Supporting Information

Inorganic-Organic Hybrid Solid Electrolytes in the Tetramethylammonium Iodide-LiI-Li$_2$S-P$_2$S$_5$ System for All-solid-state Lithium Batteries

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**Experimental procedure for the results reported in supporting information**

The morphology and elemental mapping images of the sulfide solid electrolyte particles were observed by scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) performed on JSM-IT500. A glove box was attached to the SEM, and N_2 was introduced before observation until the dew point value reached approximately -20 ℃.

The electronic conductivities were measured by direct current polarization under the 0.1 V, -0.1 V, 0.2 V, -0.2 V, 0.3 V, -0.3 V applying voltage on the SUS / (1-x) $Li_7P_2S_8I \cdot xTMAI$ (x = 0, 0.2) (100mg)/SUS cells. The sample preparation procedure and the device are the same as for ionic conductivity measurement.

Li//Li symmetrical cells assembled with (1-x) $Li_7P_2S_8I \cdot xTMAI$ (x = 0, 0.2) were evaluated. The electrolyte (100mg) was pressed at 25 MPa for 5min, and then two lithium foils were pressed at 8 MPa for 2min on both sides of the electrolyte pellet (Φ10mm). The measurement device is the same as the charge/discharge curve device.
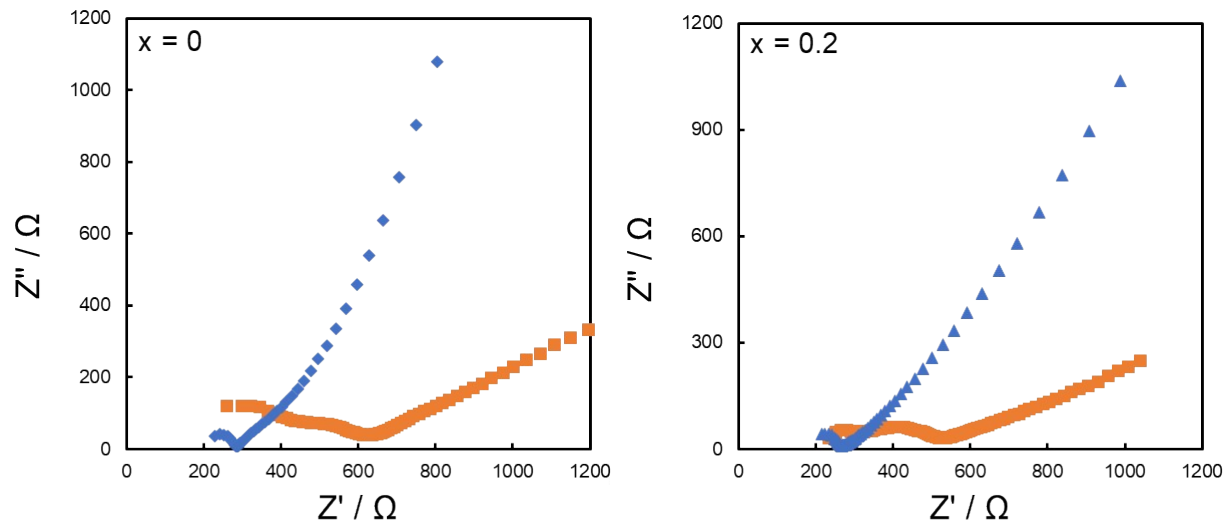
x = 0

