

Mixed silicon–graphite composites as anode material for lithium ion batteries

Influence of preparation conditions on the properties of the material

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Abstract

Mixed silicon–graphite composites were studied as an anode material for LIB. Estimation of the capacity of the composite as a function of silicon mass fraction as well as the lithium mole fraction in the final Li–Si alloy was performed. Based on this estimation, appropriate cycling test was introduced. Possible cycling stability region in terms of Si mass fraction, mole fraction of Li in the Li–Si alloy and average particle size was evaluated.

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1. Introduction

Further improvement of LIB requires the development of second generation cathode and anode materials with higher capacity. Although in the present day LIB the specific capacity of the cathode material is often about half of the value of the carbonaceous anodes, it is unlikely that significant advancement can be made in the near future. On the contrary, there are materials with theoretical capacities many times higher than the carbonaceous anodes. Possible candidates to replace carbon are the elements from the third, fourth, and fifth row of groups III, IV, and V from the periodic table their alloys and mixtures with other metals. However, due to the large volume mismatch of the initial and lithiated phases such electrodes deteriorate in just a few cycles. To overcome this problem specific for all (inter) metallic electrodes, preparation of active materials with small grain size was proposed [1]. In most of the cases the materials consist of an active metal towards Li^+ (e.g. Sn, Si) with fine grain size uniformly distributed within an inactive matrix (like Li_2O [2], TiN [3], etc.). The inactive matrix serves as a media preventing the active particle–particle interaction, thereby increasing the cycling performance. However the use of an inactive matrix leads to considerable decrease in

the energy density. Moreover, in the case of in situ inactive matrix formation (e.g. convertible oxides) there is a severe irreversible capacity loss at the first cycle due to a reduction/replacement reaction, which limits the use of convertible oxides in practical LIB.

To avoid the aforementioned problems we have tried to employ carbon-coating technique as a method to prepare silicon-based anode [4–8] for LIB. During this study we found that the graphite phase plays an important role in the improving of the cycling performance of the material. It acts as a mechanical and electrochemical buffer [7] thereby reducing the electrochemical sintering of silicon particles. Moreover the presence of carbonaceous phases increases significantly the electrical conductivity, which allow working at current density as high as 0.3 mA/mg. Although the carbonaceous phase is considered as a matrix for the silicon active component, it also contributes significantly to the overall capacity of the composite. Therefore these composites can be regarded as a double phased materials where both phases are active towards Li^+ within the same potential window.

2. Experimental

Several compositions with various Si/graphite weight ratios were studied. As a carbonaceous phase two types of nat-

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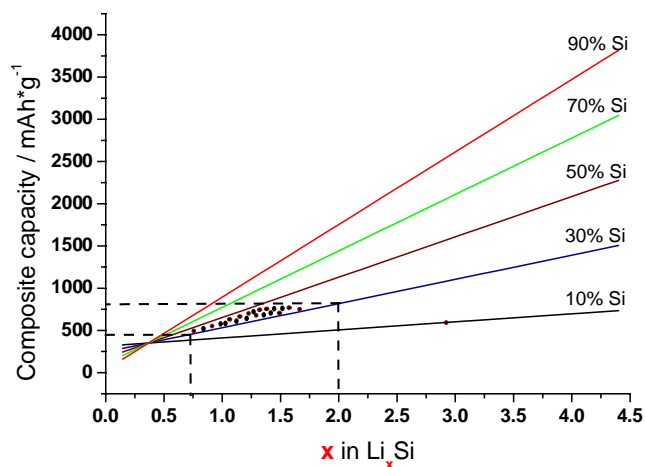


Fig. 1. Estimation of the overall capacity of Si/C composites as a function of silicon mass fraction and Li mole fraction in the final Li_xSi alloy. The expected cycling stability region is indicated with black dots as explained in the text.

