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: $Li_{10}SnP_2S_{12}$; LLCZNO: $Li_7La_{2.75}Zr_{1.75}Nb_{0.25}O_{12}$; SEBS: polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene; SN: succinonitrile; PI: polyimide; KF: Kevlar fiber; PES: polyethylene sulphide; NW: poly(paraphenyleneterephthalamide) nonwoven; LiBETI: $LiN(SO_2CF_2CF_3)_2$; SBC: Styrene-butadiene copolymer; LGTP: Gallium-doped $LiTi_2(PO_4)_3$; PEGDME: Poly(ethylene glycol) dimethyl ether; polyDOL: poly (1,3-dioxolane); PEGDA: poly(ethylene glycol) diacrylate; PEGDE: poly(ethylene glycol) diglycidyl ether).

Fabrication method	SSE	Thickness (μm)	Application	Reference
Slurry casting	Li_6PS_5Cl	30	Ag-C/NMC90.50.5 (Pouch cell+)	1
	β-Li_3PS_4	21	Li/NMC622	2
	LLZO	5	Li/LCO	3
	Li_3PS_4	59	Graphite/NMC111	4
	PAN-LAGP-PEGDA	25	Li-NMC811 (Pouch cell+)	5
	LLZO	3-5	Li/LFP	6
	Li_3PS_4	50	Graphite-NMC111 (Pouch cell+)	7
	Li_6PS_5Cl	30	Graphite-NMC622 (Pouch cell+)	8
Solution casting	PEO-CDQs	80	Li/LFP	9

	PEO-LSPS	70	Li/S	[10]
	PEO-LLTO	15±5	Li/S	[11]
	PEO-$Li_7P_3S_{11}$	50	-	[12]
	PEO	40	Li/LCO (Pouch cell)	[13]
	PEO	9.5	Li/LFP	[14]
	polyether-LiTFSI	29	Li/LFP (Pouch cell+)	[15]
	PEO-MIL-53(Al)	60	Li/S	[16]
	PEO-LLZO	20-75	Li/S	[17]
	MIL-53(Al)	60	Li/LFP	[18]
	PEO-SiO_2	30-150	Li/LFP	[19]
	PAN–$LiClO_4$–BNNF	12	Li/NMC811	[20]
Tape casting	Garnet	15	Li/S (Pouch cell)	[21]
	LAGP	75	-	[22]
	LLTO	25-160	Li/LFP	[23]
	LLZO	14-20	Li/S (Pouch cell+)	[24]
	LLCZNO	35	Li/S	[25]
	LLZO	20	Li/NMC622	[26]
	Garnet	30	-	[27]
	LLZO	<30	-	[28]
	LLZO	25	-	[29]
	LLZO	20	Li/S	[30]
	LAGP	70	-	[31]
Solution infusion	PEG-Ti- $Li_7P_3S_{11}$	10	Li/LFP	[32]
	PEO-LATP	100	-	[33]
	LLZTO-SN-LITFSI	100	Li/LFP&Li/NMC532	[34]

	LLZTO-PAN-$LiClO_4$	25	Li/LNMO	[35]
	Polyethylene-PEO	7.5	Li/LFP&Li/S (Pouch cell)	[36]
	PI-PEO	8.6	Li/LFP (Pouch cell)	[37]
	PI-$Li_6PS_5Cl_{0.5}Br_{0.5}$	40-70	Graphite/NMC622	[38]
	PEO-LLZO	40-50	-	[39]
	Celgard3501-PEGDME	50	Li/LFP&Li/NMC532 (Pouch cell+)	[40]
	KF-PES-Li_3PS_4	60	Li/NCA	[41]
Cold/Hot press	KF-Li_3PS_4	100	Li/S	[42]
	[C2mpyr][BF4]-PVDF	30	Li/LFP	[43]
	NW-Li_3PS_4	70	LTO/LCO	[44]
	77.5Li_2S-22.5P_2S_5	100	Li/FeS_2	[45]
	β-Li_3PS_4	6-35	-	[46]
	PEO-LGPS	100	Li/S	[47]
Extrusion	PEO-LLZO	<100	-	[48]
	PEO-LiBETI	80-90	Li/V_2O_5 (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-Li_3PS_4	30	-	[54]
	75.51Li_2S-24.49P_2S_5	1.5	-	[55]
In-Situ polymerization	PolyDOL	~25	Li/NMC622&Li/S	[56]
	LLZO-PEGDA	36	Li/LFP	[57]
	PEGDA-PEGDE	90	Li/LFP	[58]

			(Pouch cell)	
	LLTO	19.8	Li/O_2	[59]
Spin coating	LATP	36	Li/O_2	[60]
	LATP	20	Li/O_2	[61]

Table S2. The criteria of the SSEs to meet the requirements of different SSLBs.

