SUPPORTING INFORMATION

Hybrid sulfide-based solid electrolyte-liquid electrolyte systems for solid-state batteries: Why, how, and where to?

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Table S1. Time-dependent aerial resistances for various hybrid solid electrolyte/liquid electrolyte systems. Resistance values were digitized from the specified references and the data was used to prepare Figure 3a in the main manuscript.

Solid Electrolyte	Liquid Electrolyte	Aerial Resistance / $\Omega \cdot cm^2$			
		Initial	t = 50 h	t = 100 h	Reference
$Li_{1+x}Al_xGe_{2-x}(PO_4)_x$ (LAGP)	1 M LiTFSI (DME/DOL) [50:50 (vol%)])	57.4	65.6	77.8	1
$Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$ (LLTZO)	1 M $LiPF_6$ (EC/DMC) [50:50 (vol%)])	233	456	5722	2
$Li_xPO_yN_z$ (LiPON)	1 M LiTFSI (DME/DOL [50:50 (vol%)])	184	230	253	3
Ohara glass-ceramic	1 M LiTFSI (DME/DOL [50:50 (vol%)])	76	70.9	70.6	3
$Li_{6.6}La_3Zr_{1.6}Ta_{0.4}O_{12}$ (LLZO)	x M $LiPF_6$ (EC/DMC [1:1 (w/w)])	350	350	350	4
$Li_{10}GeP_2S_{12}$	7 M LiTFSI-TTE[a] (DME/DOL)	6.6	2350		5
Li_3PS_4	7 M LiTFSI-TTE[a] (DME/DOL)	59.2	37486.7		5
Li_3PS_4	1 M LiTFSI-TTE[a] ((MeCN)$_{2)}$	131	273	240	6
Li_3PS_4	1 M LiTFSI (DOL) [50:50 (vol%)])	8	540	610	7
Li_3PS_4	1 M LiTFSI (DME) [50:50 (vol%)])	8	83	100	7
Li_3PS_4	LiTFSI (DME/DOL) [50:50 (vol%)])	8	112	150	7

1. Values digitized from Busche *et al. Nature Chem,* 2016, **8**, 426-434
2. Values digitized from Liu *et al. Joule,* 2020, **4**, 101-108
3. Values digitized from Busche *et al. Adv. Mater. Interfaces,* 2020, **7**, 2000380
4. Values digitized from Schleutker *et al. Phys. Chem. Chem. Phys,* 2017, **19**, 26596-26605
5. Values digitized from Philip *et al. ACS Appl. Mater. Interfaces,* 2019, **11**, 2014-2021
6. Values digitized from Shin *et al. Adv. Energy Mater,* 2019, **9**, 1900938
7. Values digitized from Fan *et al. ACS Appl Mater Inter,* 2022,**14**,933-942

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[a] TTE=1,1,2,2 tetrafluroethyl 2,2,3,3,-tetraflouropropyl ether cosolvent used to reduce the viscosity of liquid electrolytes

Table S2. Summary of solvent properties and the calculated ratios of the ionic conductivity of processed thiophosphate electrolyte samples to the ionic conductivity of the pristine sample measured at room temperature.

