Electronic Supporting information

PEG-boron ester solid-state polymer electrolyte to fabricate Li_6PS_5Cl-rich composite for Li metal battery

Junghan Son*[a,c], Cedric Barcha[a,c], Sylvie Grugeon [b] , David Sicsic[c], Nicolas Besnard[c], Matthieu Courty[a], Matthieu Becuwe*[a,b]

S1. Reagents

Li_6PS_5Cl (Ampcera, particle size 100 microns) and LiTFSI (Sigma-Aldrich, 99.95%) were used in an Ar-filled glove box (O_2 < 1ppm, H_2O < 1ppm) directly without pretreatment. PEG average molecular weight 400g/mol (Alfa Aesar), 1Kg/mol (Acros Organics), 2Kg/mol (Fluka), and 3~3.6Kg/mol (Sigma-Aldrich) are dried under vacuum at 60°C for overnight before use. Tetrahydrofuran (Acros Organics, 99.5%, extra dry) and acetonitrile (Acros Organics, 99.5%, extra dry) were freshly opened and used without treatment.

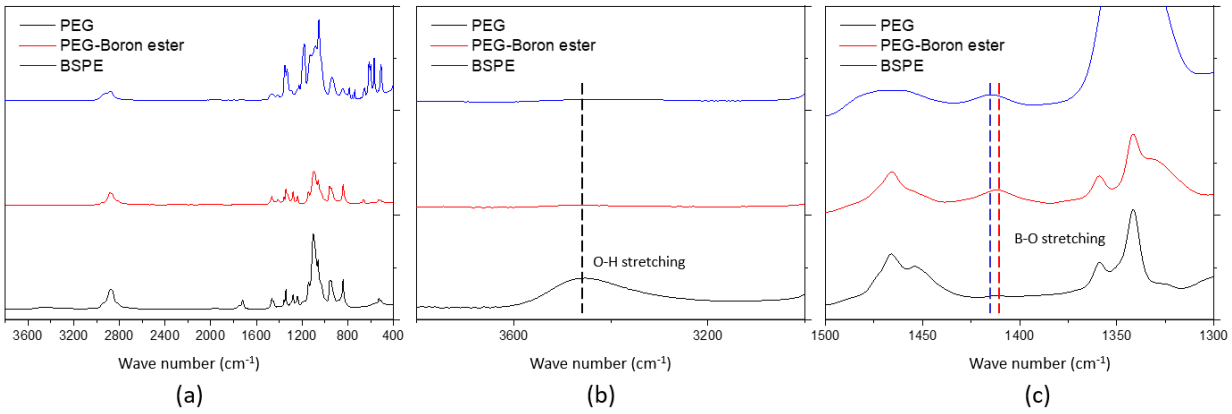
S2. Synthesis of PEG-boron ester.

BSPEs were synthesized with several sizes of PEG chains. The PEG was dissolved in acetonitrile (10 ml per 1g of PEG) under an Ar atmosphere. After PEG was dissolved, 2/3 molar equivalent of triethyl borate was added and heated to 80°C. The solution was stirred overnight under an Ar atmosphere. The solvent was removed by the rotor evaporator. The polymer was washed with ice-cold diethyl ether. The resulting white solid is dried again under vacuum at 60°C for 12 hours.

S3. Prepare BSPE

PEG-boron ester was dissolved in THF (1ml per 1g of PEG-boron ester) at 40°C, under Ar atmosphere. LiTFSI (3 molar equivalent of boron) was added, and the solution became viscous immediately. The solution was heated to 60°C and stirred for 6 hours. The solvent was removed under a vacuum at 40°C for 1 hour. The resulting yellowish-white solid was dried under a secondary vacuum at 80°C. The obtained BSPE was stored in the Ar-filled glove box.