P-K S-K I-L

IMG

I-L

P-K

S-K

x = 0.2

P-K S-K I-L

IMG

I-L

P-K

S-K
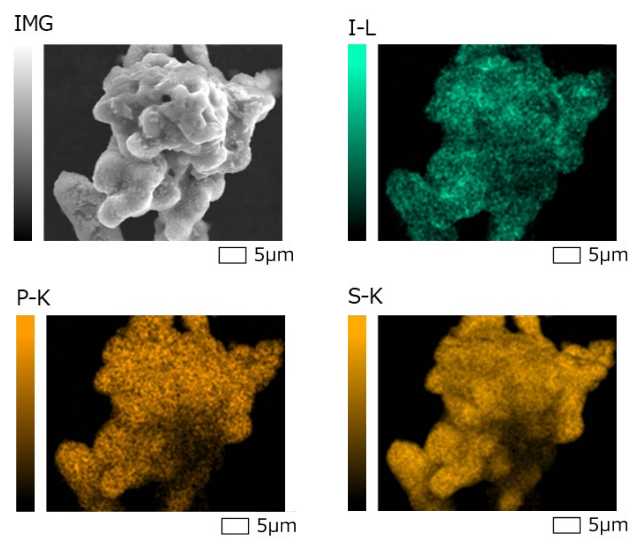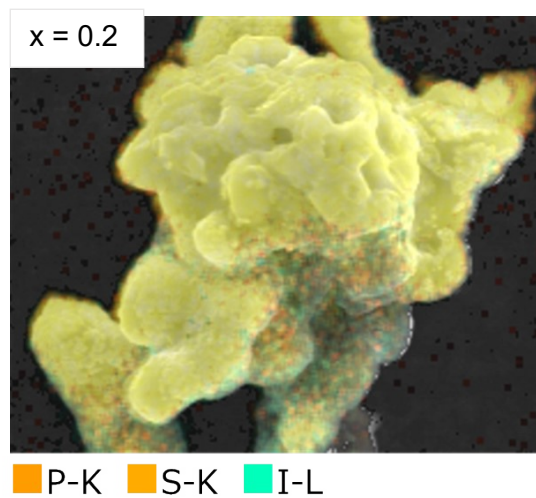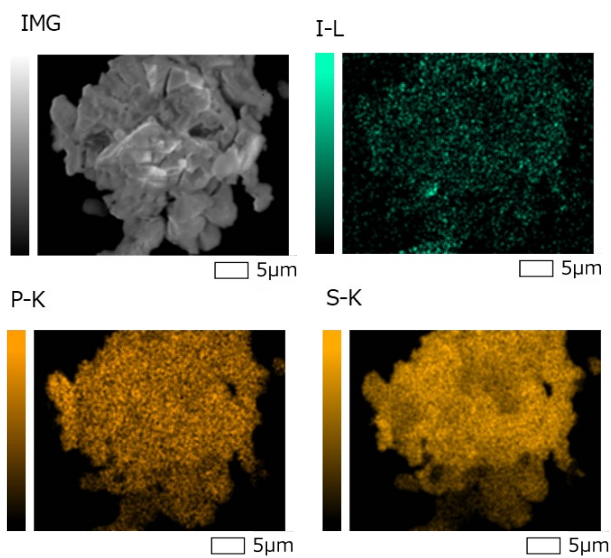