ural graphite: NG-7 (Kansai Chemical, Japan) and LF-18A (Chuetsu Graphite Works, Japan) were studied. In addition, synthetic graphite material MCMB 6–28, heated at 2800°C (Osaka Gas, Japan) was used. Preliminary experiment had shown that best results are obtained when the mass fraction of silicon lies in the range of 30–50 wt.%. Lower silicon content will result in a more stable composite, however the total capacity of the composite would be considerably lower as explained later (Fig. 1). All samples were prepared as follows. At first silicon was milled until an average particle grain size reduced to approximately $1\ \mu\text{m}$ was reached ($\text{BET}\ 5\text{--}7\ \text{m}^2\ \text{g}^{-1}$). Then it was mixed with one of the three types of carbonaceous phases and milled for predefined time intervals. Electrode preparation technique was the common one for the LIB industry. Dry Si/C composite was mixed with an appropriate amount of 5 wt.% PVDF in NMP solution. It was agitated and the resulting slurry was pasted on a copper foil current collector and dried under a flow of dry hot air at 120°C . The electrodes were prepared by punching the copper foil. Further they were pressed ($1.5\ \text{t}\ \text{cm}^{-2}$) and cycled in a coin cell versus Li metal.

3. Results and discussion

At the beginning it is convenient to divide the total capacity C_{tot} [$\text{mAh}\ \text{g}^{-1}$] as originating from the carbonaceous and silicon phases: C_{C} [$\text{mAh}\ \text{g}^{-1}$] and C_{Si} [$\text{mAh}\ \text{g}^{-1}$]. Previous studies on Si/C composites [7] had shown that over the first cycle (Li^+ insertion), Li^+ first saturates preferentially the carbonaceous phase (intercalation), and then the formation of Li_xSi takes place (alloying). Having this in mind one can show that the total capacity is expressed as

$$C_{\text{tot}} = \frac{C_{\text{C}} \times C[\text{wt.}\%] + C_{\text{Si}} \times \text{Si}[\text{wt.}\%]}{100} \quad (1)$$

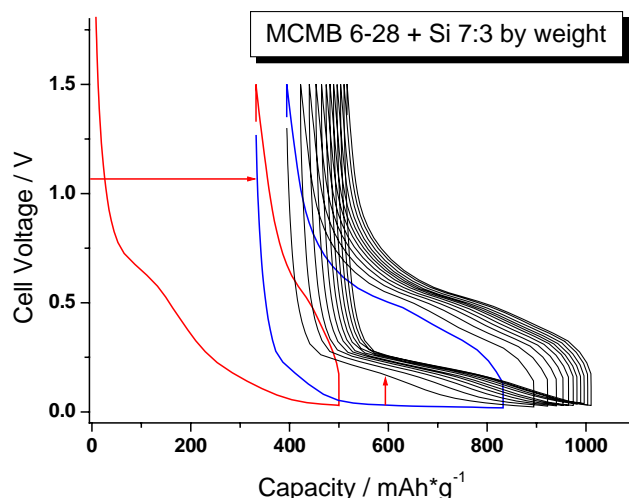


Fig. 2. Typical voltage profile of Si/C composite material (BET surface area $\sim 70\ \text{m}^2\ \text{g}^{-1}$) cycled vs. Li metal. Test performed as capacity cutoff at $500\ \text{mAh}\ \text{g}^{-1}$ in CCCV (Li^+ insertion) and CC until 1.5 V (extraction) at room temperature. Due to the highly developed surface area of such material there is a large irreversible capacity loss over the first cycle, indicated by a horizontal arrow. Another feature of such materials is the polarization between the first Si/Li alloying and the next ones, indicated with a vertical arrow.

If a carbonaceous phase with fixed capacity is given, one can find the total capacity as a function of the mole fraction x in the final Li_xSi composition. Graphically total capacity versus mole fraction of Li in the Li_xSi alloy for each Si/C composite is shown in Fig. 1. It can clearly be seen that all possible compositions will be represented with a family of straight lines with a common cross point.

