Supplementary Information

to accompany

Electrochemical and physicochemical properties of small phosphonium cation ionic liquid electrolytes with high lithium salt content

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1 Preparation of trimethyl(isobutyl)phosphonium bis(fluorosulfonyl)imide (P$_{1114}$FSI)

Isobutylphosphine (CYTOP®141, Cytec Industries) was reacted with trimethyl phosphate (>3 mol) at a temperature 110-130 °C using the process described in US patent 7,829,744 B2. The trimethyl(isobutyl)phosphonium dimethylphosphate intermediate was further reacted with 1.05 equivalents of potassium bis(fluorosulfonyl)imide (KFSI) in the presence of dichloromethane. The organic phase was treated with saturated NaHCO$_3$ in water followed by additional washes with H$_2$O, hexanes, and a number of washes with deionized H$_2$O and checked for the presence of any residual halide with the use of AgNO$_3$ in water. After removal of the volatiles on the Rotovap, the resulting product was additionally purified using short-path evaporator. Its structure was confirmed by $^1$H, $^{13}$C, $^{19}$F and $^{31}$P NMR analyses (deuterated acetone ((CD$_3$)$_2$CO)).

2 Nuclear Magnetic Resonance spectra of P$_{1114}$FSI

Figure S3 $^{31}$P NMR spectrum of P$_{1114}$FSI
Figure S4 $^{19}$F NMR spectrum of $P_{11114}$FSI

Figure S5 $^1$H NMR spectrum of $P_{11114}$FSI
Figure S6 $^{13}\text{C}$ NMR spectrum of P$_{1114}$FSI
3 Electrospray mass spectra of $P_{11i4}FSI$

Figure S7 Mass spectra of $P_{11i4}FSI$

4 Transport properties – VTF parameters

(a) (b)

Figure S1 VTF plots of ionic conductivity (a) and dynamic viscosity (b) for $P_{11i4}FSI$ electrolytes and various concentrations of LiFSI
$$\sigma = \sigma_0 \exp\left\{ \frac{-B}{T - T_0} \right\}$$

<table>
<thead>
<tr>
<th>LiFSI concentration</th>
<th>Molar ratio Li⁺: P⁺</th>
<th>Ln $\sigma_0$ / mS.cm⁻¹</th>
<th>B (K)</th>
<th>$T_0$(K)</th>
<th>R (correlation coefficient)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>0.19:0.31</td>
<td>6.36±0.09</td>
<td>791±24</td>
<td>160±2</td>
<td>0.9999</td>
</tr>
<tr>
<td>3.2</td>
<td>0.25:0.25</td>
<td>6.07±0.02</td>
<td>768±5</td>
<td>173±0.3</td>
<td>0.9999</td>
</tr>
<tr>
<td>3.8</td>
<td>0.27:0.23</td>
<td>6.35±0.04</td>
<td>844±8</td>
<td>171±0.5</td>
<td>0.9999</td>
</tr>
</tbody>
</table>

$$\eta = \eta_0 \exp\left\{ \frac{-B}{T - T_0} \right\}$$

<table>
<thead>
<tr>
<th>LiFSI concentration</th>
<th>Molar ratio Li⁺: P⁺</th>
<th>Ln $\eta_0$ / P⁻</th>
<th>B (K)</th>
<th>$T_0$(K)</th>
<th>R (correlation coefficient)</th>
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</thead>
<tbody>
<tr>
<td>2.0</td>
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<td>-4.84±0.38</td>
<td>589±100</td>
<td>188±11</td>
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<td>3.2</td>
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<td>-5.69±0.39</td>
<td>863±117</td>
<td>173±10</td>
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<td>3.8</td>
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<td>-5.16±0.64</td>
<td>742±170</td>
<td>186±15</td>
<td>0.9996</td>
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</table>
Electrochemical measurements of tri(methyl)isobutylphosphonium bis(fluorosulfonyl)imide (P$_{111i4}$FSI)

Figure S2 Linear sweep voltammograms for neat P$_{111i4}$FSI at a glassy carbon working electrode with a potential sweep rate of 20mV.s$^{-1}$ at different temperatures 25-50-75-100°C.