Cyclability evaluation on Si based Negative Electrode in Lithium ion Battery by Graphite Phase Evolution: an operando X-ray diffraction study

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Artificial graphite (FSN) additive is employed as internal structural label for projecting cyclability of Si material native electrode in a mass ratio of Si/FSN = 1.0 in Li ion battery (LIB). Results of operando X-ray diffraction analysis on Si-FSN negative electrode in LIB demonstrate that one can evaluate the lithiation and delithiation affinity of active material by referring phase transition delay of graphite as affected by experimental splits in a formation process of LIB. We prove that a thin layer of surface amorphous structure and residual lattice strain are formed in Si by high energy ball-milling treatment. Those manipulations improve Li intercalation kinetics and thus enabling a capacity fading of less than 10% (from 1860 to 1650 mAh g⁻¹) for Si negative electrode in 50 cycles. Of utmost importance, this study discloses a robust assessment for revealing mechanism on amorphous and strain related silicide formation and predicting cyclability of negative electrode by quantitative phase evolution rate of FSN additive in LIB.

With raising demand of power consumption in transportation platforms, portable electronics, as well as high energy density modulation and storage system, high capacity materials are inevitable issues for development of Li ion battery (LIB). With such a consideration, silicon based materials are no doubt the next generation negative electrode material in LIB due to its highest theoretical capacity among studied materials. However, as compared to existing negative electrode materials, the lithium diffusion coefficient and intrinsic conductivity of Si are relatively low hindering its steps into the market. Furthermore, Si possesses a volume expansion up to 400% due to a solid-state alloying reaction in lithiation (charge) process. It induces extensive stress between residual Si and Li interacted domain, therefore, leading to pulverization of silicon powder in negative electrode and instability of the solid electrolyte interphase (SEI) layer. Those characteristics pill off Si powders from current collector and increase electrical contact resistance in electrode. Meanwhile, crashed Si powders exposes fresh surface to electrolyte thus causing overgrowth of solid electrolyte interface (ESI). In past decades, improvements in the cyclability and rate capability of silicon negative electrodes have been demonstrated by reducing particle size to the nanoscale, seeking conductive coatings or conductive networks, providing void space to accommodate volume expansion, and introducing highly elastic phases to mitigate the deleterious effect of large volume changes. Regardless of attempts been utilized, cyclability of LIB has been partially improved and is still far from criteria of the commercialization.
short range disorder structure (sub-nanometer domains), and increased preferential (111) facets in Si. XRD analysis (Table 1), those characteristics can be ascribed for formation of amorphous Si species, certain As consistently proved by high resolution transmission electron microscopy (HRTEM) images in Fig. S2 and stronger diffusion scattering background (denoted by Q and Q” in inset) as compared to those of Si P. Accordingly, all diffraction peaks of SiH increase with SiP electrodes. Inset presents room in for the two diffraction patterns in a range from 11.4° to 13.2°. Wavelength of incident X-ray is 0.689 Å (18 keV).

Figure 1. XRD patterns of as-prepared SiP + FSN and SiH jako + FSN electrodes. Inset presents room in for the two diffraction patterns in a range from 11.4° to 13.2°. Wavelength of incident X-ray is 0.689 Å (18 keV).

Results and Discussion

Physical Structure Characterizations on Si based materials. Crystal structure of SiP and SiH jako is revealed by using XRD analysis. Structure parameters are quantitatively determined by Rietveld refinement on their diffraction patterns (Fig. S1) and corresponding lattice parameters of SiP + FSN and SiH jako + FSN are listed in Table S1. Accordingly, lattice parameter is 5.435(6) Å and unit cell volume (V) is 160.598(9) Å³ for SiH jako. For SiP, lattice constant is 5.431(3) Å and unit cell volume is 160.218(0) Å³. As a result, one can notice a slight distortion and lattice expansion by 0.24% on Si crystal (SiP) by high energy ball-milling treatment. Diffraction patterns of the two electrode are compared in Fig. 1 and intensity is normalized by that of FSN (002) peak. Accordingly, all diffraction peaks of SiH jako + FSN possess lower intensity, broader peak width accompanied with stronger diffusion scattering background (denoted by Q and Q” in inset) as compared to those of SiP + FSN. As consistently proved by high resolution transmission electron microscopy (HRTEM) images in Fig. S2 and XRD analysis (Table 1), those characteristics can be ascribed for formation of amorphous Si species, certain short range disorder structure (sub-nanometer domains), and increased preferential (111) facets in SiH jako by HEMM. Quantitative structural parameters are summarized in Table 1. Accordingly, crystal structure of Si phase remaining unchanged by HEMM treatment. For SiP + FSN, average coherent length (D_avg) is 834.9 Å for (111), 790.5 Å for (220), and 757.1 Å for (311) facets in Si phase. After HEMM treatments, D_avg of SiH jako + FSN is respectively reduced by 20% in (111) facet (624.2 Å), ~43% in (220) facet (451.7 Å), and 46% in (311) facet (455.4 Å) as compared to those of SiP + FSN. Changes of those parameters resembles the “damage” of Si phase by high energy treatment and thus increasing the asymmetric crystal ratio in (111) facet.

