Supplementary Information

Anisotropic Mass Transport using Ionic Liquid Crystalline Electrolyte to Suppress Lithium Dendrite Growth

Deepesh Gopalakrishnan\textsuperscript{a}, Samia Alkatie\textsuperscript{a}, Andrew Cannon\textsuperscript{b}, Sathish Rajendran\textsuperscript{a}, Naresh Kumar Thangavel\textsuperscript{a}, Neha Bhagirath\textsuperscript{a}, Emily M. Ryan\textsuperscript{b} and Leela Mohana Reddy Arava\textsuperscript{*a}

\textsuperscript{a}Department of Mechanical Engineering, Wayne State University, Detroit, MI 48202, USA
\textsuperscript{b}Department of Mechanical Engineering, Boston University, Boston, MA 02215, USA

Synthesis Methods

Preparation of 1-(12-bromododecoxy)-3-pentadecyl benzene (BDDPB)

3g of 3-pentadecyl phenol is accurately weighed out in a round bottomed flask containing 1g of 1,12-dibromododecane. Then the mixture is stirred magnetically for 1 hour at 70 °C for the complete dissolution to make a pure phase orange colored composite. KOH (1g) is weighed, powdered, and added to the reaction mixture to be continuously stirred for 48 hours. The progress of the reaction is monitored every 12 hours by conducting Thin Layer Chromatography (TLC) using 5% ethyl acetate in hexane. After confirming the completion of the reaction, the solid residue is filtered off using a filtration set up and then purified by passing through a silica column with different weight percentages of ethyl acetate in hexane solution. The product is then Rota vapoed to get a slight yellowish powder and used for the second step.

Preparation of 3-(12-(3-pentadecylphenoxy) dodecyl)-1-methylimidazole_3-3ium hexafluoro-phosphate (PDDMHP)

1g of BDDPB is added to 2g of 1-methyl imidazole at 0° C under vigorous stirring conditions and then further heated to reflux at around 75° C for 48 hours, then cooled to room temperature. The solid residue is washed with diethyl ether several times to remove unreacted reactants from the
compound. The white solid precipitate is collected and dried under vacuum to obtain the product in good yield. Bromide salts are highly moisture sensitive, so to make them environmentally stable they are diluted with distilled water and further converted into corresponding hexafluorophosphate salt by a simple anion metathesis reaction using a large amount of sodium hexafluorophosphate. An aqueous solution of bromide salt is stirred magnetically for 12 hours with a high molar solution of sodium hexafluorophosphate, which is added drop wise. The ILC with hexafluorophosphate salt is precipitated and later filtered and washed with water to remove unreacted bromide salts and excess sodium salts. It is dried under vacuum for 12 hours to obtain PDDMHP in dry form. Thus, overall synthesis procedure involves O-Alkylation of 3-PDP followed by quaternization with 1-methyl imidazole to synthesize this imidazolium based ionic liquid crystals.

<table>
<thead>
<tr>
<th>Phase transition</th>
<th>Phase transition temperatures</th>
<th>ΔH (kJ/mol)</th>
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<tbody>
<tr>
<td>Cryst - SmA</td>
<td>55 °C</td>
<td>65.69</td>
</tr>
<tr>
<td>SmA - Iso</td>
<td>165 °C</td>
<td>0.72</td>
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</tbody>
</table>

Table S1. Phase transition temperatures (°C), enthalpy changes (kJ/mol) of the PDDMHP

Scheme S1. Schematic representation of synthesis of thermotropic ILC, PDDMHP.
Figure S1. NMR Spectrum of PDDMHP
Figure S2. FT IR spectrum of PDDMHP
Figure S3. Chronoamperogram of Li/PDDMHP-LiTFSI/Li symmetric cell at RT.
Figure S4. Nyquist plot of Li/PDDMHP-LiTFSI/Li at RT before and after polarization.
Figure S5. Cross-sectional FE-SEM image of the 1 mAh cm$^{-2}$ electrodeposited Li on Cu foil using a) PC/LiTFSI and b, c) ILC/LiTFSI electrolytes.