

Electrochemical Properties of Si-Ge Heterostructures as an Anode Material for Lithium Ion Batteries

Taeseup Song, Huanyu Cheng, Kaitlin Town, Hyunjung Park, Robert W. Black, Sangkyu Lee, Won II Park, Yonggang Huang, John A. Rogers, Linda F. Nazar,* and Ungyu Paik*

Si-Ge composites have recently been explored as an anode material for lithium-ion batteries due to their stable cycle performance and excellent rate capability. Although previous reports show the benefits of Si-Ge composites on electrochemical performance, the specific mechanism and structural effects have been overlooked. Here, the structural effect of Si-Ge heterogeneous nanostructures on both mechanics and kinetics is systematically studied through theoretical analysis and detailed experimental results. Si-Ge and Ge-Si core–shell nanowires are employed for this study. The Si-Ge core–shell nanowires show a much improved electrochemical performance, especially cycle performance and rate capability, when compared to those of the Ge-Si core–shell nanowires electrode. On the basis of the detailed experimental results and associated theoretical analysis, its is demonstrated that the strain distribution and Li diffusivity and/or diffusion path are significantly affected by the Si-Ge heterostructure, which induce different mechanics and kinetics associated with lithium.

1. Introduction

In the past decade, group IVA materials have received significant interest as negative electrodes for lithium-ion batteries

Dr. T. Song, Dr. S. Lee, Prof. W. I. Park Department of Materials Science Engineering Hanyang University Seoul, 133–791, Korea Dr. T. Song, K. Town, R. W. Black, Prof. L. F. Nazar University of Waterloo and Waterloo Institute of Nanotechnology (WIN) 200 University Av. West, Waterloo, ON N2L 3G1, Canada E-mail: lfnazar@uwaterloo.ca H. Cheng, Prof. Y. Huang Departments of Mechanical Engineering and Civil and Environmental Engineering Center for Engineering and Health, and Skin Disease Research Center Northwestern University Evanston, Illinois, 60208, United States H. Park, Prof. U. Paik WCU Department of Energy Engineering Hanyang University Seoul, 133-791, Korea E-mail: upaik@hanyang.ac.kr Prof. J. A. Rogers Department of Materials Science and Engineering University of Illinois at Urbana Champaign Urbana, Illinois, 61801, United States

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due to their high theoretical capacity.^[1-4] Among them, Si is the most promising candidate due to its high theoretical specific capacity (4200 mAh g⁻¹).^[5] However, its practical use in commercial application is limited by both poor cycle retention, caused by high volume change during cycling, and poor rate capabilities, due to its inherent low electron conductivity and ion diffusivity. There are two general approaches to overcome these problems. One approach is to use one-dimensional nanostructures, such as nanowires and nanotubes for their ability to better accommodate mechanical strain, facilitate fast electron transport along 1D geometry, and short lithium diffusion length.[6-10] Although 1D nanostructured Si shows promise, further improvements in the cycle retention and rate capability are needed. The other approach is the incor-

poration of either carbonaceous materials or highly conducting metals as a mechanical support and/or electron transport network within the Si electrode, which provides an improvement in cycle retention and rate capability.^[11–19] However, this approach results in a significant decrease in the specific energy density of the electrode. Through the replacement of carbonaceous materials or highly conducting metals with active materials which exhibit high capacity, greater energy storage can be achieved.

In a previous study, we demonstrated that a Si-Ge composite benefits both the mechanics and kinetics associated with lithium while maintaining its high specific capacity, especially volumetric capacity.^[20] Although the previous report defines the benefits of Si-Ge heterogeneous structures, the specific mechanism requires further study.^[21,22] As Si and Ge have different reaction voltages associated with lithium as well as different physicochemical properties, this leads to different electrochemical behavior, especially mechanics and kinetics. During lithiation, crystalline and amorphous Si have voltage plateaus at about 120 mV and 220 mV, respectively.^[8,23,24] On other hand, crystalline and amorphous Ge have respective voltage plateaus at about 250 mV and 450 mV.^[2,3,25-28] From this, it can be determined that the Ge first reacts with lithium, followed by the reaction of both Ge and Si with lithium together in the Si-Ge heterostructures. The strain distribution and Li diffusivity are significantly affected by the structural features of Si-Ge heterostructure. Therefore, the study of structural effects of the