Interface Properties of Experimental Si based Negative Electrode Materials by DFT calculation and EIS characterization. Affinity of Li silicide formation is a crucial factor in performance of Si materials as negative electrode in LIB. This factor is a combination results including atomic packing density of facets, size of Si crystal, and anchoring ligands as dock for Li intercalation. Effects of proposed high energy milling treatment on Li silicide formation affinity are evidenced by cross-referencing DFT (with structure models determined by XRD fitting) and XRD determined crystal structure evolution of experimental materials in operando LIB. Figure 2 compares top view of DFT calculated atomic packing structure for models of LiSi clusters in Si
slabs and corresponding formation energy \( E_{\text{form}} \) (eV/atom) with facets indexed by the first three diffraction peaks in Fig. 1. Accordingly, the two \( \text{Li}_{15}\text{Si}_4 \) clusters built from its primitive bulk structure (ICSD no.167674) are homogeneously packing on surface with a slab size of 116.5–134.5 Å². Such a result can be rationalized by steric effects when two \( \text{Li}_{15}\text{Si}_4 \) clusters are stacked in a surface with an area smaller than their close packed dimension (cross section area). Formation energies \( E_{\text{form}} \) are −0.019 (eV/atom) for (111), 0.02 (eV/atom) for (220), and 0.028 (eV/atom) for (311) facets. A negative value of \( E_{\text{form}} \) indicates an exothermic reaction meaning the strong preference of silicide formation in (111) facet when slab size is 3×3 (134.5 Å²). As for models with slab sizes of 207.1 to 253.7 Å², \( E_{\text{form}} \) follows the same trend to that of model with small slabs (126.8 to 134.5 Å²). Among them, \( E_{\text{form}} \) of (111) is 0.019 (eV/atom). This value is reduced respectively by 52.5% and 65.4% as compared to that of

| Sample  | Facet  | 2θ  | \( D_{\text{avg}} \) (Å) | \( d \) (Å) | \( H_{\text{111}}/H_{\text{hkl}}^{**} \) |
|---------|--------|-----|---------------------------|-----------|---------------------|
| \( \text{Si}_p + \text{FSN} \) | (002)* | 11.787 | 445.4 | 3.355 |
| (111)   | 12.634 | 780.2 | 3.130 |
| (220)   | 20.698 | 790.5 | 1.917 | 1.724 |
| (311)   | 24.326 | 849.1 | 1.635 | 3.031 |
| \( \text{Si}_{15}\text{W} + \text{FSN} \) | (002)* | 11.787 | 445.4 | 3.355 |
| (111)   | 12.634 | 624.2 | 3.130 |
| (220)   | 20.698 | 451.7 | 1.917 | 2.215 |
| (311)   | 24.315 | 455.4 | 1.636 | 4.493 |

Table 1. XRD analysis determined structure parameters of \( \text{Si}_p + \text{FSN} \) and \( \text{Si}_{15}\text{W} + \text{FSN} \). *diffraction peak of FSN (002) facet. **\( H_{\text{111}}/H_{\text{hkl}} \) denotes the ratio of peak intensities for (111) and (hkl) facets. In an ideal Si crystal with a symmetric group of 227, \( H_{\text{111}}/H_{\text{220}} \) is 1.497 and \( H_{\text{111}}/H_{\text{311}} \) is 1.794. (source: Materials Project ID: mp-149, [https://doi.org/10.17188/1190959](https://doi.org/10.17188/1190959)).

