

## Supporting information

# Influence of compositing conditions for Si-composite negative electrodes in sulfide-type all-solid-state lithium-ion batteries

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## 1. Experimental

### 1.1 Preparation of the solid electrolyte and Si composite electrodes

#### 1.1.0 Starting materials

Reagent-grade  $\text{Li}_2\text{S}$  (Mitsuwa Chem),  $\text{P}_2\text{S}_5$  (Sigma Aldrich), LiI (Sigma Aldrich), Si (<100 nm nanopowder, Sigma Aldrich), and activated carbon (AC, Kansai Coke and Chemicals Co., Ltd.) were used as starting materials.

#### 1.1.1 Preparation of $\text{Li}_3\text{PS}_4\text{-LiI}$ as a solid electrolyte

$\text{Li}_3\text{PS}_4\text{-LiI}$  (SE) was prepared by mechanical milling using a planetary ball-mill apparatus (Premium Line P-7, Fritsch Co.); a  $\text{ZrO}_2$  pot and 160 g of  $\text{ZrO}_2$  balls (4 mm diameter) were used in the mechanical milling treatment in Ar atmosphere to mix  $\text{Li}_2\text{S}$ ,  $\text{P}_2\text{S}_5$ , and LiI (molar ratio = 3:1:2) with a rotational speed of 500 rpm for 10 h.<sup>1</sup>

#### 1.1.2 Preparation of Si composite samples for confirming Si-SE reaction

For confirming the Si-SE reaction, Si composite samples were prepared by mechanical milling using a planetary ball mill apparatus. Mechanical milling was performed in a  $\text{ZrO}_2$  pot using  $\text{ZrO}_2$  balls (ball diameter: 5 mm; total mass: 40 g) in Ar atmosphere. The preparation conditions are summarized in Table S1. Here, “L” and “H” in sample name mean low-speed treatment (100rpm) and high-speed treatment (370rpm), respectively.

Table S1. Ball milling conditions for Si composite samples for confirming the Si-SE reaction.

Samples	Component ratio (wt%)	Rotation speed / rpm	Treatment time / h
Si-H	Si = 100	370	2
(Si-SE)-H	Si:SE=50:40	370	2
(Si-SE)-L	Si:SE=50:40	100	2
(Si-AC)-H	Si:AC=50:10	370	2

### 1.1.3 Preparation of Si composite electrodes

Si composite electrodes were prepared by mechanical milling using a planetary ball mill apparatus in a manner similar to the preparation of Si composite samples for confirming the Si–SE reaction. Mechanical milling was performed in a ZrO<sub>2</sub> pot using ZrO<sub>2</sub> balls (ball diameter: 5 mm; total mass: 40 g) in Ar atmosphere. The preparation conditions are summarized in Table S2.

Table S2. Ball milling conditions for Si composite electrodes.

Samples	1st step			2nd step		
	Component ratio (wt%)	Rotation speed / rpm	Treatment time / h	Component ratio (wt%)	Rotation speed / rpm	Treatment time / h
(Si-SE-AC)-H	Si:SE:AC=50:40:10	370	2	-	-	-
(Si-SE-AC)-L	Si:SE:AC=50:40:10	100	2	-	-	-
{(Si-SE)-AC}-HL	Si:SE=50:40	370	2	(Si:SE):AC=(50:40):10	100	2
{(Si-AC)-SE}-HL	Si:AC=50:10	370	2	(Si:AC):SE=(50:10):40	100	2
{(Si-SE)-SE-AC}-HL	Si:SE=50:20	370	2	(Si:SE):SE:AC=(50:20):20:10	100	2

## 2. Characterizations

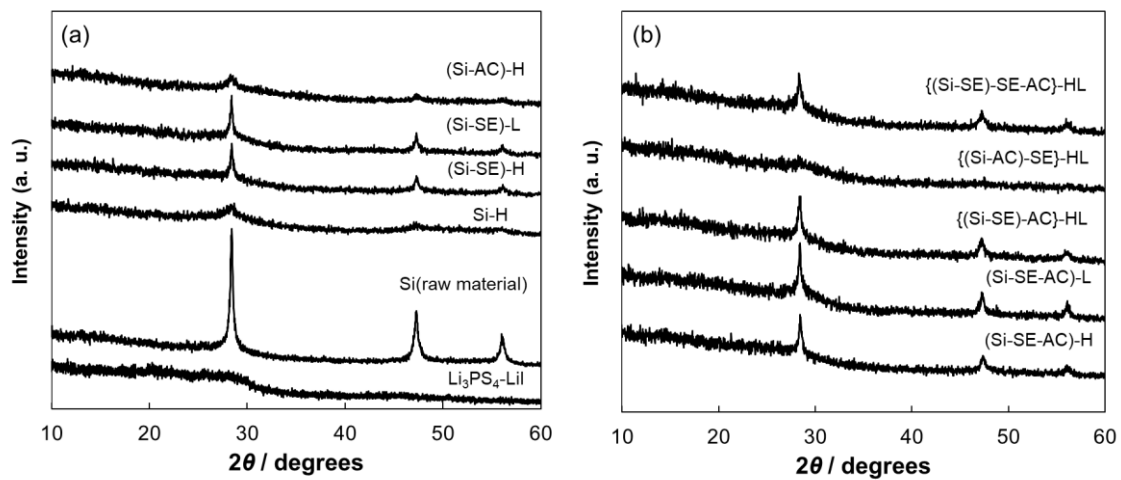
The crystalline phases in the aforementioned Si composite samples and Si composite electrodes were determined by X-ray diffraction (XRD, Cu K $\alpha$ 1) analysis using SmartLab II instrument (Rigaku Co.). The XRD measurement was performed in a closed cell assembled in an Ar-filled glove box for evaluation under Ar atmosphere, as described in our previous studies.<sup>2</sup>

