Supporting Information

A Li⁺ Conductive Metal Organic Framework Electrolyte Boosts the High-Temperature Performance of Dendrite-Free Lithium Batteries

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Experimental Section

Materials: Reagents included Co(NO₃)₂·6H₂O (99.99%, J&K Chemicals, China), anhydrous methanol (99.9%, Aladdin, China), 2-methyl imidazole (99%, J&K Chemicals, China), N-propyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide ([Py13][TFSI], >99%, Shanghai Cheng Jie, China), and lithium bis(trifluoromethylsulfonyl) imide (LiTFSI, >99%, 3M, USA, dried at 80 °C under vacuum for 48 h and subsequently placed in a glove box). Other materials were purchased and used without further purification.

Synthesis: ZIF-67 was prepared by a melt-stirring method. Co(NO₃)₂·6H₂O (8.22 g) and 2-methyl imidazole (18.5 g) were dissolved separately in 400 mL quantities of anhydrous methanol, after which the two solutions were mixed using a peristaltic pump at a flow rate of 100 mL·min⁻¹. During this process, the color of the Co(NO₃)₂·6H₂O solution changed from red to purple. The solution was allowed to sit overnight at room temperature (25 °C) and a purple solid precipitate was obtained. After centrifugation at 5 °C and drying at 60 °C for 24 h, the ZIF-67 was collected. The ionic liquid electrolyte (ILE) was obtained by mixing [Py13][TFSI] with LiTFSI in a glove box. The ILE@MOF electrolytes were prepared by high energy ball milling. In this process, the desired amounts of ZIF-67 and ILE were combined at a 2:3 mass ratio in a zirconia vial and subjected to high energy ball milling for 1 h in an Ar-filled dry box at a rate of 300 r·min⁻¹. The resulting ILE@MOF was rolled into a 50-μm-thick film and cut into free-standing pieces to allow for electrochemical measurements.

Characterization and instruments: The morphologies and microstructural features of the materials were examined using scanning electron microscopy (SEM; FEI Quanta 600). Surface areas were determined by nitrogen gas absorption in conjunction with the Brunauer–Emmett–Teller (BET) method, using an Autosorb-iQ2-MP analyzer. X-Ray powder diffraction (XRD) was performed over the 20 range from 5° to 90° at a scanning rate of 2°·min⁻¹ with an X-ray diffractometer (Rigaku, Japanese), employing Cu-Kα radiation at 40 kV and 40 mA. Thermogravimetric analysis (TGA) was carried out under an Ar flow from ambient to 700 °C at a heating rate of 10 °C·min⁻¹ using a Netzsch TG209F1 analyzer. Fourier Transform
infrared spectroscopy (FTIR) was performed with a Nicolet 6700 FTIR spectrometer over the wavelength range of 400–4000 cm\(^{-1}\) and at a resolution of 4 cm\(^{-1}\). Flammability tests of the ILE@MOF were carried out using an electronic Bunsen burner. In these trials, the ILE@MOF electrolyte was placed in the middle of a Petri dish and heated directly with the Bunsen burner. ESCALAB 250Xi was used to execute XPS. Bruker AV 300 was used to execute solid-state NMR.

**Electrochemical measurements:** The ionic conductivity of the ILE@MOF was measured by electrochemical impedance spectroscopy (CHI660D, China) at various temperatures within the range from -10 to 80 °C and in the frequency range from 10 to 10\(^5\) Hz using an SS/ILE@MOF/SS cell, where SS is stainless steel. The electrochemical anodic stability of the ILE@MOF was assessed by linear sweep voltammetry (LSV) at room temperature, employing a CHI660D workstation at a scan rate of 0.1 mV·s\(^{-1}\) in conjunction with a Li/ILE@MOF/SS cell. The electrochemical cathodic stability of the ILE@MOF was evaluated by acquiring cyclic voltammograms (CV) at a scan rate of 0.1 mV·s\(^{-1}\) using the Li/ILE@MOF/SS cell. Li/ILE@MOF/Li symmetric cells were employed during interface stability trials and Li stripping/plating tests. Li/ILE/Li symmetric cells were used for control experiments, with 1 M LiTFSI as the electrolyte and a Celgard separator. Li metal electrodes were collected after stripping/plating tests and were washed with methyl ethyl carbonate in an Ar-filled glove box prior to SEM analysis.