Figure 2. DFT calculated atomic packing structure and corresponding formation energy \( E_{\text{form}} \) (eV/atom)) for models comprising two \( \text{Li}_{15}\text{Si}_4 \) clusters in Si slabs surface with facets indexed by the first three diffraction peaks of experimental samples.

![Figure 2](https://doi.org/10.1038/s41598-018-38112-2)
respectively. As can be seen, a lower electrode impedance of SiH ranges, which are attributed to kinetics of charge transfer in interface and Li ions diffusion in bulk electrodes, at 0% lithiated state. These cells exhibited a semicircle in high frequency and a straight line in low frequency Nyquist plots of electrochemical impedance spectra (EIS) obtained from experimental Si based negative electrode.

Effects of preferential facet and particle size (predicted by DFT calculation and XRD analysis) on Li intercalation and Li silicide formation are complementary revealed combining electrochemical and operando XRD analysis on LIB with experimental Si materials (SiP and SiH+FSN) as negative electrode. Figure 3 displays the Nyquist plots of electrochemical impedance spectra (EIS) obtained from experimental Si based negative electrode at 0% lithiated state. These cells exhibited a semicircle in high frequency and a straight line in low frequency ranges, which are attributed to kinetics of charge transfer in interface and Li ions diffusion in bulk electrodes, respectively. As can be seen, a lower electrode impedance of SiH+FSN indicates its smaller interfacial charge-transfer resistance (Rct) as compared to that of SiP. Such a phenomenon reveals the facilitation of Li intercalation in SiH+FSN surface due to the surface amorphization (probed by HRTEM images), preferential (111) facets, and reduced Davg (at (220) and (311) facets) in SiH+FSN. In a meantime, a uniform and local disordered amorphous Si thin layer (as consistently proved by HRTEM and XRD analyses) is formed in fresh silicon surfaces by wet milling which provides an easy access for Li intercalation. In addition, physical impacts of high energy mechanical milling and wet milling process reduce the primary and agglomerate size which shorten the Li ion diffusion length in a silicon particle. Presence of FSN provide additional Li storage sites. Those Li storage sites share the redox loading and thus reduce chemical stress in Si surface. As denoted by reducing of semicircle diameters, presence of FSN modulates the redox kinetics and thus reduces impedance of Li intercalation in silicon-based electrode.

Internal standard structure labelling on Li affinity of Si based materials. Synchrotron based operando XRD analysis further confirms the effects of crystal size, facet selectivity on silicide formation affinity, therefore, projects cyclability of Si materials in LIB. XRD patterns of LIBs containing negative electrodes of SiP + FSN and SiH+FSN in the first lithiation/delithiation cycle are compared in Fig. 4a,e, respectively. As can be seen, the three peaks at 11.3° (P), 11.8° (Q), and 12.6° (R) are diffraction lines from LiC12 (002), graphite (002) (C (002)), and Si (111) facets. Rest of peaks at 9° and 10.48° are diffraction lines for (211) (peak S) and (220) facets (peak T) of Li15Si4. For SiP + FSN (Fig. 4a), intensities of diffraction peaks for silicon phase gradually decrease with increasing lithiation ratio to 50%. After that, Si phase is dramatically vanished and Li15Si4 crystal phase by the end of lithiation. In delithiation process, intensity of peak S and T is decreased indicating a gradual extraction of Li-ions from Li15Si4. As consistent revealed in literature, no silicon peaks are found at the end of delithiation process. This phenomenon can be rationalized by formation of amorphous Si due to a severe Li retention. As compared to those of SiP + FSN, structure evolutions of Si and silicide phases go even faster in SiH+FSN (Fig. 4e).
For clarifying lithiation affinity of SiP + FSN (SiH+W + FSN), quantitative results for crystal structure evolution of graphite (C), Si, and Li15Si4 phases in the first lithiation and delithiation cycle of LIB are cross-referenced in Fig. 4b–d (Fig. 4f–h). In these figures, unit of x-axis is number of diffraction patterns, that of y-axis is d-spacing. Shown in Fig. 4b and Fig. 4f, insertion of Li ions induces a graphite phase transformations in several stages including stage 4L (whose composition is not well defined), stage 3L (LiC24, d(002)G ~3.47 Å), dilute lattice-gas disordered stage 2 (LiC18), stage 2 (LiC12, d(002)G ~3.53 Å), and stage 1 (LiC6, d(001)G ~3.70 Å) both in SiP + FSN and SiH+W + FSN. In those stages, numerals (1, 2, 3, and 4) refer to number of empty layers between each Li-filled layer, and different stage reflects different d-spacing. By cross-referencing changes of d-spacing between crystal structures of graphite and active material, an interesting correlation to the affinity of Si with adopted treatments are revealed in Fig. 4b–d.

