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In-situ X-ray tomographic study of the morphological changes of a Si/C paper anode for Li-ion batteries

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HIGHLIGHTS

- Morphological changes of a Si/C paper electrode are investigated by *in-situ* XRCT.
- The reductive electrolyte decomposition induces the formation of gas channels.
- The electrode cracking initiates during the 1st charge (delithiation).
- The cracks close during the subsequent discharge.
- The volume change of the electrode is larger and less reversible in its bottom part.

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ABSTRACT

The evolution of the three-dimensional (3D) morphology of a Si-based electrode upon cycling (1st discharge, 1st charge and 2nd discharge) is studied by *in-situ* synchrotron X-ray tomography. The Si-based electrode is constituted of silicon/carbon black/carboxymethylcellulose (Si/CB/CMC) embedded in a commercial carbon fiber paper, acting as a flexible 3D current collector. Its initial areal discharge capacity is 4.9 mAh cm^{-2}. A reconstructed volume of 293 × 293 × 137 μm^3 is analyzed with a resolution of ~0.3 μm. Three phases are identified: *(i)* the solid phase (C fibers + Si + CB + CMC), *(ii)* the electrolyte phase (pores filled with electrolyte) and *(iii)* the gas phase (electrolyte-free pores). Their respective volume fraction, size distribution and connectivity, and also the dimensional changes of the electrode along the three axes are quantified during cycling. At the beginning of the 1st discharge (lithiation), the formation of gas channels attributed to the reductive electrolyte decomposition is observed. During the 1st charge, large cracks are formed through the electrode, which reclose during the subsequent discharge. The electrode expansion/contraction due to the Si volume change is partially irreversible, occurs mainly in the transverse direction and is much larger in the bottom part of the electrode.

1. Introduction

One of the biggest technological challenges facing the human race is probably to secure its future access to carbon free energy. Renewable energy is part of the solution to secure this access provided that we improve our ability to store this energy. The Li-ion battery is one of the most efficient technologies for electric energy storage. However, the energy density needs to be enhanced, especially for transport applications, and for that purpose alternative electrode materials must be considered. In this context, silicon is a very promising anode material due to its high theoretical gravimetric capacity of 3579 mAh g^{-1} ($Li_{15}Si_4$) compared to the 372 mAh g^{-1} of graphite (LiC_6) [1,2]. However, it is very challenging to obtain stable Si-based anodes due to the large volume change of silicon during its lithium alloying (up to ~280% for $Li_{15}Si_4$) [1,3], which induces the disintegration (cracking, peeling-off) of the electrode, and leads to the instability of the solid electrolyte interphase (SEI). In the last years, different strategies have been evaluated to solve these issues, especially by using nanosized Si materials (nanoparticles, nanowires, nanocomposites, nanoporous structures, thin films …) [4–6], which are able to accommodate a

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large volume change without extensive cracking. The production of such materials at low cost and large scale as required for commercial implementation is however challenging. Moreover, their high surface area, which enhances SEI reactions and related irreversible Li consumption, and their low compactness resulting in low volumetric and areal electrode capacities are major drawbacks for their practical application.

We have recently shown that the cycle life and power performance of micrometric Si-based electrodes with large Si mass loadings (up to 10 mg cm^{-2}) can be greatly improved by using a copper foam (3D geometry) instead of conventional copper foil (2D geometry) as the current collector [7]. The small thickness of the composite Si coating on the Cu foam walls compared to that on a flat Cu substrate is assumed to favor a better preservation of the electronic wiring upon cycling. As a result, we have shown that an areal electrode capacity as high as 10 mAh cm^{-2} can be maintained for more than 400 cycles. However, our calculation based on a virtual stack consisting of a Si/Cu foam negative electrode and a $LiFePO_4$-based positive electrode indicates that thinner and lighter Cu foam (*e.g.* ≤125 μm thick rather than the 300 μm thick Cu foam that was used) is required to get a significant gain in gravimetric and volumetric energy densities compared to the traditional $LiFePO_4$/graphite cell. However, the production of thin (<300 μm) and highly porous (>80%) Cu foams is not an easy task.

In this context, the use of carbon fiber papers as 3D current collectors appears highly relevant since such materials are thinner and lighter than Cu foams in addition to being commercially available at low cost and large scale. For instance, these carbon papers have been commonly used for decades as gas diffusion layers for fuel cell applications. In the last years, various Si/3D carbon substrate architectures have been evaluated as anodes for Li-ion batteries but only a few studies have been published on Si materials supported on commercial carbon papers [8–10]. Moreover, the morphological evolution with cycling of such complex 3D microstructures has never been investigated in detail, which is essential for a better comprehension of their failure mechanisms and for optimizing their formulation and architecture.