It is interesting to notice that the results obtained using such composites are sensitive to the mode of testing. Typical voltage profiles of the Si/C composite cycled versus Li metal are shown in Fig. 2. It is notable, that there is a large gap between the first and subsequent cycles. Moreover cycling behavior depends on the capacity inserted over the first cycle. Dahn et al. proposed to cycle lithium-alloying anodes within a narrower potential window in order to improve the cycling performance [9]. For the silicon carbon composites this approach is harder to apply. Even using the same composite, current density and same cutoff voltages generally provides different initial charging capacity. The result is sensitive to the electrode preparation technique—the amount and the type of the binder as well as the viscosity of the slurry and drying conditions.

We believe that a natural way to test silicon containing materials is to limit the insertion capacity to a given value, as suggested by Jung et al. [10]. Thus the cycling could be performed at x in Li_xSi which is clearly defined at least during the initial cycles. There is one more reason to work under such conditions. In the real LIB the insertion capacity is limited by the materials balance ratio. Therefore the cycling test was performed as follows: Li^+ insertion at high current density ($1.5\ \text{mA}\ \text{cm}^{-2}$ or $\sim 0.35\ \text{mA}\ \text{mg}^{-1}$)

until reaching the capacity required. If the capacity was not reached yet, the potential was held 5 mV and current was decreased accordingly in order to keep the cell voltage 5 mV versus Li. Exhaustion denotes the situation when the current approaches 0 mA without reaching the required capacity. The cycle when this occurs is regarded as the last cycle of the test. Charging (Li^+ extraction) was performed at 1.5 mA cm^{-2} until 1.5 V, because the extraction of Li^+ under CCCV mode does not give better extraction efficiency and therefore extraction was performed in CC mode. This confirms that in this case Li^+ extraction will correspond to discharge (work) of the real LIB, normally performed under CC mode.

In the composite electrodes, the integrity (or state of health) of the electrode can be defined as the ratio between the amount of electrochemically active silicon to the total amount of silicon present in the electrode. Since the practical measuring of this value cannot be easily performed, this test as well as the amount of ICL value can be used as an index of the rate at which capacity diminishes. Representative cycling test with one type of composite is shown in Fig. 3. This sample was ground for 5 h and its BET surface area was found to be $70 \text{ m}^2 \text{ g}^{-1}$ (estimated particle size $\sim 0.2 \mu\text{m}$). Grinding for longer time can lead to considerable increase in the BET surface area (approx. $200 \text{ m}^2 \text{ g}^{-1}$). However in such a case there was a much higher initial irreversible capacity loss over the initial cycle. Moreover, to have further substantial decrease in the particle size, the grinding time should be an order of magnitude longer (20–50 h), which is not favorable from a practical point of view. All samples (using different carbonaceous phases) exhibit the same behavior and the composite MCMB:Si 7:3 will be considered as a representative example. Typical values are given in Table 1 for the case of a capacity cutoff test performed at 500, 700 and 900 mA h g^{-1} .

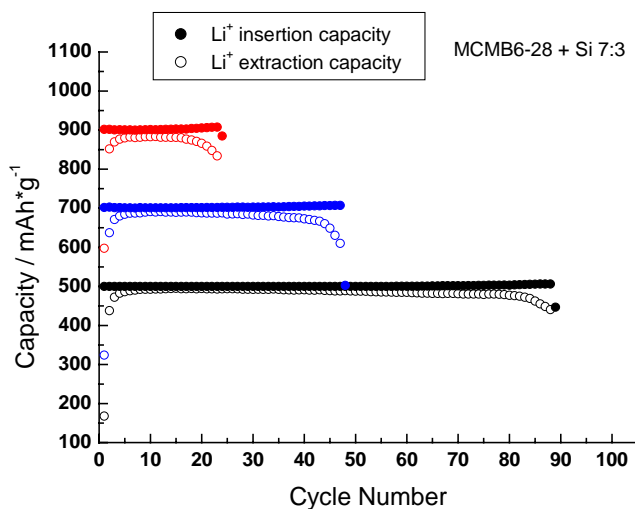


Fig. 3. Capacity cutoff cycling test performed at three different capacities 500, 700 and 900 mA h g^{-1} . Cycling efficiency and dynamics of ICL are given separately for clarity.

