

## **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/ $\text{Al}_2\text{O}_3$  nanoparticles. (a) Shear rate-dependent viscosity and photographs (inset images). The GCE paste (gel electrolyte/ $\text{Al}_2\text{O}_3$  = 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 ( $1610\text{--}1625\text{ cm}^{-1}$ ) 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 ( $1610\text{--}1625\text{ cm}^{-1}$ ) 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 50<sup>th</sup> 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<sub>6</sub> 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 1<sup>st</sup>, 25<sup>th</sup> and 50<sup>th</sup> cycles. (b) Capacity retention as function of cycle number.

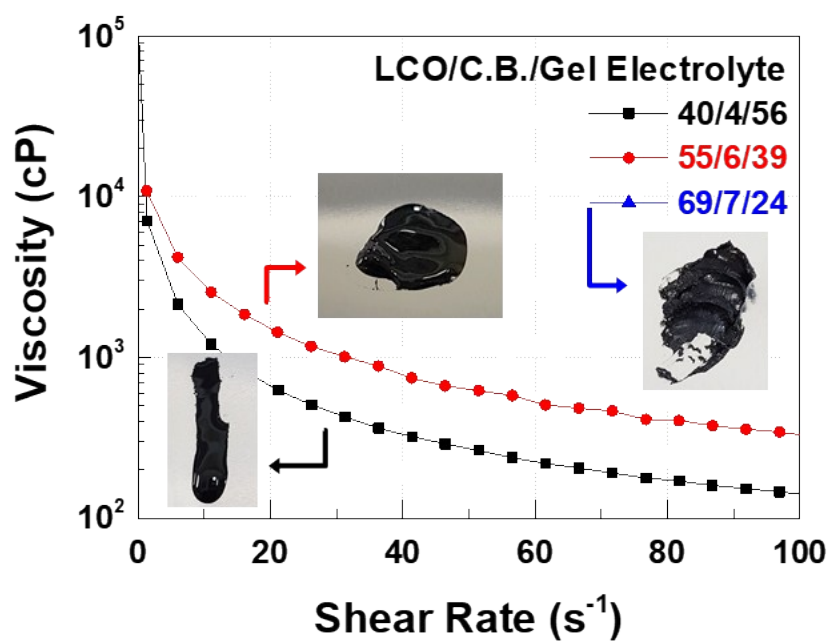
**Fig. S12** A video clip showing the safety robustness (cutting test) of the printed bipolar 2-stacked cell.

**Fig. S13** Video clips showing the safety robustness (nonflammability test) of the printed bipolar 2-stacked cell that was fabricated

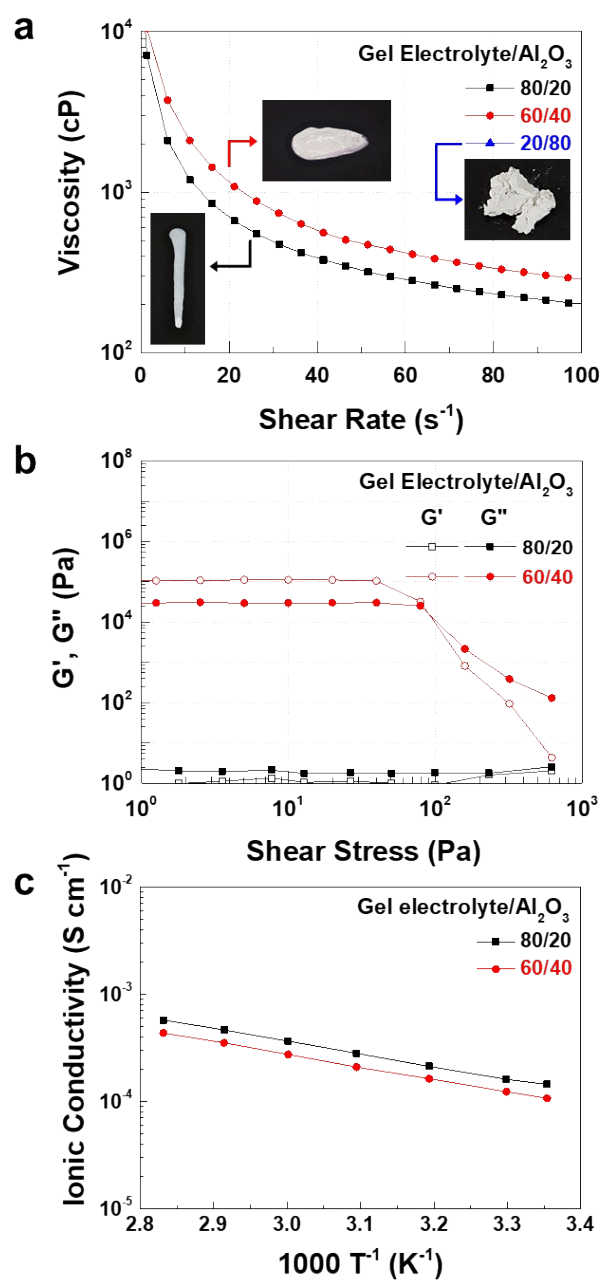
directly on the curved roof of a miniature toy car. A control cell (consisting of an LCO cathode, LTO anode, carbonate-based electrolyte (1 M LiPF<sub>6</sub> in EC/DMC = 1/1 (v/v)) and PE separator)) was also tested for comparison.