Figure 4b shows 2D contour for changes of inter-planar spacing of graphite (002) facet (C (002)) in SiP + FSN. As shown, increasing d-spacing at graphite (002) facet (d(002)G) from 3.36 Å to 3.52 Å indicates a successive evolution of Li-intercalated LiCn to stage 2 phase with capacity from 0 to 150 mAh g⁻¹ in lithiation process. By increasing capacity to 150 mAh g⁻¹, d(002)G is linearly expanded to that of Li enriched stage (stage 2, LiC12). Given that mass ratio of FSN is 50 wt% (equivalent to an ideal capacity of ~170 mAh g⁻¹) in active material, transformation of graphite to stage 2 (LiC12) suggests that Li ions are mostly intercalate in FSN. In this event, FSN performs a substantial higher affinity for Li intercalation as compared to that of SiP in active material. After capacity higher than 150 mAh g⁻¹, d(002)G is slightly increased by 0.01 Å (from 3.52 to 3.53 Å) by a subsequent lithiation to 1720 mAh g⁻¹. For structural interpretation in details, changes of peak intensity for Si phases in SiP + FSN and SiH+W + FSN with lithiation ratio are compared in Figs S3a and S3b. Accordingly, with an absence of LiC6 phase and vibration of Si (111) peak intensity (Fig. 4c), one can notice that most of Li is intercalated in Si phase with lithiation ratios.
from 15 to 100% in SiP + FSN with a capacity of ~1570 mAh g\(^{-1}\). With a mass ratio of 50 wt% in active materials, this value is decreased by ~18% as compared to theoretical capacity of Si (1850 mAh g\(^{-1}\)) and is possibly due to a crack of Li-Si phases from Si surface in a SiP + FSN electrode.

In a SiH\(^{+}\)W + FSN electrode (Fig. 4e), four stages including stage 4L (100–590 mAh g\(^{-1}\)), 3L (590–1200 mAh g\(^{-1}\)), stage 2 (1200–1890 mAh g\(^{-1}\)), and stage 1 (1900–2030 mAh g\(^{-1}\)) are found in graphite phase evolution by lithiation from 0 to 100% (2030 mAh g\(^{-1}\)). Among them, stage 1 is fully lithiated graphite phase and can only be formed by a kinetics balance between intercalation and diffusion rates of Li ions in graphite surface in a negative electrode lithiated higher than 94%. It is important to note that active materials possess a higher than 98% of ideal capacity of graphite and Si phases in SiH\(^{+}\)W + FSN; where capacity contribution is ~170–180 mAh g\(^{-1}\) for graphite phase and ~1800–1900 mAh g\(^{-1}\) for Si phase. Compared to that of SiP + FSN, graphite phase delay with lithiation ratio indicates that affinity of Li ion to surface modified Si phase is substantially higher than that of graphite phase in SiH\(^{+}\)W + FSN. Those scenarios are direct evidences rationalizing the strong lithiation preferential of Si (111), amorphous Si, and defect regions in SiH\(^{+}\)W + FSN electrode. Facile delithiation from SiH\(^{+}\)W + FSN is consistently revealed by phase transition of graphite. Shown in Fig. 4f, d(002)G hold in stage 1 by delithiation from 0 to 125 mAh g\(^{-1}\) and then move to stage 2 until 235 mAh g\(^{-1}\). Further delithiation from 235 to 375 mAh g\(^{-1}\) results in a transition from stage 3L to stage 4L in graphite. In this region, this delithiation value is doubled to that can be offered by graphite meaning that Li extraction is mainly from Si phase in a SiH\(^{+}\)W + FSN electrode. On the other hand, in delithiation process of a Si P + FSN electrode (Fig. 4b), stage 2 to stage 4L transition is found by delithiation from 0 to 160 mAh g\(^{-1}\) meaning that most of capacity is contributed from graphite phase (i.e., activation energy for Li extraction from graphite is lower than that from Si phase). Preference of lithiation/delithiation remaining hold even at the 50th cycles and is consistently revealed by comparing changes of d(002)G between SiP + FSN and SiH\(^{+}\)W + FSN with respect to lithiation ratios of LIBs (Fig. S3).

