*Electronic Supplementary Information*

# Impact of the Crystal Phase of Binary Silicide on its Lithiation and Delithiation Properties

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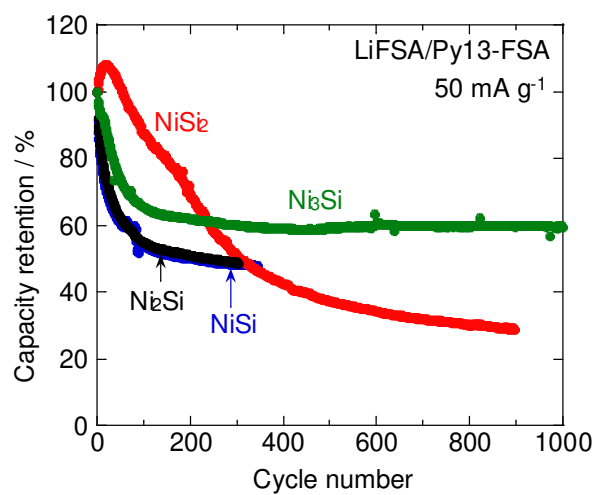
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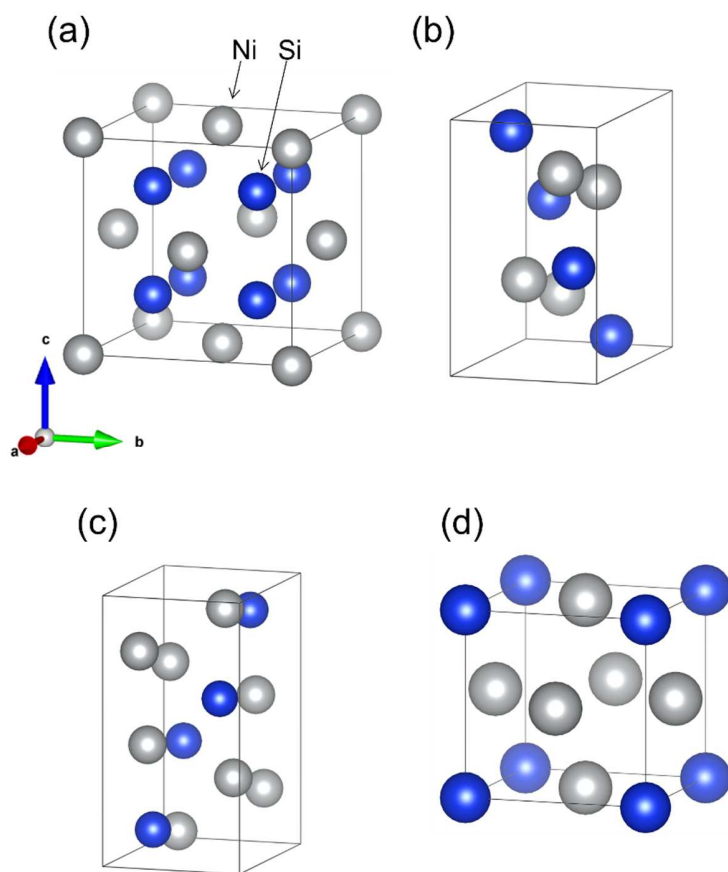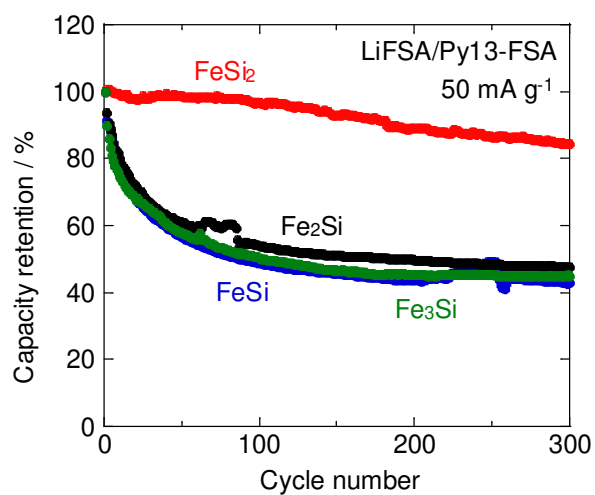
**Fig. S1.** Crystal structure of (a) NiSi$_2$, (b) NiSi, (c) Ni$_2$Si and (d) Ni$_3$Si.
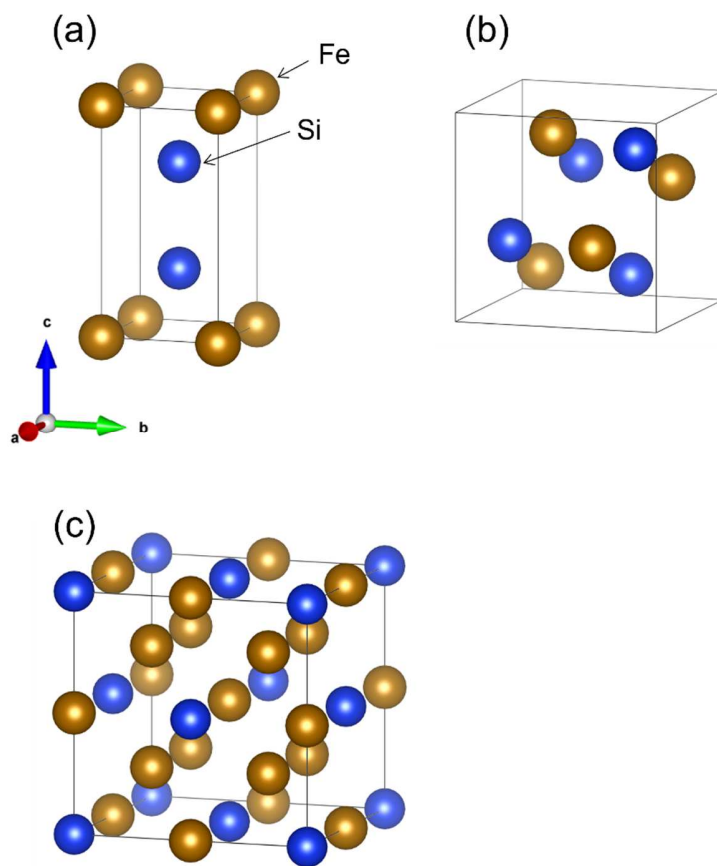
**Fig. S2.** Crystal structure of (a) $FeSi_2$, (b) FeSi and (c) $Fe_3Si$. The structure of $Fe_2Si$ cannot be determined because Z number is unknown.

