

Supporting information for:

High Rate Capability of Graphite Anode by Lithium Iodide Surface Modification for All-Solid-State Batteries

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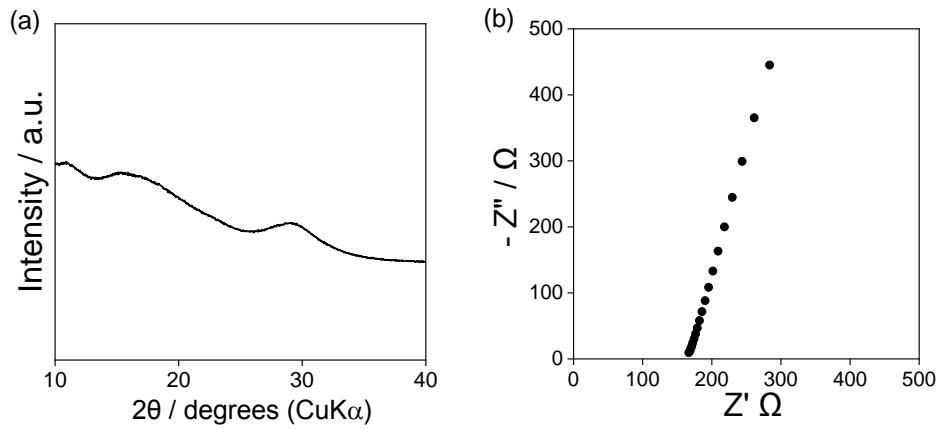


Figure S1. (a) XRD patterns and (b) Nyquist plot for prepared Li_3PS_4 .

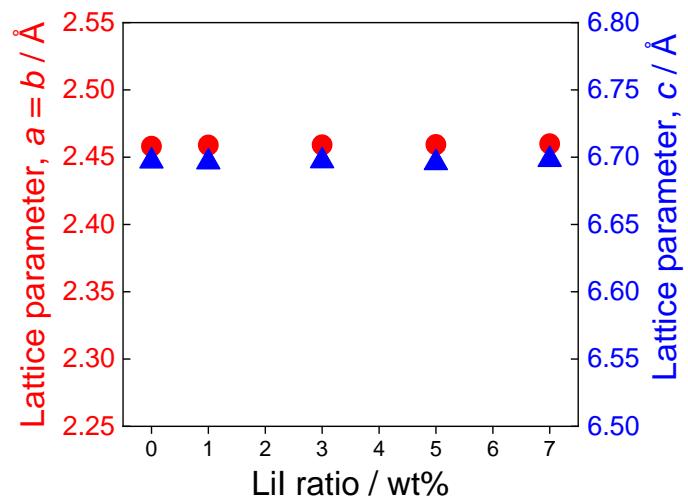


Figure S2. The lattice parameter of the graphite powders with Lithium iodide contents based on XRD patterns.

