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Degradation of Si/Ge core/shell nanowire heterostructure during lithiation and delithiation at 0.8 and 20 A/g

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Abstract

Si/Ge core/shell nanowire heterostructures have been expected to provide high energy and power densities for lithium ion battery anodes due to the large capacity of Si and the high electrical and ionic conductivities of Ge. Although the battery anode performances of Si/Ge core/shell nanowire heterostructures have been characterized, the degradation of Si/Ge core/shell nanowire heterostructures has not been thoroughly investigated. Here we report compositional and structural changes of Si/Ge core/shell nanowire heterostructure over cycling of lithiation and delithiation under different charging rates. Si/Ge core/shell nanowire heterostructure holds the core and shell structure at the charging rate of 0.8 A/g up to 50 cycles. On the other hand, compositional intermixing and loss of Si occurs at the charging rate of 20 A/g within 50 cycles. The operation condition-dependent degradation provides a new aspect of materials research for development of high performance lithium ion battery anodes with long cycle life.

Introduction

Lithium ion batteries (LIBs) have become essential means of electrical energy storage and have been deployed in consumer electronics, automobiles, and energy storage facilities. Modern LIB development demands larger capacity and energy with lower production cost and elongated lifetime. Current carbonaceous LIB anodes cannot fulfill these requirements because the capacity of commercialized graphite anode (360 mAh/g) is already close to the theoretical maximum of 372 mAh/g.¹ Therefore, novel materials are the breakthrough of LIB anode research. Group IV elements, such as silicon (Si, 3,579 mAh/g in Li₁₅Si₄ at room temperature), germanium (Ge, 1,624 mAh/g in Li₂₂Ge₅), and tin (Sn, 994 mAh/g in Li₂₂Sn₅), are ideal LIB anode materials in terms of specific capacity.¹ However, these group IV materials are limited by an inherent mechanical instability associated with the large capacity, resulting in battery failure during repeated cycling. Group IV-nanowires (NWs), especially Si and Ge NWs, have attracted great attention because mechanical failure can be significantly mitigated by the elongated shape, where volume expansion mainly occurs along one principal direction.²

Since the introduction of NWs for use in LIBs, a myriad of strategies has been suggested to improve the electrochemical performance of LIB anodes based on Si-Ge NWs. These include mechanical reinforcement via coatings,³ doping and alloying to obtain faster ion transport,⁴ controlling process variables to minimize unintentional metal silicide formation,⁵ And various forms of heterostructuring.⁶⁻¹¹ Coating, doping, and alloying alter the materials' characteristics in a homogeneous manner. Alloying and heterostructuring with Si and Ge are expected to yield additional benefits in LIB anodes. Single elements are not appropriate to achieve high energy and high power densities. Although Si boasts a great energy density represented by its specific capacity of 3,579 mAh/g, the low diffusivity of Li ion in Si $(1.9 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1})$ severely limits

the capacity of Si-based anodes at fast charging rates. Conversely, compared with that of Si, Ge has two orders of magnitude higher Li ion diffusivity $(6.25 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1})$, which enables much faster charging.^{12, 13} Reports on SiGe alloy-based anodes show enhanced capacity retention at fast charging rates.⁴ Meanwhile, heterostructuring, which introduces chemical potential discontinuities at interfaces between different materials, provides a unique means of controlling the Li ion insertion route.^{11, 14, 15} For instance, *in situ* transmission electron microscopy studies in an open-cell configuration have shown interesting phenomena, such as the lithiation of a Ge NW solely along axial direction in a Ge/Si core/shell NW heterostructure.¹⁵ Furthermore, Si/Ge core/shell NW heterostructures and SiGe NWs with composition gradients along the radial direction and block of lithiation in the core region, respectively.¹¹

It is generally assumed that the initial Si-Ge NW heterostructures in an LIB anode are preserved throughout the cycling process. Reported results focus on structural characterization before and after the first charging/discharging cycle.^{6, 9} Although amorphization and pore formation in homogeneous Si and Ge NWs have been studied extensively,^{16, 17} time-dependent structural changes in NW heterostructures have not been thoroughly examined. Amorphization and increase in the number of pores accompany a volume expansion of 300–400% in Si and Ge regions. This significantly changes the Si/Ge interface in NW heterostructures and provides a discontinuity in chemical potential. Therefore, an integrated study of electrochemical performance and structural changes of over cycling beyond the initial phase of LIB operation is necessary to develop advanced LIB anodes based on NW heterostructures.