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

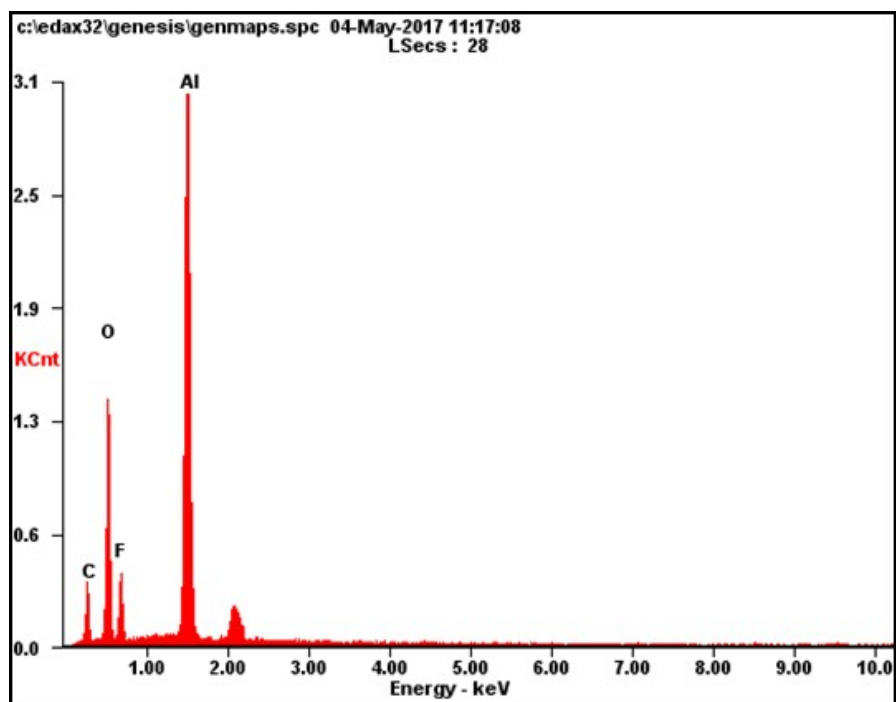
**Table S2** Comparison of this work with the previously reported bipolar LIBs.



