ECS Transactions, 64 (23) 1-10 (2015)
10.1149/06423.0001ecst ©The Electrochemical Society

Dependence of the lithiation/delithiation potentials of silicon microwire anodes on their state of charge and sizes

S.Nöhren[a], E. Quiroga-González[b], J. Carstensen[a], and H. Föll[a]

[a] Institute for Materials Science, Christian-Albrechts-University of Kiel. 24143 Kiel, Germany
[b] Institute for Physics, Benemérita Universidad Autónoma de Puebla (BUAP). 72570 Puebla, Mexico

Cycle life and cycle stability are the crucial parameters when talking about batteries. The cycle life is affected when the operational voltage range is not correctly selected. In Si anodes, their intrinsic voltage limits are given by the phase transformation potentials. The voltage limits depend not only on external parameters like the voltage sweep rate, but mostly on internal parameters like the dimensions of the Si anode, and parameters of state like the state of charge. This is investigated in the present study, using Si microwires with different thicknesses and lengths. Additionally, the wires have been pre-lithiated to specific capacity limits. The analysis has been performed through cyclic voltammetry. It has been found that while short wires exhibit a lithiation limit at 50 % state of charge (SOC), the diffusion limitations are larger in long wires, which can be easily lithiated to a higher state of charge. The study showed that the optimal wire dimension has to be found to achieve better and stable cycling performance.

Introduction

The market for Li ion battery technology is growing and is starting to replace the lead-acid or Ni-Cd-battery systems [1, 2]. Compared to those technologies, the volumetric as well as the gravimetric energy density for Li ion batteries is ten times larger, which makes them smaller and lighter. Even for automotive applications, these technologies are advancing to extend the driving ranges of electric vehicles. In order to realize these aims, high-capacity materials for the anode and cathode have to be developed. Due to its much higher gravimetrical capacity than graphite (4200 mAh/g in comparison to 372 mAh/g), the most commonly used anode material; Si becomes the material of choice for high-capacity anodes. Nano- or microstructured Si offers the possibility to overcome the large stresses that the material has during Li ion incorporation caused by volume expansion. The standard Si microwire array anodes fabricated by the authors, of 1 µm in diameter and 70 µm in length, contain a high amount of active material (Si) of 1.35 mg/cm^2. By using these anodes, conductive additives are not necessary. They exhibit a high cycling stability with small irreversible losses. Under the optimal charging/discharging conditions and limiting the incorporation of Li to 75 % of the nominal capacity, the Si microwire anodes have a capacity of 3150 mAh/g over 100 cycles [3, 4]. An important point for the optimal charging conditions is the voltage range in which the anode is cycled. In the present study, the potential limits depending on the state of charge of the anodes have been determined by cyclic voltammetry for different sizes of Si wires. To facilitate the fabrication process, paste electrodes have been produced.

Experimental Details

The Si microwire anodes used in this study were fabricated by a series of electrochemical and chemical etching steps [5, 6]. A pre-condition for the success of these etching steps is the homogeneous pre-structuring of the 6”-p-type Si substrate (R = 15-25 Ohm*cm) via photolithography and reactive ion etching (RIE). Another pre-requirement is the etching of inverted pyramids into Si. The tips of these pyramids have a higher probability to nucleate pores during the electrochemical pore etching, thus pores with the desired spatial distribution are obtained.

The electrochemical etching step is performed in a mixture of an organic and aqueous electrolyte with 10 wt. % of hydrofluoric acid (HF). The addition of water in the electrolyte oxidizes the pore walls during the etching. The added HF in the solution dissolves the oxide of the pore walls and facilitates the electrochemical and chemical etching of the pores and wires [7]. During the electrochemical etching, a specific and well-modified current-time profile is applied. This current-time profile is characteristic for each pore size. The time of this etching step determines the length of the resulting pores. For this study, four different lengths were considered: 36, 46, 60 and 75 µm. Figure 1 shows some examples for the Si microwires in different dimensions.