**Fig. S3.** Capacity retention of NiSi$_x$ ($x$ = 2, 1, 1/2 and 1/3) electrodes under a current density of 50 mA g$^{-1}$ in 1 M LiFSA/Py13-FSA.

**Fig. S4.** Capacity retention of FeSi$_x$ ($x$ = 2, 1, 1/2 and 1/3) electrodes under a current density of 50 mA g$^{-1}$ in 1 M LiFSA/Py13-FSA.
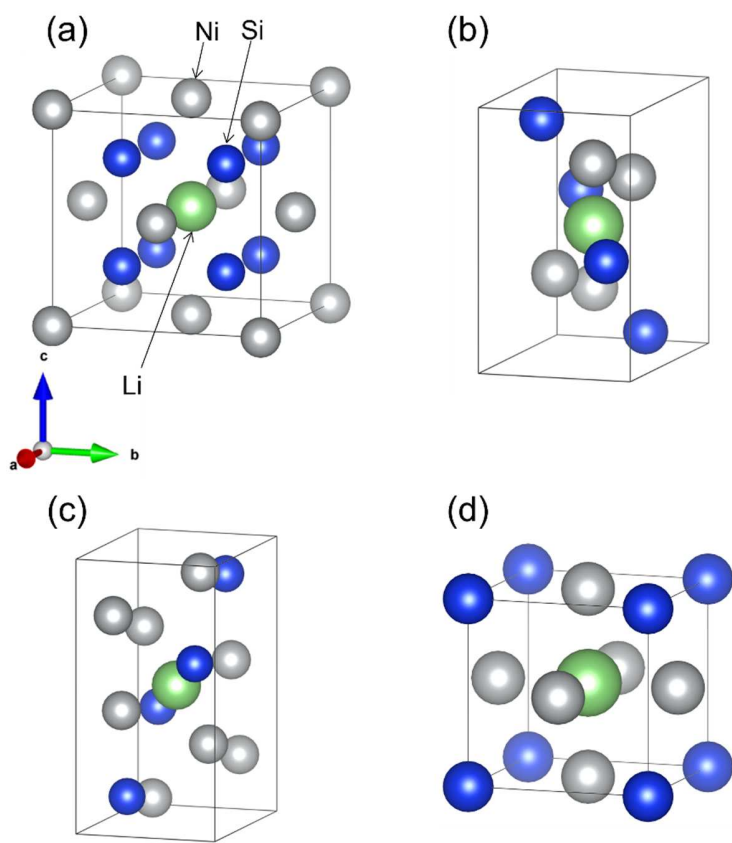
**Fig. S5.** Crystal structure of each lithiated $NiSi_x$ ($x$ = 2, 1, 1/2 or 1/3). While $Li_{0.25}NiSi_2$, $Li_{0.25}NiSi$ and $Li_{0.25}Ni_2Si$ were optimized crystal structure, $LiNiSi_3$ did not converge. Hence, the charge density was calculated with Li at the center of the lattice as in the former three crystals.
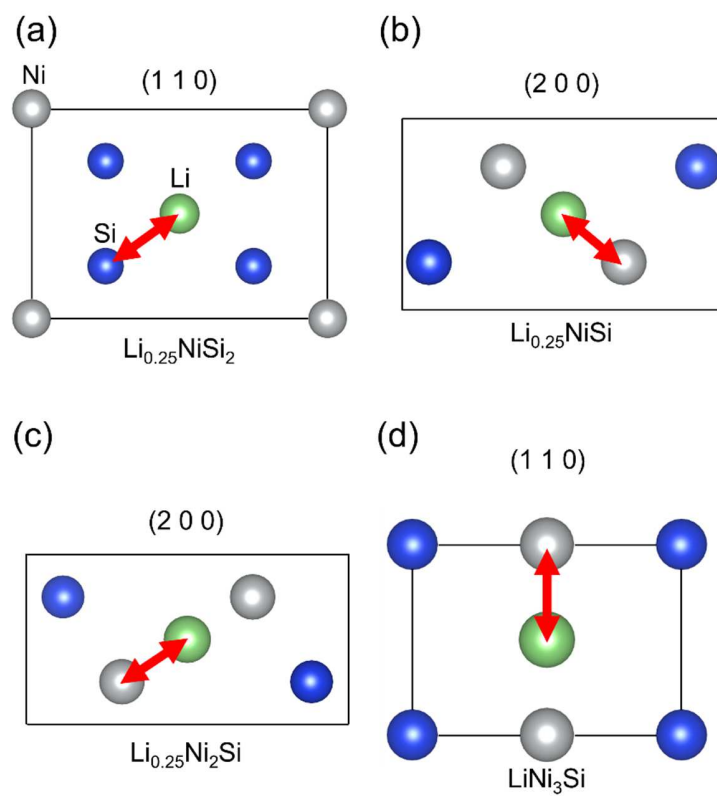
**Fig. S6.** Distance of between Li and nearest–neighbour atom in each Ni-Si lattice.