Table 1
Summary of the cycling tests

No.	Capacity cutoff [mA h g^{-1}]	Cycle no. at exhaustion	ICL value [mA h g^{-1}]
1	500	90	1720
2	700	48	1500
3	900	25	950

ICL value defined as $\text{ICL} = \sum_{i=1}^{i=i_{\text{exh}}} (\text{Li}_{\text{ins}}^+ [\text{mA h g}^{-1}] - \text{Li}_{\text{ext}}^+ [\text{mA h g}^{-1}])$.

A clear trend can be seen: the increase of the cutoff capacity leads to a decrease in the ICL value at the end of the test. At higher insertion levels the silicon component becomes inactive within fewer cycles, probably due to faster mechanical/electrical separation from the carbonaceous matrix. At moderate insertion levels the mechanical stress accumulated in the silicon phase is not high enough to cause electrode degradation. There is a gradual detachment or preferential thick film formation on the moving phase boundary of the silicon particles dispersed within the carbonaceous matrix. The accumulation of ICL does not proceed regularly. As can be seen in Fig. 4 the samples with a lower cutoff limit (500 and 700 mA h g^{-1}) show similar behavior. For every test there are two distinctive linear regions. Most of the cycles lie on the first one with a lower slope and better cycling efficiency respectively. A few cycles prior exhaustion, the coulombic efficiency decreases drastically, which is seen as a straight line with sufficiently higher slope passing through the last points. The coulombic efficiency of all Si/C composites studied so far change in the same manner. It suggests that there is a critical point beyond which the electrode quickly loses its cycling performance.

It is interesting to compare samples with the same average composition after different milling time. When the ingredi-

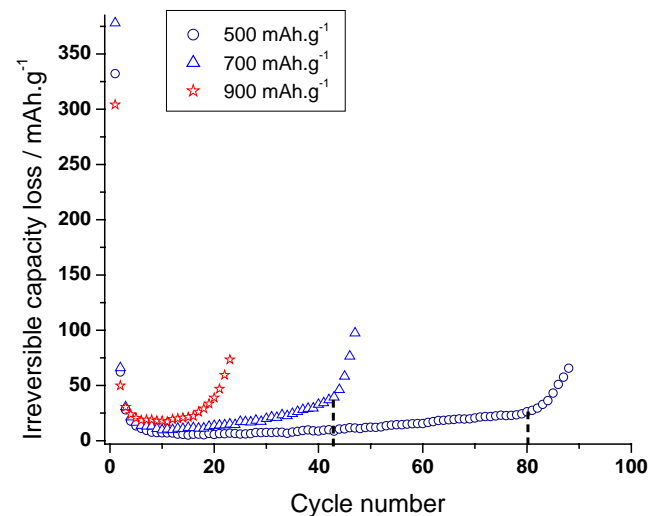


Fig. 4. Dynamics of ICL accumulation. For the levels 500 and 700 mA h g^{-1} there are linear regions (80 and 45 cycles, respectively) where the coulombic efficiency decreases slightly. Prior the exhaustion of the electrode there is a sharp decrease in the coulombic efficiency. The straight lines are shown as an eye guide.