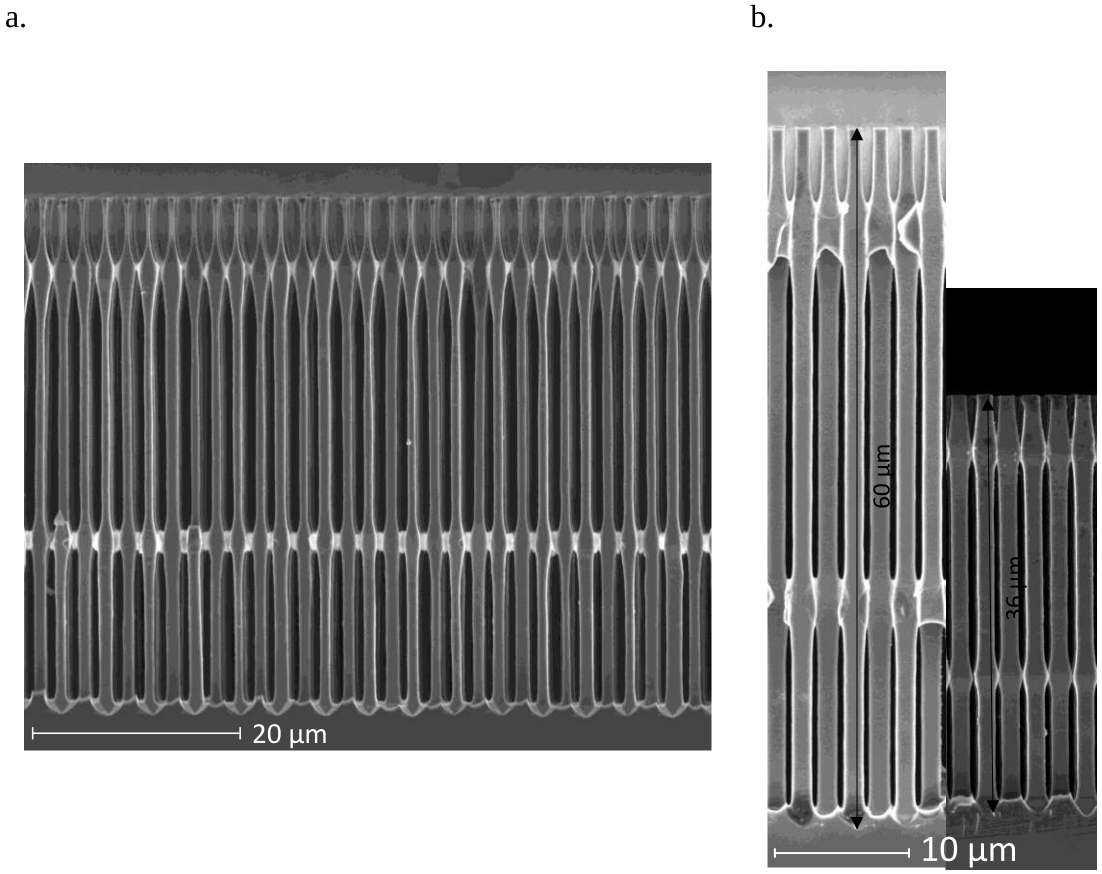


Figure 1. Examples of typical Si microwire arrays a) wires 1.2 µm thick, 60 µm long, b) comparison between different wire lengths.

The chemical etching step leads to the free-standing Si microwire array. With a 0.45 % KOH solution, the pore diameter increases until the pores merge [6]. The size of the wires is also controlled by the time. The longer the etching is running, the thinner will be the resulting Si wires. The time limit is reached if the wires and their supports are too thin and start to collapse, i.e. they stick to each other and no longer remain standing. Wire thicknesses of 1.8, 1.6, 1.4 and 1.2 µm have been produced to investigate the size dependency [3].

Paste electrodes were produced with the wires. These electrodes consist of an equal amount of active Si material and conductive carbon black (CB) (45 wt. %, Sigma Aldrich). Carboxylmethylcellulose (CMC) (45 wt. %, Sigma Aldrich) is used as binder. In comparison to polyvinyldifluoride (PVdF), CMC is more stable in the used battery electrolyte LP30 and can withstand the volume expansions of 300 % during cycling [8 - 10]. These three ingredients are mixed in a mortar with 1 wt. % deionized water and casted on a thin copper foil. The anodes have a size of 1 cm in diameter.

The Si microwire anodes have been tested in a standard, stainless-steel half cell at room temperature. For these tests, standard electrolyte LP 30 (BASF) was used. The separator was a glass fiber from Whatmann, with a pore size of 1.5 µm.

