Silicon and its Composites as Anode Materials in Li-ion Batteries

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Abstract

Recent technological advances need a reliable and sustainable energy storage system with a high energy density. $LiCoO_2$ and graphite are the cathode and anode materials used in current Li-ion batteries, respectively, however their capacity is restricted. The anode side of the battery plays an important function in storing Li-ions during charging and discharging cycles. Si has evolved as a unique anode material in recent decades with a theoretical capacity almost ten times that of traditional graphite. But there are various issues with Si, like massive volume expansion, electrode pulverization, decreasing cell capacity over time, etc. The electrochemical output of Si and its composites is determined by the materials utilized. Direct alloying of Si with Li yields stable phases such as $Li_{12}Si_7$, Li_7Si_3, $Li_{13}Si_4$ and $Li_{21}Si_5$ with the highest theoretical capacity. Composites of Si, which include carbon, polymer and other elements, exhibit promising outcomes. This paper summarizes and discusses current breakthroughs in Si and its composites tested as anodes in Li-ion batteries. The use of 1D, 2D and 3D carbon with various matrices for Si composite helps to accommodate volume expansion. Structural and morphological changes as well as the electrochemical performance of thus synthesized batteries have also been described.

Keywords: Li-ion battery, Anode, Silicon, Graphite, Energy storage, Cyclic stability.
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Introduction

We require a dependable energy storage system as technology advancements and energy consumption continue to rise. A system that can supply more energy in less space while being economical, portable, and with a long shelf life. There are several rechargeable energy storage options on the market with diverse chemistries such as NiCd, lead acid, NMH, Li-ion, Na-ion and K-ion. Li-ion batteries are one of the broadly used and investigated battery chemistries. It has a standard graphite anode and $LiCoO_2$ cathode with theoretical capacity of 374 $mAhg^{-1}$ and 160 $mAhg^{-1}$ respectively. Nevertheless, the demand for batteries with high energy density poses a new challenge to current technology due to its restricted capacity as the battery's capacity is solely determined by the material used.

In order to meet modern technology needs, a variety of materials have been tested to provide high energy density while remaining sustainable. Si may exhibit several advantages over the traditional anode material, graphite such as high energy density, cost effectiveness, ecologically sound and abundance. The chemistry of forming distinct phases with Li produces phases with the highest degree of lithiation. Phase diagram of Li and Si shows formation of various phases such as $Li_{12}Si_7$, Li_7Si_3, $Li_{13}Si_4$ and $Li_{21}Si_5$, where $Li_{21}Si_5$ has the highest degree of lithiation with chemistry of single Si atom forming bond with 6 Li atom giving advantage over graphite where 6 carbon makes bond with single Li atom. Figure 1 depicts the Li-Si phase diagram [1]. Si is the second most prevalent element on earth, accounting for around 27.7% of the planet's crust, making it a promising research topic [2]. Silicon does not occur in pure metallic form in nature, so we need to separate it from silica or silicates. Electronic structure of Si is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$, where two electrons (first shell), 8 electrons (second shell), and 4 electrons (outermost shell). These four electrons in the outermost shell determine Si's conductivity and structure. It has a 3D diamond like structure with a lattice constant of 5.431 angstrom having an Fd-3m space group. Before we can address Si composites, we must first understand the chemistry of Si with lithium. Li has an atomic number equal to three, making it the lightest metal on Earth. It has higher charge density, which means a lower atomic radius in comparison to its nuclear charge, making it extremely reactive and bond-forming. Because of this capacity, Li can easily polarize other molecules but not itself because of the double helium shell surrounding it. It is also the most active metal available due to its highly negative electrode potential. Figure 1 depicts the creation of different phases. The most lithiated phase is $Li_{22}Si_5$, with one Si atom hosting 4.4 Li atoms, resulting in the largest theoretical capacity. Lithiation of Si also shows formation of $Li_{15}Si_4$ at room temperature. Lithiation of Si starts with the formation of crystalline and amorphous phases of Li_xSi. Equation 1 shows the reaction process of lithiation of Si. Figure 2 depicts the galvanostatic profile for lithiation at room temperature. But there are several problems with Si as anode such as (i) huge volume expansion, (ii) low electrical conductivity, (iii) structural deformation on every cycle, (iv) low rate of Li^+ diffusion, (v) loss of contact in middle of active material with substrate, (vi) repeated formation of SEI, (vii) continuous consumption of electrolyte and Li^+ to form SEI and (viii) puffing of battery unit. In 1976, General Motors Corporation tested Si as an anode for the first time [3], sparks research on the material. Even graphite was commercialized several years later, circa 1990-1992, as a secondary battery. Since then, several research publications on Si as anode in alkali-ion batteries have been published. Many Si composites have been tested for anode in Li-ion batteries to mitigate the problems with Si anode, such as alloying Si with other elements of lower band gap to reduce the band gap for better electronic conductivity, synthesizing carbon-based yolk and core shell structure to compensate volume change, nano-structuring to avoid cracks inside the particle of active material and surface engineering to increase Li^+ diffusion and conductivity.