Real-time structural characterization of a single NW-based LIB anode has been demonstrated by *in situ* transmission electron microscopy (TEM) in an open-cell configuration using a solid electrolyte and a liquid cell holder.^{18, 19} Recent *operando* TEM techniques have elucidated lithiation/delithiation processes under realistic conditions.^{20, 21} Nevertheless, *in situ* and *operando* TEM techniques to explore lithiation/delithiation mechanisms under real operational conditions are not ideal because the electron beam can induce radiolysis of the electrolyte.^{22, 23} Post-mortem characterization, including *ex situ* TEM, excludes the unintentional artifacts of *in situ* characterizations.

We performed integrated electrochemical and structural characterizations of Si(P)/Ge core/shell NW heterostructures up to several tens cycles at various charging rates. A series of electrochemical performance tests including electrochemical impedance spectroscopy and *ex situ* TEM revealed time-dependent structural changes in core/shell NW heterostructures that affected their electrochemical performances.

Preparation of Si(P)/Ge core/shell nanowire heterostructures

Homogeneous Si(P) NWs and Si(P)/Ge core/shell NW heterostructures were prepared in order to investigate their electrochemical characteristics. To improve Li ion diffusivity and electrical conductivity, the core NWs were composed of phosphorus (P) doped *n*-type Si(P). Au-catalyzed vapor-liquid-solid growth via low-pressure chemical vapor deposition (CVD) was employed to grow Si(P) NWs and Si(P)/Ge core/shell NW heterostructures on stainless steel (SS) 304 disks. 3 nm-thick Au thin films were deposited onto polished SS304 disks. Prior to the growth, the Au thin film was converted to Au nanodots by thermal annealing. Silane (SiH₄), germane (GeH₄), and phosphine (PH₃) diluted in hydrogen (H₂) were used as the precursors of Si, Ge, and P, respectively. Details of growth of Si(P) NWs and their heterostructures are described elsewhere.⁵

Figure 1 shows electron microscopy images and element analysis of a Si(P)/Ge core/shell NW heterostructures. As shown in Figure 1(a), Si(P)/Ge core/shell NW heterostructures were grown directly on a polished SS304 disk. The diameters of core Si(P) NWs ranged from 50 to 80 nm. The magnified SEM image in Figure 1(b) shows that the surfaces of the Si(P)/Ge core/shell NW heterostructures were wavy, indicating non-uniform Ge shell thickness over the longitudinal direction of a Si(P) NW. This is because crystalline Ge coalesces on Si, forming dots due to compressive strain in Ge originating from a 4.5% lattice mismatch between Ge and Si.²⁴ The thickness of the Ge shell in the region between nodes ranges 10 to 20 nm. The average weight fraction of the Ge shell in the NW heterostructure was $\sim 22\%$, corresponding to a volume fraction of $\sim 12\%$. Figure 1(c) shows that the Si(P) core NW and the Ge shell were crystalline. The crystallographic orientation of the Si(P) core NW was [112]. There is a twin boundary at the center of the Si(P) NW due to twin re-entrant mechanism during Au-catalyzed growth.^{25, 26} The Ge shell also exhibits stacking faults and dislocations. Stacking faults and additional twins are observed in the core Si(P) NW region because of induced strain by the Ge shell.²⁷ Compositional modulation along the radial direction is seen clearly by the contrast in the scanning TEM (STEM) image (Figure 1(d)) and the spatially separated energy dispersive X-ray (EDX) analysis curves of Si and Ge (Figure 1(e)).