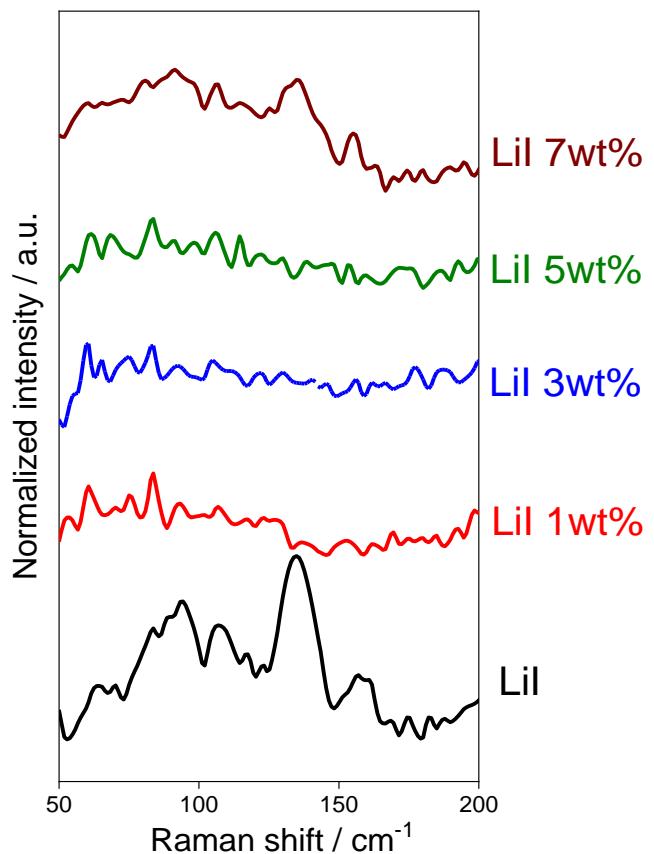


Figure S3. Raman spectra in the range from 50 to 200 cm⁻¹ corresponding to crystalline lithium iodide.

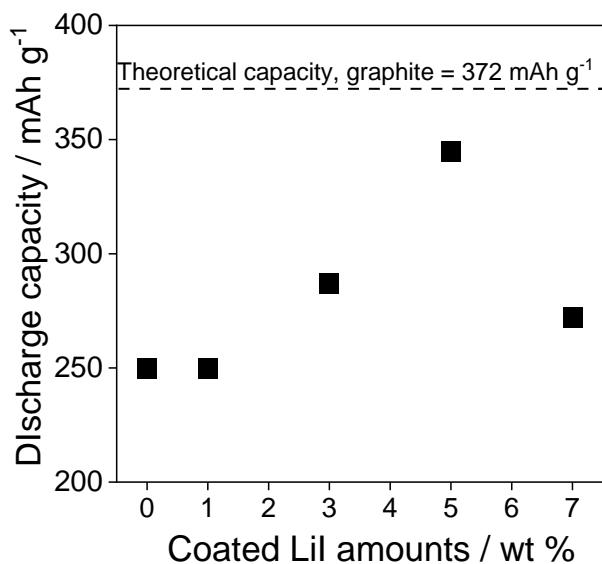


Figure S4. First discharge capacities for the LiI coated graphite under the current density of 0.10 mAcm⁻² (0.05 C) at 25 °C.

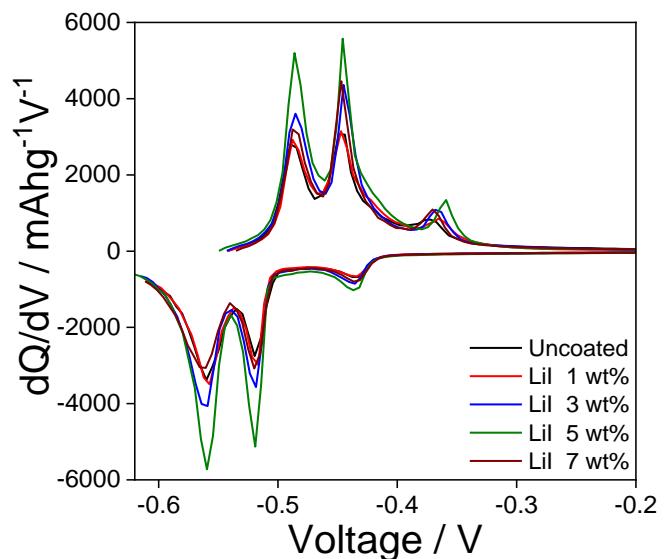


Figure S5. Total scale dQ/dV plots corresponding to 1st charge and discharge of each graphite composite with LiI amounts under the current density of 0.10 mA cm^{-2} (0.05 C) at 25°C .

