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Corset-like solid electrolyte interface for fast charging of silicon wire anodes

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HIGHLIGHTS

- Propylene Carbonate as old candidate leads to elastic SEI layer.
- Silicon microwire anodes do not need any graphite material.
- Silicon allows very fast charging with high capacity.

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ABSTRACT

The most challenging tasks in today's batteries are the need for fast charging and large energy densities for longer lifetimes. Micro-structured silicon microwire anodes show a nine-fold increase in gravimetric capacity over standard graphite batteries. The anodes exhibit an areal capacity of 4.25 $mAhcm^{-2}$ with a specific capacity of 3150 $mAhg^{-1}$. The high specific capacity implies a 400% volume expansion of the Si wires. This paper demonstrates that by modifying and adapting the electrolyte composition a charging speed of 5 *C* (12 min charging time) can be reached completely maintaining the area and gravimetric capacity of the silicon anodes. Detailed analysis of the charge transfer processes across the solid electrolyte interface into the silicon wires reveals highly relevant mechanisms for this stable performance. A well-established solvent candidate, like propylene carbonate, which was rated not at all suitable for graphite electrodes, is very promising and advancing fast for pure silicon anodes. This addition into the electrolyte allows modifying the mechanical properties of the SEI layer in oder to support revery individual silicon wire to buffer the inevitable volume expansion.

1. Introduction

Electrolytes for graphite electrodes in Li-ion batteries have been under constant investigation for the last 30 years. All electrolytes for Li-ion batteries need to fulfill some general requirements [1–4]. First, they must have a high ionic conductivity. This guarantees lithium diffusion and ionic mobility for a long lifetime, otherwise diffusion limitation sets in. As a consequence, the internal resistance increases and the capacity decreases. Most common electrolytes using $LiPF_6$ in EC-DMC mixtures have an ionic conductivity of 11 $mScm^{-1}$. Different salts containing for example As, Br or Cl give strong ionic pairs or conglomerates, as their charge is not localized [1]. Second, electrolytes must be thermally and chemically stable in order to prevent unwanted side reactions at the electrode-electrolyte interface. Third, every electrolyte component has to be electrochemically stable in their specific voltage region during cycling without irreversible decomposition. This is essential for high-power applications of up to 5 V. Specific salts, for example $LiNO_3$, irreversibly decompose below 1.7 V and do not contribute to the battery performance anymore [5–7]. Anyhow, the key requirement of any type of electrolyte is the formation of a stable solid electrolyte interface (SEI) balancing the potential differences between the anode, cathode, and the electrolyte and minimizes any oxidation or reduction of the electrolyte [1,8].

A standard non-aqueous electrolyte for Li-ion batteries consists of a Li salt dissolved in a heterocyclic carbonate, like ethylene carbonate (EC) combined with a linear carbonate like dimethyl carbonate (DMC). Especially for graphite electrodes, the EC is an essential electrolyte component for stable cycling [9]. Graphite anodes have a low gravimetrical capacity of only 372 $mAhg^{-1}$, corresponding to LiC_6. The major drawback of graphite electrodes is the possible exfoliation of the

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basal planes. This oxidation of the edges leads to complete disintegration of the active material and naturally to a very poor cycling stability. Increasing the EC concentrations should help forming a stable SEI layer on graphite ($>$ 44.1 wt %), suppressing the disintegration along the basal planes, and other kinds of degradation [9]. Propylene carbonate (PC), on the other hand, is chemically very similar to EC. For a long time, it was the solvent of choice because it exhibits very promising properties. Unfortunately, the decomposition products of PC severely degrade the graphite electrode by co-intercalating into the structure, especially at grain boundaries, opening the structure for further electrolyte flow [9–11]. This vicious circle repeats until the electrode is completely destroyed.

When considering lithium-rich silicides, e.g. $Li_{22}Si_5$ and $Li_{13}Si_4$, for electrode, the volume expansion increases significantly (i.e. up to $\sim$400%) and completely different problems on the side of the electrolyte and SEI part are occurring [12–14]. Researchers were not aware of these problems before, because the silicon content in anodes is typically small (10–20 wt %) [15,16]. For the first time, this study focuses on pure silicon electrodes and their specific electrolyte and SEI development without any additional graphite. We show that it is possible to benefit from long-known solvents like PC and electrolytes developed for graphite electrodes, and establish them now for silicon anodes. Some groups discussed about the chemical nature of PC and its interaction with different solvents. But its influence and contribution on the cycling performance of pure silicon anodes have not been investigated before.

The here described silicon microstructure is a completely freestanding microwire array anode, produced with a tailored top-down approach involving standard MEMS- and silicon technology [17,18]. The benefit of pure silicon anodes is the complete elimination of heterogeneous particles, which can disturb the local SEI formation, and can even act as arbitrary nucleation sites for failure. These situations cannot be controlled easily and negatively influence the cycling performance [19]. Therefore, the here discussed architecture does not require any additional graphite enhancing the energy density due to the lack of any inactive material. Our anodes have a specially designed geometry with pre-defined space to cope with the volume expansion.

