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# Size-dependent cyclic voltammetry study of silicon microwire anodes for lithium ion batteries

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ABSTRACT

Silicon microwires as anodes for Li-ion batteries may show good cycling performance over 100 cycles as anodes for Lithium ion batteries without significant capacity losses. The life time of the anode, however, strongly depends on the way the battery is charged. Overcharging or undercharging may have severe negative consequences. This paper studies with the study of the operational voltage range of Si microwire anodes and its dependence on the dimensions of the wires. Cyclic voltammetry is used to identify the potentials for the different lithiation/delithiation events, while a modified cyclic voltammetry technique is used to study the dynamics of those processes. Specially prepared anodes with Si wires of different lengths and widths were used for the study.



## 1. Introduction

Graphite is the most commonly used anode material for Li ion batteries due to its low cost and large cycle life, although it presents low capacities of around 370 mAh/g [1,2]. Nevertheless, this capacity is not enough to satisfy the demands for higher capacity of several applications. Besides being able to store large amounts of charge, the anode has to withstand many cycles without being damaged. Silicon, offering the highest gravimetric capacity for anode materials, of 4200 mAh/g pulverizes when used in bulk state due to volume expansions during cycling. However, if it is micro-/nano-structured, it can withstand large volume changes during lithiation/delithiation [3–5]. In particular, Si microwire array anodes with wires of 1 $\mu$m in diameter have shown exceptionally good performance [6,7]. To achieve this performance, it is important to charge the batteries in the correct potential range.

Charging outside the proper operating range of the battery produces large leakage currents that may lead to temperature increase inside the battery, producing electrolyte decomposition or an explosion of the battery in the worst case [1,8]. On the other hand, Li-ion batteries in general suffer from memory effects, which occur when a battery is charged within its voltage limits but in a smaller voltage range. The system remembers the smaller limits and for the next charging cycles it can only be charged to these limits [1], decreasing the usable capacity. All these factors affect the life time of a battery. Therefore, it is important to find the correct potential limits of the Si microwire anode.

It can be deduced from different reports of electrode materials that the lithiation and delithiation voltages depend on the size and geometry of the anode itself [9–13]. For example, for Si wires thinner than 100 nm, the potential of fully lithiated wires is in the range of 50 mV to 70 mV vs. $Li/Li^+$ [9–12]. On the other hand, if the wires are thicker than 100 nm, a shift to higher potentials has been observed [11]. Up to now, no research has fully clarified how the dimensions of the electrodes affect the lithiation/delithiation potentials. In order to determine if variations of the size of the Si microwires induce a voltage shift in the lithiation or delithiation process, the diameter as well as the length of the wires have been varied in this work, and have been tested by cyclic voltammetry. To reduce the resistances outside the wires and to minimize process differences (e.g. during deposition of the current collector), they have been tested in a paste electrode configuration, with a large amunt of conductive carbon. Compared to the highly-ordered array anodes without any additives, paste electrodes as used in this study show a ten times lower capacity when cycled under same conditions. However, the objective of the work is not to present top performing anodes, but to study some phenomena occurring in Si wires using cyclic voltammetry. This technique is the method of choice in this paper to estimate the size dependency. Additionally, the current relaxation in the anode is studied with a special

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voltammetry method to determine the lithiation/delithiation kinetics in relation to the size of the wires.

## 2. Experimental Details

The preparation of the Si microwires consists of a two-step process starting with a pre-structured (100) p-type Si wafer with a resistivity of 15–25 Ωcm. The finished, pre-structured pattern on the wafer is a quadratic array of inverted quadratic pyramids, with a pitch of 3 μm; for details about pre-structuring see [3,14]. The first step of the fabrication process is the electrochemical etching of macropores (Fig. 1a-c). Fig. 1 shows a schematic of the process to produce Si microwires, step by step, beginning with pre-structuring of Si substrates.

The pores grow at the pits of the pyramids due to sharp tips increasing the probability of nucleation at those points, as described by the current burst model (see Fig. 1c-d) [15]. The process is temperature controlled at 18 °C. The mixed aqueous and organic electrolyte allows to control the pore diameter modulation as well as the pore wall passivation, which is necessary to fine control the wire thickness of the wires. By adjusting the current density during electrochemical etching and due to the addition of PEG into the electrolyte, the pores can be modulated [3,16]. The etching current profile was optimized to get a homogeneous pore diameter along the length of the pores. Depending on the current profile, different pore lengths (translated in different wire lengths at the end of the process) can be obtained. The second step is a chemical over-etching process of the pore walls in an aqueous low concentrated KOH-based solution at 50 °C (Fig. 1e). After this process the Si microwires are obtained. Depending on the etching time, wires with different thicknesses can be prepared.

