotated 2° along the  $\phi$  direction. For each sample,  
425 a total of 6 images each with 30 s exposure time was collected and summed to increase signal-to-  
426 noise ratio. The software CrysAlisPro (v1.171.37.35, Rigaku Oxford Diffraction, 2015, Rigaku  
427 Corporation, Oxford, UK) was used for data collection and analysis.

428 *Cyclic voltammetry*: A stainless steel working electrode and a Li-metal foil counter electrode  
429 were employed for cyclic voltammetry. The CV measurements were performed against Li|Li<sup>+</sup>  
430 redox potential.<sup>33</sup> All scans were performed at 25°C with 5 mV s<sup>-1</sup> scan rate using a Biologic SP-  
431 200 controlled by EC-Lab (ver. 10.40) software.

432        *Symmetric lithium metal coin cells:* The coin cells were prepared with CR2032 cases with two  
433        3.2 mm (1/8 inch) diameter lithium electrodes in an Ar-filled glove box. The coin cells were used  
434        for impedance spectroscopy and cycling measurements. A VMP3 (BioLogic) system and a Neware  
435        system were used for battery testing.

436        *Ionic conductivity:* The ionic conductivity was measured via dielectric response over a 1 Hz –  
437        1 MHz frequency range (to emphasize the electrode-electrolyte interfacial resistance) at an  
438        amplitude of 20 mV. A temperature scan range 20 °C to 100 °C was selected, and the temperature  
439        was controlled by a Eurotherm 2204 temperature controller. Conductivity of the LiMIC was  
440        extracted using a value of electrical resistance obtained by fitting the data to an equivalent circuit  
441        model using EC-Lab (ver. 10.40) software®. Two heating scans with 10 °C intervals were  
442        conducted, and the data shown in this study were extracted from the second heating scan.

443        *Li Transference Number ( $t_{Li}^+$ ):* The transference number was electrochemically determined by  
444        direct current (DC) polarization. An AC impedance test was firstly performed over a 0.1 Hz to 1  
445        MHz range to obtain a total resistance  $R_{cell}$ . Then the polarization was carried out to obtain a stable  
446        current. Cells were polarized at ambient temperature with a constant potential of 10 mV for 2 h.

447        *Dynamic Mechanical Analysis (DMA):* The mechanical properties of the composites were  
448        investigated at 1Hz frequency using a DMA 8000 (PerkinElmer) from -50 to 200 °C. The sample  
449        preparation was finished in a N<sub>2</sub>-filled glovebox (H<sub>2</sub>O < 100 ppm). The compression mode was  
450        used to determine the storage modulus and loss modules of each electrolyte. The test sample was  
451        first cooled to -50 °C and then heated to 200 °C at a heating rate of 2 °C/min.

452        *Differential scanning calorimetry (DSC):* A Netzsch DSC (214 polyma), calibrated with  
453        cyclohexane, was used to investigate the thermal behaviour of the MICs. The heating and cooling  
454        rate were 10 °C min<sup>-1</sup>. Samples were cooled to -100 °C and then three heating scans were followed.

455 *Nanoindentation* results were measured at room temperature using a hysitron triboindenter.  
456 *Scanning electron microscopy* was performed using a JSM IT 300 series microscope and  
457 energy dispersive X-ray spectroscopy was measured with an Oxford X-Max 50 mm<sup>2</sup> EDX detector.

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595 **Data availability**

596 All data generated and analyzed in this study are included in this published article and its  
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604 **Author contributions**

605 YW designed and executed all major experiments and composed and edited article drafts. XW,  
606 RK, LJ, and MF performed and assisted with electrochemistry and impedance experiments and  
607 contributed written sections and editing to the article. CJZ performed solid-state NMR experiments  
608 and contributed written sections and editing to the article. WHK analyzed the XRD data and  
609 contributed written sections to the article. TJD modified and supplied polymer, conceived  
610 experiments and contributed written sections and editing to the article. LAM conceived ideas,  
611 oversaw experiments, and composed and edited the article.