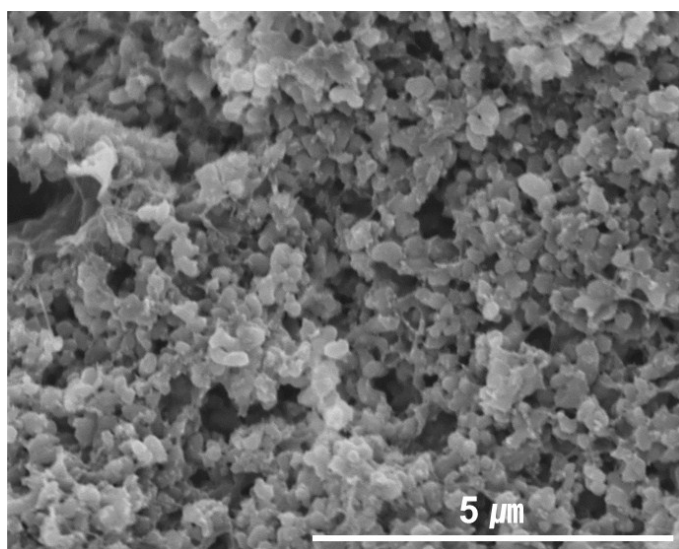
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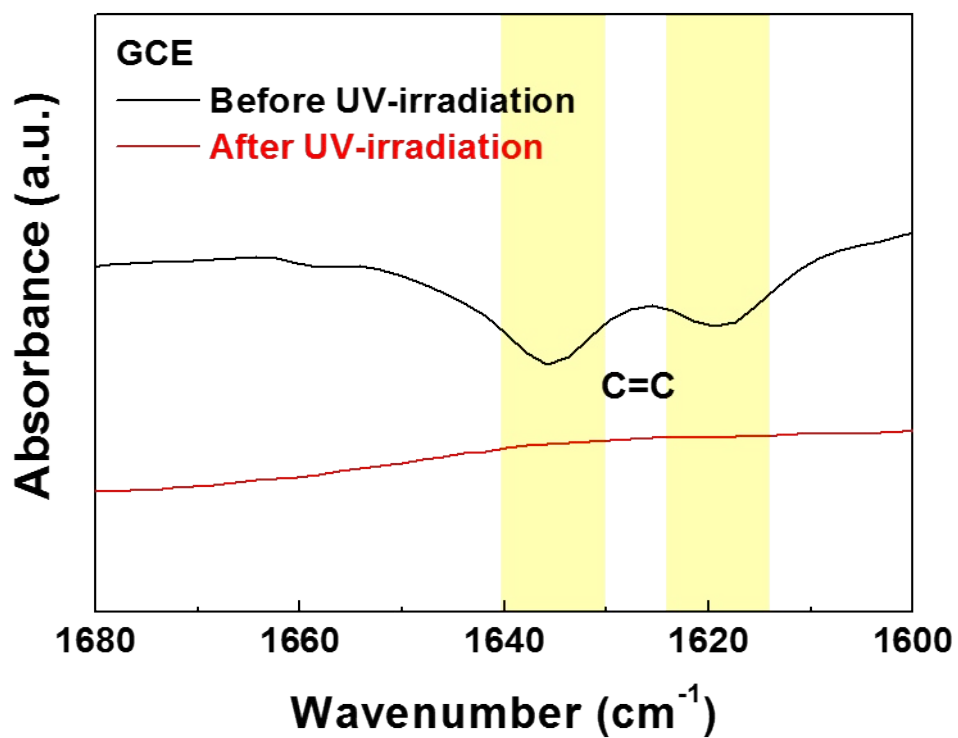


