Minimized lithium trapping by isovalent isomorphism for high initial Coulombic efficiency of silicon anodes

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Silicon demonstrates great potential as a next-generation lithium ion battery anode because of high capacity and elemental abundance. However, the issue of low initial Coulombic efficiency needs to be addressed to enable large-scale applications. There are mainly two mechanisms for this lithium loss in the first cycle: the formation of the solid electrolyte interphase and lithium trapping in the electrode. The former has been heavily investigated while the latter has been largely neglected. Here, through both theoretical calculation and experimental study, we demonstrate that by introducing Ge substitution in Si with fine compositional control, the energy barrier of lithium diffusion will be greatly reduced because of the lattice expansion. This effect of isovalent isomorphism significantly reduces the Li trapping by ~70% and improves the initial Coulombic efficiency to over 90%. We expect that various systems of battery materials can benefit from this mechanism for fine-tuning their electrochemical behaviors.

RESULTS AND DISCUSSION

Our own experiment through a careful study of inductively coupled plasma mass spectrometry (ICP-MS) (fig. S1) also confirms that a significant amount (about one-third) of the Li loss in the initial cycle is due to Li trapping in the Si anode. The mechanism behind this Li trapping can be illustrated by the diffusion modeling (21, 38, 39). During the lithiation of the Si anode, Li diffuses into the interior parts of the Si electrode until full lithiation to form Li12Si4 (fig. S1A). In the process of delithiation, as Li with limited capability of diffusion cannot diffuse out completely, some Li will be trapped in the Si electrode (fig. S1B).

Isovalent isomorphism, the increase of lattice constants because of partial substitution of a larger isovalent ion, has been previously used to achieve higher ionic conductivity of solid electrolytes (40–43). We first used a Ge isovalent ion to alloy with the Si anode. As shown in Fig. 1 (A and B), because of the partial replacement of Si by Ge, the lattice of the Li-Si-Ge phase is expanded compared to the original Li-Si phase, as illustrated in table S1. That generates two competing effects on Li atoms, depending on their positions relative to Ge atoms. For Li atoms far away from Ge, lattice expansion results in the larger local volumes occupied (the effect of “local expansion”). The lattice expansion causes the bond lengths (BLs) between Li and Si atom to increase. However, there is no change in the relative positions of Li and Si atoms. Thus, Li atoms can occupy larger local volumes to be helpful for Li diffusion in Li-Si anodes. For Li atoms close to Ge, such as those first neighbor atoms, the diffusion channels are narrowed because of the larger ionic radius of Ge (the “narrow channel” effect). Therefore, we surmise that as trace amounts of Ge atoms are added to replace Si, most of the Li atoms are far away from Ge atoms. The local expansion effect should dominate, which initially reduces the energy barrier of Li migration in the Si anode. If more Ge atoms are added in, then there would be more Li atoms sitting close to Ge atoms and the narrow channel effect is expected to dominate, which increases the energy barrier of Li migration.

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Hence, we hypothesize that there exists an optimum atomic ratio of Si-Ge for minimized energy barrier and Li trapping.

To verify this mechanism, we first performed density functional theory (DFT) calculations to examine the energy barriers of Li diffusion in Li$_{15}$Si$_4$Ge$_x$ ($x = 0, 0.25, 0.5, \text{ and } 4.0$) alloys. It was demonstrated in a previous study (44) that Li ions typically diffuse along two pathways: the Li$_{2\alpha}$ vacancy defect moves to Li$_1$ as Path 1 and the Li$_{2\beta}$ vacancy defect moves to Li$_2$ in adjacent groups as Path 2 (Fig. 1E; see more details in Materials and Methods). As shown in Fig. 1F, when the amount of Ge is small, as in the case of Li$_{15}$Si$_{3.75}$Ge$_{0.25}$ (atomic ratio of Si:Ge, 15:1), the effect of local expansion dominates Li diffusion; therefore, Li atoms have smaller energy barriers of diffusion. The energy barriers of Li diffusion in Li$_{15}$Si$_{3.75}$Ge$_{0.25}$ (atomic ratio of Si:Ge, 15:1) along these two pathways decrease by 33.6% (from 0.113 to 0.075 eV for Path 1) and 54.2% (from 0.048 to 0.022 eV for Path 2), respectively. However, as the composition of Ge increases, as in the case of Li$_{15}$Si$_{3.5}$Ge$_{0.5}$ (atomic ratio of Si:Ge, 7:1), the narrow channel effect plays a dominant role; thus, the energy barriers of Li diffusion along Path 1 and Path 2 increase sharply to 0.124 and 0.072 eV, respectively. This can also be verified by the increase of binding force on each Li atom with Ge content, as illustrated in table S1 and fig. S2. Therefore, DFT calculations clearly indicate that Li diffusion in Li-Si-Ge is dominated by the two competing effects of local expansion and narrow channel: a small amount of Ge alloyed into Si (atomic ratio of Si:Ge, 15:1) can lower the energy barriers of Li migration and reduce Li trapping.

