High capacity lithium ion battery anodes of silicon and germanium
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Lithium ion batteries with significantly higher energy and power density desired for new personal electronic devices, electric vehicles, and large-scale energy storage, require new materials. This review focuses on the replacement of the graphite anode with silicon or germanium. Si and Ge both have significantly higher Li storage capacities than graphite, but also undergo significant volumetric expansion and contraction during lithiation and delithiation. Si and Ge nanomaterials can tolerate these mechanical stresses, but solvent decomposition and loss of electrical contact with the current collector tend to lead to failure. Si and Ge anodes must therefore be formulated with appropriate binder, conductive carbon, and stabilizing additives in the electrolyte solvent to achieve stable cycling and high capacity, as described herein.

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Current Opinion in Chemical Engineering 2013, 2:286–293
This review comes from a themed issue on Energy and environmental engineering
Edited by Rakesh Agrawal and Subhas K Sikdar
For a complete overview see the Issue and the Editorial
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http://dx.doi.org/10.1016/j.coche.2013.07.001

Introduction
More advanced portable electronic devices, electric vehicles, and large-scale energy storage for the electrical grid, need rechargeable lithium ion (Li-ion) batteries with higher energy and power density, and lighter weight than currently available [1]. The energy density of Li-ion batteries has increased 8–9% per year since the early 1990s, but meeting future needs requires a breakthrough in materials design [2]. The Li-ion battery now consists of a Li metal oxide cathode and a graphite anode. Charge and discharge occurs by a redox process in which Li ions shuttle between electrodes and the charge capacity depends on how much Li can be incorporated into the electrode materials. Many aspects of Li-ion batteries can be improved, as documented by some excellent reviews [1–3,4*,5*]. In particular, various nanostructured electrode materials have the potential for much higher charge storage capacity [3,4*]. This review focuses on replacing the graphite anode with much higher capacity Si or Ge.

Graphite has a Li charge storage capacity of 372 mA h g⁻¹, corresponding to a lithiated state of LiC₆ — Li is stored in graphite by intercalating between graphitic sheets. Si, on the other hand, can soak up large amounts of Li to form an alloy of Li₅Si₄ when fully lithiated, resulting in a lithium storage capacity of 3579 mA h g⁻¹ that is nearly ten times higher than graphite [6,7]. The caveat is that the host Si lattice must expand by up to 280% to accommodate the Li. Nanoscale Si can tolerate this volumetric expansion (and contraction upon delithiation), whereas bulk Si pulverizes [8,9]. Ge also alloys with Li and forms Li₅Ge₄ when fully lithiated with four times the lithium storage capacity of graphite (1384 mA h g⁻¹) [10,11], and a volumetric capacity similar to Si (7366 A h L⁻¹ for Li₁₅Ge₄ versus 8334 A h L⁻¹ for Li₁₃Si₄). Also compared to Si, Ge anodes have performed especially well at high cycle rates and high current density [12*,13***,14–17].

Significant advancements in Si and Ge anode development have occurred in recent years. For example, lithiation and delithiation of Si and Ge has been observed directly in real time by in situ transmission electron microscopy (TEM), providing insight about how to design stable Si and Ge anodes. [18**,19**,20**] Advancements in conductive nanomaterials coatings, binder materials, and electrolyte additives have also significantly improved charge storage capacity and cycle stability. Recent findings are highlighted here, as well as some remaining challenges.