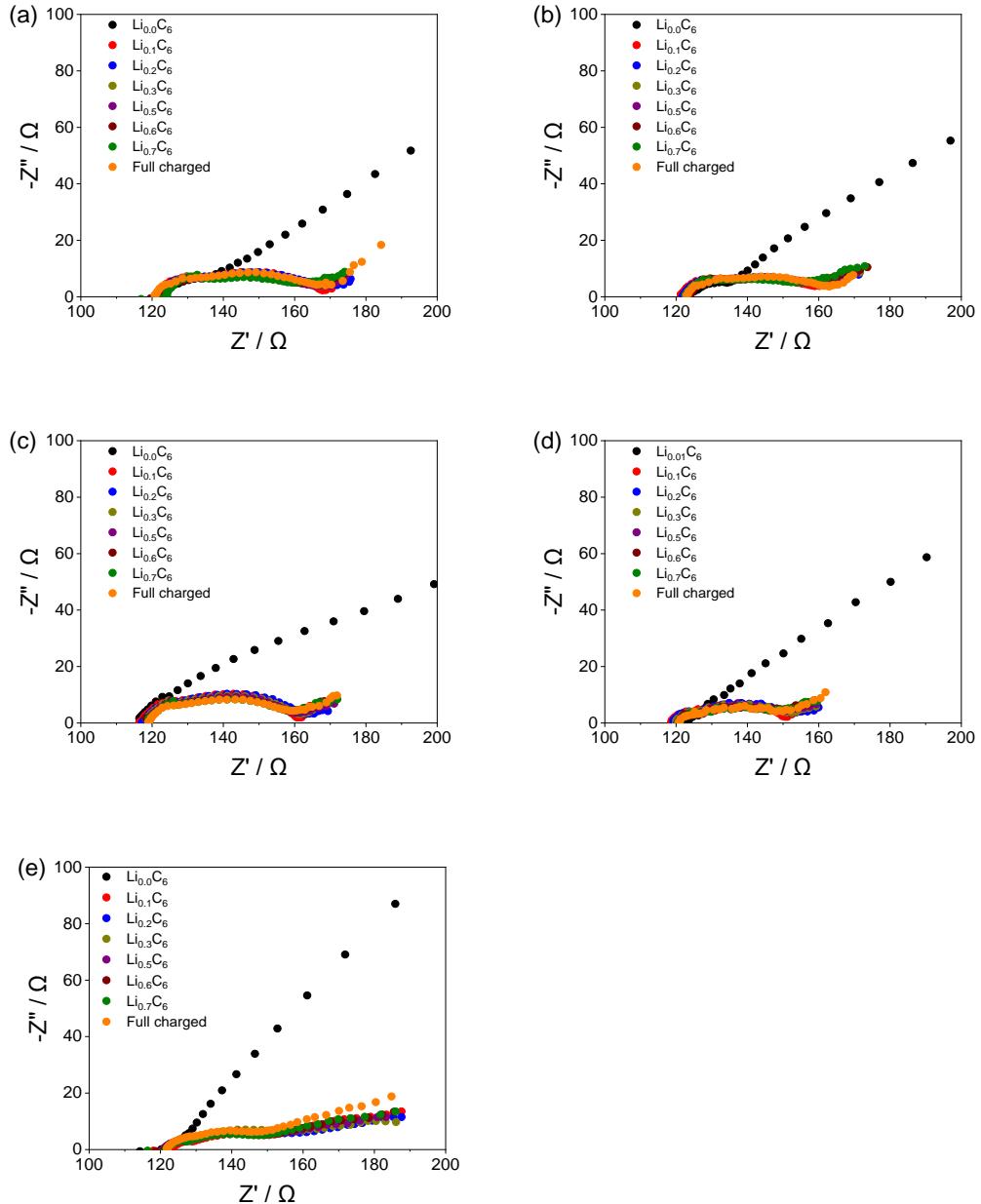
