Energy Materials
Low-concentrated sulfone electrolyte enables high-voltage chemistry of lithium-ion batteries

Manuscript ID: EM-2022-38
Manuscript Title: Low-concentrated sulfone electrolyte enables high-voltage chemistry of lithium-ion batteries
Manuscript Type: Article
Special Issue:
Keywords: Electrolyte, sulfone, fluorobenzene, interphase, lithium-ion battery
Corresponding Author(s): Xiulin Fan
Corresponding Author' Email: xlfan@zju.edu.cn
Corresponding Author's Department: State Key Laboratory of Silicon Materials, School of Materials Science and Engineering
Corresponding Author's Institution: Zhejiang University
Country/Region: China
Order of Author (Only first three authors will be listed):
1. Ling Lv
2. Haikuo Zhang

Abstract: Commercial carbonate electrolytes with poor oxidation stability and high flammability limit the operation voltage of Li-ion batteries (LIBs) up to \( \sim 4.3 \) V. As one of the most promising candidates for electrolyte solvents, sulfolane (SL) has received great interest because of its wide electrochemical window, low flammability and high dielectric permittivity. Unfortunately, SL-based electrolytes with normal concentration cannot achieve highly reversible Li+ intercalation/de-intercalation in graphite anode due to an ineffective solid electrolyte interface (SEI), thus undermining its application in LIBs. Here, a low-concentrated SL-based electrolyte (LSLE) was developed for the high-voltage graphite||LiNi0.8Co0.1Mn0.1O2 (NCM811) full-cells. The highly reversible graphite anode can be achieved through the preferential decomposition of dual-salt LiDFOB-LiBF4 in LSLE. The addition of fluorobenzene (FB) further restrains the
decomposition of SL, endowing uniform, robust and inorganic-rich interphases on the surface of electrodes. As a result, the LSLE with improved thermal stability can support the MCMB||NCM811 full-cells at 4.4 V, evidenced by an excellent cycling performance with capacity retentions of 83% after 500 cycles at 25 °C and 82% after 400 cycles at 60 °C. We believe that the design of FB-containing LSLE offers an effective routine for next-generation low-cost and safe electrolytes of high-voltage LIBs.

Funding Agency and Grant Number:
Supplementary Material

Low-concentrated sulfone electrolyte enables high-voltage chemistry of lithium-ion batteries

Ling Lv\textsuperscript{a}, Haikuo Zhang\textsuperscript{a}, Di Lu\textsuperscript{a}, Yuan Yu\textsuperscript{b*}, Jiacheng Qi\textsuperscript{a}, Junbo Zhang\textsuperscript{a}, Shuoqing Zhang\textsuperscript{a}, Ruhong Li\textsuperscript{a}, Tao Deng\textsuperscript{c}, Lixin Chen\textsuperscript{a,d} and Xiulin Fan\textsuperscript{a*}

