

# The formation and properties of amorphous silicon as negative electrode reactant in lithium systems

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## Abstract

Essentially all of the present commercial rechargeable lithium batteries use lithium-carbons as the negative electrode reactant. However, the announcement of Fujifilm in 1997 of the potential use of convertible oxides called attention to the possibility of alternatives, and a variety of different materials and approaches has been investigated in an number of laboratories.

Recent work on the potential of the use of metal–metalloid alloys has led to the recognition of several potentially attractive possibilities. Among the most interesting are a group of materials containing silicon, a boro-silicide, several silicides, and SiO. In all of these cases an irreversible reaction takes place during the first lithium loading. The result is the formation of fine particles of amorphous elemental silicon in a matrix related to the precursor. Upon further cycling, lithium reversibly reacts with this amorphous silicon. The resulting specific capacities can reach attractive values, depending upon the weight of the precursor. Their relatively flat potential profiles at low potentials make them of interest for application as negative electrodes.

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## 1. Introduction

The first ambient-temperature rechargeable lithium cells used elemental lithium as the negative electrode reactant. Due to severe safety problems and significant loss of capacity during cycling when such electrodes are used with organic solvent liquid electrolytes, this approach has been almost fully discarded. Negative electrodes in the currently available small commercial rechargeable lithium-based cells typically employ solid solutions of lithium in one or another form of carbon.

There is considerable interest in finding alternative materials that might be more attractive than the lithium-carbons. Improvements might involve the ability to operate safely at higher current densities, less first-cycle irreversible capacity loss, reduced loss of capacity upon cycling, smaller specific volume, and lower cost.

Instead of metal–metal alloys or compound semiconductors, alloys of metals and metalloids have been receiving attention in several laboratories [1–10]. These have included initial experiments on boron and a group of borides (AlB<sub>2</sub>, B<sub>4</sub>C, BN, CaB<sub>6</sub>, LaB<sub>6</sub> and SiB<sub>3</sub>) and silicides (CaSi<sub>2</sub>, CoSi<sub>2</sub>,

FeSi<sub>2</sub>, NiSi<sub>2</sub> and Mg<sub>2</sub>Si), as well as crystalline and amorphous Si and SiO.

Although it was shown some time ago that lithium will react with boron at intermediate [11–15] and elevated [16] temperatures to form a number of intermediate binary phases, neither elemental boron nor the silicon-free borides that were investigated in these studies exhibited any significant reactivity with lithium at ambient temperatures. An exception was SiB<sub>3</sub>, as will be described later. SiB<sub>3</sub> is an intermediate phase in the silicon–boron system that, according to the phase diagram, is only stable up to 1270 °C.

The reaction of lithium with elemental silicon has been known for a long time, for Li–Si alloys were of interest for use as negative electrodes in elevated temperature molten salt electrolyte batteries that operate at about 400 °C [17–20]. The reaction of lithium with a number of binary silicon alloys was also considered, and predictions made on the basis of thermodynamic considerations. Mg<sub>2</sub>Si was predicted to be a promising candidate, and experiments showed that its reaction with lithium is very attractive, with a very large capacity at a useful potential at elevated temperatures [21–24]. Experiments on the reaction of lithium with Mg<sub>2</sub>Si at ambient temperature have also been reported subsequently [6,7,10,25–27].

There has also been some interest in amorphous negative electrode materials containing silicon, including silicon oxides and lithium silicate glasses [28] and other silicon-

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containing oxides, such as amorphous SiO–SnO mixtures that were prepared by mechanical milling [29].

A number of observations have shown that the operation of oxide or alloy electrodes at very high lithium activities can result in the formation of amorphous, rather than crystalline, products, whose properties are different from those of the corresponding crystalline materials. This includes some materials of potential interest as positive electrode reactants, such as vanadium-based materials with the general formula  $RVO_4$ , in which R is Al, Cr, Fe, In, or Y [30].