To experimentally finely control the atomic ratio of Si to Ge, we prepared Si-Ge alloy particles with various atomic ratios (Si$_{15}$Ge in Fig. 2A; other ratios are in fig. S4) by a convenient ball milling process (see more details in Materials and Methods). Si particles with a diameter of 150 nm were chosen to avoid self-pulverization, which is consistent with previous studies (45, 46). A transmission electron microscope (TEM) image of Si$_{15}$Ge particles and the diffraction pattern (Fig. 2B) confirm that the obtained Si$_{15}$Ge particles are crystalline (inset of Fig. 2B) with a diameter around 150 nm. It is seen from the high-resolution TEM micrograph of the selected area in the Si$_{15}$Ge particle that atomic lattice planes are separated by 3.13 Å, slightly larger than that of Si (3.10 Å) (Fig. 2C) (47). Images of scanning TEM (STEM) and corresponding energy-dispersive x-ray (EDX) spectroscopy elemental mapping reveal a uniform atomic scale mixing (Fig. 2D) of Si and Ge of Si$_{15}$Ge particles. Scanning electron microscope (SEM) EDX
results confirm the precise atomic ratios of the obtained particles (fig. S4). The lattice expansion of Si-Ge alloy with more Ge is verified by a clear peak shift to smaller angles in x-ray diffraction (Fig. 2E) (48, 49). The Si-Si peak also shifts to lower wave numbers as the Ge content increases in Raman spectra (Fig. 2F), confirming that Ge atoms disrupted the Si lattice to form the Si-Ge alloy. These results together suggest that Si-Ge alloy particles with various atomic ratios of Si to Ge have been successfully prepared through ball milling.

To examine the electrochemical performance of Si-Ge alloy electrodes, half-cell measurements were first carried out using Li metal as a counter/reference electrode. For comparing CE, the thickness of each electrode was controlled to be around 10 μm. Figure 3A presents the typical cyclic voltammetry (CV) results of different Ge concentrations alloyed with Si in the first and second cycle at a scanning rate of 0.1 mV/s between 0 and 1 V versus Li/Li+’. In the CV of Si, a sharp redox peak below 0.1 V appears during the first Li insertion process, indicating the initial lithiation of crystalline Si. Along with the increase of Ge concentration, the redox peak shifts to a higher voltage, which is consistent with the Si-Ge alloy anode reported before (49). The discharge/charge profiles at the same current density of 0.1 C of these electrodes exhibit the precise lithiation platforms, clearly elucidating the differences of Ge addition in the Si anodes (Fig. 3B). It is observed that the Si15Ge alloy anode delivered a charge and discharge capacity of 3200.8 and 3010.9 mA-hour/g at the initial cycle, corresponding to a high initial CE of 94.1% (Fig. 3B), which is higher than that of pure Si and other Si-Ge alloy electrodes, comparable to that of commercial graphite anodes. To avoid the interference, we measured 10 samples for each electrode at the same rate of 0.1 C and obtained the statistical results, as shown in Fig. 3C. It is obvious that the Si15Ge alloy electrodes exhibit higher initial CE ranging from 89.4 to 94.1% as compared with that of other Si-Ge alloy electrodes, which are almost always below 80% (21–29). Figure 3D lists the value of initial CE from this work, in comparison with other strategies reported previously such as electrolyte additives, structure design, and prelithiation. We also prepared new samples of each electrode for long cycles. Note that in the subsequent cycles, a Si15Ge electrode still maintains higher CE than other electrodes, which reaches up to 99% after only the third cycle (fig. S5B). It illustrates that isovalent isomorphism can minimize lithium trapping in each lithiation/delithiation cycle. Moreover, the various Si-Ge alloy anodes show a difference in terms of capacity retention (fig. S5A). With the increase of Ge concentration, the electrodes present more stable cycles (such as Si2.6Ge, SiGe2.7, and Ge) due to the higher intrinsic electronic/ionic conductivity, which is similar with that reported previously (48). For SiGe anodes with high