The experiments consist of a pre-lithiation step followed by the cyclic voltammetry measurements. The pre-lithiation consists of a galvanostatic and a potentiostatic step. The cycling is switched from galvanostatic to potentiostatic mode when the potential limits are reached, and this step finishes when the current reaches 10 % of its initial value, or the capacity limit is reached. The capacity limit for these tests was varied from 25 % of the maximum capacity of 4200 mAh/g (refered to as 25 % state of charge (SOC)) to 75 % of the maximal capacity (always referred to as 75 % SOC). 25 % SOC therefore means that the capacity of Si is limited to 1050 mAh/g. The experiments were performed with a cycling rate of C/10 [3, 4].

Cyclic voltammetry is the characterization method of choice. Five scans from 1 V to 0.02 V (and vice versa) with a scan rate of 0.1 mV/s have been recorded. This slow scan rate is needed to perform a quasi steady-state measurement.

Experimental Results & Discussion

Voltammetry measurements detect phase transformations at different potentials through current peaks. The lithiation/delithiation process for Si is a two-step process, which is fully reversible, indicated by two peaks occuring during the lithiation as well as during the delithiation. A typical cyclic voltammogram of a Si anode is shown in Figure 2.

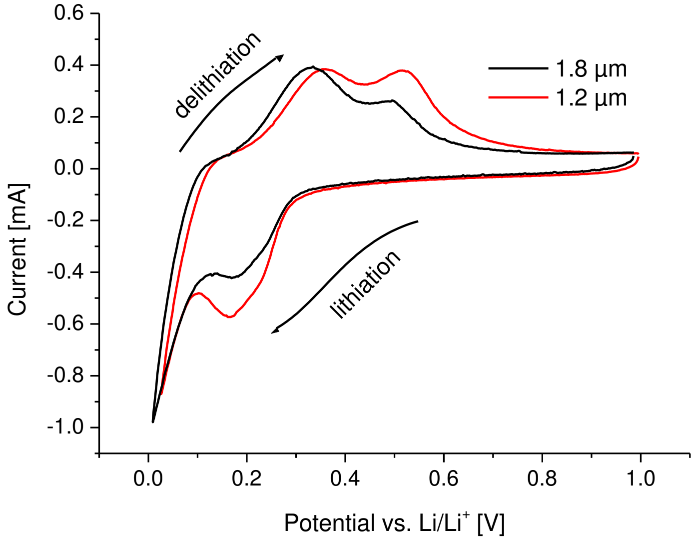


Figure 2. Typical cyclic voltammogram of a Si anode for different thicknesses.

In two steps, the Si is converted from crystalline to partially amorphous Li_xSi_y phases. The peak at which the Li^+-ions are fully incorporated into the Si is referred to as the fully lithiation peak. The same holds for the delithiation. During this analysis, only the fully lithiation and the partial delithiation peak are discussed because they contain the most reliable information.

The current (amplitude) could be expressed by the Cotrell equation which defines the dependency of the diffusion coefficient and its layer thickness on the current [11]:

$$I = \frac{nFA\sqrt{D}c^*}{\sqrt{\pi t}} \quad (1),$$

where A is the sample area, c^* is the concentration of the active species, t is the time of the experiment, F is the Faraday constant and n are the number of moles.

$$\delta = \sqrt{Dt} \qquad (2)$$

Thickness variation

Cyclic voltammetry measurements have been performed while changing the thickness of the Si microwires. During these experiments, the peak potentials as well as the current have been analyzed and compared. At first the trend in the peak potentials has been analyzed. Figure 3 shows the trend in the peak potentials for different wire thicknesses.