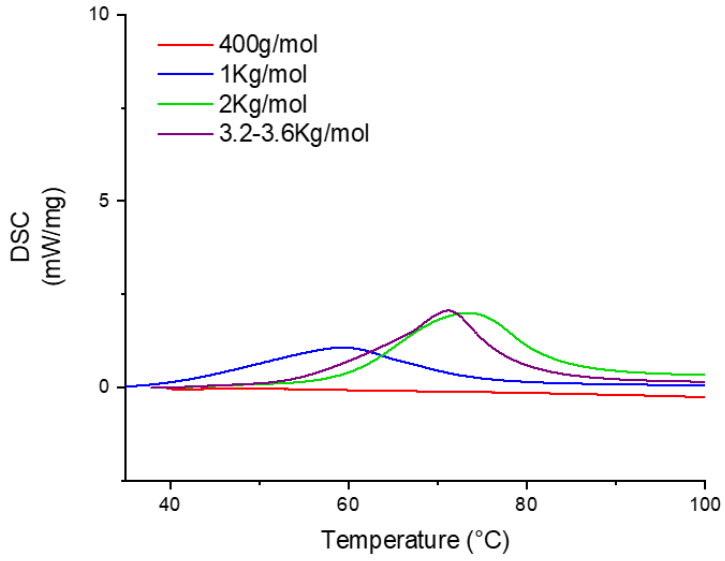
S4. FTIR spectra



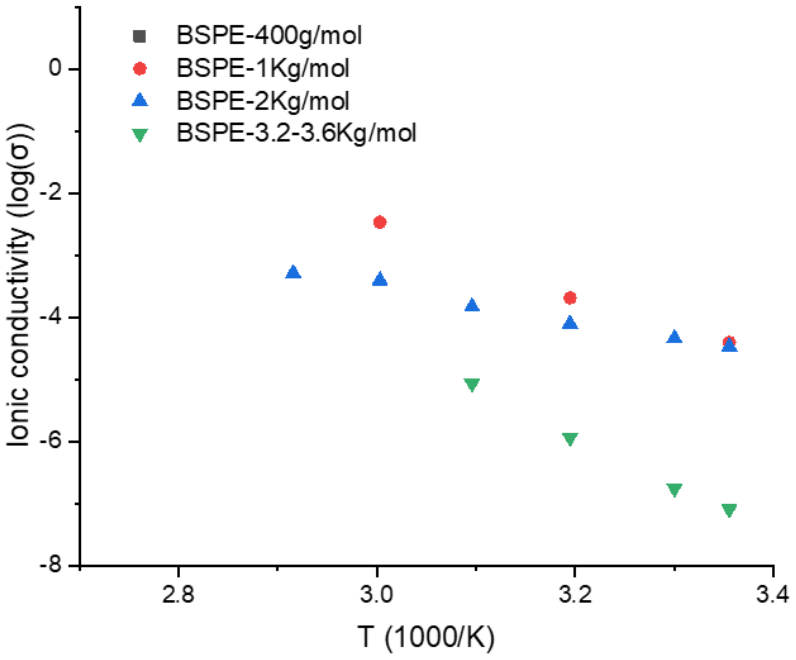
S4. FTIR spectra showed the progress of reaction (a). The O-H stretching absorption bands (3200-3600 cm^{-1}) are derived from PEG, it is disappeared after PEG-Boron ester (b). The B-O stretching absorption bands (1370-1420 cm^{-1}) are slightly blue-shifted after the LiTFSI addition, we assumed that there is interaction between TFSI anion and boron of PEG-Boron ester (c).

S5. Selection of BSPE

The molecular weight of PEG highly influences the mechanical properties and ionic conductivity of BSPE. From bibliographic and brief testing, we used PEG with 2Kg/mol to make the composites. (BSEP with 1Kg/mol of PEG has better ionic conductivity; however, its mechanical stability is not enough as an SPE)



