

## *Supporting Information*

### Electrochemical Lithiation Mechanism of Nickel Silicide Electrode

Yasuhiro DOMI,<sup>a,c,\*</sup> Hiroyuki USUI,<sup>a,c</sup> Takumi ANDO,<sup>b,c</sup> Ryuto TANAKA,<sup>b,c</sup> Kazuma GOTOH,<sup>d</sup>  
Takeo HOSHI,<sup>e</sup> Kei NISHIKAWA,<sup>f</sup> and Hiroki SAKAGUCHI,<sup>a,c,\*</sup>

<sup>a</sup> Department of Chemistry and Biotechnology, Graduate School of Engineering, Tottori University, Minami 4–101, Koyama-cho, Tottori 680–8552, Japan

<sup>b</sup> Course of Chemistry and Biotechnology, Department of Engineering, Graduate School of Sustainability Science, Tottori University, Minami 4–101, Koyama-cho, Tottori 680–8552, Japan

<sup>c</sup> Center for Research on Green Sustainable Chemistry, Tottori University, Minami 4–101, Koyama-cho, Tottori 680–8552, Japan

<sup>d</sup> Center for Nano Materials and Technology, Japan Advance Institute of Science and Technology, 1–1, Asahidai, Nomi, Ishikawa 923–1292, Japan

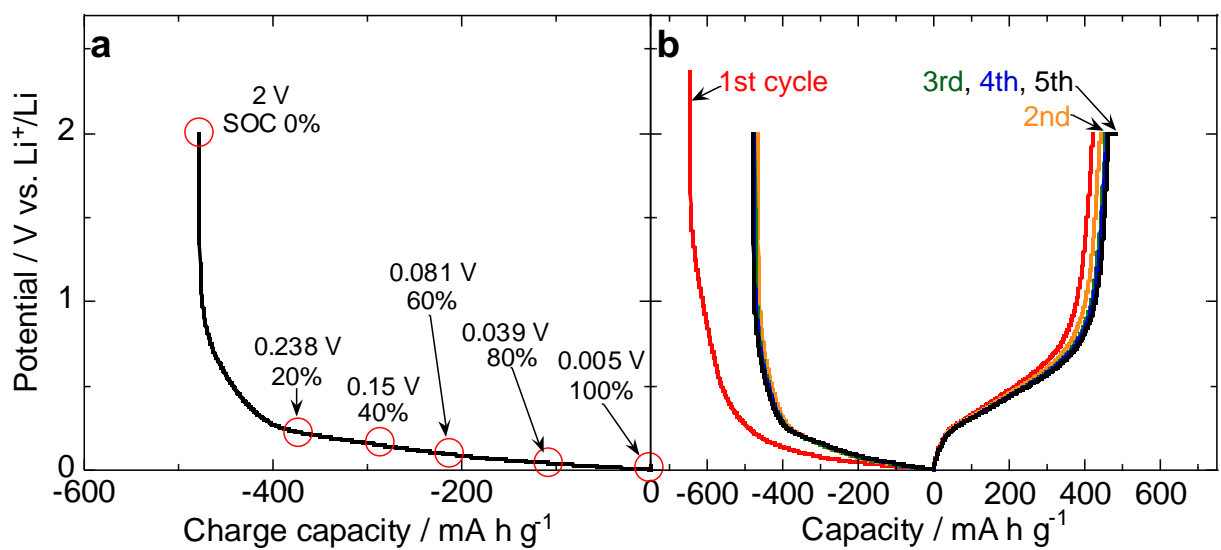
<sup>e</sup> Plasma Quantum Process Unit, National Institute for Fusion Science, 322–6, Oroshi, Toki-shi, Gifu 509–5292, Japan

<sup>f</sup> Center for Green Research on Energy and Environmental Materials, National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba 305-0044, Japan