$$Li_xSi \leftrightarrow xLi + Si + xe^- \qquad (1)$$

Various strategies were and are being applied to mitigate these problems with silicon being used as anode in Li-ion batteries such as pre-lithiation, alloying Si, surface modification, structural modification, nano particle synthesis etc.

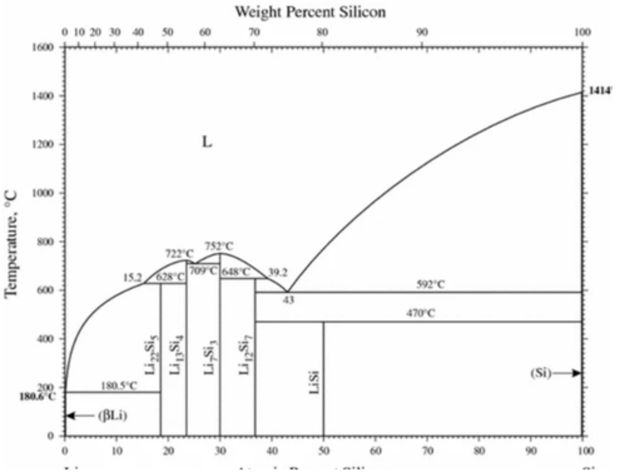

Figure 1: Phase diagram of Li-Si alloy [1]. Reprinted with permission from ACS Nano © 2013 American Chemical Society.

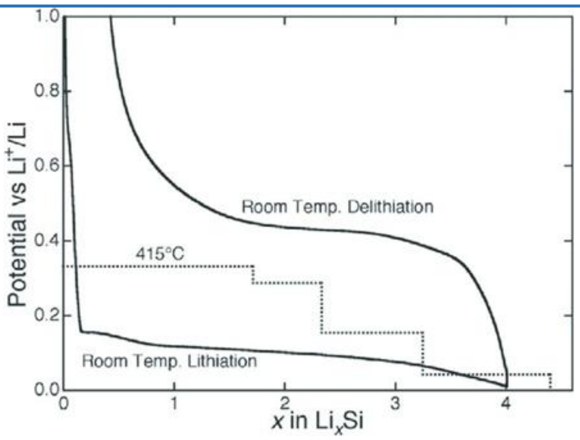

Figure 2: Graph of open circuit voltage as a function of lithium, shows formation of plateaus at elevated temperatures [4]. Reprinted with permission from Advanced Materials © 2013 John Wiley & Sons.

Silicon/Carbon (Si/C) Composites

Silicon/Carbon composite strategies were tested, including structural modification, synthesis of core and yolk shell structures, and production of nanoparticles, nanowires, and nanorods. Si/C materials demonstrate improved outcomes with increased cycling stability, longer life, and the problem of low conductivity. Si/C composite such as carbon nanotubes (CNT), synthesis of nano porous spheres helps in aiding to compensate the structural change and easing diffusivity by shortening the path of Li-ion diffusion. Si/C materials are synthesized using a variety of methods, including high-energy ball milling, pyrolysis, chemical vapour deposition, etching, and mechanofusion. Materials like conductive carbon obtained from various sources are used to synthesize Si/C to mitigate the problem of low conductivity of Si. Carbon's strong conductivity aids in obtaining a high value of charging and discharging during operation; in fact, we have traditionally used graphite, one of the allotropes of carbon, as an anode. However, despite these advantages, the continual volume expansion of Si in the composite consumes Li-ions, resulting in a paucity of active Li-ions inside the battery unit.

Table 1: Some of the Si/C materials together with synthesis roots and performance.