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Scheme 1. Schematic illustration of morphological changes for the both Si-Ge and Ge-Si coreshell nanowires during cycling. Above the charge voltage of 0.25 V, Li ion reacts with only Ge. Si core of the Si-Ge core shell nanowire and Si shell of the Ge-Si core shell nanowire experience large stress induced by the expansion of Ge layer, respectively, which lead to a generation of cracks in Si. Ge has higher Li ion diffusivity and lower adsorption energies of the Li ion on the surface (E_{ad}), which results in more favorable Li kinetics in Si-Ge core shell nanowires. After the full lithiation up to 0.01 V, both Si and Ge react with lithium ion. After the cycling, the swelled core and wall were reversibly restored to their initial morphology.

Si-Ge heterostructure on the electrochemical performance is essential.

Herein, we demonstrate the structural effect of Si-Ge heterogeneous nanostructures on electrochemical performance, including mechanics and kinetics through theoretical analysis and galvanostatic intermittent titration (GITT). The Si-Ge and Ge-Si core–shell nanowires were employed as electrodes for this study since, as described above, one-dimensional nanostructures provide a relatively stable cycle performance which allows the effect of the Si-Ge heterostructure on the electrochemical performance to be examined.

pre-shell nanowires 2. Results and Discussion

The morphological change of Si-Ge and Ge-Si core–shell nanowires during cycling is described in **Scheme 1**. Since Ge has higher reaction voltage associated with lithium than Si, the Ge shell or core in the Si–Ge (Ge-Si) core–shell nanowires reacts with lithium prior to a reaction between Si and Li. This leads to a localized volume expansion in the Ge region alone, that causes strain in the Si-Ge heterostructure. Furthermore, the Li

diffusion path and Li adsorption energy are affected by the nanowire structure, which

results in different Li kinetics. Figure 1 shows the electron microscope images and elemental analysis of Si-Ge and Ge-Si core-shell nanowires. Single crystalline Si and Ge core nanowires were synthesized using vapor-liquid-solid growth on a stainless steel substrate. Amorphous Ge or Si shell layers were then deposited on the crystalline Si or Ge nanowires via chemical vapor deposition method, respectively. As shown in scanning electron microscope (SEM) images, both the Si-Ge and Ge-Si core-shell nanowires have random growth orientation and identical morphology on the current collector. Low magnification transmittance electron microscope (TEM) images clearly show

the core–shell structure. The core diameter of the nanowires is 30–40 nm, coated with a shell thickness of 30–40 nm. High resolution (HR) TEM images reveal that the core nanowire and shell layer are crystalline and amorphous phases, respectively. The cross sectional composition line profiles validate the Si-Ge and Ge-Si core–shell microstructures and the absence of any noticeable impurity.

The electrochemical performance of both core–shell nanowires were evaluated using Li half cells in the range of 0.01–2 V versus Li/Li⁺. The voltage profiles of the first cycle clearly show their differing electrochemical behavior (**Figure 2**a). Si-Ge and Ge-Si core–shell nanowire electrodes exhibit different voltage



Figure 1. Electron microscope images and elemental line profile analysis of both Si-Ge and Ge-Si core–shell nanowires. a,e) SEM images. b,f) Low magnification TEM images. c,f) High resolution TEM images. d,f) Cross-sectional EDX elemental mapping.