In recent years, X-ray computed tomography (XRCT) has been used to characterize the porous microstructure of various Li-ion battery electrodes, including Si-based anodes [11–16]. However, these latter have been performed with a conventional electrode architecture (*i.e.* by casting the slurry on a 2D rigid current collector such as a steel or Cu rod) in contrast to the present study in which the slurry is embedded in a 3D and flexible C paper current collector. The XRCT technique permits 3D imaging of the analyzed electrodes with a quantification of key morphological parameters of the constitutive solid and pore phases (tortuosity, connectivity, volume fraction, size distribution …). Moreover, *in-situ* acquisition can be performed with an appropriate setup in order to assess the morphological evolution of the electrode upon cycling. In a conical beam configuration, the XRCT spatial resolution is determined by the X-ray spot size, which depends on the X-ray source and the source-sample working distance. Micrometric spatial resolution is usually obtained with a conventional laboratory X-ray source whereas tens of nm resolution can be reached with a synchrotron X-ray source. The main limitation of the XRCT technique is the difficulty to distinguish materials having low and/or similar X-ray attenuation coefficients. In that case, phase-contrast XRCT may be required [17].

In the present work, synchrotron XRCT analyses are performed to visualize and quantify the morphological changes occurring during the first lithiation/delithiation stage of a Si/C paper electrode. It is shown that major changes in the 3D structure of the Si/C paper electrode occur upon cycling due to the electrolyte decomposition, electrode volume expansion/contraction and electrode cracking.

2. Experimental

2.1. Materials

Ball-milled Si powder was used as active material. Si powder (99.999%, 20 mesh, Materion) was milled under argon atmosphere for 20 h using a SPEX 8000 mixer with a ball-to-powder mass ratio of 5:1. The as-milled Si powder consists of micrometric agglomerates (median size ~6 μm) made of sub-micrometric particles more or less welded together. More details on the characteristics of the as-milled Si powder are presented elsewhere [18]. During the slurry mixing for the electrode preparation (see below), the Si agglomerates are broken, resulting in a Si powder with a median diameter of ~0.2 μm [19]. Super P carbon black (CB) (particle size ~40 nm, Timcal) was used as the conductive additive. Carboxymethyl cellulose (CMC) (DS = 0.7, Mw = 90 000 g mol^{-1}, Sigma-Aldrich) was used as binder. Citric acid and KOH salts (Sigma-Aldrich) were used to prepare a pH3 buffer solution (0.17 M citric acid + 0.07 M KOH) as slurry medium. As previously shown, the pH3 buffering promotes covalent bonding between −OH groups present on the surface of the Si particles and −COOH groups of CMC, which improves the mechanical strength and cycling performance of the Si electrode prepared on a conventional copper foil [20,21]. AvCarb EP40 carbon paper (Fuel Cell Store) was used as 3D current collector. The EP40 carbon paper consists of non-woven carbon fibers bound by a binder filled with micrometric carbon particles (see Supplementary Fig. S1). Its mean thickness measured with a micrometer is 163 ± 2 μm and its areal weight is 3.37 ± 0.05 mg cm^{-2}. According to its characterization by standard laboratory XRCT, its mean porosity is ~82% with a median pore size of 36 μm and a median fiber diameter of 8 μm (see Supplementary Fig. S2).

2.2. Electrode preparation and cell assembly

A slurry was prepared by mixing 200 mg of 80 wt% Si, 8 wt% CMC and 12 wt% CB in a 0.5 ml pH3 buffer solution. Mixing was performed at 500 rpm for 1 h using a Fritsch Pulverisette 7 mixer with 3 silicon nitride balls (9.5 mm diameter). The Si composite electrode was obtained by successive soakings (typically 2–3 times) of the carbon paper (0.3 cm diam. disc) in the slurry. Slurry excess was removed from the carbon paper surface by using an absorbent paper. This was followed by a short drying period of ~2 min in air at each step of impregnation. Finally, the electrode was dried at room temperature for 12 h and then at 100 °C in vacuum for 2 h. Electrodes with a Si mass loading of 1.39 mg cm^{-2} were selected for the present study.

A two-electrode Swagelok® cell made of perfluoroalkoxy alkane (PFA) polymer was designed for *in-situ* XRCT experiments. A schematic representation of the cell is shown in Supplementary Fig. S3. The cell was assembled in an argon-filled glove box and included: *(i)* a Si/C paper (3 mm diameter disc) working electrode; *(ii)* a Whatman GF/D borosilicate glass-fiber separator soaked with 20 μl of LP30 electrolyte made of 1 M $LiPF_6$ in 1:1 ethylene carbonate/dimethyl carbonate (battery grade from BASF); *(iii)* a lithium foil (3 mm diameter, 1 mm thick) as counter and reference electrode. In order to ensure a better contact between the cell components, the cell was slightly compressed with a spring installed on the counter electrode side (load estimated at 6.2 N).

2.3. SEM characterization after ion polishing

Ion beam cross sectioning of the pristine Si/C paper electrode