



In situ Scanning electron microscope study and microstructural evolution of nano silicon anode for high energy Li-ion batteries



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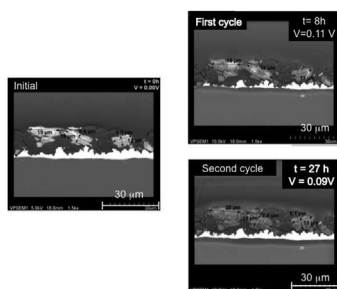
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HIGHLIGHTS

- Volumic expansion of nano Si was observed by in situ SEM.
- Si keep their integrity when the discharge is stopped at a voltage 0.1 V.
- Particles of size $d < 2 \mu\text{m}$ do not crack.

GRAPHICAL ABSTRACT



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ABSTRACT

In situ and ex situ scanning electron microscopy of nano Si and SiO anode particles was carried out during the first cycles, and at various stages of charge. The particle size effects were explored in the range 0.1–20 μm , providing a new insight into the micro-structural evolution of the particles as a function of their size, and into the ‘mechanical’ resistance upon important volume change upon phase transformation of these anodes. For small particles, the failure of the battery comes from an electrochemical sintering that compacts the whole electrode, which results in its cracking. The particles keep their integrity when the discharge is stopped at a voltage 0.1 V, which corresponds to the chemical composition $\text{Li}_{12}\text{Si}_7$, while the particles are known to crack at deeper discharge up to $\text{Li}_{22}\text{Si}_5$. Replacing the Si particles by SiO particles in an attempt to avoid these structural effects did not help, because of the different chemical reactions during cycling, with the loss of oxygen.

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1. Introduction

Lithium-ion batteries have become the most popular technology for electric energy storage, with applications as power source for portable electronics, and more recently for hybrid and electric

vehicles. This success is due to the development and optimization of active materials as positive electrodes (see Refs. [1–3] for a review), and negative electrodes (see Ref. [4] for a review). Many efforts are currently made to increase the energy density, the power density and the intrinsic safety of the battery. The commercialized anode is usually graphite carbon, although $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is presently used for applications that demand a lot of power [5,6]. The capacity of carbon graphite is 370 mAh g^{-1} . This is much smaller than silicon that has a gravimetric capacity 4200 mAh g^{-1} when lithiated to

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$\text{Li}_{4.4}\text{Si}$, and volumetric density 9786 mAh cm^{-3} based on the initial volume of Si, respectively [7–9]. These are the highest capacities among all the anode elements for Li-ion batteries, except Li metal itself. For this reason, Si has been considered as the promising element to increase the energy density of the Li-ion batteries since many years [10–12]. It is, however, difficult to believe it, because the cathode limits the energy density of a Li-ion cell, not by the anode element. The capacity of LiFePO_4 olivine is 170 mAh g^{-1} , that of lamellar compounds slightly larger, but still much smaller than that of graphite, and at the price of thermal instability that reduces the intrinsic safety of the batteries [13]. Nevertheless, the investigation on the Si anode is of interest for another reason, as the performance of the graphite anode depends strongly on the stabilization and control of the solid–electrolyte interface that limits the performance and calendar life of the battery. So far however, Si-based anodes suffer from numerous problems that prevent them being commercialized. In particular, the performance degrades during the first cycles due to the large variations of the volume during the charging/discharging process [14–20]: when transforming from Si to $\text{Li}_{4.4}\text{Si}$, the volume expansion is 420% [21–25]. This large volume expansion/contraction during lithium insertion/extraction is responsible for the cracking of the Si particles, observed by atomic force microscopy during the Li-extraction [26–28]. In an attempt to overcome this problem, many efforts have been made to reduce the size of the Si particles to the nanoscale, which have been recently reviewed [29], in order to reduce the internal stress. Indeed, the electrochemical properties have been improved when Si is under the form of clamped hollow structures, such as double-walled nanotubes and yolk-shell nanoparticles. Such a structure, with Si nanotubes coated with a SiO_x layer showed a remarkable capacity of 1000 mAh g^{-1} at rate 12C, with long cycling life (6000 cycles with 88% capacity retention) [30]. Such devices, however, are still too expensive to be commercialized. In this context, the size dependence of the Si-properties and the nature of the solid–electrolyte interface need to be studied and are identified as two areas where research is needed [29]. For this purpose, in-situ electron microscopy measurements are a very

useful tool, since they allow real-time observation of the charging/discharging behavior of individual particles. This strategy has already been used to investigate the effect of metallic coating on Si expansion [20], and the behavior of individual Si nanowire electrodes [31–34].