Figure 2. Electrochemical characteristics of both Si-Ge and Ge-Si coreshell nanowires electrodes. a) Voltage profiles of both electrodes at rate of 0.2 C. b) Cycle performances. c) Rate capabilities at various C rates.

plateaus during the charge, which arises from the different Li reactivity of both the Si and Ge. From the second cycle, both electrodes show identical voltage profiles due to the amorphisation of the crystalline core of the nanowires during the first cycle (Figure S1, Supporting Information). This result is also well corelated with dQ/dV derivatives curves of the Si-Ge ans Ge-Si core–shell nanowires for the first and second cycles. (Figure S2, Supporting Information). In the first cycle, the Si-Ge core–shell nanowires show charge and discharge capacity of about 1426 and 1346 mAh g⁻¹ respectively, with a Coulombic efficiency of 94.4%. Si-Ge core–shell nanowires show lower discharge capacity compared to that of previously reported Si/Ge double layered nanotubes arrays (1544 mAh g⁻¹)²⁰ due to its



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lower Si content. The weight ratio of Si and Ge for Si-Ge coreshell nanowires and Si/Ge double layered nanotubes arrays are 1:2.6 and 1:6.8, respectively. Comparatively, the first charge capacity of Ge-Si core–shell nanowires is found to be 1276 mAh g^{-1} with a Coulombic efficiency of 89.8%. The higher Coulombic efficiency of the Si-Ge core–shell nanowires is attributed to the high resistance of Ge to oxidation.

The cycle performances of both core–shell nanowires were monitored for 50 cycles (Figure 2b). After 50 cycles, the Si-Ge nanowires maintained a capacity retention of 72.4% and the Ge-Si nanowires had a capacity retention of 62.4%. Both electrodes showed improved cycle performances compared to a previously reported result of Si nanowires synthesized directly on the current collector.^[29] This implies that the heterogeneous system provides more favorable mechanics over the homogeneous system. More interestingly, the Si-Ge core–shell nanowires exhibit better cycle performance compared to that of the Ge-Si nanowires. The improved cyclability of Si-Ge core–shell nanowires could be attributed to better structural stability during cycling.

The effect of structural alteration on the electrochemical kinetics was also explored (Figure 2c). The Si-Ge core–shell nanowires show much improved rate capability at all current rates. For example, the Si-Ge core–shell nanowires delivered a charge capacity of 90% at a rate of 3 C, which is about 30% higher than that of the Ge-Si core–shell nanowires. It is unexpected that the microstructure of the electrodes results in significantly different kinetics, while the 1D geometry and composition is identical. To explore the origin for this phenomenon, GITT was employed. Detailed discussion is described in Figure 5.

The degradation of the system results from the mechanical strain induced during cycling, and the strain in the core–shell heterostructures consists of volumetric expansion due to lithiation and the elastic mismatch between the core and shell. The different volumetric expansion of bulk Si $\Delta V_{\text{Si}} = 400\%$ and bulk Ge $\Delta V_{\text{Ge}} = 370\%$ based upon final compositions of Li_{4.4}Si and Li_{4.4}Ge respectively leads to compressive (tensile) strain in the lithiated Si-Ge (Ge-Si) core–shell structure, and accounts for the aforementioned improved cyclability of Si-Ge core–shell nanowires.

Prior experiments^[20] show that the expansion in the radial direction is much larger than that in the axial direction of nanowires, thereby indicating the expansion in the axial direction is negligible and the expansion is mainly in the radial direction. For the Si-Ge core–shell nanowires electrode, let $R_{\rm interface}$, $R_{\rm Ge}$ denote the radius of Si core and the outer radius of Ge shell before lithiation. The minimization of energy in the system given below will show that the expansion is mainly in the radial direction; therefore, the radius of Si core changes from $R_{\rm interface}$ to $\sqrt{\Delta V_{\rm Si}} R_{\rm interface}$ for a free expansion. Similarly, the inner and outer radii of Ge shell $R_{\rm interface}$ and $R_{\rm Ge}$ change to $\sqrt{\Delta V_{\rm Ge}} R_{\rm interface}$ is smaller than the radius of Si core $\sqrt{\Delta V_{\rm Si}} R_{\rm interface}$, which results in a compressive normal stress on the interface.

