

Si Nanowire Arrays as Anodes in Li Ion Batteries

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Si nanowires can incorporate large amounts of Li without fracturing and are thus prime candidates for anodes in Li ion batteries. Anodes made from Si nanowires offer a specific capacity per g more than 10 times larger than the present graphite standard. It is shown how optimized Si nanowire arrays embedded in Cu can be produced in a relatively simple way

employing macropore etching in Si followed by chemical etching and Cu galvanic deposition. First tests of these arrays in half-cells and batteries demonstrated a substantially increased capacity, small irreversible losses and cycle stability. In particular more than 60 charge / discharge cycles could be realized without loss of capacity.

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Introduction Applications of the Li ion battery for large-scale energy storage, e.g. for electrical cars, requires substantial improvements of the performance/cost relationship and thus a substantially increased capacity (as measured in Wh/kg). The capacity is directly related to the amount of Li that can be intercalated in the anode (and cathode). It has been known for some time that Si can incorporate large amounts of Li with a specific capacity of 4200 mAh/g, about a factor of 11 larger than for state-of-the-art graphite anodes [1]. However, upon driving Li into Si, various phases like $\text{Li}_{12}\text{Si}_7$, Li_7Si_3 , $\text{Li}_{13}\text{Si}_4$, and $\text{Li}_{22}\text{Si}_5$ form with a concomitant volume change of about a factor of 4 for full loading. This invariably leads to mechanical stresses large enough to fracture bulk Si into powder after the first few cycles of charging / discharging.

In [2] it was shown that Si nanowires, while doubling their diameter during the intercalation of Li, do not fracture and that some random arrangement of nanowires with some diameter distribution centered around 89 nm can withstand more than 10 charging / discharging cycles without significant loss of capacity. In this letter we demonstrate a technique for the production of Si nanowire anodes that provides for improved performance relative to what has been reported in [2] and has the potential for mass production.

Optimized Si Nanowire Anode Production

Three basic steps are required: 1. Electrochemical etching of macropores in an optimized (lithographically determined) arrangement. 2. Uniform chemical etching of the macroporous substrate in order to increase the pore diameters to a point where the pores touch, resulting in a nanowire, and 3. Galvanic deposition of Cu onto the substrate so that the nanowires are now encased in Cu. Fig. 1 illustrates these points schematically.

p-type 20 Ωcm Si wafers were first structured (square lattice of openings in the 2 μm range) in a Si_3N_4 layer by standard lithography; experiments were performed with $\approx 1\text{ cm}^2$ pieces cut from the wafer. Macropore etching was performed in an "ELYPORE" apparatus [3] employing an HF : DMF electrolyte for about 112 min. Pores with a length of about 160 μm result; details of the macropore etching can be found in [4, 5].

Chemical etching was performed in a HF : HNO_3 : Ethanol : HAc solution for ≈ 24 hrs., conceptually similar to [6]. Galvanic Cu deposition onto the bottom of the nanowires is far from trivial (cf. [7 - 9]) but possible with an optimized process as described in the above cited publication. Fig. 2 gives an example for the nanowire structure obtained before Cu deposition.

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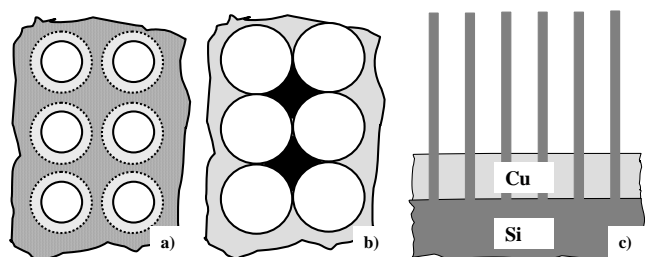


Figure 1 a) Schematic top view of macropores (diameter around 2 μm) and their enlargement by chemical etching (dashed lines), b) Formation of nanowires (black) by overlap of the enlarged pores. c) Schematic cross-section with the Cu layer (thickness $> 10 \mu\text{m}$).