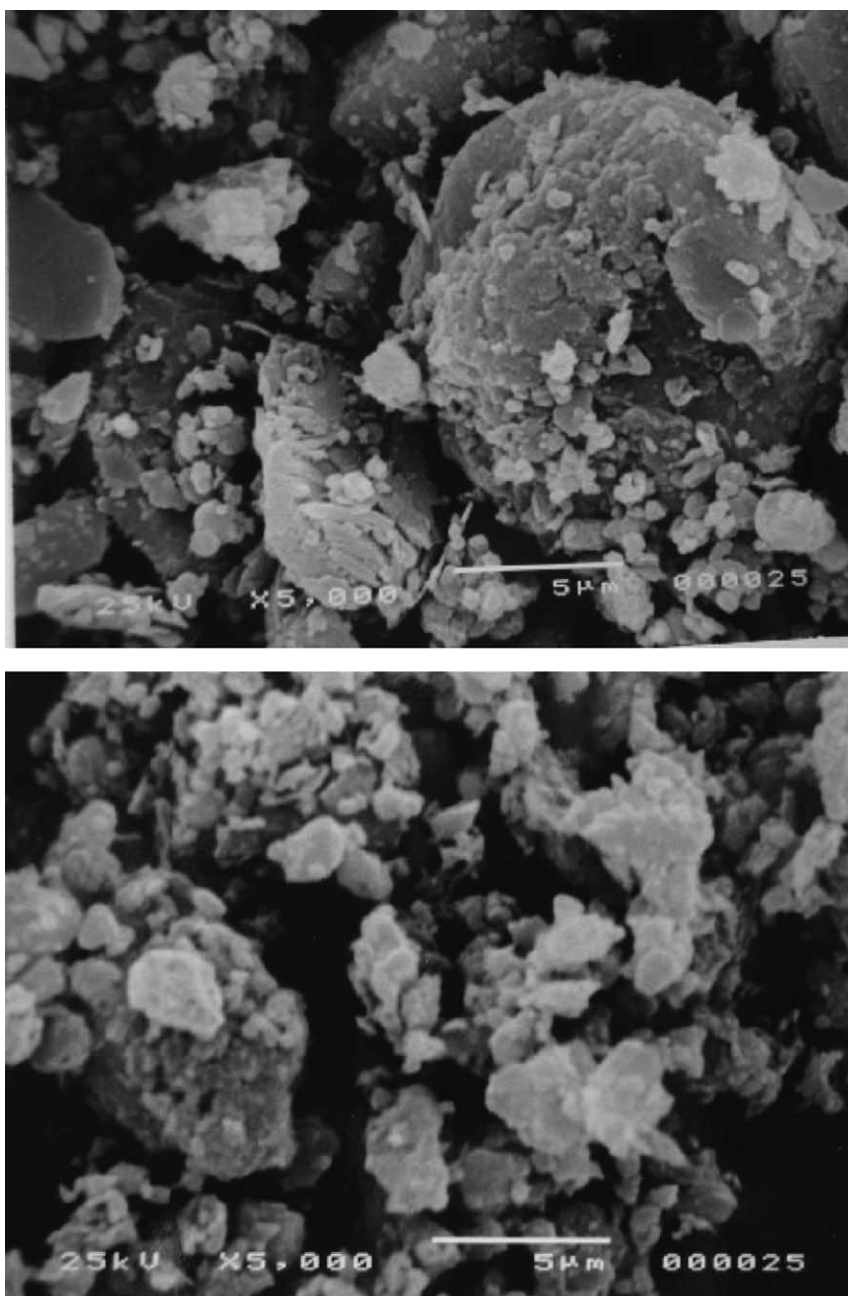


Fig. 5. Initial morphology of the composites MCMB:Si 7:3. Upper image: after 15 min milling, bottom image: after 5 h milling.

ents are just mixed (15 min milling), MCMB particles retain their initial morphology shown in the upper part of Fig. 5. As expected, longer milling time leads to a change of the material's morphology as shown in Fig. 5 below. Electrodes prepared with a composite containing MCMB particles, retaining their initial morphology could not be cycled—they become inactive in just few cycles. Cycling efficiency in this case is very low. To understand the reason, cross-sectional view of both electrodes is shown in Fig. 6. The electrode prepared with the composite ground for a longer time retained its morphology even after 90 cycles at 500 mA h g^{-1} . Contrary to that, electrode prepared by composite with larger

particle size is not stable over the cycles. Even after a few cycles there are severe morphological changes. Moreover, the active material loses the electrical contact with the current collector as shown in the upper side of Fig. 6.