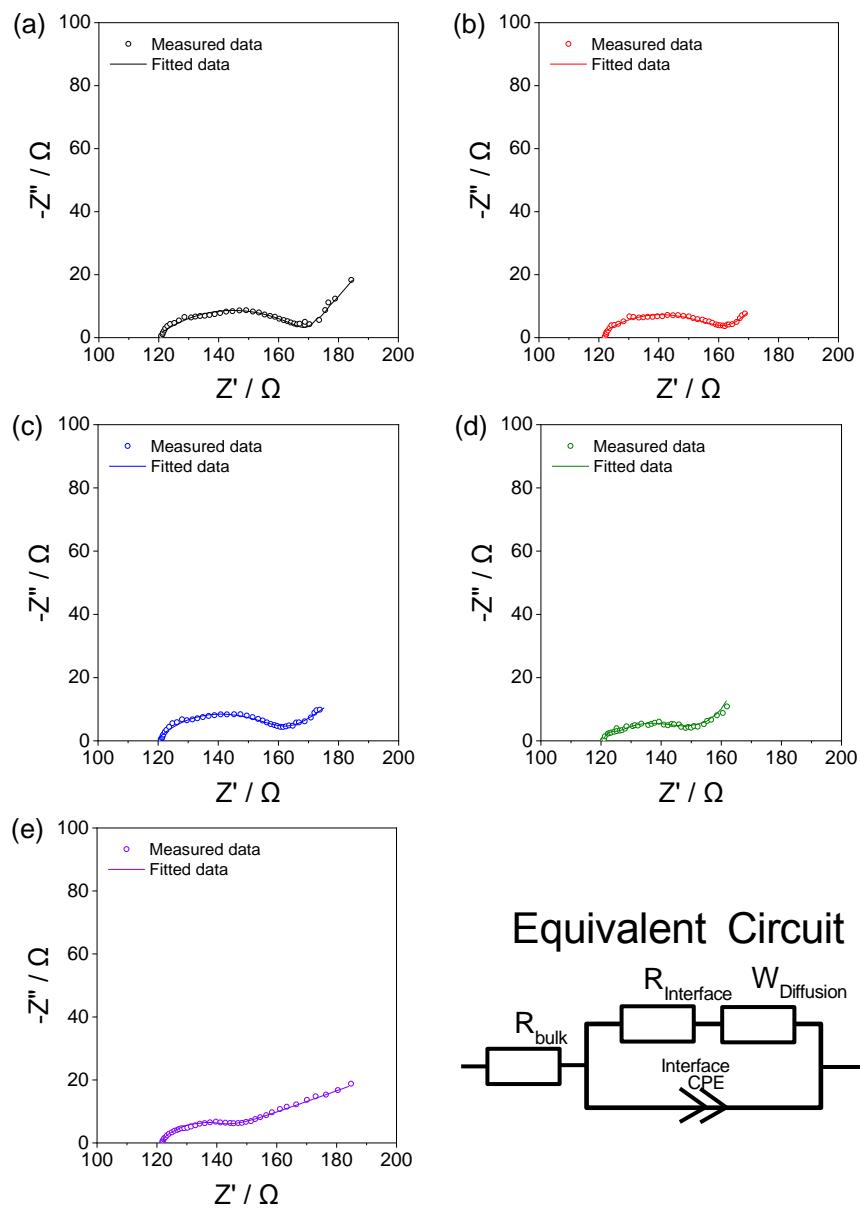