Li-ion batteries
The electrodes of a Li-ion battery are separated by an electrically insulating, Li⁺ ion permeable membrane and immersed in an ionically conductive electrolyte solution. During discharge, Li⁺ ions shuttle from the anode to the cathode and electricity flows through the external circuit to power the device (Figure 1f). The battery is recharged by applying a voltage that forces Li back into the anode. The stored electrical energy depends on the open circuit voltage determined by the difference in anode and cathode redox potentials and the charge storage capacity of the anode and cathode. Si and Ge have much higher lithium storage capacities than graphite and similar operating voltages thereby providing significantly higher energy density, but the batteries must undergo hundreds of cycles without significant capacity fade. Cycle rate, typically reported as C/X where X is the number of hours required to fully charge or discharge, also affects the charge storage capacity as faster cycle rates and higher current densities can induce kinetic limitations that lower the capacity (Figure 1g and h). To isolate battery
Nanowire batteries. (a) SEM and high-res TEM images of nanowires. (b) Structure of different polymeric binders (NaAlg and PVdF) and electrolytes (ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), fluoroethylene carbonate (FEC), and propylene carbonate (PC)). (c) Slurry of nanowires with binder and conductive carbon in n-methylpyrrolidone (NMP) (d) and (e) doctor-bladed onto a copper foil current collector. (f) Cartoon representation of electron and Li⁺ ion flow during charge and discharge of the battery. (g) and (h) Capacity of Si and Ge nanowire batteries cycled at C/10 for 100 cycles and at various faster rates for periods of 10 cycles.

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performance limitations to the Si and Ge anodes, coin cells are made using Li metal as the counter electrode — so-called ‘half-cells’ — to ensure that the performance is not limited by the cathode. In these tests when Li metal is used as the counter electrode, the Si and Ge electrode is actually the cathode, or positive electrode, due to their relative redox potentials.

**Silicon and germanium lithiation**

Crystalline Si (c-Si) lithiates to form an amorphous Li₅Si alloy before reaching the fully lithiated crystalline phase of Li₁₅Si₄:

\[
\text{Si} \rightarrow a-Li₅Si \rightarrow Li₁₅Si₄
\]  

Lithiation and delithiation of Si gives rise to two distinct plateaus in the capacity versus voltage plots, or correspondingly, two peaks in the differential capacity data (Figure 2c). This indicates that lithiation occurs by the formation of two chemically distinct amorphous lithiated phases. Mössbauer spectroscopy studies have revealed that these two peaks correspond to lithiation up to a Li content of Li₂₅Si, at which point each Si atom becomes completely surrounded by Li nearest neighbors [23**]. At this point, the lithiation redox potential shifts. More Li then incorporates into the a-Li₅Si until saturation at Li₁₅Si₄. In situ TEM imaging of a-Si disks as they lithiate has confirmed this two-phase, or two-step, process [18**]. The entire a-Si does not uniformly take up Li, but rather forms a shell of a-Li₅Si that migrates into the core of the structure as lithiation proceeds. After the entire disk has become a-Li₅Si (x ~ 2.5), further lithiation takes place to form a-Li₃Si by a single-phase alloying process [18**]. This two-phase lithiation process has also been observed in c-Si, in which the a-Li₅Si/c-phase boundary moves into the center of the nanostructure [19**,24]. This interphase boundary creates significant mechanical stress and c-Si particles larger than 150 nm fracture during lithiation [24]. After the first delithiation cycle, Si remains amorphous [19**]. Amorphous Si particles appear to be much more stable than c-Si particles and a-Si nanoparticles up to 870 nm in diameter do not fracture upon lithiation [19**,25] (Figure 2a and b). Beyond the initial cycle, c-Si and a-Si nanoparticles show no difference with repeated cycling [19**].

Si nanowires have also been studied to determine if there are any significant differences compared to nanoparticles. Ryu et al. have reported that c-Si nanowires with diameter less than 300 nm do not fracture, even if pre-existing
Lithiation of Si and Ge nanomaterials. In situ TEM observation of lithiating (a) c-Si and (b) a-Si nanoparticles undergoing a two-phase lithiation mechanism with fracture of the c-Si nanoparticle and no fracture of the a-Si nanoparticle. In situ TEM observation of lithiating (c) Si and (d) Ge nanowires. The Si nanowire exhibits anisotropic expansion and fracture, whereas the Ge nanowire exhibits isotropic expansion. (e) and (f) Differential capacity plots of Si and Ge nanowires showing the lithiation (bottom) and delithiation (top) peaks through repeated cycling. Parts (a, c, and d) reproduced with permission from [20], copyright 2012 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim. Parts (b), (e), and (f) reproduced with permission from [19**,22*,13**], copyright 2013, 2012, and 2012 American Chemical Society.