Given the inner and outer radii r_i and r_o for a tube subjected to internal and external pressures P_i and P_o and axial stress σ_z , the displacements in the radial and axial directions are given by

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$$\begin{split} u_{\rm r} &= \frac{1}{(r_{\rm o}^2 - r_{\rm i}^2)E} \quad \left[(1 - v) \left(r_{\rm i}^2 P_{\rm i} - r_{\rm o}^2 P_{\rm o} \right) r + (1 + v) r_{\rm i}^2 r_{\rm o}^2 \left(P_{\rm i} - P_{\rm o} \right) \frac{1}{r} - v \left(r_{\rm o}^2 - r_{\rm i}^2 \right) \sigma_{\rm z} r \right] \text{ and } u_{\rm z} = \frac{1}{(r_{\rm o}^2 - r_{\rm i}^2)E} \left[-2v \left(r_{\rm i}^2 P_{\rm i} - r_{\rm o}^2 P_{\rm o} \right) + \left(r_{\rm o}^2 - r_{\rm i}^2 \right) \sigma_{\rm z} \right] z, \end{split}$$
where E and v are the Young's modulus and Poisson's ratio of the tube, r and z are the distances from and along the central axis, respectively.^[30] The displacements $(u_r)_{s_i}$ and $(u_z)_{s_i}$ at the outer surface of Si core are obtained by setting $r = r_0 =$ $\sqrt{\Delta V_{\rm Si}} R_{\rm interface}$ and $r_{\rm i} = 0$. The displacements $(u_r)_{\rm Ce}$ and $(u_z)_{\rm Ce}$ at the inner radius of Ge are obtained by $r_0 = \sqrt{\Delta V_{Ge}} R_{Ge}$, $r = r_i = \sqrt{\Delta V_{Ge}} R_{interface}$ and external pressure $P_0 = 0$. The radial displacement is continuous across the Si/Ge interface, that is, $\sqrt{\Delta V_{\text{Si}}} R_{\text{interface}} + (u_{\text{r}})_{\text{Si}} = \sqrt{\Delta V_{\text{Ge}}} R_{\text{interface}} + (u_{\text{r}})_{\text{Ge}}$, while continuity of axial displacement across the interface gives a similar equation. Force equilibrium requires $(\sigma_z)_{\rm Si} \Delta V_{\rm Si} R_{\rm interface}^2 + (\sigma_z)_{\rm Ge} \Delta V_{\rm Ge} (R_{\rm Ge}^2 - R_{\rm interface}^2) = 0$ for axial stresses in the Si core and Ge shell. A similar equation is established for the pressures at the Si/Ge interface. Analytic expression of the interfacial pressure on Si core is obtained as

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 $P_{\text{interface}} =$

$$\frac{E_{\text{Li}_{4,4}\text{Si}}\frac{\sqrt{\Delta V_{\text{Si}}}}{\sqrt{\Delta V_{\text{Ge}}}}\left(1-\frac{\sqrt{\Delta V_{\text{Si}}}}{\sqrt{\Delta V_{\text{Ge}}}}\right)}{(1-v_1)\frac{\Delta V_{\text{Si}}}{\Delta V_{\text{Ge}}} + \left[1-v_2+(1+v_2)\frac{R_{\text{Ge}}^2}{R_{\text{interface}}^2}\right]\kappa - \frac{2\left(v_2\kappa + v_1\frac{\sqrt{\Delta V_{\text{Si}}}}{\sqrt{\Delta V_{\text{Ge}}}}\right)^2}{1+\kappa}}$$
(1)

where κ is defined as $E_{\text{Li}_{4,4}\text{Si}}\Delta V_{\text{Si}} R_{\text{interface}}^2 / [E_{\text{Li}_{4,4}\text{Ge}}\Delta V_{\text{Ge}} (R_{\text{Ge}}^2 - R_{\text{interface}}^2)]$, $E_{\text{Li}_{4,4}\text{Si}} = 15.2 \text{ GPa}$ and $v_{\text{Li}_{4,4}\text{Si}} = 0.328$ are the Young's modulus and Poisson's ratio of lithiated Si, and $E_{\text{Li}_{4,4}\text{Ge}} = 15.6 \text{ GPa}$ and $v_{\text{Li}_{4,4}\text{Ge}} = 0.326$ are for lithiated Ge.