Some nitride alloys have been reported to be of interest as potential negative electrode reactants. Among the more interesting are those with structures related to that of  $Li_3N$ , which is known to be a fast ionic conductor for lithium. In these materials some of the lithium is replaced by a transition metal, such as Co. The crystalline structure changes upon the first insertion of lithium, and is found to be amorphous during subsequent cycling [31–34].

Structural evidence for the electrochemical amorphization of alloys as the result of a reaction with lithium in the Li–Si, Li–Sn, and Li–Ag systems was studied by Limthongkul [35]. In the latter two cases, this was only a transient phenomenon, and the structures became crystalline again at later times.

The purpose of this paper is to point out that it appears as though an irreversible reaction takes place during the first lithium loading of a number of silicon-containing materials that results in the formation of fine particles of amorphous elemental silicon in an inert matrix of a residual phase that is related to the precursor. Upon further cycling, lithium reversibly reacts with the amorphous silicon particles.

## 2. Experimental set-up and procedures

A series of experiments were carried out using a so-called “coffee bag” cell, which is a flat test cell similar to those used in a number of commercial lithium-ion batteries.

The working electrodes were prepared by mixing the electroactive material with PVdF as binder and acetylene black as electronic conductor in the weight ratio 85:10:5. The mixture was ballmilled at 30 Hz using a mixer mill MM200 from Retsch to get fine and uniform particles. Thereafter NMP (from Merck) was added dropwise while stirring the mixture to get a slurry with the desired viscosity. The slurry was coated in a thickness of 30  $\mu\text{m}$  onto a thin copper foil using doctor blade equipment. The resulting film was dried under infrared light for 15 h at 200 °C. This corresponds to a temperature of 110 °C on top of the foil. In the case of the moisture-sensitive silicides all the preparation steps were performed in an argon-filled glove box.

The dried foil was cut into pieces with an area of 6  $\text{cm}^2$ . These pieces were assembled as working electrodes in “coffee bag” cells using GF/A glass fiber sheets (from Whatman) as the separator and lithium foil (from Aldrich) as counter and reference electrodes. A solution of 1 mol/l  $LiPF_6$  in EC:DEC (2:1) (from Merck) was employed as the electrolyte. The whole assembly of the cell was done in an argon-filled glove box with oxygen and nitrogen purification. The bags were sealed in the glove box with a vacuum sealer from Multivac.

Electrochemical testing was performed outside the glove box. Galvanostatic cycling was done at a current density of 0.1  $\text{mA}/\text{cm}^2$  in the voltage range from 1.5 V to 25 mV, if not specified otherwise elsewhere. The samples were each cycled three times at ambient temperature.

## 3. Experimental results

### 3.1. Silicon boride

The most attractive of the boron-based compounds that we have investigated was  $SiB_3$ . The potential–capacity relation observed upon the initial galvanostatic cycle of

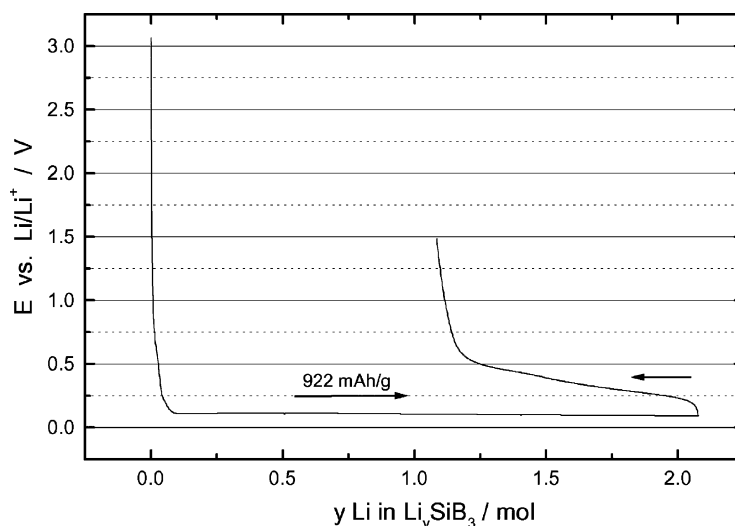


Fig. 1. Initial galvanostatic cycle of  $SiB_3$  at a current density of 0.1  $\text{mA}/\text{cm}^2$  between 90 mV and 1.5 V.

