Supporting Information

A highly concentrated phosphate-based electrolyte for high-safety rechargeable lithium batteries

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Experimental

Preparation of the electrolyte and the electrodes

The highly concentrated electrolyte was prepared by mixing 5 M LiFSI (Guotai Super Power Co., LTD.) with TMP (Energy Chemical Co., LTD.) in an Ar-filled glove box (MBraun) with both the O₂ and H₂O contents below 0.1 ppm. For comparison, a conventional electrolyte of 1 M Li hexafluorophosphate (LiPF₆)/ethylene carbonate (EC)-diethyl carbonate (DEC) (1:1, w/w) (Capchem Technology Co., LTD) was used as the control electrolyte.

LiNi₁/₃Co₁/₃Mn₁/₃O₂ or LiFePO₄ positive electrodes are composed of 84 wt.% active material (LiNi₁/₃Co₁/₃Mn₁/₃O₂ or LiFePO₄, Guoxuan High-tech Power Energy Co., Ltd.), 8 wt.% Super-P (TIMCAL) conductive additive and 8 wt% polyvinylidene fluoride (PVDF, Solvey HSV900) on an Al current collector. Graphite negative electrodes are composed of 90 wt.% graphite powder (Shanshan Co., LTD.), 3 wt.% Super-P and 7 wt.% PVDF on a copper current collector. All electrodes were punched into discs (Φ14 mm) for coin-cell assembly. The mass loadings of positive electrode (LiNi₁/₃Co₁/₃Mn₁/₃O₂ or LiFePO₄) and graphite negative electrode were controlled at ~5.0 and ~2.4 mg cm⁻², respectively.

Electrochemical measurements

Electrochemical performance of the highly concentrated electrolyte was tested on a Neware BTS2300 battery cycler (Shenzhen, China) by using 2032-type coin cells, along with the control electrolyte of 1 M LiPF₆/EC-DEC (1:1, w/w) for comparison. The homemade SiO₂-coated polyethylene microporous membrane was used as a separator.[1] The Li|LiNi₁/₃Co₁/₃Mn₁/₃O₂, graphite|LiNi₁/₃Co₁/₃Mn₁/₃O₂ and Li|LiFePO₄ cells were all cycled between 2.5 and 4.2 V. The Li|graphite cells were tested at 0.05 C between 1.2 and 0.005 V.

Material Characterizations

The flammability tests were conducted by igniting a cotton ball (0.5 g) that had absorbed about 0.5 g electrolyte of the control electrolyte or highly concentrated electrolyte of 5 M LiFSI/TMP. The conductivity of various electrolytes were tested by
conductivity meter (DDS 307A). The Li\(^+\) transference number (\(t_{\text{Li}^+}\)) of the highly concentrated 5 M LiFSI/TMP electrolyte was also measured by dc-polarization and ac-impedance spectroscopic analysis in a symmetric Li|Li cell.\(^2\) The \(t_{\text{Li}^+}\) is calculated by following equation:

\[
t_{\text{Li}^+} = \frac{I_{\text{ss}}(\Delta V - I_0 R_0)}{I_0(\Delta V - I_{\text{ss}} R_{\text{ss}})}
\]

where \(I_{\text{ss}}\) is the steady-state current, \(I_0\) the initial current, \(\Delta V\) is the applied potential of 0.05V, \(R_{\text{ss}}\) and \(R_0\) the electrode resistances after and before the polarization, respectively. Solvation structures of the various concentration LiFSI/TMP electrolytes were measured by Raman (HR Evolution) employing a 10 mW helium/neon laser with a wavelength of 532.8 nm. Linear sweep voltammetry (LSV) of Li|Al cells with various LiFSI/TMP electrolytes were performed on a CHI 604 electrochemical workstation (Shanghai Chenhua). Electrochemical impedance spectroscopy (EIS) of Li|Li\(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2\) and Li|Li\(\text{FePO}_4\) cells were also measured on the electrochemical workstation above, with a frequency range from 100 kHz to 0.1 Hz. Cycled Li anodes obtained from Li|Li\(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2\) cells were used for various characterizations. Before the measurements, the Li electrodes were immersed in fresh DMC for 20 h and then rinsed with fresh DMC three times to remove the reserved Li salts before drying under vacuum. The morphologies of the Li electrodes were observed by field-emission scanning electron microscopy (FE-SEM, Germany Zeiss). Chemical compositions of the solid electrolyte interphase (SEI) formed in various electrolytes were measured by X-ray diffraction (XRD, D/MAX2500 V, Cu K\(_\alpha\) radiation) and X-ray photoelectron spectroscopy (XPS, America Thermo ESCALAB250).
**Table S1** Ionic conductivities of various electrolytes

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Conductivity (mS cm(^{-1}))</th>
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<tbody>
<tr>
<td>1 M LiPF(_6)/EC-DEC</td>
<td>6.8</td>
</tr>
<tr>
<td>1 M LiFSI/TMP</td>
<td>6.4</td>
</tr>
<tr>
<td>3 M LiFSI/TMP</td>
<td>1.9</td>
</tr>
<tr>
<td>5 M LiFSI/TMP</td>
<td>0.9</td>
</tr>
</tbody>
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![Figure S1](image)

**Fig. S1.** (a) Chronoamperometries of symmetric Li|Li cell at a potential step of 0.05V, (b) EIS spectra of the same cell before and after polarization.
Fig. S2. Schematic illustration of the solvation structure in the dilute and highly concentrated electrolytes.

Fig. S3. Initial discharge-charge curves of graphite|Li cells with various electrolytes at 0.05 C.
Fig. S4. (a) Oxidation stability of various LiFSI/TMP electrolytes on Al electrode measured by LSV at a scan rate of 0.2 mV s\(^{-1}\). SEM images of (b) pristine Al current collector, (c) Al foil after LSV measurements in the dilute electrolyte of 1 M LiFSI/TMP, and (d) Al foil after LSV measurements in the highly concentrated electrolyte of 5 M LiFSI/TMP.

Fig. S5. Performances of the Li||LiNi\(_{1/3}\)Co\(_{1/3}\)Mn\(_{1/3}\)O\(_2\) cells in 1 M LiPF\(_6\)/EC-DEC and 5 M LiFSI/TMP electrolytes (a) dQ/dV curves; (b) EIS curves after 100 cycles.
Fig. S6. Electrochemical performances of the Li||LiFePO_4 cell cycled in 1 M LiPF_6/EC-DEC and 5 M LiFSI/TMP electrolytes (a) Initial charge and discharge curves; (b) Cycling performance. The cells were cycled at 1C for 400 cycles after 2 formation cycles at 0.1C; (c) EIS plots of cells after 400 cycles; (d) Rate performance from 0.1 to 12 C.

Fig. S7. XRD patterns of the interphase layers on the Li metal electrode obtained from Li||LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2 cells after 100 cycles.
Fig. S8. XPS spectra of the SEI formed in various electrolytes (a) wide scans and (b) the corresponding element ratios in the SEI layer

Reference