Structure evolutions of Si phases provide complimentary information to the preferential lithiation of active materials in negative electrode of LIB. Shown in Fig. 4g, position of Si(111) peak for SiP + FSN remaining unchanged in lithiation process. In this region, intensity of Si(111) peak is vibrating between 200 to 1100 a.u. with increasing capacity to 1490 mAh g\(^{-1}\) and then dramatically decreased to 0 by a subsequent lithiation till 1570 mAh g\(^{-1}\) (Fig. S3a). A dramatic vibration of peak intensity implies a crack of Si powder due to a strong lattice mismatch between Li silicide. This hypothesis is proved by presence of wide range scattering signals (denoted by yellow arrows) and diffraction line of Li\(_{15}\)Si\(_4\) (211) by increasing capacity higher than 500 mAh g\(^{-1}\) in Fig. 4d. Schematic representation for silicide formation induced interface crack in SiP is shown in Fig. 5. For SiH\(^{+}\)W + FSN, Li\(_{15}\)Si\(_4\) (211) peak intensity is increased from 0 to 40 a.u. by delithiation from 0 to 500 mAh g\(^{-1}\) and then progressively decreased to 0 in a subsequent delithiation till 1200 mAh g\(^{-1}\) (Figs 4b and 5b). As compared to those of in SiP + FSN, substantially weakened intensity with a broad width and delayed response of Li\(_{15}\)Si\(_4\) (211) peak reveal a suppression of Li silicide. Such a characteristic can be attributed to formation of local disordered Si/SiO\(_x\).

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**Figure 5.** Schematic representation to Li intercalation manners in Si materials with (SiH\(^{+}\)W) and without (SiP) high energy ball milling treatment. Strain regions in amorphous layer possess large local space for Li intercalation and flat surface (i.e., (111) facet) reduce formation energy for Li silicide in Si powder surface. The two pathways facilitate Li intercalation in SiH\(^{+}\)W reducing crack in Si crystal. In SiP ratios of open facets (i.e., (220) and (311)) are higher than that in SiH\(^{+}\)W. In open facets, silicide tend to cluster in corner region defect sites to form strong strain. In this event, Li\(^{+}\) ions would either extrude in bulk or induce a strong interface lattice mismatch to crack Si crystal.
and increased ratio of (111) facets dimension with proper interface to facilitate Li intercalation and formation of amorphous Li silicide in SiH_{1.4} + FSN surface (Fig. 1 and Table 1). Effects of HEMM treatments on facilitating Li accommodation in Si surface remaining hold in long-term cycling test till the 50th cycle which again consistently proved the facilitations of silicide formation in (111) facets and reduced Δd_{002} as predicted by DFT calculation and EIS analysis. Meanwhile, the same scenario on graphite phase evolutions delay proves the substantial improvement of Li intercalation/extraction performances of Si materials even hold after 50 cycles of LIB. Details of graphite evolutions in 50th cycles are given in ESI (Fig. S2) and latter sessions. Rates of d_{002} to lithiation ratio (Δd_{002G}/ΔL) of negative electrodes are compared Fig. S4 and corresponding peak area (which can be serve as a qualitative index for extent of graphite phase transition) are compared in Table S2 for further revealing the graphite evolution as affected by affinity of Si to Li^+ ions. Shown in Fig. S4a, the four Δd_{002G}/ΔL peaks in (1) 3.9%, (2) 6.8%, (3) 8.1%, and (4) 94.8% of lithiation ratios correspond to the maximum rate for graphite phase transition (i.e., stage 4L, stage 3L, stage 2, and stage 1) in SiP + FSN. The first three peaks incur 97.8% of area indicate that most of active sites in graphite phase are lithiated in a lithiation ratio of 8.1% (i.e., ~260 mAh g^{-1}) for negative electrode. For the case of SiH_{1.4} + FSN, the Δd_{002G}/ΔL peaks at lithiation ratios of (1) 4.6%, (2) 28.6%, (3) 30.2%, (4) 36.1, and (5) 51.8% suggest the presence of five transient states in graphite phase of SiH_{1.4} + FSN. In this event, as revealed by area of all Δd_{002G}/ΔL peaks, most active sites (~96.1%) in graphite phase are lithiated at 36.1% of lithiation (~1240 mAh g^{-1}) for SiH_{1.4} + FSN. In a subsequent lithiation, a broad peak across 36.1 to 51.8% can be attributed to formation of LiC_{6} transient state. As compared to that of SiP + FSN, transition of graphite phases is delayed by 20–25% of lithiation ratio in SiH_{1.4} + FSN. Given that phase transition rate of active materials is dominated by their affinity to Li^+ ion, such a phase delay again consistently revealed the improvement of Li affinity on Si phase in SiH_{1.4} + FSN. Taking results of operando XRD analyses together, changes of graphite and Si phases with lithiation/delithiation ratios of SiH_{1.4} + FSN and Si first lithiation step of SiH_{1.4} + FSN can be respectively summarized in S4a and S4B. As compared to that of the first cycle, transition of graphite phase is further delayed by ~14 in SiP + FSN and ~10% in SiH_{1.4} + FSN. Such a scenario can be attributed to a reduced lithiation/delithiation barrier by LiSiL formation again proving the concept of graphite phase evolution as internal structural label to Li^+ ion affinity of active materials in LIB.