Solvent	ε	Donor number[a] / kcal·mol^{-1}	Relative Polarity[b]	$\sigma_{processed}/\sigma_{pristine}$			
				Li_6PS_5Cl[c] $\sigma_{pristine}$=1.7 mS cm^{-1}	Li_3PS_4[d] $\sigma_{pristine}$=0.41 mS cm^{-1}	$Li_7P_3S_{11}$[e] $\sigma_{pristine}$=1.2 mS cm^{-1}	tetra-Li_7SiPS[f] $\sigma_{pristine}$=4 mS cm^{-1}
cyclohexane	2	0	0.006				0.26
decane	2.1	0	0.009		0.95		
dioxane	2.2	14.3	0.164		0.061		
xylene	2.3	5	0.074			0.99	0.53
toulene	2.4	1	0.099	0.040		0.93	0.24
dimethylcarbonate	3.08	17	0.231			0.92	0.044
anisole	4.3	9	0.197		0.81		0.66
diglyme	7.23	19.5	0.244		0.0075		
tetrahydrofuran	7.5	20	0.207	0.26			0.12
1,2-dichloroethane	10.3	0	0.327		0.95		
pyridine	13	33	0.302				0.011
propanenitrile	27.7	16	0.398				0.088
triethylamine	32	61	0.043				0.0005
N-methyl-2-pyrrolidone	32.3	27	0.354				0.015
acetonitrile	35.7	14.1	0.460	0.43		0.0006	0.38
dimethylformamide	38.25	26	0.386				
propylene Carbonate	64.9	15	0.472				0.02

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[a] Marcus, Y. *Chem. Soc. Rev.* 1993, **22**, 409-416.

[b] The values for relative polarity are normalized from measurements of solvent shifts of absorption spectra and were extracted from Christian Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, Wiley-VCH Publishers, 3rd ed., 2003.

[c] Values calculated from digitized data reported by Ruhl *et al*. *Adv. Energy Sustain. Res.* 2021, **2**, 200077

[d] Values calculated from digitized data reported from Yamamoto *et al*. *Sci.Rep*, 2018, **8**, 121

[e] Values calculated from digitized data reported from Tan *et al*. *ACS Appl. Energy Mater*. 2019, **2**, 6542-6550

[f] Values calculated from digitized data reported by Hatz *et al*. *ACS Appl. Energy Mater*. 2021, **4**, 9932-9943