Si 2p X-ray photoelectron spectroscopy (XPS) analyses of the composite electrodes and raw materials were performed using a spectrometer (KRATOS Nova, KRATOS ANALYTICAL) with a monochromatic Al–K $\alpha$  source. The measurement samples were prepared in an Ar-filled glove box and inserted into the spectrometer using an unexposed transporter in vacuum, as described in our previous studies.<sup>2</sup> The binding energies of all spectra were calibrated to the binding energy (284.8 eV) of C 1s corresponding to adventitious carbon. Here, the energy split and area ratio of 2p<sub>3/2</sub> and 2p<sub>1/2</sub> were set to 0.6 eV and 0.5, respectively. After subtracting the Shirley background, the XPS spectra were evaluated by curve-fitting to a Lorentzian asymmetric (LA) line shape using CasaXPS V2.3.23 software.

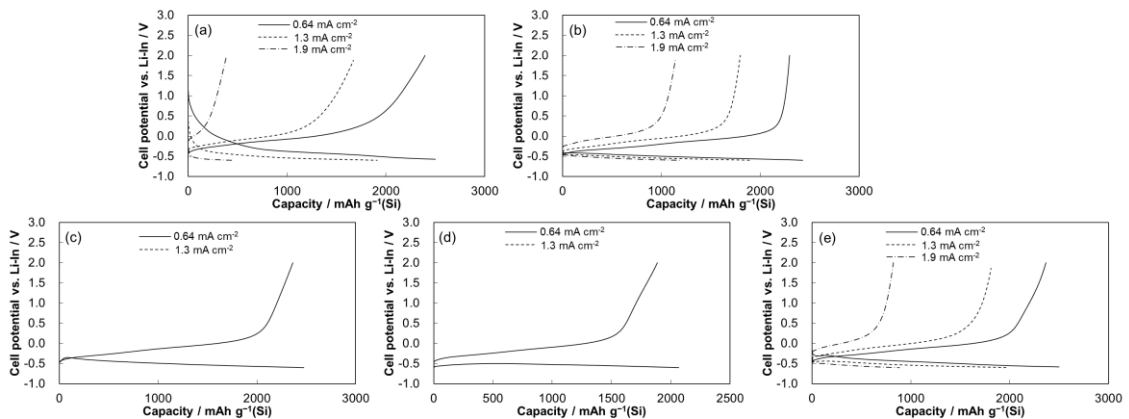
The half-battery cell structure was as follows: Si composite electrode/SE as the solid electrolyte layer/Li-In alloy as the counter electrode. Similar structures were reported in previous studies.<sup>1,2</sup> The Si composite electrode powder (4.0 mg) and SE powder (80 mg) were placed in a polycarbonate tube (inner diameter = 10 mm) and subjected to a pressure of 200 MPa applied by stainless steel rods, forming a two-layered pellet. The counter electrode of the Li-In alloy was formed by applying pressure less than 80 MPa. The Li foil and In foil were stacked on the surface of the two-layered pellet, and

thus, the foils were in contact with the SE. The molar ratio of Li/In in the negative electrode was 0.64. In  $\text{Li}_x\text{-In}$  ( $x < 1$ ), the potential of the Li-In alloys was constant at 0.62 V vs. Li.<sup>3</sup> The resulting three-layered pellet was sandwiched between two stainless steel rods, which acted as current collectors. The half-battery cells were assembled in an Ar-filled glove box and placed in a sealed vessel. Their battery performances were evaluated in Ar atmosphere.

The battery performances of the half cells were evaluated at a constant current density of 0.25–1.9  $\text{mA cm}^{-2}$  at 25°C between -0.6 and 2.0 V using a charge–discharge measuring device (ACD-01, Asuka Electronics Co. Ltd.).



**Figure S1.** X-ray diffraction (XRD) patterns of Si samples for confirming the Si–solid electrolyte (Si–SE) reaction (a) and Si composite electrodes (b).



**Figure S2.** Charge–discharge curves of Si composite electrodes at 0.64, 1.3, and 1.9  $\text{mA cm}^{-2}$  and 25°C between -0.6 and 2.0 V vs. Li-In. (a) (Si-SE-AC)-H, (b) (Si-SE-AC)-L, (c) {(Si-SE)-AC}-HL, (d) {(Si-AC)-SE}-HL, and (e) {(Si-SE)-SE-AC}-HL.

## References

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3. N. Aotani, K. Iwamoto and S. Kondo, *Solid State Ionics*, 1996, **86–88**, 877–882.