Crystal structure affinity to formation of Li silicide in long-cycle LIB cells. Quantitative structural parameters on influences of surface modification to cyclability of silicon are determined by fitting the experimental diffraction patterns by the LAMP program. Results of graphite phase evolution (changes of d_{002G}) with lithiation/delithiation ratios of SiP + FSN in the 1st and 50th cycles are shown Fig. S5a. In lithiation process, Li^+ ions move from Li metal to the negative electrodes. In SiP + FSN, d_{002G} is significantly increased to a value of ~3.53 Å by increasing lithiation ratios from 5 to ~15%. Such a value is commonly known as a d-space of fully lithiated graphite (LiC_{12}). Without significant differences of Si phase evolution in LIB, such a result suggests a lower diffusion barrier for Li^+ ions in solid electrolyte interface (SEI) and graphite surface as compared to that in Si surface. For the case of SiH_{1.4} + FSN situation goes to the opposite. As shown in Fig. S5b, d_{002G} is increased to that of stage 4L (3.37 Å) by increasing lithiation ratios from 5% to 30%. After that, d_{002G} is then dramatically increased to that of stage 3L (3.47 Å) when ratio of lithiation is 40% and then progressively increased to 3.53 Å (stage 2) till 100%. Hereafter, one can notice a delay of d_{002G} in SiH_{1.4} + FSN as compared to that in SiP + FSN in lithiation/delithiation processes. Such a delay on d_{002G} with lithiation extent coincides to an inverse proportional of formation energy of LiSiL, in SiH_{1.4} surface as consistently proved by DFT calculations.

Changes of d_{002G} with capacity in lithiation and delithiation processes of SiP + FSN and SiH_{1.4} + FSN in the 50th cycle are respectively shown in Fig. S6c and S6d. Accordingly, trends of d_{002G} evolutions in SiH_{1.4} + FSN in the 50th cycle is differed from that in the 1st cycle. Shown in Fig. S6c, changes of d_{002G} in SiP + FSN is significantly retarded in the 50th delithiation process as compared to that in the 1st delithiation process. Such a delayed response on graphite phase and be explained by formation of significant amount of amorphous Si and retained Li silicide (i.e., irreversible capacity) in SiP + FSN in long-cycle test. Meanwhile, as consistently explained by vibration of Si(111) peak intensity, loss of capacity reveals a crack (pulverization) of Si particle in SiP + FSN in long cycle test which increases internal resistance between Si phases and back contact electrode. Changes of d_{002G} for SiP + FSN and SiH_{1.4} + FSN in delithiation process are compared in Fig. S6d. As depicted, SiP + FSN and SiH_{1.4} + FSN perform a similar decay trend on d_{002G}. It means that graphite phase possesses a similar energy barrier for Li intercalation in both the two electrodes in the 50th delithiation process. It is worth to note that, as compared to that of SiH_{1.4} + FSN in the 1st cycle, d_{002G} is suspended in stage IV by further increasing delithiation by 8–9%. It rationalizes the Li intercalation in Si phase is further facilitated in the 50th cycle for SiH_{1.4} + FSN in a LIB. Those results prove that formation of surface amorphous Si layer and increase ratio of (111) facet domain size with local distortion and surface modification by HEMM treatments improve the affinity of Li intercalation and extraction in Si surface (Fig. S3). Such a method is easy assessable therefore promising the development of Si based materials in LIB applications.