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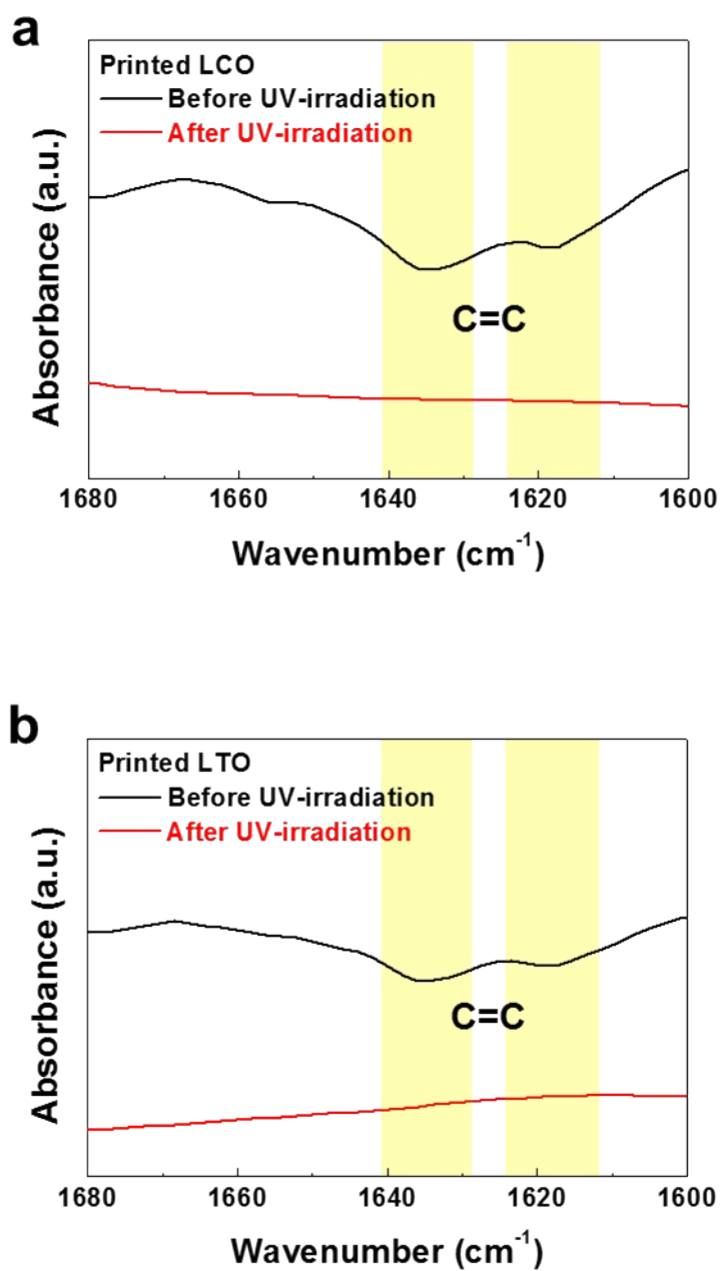


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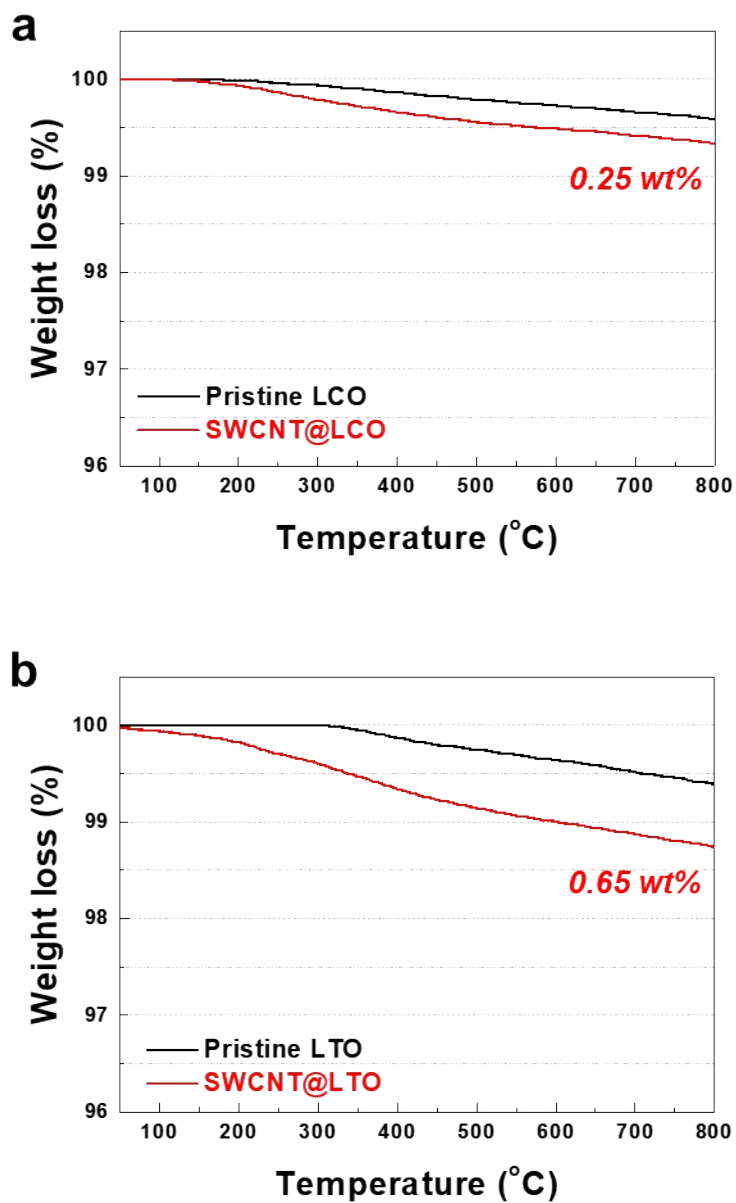