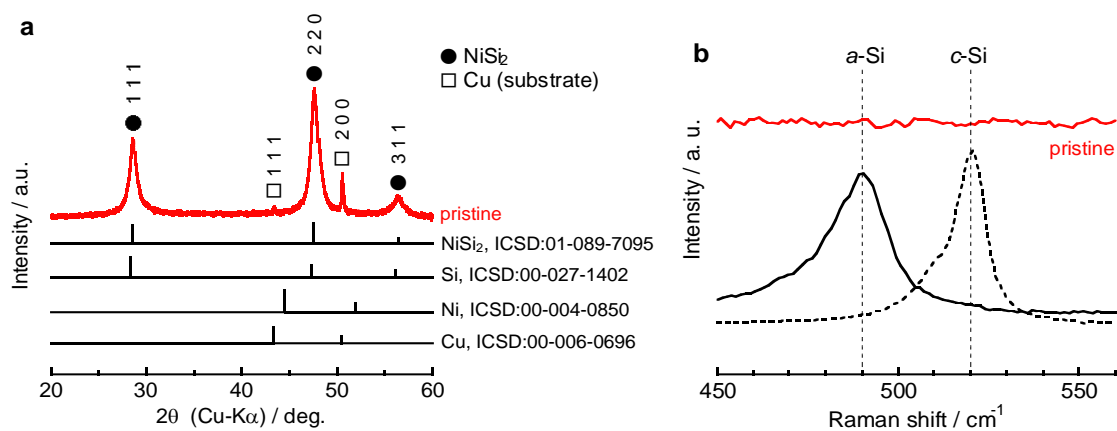
\*Corresponding authors:

Yasuhiro Domi      Tel/Fax: +81-857-31-5249, E-mail: domi@tottori-u.ac.jp

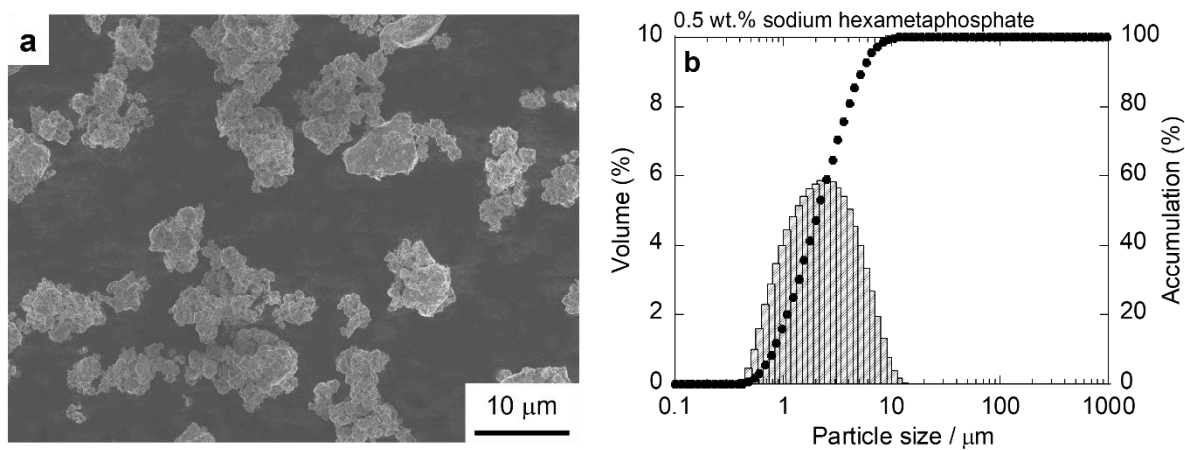
Hiroki Sakaguchi      Tel/Fax: +81-857-31-5265, E-mail: sakaguch@tottori-u.ac.jp