Figure S6. Nyquist plot behaviors during each lithiation process under 0.10 mA cm^{-2} (0.05 C) at 25°C , (a) Uncoated, (b) LiI 1 wt%, (c) LiI 3 wt%, (d) LiI 5 wt%, and (e) LiI 7 wt%.



Equivalent Circuit

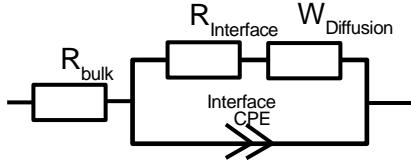


Figure S7. Fitted results for the uncoated (a) LiI 1 wt%, (b) LiI 3 wt%, (c) LiI 5 wt%, (d), and LiI 7 wt% (e) based on equivalent circuit model.

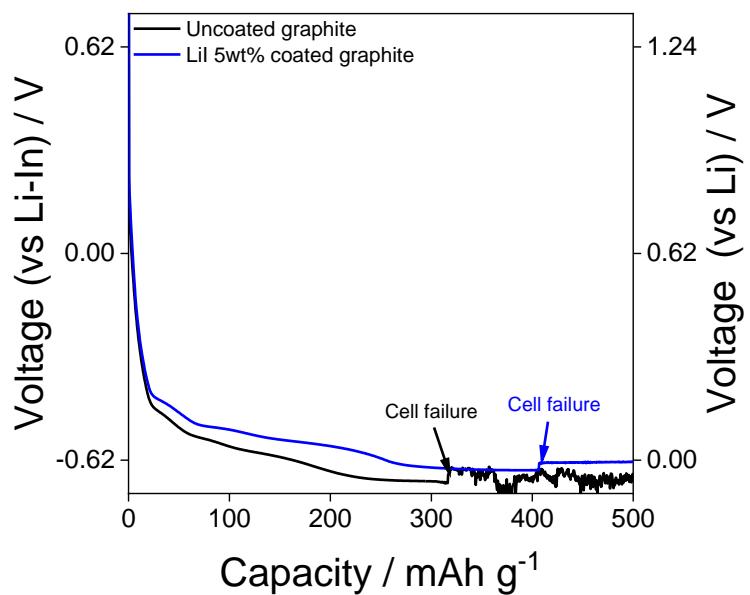


Figure S8. Voltage profiles of Li deposition for uncoated graphite composite (Black line) and LiI 5wt% coated graphite composite (blue line) under 0.23 mAcm^{-2} at 25°C .

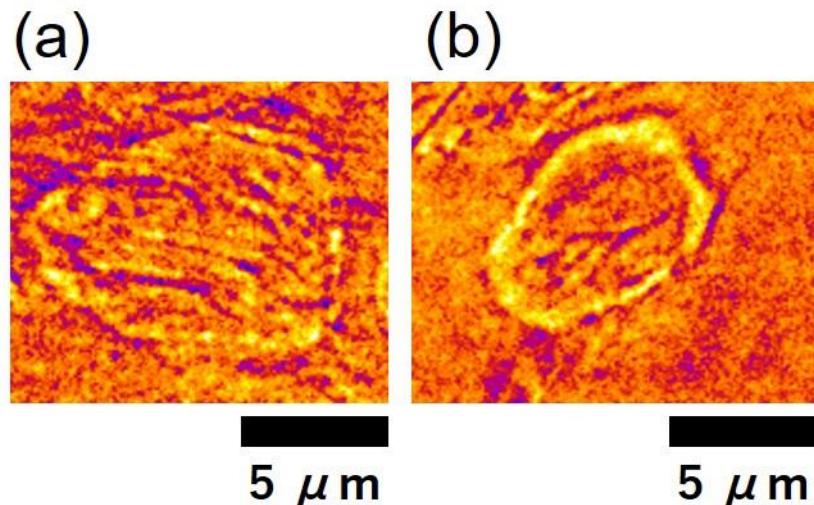


Figure S9. X-ray computed tomography images for (a) uncoated graphite and (b) LiI 5 wt% coated graphite. The X-ray CT measurements were carried out at BL20XU on the SPring-8 using a transmission X-ray microscope with 30 keV of a monochromatic X-ray beam. The X-ray beam was focused onto the sample using an elliptical glass capillary and the images were projected onto a scintillator using a Fresnel zone plate. The images were also recorded using a charge-coupled device camera (2048×2048 pixels). The image with a voxel size of 32 nm and a $65 \times 65 \mu\text{m}^2$ field of view was measured. 1800 radiographs were collected using an exposure time of 500 ms during 180° rotation.