The white arrows in Fig. 6 show the line between the current collector and the active material. In the case of composites with a smaller particle size (Fig. 6, down part) the arrows again show the interface between the current collector and the active material. This effect can be understood qualitatively if we consider the factors responsible for the failure of such electrodes. As shown by Huggins [11], when the host particles undergo drastic volumetric changes, there

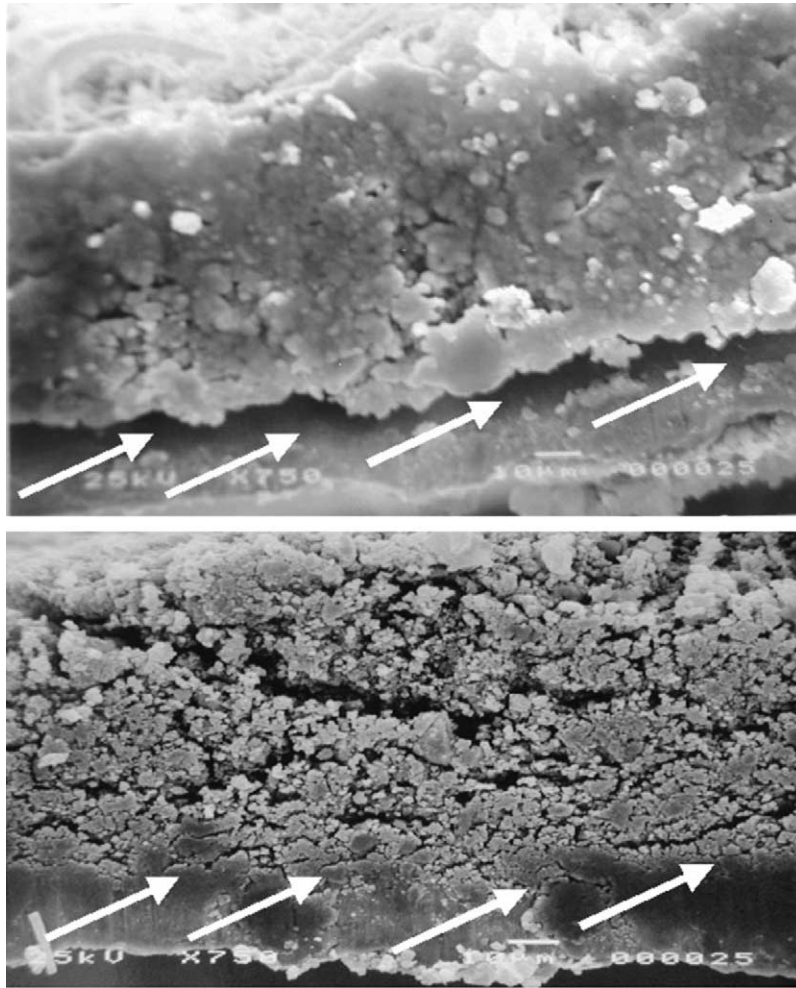


Fig. 6. Profile of the MCMB6-28/Si 7:3 exhausted composite electrodes. Upper picture: composite with BET surface area $4 \text{ m}^2 \text{ g}^{-1}$ after three cycles at 700 mA h g^{-1} capacity cutoff test. The detachment of the active material from the current collector is clearly visible. Bottom image: composite with BET surface area $70 \text{ m}^2 \text{ g}^{-1}$ after 90 cycles at 500 mA h g^{-1} capacity cutoff cycling test. Even after extended cycling the electrode retains its initial morphology. Moreover the active material does not lose the electric contact with the copper current collector. Current density in both cases was $\sim 0.35 \text{ mA mg}^{-1}$.