For the voltammetric studies two sets of Si microwires were produced: a) wires 60 μm long with thicknesses of 1.8 μm, 1.6 μm, 1.4 μm, 1.2 μm; b) wires 1.4 μm thick with lengths of 75 μm, 60 μm, 46 μm, 36 μm.

Examples of the produced wires with different thicknesses and lengths are shown in the SEM images in Fig. 2.

Fig. 2a and b show wire arrays with two different thicknesses of 1.4 and 1.6 μm at a fixed length of 60 μm. In the figure, the wires are still attached to the Si substrate. The wires show two diameter modulations which are used as diffusional barrier and to stabilize the diameter. Fig. 2c and d show wires with different lengths, but with the same thickness, in order to systematically investigate the influence of the thickness and the length of the Si microwires on the peak potentials and with it on the voltage limits during cycling experiments. With this electrochemical etching method, highly reproducible and reliable anodes were produced, by step-by-step adapting thickness or length of the wires.

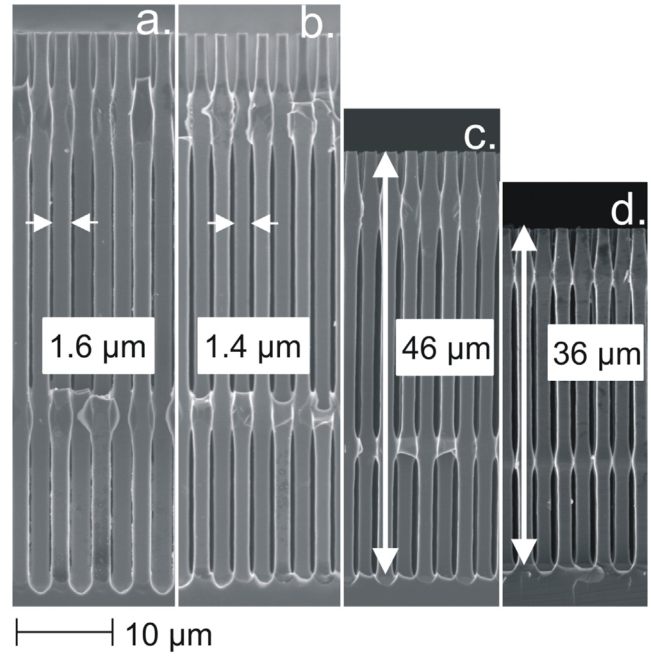


**Fig. 2.** Examples of wires with different thickness and length: Wires of a. and b. have the same length of around 60 μm, and widths of 1.6 and 1.4 μm, respectively. The wires of c. and d. have the same thickness of 1.4 μm, but different lengths of 46 and 36 μm, respectively.

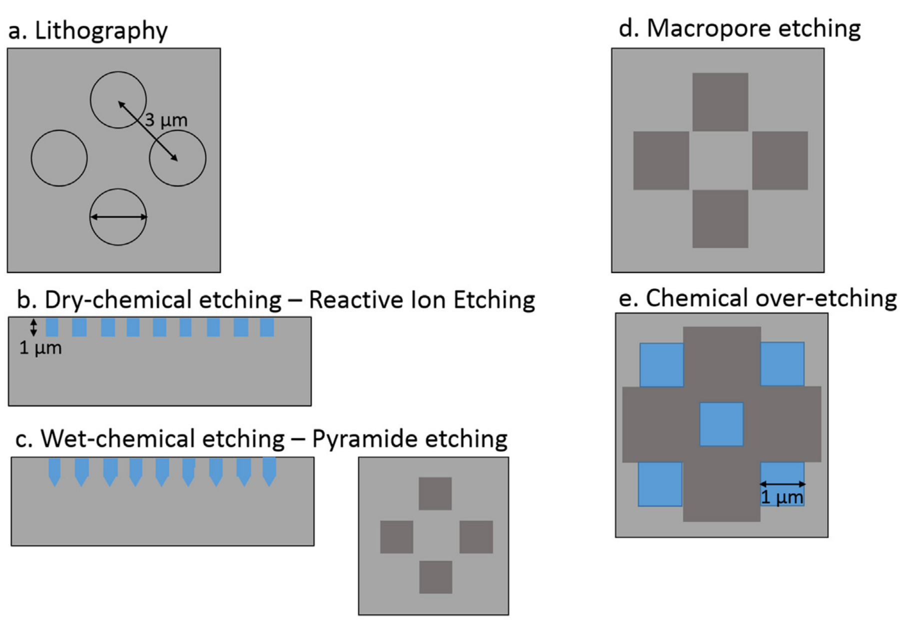


**Fig. 1.** Schematic of the fabrication steps of the Si microwires. a. It shows the pre-structuring via lithography with a highly ordered pattern. b. and c. It includes the dry and wet chemical pre-structuring process which are a requirement for the essential macropore etching step. The essential macropore step is shown in d in a top view. During the over-etching step, the interstices between the pores is dissolved and the wires remain free-standing.