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**Fig. 2. Characterizations of the obtained Si-Ge alloy nanoparticles.** (A) SEM and (B) TEM image of Si15Ge nanoparticles (inset: diffraction pattern). (C) High-resolution TEM of the selected part in (B). (D) STEM and corresponding EDX mapping images of Si and Ge (scale bar, 50 nm). (E) X-ray diffraction and (F) Raman results of various ratios of Si-Ge alloy nanoparticles. a.u., arbitrary units.
Si composition as in the case of Si and Si15Ge, they exhibit obvious capacity decay after 100 cycles, while their initial capacities are higher than that of other Si-Ge alloy anodes. It has been proved that structure design such as carbon coating can be effective to improve the long cycle stability of Si15Ge anodes (fig. S5C).

It is critical to figure out the exact cause of high initial CE of Si15Ge electrodes. Besides the formation of SEI and some Li trapped in the electrodes, the unstable structure due to volumetric change can also cause the first irreversible Li consumption in electrode. The volume expansion of Si-Ge alloy electrodes was unveiled by the SEM (Fig. 4, A and B, and fig. S6). The top-view images of Si and Si15Ge electrodes portray similar results. Both electrodes were maintained coalesced and intact; no pulverization or cracks were observed because of the small size of nanoparticles (<150 nm). The cross-sectional images reveal that the electrodes of Si and Si15Ge have similar thickness at pristine states (10.1 and 11.2 μm, respectively). For both of these two electrodes, thickness remains unchanged (10.8 and 11.4 μm, respectively) after the initial cycle, reflecting the cycle stability of electrodes. Therefore, it is safe to conclude that the initial Li loss due to pulverization induced by volume expansion should be negligible.

To identify the influence of SEI formation, we performed a TEM study of Si-Ge alloy electrodes after the initial cycle. The obvious evidence comes from TEM images of the cycled Si and Si15Ge, whose surfaces are found to be covered with an approximately 10-nm-thick SEI layer (Fig. 4, C and D), when compared with the pristine state. Other Si-Ge alloy particles with different atomic ratios present similar SEI thickness after the first cycle, while Ge particles exhibit a thicker SEI layer (fig. S7). X-ray photoelectron spectroscopy was exploited to characterize the SEI components of Si and Si15Ge, suggesting the same SEI components for Si and Si15Ge (Fig. 4E).

To further study the growth kinetics and Li ion/electron transport of SEI films, electrochemistry impedance spectroscopy (EIS) was carried out. The electrochemical impedances of all cells based on Si-Ge electrodes with various atomic ratios were measured after the first cycle. Figure 4F presents the EIS of Si and Si15Ge after the first charge to 1.5 V. It is clear that both curves are composed of two high-frequency suppressed semicircles and a sloping line in the low-frequency region, which correspond to the SEI film formation, the charge-transfer reaction, and the Li⁺ diffusion effect on the electrode-electrolyte interfaces, respectively. On the basis of the equivalent circuit model (inset of Fig. 4F), the $R_{SEI}$ (SEI film resistance) of a Si15Ge cell is about 128.2 ohms, which approximates to 123.1 ohms of the Si cell’s $R_{SEI}$. It is consistent with the TEM results (Fig. 4, C and D) that SEI with a similar thickness was formed during electrochemical cycling for Si and Si15Ge. The SEI impedances of other Si-Ge alloy cells were fairly similar (around 150 ohms), while that of the Ge cell showed a higher value of 175 ohms (fig. S8). In general, it seems that, from the statistical results of $R_{SEI}$ and SEI thickness, no distinct differences are shown in the formed SEI for five different samples of Si-Ge electrodes with different atomic ratios (Fig. 4G).