Figure 1. (a) SEM image of Si(P)/Ge core/shell NW heterostructures directly growth on stainless steel 304 disk. (b) A magnified SEM image of Si(P)/Ge core/shell NW heterostructures. (c) TEM image of a single Si(P)/Ge core/shell NW heterostructure. The dotted yellow line indicates the interface between the Si(P) core and Ge shell. (d) STEM image of a single Si(P)/Ge core/shell NW heterostructure. The bright and dark regions correspond to Ge shell and Si(P) core NW, respectively. (e) Composition profile of Si and Ge along the dotted yellow line in (d). Ge shell surrounds the core Si(P) NW.

Charging rate-dependent electrochemical characteristics of Si(P) nanowires and Si(P)/Ge core/shell nanowire heterostructures

The specific gravimetric capacities of Si(P) NWs and Si(P)/Ge core/shell NW heterostructures were characterized by potentiostat measurements in a type 2032 half-coin cell configuration. The Si(P) NWs and Si(P)/Ge core/shell NW heterostructures grown directly on SS304 disks were loaded in coin cell cases. There was no additive in the half-coin cell. Details of the coin cell assembly are described in the supporting information. For every electrochemical characterization, the cells were cycled at a low current rate of 200 mA/g (0.05 C for Si) in the voltage window between 0.005 and 1.5 V before the first cycle at targeted current rates. This cycle aimed at formation of smooth solid electrolyte interphase. To control the current rate, current was applied to both Si(P)/Ge NWs and Si(P) NWs based on the theoretical properties of neat Si (1 C = 4 A/g). Charging (C-) rates of 0.8 A/g (0.2 C), 2 A/g (0.5 C), 4 A/g (1 C), 12 A/g (3 C), 20 A/g (5 C) and then back to 0.8 A/g (0.2 C) were applied. As shown in Figure 2, the gravimetric capacities of the Si(P) NWs and Si(P)/Ge core/shell NW heterostructures were 2,358 and 2,070 mAh/g at 0.8 A/g (0.2 C for Si), respectively. The lower capacity of the Si(P)/Ge core/shell NW heterostructures, compared with that of Si(P) NWs at 0.8 A/g, can be explained by the larger theoretical capacity of Si than that of Ge.¹ The C-rate-dependent gravimetric capacities of Si(P) NWs and Si(P)/Ge core/shell NW heterostructures show structure-dependent capacity retention. Figure 2 shows that the capacities of the Si(P) NWs and Si(P)/Ge core/shell NW heterostructures decreased as the C-rate increased from 0.8 to 20 A/g. Although the specific capacity of Si(P) NWs was larger than that of Si(P)/Ge core/shell NW heterostructures at 0.8 A/g, the capacities of Si(P)/Ge core/shell NW heterostructures were larger than those of Si(P) NWs at charging rates over 2 A/g. For the fastest current rate of 20 A/g in the characterization, the capacity (950 mAh/g)

of Si(P)/Ge core/shell NW heterostructures was 2.4 times higher than that (390 mAh/g) of Si(P) NWs. The C-rate was returned to 0.8 A/g after 5 cycles of charging and discharging at 20 A/g (5 C for Si) to check recovery of specific capacity. The Si(P) NWs and Si(P)/Ge core/shell NW heterostructures showed 2,250 and 1,990 mAh/g, respectively, at the current rate of 0.8 A/g during the recovery tests. The specific capacity of Si(P) NWs decreases steeply down to 60, 40, 23, and 18 % of the maximum capacity at 0.8 A/g as the C-rate increased from 2, 4, 12, and 20 A/g, respectively. Meanwhile, until the current rate reached to 4 A/g, the specific capacity of Si(P)/Ge core/shell NW heterostructures was consistently >80% of the maximum capacity at 0.8 A/g. When the current rate was >12 A/g, the specific capacity of the core/shell NW heterostructures dropped to <60% of the maximum. There have been reports showing that Gecontaining Si structures, such as Si_xGe_{1-x} alloy and Si/Ge NW heterostructures,^{4, 6, 8, 9} provide enhanced capacity retention of at C-rates over 1 A/g because of the electrical conductivity and Li ion diffusivity of Ge. Our Si(P)/Ge core/shell NW heterostructures have n-type Si core region that exhibits electrical conductivity comparable to that of Ge.²⁸ Therefore, the Li ion diffusivity in Ge can be a crucial factor that affects the electrochemical performance of Si(P)/Ge core/shell NW heterostructures.