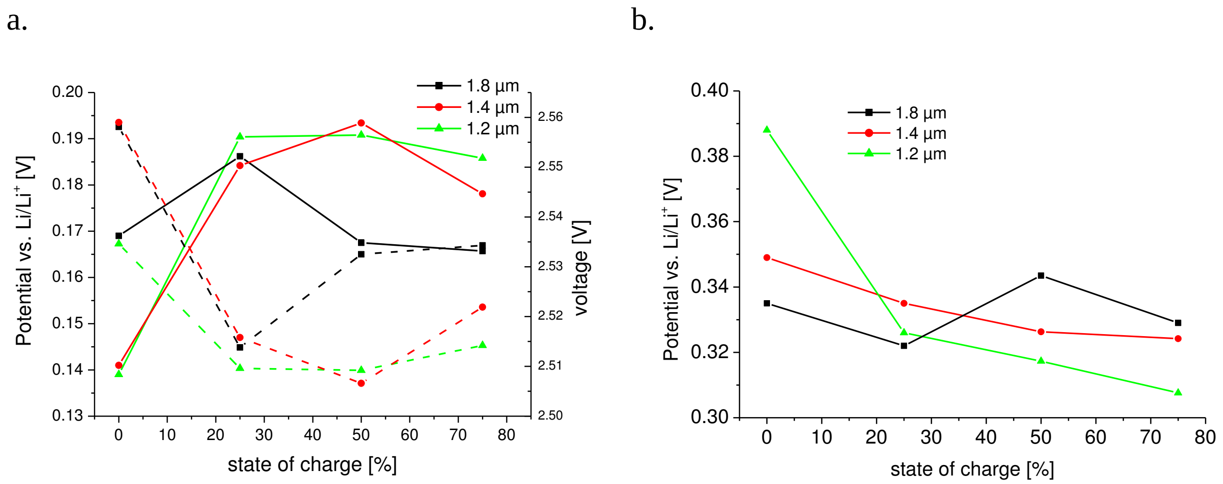


Figure 3. Peak potential vs. state of charge for different thicknesses and constant length of 60 µm. a) Fully lithiation peak, b) Partial delithiation peak in cycle 3.

Figure 3a compares the different thicknesses according to their state of charge for the fully lithiation peak. Starting from the non-pre-lithiated samples at 0 % SOC, thick wires show higher potential values. Comparing that with the voltammogram, higher values would mean a peak shift to the right. With increasing SOC values, the trend changes in favour to thin wires. They show an increase in the potential values. The peak potential can be translated into actual battery voltages. For the reverse scan, an increase in potential or a shift to higher values translates into smaller voltages for the lithiation. To calculate this, the open circuit potential is subtracted with the (actual) peak potential. The observed peak potential trend shows smaller voltages when the thickness is decreased. This leads to easier incorporation of Li$^+$-ions. Peak potential shifts can indicate if the lithiation/delithiation process is easier or hindered by diffusion. They restrict also the charging range during cycling experiments. The minimum and maximum voltages are taken always right after the last lithiation or delithiation peak/transformation occurred. Those minimum and maximum values determine the charging range.

The partial delithiation peak shown in figure 3b can support this behavior. Here, the non-pre-lithiated samples show larger voltage values for thin wires, which also change rapidly once the samples are pre-lithiated. For the forward scan, not the open circuit potential but 0 V is taken as reference for the calculation of the voltage. A peak shift to higher values translates therefore automatically to higher voltage values. From the peak potential trend or the translation into voltages, it could be deduced that thin wires also show easier delithiation behavior. The fully lithiation peak represents the complete incorporation of Li$^+$-ions in the anode. With this incorporation a phase transformation from crystalline Si to (amorphous) Li-rich Si_xLi_y phases occur. Due to the fact that the samples were already pre-lithiated to a certain amount of charge, they have undergone a previous phase transformation [12]. During the initial lithiation, Si bonds have to be broken in order to incorporate Li$^+$-ions in the anode.

The voltage increases in thick wires if the samples are pre-lithiated to a higher degree. For thick wires the mass transport is hindered when the ions are removed from the anode.

The change in the lithiation/delithiation behavior can be explained by the different surface to volume ratio. The wires can be considered as cylindrical with a radius of r. Two different wire geometries with a thick radius r_1 and a thin wire with a radius r_2 ($r_1 > r_2$) are considered.

Thin wires with r_2 have a higher surface to bulk ratio. An increase in the surface area leads to an increase of active activation sides for the Li$^+$-ions. A higher surface area at the same volume leads to an increase in activation sides for Li$^+$-ions. Additionally, bonds have to be broken initially to incorporate Li along the larger surface. Pre-lithiated samples cannot be lithiated to their full extent. 25 % SOC means that it can only be lithiated 75 %. At 75 % SOC, on the other hand, only a limited amount of ions can still be incorporated into the anode. During pre-lithiation, the necessary bonds were broken (energy consumption) and a stable solid electrolyte interphase (SEI) is formed. For the rest ions, less energy (and less voltage) is needed for the incorporation or removal especially when the diameter is decreased and less activation sides are available. In samples that were only pre-lithiated to 25 % SOC less charge was previously incorporated into the sample and therefore could have still more crystalline parts inside which would result in a higher current. The current is correlated to the (activation) energy, which has to be overcome for the Si bonds to be broken.