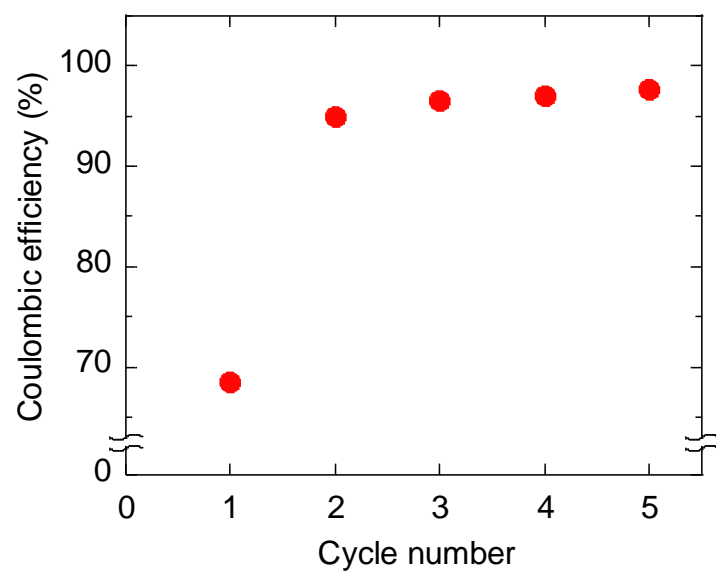
**Figure S1.** (a) Fifth charge curve and (b) initial five charge–discharge curves of the  $\text{NiSi}_2$  electrode in 1 M LiFSA/Py13-FSA at current density of  $50 \text{ mA g}^{-1}$ .



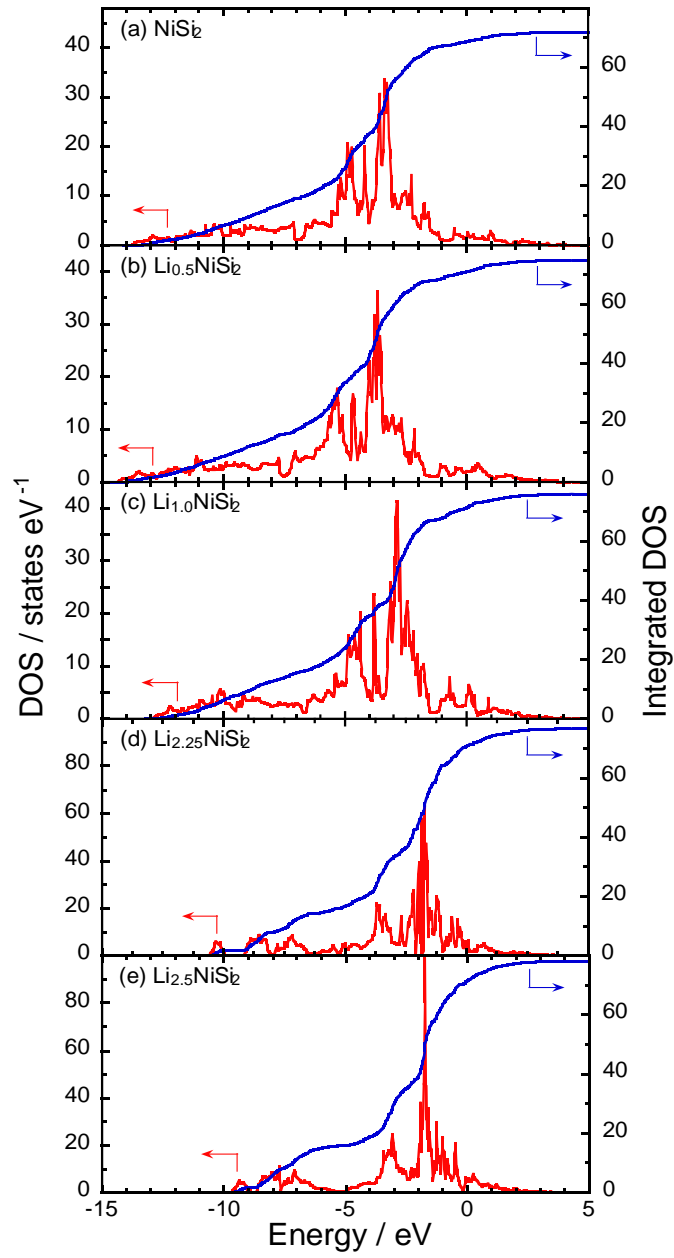
**Figure S2.** (a) XRD pattern of the powder synthesized from elemental Ni and Si and (b) its Raman spectrum. The results of *a*-Si and *c*-Si were also shown in part (b).



