Investigation of failure mechanisms in silicon based half cells during the first cycle by micro X-ray tomography and radiography

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HIGHLIGHTS

- Two prototypes of lithium ion batteries were manufactured for micro X-ray imaging.
- The first cycle of Si based half cells is investigated.
- Volume change of electrochemically active Si particles are shown in 3D and 2D.
- Electrochemical deactivation process is proved from the un-shifted X-ray attenuation.
- Some of Si particles never experience the battery level electrochemical de/lithiation.

ARTICLE INFO

ABSTRACT

Two proof-of-concept batteries were designed and prepared for X-ray microtomography and radiography characterizations to investigate the degradation mechanisms of silicon (Si) based half cells during the first cycle. It is highlighted here for the first time that, apart from the significant volume expansion-induced pulverization, the electrochemical "deactivation" mechanism contributes significantly to the capacity loss during the first charge process. In addition, the unexpected electrochemically inactive Si particles are also believed to substantially decrease the energy density due to the inefficient utilization of loaded active material. These unexpected findings, which cannot be deduced from macroscopic electrochemical characterizations, expand the inherent explanations for performance deterioration of Si-anode material based lithium ion batteries (LIBs) and emphasize the vital value of microscopic techniques in revealing the correlation between macroscopic electrode structure and the overall electrochemical performance.

1. Introduction

Following their commercial introduction in the early 1990s, lithium ion batteries (LIBs) have penetrated ubiquitously into the market for energy storage systems, e.g. laptops and mobile phones [1,2]. More recently, advanced LIBs with a larger specific energy, higher power density and longer cycle life have been considered for powering clean electric vehicles (EVs) and plug-in hybrid vehicles (PHVs), as well as for the storage and distribution of energy from sustainable sources, such as solar and wind energy [3–6]. The key

to fabricate such next-generation LIB is to exploit high-performance electrode materials. From the material's point of view, silicon (Si) is a promising candidate for the anode of LIBs because it possesses the highest theoretical capacity of 3579 mAh/g when lithiated to $Li_{21}Si_5$, that is about 10 times larger than the currently commercialized carbonaceous anode, which features 372 mAh/g for LiC_6 [7–9]. This promising potential of the high specific capacity has spurred considerable investigations of Si thin films [10], carbon mixed [11,12] and metal coated [13] Si composites, along with various Si nanostructures, such as nanoparticles [14], nanowires [15], nanospheres [16] and nanotubes [17] that could serve as building blocks for high-performance anodes. Despite these extensive efforts, Si-based anode LIBs still inevitably suffer from substantial capacity decay during lithium insertion and

extraction and thus they are now below the requirements for practical applications.

To shed light on the underlying degradation mechanisms, a range of investigation techniques such as scanning electron microscopy (SEM) [18], transmission electron microscopy (TEM) [19], X-ray diffraction (XRD) [20], nuclear magnetic resonance (NMR) [21] and Raman spectroscopy [22] have been adopted. As a result, our knowledge of the intrinsic behavior of Si upon lithium insertion and extraction has been significantly enhanced [23] and various possible explanations for the performance deterioration have been proposed. For instance, it has been discovered that, apart from the loss of the lithium inventory and electrolyte/binder decomposition [24], the preferential volume expansion along Si [110] directions is as large as ~300% during lithium insertion and this extraordinary volume change has been proposed as the primary factor contributing to the fatal capacity decay [25]. Nevertheless, prior analytical tools are inherently limited. For example, most of the measurements abovementioned explore the degradation mechanisms on the atomic or single nanoparticle level, overlooking the interplays amongst a multitude of particles and the interactions between the active material and the conductive/binder agent. What is more, a particular battery design, such as open structure and specialized electrolyte that does not adequately simulate the real battery operating conditions is widely employed. On the other hand, most conventional tools only specialize in revealing the structural and compositional information without imaging capability, lacking effective spatially resolved information about the degradation mechanisms. In parallel, some investigations are carried out *ex situ*, i.e. post-mortem, as opposed to *in situ* characterizations of dynamic processes. Considering that a realistic composite electrode includes an assembly of ensembles of active particles, an organic polymeric binder and a conducting agent, the ability to probe the dynamic deterioration mechanisms on a multi-particle electrode level is of technological and practical importance. Therefore, it is crucial and emergent that fundamental research techniques are highly needed to further promote the exploration of electrode degradation.