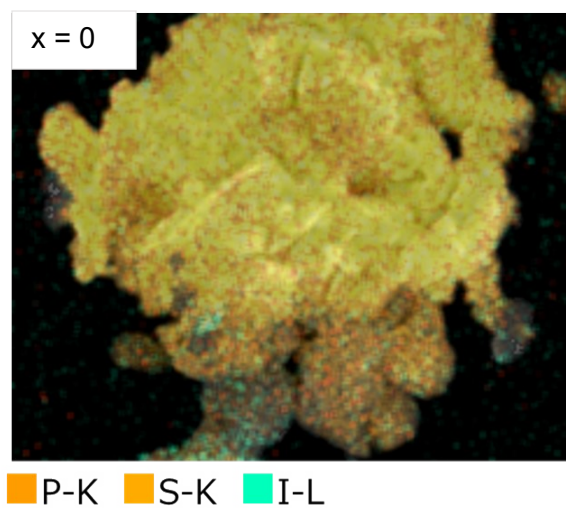
Figure S1. The EDS images of (1-x) $Li_7P_2S_8I \cdot x$ TMAI (x = 0, 0.2) after ball milling.
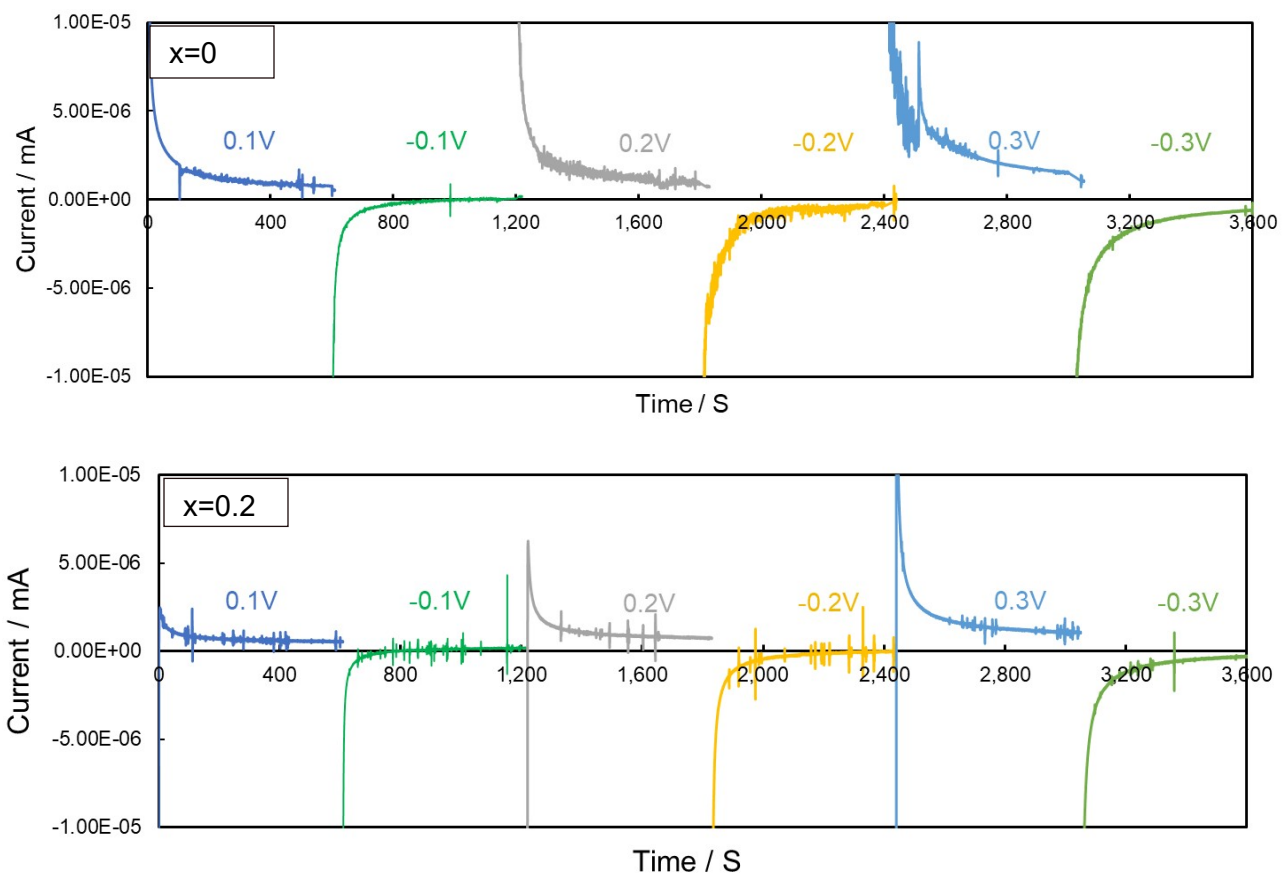