In general, the radial and axial expansions of Si can be designated by $(\Delta V_{\rm Si})^n$ and $(\Delta V_{\rm Si})^{1-2n}$, respectively, such that the total volumetric expansion is $\Delta V_{\rm Si}$, where *n* is a parameter to be determined. Similarly, the radial and axial expansions of Ge are expressed as $(\Delta V_{\rm Ge})^n$ and $(\Delta V_{\rm Ge})^{1-2n}$, respectively. The radii and heights of lithiated Si core and Ge shell in continuity and force equilibrium equations will be changed accordingly in the above analysis. Minimization of total energy in the system gives *n* = 0.48, that is, expansion mainly in the radial direction, which is consistent with the experiment of free expansion of silicon nanotubes.^[6]

The strains in Ge shell in the circumferential and radial directions are given by

$$\varepsilon_{\theta,r} = \frac{P\sqrt{\frac{\Delta V_{\rm Si}}{\Delta V_{\rm Ge}}}}{E_{\rm Li_{4,4}Ge} \left(\frac{R_{\rm Ge}^2}{R_{\rm interface}^2} - 1\right)} \times \left[1 - v_{\rm Ge} \pm \frac{R_{\rm Ge}^2}{r^2} \left(1 + v_{\rm Ge}\right) - 2v_{\rm Ge} \frac{v_{\rm Ge}\kappa + v_{\rm Si}\sqrt{\frac{\Delta V_{\rm Si}}{\Delta V_{\rm Ge}}}}{1 + \kappa}\right] (2)$$

and the strains in Si core are constant in both circumferential and radial directions:

$$\varepsilon_{\rm Si} = \left[2v_{\rm Li_{4,4}Si} \sqrt{\frac{\Delta V_{\rm Si}}{\Delta V_{\rm Ge}}} \frac{v_{\rm Ge} \frac{R_{\rm Ge}}{R_{\rm interface}} - v_{\rm Li_{4,4}Si} \sqrt{\frac{\Delta V_{\rm Si}}{\Delta V_{\rm Ge}}}}{\frac{\Delta V_{\rm Si}}{\Delta V_{\rm Ge}} + \frac{E_{\rm Li_{2,G}}}{E_{\rm Li_{4,4}Si}} \left(\frac{R_{\rm Ge}^2}{R_{\rm interface}} - 1\right)} \right] \\ \times \left[+ \left(v_{\rm Li_{4,4}Si} + 1 \right) \left(2v_{\rm Li_{4,4}Si} - 1 \right) \right] \frac{P_{\rm interface}}{E_{\rm Li_{4,4}Si}}$$
(3)



%

Strain in the shell ε ,

-3

20

Distance x, nm

40

Figure 3. Strain distribution in the Si-Ge and Ge-Si core-shell structures.

For Ge-Si core–shell nanowires electrode, the strains in the Ge core and Si shell can be obtained following the same approach. Given $R_{interface} = 18$ nm and $R_{Ge} = 54$ nm, Figure 3 shows that the strain distribution in the shell from Equation 2 is comparable in both Si-Ge and Ge-Si electrodes. However, it changes from tensile strain in the Ge core of Ge-Si electrode to compressive strain in the Si core of Si-Ge electrode obtained in Equation 3, thereby leading to improved cyclability of Si-Ge electrode.