The voltages at which lithiation and delithiation occur in Si and Ge during cycling are observed in differential capacity plots (Figure 2e and f). a-Si lithiation occurs at 250 mV initially until Li2.5Si has formed and then the lithiation potential shifts to just below 100 mV until the saturated Li13.75Si phase has formed (Figure 2c) [22*,23**]. Similarly for Ge, after the first cycle the differential capacity plot shows three relatively broad lithiation peaks at 500, 350, and 200 mV corresponding to the lithiation of amorphous Ge (Figure 2f) [13**]. Like Si, Ge remains amorphous after the first cycle. For both Si and Ge, full delithiation does not occur until reaching a potential of 500 mV, which is 400 mV higher than graphite delithiation. This means that replacing graphite with Si or Ge comes with a 0.4 V loss in open circuit voltage of the battery. This can be a problem for applications that require higher voltage batteries; however, it can be corrected through the use of higher voltage cathodes.

Anode formulation and materials

Vapor deposited nanowire anodes

Si and Ge nanowires have been grown by chemical vapor deposition (CVD) on copper, titanium, or stainless steel current collectors to ensure good electrical contact [28–32]. Si nanowire anodes made by fabricating nanowires directly on the current collector [28–31] have exhibited capacities of more than 3500 mA h g⁻¹ after 25 cycles at a rate of C/20, which is nearly the theoretical maximum capacity [30]. The capacity of the Si nanowire anodes is reduced at faster cycle rates, with capacity decreases of more than 40% when cycled at 1 C or faster [28,30]. Ge nanowires grown on stainless steel as a current collector have shown capacities up to 1141 mA h g⁻¹, 82% of the maximum capacity, after 100 cycles at a rate of C/20 [32]. Ge has exhibited better cycle retention than Si at higher rates. For example, Ge nanowires have recently been reported with 580 mA h g⁻¹ cycled at 2 C, which is almost double the theoretical capacity of graphite [32]. The problem with CVD nanowire growth is that it is relatively expensive, yielding very small amounts of material after several hours of deposition.
Solution-grown nanowires for anodes

Slurry-based Si and Ge anodes have also been extensively studied. Si and Ge nanoparticles are commercially available and Si and Ge nanowires can be grown in large quantities in solution [11,13**]. Initial attempts to make anodes from these materials resulted in low capacities and poor cyclability due to low film conductivity and poor electrical contact [36,37]. These problems have been addressed by introducing binders like polyvinylidene fluoride (PVdF) or sodium alginate (NaAlg) and additional conductive carbon or coatings. Typically, the active material is mixed with binder and carbon with a minimal amount of solvent to form a slurry that is doctor-bladed onto a metal foil current collector (Figure 1a–e).

Binder materials

Poly(vinylidene fluoride) (PVdF) is currently used commercially as a binder for Li-ion cathodes and graphite anodes and has also been relatively effective for Ge anodes [13**]. For Si, however, PVdF has met limited success. Heating to about 200 °C is needed to infuse PVdF into Si anodes [38] and weak bonding between Si and PVdF has led to anode failure with repeated cycling [39].

Other binders have shown reasonably good success with Si. Carboxymethyl cellulose (CMC) has carboxylic acid functional groups that can bond to the native oxide surface layer and has exhibited good cycle stability [40]. Alginate (Alg), which is naturally occurring from brown algae, is structurally similar to CMC and has also been shown to be effective as a Si anode binder [41]. Binders with the ability to hold the anode together and improve adhesion to the copper current collector have also been studied. Poly(acrylic acid) (PAA) adheres much more strongly to the copper collector than PVdF and CMC based on measurements of the load (N cm⁻¹) required to peel the anode off the Cu collector [42]. Enhanced adhesion of the anode to the current collector with the addition of PAA has improved cycling reversibility of Si anodes [39,42-44,45*], especially when it was cross-linked with additional CMC binder [45*].