\textsuperscript{a}State Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China. Email: xlfan@zju.edu.cn
\textsuperscript{b}Zhejiang Provincial Key Laboratory of Fiber Materials and Manufacturing Technology, Zhejiang Sci-Tech University, Hangzhou 310018, China. Email: yuyu@zstu.edu.cn
\textsuperscript{c}Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, MD, USA.
\textsuperscript{d}Key Laboratory of Advanced Materials and Applications for Batteries of Zhejiang Province, Hangzhou 310013, China
**Supplementary Table 1.** Surface resistance ($R_{SEI}$), charge transfer resistance ($R_{ct}$) and interfacial resistance ($R_i$) of MCMB||NCM811 full-cells using different electrolytes corresponding to the EIS data of fitting equivalent circuit in Figure S8.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$R_{SEI}$ (Ohm)</th>
<th>$R_{ct}$ (Ohm)</th>
<th>$R_i$ (Ohm)</th>
<th>Cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10th</td>
</tr>
<tr>
<td>LiDFOB-LiBF₄/SL-FB</td>
<td>39.4</td>
<td>262.4</td>
<td>301.8</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>101.9</td>
<td>103.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.3</td>
<td>0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiDFOB-LiBF₄/SL</td>
<td>24.3</td>
<td>248.1</td>
<td>272.4</td>
<td>111.2</td>
</tr>
<tr>
<td></td>
<td>1.3</td>
<td>1.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BE</td>
<td>303.6</td>
<td>341.4</td>
<td></td>
<td>134.7</td>
</tr>
<tr>
<td></td>
<td>135.9</td>
<td>145.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure S1. Density of states (DOS) obtained in quantum mechanical DFT-AIMD simulations of LiDFOB-LiBF$_4$/SL.
Figure S2. AIMD simulation results of LiDFOB-LiBF₄/SL electrolyte. (A) AIMD simulation snapshots of LiDFOB-LiBF₄/SL. (B) Radical distribution functions calculated from AIMD simulation of LiDFOB-LiBF₄/SL electrolyte.
Figure S3. Schematic diagram of reaction at LiDFOB-LiBF₄/SL electrolyte /graphite interphase.
Figure S4. Wettability of LiDFOB-LiBF₄/SL (left) and LiDFOB-LiBF₄/SL-FB (right) toward polyethylene (PE) separator.
**Figure S5.** Cycling performance and Coulombic efficiency versus cycle number of Li||MCMB half-cells with various electrolytes at a constant rate (0.1C) between 0.005 V to 1.5 V.
Figure S6. Voltage profiles of MCMB||NCM811 full-cells with BE (A), LiDFOB-LiBF₄/SL (B), and LiDFOB-LiBF₄/SL-FB (C) at a constant rate (0.5C) between 2.8 V to 4.4 V at 25 ℃.
Figure S7. Discharge curves of MCMB||NMC811 full-cells using BE (A), LiDFOB-LiBF₄/SL (B), and LiDFOB-LiBF₄/SL-FB (C) under varying discharge rates (xC).
Figure S8. Electrochemical impedance spectra (EIS) measurements of MCMB||NCM811 full-cells after 10 cycles (A) and 50 cycles (B) with different electrolytes. The solid lines represent the fits results using an equivalent circuit shown in the Figure S8A.
**Figure S9.** H-transfer reaction from DMC/DMC (-H) to the delithiated NCM811 (003) cathode surface from periodic DFT calculations.
Figure S10. XRD patterns of uncycled pristine NCM811 cathode and cycled NCM811 cathodes recovered from MCMB||NCM811 full-cells after 50 cycles with different electrolytes.
Figure S11. Typical SEM images of uncycled NCM811 electrode (A) and cycled NCM811 electrodes recovered from NCM811/MCMB full-cells after 50 cycles with BE (B), LiDFOB-LiBF$_4$/SL (C) and LiDFOB-LiBF$_4$/SL-FB (D), respectively.
Figure S12. XPS C 1s, P 2p spectra for NCM811 cathodes recovered form MCMB||NCM811 full-cells after 50 cycles with various electrolytes.
Figure S13. XRD patterns ((002) diffraction peak) of uncycled pristine MCMB anode and cycled MCMB anodes recovered form MCMB||NCM811 full-cells after 50 cycles with different electrolytes.
Figure S14. Typical SEM images of uncycled MCMB electrode (A) and cycled MCMB electrodes recovered from MCMB||NCM811 full-cells after 50 cycles with BE (B), LiDFOB-LiBF$_4$/SL (C) and LiDFOB-LiBF$_4$/SL-FB (D), respectively.
Figure S15. XPS C 1s, P 2p spectra for NCM811 cathodes recovered from MCMB||NCM811 full-cells after 50 cycles with various electrolytes.
Figure S16. Voltage profiles of MCMB||NCM811 full-cells with BE (A), LiDFOB-LiBF₄/SL (B), and LiDFOB-LiBF₄/SL-FB (C) at a constant rate (0.5C) between 2.8 V to 4.3 V at 60 °C.