Effects of LiBOB on Salt Solubility and BiF₃ Electrode Electrochemical Properties in Fluoride Shuttle Batteries

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Supporting information

Table S1 Reference solutions prepared using tetraglyme (G4) and lithium bis(oxalato)borate (LiBOB)

<table>
<thead>
<tr>
<th>Code</th>
<th>LiBOB (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBOB₀.₀₆/G₄</td>
<td>0.06 (1 wt%)</td>
</tr>
<tr>
<td>LiBOB₀.₂₅/G₄</td>
<td>0.25 (4.4 wt%)</td>
</tr>
<tr>
<td>LiBOB₀.₅/G₄</td>
<td>0.5 (9 wt%)</td>
</tr>
</tbody>
</table>

Fig. S1 X-ray diffraction patterns of BiF₃/C in the pristine state; * represents the peak related to the pocket.
Fig. S2 Temperature and concentration dependence of the ionic conductivity for the (a) LiBOB\textsubscript{0.06}/CsF/G4 and (b) LiBOB\textsubscript{0.06}/G4 electrolyte solutions (LiBOB: lithium bis(oxalato)borate; G4: tetraglyme; n: LiBOB molar concentration).

Table S2 Comparison between the temperature dependence of the conductivity of the LiBOB\textsubscript{0.06}/CsF/G4 and LiBOB\textsubscript{0.06}/G4 solutions (LiBOB: lithium bis(oxalato)borate; G4: tetraglyme, Ea: Activation Energy)

<table>
<thead>
<tr>
<th></th>
<th>25°C</th>
<th>35°C</th>
<th>45°C</th>
<th>55°C</th>
<th>Ea (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBOB\textsubscript{0.06}/G4</td>
<td>3.98 x 10^{-4}</td>
<td>4.65 x 10^{-4}</td>
<td>5.08 x 10^{-4}</td>
<td>5.87 x 10^{-4}</td>
<td>15.6</td>
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<tr>
<td>LiBOB\textsubscript{0.06}/CsF/G4</td>
<td>3.64 x 10^{-4}</td>
<td>4.21 x 10^{-4}</td>
<td>4.57 x 10^{-4}</td>
<td>5.37 x 10^{-4}</td>
<td>16.18</td>
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<tr>
<td>LiBOB\textsubscript{0.25}/G4</td>
<td>1.28 x 10^{-3}</td>
<td>1.57 x 10^{-3}</td>
<td>1.88 x 10^{-3}</td>
<td>2.19 x 10^{-3}</td>
<td>14.32</td>
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<tr>
<td>LiBOB\textsubscript{0.25}/CsF/G4</td>
<td>1.31 x 10^{-3}</td>
<td>1.63 x 10^{-3}</td>
<td>1.95 x 10^{-3}</td>
<td>2.28 x 10^{-3}</td>
<td>14.7</td>
</tr>
<tr>
<td>LiBOB\textsubscript{0.5}/G4</td>
<td>2.24 x 10^{-3}</td>
<td>2.81 x 10^{-3}</td>
<td>3.43 x 10^{-3}</td>
<td>4.00 x 10^{-3}</td>
<td>10.21</td>
</tr>
<tr>
<td>LiBOB\textsubscript{0.5}/CsF/G4</td>
<td>2.27 x 10^{-3}</td>
<td>2.86 x 10^{-3}</td>
<td>3.49 x 10^{-3}</td>
<td>4.17 x 10^{-3}</td>
<td>10.15</td>
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</table>

Fig. S3 Raman spectra of LiBOB\textsubscript{0.25}/CsF/G4, LiBOB\textsubscript{0.5}/CsF/G4, LiBOB\textsubscript{0.25}/G4, LiBOB\textsubscript{0.5}/G4, and pure G4 in the of 200–3800 cm\textsuperscript{-1} region (LiBOB: lithium bis(oxalato)borate; G4: tetraglyme).
Fig. S4 19F NMR spectra of (a) LiBOB_{0.06}/CsF/G4, (b) LiBOB_{0.25}/CsF/G4, and (c) LiBOB_{0.5}/CsF/G4 electrolytes. Chemical shift related to the reference of trifluoroacetic anhydride (TFAA) at −76.5 ppm is shown with an asterisk (*).
Fig. S5 Linear sweep voltammograms of the glassy carbon electrode in LiBOB$_{0.25}$/CsF/G4 (LiBOB: lithium bis(oxalato)borate; G4: tetraglyme) in the potential range from −4.0 to 0.0 V (vs reference electrode) at a scan rate of 1 mV s$^{-1}$.

Table S3 Relation between capacity and cycling number for LiBOB$_{0.25}$/CsF/G4 (LiBOB: lithium bis(oxalato)borate; G4: tetraglyme) at 1/40 C rate

<table>
<thead>
<tr>
<th>Cycle Number</th>
<th>1$^{st}$</th>
<th>2$^{nd}$</th>
<th>3$^{rd}$</th>
<th>4$^{th}$</th>
<th>5$^{th}$</th>
<th>6$^{th}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Discharge capacity (mAh g$^{-1}$)</td>
<td>340</td>
<td>116</td>
<td>93</td>
<td>80</td>
<td>72</td>
<td>70</td>
</tr>
<tr>
<td>Charge capacity (mAh g$^{-1}$)</td>
<td>117</td>
<td>86</td>
<td>75</td>
<td>70</td>
<td>65</td>
<td>70</td>
</tr>
</tbody>
</table>