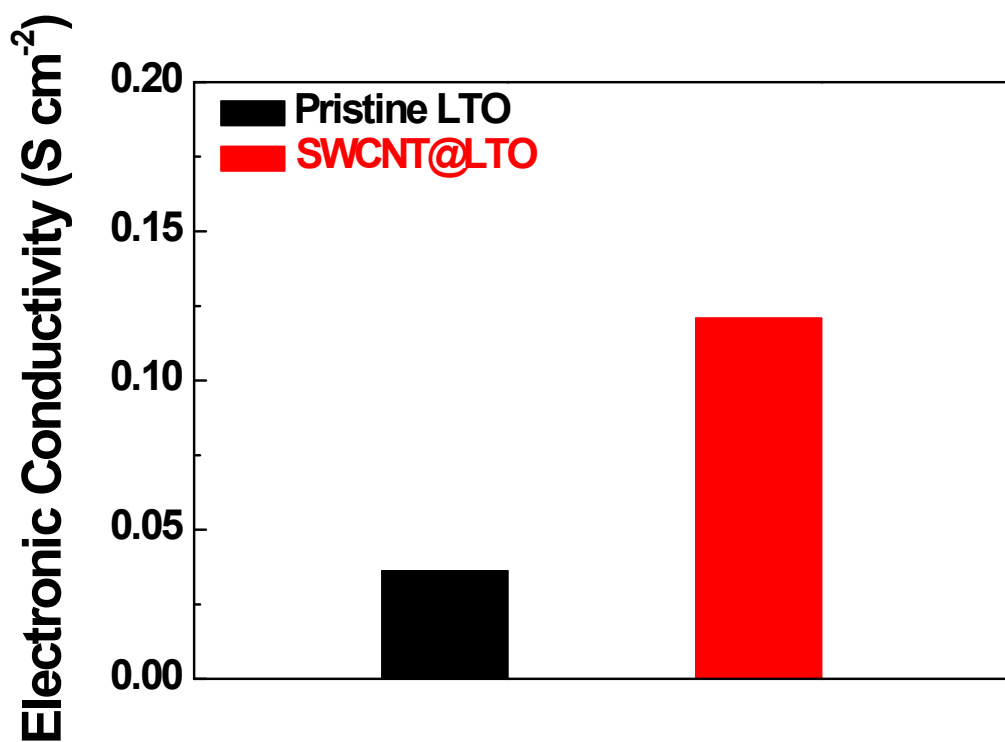
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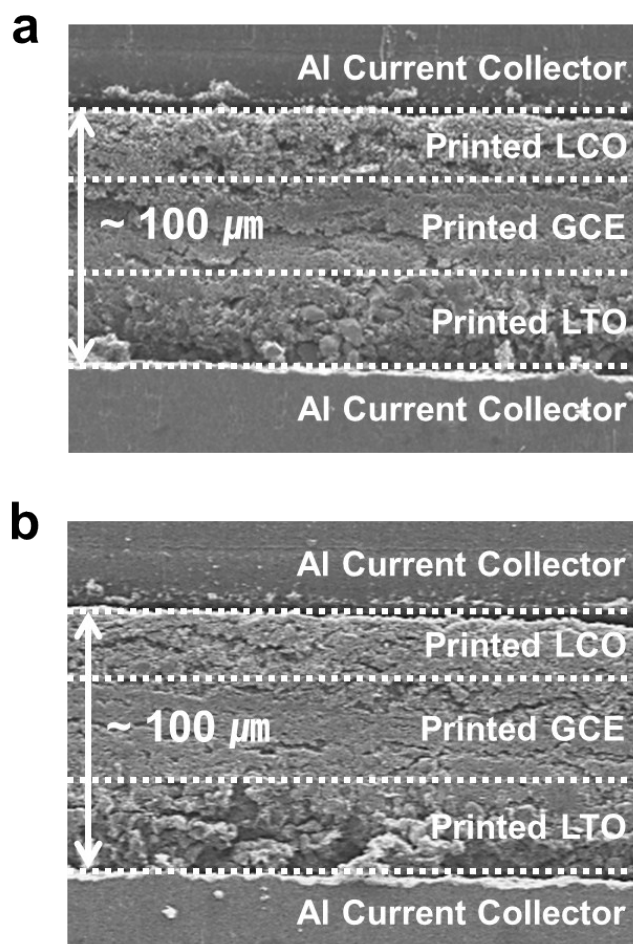
**Fig. S6** Change in the characteristic FT-IR peaks assigned to the acrylic C=C bonds (1610–1625  $\text{cm}^{-1}$ ) of the ETPTA before/after UV irradiation: (a) printed LCO cathode and (b) printed LTO anode.