2. DSC curves of PEG-Boron ester. The polymer with PEG (400g/mol) is a amorphous at room temperature.



3. The ionic conductivity of BSPE with various PEGs

S6. **Synthesis of composites**

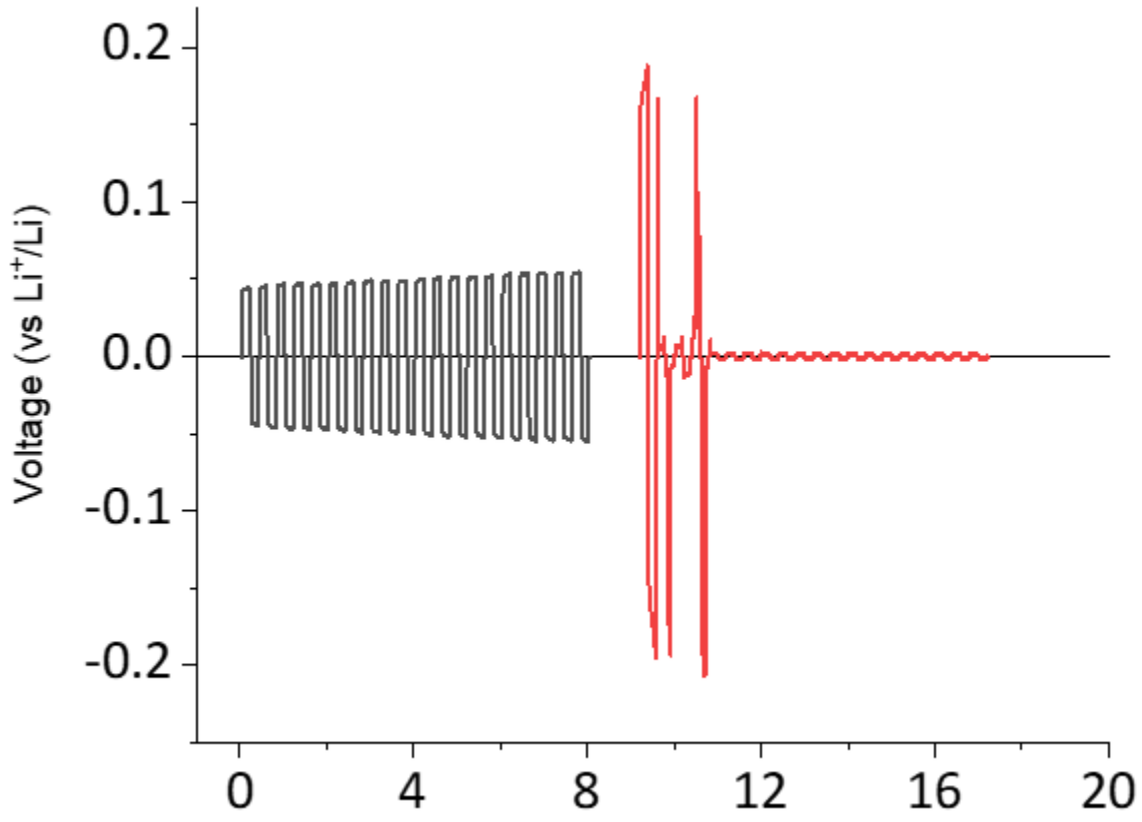
All the process was conducted in an Ar-filled glove box. The BSPE of PEG (2Kg/mol) was dissolved in dry acetonitrile, and Li_6PS_5Cl was added. The acetonitrile turned blue due to S_3^- anions from the reaction between Li_6PS_5Cl and acetonitrile. Acetonitrile is used because it influences less the ionic conductivity of Li_6PS_5Cl than other solvents such as THF, toluene, ethanol, and methanol[1]. The mixture is stirred vigorously for 5 minutes, the slurry was dried at room temperature. To remove a trace of acetonitrile that may exist in the BSEP, the resulting solid was dried under vacuum at 40°C overnight. The composite powder was pressed into pallets under 125 MPa (1 ton for 10mm diameter pallet) for 5 minutes.

S7. Potential evolution during cycling

We calculated how fast the potential increasing during cycling (table below). The potential increased faster in Li_6SP_5Cl, it became slower as the content of BSPE increased. The effect is greater in step 2, where Li striping/plating occurs faster.

	Step1 (0.05mA/cm²)	**Step2 (0.1mA/cm²)**
	1st → last cycle (mV)	1st → 9th → last cycle (mV)
	(Initial/last ×100)	(Initial/9th ×100)
Li_6SP_5Cl	25.0 →42.0	162→340→980

	(168)	(209)
Composite 5 wt.%	15.0→23.1	82.5→119→176
	(154)	(144)
Composite 15 wt.%	28.6→38.5	131→162→short circuit
	(134)	(122)



4. Second trial for the composite with 15 wt. % of BSPE

S8. SEM images