Conductive additives

Because Si is a poor electrical conductor, additives are needed to improve electrical conductivity and lower the series resistance in the anode. Usually 10–30 wt% of conductive carbon powder is mixed into the battery formulation. Segregation of the carbon particles decreases the performance of the anode [46], so Si nanomaterials with electrically conductive coatings have also been made and studied. For example, Si coated with carbon or metals such as copper has exhibited significantly improved battery performance compared to anodes made without any conductive additive [37,47–51]. With its smaller band gap than Si, Ge has an electrical conductivity that is more than two orders of magnitude higher than Si. The more efficient electrical transport in Ge anodes results in better rate capability. Recently, composite anodes with both Si and Ge combined with graphene sheets or carbon nanotubes have been made and have exhibited relatively good performance, even without added binder [34,52–56].

Electrolyte solvent and SEI formation

Li-ion battery electrolyte solutions are comprised of a Li salt, generally LiPF₆, dissolved in a nonaqueous, carbonate-based solvent. Si and Ge anodes operate at potentials close to that of metallic lithium, resulting in solvent decomposition and the formation of a solid electrolyte interphase (SEI) layer primarily composed of carbonate byproducts including lithium alkyl carbonates, lithium carbonate, lithium alkoxide, polycarbonates, and ethers [57–60]. The SEI increases electrical resistance in the electrode and hinders Li-ion diffusion to the active anode material. The SEI layer can also trap a significant amount of Li and decrease storage capacity [47,58,61]. However, the SEI layer can also protect the anode surface and prevent degradation. Therefore, a robust, yet thin, SEI layer is needed for optimum battery performance. This has been a challenge in Si and Ge anodes because of the large volumetric expansion and contraction that occurs during charging and discharging. During cycling, the SEI layer can crack and expose the anode to the electrolyte solution, resulting in additional SEI growth and further oxidation of the anode material, decreasing battery performance over time [62,63**]. Electrode-stabilizing electrolyte solvents represent one of the most important aspects needed for stable Si and Ge anode cycling.

Commercial graphite anodes use solvent mixtures of ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC). In carbon anodes, electrochemical decomposition of these carbonates forms a stabilizing SEI layer and is one of the key attributes of carbon-based anodes. In many studies, these typical carbonates have not provided stable SEI layers and cycling for Si and Ge anodes. Fluoroethylene carbonate (FEC) additive has been found to be particularly effective at stabilizing Si and Ge anode cycling [13**,22**,33,35,63**,64,65]. FEC is less susceptible to oxidation and appears to induce the formation of a relatively stable SEI layer [63**,64]. Vinylene carbonate (VC) has also been shown to improve thermal stability and electrochemical performance of Si anodes and has been combined with FEC in some cases [66–69].

Silicon and germanium anode performance

Figure 3 provides a summary of recent literature reports on the capacities demonstrated for both Si and Ge nanomaterials at different cycle rates. Si and Ge anodes have exhibited charge capacities close to their maximum...
capacities, as high as 3500 mA h g\(^{-1}\) and 1475 mA h g\(^{-1}\), respectively [30,70]. Si nanowires have shown higher capacities than Si nanoparticles when cycled at slower rates (C/20 to 1C), but lower capacities when cycled at faster rates (2C to 10C) [30,71,72]. Ge nanowires have generally shown higher capacities than Ge nanoparticles [12*,13**,16,70]. At higher cycle rates, Ge has exhibited better capacity retention than Si, retaining about 55% of its capacity when rates have been increased from C/20 to 10C compared to Si, which has retained only 35% of its capacity [13**,30,72]. While, Ge has better capacity retention, the actual capacities exhibited by Si and Ge at higher rates are relatively similar making them both attractive alternatives to graphite for rapid charging and high power delivery applications.