In the present work, we report both in-situ and ex-situ SEM experiments to observe the charging/discharging behavior of bigger particles to investigate the micro-structural evolution of nano Si particles during electrochemical cycling as a function of their size, completed by an analysis of SiO -based anode, aiming to determine the critical size above which cracking of bare particles cannot be avoided. We also investigate dynamically the micro-structural change of morphology of the whole Si and SiO electrodes to investigate the effect of the changes of the volumes of the particles at the level of the entire electrode (active material, binder, conductive carbon).

2. Experimental

2.1. Materials

Different sources of Si were selected to cover a broader range of particle sizes: nano-Si particles (average particle size ca. 100 nm); bigger SiO_x particles (2–8 μ). 0.8 cm \times 0.8 cm cells were assembled and prepared for SEM cross-section observation using a cryo-microtome. The electrodes were prepared by mixing Si and graphite (1:1 weight ratio) with the binder dissolved in *N*-methyl-2-pyrrolidinone (NMP) in the ratio 10%. The graphite (OMAC1S, 15- μ m average particle size) was obtained from Osaka Gas (Japan). The SiO_x powder is the same as that used in Ref. [35]. Since the changes in volume of the Si particles are large upon cycling, the electrochemical properties strongly depend on the binder [35]. The binder used in the Si experiments was algae, chosen because it has been recently proved to give much better electrochemical properties than the conventional poly (vinylidene fluoride) (PVDF) [36]. A small fraction of vapor-grown carbon fibers (2% VGCF from Showa-Denko (Japan)) was added to the electrode composition. These

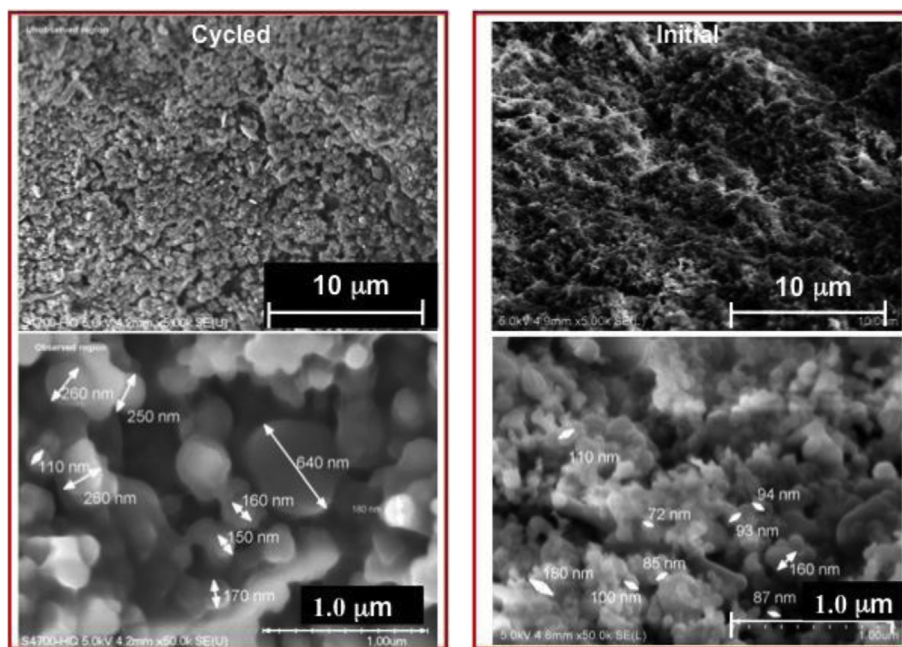


Fig. 1. Right side: Field emission gun (FEG-SEM) images of the Si anode before cycling at two different magnifications. The average size of the Si particles is 100 nm. Left side: same electrode after the two cycles shown in Fig. 2.

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