Figure 4 shows the trend for the current amplitudes for both the fully lithiation as well as for the partial delithiation peak.

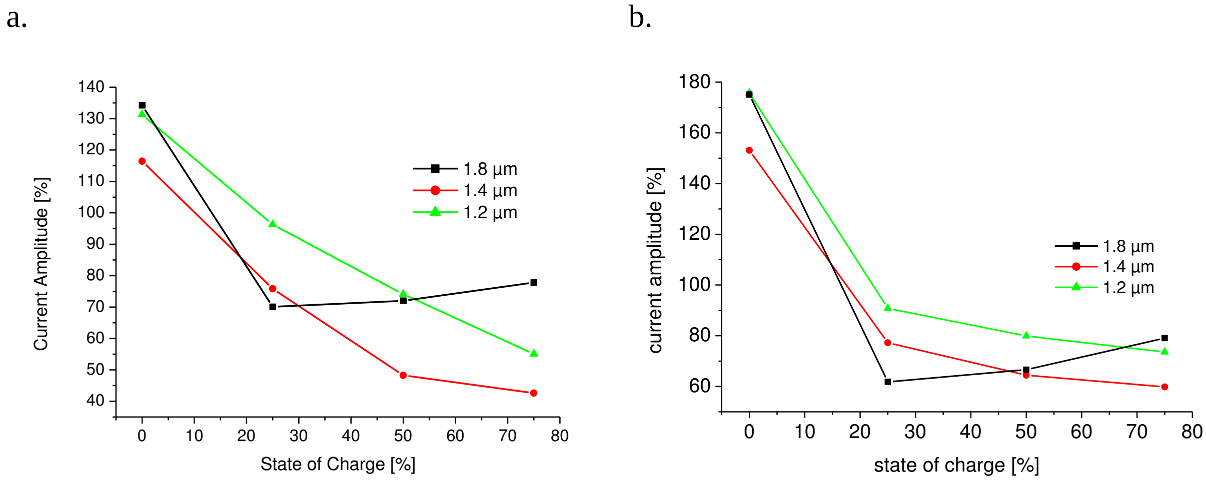


Figure 4. Current amplitude vs. state of charge. a) Fully lithiation peak for different thicknesses, b) Partial delithiation peak for different thicknesses for cycle 3 at 60 µm length.

For the current amplitude, the normalized current for each sample was calculated and compared to the first cycle where the current is considered to be 100 %. The other values represent the change (increase/decrease) in current with the state of charge.

During the first cycle, the SEI is formed for non-pre-lithiated samples. The SEI is composed of bi-products of the electrolyte that decompose during the application of current or voltage. This layer formation occurs only in the beginning of the cycling and is stabilized in the following cycles.

The current amplitude decreases in the course of the different SOCs. Comparing first again only the non-pre-lithiated samples, the current amplitude increases.

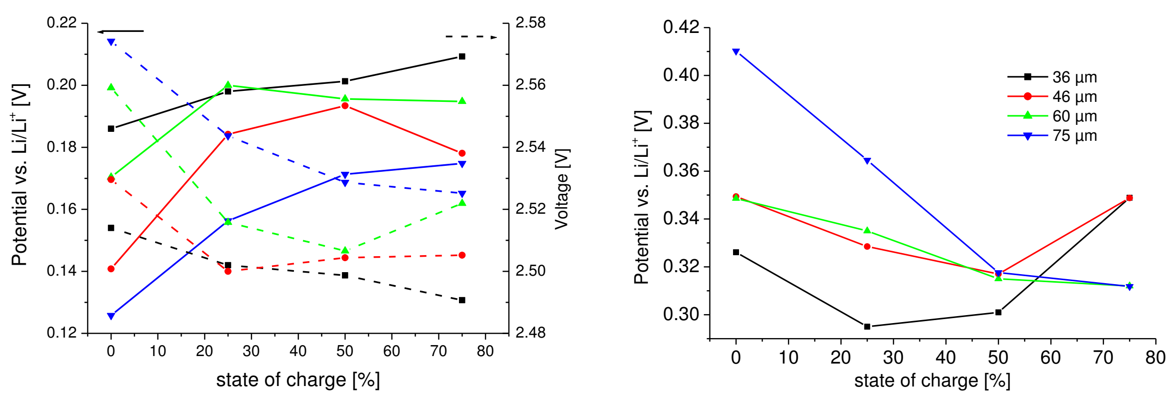
Thus more charges can be incorporated into the anode without any diffusion limitation (due to the correlation of charge and current). Figure 4a describes the fully lithiation peak for the thickness variation. The current amplitude for the smallest dimension decreases almost linearly to its minimum at 75 % SOC. The same holds for the next dimension.