**Assembly and performance testing of LMBs:** Electrodes were fabricated by mixing 80 wt% electrode material (LiFePO\(_4\), LiNi\(_{0.33}\)Mn\(_{0.33}\)Co\(_{0.33}\)O\(_2\), LiNi\(_{0.8}\)Mn\(_{0.1}\)Co\(_{0.1}\)O\(_2\) or Li\(_4\)Ti\(_5\)O\(_12\)), 10 wt% acetylene black and 10 wt% polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP) to form a viscous slurry that was then cast onto Al foil. The electrodes were heated at 80 °C for 24 h to evaporate the residual solvent then were cut into circular discs with a diameter of 11 mm. The average loading of LiFePO\(_4\) was approximately 4.2 mg·cm\(^{-2}\), corresponding to 0.7 mAh·cm\(^{-2}\) based on the theoretical capacity of LiFePO\(_4\) (170 mAh·g\(^{-1}\)). The average loadings of the LiNi\(_{0.33}\)Mn\(_{0.33}\)Co\(_{0.33}\)O\(_2\), LiNi\(_{0.8}\)Mn\(_{0.1}\)Co\(_{0.1}\)O\(_2\) and Li\(_4\)Ti\(_5\)O\(_12\) were 3.7, approximately 4.0 and 3.9 mg·cm\(^{-2}\). LMBs were prepared in an Ar-filled glove box by placing the electrodes, ILE@MOF and Li metal in a CR2032 button cell to form a cell without any separator. The charge/discharge cycling of LMBs was performed using a Land instrument. The Li/LiFePO\(_4\) cells were discharged between 2.7 and 4.2 V at 0.1 C (1.0 C=170 mA·g\(^{-1}\)) at 60 °C. The Li/LiNi\(_{0.33}\)Mn\(_{0.33}\)Co\(_{0.33}\)O\(_2\) cells were charged/discharged between 2.8 and 4.2 V at 2.0 C (1.0 C=140 mA·g\(^{-1}\)) at 60, 90, 120 and 150 °C. The Li/LiNi\(_{0.8}\)Mn\(_{0.1}\)Co\(_{0.1}\)O\(_2\) cells were charged/discharged between 2.7 and 4.3 V at 2.0 C (1.0 C=150 mA·g\(^{-1}\)) at 150 °C. The Li/Li\(_4\)Ti\(_5\)O\(_12\) cells were charged/discharged between 1.0 and 2.5 V at 1.0 C (1.0 C=170 mA·g\(^{-1}\)) at 150 °C. The Li metal electrode, ILE@MOF electrolyte and cathode electrode were washed with methyl ethyl carbonate and stored in an Ar-filled glove box for SEM analysis. Electrochemical impedance spectroscopy was performed with a CHI660D apparatus at various temperatures. Electrochemical stability data were obtained from CV results acquired with a CHI660D workstation at a scan rate of 0.1 mV·s\(^{-1}\).
Figure S1. XRD pattern of MOF, ILE@MOF electrolyte, and ILE@MOF after wash with acetonitrile to removal of the ILE.

Figure S2. FTIR spectra of MOF, ILE@MOF and ILE.
**Figure S3** $^7$Li NMR spectra for ILE and ILE@MOF.

**Figure S4** a) SEM images of a fresh Li metal. b) SEM images of Li metal surface in the Li/ILE@MOF/Li cell before cycling.
Figure S5  a) Voltage profiles for Li/ILE@MOF/Li cell cycling at a current density of 0.1 mA·cm$^{-2}$ at 60 °C. Each cycle is set to be 10 h. b) Voltage profiles for Li/ILE /Li cell cycling at a current density of 0.1 mA·cm$^{-2}$ at 60 °C. Each cycle is set to be 10 h.

Figure S6 f) SEM morphology for Li anode in Li/ILE /Li cell after 1000 h cycling at 0.1 mA·cm$^{-2}$ at 60 °C.
Figure S7 Voltage profiles for Li/ILE@MOF/Li cell cycling at a current density of 0.5 mA·cm⁻² at 120 °C. Each cycle is set to be 2 h.
Figure S8 a) Co 2P XPS spectra for the thin particles layer of Li metal after 100 h stripping/plating at 150 °C. b) Co 2P XPS spectra of fresh ILE@MOF electrolyte.

Figure S9 Cycle performance of the Li/LiFePO₄ cells using the ILE@MOF electrolyte at 60 °C.
Figure S10 Galvanostatic charge/discharge plots of Li/LiFePO₄ cell using the ILE@MOF electrolyte.

Figure S11 Cyclic voltammograms of the Li/LiFePO₄ cell using ILE@MOF electrolyte.
Figure S12 Cyclic voltammograms of the Li/LiNi$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$ cell using ILE@MOF electrolyte.

Figure S13 Electrochemical impedance spectra (EIS) of Li/LiNi$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$ cell using ILE@MOF electrolyte at 60, 90, 120, and 150 °C.
Figure S14 SEM images of LiNi_{0.33}Mn_{0.33}Co_{0.33}O_{2} electrode surface after initial discharged at a) 90 °C and b) 120 °C.

Figure S15 SEM images of dense MOF on the surface of cycled LiNi_{0.33}Mn_{0.33}Co_{0.33}O_{2} electrode.