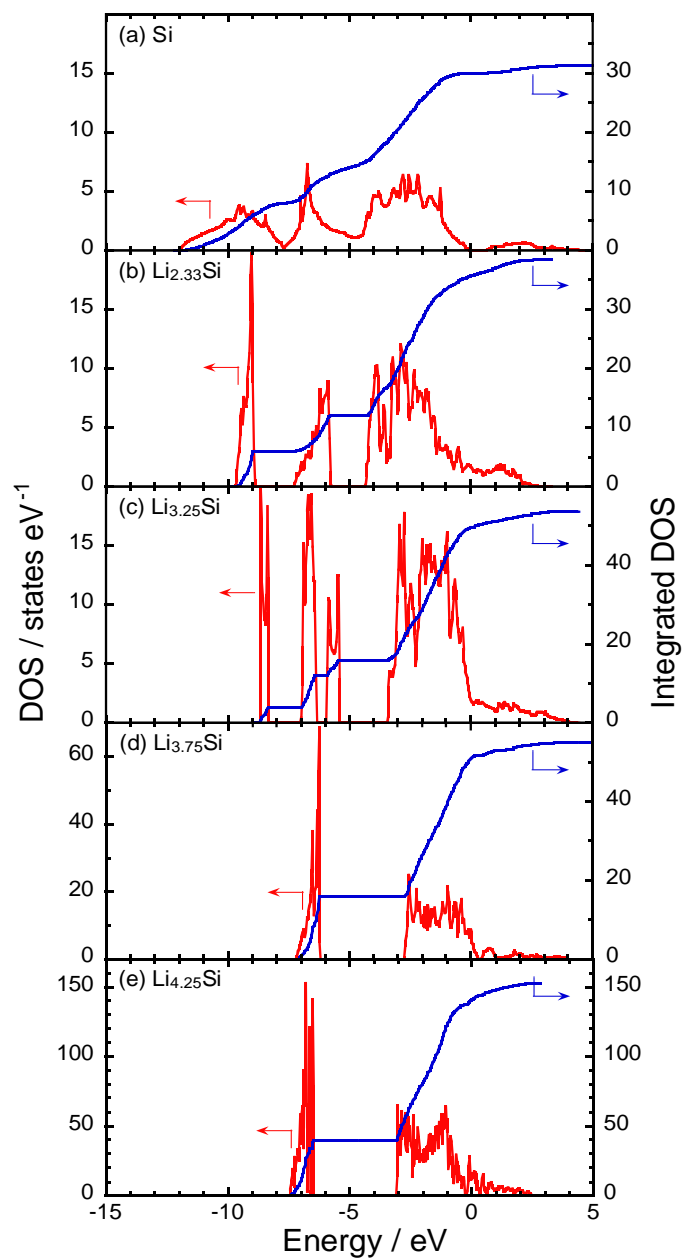
**Figure S3.** (a) FE-SEM image and (b) particle size distribution of  $\text{NiSi}_2$  powder.



**Figure S4.** Cycle-dependency of Coulombic efficiency of the NiSi<sub>2</sub> electrode in 1 M LiFSA/Py13-FSA at 50 mA g<sup>-1</sup>.



**Figure S5.** DOS (red line) and integrated DOS (blue line) for  $y =$  (a) 0, (b) 0.5, (c) 1.0, (d) 2.25, and (e) 2.5 in  $\text{Li}_y\text{NiSi}_2$ . The Fermi energy is located at  $E = E_F = 0$ .



**Figure S6.** DOS (red line) and integrated DOS (blue line) for  $x =$  (a) 0, (b) 2.33, (c) 3.25, (d) 3.75, and (e) 4.20 in  $\text{Li}_x\text{Si}$ . The Fermi energy is located at  $E = E_F = 0$ .

**Table S1.** Lattice volume of  $\text{Li}_y\text{NiSi}_2$  ( $y = 0, 0.5, 1.0$  and  $2.25$ ) calculated by first-principles calculations.

$y$ in $\text{Li}_y\text{NiSi}_2$	Lattice volume / $\text{nm}^3$
0	0.161
0.5	0.179
1.0	0.193
2.25	0.299