This behavior can be supported by the tendency for the partial delithiation peak (compare Fig. 4b). Although the long wires have higher overall current amplitude compared to the others thick wires show an increase in the current when the pre-lithiation is higher than 25 % for the partial delithiation peak. Taking also the battery voltages into account where thin wires showed low values at high SOC, it means that a smaller amount of ions (25 % still remaining) can be incorporated easier due to its structural change and surface area. At higher SOC values, only 25 % of the wire can still be lithiated. This translates into less charge that has to pass the diffusion layer and have to overcome energy barriers which could lead to higher voltages in the end.

Length variation

To understand the contribution of the different wire lengths, the same characterization and comparison of potentials and currents are performed.

Figure 5 compares the trend in the potentials for the fully lithiation and partial delithiation peak.


a.

b.

Figure 5. Trend in the potential vs. state of charge a) Fully lithiation peak for different lengths, b) Partial delithiation peak for different lengths in cycle 3 with a thickness of 1.4 µm.

Figure 5a shows the peak trend for the fully lithiation peak. Comparing the long with the short wires (going from bottom to top), there is a trend to higher potentials for short wires. But with increasing state of charge up to 75 %, the potential for all the wires increase. For the SOC dependency on the wire lengths, this would mean that the higher potential values for the short wires translate into smaller voltages needed to incorporate the Li$^+$-ions. Due to the steep increase of all the wire lengths with the state of charge, the incorporation of ions into pre-lithiated samples is becoming easier the more charge is previously incorporated.

Figure 5b shows the trend in the partial delithiation peak in comparison for all the states of charge. Although the potential for shorter wires increases at 50 % SOC, their potential values for the delithiation are smaller of about 0.1 V. The overall tendency for the different wire length for the partial lithation peak is a reduction in the potential and therefore voltage.

Comparing the different length with each other in each state of charge, the longer wires suffer from the diffusion as well as from the resistance contributions.
The following figure 6 shows exemplary the trend for the current amplitude during the five cycles of the voltammogram of the partial delithiation peak for wires with a length of 46 µm.

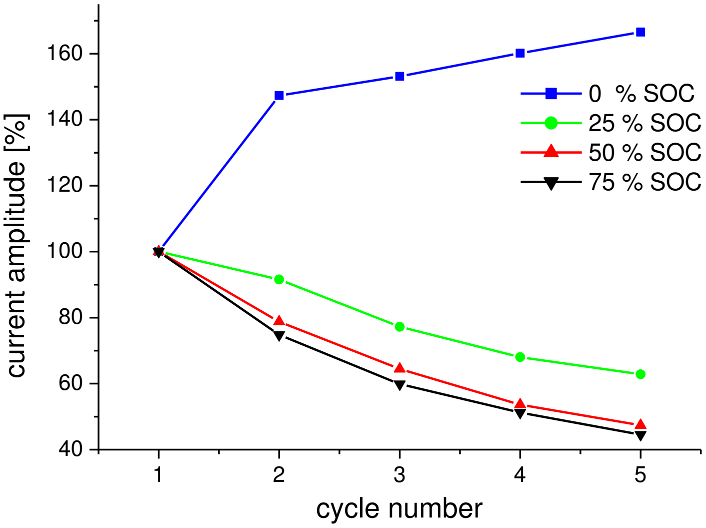


Figure 6. Trend for the current amplitude vs. cycle number in dependency of the state of charge for 46 µm wires for the partial delithiation peak.

The blue line in figure 6 represents the non-pre-lithiated samples. The current amplitude increases with number of cycles referring to a current gain during cycling. Compared to that, the pre-lithiated samples show an exponential decrease of the current amplitude. During delithiation, the current is lost. The higher the SOC (compare green, Fig. 6) the higher is the loss of the current amplitude. In cycle 5, the current amplitude is reduced to almost 50 % of the initial current amplitude.
In order to compare the lithiation/delithiation behavior, different lengths are considered in figure 7 for the fully lithiation and partial delithiation peak.