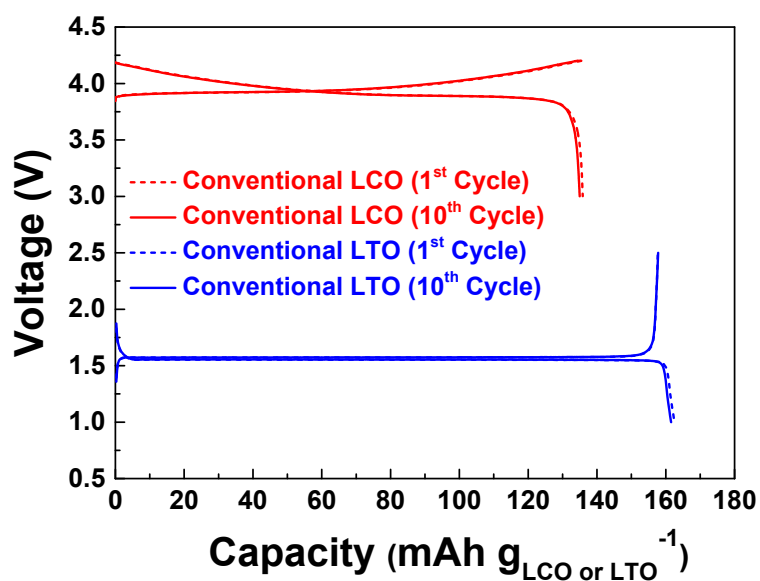
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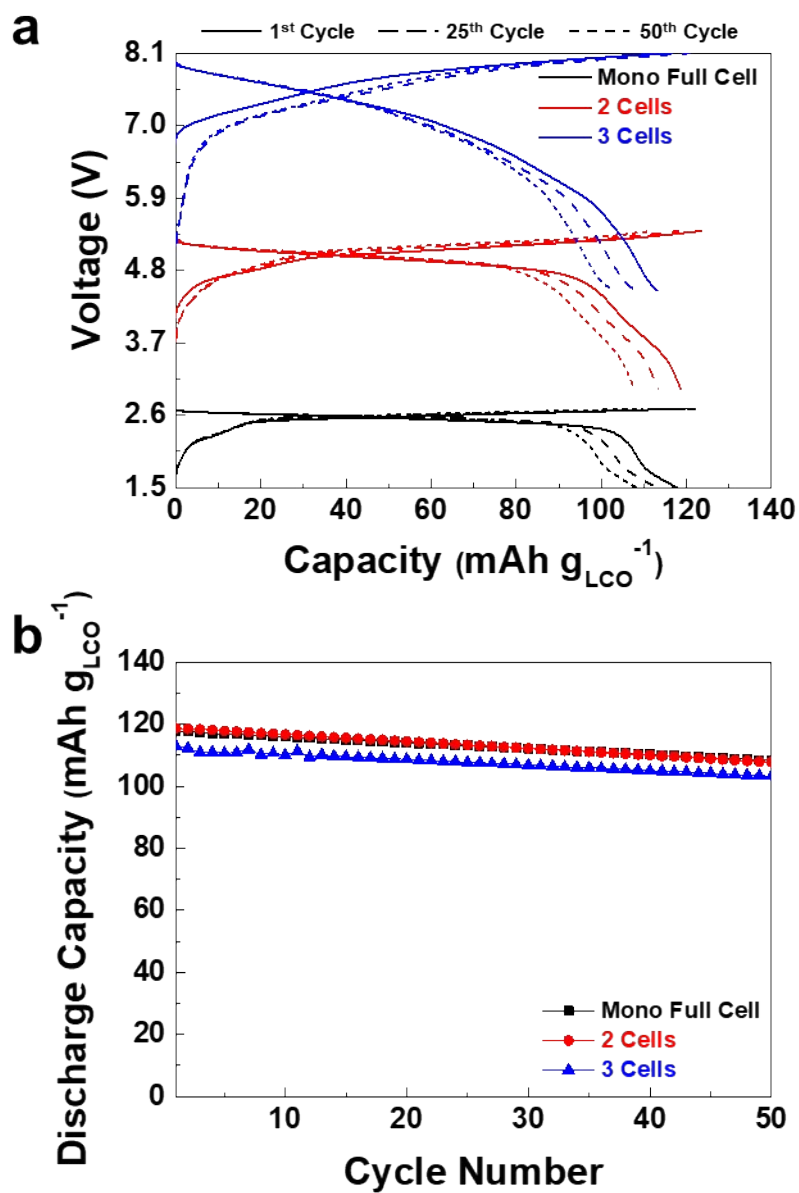
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