Composition / Material	**Synthesis roots**	**Anode Performance**	**Reference**
Si/C core shell	pyrolysis	high reversible capacity 1328.8 $mAhg^{-1}$ and high retention (97%) after 30 cycles at $J=50\ mAg^{-1}$	[5]

Si/C core shell	electrospinning	high capacity 1384 $mAhg^{-1}$ and retention of 97% after 300 cycles	[6]
Si/C	ball milling, mixing carbon black, graphite and carboxymethyl cellulose (CMC)	reversible capacity of 1000 $mAhg^{-1}$ after 1200 cycles in ratio Si:CB:graphite:CMC= 60:15:10:50	[7]
Si/C	magnetic stirring, freeze drying and calcination	specific capacity of around 792 $mAhg^{-1}$ after 100 cycles at J = 0.1 $mAhg^{-1}$	[8]
Si/C, Si and starch	mechanical stirring pyrolyzation and mortar pestle for grinding	reversible capacity of about 781 $mAhg^{-1}$ with 91.3% capacity retention after 50 cycles at J= 100 mAg^{-1}	[9]
SiNP, SiOx as sacrificial layer and polydopamine layer for carbonization	sol-gel and self-polymerization	reversible capacity of 2833 $mAhg^{-1}$ at C/10 with 88% retention after 500 cycles	[10]

Metal-Silicide Composites

Table 2: Various metal-silicide with synthesis roots and performance.

Composition / Material	**Synthesis roots**	**Anode Performance**	**Reference**
$Li_{21}Si_5$, Li and Si powder	Prelithiation melt solidification and ball milling	1007 $mAhg^{-1}$ delithiation capacity	[11]
Si-Mg, Si and Mg powder	ball milling	discharge capacity of discharge capacity of 830 $mAhg^{-1}$ over 5-650 mV against Li	[12]
Si-Al thin films	magnetron sputtering	Li_9AlSi_3dominant phase with specific capacity 650 $mAhg^{-1}$ post 100 cycles at C/20	[13]
Si-Sn, Si and Sn powder	mechanical milling	1400 $mAhg^{-1}$ as initial capacity with 78% retention after 50 cycles	[14]
Si-Cu, Si and Cu-Zn powder	ball milling	specific capacity of 608 $mAhg^{-1}$ with 66.8% retention after 200 cycles	[15]
Si, boron nanoparticle	plasma enhanced chemical vapour deposition (PECVD)	more than 80% capacity retention after 1000 cycles	[16]

Li-Si, Ca-Si, Mg-Si, Ti-Si, Co-Si, Fe-Si, Mn-Si, Ni-Si, Cr-Si, Cu-Si, Ag-Si, Al-Si, Sn-Si, Ge-Si, and other metal silicide composites have been produced as anodes for Li-ion batteries. The integration of Li-Si alloy as an anode is viewed as a pre-lithiation process for the active anode material. Table 2 shows some metal silicide materials. This approach aims to minimize the loss of active lithium within the battery unit, which occurs during various operational stages, including the creation of the solid electrolyte interface (SEI), expansion and irreparable reactions. Si's high band gap adds to its low conductivity, which ranges between 0.7 and 1.1 eV, and alloys with other metals with low band gaps could help to alleviate the problem of low conductivity.

Silicon Oxides (SiO_x)

Comprehensive research has been published on Si oxides to construct negative electrodes by looking at its improved theoretical capacity (1950 $mAhg^{-1}$) matching to SiO_2. These are the kinds of oxides that occur naturally and in abundance, influencing the market dynamics of energy storage. SiO_x outperforms pure Si as an electrode material in terms of volume expansion. However, a number of other difficulties with SiO_x prevent its commercial usage, including its insulating properties, limited electrical conductivity, and low initial coulombic efficiency. Table 3 shows some SiO_x based anode material with synthesis roots and performance. Several approaches are being used to synthesize SiO_x such as hydrothermal, sol-gel, chemical vapour deposition and electrospinning.

Table 3: SiO_x materials with synthesis roots and their performance.