To understand the origin of the increase of initial CE for the Si15Ge electrode, we exploited ICP-MS to determine the Li contents of different Si-Ge alloy electrodes after the first cycle (seen in Materials and Methods). It was found that Si15Ge electrodes have much less amounts of trapped Li (0.9 to 1.2%) compared to other electrodes (4.6 to 11.1%). For clarity, we define a value ($\eta$) to represent the concentration of...
trapped Li in the initial entire Li loss (η = trapped Li/Li loss and Li loss = SEI Li + trapped Li). It is interesting to find that the η of Si15Ge electrodes was 9.2 to 11.1%, far lower than that of other electrodes (~30%), suggesting minimized Li trapping in the Si15Ge electrode, which is consistent with the DFT calculation (Fig. 1F). It is also noted that, although the thickness of SEI for Si and Si15Ge is similar (Fig. 4G), the concentration of Li from the SEI (LiSEI) also reduced from ~8.5 to 15.3% (Si) to ~7.7 to 9.5%. This reduced LiSEI in a Si15Ge anode may be attributed to improved Li kinetics because of lower energy barriers of Li migration, consequently resulting in the formation of SEI with low density (50–53).

To examine whether this mechanism of isovalent isomorphism can be applied to other isovalent atoms, we also performed the same study for Si-Sn alloys. The energy barriers of Li migration along two pathways in Li-Si-Sn alloys were calculated (see more details in tables S3 and S4), which show a similar trend as that in Li-Si-Ge alloys (fig. S2 and Fig. 1F). We also prepared Si-Sn alloy particles with various atomic ratios as anodes to examine the electrochemical performance. As shown in fig. S9, the Si-Sn alloy with small percentage of Sn (Si18.2Sn) shows the highest initial CE reaching 93.6%. According to ICP results (table S5), the η value of Si18.2Sn is 12.03%, the lowest among all the Si-Sn alloys, consistent with the calculation result (fig. S3B). Therefore, our proposed mechanism is generalized for isovalent atoms to minimize Li trapping.

In summary, we demonstrated that through a fine compositional control of alloy anodes, isovalent isomorphism can be used to effectively reduce the energy barriers of Li diffusion and therefore reduce Li trapping and increase initial CE. As an example, anodes based on a Si-Ge alloy (atomic ratio of Si:Ge, 15:1) have significant reduced Li trapping (70% decrease compared to Si) and high initial CE reaching 94.1%. This practical approach can be applied to other isovalent atoms (such as tin) and complementary to other structural designs and engineering methods. Therefore, this effect based on isovalent isomorphism provides an extra knob for fine-tuning electrochemical Li behaviors in various material systems.

MATERIALS AND METHODS
Computational methods
It is known that the Li15Si4−xGex phase is in the fully lithiated state at room temperature, in which all the Si (and Ge) atoms at 16c sites are surrounded by Li atoms while Li atoms are classified into two groups according to the symmetry: L11 atoms at 12a sites and Li2 atoms at 48e sites (Fig. 1, C and D). To theoretically find out the stable structures of Li15Si4−xGex (x = 0, 0.25, 0.5, and 4.0) alloys, their structure optimizations were first performed in the frame of DFT with the program package CASTEP (54, 55), using the plane-wave (PW) ultrasoft pseudopotential method and the Perdew-Wang (PW91) form of generalized gradient approximation (GGA) exchange-correlation energy functional (56). To quantificationally estimate the covalent interactions on each Li atom in Li15Si4−xGex, the average bond orders (BO) and BLs were calculated.

Fig. 4. Characterizations of Si-Ge alloy anodes before/after initial cycle. (A) Top view and cross section of Si electrode and (B) Si15Ge electrode before and after initial cycle [scale bars, 10 μm (top view) and 5 μm (cross section)]. (C) TEM of Si and (D) Si15Ge nanoparticle after initial cycle (scale bar, 10 nm). (E) X-ray photoelectron spectroscopy results of Si and Si15Ge electrodes after initial cycle. (F) Electrochemistry impedance spectroscopy (EIS) result of Si and Si15Ge after initial cycle. (G) The statistical results of RSEI and SEI thickness from five different samples. (H) LiSEI and trapped Li from ICP results and η value.

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by using a projection of PW states onto a molecular orbital basis in the Mulliken population analysis (57).

Then, depending on the type of Li atoms and the distances between them, we chose two sets of pathways for Li migration in Li15Si4 to examine the energy barriers by performing transition state (TS) searches. As seen in Fig. 1E, for the first set of pathways (Path 1), the Li2α vacancy defect moves to Li1, while for the second set of pathway (Path 2), Li2α vacancy defect migrates to Li2β in adjacent groups. The TS searches of Li migration in Li15Si4−Ge were carried out using the program package DMol3 (58, 59) with double numerical with polarization basis sets and the complete linear synchronous transit/quadratic synchronous transit method (60).