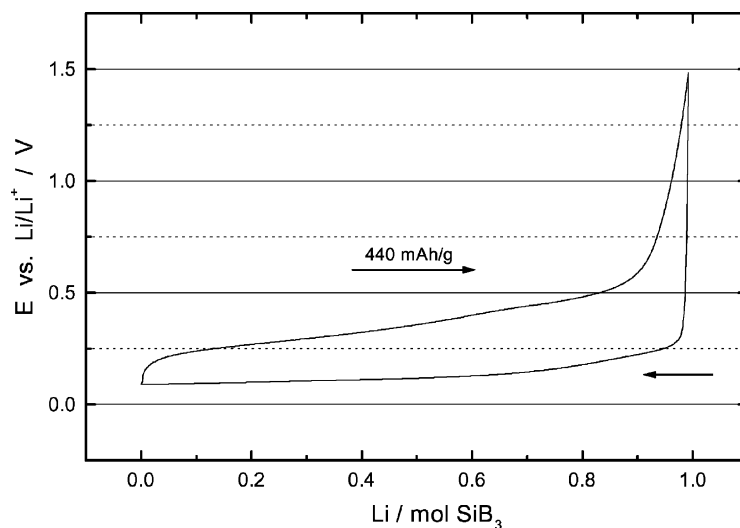


Fig. 2. Reversible lithium extraction and reloading of  $\text{SiB}_3$  at  $0.1 \text{ mA/cm}^2$  between 90 mV and 1.5 V after the initial lithiation.

$\text{SiB}_3$  between 1.5 V and 90 mV versus lithium at a current density of  $0.1 \text{ mA/cm}^2$  is shown in Fig. 1. It can be seen that the potential decreased rapidly down to a plateau around 100 mV. Up to 2 mol of lithium could be inserted per mol of  $\text{SiB}_3$  before the potential reached 90 mV, which corresponds to a lithium absorption capacity of 922 mAh/g.

The amount of extractable lithium from the lithiated electrode was much less, however, only about 1 mol of lithium per mol of  $\text{SiB}_3$ . This is equivalent to an extraction capacity of 440 mAh/g of the original  $\text{SiB}_3$ . Thereafter the reaction was reversible, and about 1 mol of lithium could be inserted again during the next galvanostatic lithiation. The potential profile during the second lithiation was significantly different from that which was observed during the first lithiation, indicating a substantial change in the sample. This can be seen in Fig. 2, which shows the variation of the potential during both the first extraction and the second loading. It is seen that the capacity was the same in both directions after the initial lithiation. These potential profiles are reasonably flat and in an attractive potential range for use as a negative electrode reactant.

### 3.2. Silicides

As mentioned earlier, there has been a significant amount of work on the properties of  $\text{Mg}_2\text{Si}$ , both at elevated and ambient temperatures. This material has the relatively stable anti-fluorite structure, and there are octahedral sites into which lithium can be reversibly inserted. Galvanostatic experiments show a rather reversible potential profile in early, or relatively shallow, cycles that has a series of four small plateaus, probably due to the successive occupation of the available crystallographic sites in the host structure. Both the capacity and potential profiles gradually change upon further cycling, especially if the potential goes down toward that of pure lithium. In addition, there is not a substantial

capacity loss during the initial lithiation process, as was shown above for  $\text{SiB}_3$ . This behavior is decidedly different from that of the other materials that are discussed here.

Experiments were conducted on the disilicides  $\text{CaSi}_2$ ,  $\text{CoSi}_2$ ,  $\text{FeSi}_2$ , and  $\text{NiSi}_2$ . Phase diagram information shows that there are stable phases with lower silicon contents in each case. They all showed the same general characteristics in the electrochemical experiments as were found in the case of  $\text{SiB}_3$ . There was a long plateau at about 100 mV during the initial lithiation, and a significantly lower capacity during the first delithiation, with close to reversibility thereafter. The second, and subsequent, lithiation curves were different from the first, with the lithium uptake starting at higher potentials.