Composition / Material	**Synthesis roots**	**Anode Performance**	**Reference**
SiO_x/Si	high energy mechanical milling	reversible capacity of 1000 $mAhg^{-1}$ with high retentivity rate	[17]
SiO/C	mechanically grinding SiO and C material	discharge capacity of 700 $mAhg^{-1}$ post 100 cycles	[18]
SiO thin film	radio frequency sputtering	Discharge capacity of 416-465 $mAhg^{-1}$ for first 100 cycles	[19]
SiO_2/C mesoporous	sol-gel, carbon coating	specific capacity at of 441 $mAhg^{-1}$ at J=500 mAg^{-1} post 500 cycles	[20]
SiO_x/C	mechanofusion	higher discharge capacity and higher initial coulombic efficiency	[21]

Various Structural Modifications

So far, various structural changes have been made to Si-based anodes to achieve the desired outcomes. Various approaches for generating nanoparticles have been shown to improve results over cracks during volume expansion. Liu *et. al.* reported that lowering the size of the produced nanoparticle below 150 nm resulted in no cracks during lithiation [22]. Nanostructures, such as Si nanowire (SiNw), aid in improving Li-ion kinetics and the rate of Li-ion diffusion in batteries. Porous Si structure also shows good results with accommodating volume expansion and increasing Li-ion diffusivity [26]. Some of the various morphological Si-based anode materials given in table 4 [22, 23, 24, 25, 27]. Nano structures like nanorods help in diffusion of Li-ion in one particular direction, helps in decrease in loss of Li-ion throughout the process. The nano size of the produced Si particles aids in enclosing them inside carbon-coated structures such as the core and yolk shell, reducing the problem of volume turn up by accommodating expansion within the shell. Despite these nano structuring qualities, there is one more feature: the high surface area of nano-synthesised Si particles, which allows for a strong contact between the substrate and the active electrode material. However, this high surface area has significant drawbacks, such as increased electrolyte consumption for the construction of a solid electrolyte interface, which splits amid cycling, resulting in the loss of more Li-ion and the formation of bunches of structure of active electrode material.

Table 4: Some of various morphological Si-based anode materials with synthesis roots and performance.

Composition/ Material	**Synthesis roots**	**Anode Performance**	**Reference**
Si nanoparticles	Si NP powder	No cracks below 150 nm	[22]
SiNW	Vapour-liquid-solid (VLS)	gives coulombic efficiency of 73% and 93% on first and second charge/discharge cycle from 4277 $mAhg^{-1}$ and 3541 $mAhg^{-1}$	[23]
Hollow Si sphere/CNT	template method	improves stability over cycles	[24]
Hollow Si (interconnected)	template method	increased rate capability with 2725 $mAhg^{-1}$ initial discharge capacity	[25]

Challenges and Future Perspective

Despite the advantage of Si's abundance on earth, it is still not recommended for usage as anode in Li-ion batteries. Several approaches showed enhanced results such as synthesizing nano structures, Si/C composite, metal alloys, etc., they still lack in providing overall performance for commercial availability in the market. Si-based anodes are a strong contender for future Li-ion battery materials.

However, Si's low conductivity, high energy band gap, and large volume expansion limit its commercial application. Although tech companies like TESLA use Si in their batteries for cars, its weightage is roughly 5% with 95% graphite, indicating that we cannot totally rely on Si-based anode materials. Si/C composites offer improved outcomes in enhancing Li-ion kinetics and diffusivity while compensating volume change. However, there is a lack of stability at high charge rates and long-term cyclic stability. Alloying and de-alloying metal silicide-based anode materials possess the ability to store more Li-ions inside the material using pre-lithiation techniques, reducing Li loss during battery operation caused by the creation of a solid electrolyte interface and trapping inside the damaged structure of the active material. Li-Si has the most powerful Li-ion storage phase ever discovered, possessing a storage capacity that is 10 times the energy than graphite. The abundance of Si in its oxide may have a significant impact on market dynamics if available with structural stability as an anode material. Various structural morphologies of Si-based anode materials including nanotubes, nanoparticles and nanowire, aid in the transport and kinetics of Li-ion within the material and provide necessary size for decreasing crack development. The advantage of Si nano morphologies is their high surface area, which also puts limitation because this surface area causes high decay of electrolyte for creation of SEI leading to side reactions.

Conclusion

This review paper provides insight into the Si as anode material by examining its characteristics and composite with other materials. To meet the aims of green energy, we need unique materials that can store energy in less space and endure the growing demand for portable energy storage devices. The tenfold capability of Si motivates researchers to develop novel Si-based anode materials to provide stability during operations. Significant progress has been recorded throughout time for Si anodes, although problems remain. The research community also need to handle the challenging process of manufacturing Si-based anode materials. This work also describes the synthesis of several Si-based composite materials. Considering the overall picture of present research, new strategies are required to accelerate the research in the appropriate path.

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