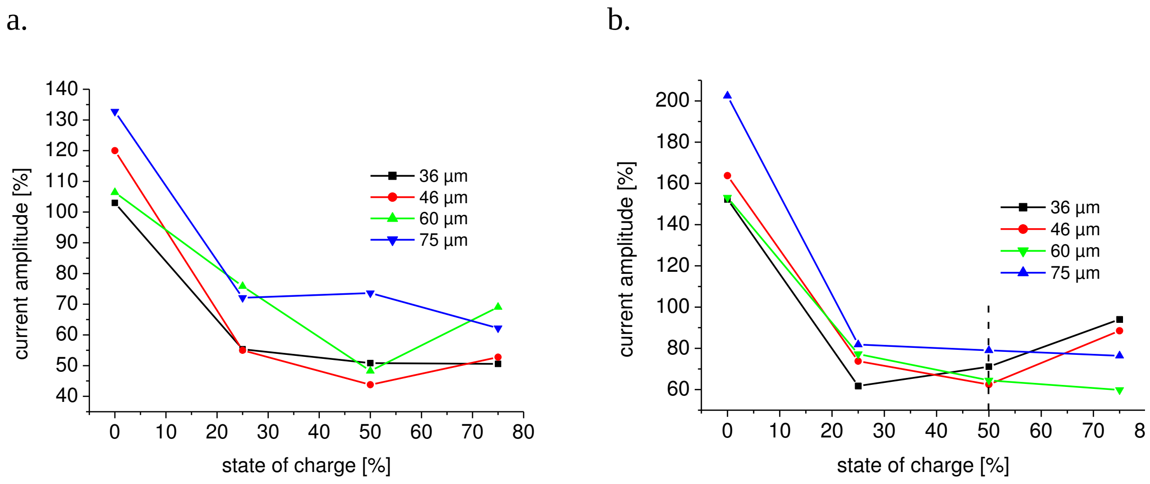


Figure 7. Trend of the current amplitude vs. state of charge. a) Fully lithiation peak for different wire lengths, b) Partial delithiation peak for different wire lengths at cycle 3 with a thickness of 1.4 µm.

As explained before, the decrease in the current amplitude (compare Fig. 6) can be justified in the trend for the fully lithiation and partial delithation peak (compare Fig. 7a and 7b). The higher the amount of pre-lithiation, the higher will be the decrease in the current amplitude. At 75 % SOC, the current amplitude increases with the length of the wires. As can be seen in equation (1), the current is inverse proportional to the square root of time. The longer the experiment/diffusion takes place the thicker the diffusion layer is going to be. An increase in the diffusion layer thickness resembles a decrease in the current.

For non-pre-lithiated samples, the Li^+-ions can be incorporated to the full extent into the Si anode. The system is not saturated and over the cycles more and more ions can be incorporated because the current amplitude increases for both the lithation/delithation peaks. Whereas pre-lithiated samples suffer from the structural change, the breaking of the Si bonds and that they cannot only be lithiated to a certain amount

Figure 7b shows the partial delithiation peak. During the delithiation process, the Li^+-ions have been removed from the anode. A decrease in the current amplitude can also be seen in this peak. But in comparison to the fully lithiated peak, here the longer wires with a pre-lithiation of 75 % SOC show a higher loss of current. For short wires, there is a limit at 50 % SOC after which those wires show a higher current amplitude again.

Another important factor is the embedding and breathing of the wires in the paste electrodes during cycling. The creation of a percolating network with the carbon black particles is an important factor. The contact has to be the same all around the wires, which expand during cycling. The radial volume expansion influences the conducting network and crack formation might occur. In the slurry paste, the carbon black connects to Si. Due to this 3D network and its better connectivity, the Li^+-ions can travel easier into the Si wires. Nevertheless, due to the length change, the diffusion length is different. If more carbon black particles are around a short Si wire, its connectivity is better, but also the ions have a shorter way to fully lithiate Si, which leads to a decrease in necessary voltage.

Conclusion

For the optimal cycling conditions of Si microwire anodes, the sizes of the Si wires and their state of charge has to be taken into account. Internal and external parameters have an effect on the cycling performance of the Si anode. The minimum voltage for the incorporation of Li^+-ions changes with the SOC and the sizes of the Si wires. Upon cycling, the charging ranges have to be adjusted according to its capacity limit in order to enhance the cycling performance.

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