**Table S1.** Molar ratio, rotational speed, and treatment time for preparation of each silicide powder.

| Silicide | Molar ratio | Rotational speed / rpm | Treatment time / h |
|---|---|---|---|
| $NiSi_2$ | Ni : Si = 1 : 2 | 380 | 20 |
| NiSi | Ni : Si = 1 : 1 | 380 | 10 |
| $Ni_2Si$ | Ni : Si = 2 : 1 | 380 | 10 |
| $Ni_3Si$ | Ni : Si = 3 : 1 | 380 | 40 |
| $FeSi_2$ | Fe : Si = 1 : 3.3 | 380 | 100 |
| FeSi | Fe : Si = 1 : 1 | 380 | 10 |
| $Fe_2Si$ | Fe : Si = 2 : 1 | 380 | 10 |
| $Fe_3Si$ | Fe : Si = 3 : 1 | 380 | 10 |

**Table S2.** Crystallite sizes of (upper) $NiSi_x$ and (lower) $FeSi_x$ ($x$ = 2, 1, 1/2 or 1/3).

| | $NiSi_2$ | $NiSi$ | $Ni_2Si$ | $Ni_3Si$ |
|---|---|---|---|---|
| Crystallite size / nm | 9.2 | 11.8 | 13.9 | 9.0 |

| | $FeSi_2$ | $FeSi$ | $Fe_2Si$ | $Fe_3Si$ |
|---|---|---|---|---|
| Crystallite size / nm | 13.7 | 22.2 | 6.3 | 11.7 |

**Table S3.** Molar mass, density and crystal structure for each silicide.

| Silicide | Molar mass / g mol$^{-1}$ | Density / g cm$^{-3}$ | Crystal system |
|---|---|---|---|
| NiSi$_2$ | 114.87 | 4.83 | Cubic |
| NiSi | 86.78 | 5.96 | Orthorhombic |
| Ni$_2$Si | 145.47 | 7.37 | Orthorhombic |
| Ni$_3$Si | 204.17 | 7.84 | Cubic |
| FeSi$_2$ | 112.02 | 5.04 | Tetragonal |
| FeSi | 83.93 | 6.17 | Cubic |
| Fe$_2$Si | 139.78 | – | Cubic |
| Fe$_3$Si | 195.62 | 7.1[40] | Cubic |