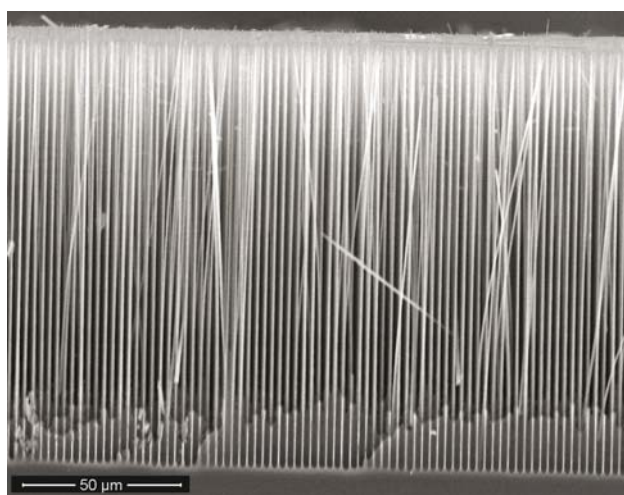


Figure 2 SEM cross-section of nanowires (diameter about 0.9 μm , lattice constant $\approx 2 \mu\text{m}$, length 140 μm).

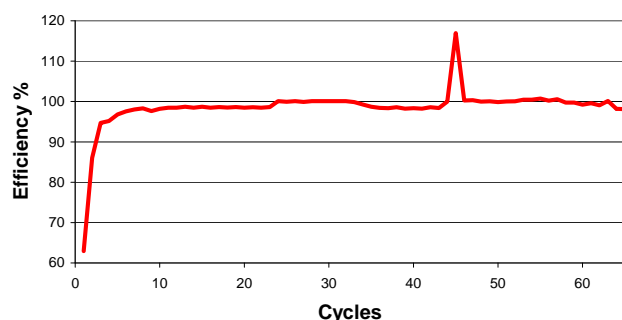


Figure 3 Anode charge/discharge efficiency in a half-cell. Shown is the difference between discharge and charge vs. cycle number. The peak around cycle 45 is an artifact caused by a failure of the temperature control.

The resulting device can be directly used as an anode in a Li half-cell or in a battery. Its basic conceptual advantages with respect to the anode in [2] that consisted of nanowires produced by the vapor-liquid-solid (VLS) technique attached to stainless steel are: i) Arrangement in a defined grid with uniform diameters and lengths allows for maximum anode capacity because of maximum nanowire volume/nanowire layer thickness ratio. ii) All geometrical parameters are adjustable in a wide range. iii) Anode production is far faster and cheaper. iv) The embedding in Cu provides for stability (no shearing off is observed) and good current collection.

Anode Properties Anodes produced as described above were tested in half-cells and batteries, primarily with respect to capacity, cycle stability, and irreversible Li losses.

The half-cell tests employed a standard LP-30 (Merck) electrolyte and glass fiber fleece in a titanium housing and is charged to $C/10$ for the first 8 cycles (C is the nominal capacity), the remaining cycles go to $C/5$. Cycling was stopped after 65 cycles because of time constraints. Relevant results are shown in Fig. 3 and Fig. 4.

The capacity as measured in mAh over 65 cycles did not noticeably decrease and remained close to 100 % (defined as charge to discharge percentage). The initial low efficiency is due to the formation of a solid electrolyte interface (SEI) and the initiation of the phase transformation from Si to Si-Li.

The result of first experiments with our Cu stabilized Si nanowire anode indicate irreversible losses of $\approx 18.8 \%$, comparable to the values reported in [10]; it is thus close to the theoretical limit.

The cycle stability of the anode is as good as it can be given by the measurement noise and present limits with time and the number of samples. This implies that the Li-loaded Si nanowires do not become detached from the current collector (the Cu film here) despite the strain at the interfaces between Cu, (cryst.) Si, and (amorphous) Si-Li compounds. Fig. 4 shows SEM cross section pictures after cycling an anode for 6 and 66 cycles, respectively.