The amounts of irreversible capacity during the first lithiation varied among the disilicides, as did the amount of subsequently reversible capacity. In addition, they all showed a small initial irreversible capacity of about  $1 \text{ C/cm}^2$  related to the formation of the SEI layer.

$\text{CaSi}_2$  and  $\text{NiSi}_2$  had the highest values of reversible capacity, 1.15 and 0.85 Li/mol, with  $\text{CoSi}_2$  and  $\text{FeSi}_2$  much lower, about 0.25 Li/mol. In all cases, however, the potential ranges and general shapes of the curves were the same when scaled to their respective capacities, and similar to what was found in the experiments on  $\text{SiB}_3$ .

### 3.3. Silicon(II) oxide, $\text{SiO}$

A substantial interest in the possibility of the use of glassy oxides containing reducible metal species followed the announcement of Fuji Photo Film Co. of their potentially attractive properties [36]. During the first lithiation the oxides are converted to a fine composite microstructure containing both  $\text{Li}_2\text{O}$  and lithium–metal (e.g. Li–Sn) alloys. After this initial irreversible reaction, the electrochemical properties are essentially those of the resulting lithium–metal alloys.

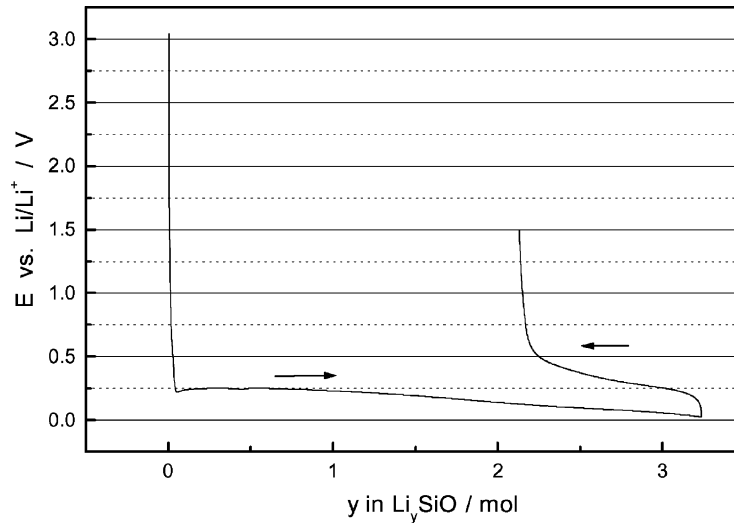


Fig. 3. Galvanostatic cycling of SiO at a current density of  $0.1 \text{ mA/cm}^2$  between 25 mV and 1.5 V vs. Li.

Experiments were undertaken to investigate the possibility of the analogous behavior of SiO. This is a potentially attractive convertible oxide, both because of its relatively light weight and its low oxygen content. In addition, it was known that lithium and silicon form as series of alloy phases, as mentioned above.

Much of the attention to date in investigations of convertible glasses has involved the reduction of dioxides. SiO only has one oxygen per mole, so that the first-cycle capacity loss should be only half of that found in those cases.

SiO was mentioned in the Seiko Instruments patent [28], and its reversible reaction with lithium was explained in terms of the formation of a lithium–silicon monoxide phase,  $\text{Li}_x\text{SiO}$ . The initial irreversible capacity that was observed was attributed to a reaction with the carbon that was present in the electrode structure.

SiO was also investigated by Klausnitzer [4], who made a slurry of amorphous SiO with nickel powder and a polymer

binder, and pressed it into a nickel screen to make an electrode. This was evaluated in a liquid electrolyte using a lithium counter and reference electrode. He observed a large excess capacity of about 2 Li/mol during the first lithiation that did not appear in later cycles, and attributed this to the irreversible formation of  $\text{Li}_2\text{O}$ . Observations of the variation of both the irreversible and reversible capacities with potential in differential capacity experiments led to the conclusion that  $\text{Li}_2\text{O}$  was formed first, and was then followed by the reaction of further lithium with the residual silicon as the potential was further reduced.

