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Supporting Information

Engineering Green and Sustainable Solvents for Scalable Wet Synthesis of Sulfide Electrolytes in High-Energy-Density All-Solid-State Batteries

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1. Investigation of the electrochemical behavior of electrolytes

Ohmic resistances (R_{SE}) of SEs were calculated by σ_{ion} from Table 2 and geometric factor (thickness l and area A) of SEs ($R_{SE} = l/(\sigma_{ion} \cdot A)$). Then, ohmic overpotentials were calculated by ohmic resistance and current density ($V = IR$). (Fig. S1)

The overpotentials of THF(8.72mV), 2-MeTHF(8.87mV), CPME(9.17 mV), G1(12.38 mV) cells were higher than ohmic polarizations of SEs (4.37 mV, 5.39 mV, 5.31 mV, and 4.59 mV, respectively). The discrepancy between the cell overpotential and ohmic polarization of SE might be originated from interfacial resistance between Li metal and solid electrolyte.

However, compared to the above samples, G2, G3, and G4 cells exhibited unstable cycle performances. The overpotentials of G2 and G3 cells suddenly dropped after cycling a few times (12 → 7.34 mV, 12 → 4.74 mV for G2, G3 cells respectively), and the overpotentials were lower than the ohmic polarization in each sample (8.11 mV and 9.26 mV, respectively). It can be considered a soft short-circuit behavior, as reported in previous studies.[1] On the other hand, the failing behavior of the G4 cell was different of the G2 and G3 cells. The overpotential of G4 samples increased abruptly after ~80 hours, and we speculate that it might be related to a large amount of impurities in the G4 sample (**Fig. 6**m – XRD).

[S1] N. J. Taylor, S. S. Molo, C. G. Haslam, A. Sharafi, T. Thompson, M. Wang, R. G. Mendez, J. Sakamoto. Demonstration of high current densities and extended cycling in the garnet Li7La3Zr2O12 solid electrolyte. Journal of Power Sources **396**, 314-318(2018). https://doi.org/10.1016/j.jpowsour.2018.06.055.