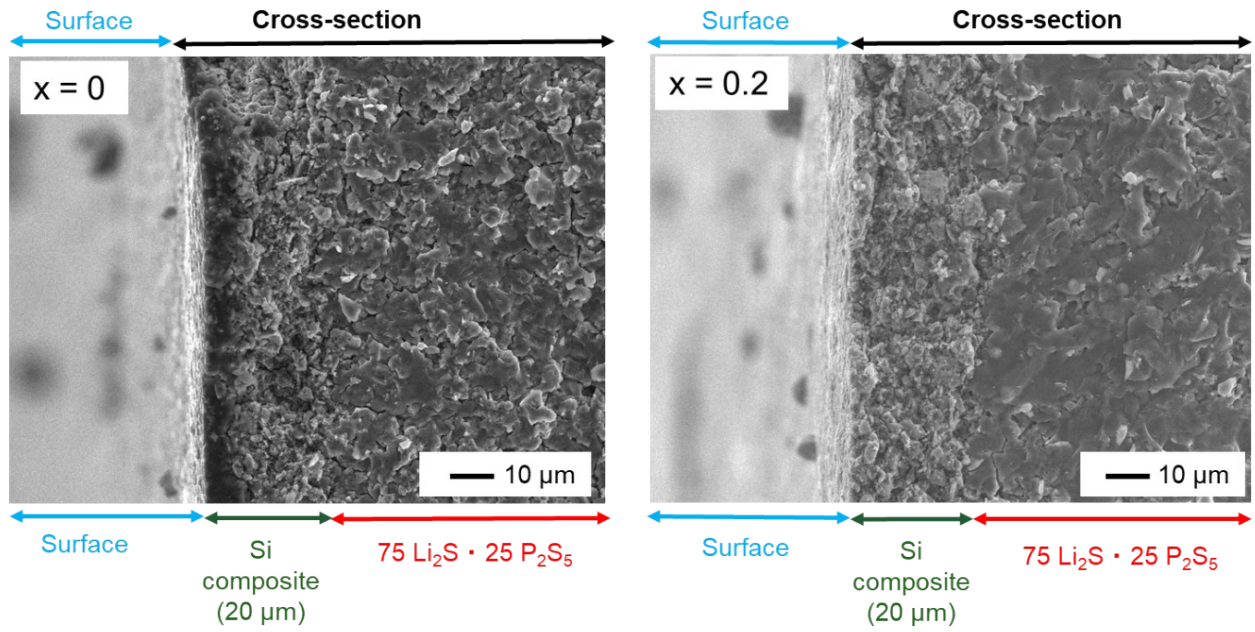**Figure S2.** Direct-current polarization curves of SUS / (1-x) $Li_7P_2S_8I \cdot xTMAI$ (x = 0, 0.2) /SUS cells.
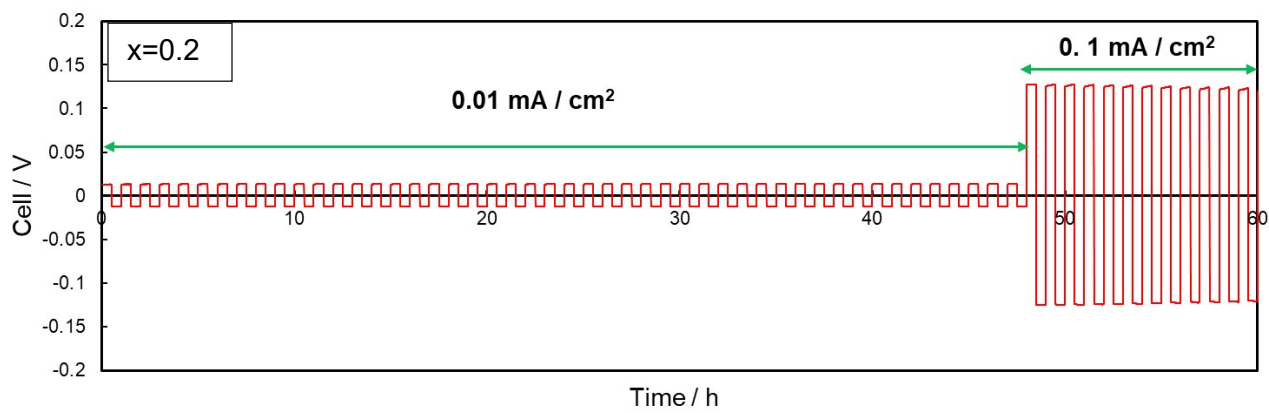