Cycle performance test further confirms the prediction on cyclability of Si materials by operando XRD analysis. Figure 6 shows the (a) specific capacity and (b) charging capacity retention (CR) of SiP, SiP + FSN, SiH_{1.4} + FSN and SiH_{1.8} + FSN negative electrodes in LIBs till the 50th lithiation/delithiation cycle. In the cycle test, rate is C/6 and potential range is 2mV to 1.5 V. Accordingly, SiP possesses a capacity of 3236 mAh g^{-1} in lithiation process and 2655 mAh g^{-1} in delithiation process in the 1st cycle (formation stage). For SiH_{1.4} + FSN capacity is 3470 mAh g^{-1} in lithiation and 2845 mAh g^{-1} in delithiation processes. It is important to note that both the SiP and SiH_{1.4} + FSN perform a columbic efficiency of ~82% in formation stage, however, with completely different fading manners of CR fading in a cycle test. For SiP, CR is exponentially decreased to 10% till the 50th cycle. On the other hand, CR is decreases by ~15% in the first five cycles (region A) and then slightly decreased by ~4% in the subsequent cycles (region B) for SiH_{1.4}. As compared to that of SiP, a substantially reduced CR decay in region A implies a reduction of energy barrier for silicide formation therefore improving cycle stability of SiH_{1.4}.
Addition of conducting graphite (FSN) further enhances the difference of capacity fading mode between SiP and SiH+W. Show in Fig. 6b, fading rate of SiP is substantially reduced by mixing FSN in a weight ratio of FSN/SiP = 1.0. Although capacity fading is improved by 19.6%, its CR fading remaining reaction control. On the other hand, CR fading of SiH+W shows the opposite way to that of SiP when mixing with FSN in the same weight ratio. In the 2\textsuperscript{nd} cycle, a slight increase of capacity might be attributed to the excess Li storage in FSN as compared to that of the 1\textsuperscript{st} cycle. Such a hypothesis is further revealed by results of \textit{operando} XRD analysis and impedance test which proving the insufficient/uncompleted Li intercalation in FSN in the first lithiation process. Similar to that of SiP, CR fading of SiH+W is improved by 12% by FSN additive with cycle number to 50.

Conclusions
Graphite phase evolution is employed to evaluate cyclability of Si based materials as negative electrode in an \textit{operando} LIB cell. At the first cycle, delay of d(002)\textsubscript{G} expansion with increasing capacity reveals a strong preference of Li ion intercalation in silicon phase in negative electrode of SiH+W comprising modified Si powder in lithiation process. As compared to that of SiH+W+FSN, d(002)\textsubscript{G} is linearly increased and stabled to that of fully lithiated graphite (3.53 Å) with respect to a capacity of ~170–180 mAh g\textsuperscript{-1} revealing that Li\textsuperscript{+} ions are mostly intercalated in graphite phase by lithiation to 5% in negative electrode of SiP+FSN comprising pristine Si powder. Those scenarios are further confirmed by cross-referencing results of XRD, HRTEM, and DFT calculation indicating that performance of Si materials are improved by formation of preferential (111) facet accompanied with certain amorphous structure by HEMM treatment. A most important finding is that d(002)\textsubscript{G} delay remaining hold in an \textit{operando} LIB cell even in the 50\textsuperscript{th} lithiation/delithiation cycle. Such a scenario, in a fact of phase evolution dominated by Li interaction, proves that changes of d(002)\textsubscript{G} with lithiation ratios is a robust qualitative index for predicting the cyclability of active materials in the formation stage of a LIB.

