Supporting Information

Recent Advances and Perspectives on Thin Electrolytes for High-Energy-Density Solid-State Lithium Batteries
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Table S1. Summary of thin SSEs with thickness of less than 100 μm and their application in SSLBs. (Items in the application column labelled with “pouch cell” in the brackets mean that pouch cells are in the references but didn’t cycle them. SSLBs with “pouch cell +” in the brackets indicate that pouch cells are shown in the references with performance testing. CQDs: Carbon quantum dots; LSPS: Li10SnP2S12; LLCZNO: Li7La2.75Zr1.75Nb0.25O12; SEBS: polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene; SN: succinonitrile; PI: polyimide; KF: Kevlar fiber; PES: polyethylene sulphide; NW: poly(paraphenyleneterephthalamide) nonwoven; LiBETI: LiN(SO2CF2CF3)2; SBC: Styrene-butadiene copolymer; LGTP: Gallium-doped LiTi2(PO4)3; PEGDME: Poly(ethylene glycol) dimethyl ether; polyDOL: poly (1,3-dioxolane); PEGDA: poly(ethylene glycol) diacrylate; PEGDE: poly(ethylene glycol) diglycidyl ether).

<table>
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<th>Fabrication method</th>
<th>SSE</th>
<th>Thickness (μm)</th>
<th>Application</th>
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<td>(Pouch cell+)</td>
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<td>Polyethylene-PEO</td>
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<td>Graphite/NMC622</td>
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<td>Li/NCA</td>
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| KF-Li₃PS₄ | 100 | Li/S | 42 |
| [C2mpyr][BF₄]-PVDF | 30 | Li/LFP | 43 |
| Cold/Hot press |
| NW-Li₃PS₄ | 70 | LTO/LCO | 44 |
| 77.5Li₂S⁻ | 100 | Li/FeS₂ | 45 |
| 22.5P₂S₅ | 6-35 | - | 46 |
| β-Li₃PS₄ | 6-35 | - | 46 |
| PEO-LGPS | 100 | Li/S | 47 |

| Extrusion |
| PEO-LLZO | <100 | - | 48 |
| PEO-LiBETI | 80-90 | Li/V₂O₅ (Pouch cell+) | 49 |

| 3D printing |
| LLZO | 5-10 | - | 50 |
| SBC-LLZO | 100 | - | 51 |

| Hydrothermal |
| LATP | 40-90 | Graphite/LFP | 52 |
| LGTP | ~100 | - | 53 |

| Solvent evaporation |
| β-Li₃PS₄ | 30 | - | 54 |
| 75.51Li₂S⁻ | 1.5 | - | 55 |

<p>| In-Situ polymerization |
| PolyDOL | ~25 | Li/NMC622&amp;Li/S | 56 |
| LLZO-PEGDA | 36 | Li/LFP | 57 |
| PEGDA-PEGDE | 90 | Li/LFP | 58 |</p>
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<th>Method</th>
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<th>Li/O₂</th>
<th>Reference</th>
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<td>LATP</td>
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Table S2. The criteria of the SSEs to meet the requirements of different SSLBs.

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<th>SSLB system</th>
<th>Requirements for SSE</th>
<th>SSE type</th>
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<td>Li-LFP</td>
<td>Oxidation stability potential: &gt;4.0 V</td>
<td>SPEs</td>
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<td>Stable against Li</td>
<td>Oxide (interface modification)</td>
</tr>
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<td></td>
<td>Ionic conductivity: &gt;10^{-3} S cm^{-1}</td>
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<tr>
<td>Li-LCO/NMC</td>
<td>Oxidation stability potential: &gt;4.2 V</td>
<td>Multi-layered SPEs (or modified SPEs)</td>
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<tr>
<td></td>
<td>Stable against Li</td>
<td>Oxide (interface modification)</td>
</tr>
<tr>
<td></td>
<td>Ionic conductivity: &gt;10^{-3} S cm^{-1}</td>
<td>Halide (considering Li reduction)</td>
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<td></td>
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<td>Sulfide (Cathode materials should be protected)</td>
</tr>
<tr>
<td>Li-S</td>
<td>Oxidation stability window: &gt;3 V</td>
<td>SPEs (Considering shuttle effect)</td>
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<td></td>
<td>Stable against Li</td>
<td>Oxide (Interface modification, Considering LiPS and Li reduction)</td>
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<td></td>
<td>Ionic conductivity: &gt;10^{-3} S cm^{-1}</td>
<td>Sulfide (Considering electrolyte decomposition by carbon)</td>
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<td>Li-O2/air</td>
<td>Oxidation stability potential: &gt;4.2 V</td>
<td>SPEs (considering high-voltage oxidation)</td>
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<td></td>
<td>Stable against Li</td>
<td>Oxide (Interface modification)</td>
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<td>Ionic conductivity: &gt;10^{-3} S cm^{-1}</td>
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<td>Air stability (O _2 and H_2O)</td>
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Table S3. Parameters used for energy density calculations of the selected battery systems.

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<th>Anode</th>
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<td>Press Density (g cm(^{-3}))</td>
<td>Reversible Capacity (mAh g(^{-1}))</td>
<td>Initial Coulomb Efficiency</td>
<td>Press Density (g cm(^{-3}))</td>
<td>Reversible Capacity (mAh g(^{-1}))</td>
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<td>Li-LFP</td>
<td>3.2</td>
<td>2.25 (90 wt.%)</td>
<td>170</td>
<td>98%</td>
<td>0.53</td>
<td>3860</td>
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<tr>
<td></td>
<td></td>
<td>2.22 (85 wt.%)</td>
<td></td>
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<td>2.18 (80 wt.%)</td>
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<tr>
<td>Li-LCO</td>
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<td>4.03 (90 wt.%)</td>
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<td>97%</td>
<td>0.53</td>
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<td></td>
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<td>3.90 (85 wt.%)</td>
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<td>3.77 (80 wt.%)</td>
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<td>Li-NMC-811</td>
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<td>Capacity (Ah)</td>
<td>14.955</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Mass (kg)</td>
<td>0.16185</td>
<td></td>
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<tr>
<td></td>
<td>Volume (L)</td>
<td>0.0753</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gravimetric energy density (Wh kg⁻¹)</td>
<td>365.0</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Volumetric energy density (Wh L⁻¹)</td>
<td>784.5</td>
<td></td>
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</tr>
</tbody>
</table>

**Table S4.** Typical technological parameters of a Li-LCO pouch cell with a fixed size of 138 mm x 81.8 mm x 6.44 mm.
References