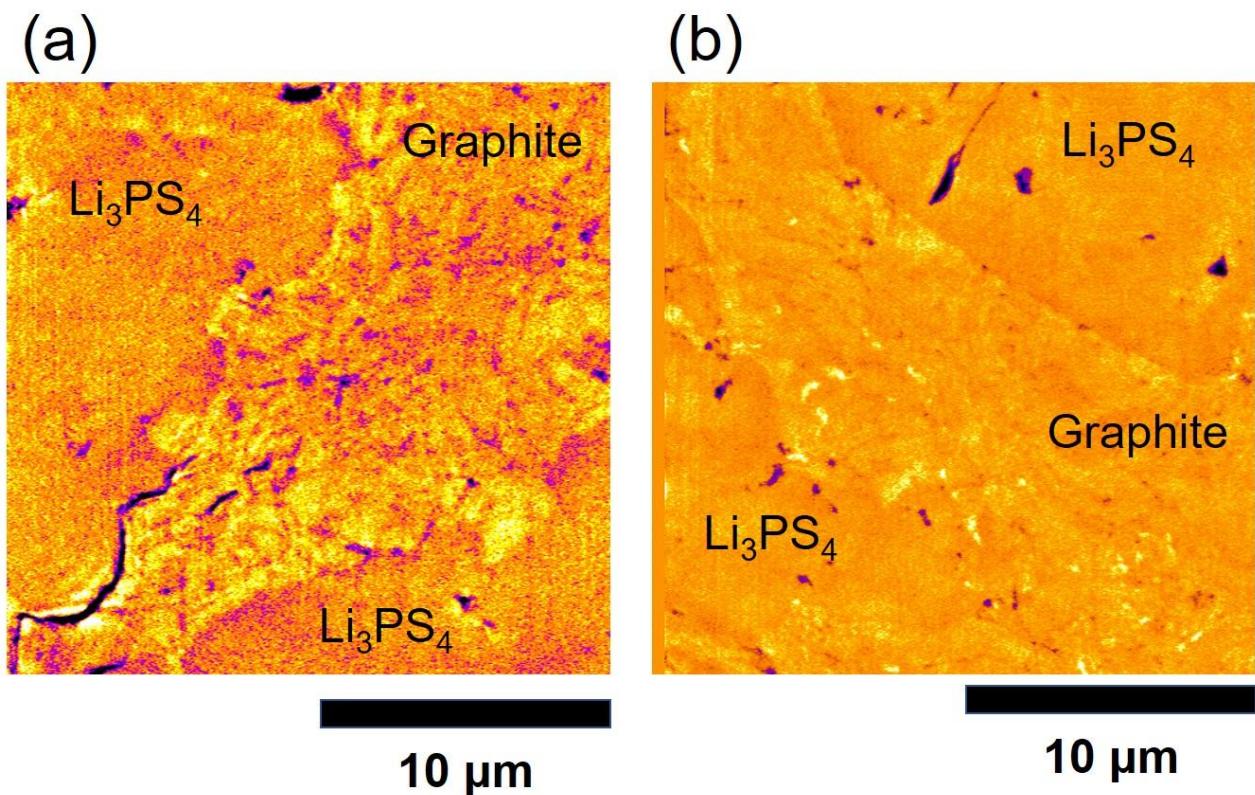


Figure S10. X-ray CT images for (a) uncoated graphite composite and (b) LiI 5wt% coated graphite composite after first charging. A large dark region, in which X-ray absorption coefficient is small, was observed along the interface between Li_3PS_4 and graphite in (a). This region may be attributed to decomposition products of Li_3PS_4 and/or formation of void associated with it, which in any case cause to poor lithium diffusion in the composite electrode. In contrast, the dark region along the interface between Li_3PS_4 and LiI coated graphite was not observed in the LiI 5wt% coated graphite composite (Figure S10(b)).

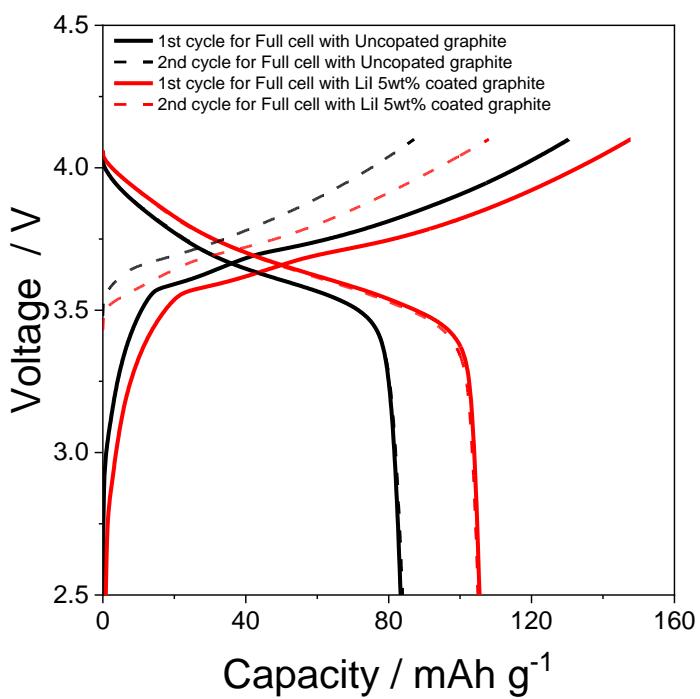


Figure S11. First cycle charge discharge of full cells corresponding to the uncoated graphite and LiI 5 wt% coated graphite under 0.05 C at 25 °C, in which the cell operation was conducted under the 0.05C and cut off voltage was 2.5 to 4.1 V. A cathode composite electrode was prepared by mixing with 1 wt% LiNbO₂ coated LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ (NMC) and Li₃PS₄ (LPS) and in the ratio of 70 wt% : 30 wt%.