Further experiments on amorphous SiO were undertaken in this work. The first galvanostatic cycle is shown in Fig. 3. It has several significant features. One is that the initial reaction showed a negative potential overshoot. This is characteristic of reactions in which the nucleation of a new phase is required, as must be case if  $\text{Li}_2\text{O}$  is formed.

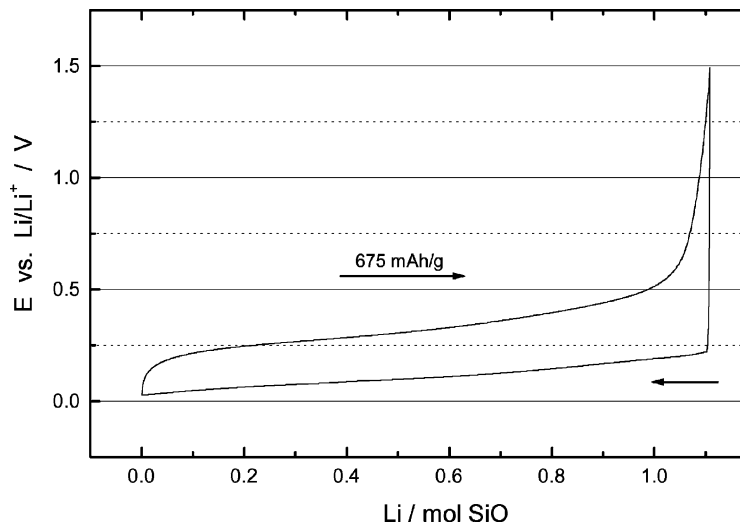


Fig. 4. Extractable lithium and further loading of SiO at  $0.1 \text{ mA/cm}^2$  between 25 mV and 1.5 V vs. Li.

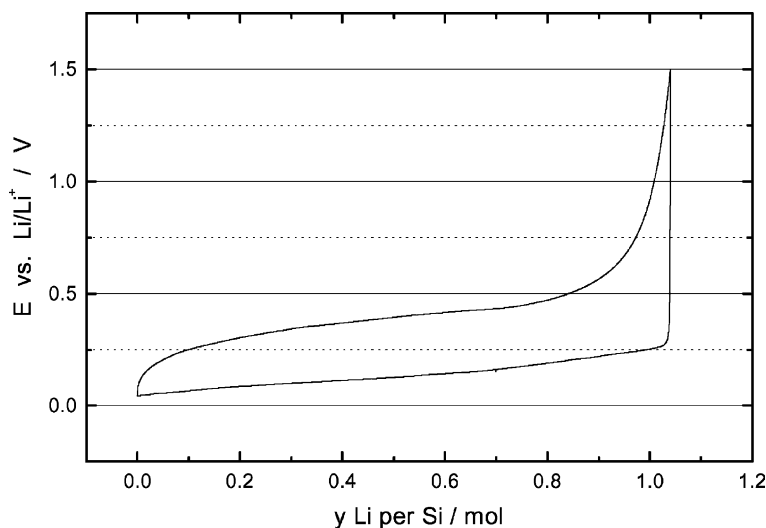


Fig. 5. Extractable lithium and further loading of amorphous silicon at  $0.1 \text{ mA/cm}^2$  between 25 mV and 1.5 V vs. Li.

A total of more than 3 mol of lithium was found to react per mol of SiO during the initial lithiation. During the first delithiation cycle, as well as during subsequent lithiation cycles, the capacity became close to 1 mol of Li per mol of initial SiO. This is consistent with the initial formation of  $\text{Li}_2\text{O}$ , and the subsequent reaction of additional lithium with the residual silicon.