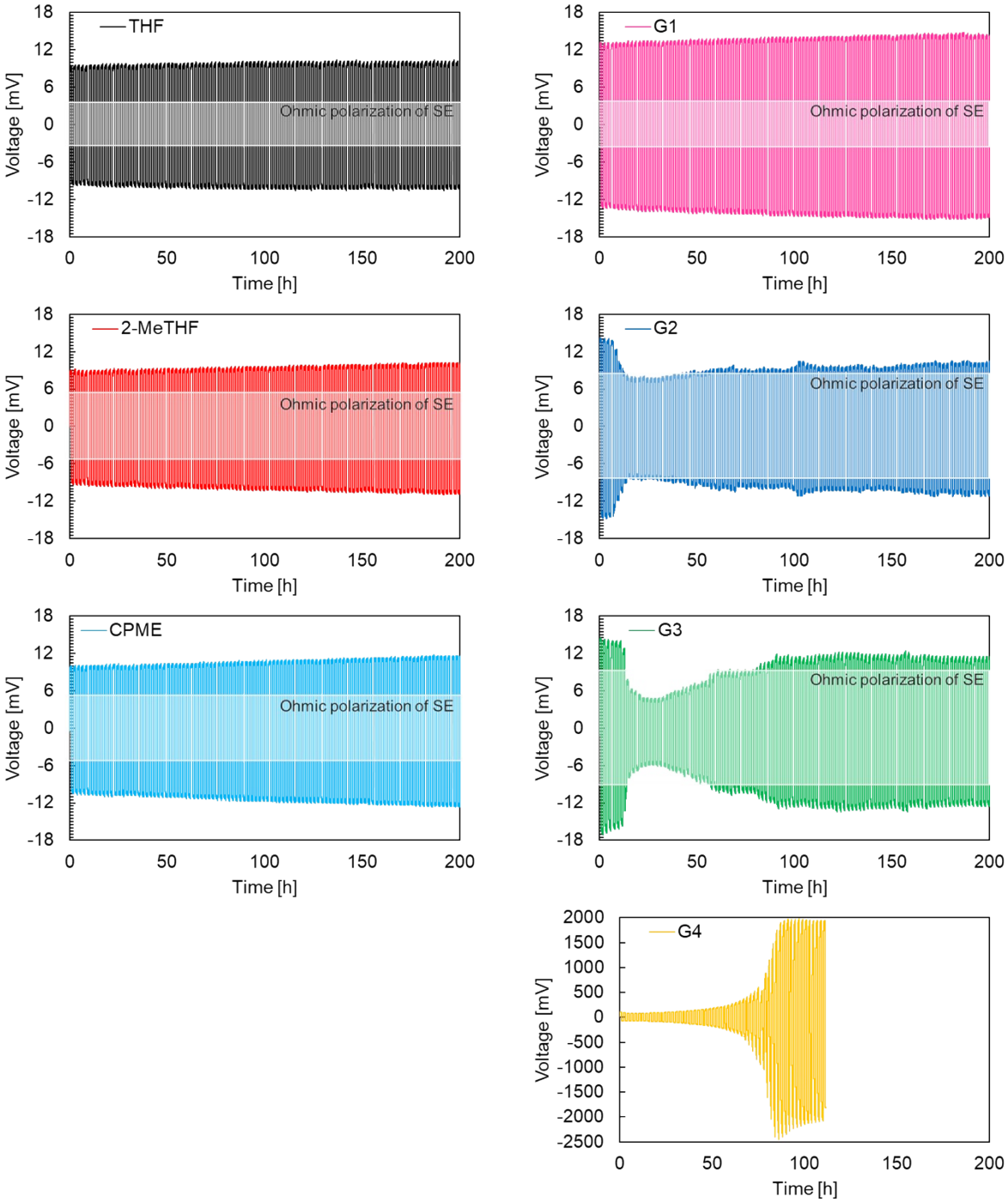

Fig. S1. Voltage profiles of the symmetrical Li/Li cells with LPSCl SEs prepared with various solvents; THF, 2-MeTHF, CPME, and glymes (G1-G4).

2. Reproducibility of ASSBs

Table S1. Discharge capacities of ASSB cells with LPSCl SEs prepared using THF and various greener alternatives and sustainable solvents; 2-MeTHF, CPME, G1, G2, G3, and G4 for each C-rates from 0.1C to 2.0C.

	Discharge capacity [mAh g^{-1}]						
C-rate	THF	2-MeTHF	CPME	G1	G2	G3	G4
0.1C	177.5278	192.5776	166.3057	169.1075	158.7253	148.9147	28.6741
	173.6746	184.6486	159.7478	160.3497	154.3544	152.4864	22.2798
	170.4677	180.4354	154.3344	166.4676	146.1359	144.6486	25.5473
0.2C	172.9806	174.5262	153.1806	161.4197	126.091	106.2834	13.90979
	166.1564	166.1548	148.3487	156.7687	123.4676	103.6841	9.5463
	165.4641	164.6425	140.6476	150.6432	113.4654	97.5954	10.3867
0.5C	162.8671	140.4844	132.5169	149.1674	74.79097	54.6562	4.829311
	154.6344	132.6487	120.9687	142.6744	70.7983	50.1347	2.6987
	156.4678	135.4687	124.6746	137.3547	62.3547	52.3647	2.1335
1C	148.2142	99.59706	111.7479	139.5137	35.43078	22.20558	0
	144.6547	85.6874	102.5468	132.8412	32.4567	20.3774	0
	139.6874	90.467	90.5467	122.6143	21.5463	12.6741	0
2C	95.1244	50.64229	82.33707	85.26075	9.413808	2.698183	0
	96.8463	39.4349	75.6541	71.3741	5.7531	2.8543	0
	89.6449	40.6797	72.1354	75.8413	0	0	0

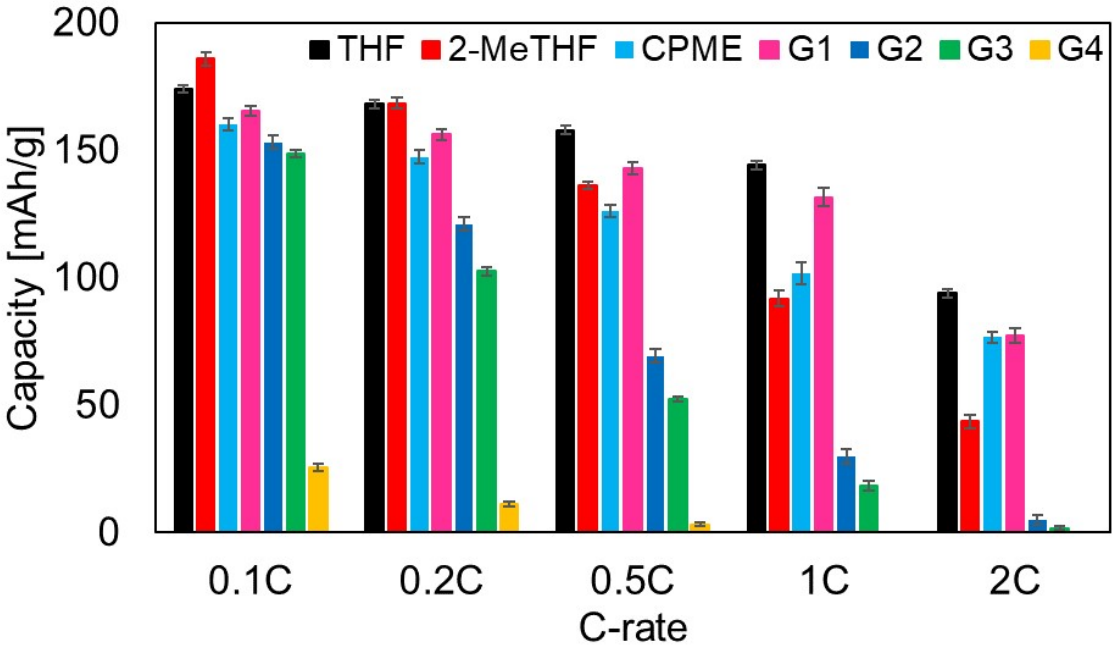

Fig. S2. Discharge capacities and corresponding standard deviation of ASSB cells with LPSCl SEs which wet-synthesized using conventional petrochemical solvent (THF) and various greener alternatives and sustainable solvents; 2-MeTHF, CPME, G1, G2, G3, and G4 for each C-rates from 0.1C to 2.0C