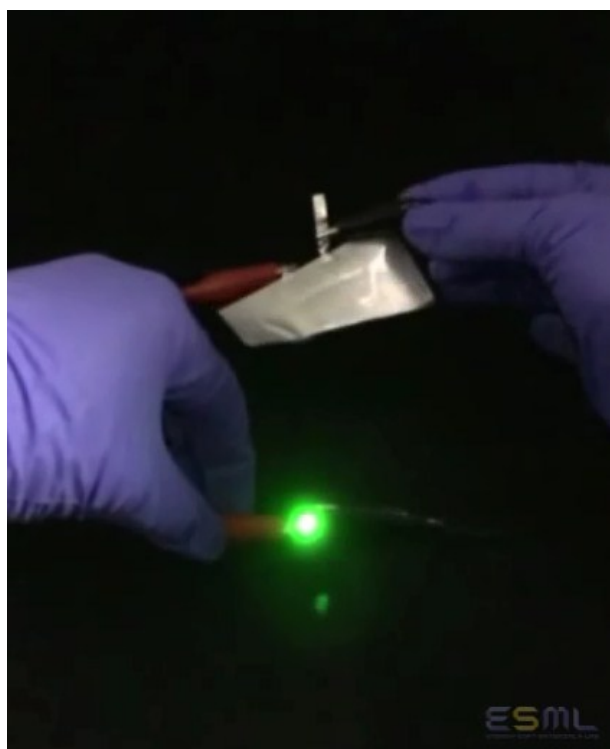
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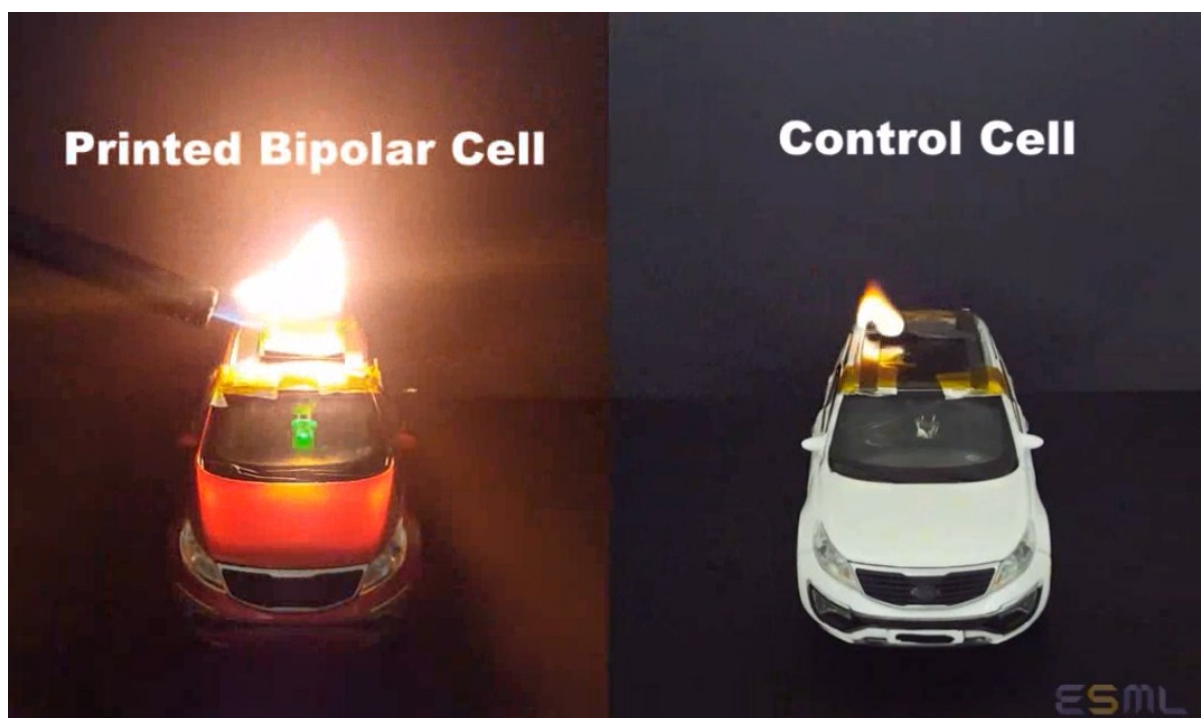