is a limiting particle size under which the particle fracture will not occur. Average value of the fracture toughness parameter for solid state materials like silicon is $10 \text{ MPa}\sqrt{\text{m}}$. For total dilation transformation strain ≈ 2 (for Li_2Si) the particle size under which the fracture will not occur is estimated to be of the order of $0.3 \mu\text{m}$. This electrode behavior suggests that there is a relationship between the morphological stability and the average particle size of the composite. If the silicon particles do not fracture, then the electrode integrity and morphology could be preserved over the cycles. Although in this case there is no distinctive gap between the current collector and the active material, and despite the much improved cycling, at the end of the test the electrode again becomes electrochemically inactive. Hence, morphological stability is a necessary but not sufficient condition to enable the composite electrode, to compete with carbonaceous anodes. Deeper insight for the process responsible for this behavior can be found in the OCV/CCV voltage profiles given in Fig. 7. The data were collected during the first,

second, and last cycle—after exhaustion. Over the first cycle the Li^+ insertion was performed in steps corresponding to 100 mA h g^{-1} . Current density was high (1.5 mA cm^{-2} or $\approx 0.35 \text{ mA mg}^{-1}$) as performed during the cycling test. After every insertion step the current was interrupted for 5 h and the potential profile recorded. The first cycle was stopped at 1100 mA h g^{-1} total capacity, the second at 800 mA h g^{-1} . Then the electrode was cycled until exhaustion at capacity cutoff 800 mA h g^{-1} (as defined above) and the OCV/CCV profile was recorded again. The curves in Fig. 7 are plotted keeping in mind the integrated capacity loss values. As can be seen the OCV values during the first Li^+ insertion lie in the range of 120–130 mV. The same value of OCV over a wide range of compositions during the first cycle is consistent with the coexistence of the two solid phases: Li rich phase close to the solid/liquid phase boundary and fresh Si in the bulk of the particles. Therefore working at higher current density leads to a layer by layer crystal lattice destruction of the silicon host as established by Li et al. [12]. This

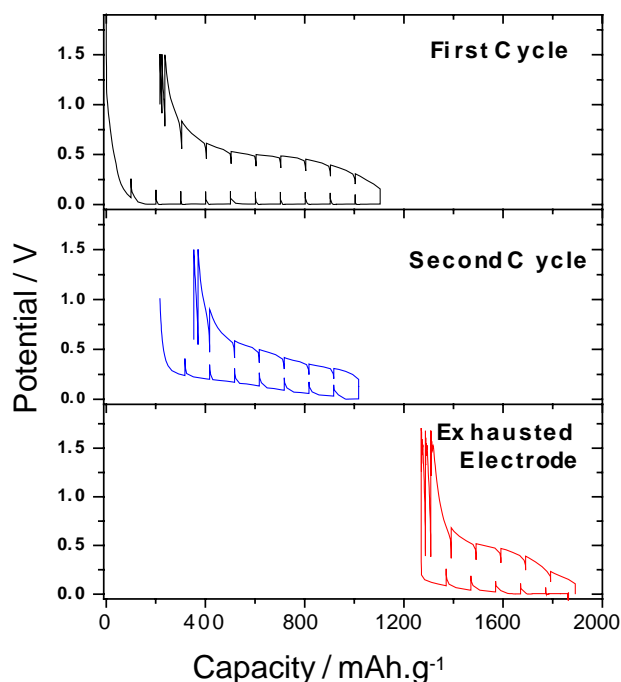


Fig. 7. OCV/CCV profiles for the MCMB/Si composite electrode over the first, second cycle, and after exhaustion performed as 800 mA h g^{-1} capacity cutoff test.

feature of the electrochemical reaction is considerably different from that expected based on the Li–Si phase diagram. Hence the reaction performed under technically interesting conditions is irreversible and far from equilibrium. From the second cycle both OCV/CCV values decrease linearly with the amount of Li^+ inserted. There are no indications for distinctive plateaus as in the case of intercalation materials. In summary, the behavior of a silicon host in a low-temperature, organic solvent is very different from those obtained in a molten salt, high temperature electrolyte, where distinctive crystal phases can be obtained.