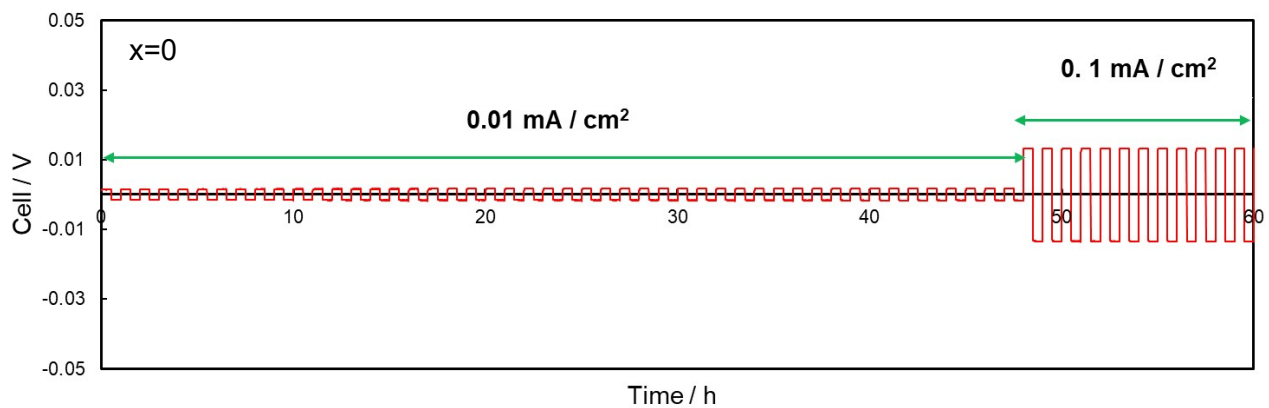
Figure S3. Cycling performances of Li / (1-x) $Li_7P_2S_8I$ ·xTMAI / Li symmetrical cells of x = 0 and x = 0.2 samples.
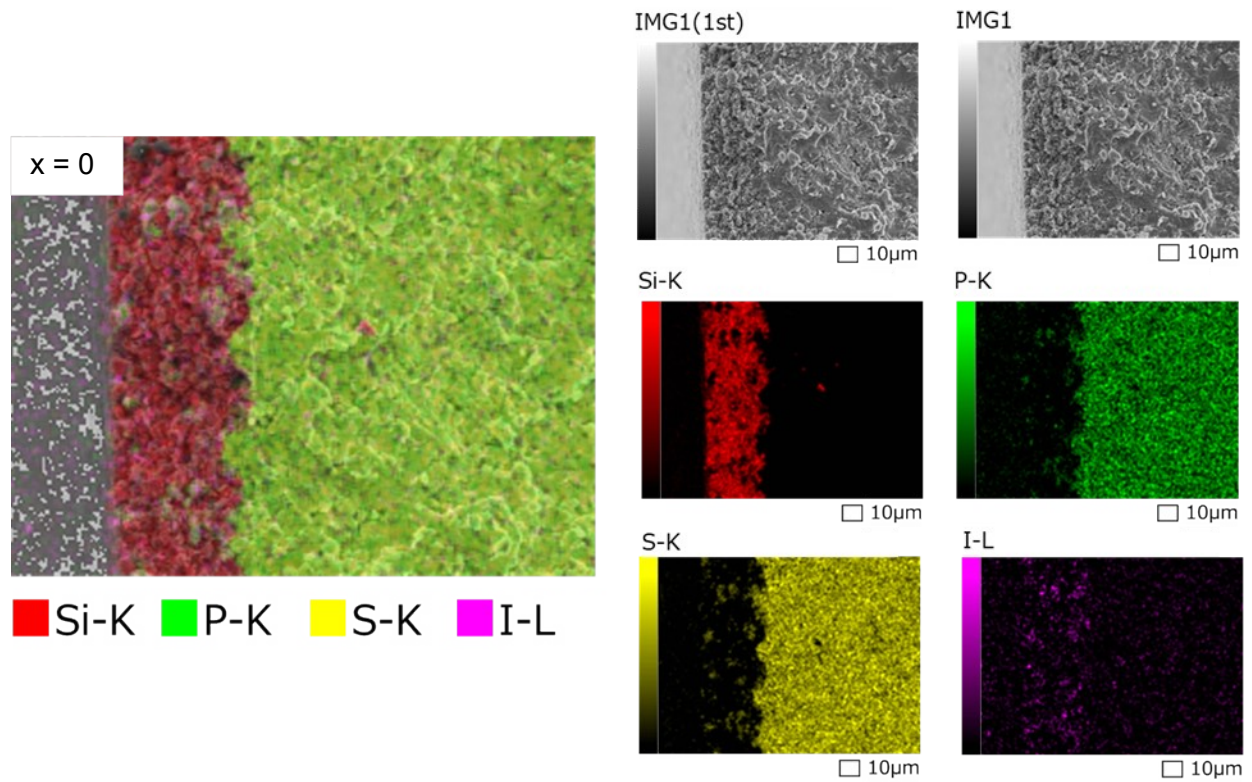