The morphological changes of both nanowires were monitored as a function of Li insertion amount: i) at a charge voltage cutoff at 0.25V, ii) after the full lithiation at 0.01 V, iii) after delithiation following the first cycle at 2.0 V. The voltage profiles of both nanowires at each state are presented in Figure S3, Supporting Information. At the charge voltage cutoff of 0.25 V, the Si-Ge and Ge-Si nanowired differed greatly in appearance from one another. Although the Si-Ge core-shell nanowires maintained their initial straight and smooth morphology, the Ge-Si core-shell nanowires appeared severely distorted and with a winded morphology. Low magnification TEM images (Figure 4a,c) clearly showed the change in the morphology. In the case of the Si-Ge core-shell nanowire, some cracks in the Si core were observed, which is attributed to the large strain induced by volume expansion of the Ge wall. The selected area diffraction (SAED) pattern (Inset of the of Figure 4b and HR-TEM image (Figure S4, Supporting Information) confirm that the Si core maintains its crystallinity, while the thickness of Ge shell was increased to ≈50 nm. In the case of Ge-Si nanowires, the cracks and breaks in the Si wall were generated due to the large expansion of the Ge core, which leads to accelerated electrolyte decomposition via the formation of additional solid electrolyte interphase (SEI) on the newly generated Ge surface. The SAED pattern (Inset of the left panel of Figure 4d) and HR-TEM image (Figure S4, Supporting Information) reveals the coexistence of both amorphous Li, Ge and crystalline Ge. At the fully lithiated state, only amorphous Li_xGe and Li_xSi phases were observed. Although both core-shell nanowires electrodes sustain the initial 1D shape without mechanical degradation,







Figure 4. Morphological changes of Si-Ge and Ge-Si core-shell nanowires during the first cycling. a) SEM images and b) low magnification TEM images for Si-Ge core-shell nanowires. White arrows indicate the cracks in Si core. c) SEM images, and d) low magnification TEM images for Ge-Si core-shell nanowires.

the Ge-Si core-shell nanowires shows severely distorted and twisted morphology compared to that of Si-Ge core-shell nanowires. After the first full cycle, the swelled core and wall were reversibly restored to their initial thickness. More interestingly, the Si-Ge and Ge-Si core-shell heterostructures were



Figure 5. a) Potentiostatic current vs voltage plot of Si-Ge and Ge-Si core–shell electrodes. b) Comparison of chemical diffusion coefficients for Si-Ge and Ge-Si core–shell electrodes.

maintained after subsequent volume contraction (Figure S5, Supporting Information).

Potentiostatic charge of both the Si-Ge and Ge-Si nanowires was conducted to 0.01 V, with a voltage step of 10 mV. During charge, two large peaks were observed at 0.48 and 0.16 V in the current-voltage curve of the Si-Ge core–shell nanow-

ires (Figure 5a). These peaks correspond to plateau-like regions in the discharge profile of the nanowires, (Figure 2a) due to lithiation of the amorphous Ge shell, and crystalline Si core of the nanowires. In the curve of the Ge-Si core-shell nanowires, peaks are observed at 0.26 and 0.18 V (Figure 5a). These peaks align with the slightly sloping region of the discharge curve (Figure 2a), where lithiation of the crystalline Ge core and amorphous Si shell occurs. The diffusion coefficients of lithium ions (D_{Li+}) in the Si-Ge and Ge-Si nanowires electrodes were obtained from GITT results.^[31] The values calculated were within the range of $10^{-16}\ to\ 10^{-13}\ cm^2\ s^{-1}$ previously reported for other group IVA compounds.^[32-35] A slightly lower Li diffusion constant for the nanowires is expected, due



to the absence of any conductive additive in the electrode. Both Si and Ge are capable of alloying with and storing Li and the dense structure of the nanowires should reflect the intrinsic diffusion kinetics of the Si-Ge and Ge-Si electrodes. Both electrodes exhibit a variation of D_{Ii^+} as a function of steady state potential. The Si-Ge nanowires have a higher D_{Li^+} when compared with the Ge-Si nanowires at potentials above 0.6 V. This phenomenon is attributed to the higher adsorption energy of Li ions on a Ge surface, when compared to Li on Si surfaces, which leads to more favorable kinetics due to a significant decrease in the system total energy.^[20] The decrease in D_{Ii^+} observed between 1.25 and 1.75 V is attributed to the onset of SEI formation, as the cell potentials were recorded as less that 0.8 V during the applied current periods. The fluctuation in D_{Ii^+} of Ge-Si nanowires below the charging potential of 0.6 V is attributed to the increased Li ion flux to both Si and Ge through cracks formed in the Si shell layer, which leads to continuous SEI formation and therefore an increased diffusion path length, and degradation in electrochemical performance.