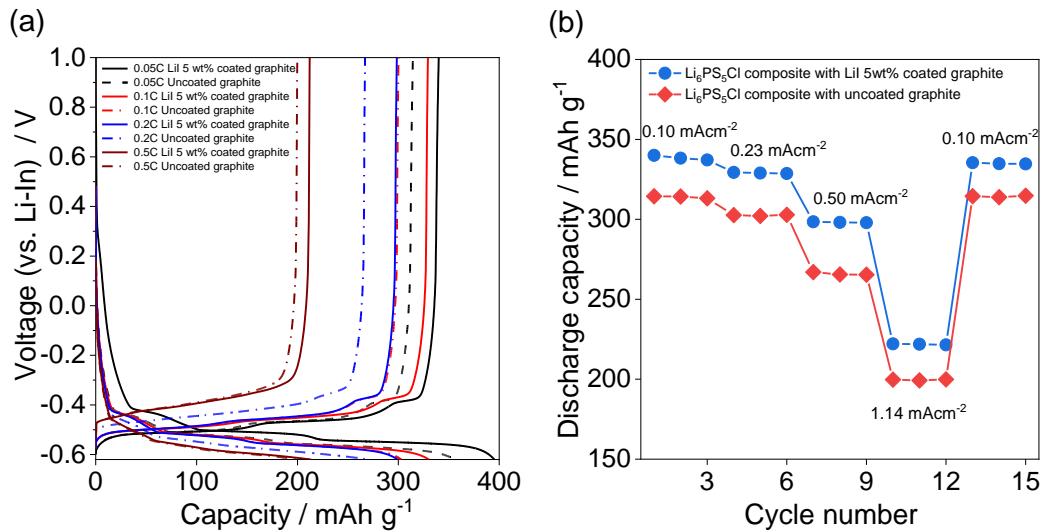


Figure S12. (a) First cycle charge-discharge for LiI 5wt% coated graphite composite with Li₆PS₅Cl, and (b) Rate performance compared with that with Li₃PS₄.

Table S1. Impedance parameters for each sample according LiI coating amounts based on the fitting process with obtained Nyquist plots.

Uncoated	Li _{0.1} C ₆	Li _{0.2} C ₆	Li _{0.3} C ₆	Li _{0.5} C ₆	Li _{0.6} C ₆	Li _{0.7} C ₆	Li _{0.75} C ₆
R _{bulk} / Ω	123.1	123.2	122.1	124.1	125.9	125.5	125.6
R _{interfacial} / Ω	45.09	45.22	45.44	47.09	48.06	50.79	52.3
CPE-T	0.000164	0.000133	0.000277	0.00377	0.00504	0.00529	0.00738
CPE-P	0.536	0.556	0.486	0.461	0.433	0.430	0.397
Capacitance / F	2.35 x 10 ⁻⁶	2.26 x 10 ⁻⁶	2.69 x 10 ⁻⁶	3.42 x 10 ⁻⁶	3.89 x 10 ⁻⁶	4.38 x 10 ⁻⁶	5.25 x 10 ⁻⁶
W-R	31.33	34.33	32.79	31.39	32.12	34.97	38.9
W-T	32.8	30.6	31.5	27.43	32.3	30.0	29.5
W-P	0.5	0.5	0.5	0.5	0.5	0.5	0.5