Figure S4. The Nyquist plots of the cell using (1-x) $Li_7P_2S_8I \cdot x$ TMAI (x = 0, 0.2) in the composite electrode, before and after 10 cycles.
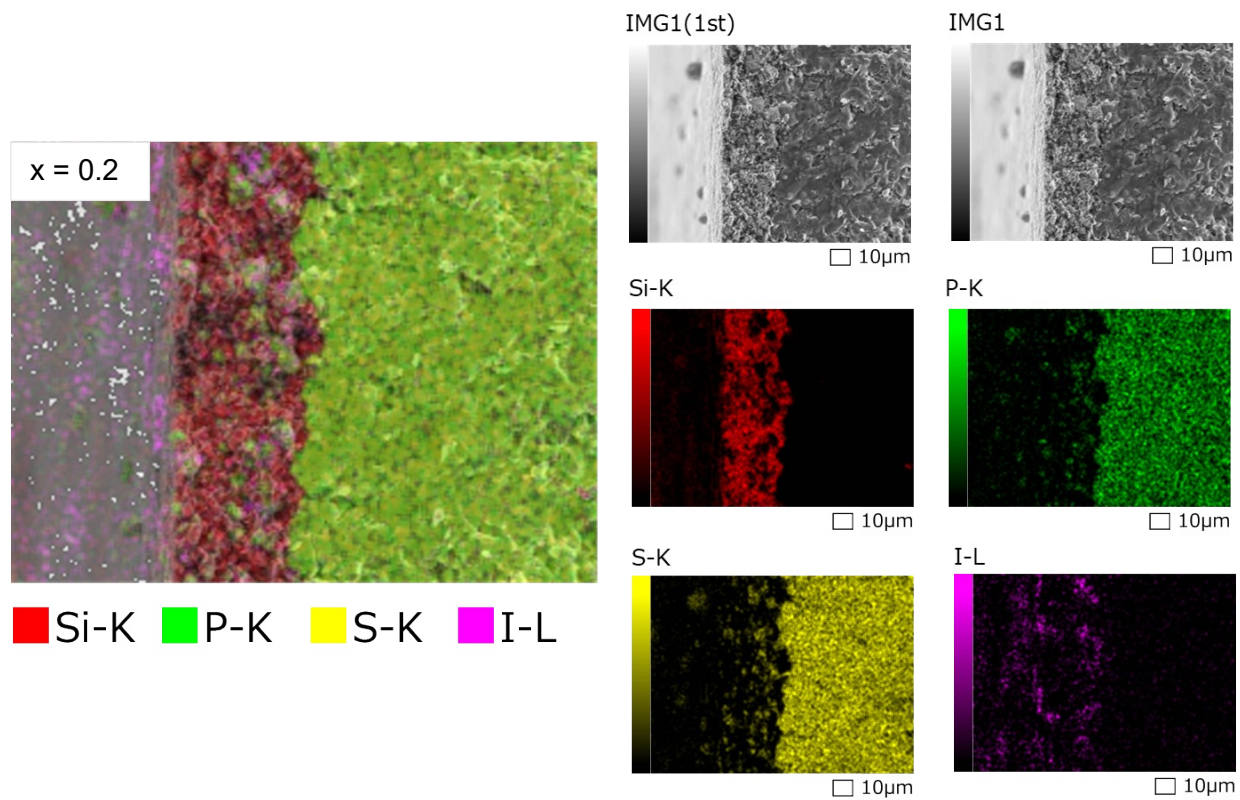
(a)