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**Fig. S12** A video clip showing the safety robustness (cutting test) of the printed bipolar 2-stacked cell.





**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  $\text{LiPF}_6$  in EC/DMC = 1/1 (v/v)) and PE separator)) was also tested for comparison.

Classification	Composition	Synthesis	Ionic Conductivity (S cm <sup>-1</sup> , R.T.)	Thickness (μm)	Flexibility	Safety	Shape Versatility	Ref.
GCE	1M LiBF <sub>4</sub> in SBN/ Semi-IPN/Al <sub>2</sub> O <sub>3</sub>	Printing/UV- Crosslinking (Room Temp., < 30 s)	10 <sup>-4</sup>	50	⊙	⊙	⊙	This work
Sulfide	Li <sub>2</sub> S-P <sub>2</sub> S <sub>5</sub>	Pelletizing (94 MPa, 280-300 °C for 2 h)	1.7 × 10 <sup>-2</sup>	-	-	⊙	-	S1
Sulfide	Li <sub>10</sub> GeP <sub>2</sub> S <sub>12</sub>	Pelletizing (30 Pa, 550 °C for 8 h)	1.2 × 10 <sup>-2</sup>	3000-4000	-	⊙	-	S2
Sulfide	Li <sub>9.54</sub> Si <sub>1.74</sub> P <sub>1.44</sub> S <sub>11.7</sub> Cl <sub>0.3</sub>	Pelletizing (240-550 °C)	2.5 × 10 <sup>-2</sup>	1000-2000	-	⊙	-	S3
Oxide (Perovskite)	La <sub>0.51</sub> Li <sub>0.34</sub> TiO <sub>2.94</sub>	Pelletizing (1350 °C for 6 h)	1.4 × 10 <sup>-3</sup>	-	-	⊙	-	S4
Oxide (Garnet)	Li <sub>7</sub> La <sub>3</sub> Zr <sub>2</sub> O <sub>12</sub>	Pelletizing (1230 °C for 36 h)	3.0 × 10 <sup>-4</sup>	980	-	⊙	-	S5
Oxide (NASICON)	Li <sub>1.3</sub> Al <sub>0.3</sub> Ti <sub>1.7</sub> (PO <sub>4</sub> ) <sub>3</sub>	Pelletizing (3 Mpa, 950-1000 °C for 24 h)	3.0 × 10 <sup>-3</sup>	1400	-	⊙	-	S6

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

# of Stacked Cells	Measurement Temp. (°C)	Cycle #	Safety	Flexibility	Ref.
3	25	50	☉	☉	This work
5	60	200	-	-	S7
2	30	1	-	△	S8
2	25	1	-	-	S9
2	39	200	-	-	S10
3	35	100	-	-	S11

**Table S2** Comparison of this work with the previously reported bipolar LIBs.

## References

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