After the exhaustion, the OCV/CCV curve exhibits strong polarization. The high ICL value ($>1000 \text{ mA h g}^{-1}$) demonstrates that not all Li^+ initially inserted in the composite electrode can be extracted. The reason could be a thick film formation on the moving phase boundaries inserted in the organic electrolyte and/or gradual detachment of active silicon particles from the carbonaceous matrix. As a result there is a gradual accumulation of Li^+ in the silicon host phase.

Further improvement of this kind of composites is probably related to the silicon surface modification aiming to make the connection between C and Si phases stronger. The importance of interfacial phenomena in silicon containing composite electrodes is demonstrated with the data in Fig. 8. It represents the capacity over the first cycle as a function of the particle grain size. Pure silicon powder was ground and electrodes were prepared using only Si powder milled for different time intervals and PVDF. As can be seen, there is a strong relationship between the silicon BET surface area (grain size) and the capacity that can be achieved practi-

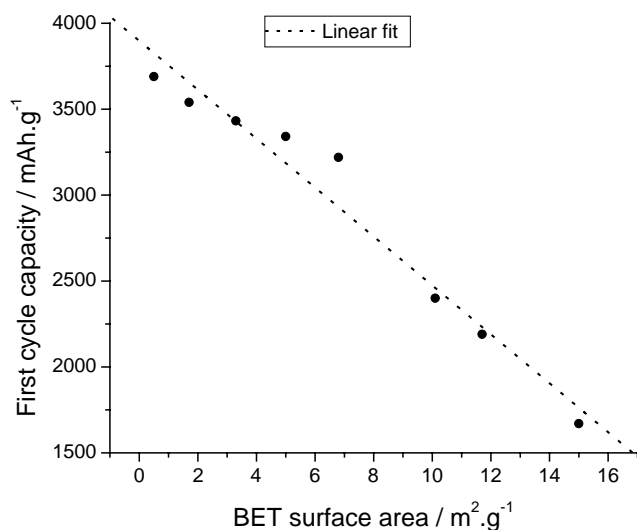


Fig. 8. First cycle insertion capacity in the pure silicon anode, prepared from silicon with different particle grain size.

cally over the first alloying. Since the electrode composed by larger particles contains void spaces, which can accommodate the volume variation upon alloying, the observed capacity is closer to the theoretical value of ca. 4000 mA h g^{-1} . As the BET surface area increases the observed capacity decreases linearly. Due to the lack of enough void spaces in the electrodes prepared with smaller grain size silicon, the surface layers of silicon particles expand, forming a layer of saturated Li_xSi . Then the fresh silicon remaining in the central area of the particles could not be further alloyed. Although this is not thermodynamic equilibrium, the capacity that can be inserted cannot exceed the values presented in the graph for a reasonable time. In this case the current reaches values as small as several μA at 5 mV versus Li and the kinetics becomes very sluggish. In the presence of a graphite matrix able to accommodate the silicon expansion most of the silicon is available for the reaction at reasonably high current density.

4. Conclusions

When the Si/C composite electrode is prepared and tested under controlled conditions (shown as dotted area in Fig. 1) it is possible to achieve stable electrode morphology even after extended cycling. Decreasing the composite particle size is essential for the improvement of the cycling performance.

Further improvement could be a difficult problem since contradictory requirements would have to be satisfied. The average particle size and BET specific surface area should be acceptable so that the first cycle irreversible capacity loss would be reduced. On the other hand, the grain particle size should be small enough to achieve stable morphology. The match between the silicon and matrix is also an important issue, since during the reversible alloying the

particles are repeatedly subjected to mechanical stress. If exposed to the electrolyte the formed surface film could serve as a barrier for the further Li^+ transport. This in turn will lead to a decrease in the cycling efficiency. A thin metal film deposited on the silicon cores could further improve the cycling efficiency in the presence of organic electrolyte.

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