Figure 2. Specific gravimetric capacities of Si(P) NWs and Si(P)/Ge core/shell NW heterostructures at different charging rates ranging from 0.8 to 20 A/g. The numbers in the parenthesis are the C-rates corresponding to Si.

The electrochemical kinetics in Si(P)/Ge core/shell NW heterostructures was investigated by cyclic voltammetry and galvanostatic electrochemical impedance spectroscopy (GS-EIS) at 0.8 A/g (0.2 C for Si). Figures 3(a) and (b) show voltage profiles and differential capacities of Si(P) NWs and Si(P)/Ge core/shell NW heterostructures recorded during the pre-cycle treatment with 0.2 A/g (0.05 C for Si). The differential capacity curve of Si(P)/Ge core/shell NW heterostructures in Fig. 3(b) shows a peak at 350 mV, which is not observable with Si(P) NWs and results from the amorphization of crystalline Ge.^{4, 29} A sharp peak at 125 mV occurs during charging of both Si(P) NWs and Si(P)/Ge core/shell NW heterostructures. The peak of 125 mV is attributed to the lithiation of Si to form a series of amorphous Li_xSi phases where 0 < x < 3.75.^{4, 30, 31} The reverse of this process occurs during discharging, with the related peaks occurring at 432 mV. After the pre-cycle treatment, the cyclic voltammograms of Si(P) NWs and Si(P)/Ge core/shell NW heterostructures corresponding to the lithiation of Si only during the first cycle at 0.8 A/g, shown in Figs. 3(c) and (d). Figure 3(d) shows two distinct plateaus at 0.24 (γ) and 0.08 (δ) V, corresponding to the formations of Li_xSi phases.^{30, 32}

GS-EIS allows one to visualize the impedance of lithiation in Si(P) and Si(P)/Ge core/shell NW heterostructures. Figures 3 (e) and (f) show the Nyquist plots obtained from Si(P) NWs and Si(P)/Ge core/shell NW heterostructures at 0.24 (γ) and 0.08 (δ)V, respectively. The impedance (Z') was estimated with the equivalent circuit depicted in Fig. 3(e), where R_S is the Ohmic resistance of the electrolyte, R_{CT} is the charge transfer resistance of the electrolyte, R_{SEI} is the resistance of Li ion migration through the SEI layer, C_{SEI} is the capacitance of the SEI layer, C_{CT} is the electrical double layer pseudocapacitance of the Si-Ge NW (heterostructures)/SEI interface, and Z_w is the Warburg impedance related to Li ion diffusion process, measured at low frequency. The diameter of the depressed semicircle corresponds to Z', obtained by the sum of R_{SEI} and R_{CT} . The depressed semicircles of Si(P) NWs and Si(P)/Ge core/shell NW heterostructures have similar intercepts (~1 Ω), which are related to surface resistance, at the low side of abscissa. The diameters of the two Nyquist plots are significantly different, however, indicating differences in the impedance (Z') of the two material systems. The surface resistance values of ~1 Ω for Si(P) NWs and Si(P)/Ge core/shell NW heterostructures indicate that the electrical conductance of surface of as-prepared Si(P) NW and Ge shell is comparable. The smaller impedance (Z') of the Si(P)/Ge core/shell NW heterostructures compared with that of the Si(P) NWs indicates that the Ge shell lowers either R_{SEI} or R_{CT}. The observed decrease in the impedance of Si lithiation by adding Ge is consistent with the previous reports.^{6, 8} In Si/Ge core/shell NW heterostructures, the surface resistance related to R_{CT} is smaller because Li ions move preferentially along the Ge shell. The lithiation of Ge-coated Si can be expedited due to the higher Li ion diffusivity in Ge compared with Si. Difference of R_{SEI} is out of scope of the article because characteristics of SEI on Ge have not been thoroughly studied.