Recently, X-ray imaging based on either laboratory X-ray or synchrotron X-ray sources has rapidly evolved into a powerful characterization tool in materials science [26–42]. Specifically, X-ray imaging has enabled researchers to obtain unprecedented insights into LIBs non-destructively on a length scale ranging from particles to entire electrodes and has contributed markedly to our understanding [29–33]. The pioneering research of employing synchrotron X-ray tomography by Ebner et al. features a direct observation and quantification of electrochemical and mechanical degradation in a SnO anode [34]. Meanwhile, Gonzalez et al. have visualized the expansion of large Si particles during the first lithiation step in three-dimensions (3D) by means of tomography based on a laboratory X-ray source [35].

Herein, by employing both laboratory X-ray tomography and radiography, we re-inspect the underlying mechanism of performance degradation of Si based half cells from the perspective of entire electrodes, which implies spanning the length scales from individual active particles to the macroscopic electrode ensemble. On the one hand, X-ray microtomography grants us the ability to track the structural evolution induced by volume changes in three dimensions. On the other hand, *in operando* micro X-ray radiography enables us to directly observe the changes of the active particles and an entire electrode during lithium insertion and extraction. By the combinatorial X-ray tomography and radiography, for the first time we highlight that, apart from the huge volume expansion/contraction of Si particles during cycles, the striking inhomogeneous lithiation/delithiation mechanism amongst ensemble active particles observed in an electrode, which cannot be easily detected in conventional electrochemical

measurements and, the unprecedented electrochemical "deactivation" of original electrochemical active particles are another two key factors contributing to the substantial performance degradation. This study expands the inherent explanations for performance deterioration of Si-anode material based LIBs, and the new sights would open new design principles and opportunities for high-capacity electrode materials for next-generation energy storage systems.

2. Experimental section

2.1. Materials

Silicon was received from Elkem AS, Norway. Polyvinylidene difluoride (PVDF) binder, carbon black, Celgard separator, CR2032 coin cells and lithium were purchased from MTI Cor. USA. *N*-methyl pyrrolidone solvent (NMP) and 1 M $LiPF_6$ in a volume-ratio (1:1) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) were purchased from Sigma Aldrich. Titanium foil is from ANKURO Int. GmbH, Germany. The housing of proof-of-concept beamline battery is made of polyamide-imide (Torlon), from McMaster-Carr company.

2.2. Characterization

Scanning electron microscopy (SEM) image were taken using a Zeiss ultraplus microscope. The electrochemical characterizations were conducted by using an Ivium CompactStat station, Iviumtechnology.

2.3. Battery preparation

The composite electrode is made of slurries with weight ratios of Si:carbon black:binder of 75:15:10 in NMP. For the tomo-cell, the slurry was first sandwiched between two glasses and put into an oven at 60 °C to dry and form a block, which was then cut into small pieces with a razor blade and put directly onto the top of the screws. The resultant Si composite electrode was a small piece of 1.7 × 1.7 × 0.2 mm (length × width × height). Before the Si composite was assembled into the tomo-cell, it was weighed by a digital balance and the amount of Si particles was determined from the origin mass ration. The Si composite electrode mass in the tomo-cell was around 0.9 mg. For the radio-cell, the slurry was casted onto the 5 μm thick titanium (Ti) foil. The area of the slurry was around 4 × 3 mm (length × width). To remove the NMP, the casted Ti foil was also dried in an oven at 60 °C. Before and after the casting process, Ti foil was weighted to determine the weight of the electrode materials. The Si composite in the radio-cell was around 1 mg. These two proof-of-concept batteries were assembled in an argon filled glovebox with humidity and oxygen levels below 0.1 ppm. During battery assembly, these two cells were only hand-assembled without exerting extra pressures. For the tomo-cell, metallic lithium (2.5 mm diameter, 1 mm thick) was placed on top of the other screw, and served as a counter and reference electrode. For the radio-cell, a lollipop shape copper foil without inner region (out diameter is 10 mm and inner diameter is 6 mm) was used as a current collector and the Ti foil was placed on top of it. Metallic lithium (6 mm diameter, 1 mm thick) was used as the opposite electrode. A polymer separator was placed between the lithium electrode and the Si electrode in both cells. After filling these two cells with sufficient electrolyte, they were sealed off and then taken out of the glovebox. For a further comparison of the electrochemical activity of Si composite electrode in the two proof-of-concept cells, commercial CR2032 coin-cell with the same Si electrode was assembled and tested.