The potential ranges and the shapes of these curves are essentially the same as those found earlier in the cases of  $\text{SiB}_3$  and the disilicides. This is shown in Fig. 4, which shows the first lithium extraction and the subsequent second lithiation cycle of SiO.

### 3.4. Amorphous silicon

The behavior of the several silicon-containing materials discussed above lead to the conclusion that amorphous silicon is formed during the initial lithiation reaction in each case, and that lithium subsequently reacts reversibly with this amorphous product. To further substantiate this model, similar electrochemical experiments were performed on amorphous silicon powder that was obtained from Alpha Aesar.

Samples prepared under argon to reduce the formation of  $\text{SiO}_2$  on the surface showed an initial lithiation capacity of about 3.2 Li/Si. It was found that about 1.1 Li/Si could be extracted upon delithiation, and that approximately the same amount reacted during the subsequent lithiation process. This is illustrated in Fig. 5.

## 4. Summary and conclusions

Experiments have shown that the initial lithiation of several silicon-containing materials,  $\text{SiB}_3$ , several disilicides, and SiO, results in the formation of a lithium-containing product from which lithium can subsequently be deleted

and reintroduced. Although extensive cycling experiments have not been undertaken, this capacity seems to be quite reversible.

Observations of the composition dependence of the potential during the first delithiation and the second lithiation cycles show that all of these materials have approximately the same potential profiles. This indicates that they have comparable thermodynamic and kinetic properties, leading to the conclusion that they have similar compositions and structures. X-ray observations show that the products of the first lithiation of these materials are amorphous. We assume that they are all lithium-containing amorphous silicon.

Experiments were also performed on similar cells in which commercially available amorphous silicon was used as the reactant. The measured capacity and potential profile of amorphous silicon corresponded quite well with the results found in the other materials after the first lithiation step. This is shown in Fig. 6, in which the potential profiles are shown for all seven of the materials discussed here,

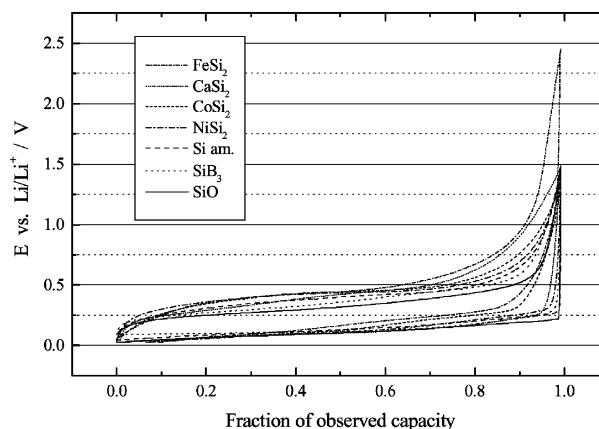


Fig. 6. Variation of the potential during the first delithiation and second lithiation processes for all of the materials investigated, plotted as a function of the fraction of their observed capacities.

Table 1  
Specific capacity data for several materials

Precursor	Molar weight	First delithiation (Li/mol)	Delithiation capacity (mAh/g)
CoSi <sub>2</sub>	115.11	0.25	58
FeSi <sub>2</sub>	112.03	0.25	60
NiSi <sub>2</sub>	114.87	0.85	198
CaSi <sub>2</sub>	96.26	1.15	320
SiB <sub>3</sub>	60.52	1.0	443
SiO	44.09	1.1	669
α-Silicon	28.09	1.05	1002

scaled by their respective capacities. This similarity reinforces the assumption of the formation of amorphous silicon containing lithium during the initial lithiation process in all of these materials.

In addition to the extent of lithium insertion, the initial weight of the precursor must be considered, of course, when considering the practical specific capacity, i.e. the capacity per unit weight, that might be obtained. The influence of both these factors is readily seen in Table 1.

It is evident that quite attractive values of specific capacity can be obtained in several cases. In addition, the potential profiles are reasonably flat, and in an attractive range for their potential use as negative electrode reactants. The question of their stability during further cycling, which often results in microstructural changes and the loss of electronic contact, has not yet been investigated.

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