Figure 3. (a) Cyclic voltammograms and (b) Differential capacities of Si(P) NWs (black, dashed) and Si(P)/Ge core/shell NWs (red, solid) at current rate of 0.2 A/g (0.05 C) for the precycle treatment. (c) Cyclic voltammograms and (b) Differential capacities of Si(P) NWs (black, dashed) and Si(P)/Ge core/shell NWs (red, solid) at current rate of 0.8 A/g (0.2 C). Impedance spectra obtained at the voltages of 0.24 V (γ in (c) and (d)) and 0.08 V (δ in (c) and (d)), respectively. The inset of (e) is the equivalent circuit used to fit impedance (Z_w) data.

The durability of electrochemical characteristics is a crucial factor in assessing LIB anode performance. Figure 4 shows specific gravimetric capacity curves of Si(P)/Ge core/shell NW heterostructures, cycled at current rates ranging from 0.8 to 20 A/g (0.2 to 5 C for Si). A comparison of the 1st-cycle capacities reveals that the specific capacity of Si(P)/Ge core/shell NW heterostructures decreased from 2,133 to 702 mAh/g as the charging rate increased from 0.8 to 20 A/g. At a current rate of 0.8 A/g, the specific capacity of Si(P)/Ge core/shell NW heterostructures decreased monotonically with the number of cycles. However, at higher current rates of 4, 12, and 20 A/g, the specific capacity plots as a parabolic curve indicating an increase in capacity in the initial cycles with a subsequent decrease. Moreover, the number of cycles at which the maximum specific capacity is achieved increases with current rate. At 4 A/g, the specific capacities at the 1st and the 10th cycles were 1,532 and 1,710 mAh/g, respectively. At

20 A/g, the specific capacities at the 1st and the 25th cycles were 702 and 1,347 mAh/g, respectively. The shift in the maximum-capacity cycle of Si(P)/Ge core/shell NW heterostructures as a function of charging rate indicates timedependent electrochemical characteristics. Another unconventional behavior of current rate-dependent specific capacity over cycling is that the specific capacities at different current rates are not inversely



Figure 4. Specific gravimetric capacities of Si(P)/Ge core/shell NW heterostructures over cycling at different current rates ranging from 0.8 and 20 A/g (0.2 and 5 C for Si).

proportional to the number of cycles.

The dynamics of electrochemical behavior in Si(P)/Ge core/shell NW heterostructures were investigated by obtaining voltage profiles and differential capacity curves, as shown in Figure 5, at 0.8 and 20 A/g. Figure 5(a) shows a decrease in specific capacity with increasing charging/discharging cycles. The plot shows two pseudo-plateaus during lithiation and one plateau during delithiation, which are typical characteristics of lithiation/delithiation of Si.⁴ The two pseudo-plateaus during lithiation are also visible in the differential capacity curves in Fig. 5(b). Broad voltage peaks at around 70 and 230 mV indicate lithiation of the Si(P)/Ge core/shell NW heterostructures. After pre-cycle at 0.2 A/g, the voltage peak related to the lithiation of Ge is not observable. At 0.8 A/g, the lithiation and delithiation of Si(P)/Ge core/shell NW heterostructures are governed by those of Si. By contrast, the lithiation/delithiation behavior of the Si(P)/Ge core/shell NW heterostructures at 20 A/g differed significantly from those acquired at 0.8 A/g and those of Si(P) NWs. Figure 5(c) shows the increase and subsequent decrease in specific capacity with increasing charge/discharge cycles, as in Fig. 4. Additional feature of voltage profile in Fig. 5(c) is the absence of the characteristic pseudo-plateaus and plateau during lithiation and delithiation, respectively. The differential capacity curves in Fig. 5(d) show broad voltage peaks and a shift in the dominant lithiation potential from ~100 to ~190 mV as the number of charge/discharge cycles approached 30. Moreover, a broad emerged during delithiation, shifting from ~450 to ~370 mV, with the shift of another peak from ~600 mV to ~550 mV with increasing cycles. The shift in lithiation potential to higher values and the concurrent shift in delitathion potential to lower values at 20 A/g indicate that the electrochemical characteristics of Si(P)/Ge core/shell NW heterostructures are process-

dependent. These characteristics become more Ge-like because the lithiation and delithiation potentials of Ge are higher and lower than those of Si, respectively.