3. Conclusion

We demonstrated that the structural feature of Si/Ge heterostructure plays an important role on the electrochemical performances through the theoretical analysis and appropriate experiments including morphological change observation and GITT analysis. The Si-Ge core–shell nanowires exhibit better cycle performance and rate capability compared with Ge-Si core–shell nanowires. Our results presented here offer general guidance for electrode configuration design of group IVA negative electrode materials.

4. Experimental Section

Si and Ge nanowires were synthesized directly on the current collector (stainless steel foil) using vapor-liquid-solid method. Colloidal Au nanoparticles with a diameter of 20 nm were used as a catalyst. The substrate decorated with Au colloids was placed in the quartz tube of a chemical vapor deposition (CVD) tube furnace. SiH, and GeH, gases were used for the synthesis of Si nanowires and Ge nanowires, respectively. For the synthesis of Si-Ge core-shell nanowires, Si nanowires were first synthesized at 500 °C and 40 Torr for 10 min. A Ge shell layer was coated on the Si nanowires at 360 °C and 100 Torr for 3 min. For the synthesis of Ge-Si core-shell nanowires, Ge nanowires were synthesized at 300 °C and 40 Torr for 10 min followed by a Si shell coating at 520 °C and 20 Torr for 2 min. Core-shell nanowires were characterized using a field emission scanning electron microscope (FE-SEM, S-4700, Hitachi, Japan), a field emission transmission electron microscope (FE-TEM, JEM 2100F, JEOL, Japan), an X-ray diffraction spectrometer (D/MAX-2500/ PC, Rigaku, Japan) and Raman spectrometer (LabRam HR, Horiba Jobin-Yvon, France). The weight ratio of Si and Ge for both Si-Ge core-shell nanowires and Si/Ge double layered nanotubes arrays was calculated based on the volume ratio obtained from Image-pro plus v. 4.5 (Media Cybernetics Manufacturing) program.

For the evaluation of the electrochemical properties of both the Si-Ge and Ge-Si core–shell nanowires, coin-type half cells (2032 type) were fabricated. The precise mass of the active material was measured using a microbalance (Sartorius SE2, resolution 1 μ g, Sartorius, Germany) before and after nanowire growth. A solution of 1.3 μ LiPF₆ in a solvent mixture of ethylene carbonate (EC) and diethylene carbonate (DEC)

(3:7 vol%) and pure Li metal were used as an electrolyte and a counter electrode, respectively. The cycle retention of the electrodes was conducted at a rate of 0.2 C between 0.01 and 2 V (TOSCAT 3000, Tovo Systems, Japan). The morphological changes of the both nanowires as a function of the lithium insertion were observed using FE-TEM (JEM 2100F, JEOL, Japan) and FE-SEM (S-4700, Hitachi, Japan). To determine the kinetics of lithiation of the Si-Ge and Ge-Si core-shell nanowires, Swagelok-type half cells was assembled with electrodes of the appropriate material. These electrodes were assembled against a Li metal electrode, separated by glass fiber (Whatman) which was wetted with an electrolyte solution of 1.3 M LiPF₆ in EC:DEC (3:7 vol%). Samples examined by potentiostatic methods were discharged to 0.01 V, with a voltage step of 10 mV (VMP3, Bio-Logic). Galvanostatic intermittent titration Technique (GITT) samples were evaluated between 2.5 and 0.01 V, at a rate equivalent to 0.02 C for 15 min, followed by a relaxation period of 15 min (VMP3, Bio-Logic). All samples were prepared in an argon-filled glovebox to prevent oxidation from air and moisture.

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