SSLB system	Requirements for SSE	SSE type
Li-LFP	Oxidization stability potential: >4.0 V Stable against Li Ionic conductivity:>10^{-3} S cm^{-1}	SPEs Oxide (interface modification)
Li-LCO/NMC	Oxidization stability potential: >4.2 V Stable against Li Ionic conductivity:>10^{-3} S cm^{-1}	Multi-layered SPEs (or modified SPEs) Oxide (interface modification) Halide (considering Li reduction) Sulfide (Cathode materials should be protected)
Li-S	Oxidization stability window: >3 V Stable against Li Ionic conductivity:>10^{-3} S cm^{-1}	SPEs (Considering shuttle effect) Oxide (Interface modification, Considering LiPS and Li reduction) Sulfide (Considering electrolyte decomposition by carbon)
Li-O2/air	Oxidization stability potential: >4.2 V Stable against Li Ionic conductivity:>10^{-3} S cm^{-1} Air stability (O_2 and H_2O)	SPEs (considering high-voltage oxidization) Oxide (Interface modification)

Table S3. Parameters used for energy density calculations of the selected battery systems.

Battery system	Average Voltage (V)	Cathode			Anode		
		Press Density (g cm^{-3})	Reversible Capacity (mAh g^{-1})	Initial Coulombic Efficiency	Press Density (g cm^{-3})	Reversible Capacity (mAh g^{-1})	Initial Coulombic Efficiency
Li-LFP	3.2	2.25 (90 wt.%) 2.22 (85 wt.%) 2.18 (80 wt.%)	170	98%	0.53	3860	100%
Li-LCO	3.95	4.03 (90 wt.%) 3.90 (85 wt.%) 3.77 (80 wt.%)	190	97%	0.53	3860	100%
Li-NMC-811	3.8	3.38 (90 wt.%) 3.28 (85 wt.%) 3.19 (80 wt.%)	210	90%	0.53	3860	100%
Li-Li-rich	4.0	2.63 (90 wt.%) 2.57 (85 wt.%) 2.52 (80 wt.%)	300	90%		3860	100%
Li-S	2.1	0.86-0.94 (70 wt.%) 0.71-0.79 (60 wt.%) 0.60-0.68 (50 wt.%)	1338	100%	0.53	3860	100%

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

Component of Cell	Parameter	Value
Cathode	Material	LCO
	Reversible capacity (mAh g^{-1})	190
	Initial Coulombic efficiency (%)	97
	Unilateral areal density (mg cm^{-2} each side of Al)	24.02
	Active material ratio (%)	85
	Press density (g cm^{-3})	3.90
	Unilateral thickness (μm)	61.6
	Thickness of Al (μm)	16
	Length (mm)	120
	Width (mm)	73
	layer	22
Anode	Material	Li
	Reversible capacity (mAh g^{-1})	3860
	Initial Coulombic efficiency (%)	100
	Unilateral areal density (mg cm^{-2} each side of Cu)	2.07
	Active material ratio (%)	100
	Press density (g cm^{-3})	0.53
	Unilateral thickness (μm)	39.10
	Thickness of Cu (μm)	8
	Length (mm)	123
	Width (mm)	76
	layer	23
Electrolyte	Material	LGPS
	Thickness (μm)	30
	Length (mm)	126
	Width (mm)	76
	layer	44
Sealing film	Thickness (μm)	152
Cell	Voltage (V)	3.95
	Capacity (Ah)	14.955
	Mass (kg)	0.16185
	Volume (L)	0.0753
	Gravimetric energy density (Wh kg^{-1})	365.0
	Volumetric energy density (Wh L^{-1})	784.5

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