Figure 5. Voltage profiles and differential capacity curves of Si(P)/Ge core/shell NW heterostructures at (a, b) 0.8 and (c, d) 20 A/g.

Effect of lithiation condition on composition modulation in single Si(P)/Ge core/shell nanowire heterostructures

Ex situ elemental analyses of Si(P)/Ge core/shell NW heterostructures after multiple charge/discharge cycles were performed to correlate structural changes and process-dependent electrochemical characteristics at current rates of 0.8 and 20 A/g. 3-5 EDX line scans were conducted at >3 different locations in an individual nanowire heterostructure. For each current rate and number of charging/discharging cycles, >3 nanowire heterostructures were investigated by TEM-EDX. Figs. 6(a)-(c) show elemental analysis results of Si(P)/Ge core/shell NW heterostructures after 7, 20, and 50 cycles of lithiation/delithiation at 0.8 A/g (0.2 C for Si). EDX line scan profiles of Si and Ge exhibit spatial separation between the two elements up to 50 lithiation/delithiation cycles. On the other hand, at 20 A/g, a comparison of Figs. 6(d) and (e) reveals a structural transition from core-shell to mixed before the number of lithiation/delithiation cycles reaches 20. Moreover, Ge becomes the dominant element in the initial Si(P)/Ge core/shell NW heterostructure after the 50th cycle at 20 A/g (5C for Si), as shown in Fig. 6(f). The compositional intermixing of Si and Ge, observed in Figs. 6(e) and (f), indicates that the core/shell NW heterostructure is not preserved under certain electrochemical conditions, such as the application of a high potential in core/shell NW heterostructure at 20 A/g. Furthermore, the Ge-dominant EDX line scan and even distribution of Si in Fig. 6(f) implies a loss of Si through reaction with electrolyte during charge/discharge cycles at 20 A/g. The observed loss of Si may occur through two steps consisting of migration of Si to the surfaces via intermixing and subsequent SEI formation at the surface.³³ According to the observation, the Si(P)/Ge core/shell NW heterostructure is being converted to Si_{1-x}Ge_x alloy nanowire along cycles of charging/discharging at the current rate of 20 A/g. The compositional and structural

transition is also consistent to the parabolic capacity-cycle curve in Fig. 4 and the shift of lithiation and delithiation potentials in Fig. 5(d). The mechanism of compositional intermixing and preferential loss of Si in Si/Ge core/shell NW heterostructure are the subjects for follow-up study.



Figure 6. STEM images and EDX line profiles of Si and Ge in single Si(P)/Ge core/shell NW heterostructures after different charging/discharging cycles at current rates of 0.8 A/g (a, b, c)

and 20 A/g (d, e, f). EDX line scan was performed along the solid yellow line in each panel of STEM image.

Conclusion

Systematic studies correlating dynamic electrochemical characteristics and the structure of Si(P)/Ge core/shell NW heterostructures at low (0.8 A/g) and high (20 A/g) current rates provide insight into the durability and dynamic behavior of nanostructure-based LIB anodes. Si(P)/Ge core/shell NW heterostructures are useful in applications requiring fast charging due to their small impedance of Li ion transport. However, the electrochemical characteristics of Si(P)/Ge core/shell NW heterostructures depend on process variables, such as current rate and number of charge/discharge cycles. The observed compositional intermixing in Si(P)/Ge core/shell NW heterostructures at high current rate of 20 A/g indicates that core/shell heterostructures are not preserved under certain electrochemical processes, especially those employing large potentials. Therefore, the design of Si/Ge heterostructure-based LIB anodes should include process-dependent structural changes to obtain high-performance batteries.

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