**Preparation of particles**

The particles with a diameter of ~150 nm were prepared by ball milling. After mixing the silicon powder (99.9%; Alfa Aesar) and germanium (99.99%; Alfa Assar), the mixture was ball-milled with a rotation speed of 750 rpm. Before fabricating electrodes, the obtained particles were etched by 5% HF for 5 min to avoid oxidation.

**Preparation of the electrodes**

The control electrode was prepared by dissolving the mixture of 60 mg of nanoparticles, 20 mg of carbon black, and 20 mg of sodium carboxymethyl cellulose binder in deionized water (0.6 ml) to make slurry. After stirring, the slurry was cast onto a copper foil and then dried in a vacuum oven at 110°C.

**Half cells for testing**

Coin-type cells (2032) were fabricated inside an Ar-filled glove box using a Celgard 2250 separator. A Si-Ge alloy electrode and Li metal foil were prepared as two electrodes. The electrolyte used was 1.0 M LiPF6 in 1:1 v/v ethylene carbonate/diethyl carbonate with 2 weight % vinylene carbonate (Guotai Huarong) added to improve the cycling stability. The electrochemical tests were performed using a LANHE system.

**SEM and TEM**

The nanoparticle samples were prepared by casting the nanoparticles on the copper colloids and observed by SEM (TESCAN MIRA3). The electrode samples were prepared by sticking the electrodes to the copper colloids directly. The electrode after cycling was treated with acetonitrile and then dried in a vacuum oven at 110°C.

**ICP–atomic emission spectroscopy test**

The electrode after 1 cycle was treated with acetonitrile to remove the electrolyte and dried in the Ar-filled glove box. Then, the electrodes were dissolved in 5 ml of deionized water overnight to completely remove the extra Li on the electrode. Then, the electrodes were treated in 0.5 M HCl to dissolve SEI; supernatants (1 ml) were extracted from the solution and were tested using an ICP-AES (atomic emission spectroscopy) instrument to get the Li+ concentration of SEI. After washing the remained electrodes with ultrapure water, 10% HCl, 20% HNO3, and 8% HF were added to dissolve Si, Ge, and the trapped Li. After centrifugation, 1 ml of solution from supernatants was tested using an ICP-AES instrument to determine the trapped Li. Last, the amount of trapped Li was calculated.

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/5/11/eaax0651/DC1

Diffusion model in the Li insertion and extraction

DFT calculations of Si-Ge alloy

DFT calculations of Si-Sn alloy

Characterizations of Si-Ge alloy with various atomic ratios

Characterizations of Si-Sn alloy anodes

Fig. S1. Schematic of diffusion modeling in lithiation and delithiation processes.

Fig. S2. Relationship between average scaled bond orders BOave and the atomic ratio Si to Ge in Li15Si4−Ge.

Fig. S3. Relationship between average scaled bond orders BOave versus the atomic ratio of Si to Sn in Li15Si4−Sn (x = 0.25, 0.5, 1.0, and 4.0) alloys.

Fig. S4. SEM images of the obtained particles after ball milling.

Fig. S5. The electrochemical performance of Si-Ge electrodes with various atomic ratios.

Fig. S6. SEM of top view and cross-sectional view of electrodes based on Si-Ge alloy before and after initial cycle.

Fig. S7. TEM images of the SEI after initial cycle of Si2.6Ge, SiGe2.7, and Ge, respectively.

Fig. S8. EIS results of Si2.6Ge, SiGe2.7, and Ge electrodes after initial cycle.

Fig. S9. The voltage profile of various Si-Sn alloy electrodes in the first cycle and statistic CE.

Table S1. Space group, experimental, and first-principles (GGA) calculated lattice parameters (Å) of Li15Si4−Ge.

Table S2. The Li migration energy barriers (eV) along two sets of pathways in Li15Si4−Ge.

Table S3. Space group, experimental, and first-principles (GGA) calculated lattice parameters (Å) of Li15Si4−Sn (x = 0.25, 0.5, 1.0, and 4.0) alloys and their scaled BOS and number (α and β) of Li-Si and Li-Li covalent bonds on each Li atom.

Table S4. The Li migration energy barriers (eV) along two sets of pathways in Li15Si4−Sn.

Table S5. The LiSEI, trapped Li, and Sn content/full/5/11/eaax0651/DC1

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