Electronic Supplementary Information

Flexible/Shape-Versatile, Bipolar All-Solid-State Lithium-Ion Batteries Prepared by Multistage Printing

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**Fig. S1** Shear rate-dependent viscosity and photographs (inset images) of the cathode pastes as a function of composition ratio. The cathode paste (LCO/C.B.(carbon black)/Gel Electrolyte = 69/7/24) failed to measure its rheological properties due to serious particle agglomeration.

**Fig. S2** Rheological properties and ionic conductivity of the GCE pastes as a function of the ratio of gel electrolyte/Al$_2$O$_3$ nanoparticles. (a) Shear rate-dependent viscosity and photographs (inset images). The GCE paste (gel electrolyte/Al$_2$O$_3$ = 20/80) failed to measure its rheological properties due to serious particle agglomeration. (b) Viscoelastic properties (G’ and G’’) of the GCE pastes as a function of shear stress. (c) Ionic conductivity of the printed GCE films as a function of temperature.

**Fig. S3** EDS mapping area of Al and F elements in the printed GCE (shown in Figure 1b).

**Fig. S4** SEM morphology of the (ETPTA/PVdF-HFP = 75/25 (w/w)) semi-IPN film; the PVdF-HFP was selectively etched prior to the SEM analysis.

**Fig. S5** Change in the characteristic FT-IR peaks assigned to the acrylic C=C bonds (1610–1625 cm$^{-1}$) of the ETPTA in the printed GCE before/after UV irradiation.

**Fig. S6** Change in the characteristic FT-IR peaks assigned to the acrylic C=C bonds (1610–1625 cm$^{-1}$) of the ETPTA before/after UV irradiation: (a) printed LCO cathode and (b) printed LTO anode.
**Fig. S7** TGA profiles of the SWCNT-coated electrode active powders. (a) SWCNT-coated LCO. (b) SWCNT-coated LTO.

**Fig. S8** Comparison of the electronic conductivity between the pristine LTO and SWCNT-coated LTO.

**Fig. S9** Cross-sectional SEM image of the printed mono full cell (composed of an LTO anode, GCE layer and LCO cathode). (a) Before the cycle test. (b) After the 50th cycle

**Fig. S10** Charge-discharge profiles of the conventional LCO cathode and LTO anode at 25 °C, where a coin-type half cell (LCO cathode (or LTO anode)/(1M LiPF$_6$ in EC/DMC = 1/1 (v/v))-soaked PE separator/ lithium metal) was cycled at a fixed charge/discharge current density of 0.1 C/ 0.1C in the voltage range from 3.0 to 4.2 V and from 1.0 to 2.5 V, respectively.

**Fig. S11** Cycling performances of the printed bipolar cells connected in series as a function of cell number (1 → 3 cells) at 25 °C, where the cells were cycled at a constant charge/discharge current density (0.1 C/ 0.1 C). (a) Charge/discharge profiles at 1st, 25th and 50th cycles. (b) Capacity retention as function of cycle number.

**Fig. S12** A video clip showing the safety robustness (cutting test) of the printed bipolar 2-stacked cell.

**Fig. S13** Video clips showing the safety robustness (nonflammability test) of the printed bipolar 2-stacked cell that was fabricated.
directly on the curved roof of a miniature toy car. A control cell (consisting of an LCO cathode, LTO anode, carbonate-based electrolyte (1 M LiPF$_6$ in EC/DMC = 1/1 (v/v)) and PE separator) was also tested for comparison.

**Table S1** Comparison of this work with the previously reported sulfide and oxide solid electrolytes.

**Table S2** Comparison of this work with the previously reported bipolar LIBs.
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Charge-discharge profiles of the conventional LCO cathode and LTO anode at 25 °C, where a coin-type half cell (LCO cathode (or LTO anode)/(1M LiPF₆ in EC/DMC = 1/1 (v/v))-soaked PE separator/ lithium metal) was cycled at a fixed charge/ discharge current density of 0.1 C/ 0.1C in the voltage range from 3.0 to 4.2 V and from 1.0 to 2.5 V, respectively.
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<table>
<thead>
<tr>
<th>Classification</th>
<th>Composition</th>
<th>Synthesis</th>
<th>Ionic Conductivity (S cm⁻¹, R.T.)</th>
<th>Thickness (㎛)</th>
<th>Flexibility</th>
<th>Safety</th>
<th>Versatility</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>GCE</td>
<td>1M LiBF₄ in SBN/Semi-IPN/Al₂O₃</td>
<td>Printing/UV-Crosslinking (Room Temp, &lt; 30 s)</td>
<td>10⁻⁴</td>
<td>50</td>
<td>☺</td>
<td>☺</td>
<td>☺</td>
<td>This work</td>
</tr>
<tr>
<td>Sulfide</td>
<td>Li₅S–P₂S₁</td>
<td>Pelletizing (94 MPa, 280-300 °C for 2 h)</td>
<td>1.7 × 10⁻²</td>
<td>-</td>
<td>-</td>
<td>☺</td>
<td>-</td>
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<tr>
<td>Sulfide</td>
<td>LiₓGeP₂S₁₂</td>
<td>Pelletizing (30 Pa, 550 °C for 8 h)</td>
<td>1.2 × 10⁻²</td>
<td>3000-4000</td>
<td>-</td>
<td>☺</td>
<td>-</td>
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<td>Sulfide</td>
<td>Liₓₓₓ⅓S₁⅓P₁⅔S₁₁⅓Cl₁⅓</td>
<td>Pelletizing (240-550 °C)</td>
<td>2.5 × 10⁻²</td>
<td>1000-2000</td>
<td>-</td>
<td>☺</td>
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<tr>
<td>Oxide (Perovskite)</td>
<td>La₀.₅₁Li₀.₃₄TiO₂.₉₄</td>
<td>Pelletizing (1350 °C for 6 h)</td>
<td>1.4 × 10⁻³</td>
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<td>-</td>
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<td>Oxide (Garnet)</td>
<td>Li₇La₃Zr₂O₁₂</td>
<td>Pelletizing (1230 °C for 36 h)</td>
<td>3.0 × 10⁻⁴</td>
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<tr>
<td>Oxide (NASICON)</td>
<td>Liₓ₁ₓ₁Al₀.₃₁Ti₁₋ₓ(PO₄)₃</td>
<td>Pelletizing (3 Mpa, 950-1000 °C for 24 h)</td>
<td>3.0 × 10⁻³</td>
<td>1400</td>
<td>-</td>
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**Table S1** Comparison of this work with the previously reported sulfide and oxide solid electrolytes.
<table>
<thead>
<tr>
<th># of Stacked Cells</th>
<th>Measurement Temp. (°C)</th>
<th>Cycle #</th>
<th>Safety</th>
<th>Flexibility</th>
<th>Ref.</th>
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<tr>
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<td>25</td>
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<tr>
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Table S2 Comparison of this work with the previously reported bipolar LIBs.
References