Methods
\textbf{Experimental details - Sample preparation, LIB assembly, and Physical Structure Characterizations.} Commercial silicon powder was purchased from Fuzhou Hokin Chemical Technology, China (Si\textsubscript{P}, ~10 um). To modify surface conformation of Si\textsubscript{P} high energy mechanical milling (HEMM) and wet ball-milling in a planetary miller for 20 hours at room temperature were employed and resulting product is named as Si\textsubscript{H+W}. Artificial graphite (FSN, Shanshan Technology, China, ~15 um) was employed as an internal structure standard for labelling lithiation and delithiation affinity of active materials in negative electrode of LIB. The
electrochemical measurements and the investigations of structural evolution of the silicon/graphite composite electrode were carried out by using CR2032 coin-cells. Experimental negative electrodes were prepared by casting 15 μm of active materials mixture in aluminum foil. The mixture contains 65 wt% of active materials (mixture of Si0.4 and Si0.45, respectively) with FSN at a weight ratio of silicon/graphite = 1, namely Si0.4 + FSN and Si0.45 + FSN, 20 wt% of carbon black (Super P), 9 wt% of poly(acrylic acid) (PAA, SigmaAldrich Co.), 3.5 wt% of styrene butadiene rubber (SBR, Zeon Co.), and 2 wt% of carboxymethylcellulose (CMC) dissolved in deionized water. Cells were assembled inside an Ar-filled glovebox. In a coin cell, counter (reference) electrode is lithium metal foil and separator is micro-porous polypropylene. The electrolyte was 1 M LiPF6 solution in a mixture of EC and DMC (1:1 in volume ratio). After assembly, experimental coin cells were stored for two days prior to electrochemical test. Electrochemical impedance spectroscopy (EIS) is employed to investigate the charge transfer resistance and the electronic resistance of activated material in lithium ion batteries. In this study, EIS characterization were performed on coin cells at open-circuit voltage (OCV) and the frequency was swept from 1 MHz to 10 mHz.

Oparado XRD analysis on experimental coin cells was conducted at Taiwan beamline (BL12B2) of Spring-8 (Aioi, Japan). XRD patterns are measured with an incident x-ray wavelength of 0.688992 Å by a area detector. Pixel resolution of detector equivalent to a step size of ~0.015° in two-theta and covers a range from 0 to 30°. The system temperature is ~30°C and exposure time is 3–4 min per pattern in transmission mode. During the data collection, the operation voltage of LIB is ranged from 2 mV to 1.5 V at a constant current (CC) of ~0.5 mA (i.e., at a rate of C/6). For conducting operando XRD analysis, one hole is punched and is covered with Kapton film on both top and bottom of case as X-ray window.

**Computational details.** All calculations were performed in the framework of density functional theory, as implemented in the Vienna Ab Initio Simulation Package (VASP) approach. The Perdew-Burke-Ernzerhof form of the generalized gradient correction (GGA-PBE) functional is used to describe the exchange-correlation interaction. The cutoff energy of 370 eV and Monkhorst-Pack k-point sampling of 12 x 12 x 12 were employed in Si bulk structure optimization, which were sufficient to converge total energies. The calculated bulk lattice constant of 5.486 Å is consistent with experimental value of 5.431 Å. We utilized large slabs of Si(100)—12L, Si(110)—8L, and Si(111)—8L to simulate silicon surfaces. The bottom two layers were fixed in its bulk structure and the dangling bonds were saturated by hydrogen atoms, all the rest atoms were optimized with the convergence threshold for energy is 10−5 eV which could provide sufficient accuracy. A vacuum larger than 12 Å is used to avoid the interaction between periodic images. To clarify the affinity of Li silicide on Si surface, we performed analyses of Li15Si4 (most highly lithiated phases) on a series of Si surfaces with different size of area. The structure of Li15Si4 primitive cell consisting of thirty Li atoms and eight Si atoms is available in Inorganic Crystal Structure Database (ICSD, #167674) by utilizing database from Material Project. The formation energy can be obtained from the formula: $E_{\text{form}} = (E_{\text{total}} - E_{\text{surface}}) - \frac{2}{N} \sum_{i} (\mu_{\text{Li}} - \mu_{\text{Si}})$, where $E_{\text{total}}$ and $E_{\text{surface}}$ are the total energies of Li15Si4 and Si bare surface, respectively. Ni and μ are atom number and chemical potential of species i (Li and Si). Here, we used bulk energy per atom as the chemical potential.

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Author Contributions
C.-W.H. analyzed the in-situ XRD data, J.-P.C. and A.H. performed the DFT calculations, S.-C.H. and W.-K.L. prepared Si powder sample, Y.-F.S. analyzed battery electrochemical properties, T.-Y.C. analyzed in-situ data and wrote the manuscript, Y.-F.L. and J.-M.C. installed XRD tool, J.-L.H. evaluated Si powder quality, C.-C.C. evaluated battery bath characterization.

Additional Information
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