(b)

Figure S5. The cross-sectional (a) SEM and (b) EDS images before cycling of Li_xSi / $75Li_2S\cdot25P_2S_5$ / Li-In cells using $(1-x)$ $Li_7P_2S_8I\cdot xTMAI$ (x = 0, 0.2) in the LixSi electrode composite.

(a)

x = 0
Surface | Cross-section

Surface | Si composite (50 μm) | 75 Li$_2$S・25 P$_2$S$_5$

x = 0.2
Surface | Cross-section

Surface | Si composite (20 μm) | 75 Li$_2$S・25 P$_2$S$_5$

(b)

x = 0

Si-K P-K S-K I-L

IMG1(1st)

IMG1

Si-K

P-K

S-K

I-L

x = 0.2

Si-K P-K S-K I-L

IMG1(1st)

20μm

IMG1

20μm

Si-K

20μm

P-K

20μm

S-K

20μm

I-L

20μm
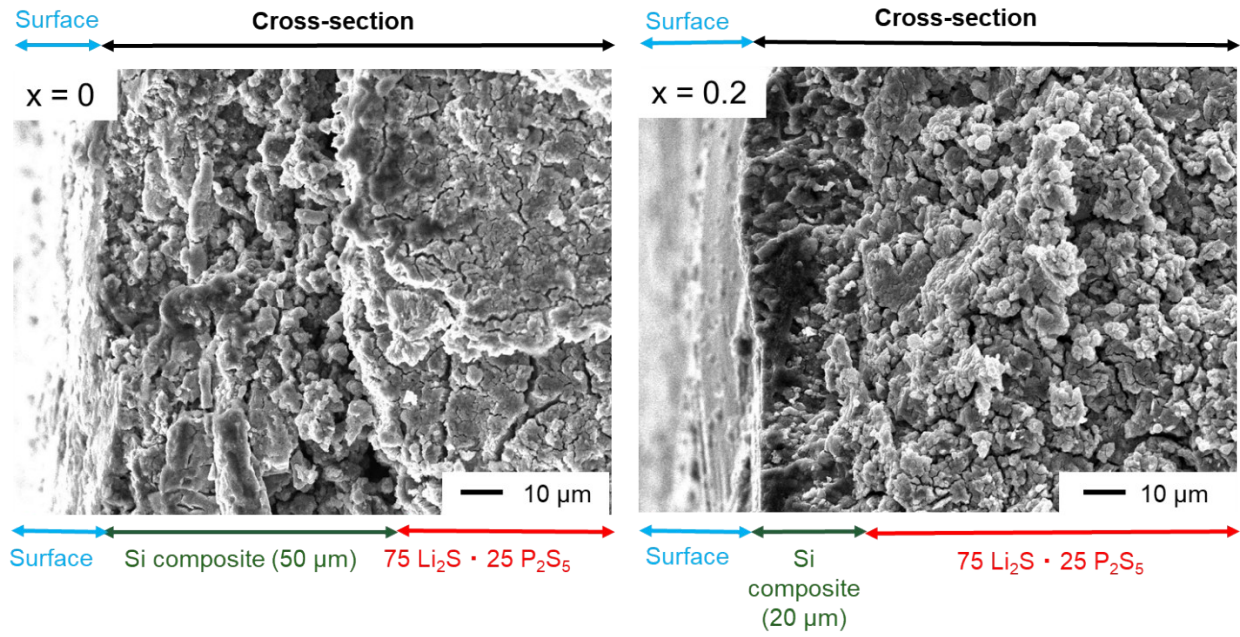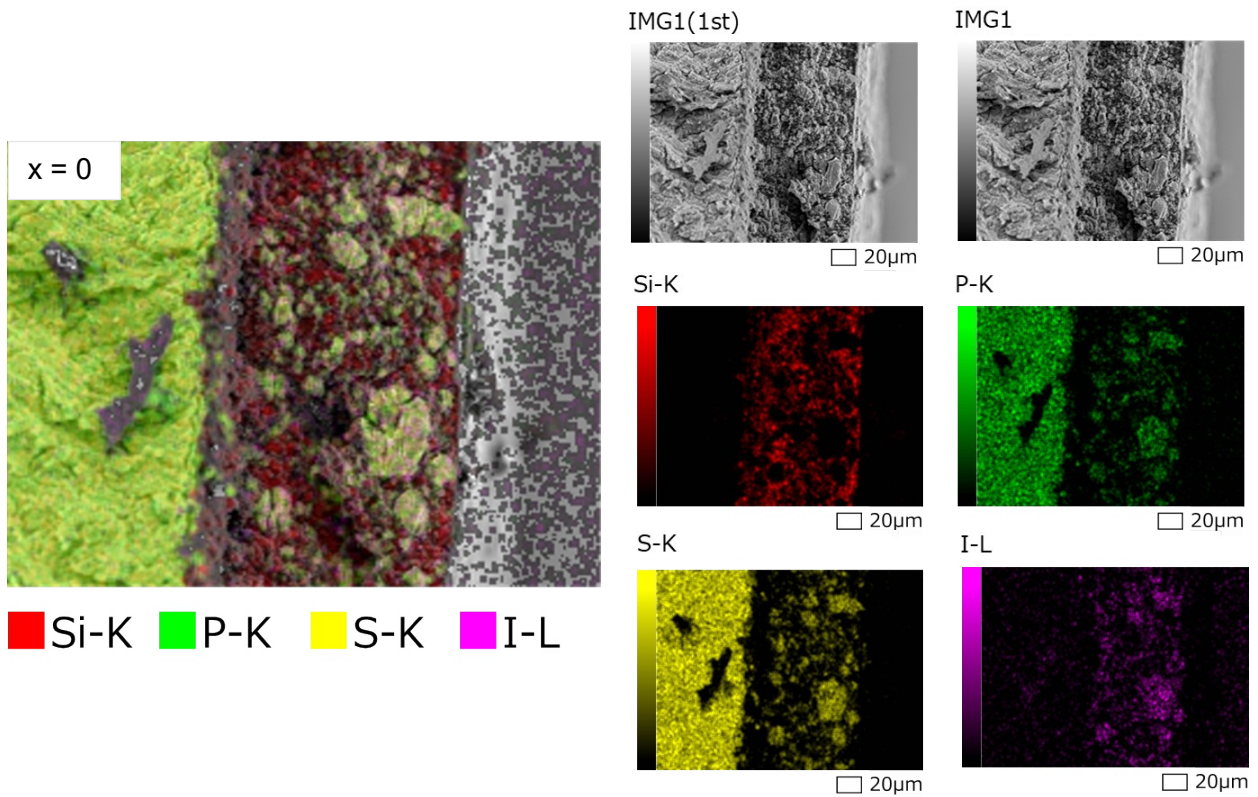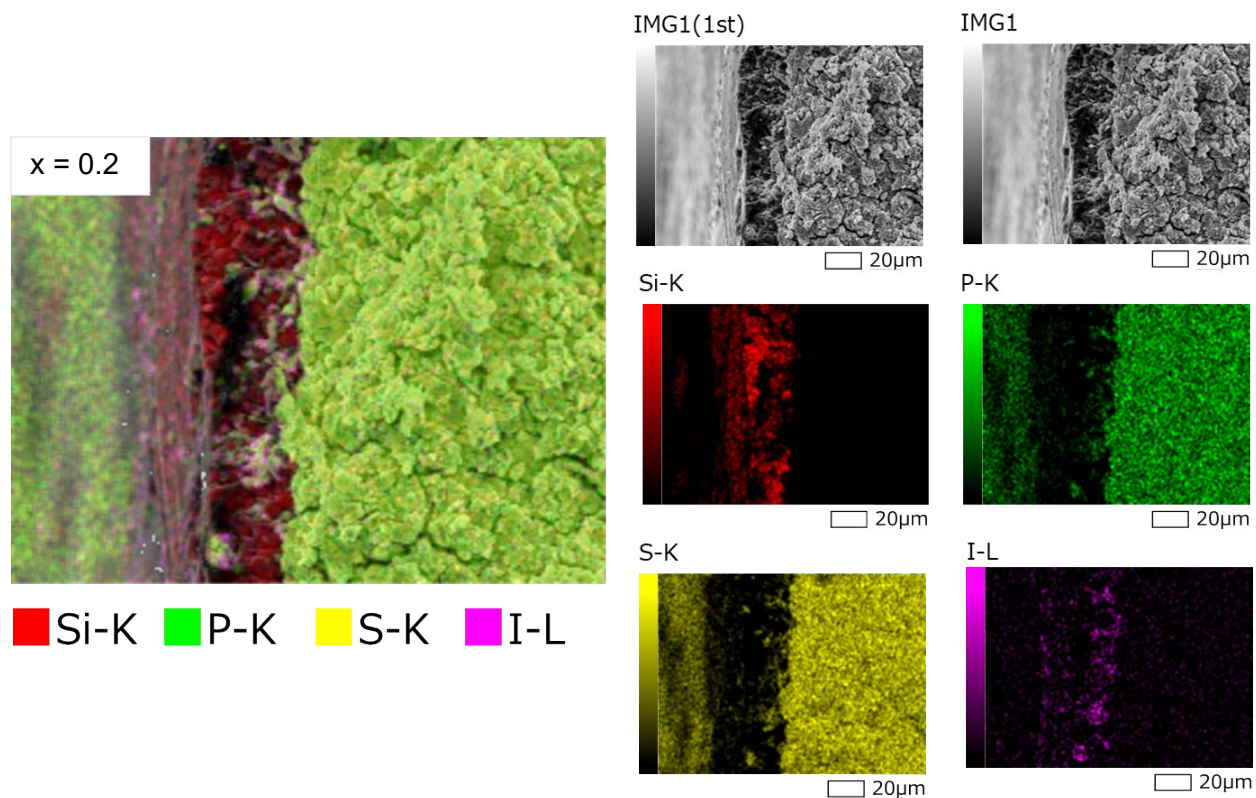
Figure S6. The cross-sectional (a) SEM and (b) EDS images after two cycles of LixSi / 75Li$_2$S·25P$_2$S$_5$ / Li-In cells using (1-x) Li$_7$P$_2$S$_8$I·xTMAI (x = 0, 0.2) in the LixSi electrode composite.