LiI 1 wt%	Li _{0.1} C ₆	Li _{0.2} C ₆	Li _{0.3} C ₆	Li _{0.5} C ₆	Li _{0.6} C ₆	Li _{0.7} C ₆	Li _{0.76} C ₆
R _{bulk} / Ω	121.2	121.6	122.1	122.9	123.5	124.5	125.2
R _{interfacial} / Ω	38.75	40.85	41.96	41.48	41.63	41.88	42.20
CPE-T	0.00301	0.00342	0.00378	0.00392	0.00414	0.00396	0.00327
CPE-P	0.515	0.501	0.486	0.479	0.470	0.473	0.496
Capacitance / F	4.59 x 10 ⁻⁶	4.87 x 10 ⁻⁶	4.72 x 10 ⁻⁶	4.45 x 10 ⁻⁶	4.26 x 10 ⁻⁶	4.12 x 10 ⁻⁶	4.18 x 10 ⁻⁶
W-R	33.9	31.6	27.7	29.5	29.2	34.2	36.0
W-T	28.7	20.7	25.7	25.9	25.8	27.4	28.5
W-P	0.5	0.5	0.5	0.5	0.5	0.5	0.5

LiI 3 wt%	Li _{0.1} C ₆	Li _{0.2} C ₆	Li _{0.3} C ₆	Li _{0.5} C ₆	Li _{0.6} C ₆	Li _{0.7} C ₆	Li _{0.84} C ₆
R _{bulk} / Ω	120.1	120.2	117.3	118.5	119.8	121.1	122.5
R _{interfacial} / Ω	29.71	32.04	32.36	32.77	33.76	33.90	34.02
CPE-T	0.000480	0.000565	0.000479	0.000377	0.000443	0.000376	0.000349
CPE-P	0.442	0.431	0.449	0.461	0.455	0.472	0.478
Capacitance / F	2.26 x 10 ⁻⁶	2.82 x 10 ⁻⁶	2.86 x 10 ⁻⁶	2.20 x 10 ⁻⁶	2.86 x 10 ⁻⁶	2.84 x 10 ⁻⁶	2.75 x 10 ⁻⁶
W-R	24.5	24.6	23.9	25.3	25.9	29.5	31.4
W-T	13.4	12.7	12.1	12.4	13.0	13.9	13.8
W-P	0.5	0.5	0.5	0.5	0.5	0.5	0.5

LiI 5 wt%	Li _{0.1} C ₆	Li _{0.2} C ₆	Li _{0.3} C ₆	Li _{0.5} C ₆	Li _{0.6} C ₆	Li _{0.7} C ₆	Li _{0.96} C ₆
R _{bulk} / Ω	118.2	119.3	119.1	119.9	119.1	119.7	120.3
R _{interfacial} / Ω	24.54	25.43	25.87	24.92	25.45	25.07	25.16
CPE-T	0.00131	0.00172	0.00169	0.00226	0.00270	0.00293	0.00187
CPE-P	0.442	0.402	0.402	0.366	0.344	0.333	0.387
Capacitance / F	1.70 x 10 ⁻⁵	1.63 x 10 ⁻⁵	1.60 x 10 ⁻⁵	1.52 x 10 ⁻⁵	1.64 x 10 ⁻⁵	1.59 x 10 ⁻⁵	1.49 x 10 ⁻⁵
W-R	23.3	20.9	24.0	26.1	23.5	26.5	28.4
W-T	9.63	9.01	8.5	7.56	7.27	6.61	6.84
W-P	0.5	0.5	0.5	0.5	0.5	0.5	0.5

LiI 7 wt%	Li _{0.1} C ₆	Li _{0.2} C ₆	Li _{0.3} C ₆	Li _{0.5} C ₆	Li _{0.6} C ₆	Li _{0.7} C ₆	Li _{0.81} C ₆
R _{bulk} / Ω	119.7	120.2	120.6	121.8	122.0	122.8	123.5
R _{interfacial} / Ω	33.2	36.1	36.8	37.8	36.4	36.4	39.0
CPE-T	0.000890	0.000753	0.000992	0.00123	0.00165	0.00164	0.00213
P	0.441	0.482	0.435	0.400	0.396	0.383	0.329
Capacitance / F	1.03 x 10 ⁻⁵	1.56 x 10 ⁻⁵	1.34 x 10 ⁻⁵	1.24 x 10 ⁻⁵	2.47 x 10 ⁻⁵	1.06 x 10 ⁻⁵	1.33 x 10 ⁻⁵

W-R	109.5	104.2	94.96	102	99.31	102.4	97.62
W-T	14.4	13.8	14.9	15.5	15.8	14.4	17.9
W-P	0.5	0.5	0.5	0.5	0.5	0.5	0.5