**Full cells**

Si and Ge anode performance is tested using Li metal as the counter electrode to ensure that the battery performance is not limited by the cathode; however, the total capacity of a practical full-cell battery using Si or Ge anodes would be hindered by the low capacity of the cathode material. As shown in Figure 4, even without a change in the cathode material, Si or Ge anodes could improve the Li-ion battery capacity by more than 25%, despite their difference in maximum storage capacity (Figure 4). To obtain more significant improvements in storage capacity using Si and Ge anodes, new significantly higher capacity cathode materials must be developed. Recent work in high capacity cathodes have explored the use of vanadium oxides (442 mA h g\(^{-1}\)), metal fluorides (300–700 mA h g\(^{-1}\)), molybdenum oxides (1230 mA h g\(^{-1}\)), and sulfur (1672 mA h g\(^{-1}\)) [80–82]. While each of these materials provides a significant improvement in the capacity of the cathode, none of them contain lithium and cannot be combined with Si or Ge as is. Recently, efforts have been made into developing a prelithiation procedure for Si nanowires to enable the use of these non-lithium containing cathodes and usher in a new era of Li-ion battery technology [83].

**Conclusions and outlook**

Si and Ge both have significantly higher Li charge storage capacity than graphite. The main challenge facing their commercial use relates to the large volume changes that take place during battery cycling. Nanomaterials can tolerate these volume changes without significant loss of structural integrity, but the entire battery cell must withstand the volume changes as well. This means that an appropriate binder is needed and stabilizing electrolyte...
solvent additives that create thin and robust SEI layers. Binder materials are selected based on their ability to adhere to the nanowires and the current collector. Promising binders include PVdF for Ge, and CMC, NaAlg, and PAA for Si. Graphene and carbon nanotube composites have also been shown to increase capacities with improved structural integrity. Electrolyte additives have been sought to improve the formation and stability of the anode SEI layer with FEC and VC providing relatively stable electrochemical performance. To date, Si and Ge nanomaterial anodes have demonstrated reversible capacities up to 3500 mAh g⁻¹ and 1475 mAh g⁻¹, close to their respective maximum theoretical capacities, which are nearly 10-fold and 4-fold improvements over carbonaceous anodes. While their performance benefits are currently limited by the low capacities of current cathodes, prelithiation efforts look to enable the use of Si and Ge anodes with higher capacity, non-lithium containing cathodes. Although there are many research challenges that remain, Si and Ge nanomaterials are one of the most promising new revolutionary approaches to creating next generation Li-ion batteries.

Acknowledgements

Financial support of this work from the Robert A. Welch Foundation (Grant no. F-1464) is acknowledged. T.D.B acknowledges the National Defense Science and Engineering Graduate Fellowship for financial support.

References and recommended reading

Papers of particular interest, published within the period of review, have been highlighted as:

- of special interest
- of outstanding interest


A current review of challenges facing the improvement of Li-ion battery cathode materials.


A recent review of the research challenges facing the development of silicon anodes for Li-ion batteries.


Authors characterize and analyze a high capacity Ge anode using solution processed nanowires demonstrating the first full cell battery pack using Ge nanowires, with LiFePO₄ as the cathode, to power an LED display.


Authors demonstrate the best performance for a Ge anode using solution processed nanowires through repeated cycling at both slow and fast rates.


In situ TEM experiments reveal that lithiation of amorphous silicon proceeds by two steps, the first of which being a two-phase process, not simple phase as previously thought.


The lithiation/delithiation of amorphous Si was compared directly to crystalline Si nanoparticles using in situ TEM lithiation experiments showing no difference between the two after the first cycle.


Anisotropic and isotropic expansion of Si and Ge nanowires, respectively, was observed directly during lithiation by in situ TEM.


Stable, high capacity cycling (1800 mAh g⁻¹) of Si anodes for more than 100 cycles was demonstrated.


Determined that the two lithiation and delithiation peaks in the differential capacitance data are the result of a transition during lithiation of Si when each Si atom becomes completely surrounded by nearest neighbor Li atoms, at the composition LiₓSi. They also propose that battery failure is the result of a loss of electrical contact between conductive carbon additive in the anode layer.


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46. A multilayer Si anode binder was demonstrated that combined the adhesion of poly(acrylic acid) to copper foil with the strong bonding of carboxymethylcellulose to Si to improve anode capacity retention during cycling.


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New anodes for lithium ion batteries  