Figure S16 The voltage profiles of Li/ILE@MOF/Li_{4}Ti_{5}O_{12} cell at rate of 0.1 C and at room temperature.
Figure S17 Cycling performances of Li/Li$_4$Ti$_5$O$_{12}$ cell using the ILE@MOF electrolyte at a current density of 1.0 C at 150 °C.
The BET result revealed that the specific surface of MOF is 1352.1974 m$^2$/g, and the specific surface of ILE@MOF decreases from 1791.88 m$^2$/g to 5.26 m$^2$/g by introducing of ILE.

Table S2 Summarized the fundamental security information of different electrolytes

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Thermal stability</th>
<th>Electrode</th>
<th>Test temperature</th>
<th>Cycle performance (mAh·g$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ILE@MOF</td>
<td>325 °C</td>
<td>LiNi$<em>{0.33}$Mn$</em>{0.33}$Co$_{0.33}$O$_2$</td>
<td>150 °C, 150 °C, 150 °C</td>
<td>143.5 at 2.0 C, 137.3 at 2.0 C, ~165 at 1.0 C</td>
<td>Our work</td>
</tr>
<tr>
<td>Liquid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1M LiPF$_6$-EC/EMC/DMC</td>
<td>40 °C</td>
<td>LiNi$<em>{0.33}$Mn$</em>{0.33}$Co$_{0.33}$O$_2$</td>
<td>25 °C</td>
<td>190 at 0.1 C</td>
<td>[2]</td>
</tr>
<tr>
<td>LiTFSI/[EMIm][FSI]</td>
<td>220 °C</td>
<td>LiNi$<em>{0.33}$Mn$</em>{0.33}$Co$_{0.33}$O$_2$</td>
<td>RT</td>
<td>163 at 1.0 C</td>
<td>[3]</td>
</tr>
<tr>
<td>1M LiPF$_6$-EC/DMC/EMC+PP13TFSI</td>
<td>100 °C</td>
<td>LiNi$<em>{0.33}$Mn$</em>{0.33}$Co$_{0.33}$O$_2$</td>
<td>RT</td>
<td>230 at 0.1 C</td>
<td>[4]</td>
</tr>
<tr>
<td>LiTFSI-EC/DMC+[Py14][TFSI]</td>
<td>100 °C</td>
<td>LiFePO$_4$</td>
<td>RT</td>
<td>150 at 0.1 C</td>
<td>[5]</td>
</tr>
<tr>
<td>Ionogel</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>h-BN/[PP13][TFSI]/LiTFSI</td>
<td>-</td>
<td>Li$_4$Ti$_3$O$_12$</td>
<td>150 °C</td>
<td>~145 at 0.5 C</td>
<td>[6]</td>
</tr>
<tr>
<td>Clay/[PP13][TFSI]/LiTFSI</td>
<td>370 °C</td>
<td>Li$_4$Ti$_3$O$_12$</td>
<td>120 °C</td>
<td>~60 at 1/3 C</td>
<td>[7]</td>
</tr>
<tr>
<td>SiO$_2$/[BMI][TFSI]/LiTFSI</td>
<td>390 °C</td>
<td>LiNi$<em>{0.33}$Mn$</em>{0.33}$Co$_{0.33}$O$_2$</td>
<td>30 °C</td>
<td>~149 at 0.1 C</td>
<td>[8]</td>
</tr>
<tr>
<td>TiO$_2$/[Py13][TFSI]/LiTFSI</td>
<td>375 °C</td>
<td>LiNi$<em>{0.33}$Mn$</em>{0.33}$Co$_{0.33}$O$_2$</td>
<td>RT</td>
<td>120 at 0.1 C</td>
<td>[9]</td>
</tr>
<tr>
<td>SiO$_2$-PP-TFSI/PC/1M LiTFSI</td>
<td>250 °C</td>
<td>Li$_4$Ti$_3$O$_12$</td>
<td>RT</td>
<td>130 at 1.0 C</td>
<td>[10]</td>
</tr>
<tr>
<td>Gel polymer</td>
<td></td>
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<tr>
<td>PVdF/(VC-VAc)-1M LiPF$_6$-EC/EMC/DMC</td>
<td>240 °C</td>
<td>LiNi$<em>{0.33}$Mn$</em>{1.5}$O$_4$</td>
<td>RT</td>
<td>127 at 0.5 C</td>
<td>[11]</td>
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<tr>
<td>PEO–LiTFSI–EMIMTFSI</td>
<td>310 °C</td>
<td>LiMn$_2$O$_4$</td>
<td>RT</td>
<td>120 at 0.1 C</td>
<td>[12]</td>
</tr>
<tr>
<td>LiTFSI-[PP14][TFSI]–P(VdF-HFP)</td>
<td>150 °C</td>
<td>LiFePO$_4$</td>
<td>60 °C</td>
<td>131 at 1.0 C</td>
<td>[13]</td>
</tr>
</tbody>
</table>

RT: Room Temperature
References