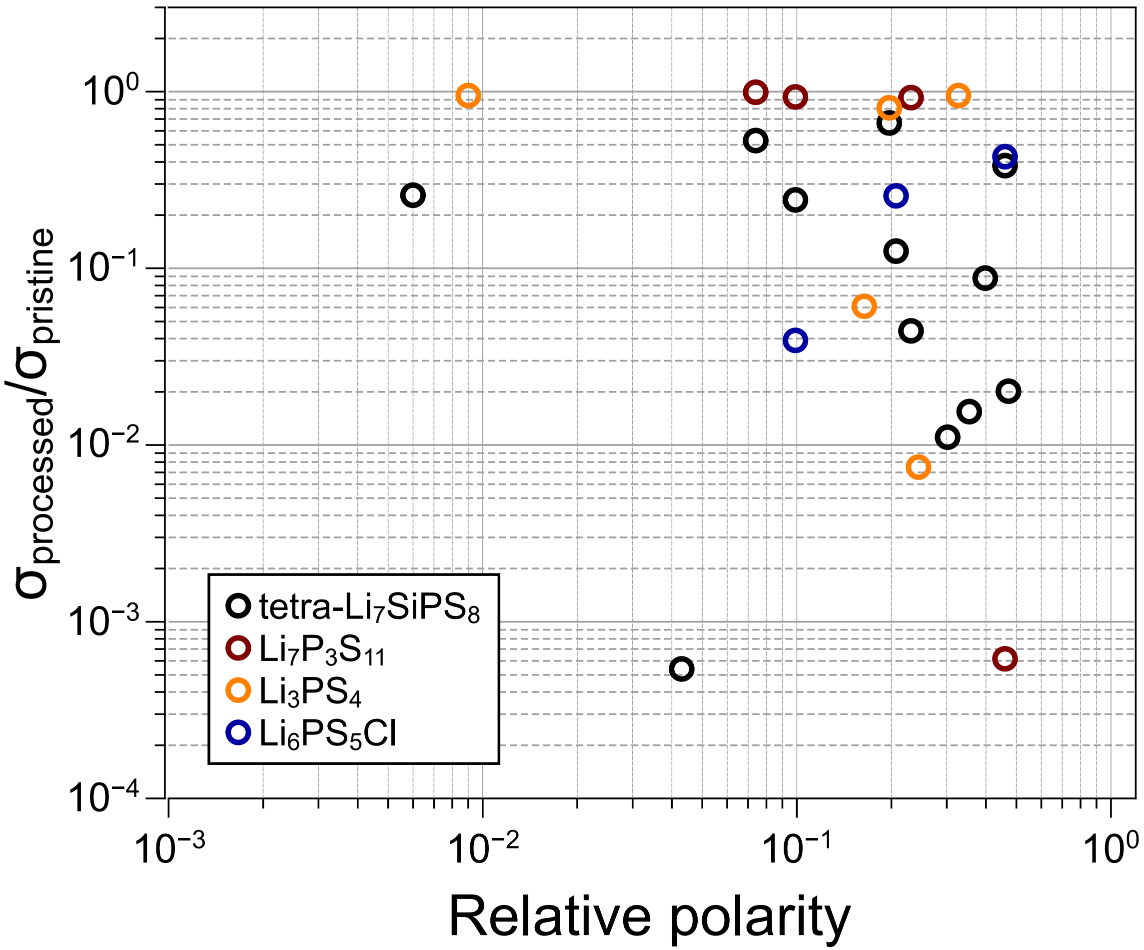

Figure S1: The influence of the relative polarity of various solvents used to process thiophosphates. On the y axis the relative ionic conductivity of the electrolytes before and after the solvent processing is shown. In general, the more polar the solvent the more likely it is to cause the decomposition of an electrolyte into a less ionically conducting electrolyte.

Estimation of energy density and round-trip efficiency losses of a Li-S solid state battery that utilizes a hybrid SE/LE electrolyte

These derivations and calculations were done based on the work of Busche et al. *Nat Chem*, 2016, **8**, 426–434.

Let us consider an ideal Li-S cell with the following features:

- Separator conductivity: 0.01 S/m (typical of an oxide electrolyte) or 1 S/m (typical of a good sulfide electrolyte)
- Separator transference number: 1
- Theoretical capacity: 1672 mAh/g
- Discharge voltage: 2.2 V vs. Li/Li^+,
- 100% sulfur utilization

To assess the effect of the separator (SE) and the resistance of the solid-liquid electrolyte interphase (R_{SLEI}) on the energy density, we utilize the following equation:

$$E = 1672\ {}^{Ah}/_{kg} \times [2.2\ V - \eta_{SE} - \eta_{SLEI}]$$

The overpotentials for the solid electrolyte and the SLEI are obtained as follows:

$$\eta_{SE} = \frac{d}{\sigma_{SE}} j$$

$$\eta_{SLEI} = R_{SLEI} \cdot j$$

Where d is the thickness of the separator (in m), j is the applied current density (in A/m^2), R_{SLEI} is the resistance of the solid-liquid electrolyte interphase (in $\Omega \cdot m^2$) and σ_{SE} is the conductivity of the separator in S/m. Note that η_{SE} will depend on both the thickness of the separator and the C-rate (due to its dependence on the current density), whereas $\eta_{SLEI}$is only influenced by the C-rate.

To estimate the round-trip efficiency (RTE) losses, we assume that the overpotentials during charging and discharging are equal and therefore, we double the effect of the overpotentials due to the solid electrolyte and the SLEI on the RTE.

$$RTE = \left[\frac{\left(1672\,{}^{Ah}\!/_{kg} \cdot 2.2\ V\right) - \left(1672\,{}^{Ah}\!/_{kg}\right)2(\eta_{SE} + \eta_{SLEI})}{1672\,{}^{Ah}\!/_{kg} \cdot 2.2\ V}\right] \cdot 100$$

Or in a simplified form that focuses on the overpotentials:

$$RTE = \left[1 - \frac{2(\eta_{SE} + \eta_{SLEI})}{2.2\ V}\right] \cdot 100$$

This calculation assumes that there are no additional ohmic losses in such an ideal cell.