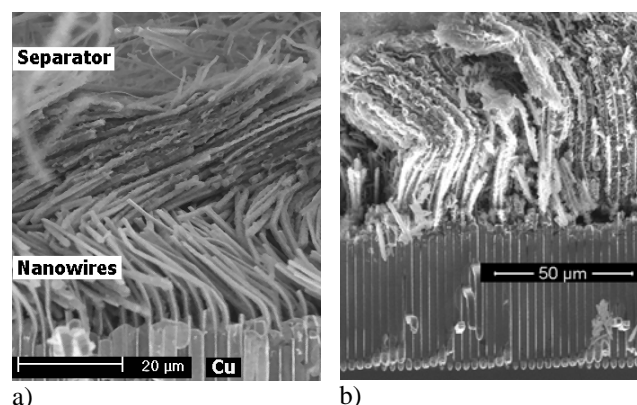


Figure 4 SEM cross-section of Si nanowire anode after 6 cycles (a) and 66 cycles (b). Note that nanowire detaching occurred during specimen preparation by cleaving.

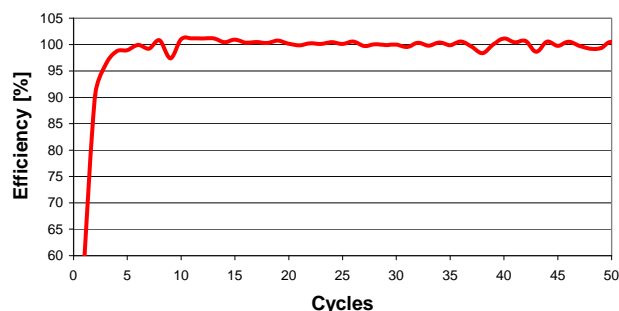


Figure 5 Charge/discharge efficiency vs. cycle of first battery.

It can be clearly seen that the nanowires are bend as would be expected upon applying some pressure via the separator (glass fibre fleece) but not destroyed, and that prolonged cycling leads to the build-up of deposits, most likely SEI, as always observed in similar cases [10]. No widening of the nanowire parts embedded in the Cu layer has been found. The mechanical stress induced by the Cu onto the nanowires is possibly the reason that no Li penetrates via the nanowires into the bulk Si.

Our Si nanowire anode was also tested in a complete battery with $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ (NCM) as cathode, LP-30 electrolyte with 1 % vinylen carbonate and glass fiber fleece separator. Due to a small leakage in the masking of the substrate there is a shift of the absolute capacity of this battery. The first battery with our Si nanowire anode is presently still running; with cycle numbers of around 50 charged with $C/5$ based on the shifted capacity. Some results are shown in Fig. 5.

The first Si - $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$ batteries produced displayed a voltage - current behavior quite similar to that of the standard graphit- LiCoO_2 . The useable voltage regime is from 3 V till 4.2 V. Due to our cathode material ($\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$) we only have chargeable Li for 84.8 % of our Si-Sample. We could only use 35.6 % of our sample as anode material. The reason is the unmasked Si-substrate in which Lithiation occurs.

Discussion The present anodes still have a substantial amount of bulk Si attached to the nanowires and the Cu layer. If the half-cell or the battery is not perfectly sealed so that Li ions can reach the bulk Si (e.g. via holes in the Cu layer or “leakage” around the edges), some Li will be also incorporated into the bulk Si, which then fractures. This may influence the measured results and some such effects were indeed observed in measurements and in SEM pictures. Leakage of this kind also accounts for a few cycle experiments where the anode lost capacity. However, all results taken together indicate clearly that the basic data given here with respect to capacity, irreversible losses and cycle stability are reflecting true properties of the nanowire anode.

Removing the substrate Si and producing a flexible Cu

foil with embedded nanowires would thus be advantageous, and some work in this direction is under way.

A conservative extrapolation of the data obtained so far leads to the following scenario: Using a standard 200 mm p-type Si wafer as used for solar cells (costs around 2 €) as an electrode involves scaling of the macropore etching process, the chemical etching process, and the Cu galvanics. The specialized equipment and necessary process development needed for this is mostly available (cf. [11]); processing is in fact easier (but costlier) than for small samples because edge effects become negligible. An optimized 200 mm Si nanowire anode would have a capacity of 6500 mAh, and only 22 wafers with a total nanowire layer thickness less than 3.6 mm and a weight (without the Si substrate) around 34 g would be needed for a 48 Ah car starter battery. The presently long processing times can be reduced substantially; the processes are also rather cheap. It is thus not unrealistic to assume that our Si nanowire anode can be manufactured at competitive costs.

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