The formation of a closed and flexible SEI is more difficult due to the large volume expansion of this material. During silicon expansion, silicon and the SEI layer can easily be perforated and break. Consequently, the SEI layer needs a self-healing property acting during each lithiation and delithiation cycle again. On the other hand, the electrode compatibility is the most important criterion for designing a full cell with silicon anodes and the cathode material of choice, e.g. a novel sulfur cathode. When combining silicon and sulfur electrodes, different lithium salts like LiTFSI compared to the $LiPF_6$ or even additional solvents are favored to enhance the cycling stability and minimize the capacity retention [20–22]. This includes ether-based electrolytes as well as LiTFSI as salt to enhance the viscosity. For the here described silicon wires, LiTFSI in combination with DME and DOL has an optimal viscosity. The direct interaction between the electrode and the surrounding electrolyte is found to be very important, including the formation of the supportive solid electrolyte interface (SEI) around the electrode as well as possible aging mechanisms of the electrolyte [1]. For pure silicon anodes, it is important to minimize the SiO_x formation leading to lithium as well as silicon disintegration [13,23].

In this paper, the reduction mechanisms of various electrolytes during the SEI formation are analyzed and modelled with respect to the SEI layer mechanically supporting the Si wires. Thus by combining several Li salts and solvents, the C-rates allowing for stable cycling could be increased by a factor of ten (compared to standard charging and discharging processes [17,18,24]) up to 5 *C*. At the same time, the gravimetric capacity remains stable at 3150 $\mathrm{mAhg^{-1}}$.

2. Experimental details

The fabrication process of silicon wires relies on lithographic microstructuring and the macropore etching in p-doped silicon. This study focuses on the macropore etching in organic (water-free) electrolyte with HF at a low concentration ($\sim$10 wt %) and PEG ($M \sim 3360\ \mathrm{g\,mol^{-1}}$). Pore modulation and etching in n-doped silicon is a standard process by adequate backside illumination and pure current density variation. The same parameters with p-doped silicon lead to deep and wide pores, without any (deliberate) diameter modification along the pore [25–27]. However, for the proposed application, the pore modulation in p-doped silicon could be achieved by increasing the electrolyte viscosity by adding PEG. Consequently, the pore walls are passivated and the local diffusional reaction is directed towards the pore tips. Locally the diffusion is reduced, to allow a controlled pore modulation. Fig. 1 shows an example of the highly-oriented silicon microwire arrays anodes with the integrated copper current collector.

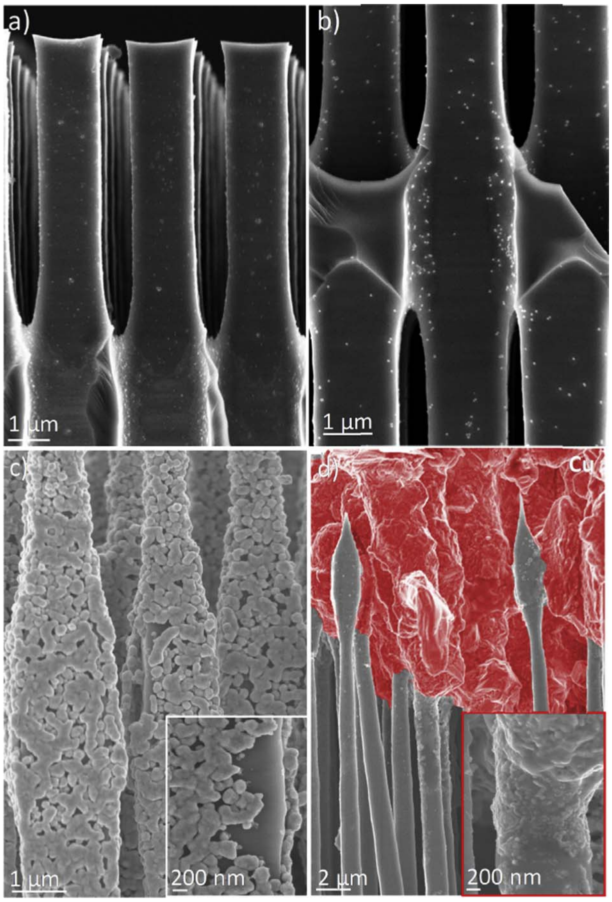

Fig. 1. Highly-symmetric silicon microwire array anodes for Li-ion batteries. The SEM images show individual process steps for the mechanically stable, freestanding array anode. a-b) Diameter variations along a wire implemented during electrochemical and chemical etching. c) A thin, chemically deposited copper layer enhances the contact between silicon and thick copper layers. d) The thick copper current collector allows a large mechanical integration and stability for the silicon wires, in order to remove the complete array from the silicon substrate. The parts covered with copper are highlighted in red. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

The pores in this study were 70 µm long (deep in $< 100 >$ direction) and have two design features: a) two diameter variations resulting in stabilizing planes along the pore (Fig. 1a–b), and b) a narrow pore tip. The pore modulation and diameter variation during the macropore etching affects the wire geometry. By deliberately adjusting the organic electrolyte and additionally, by adapting the current density profiles to the desired pore length, it is possible to obtain a defect free high quality pore array (with a diameter variation of less than 1%) [30]. Subsequent pore wall dissolution in a low concentrated KOH ($\sim$0.45 wt %) chemical etching solution leads to the desired wire