Journal of Power Sources 342 (2017) 904–912

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Microstructural degradation of silicon electrodes during lithiation observed via *operando* X-ray tomographic imaging

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HIGHLIGHTS

- Si particle evolution in early stage of lithiation was captured using X-ray CT.
- Fracturing of Si particles during incremental lithiation was visualised.
- Lithiation-induced micro-cracks propagate within particles leading to fracturing.
- Si particle lithiation as a function of distance from current collector was studied.

ARTICLE INFO

Article history:
Received 21 September 2016
Received in revised form
2 December 2016
Accepted 19 December 2016
Available online 10 January 2017

Keywords:
X-ray CT
Silicon electrode
Lithiation
Particle fracturing
Degradation

ABSTRACT

Due to their high theoretical capacity compared to that of state-of-the-art graphite-based electrodes, silicon electrodes have gained much research focus for use in the development of next generation lithium-ion batteries. However, a major drawback of silicon as an electrode material is that it suffers from particle fracturing due to huge volume expansion during electrochemical cycling, thus limiting commercialization of such electrodes. Understanding the role of material microstructure in electrode degradation will be instrumental in the design of stable silicon electrodes. Here, we demonstrate the application of synchrotron-based X-ray tomographic microscopy to capture and track microstructural evolution, phase transformation and fracturing within a silicon-based electrode during electrochemical lithiation.

1. Introduction

Lithium-ion batteries are ubiquitous as power sources in portable electronic devices due to their high energy density and long cycle life, and are now being extended to applications such as electric vehicles and grid energy storage [1,2]. To meet such demanding electronic applications, the development of high-performance lithium-ion batteries is crucial and significant research effort has been devoted to achieve this. Carbonaceous materials such as graphite are commonly used as negative electrodes in traditional lithium-ion batteries; these materials have high Coulombic efficiencies (>90%) but are limited by their rather low specific capacities (372 $mAhg^{-1}$). Materials that form alloys with lithium (e.g. Sn, Sb, Si, and Ge) [3] are being considered as replacements for graphite due to their much higher theoretical specific capacities.

Amongst alloy-type electrode materials, silicon (Si) is a particularly promising candidate studied because its reaction with lithium occurs at low discharge potentials (<0.5 V vs. Li/Li^+) [4], and it possesses a large theoretical specific capacity (ca. 4200 $mAhg^{-1}$, [5]). However, a major challenge of the application of silicon in rechargeable lithium batteries is the huge volume expansion of silicon (up to 300% [6]) upon lithiation, leading to material

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http://dx.doi.org/10.1016/j.jpowsour.2016.12.070

fracturing and pulverization, which results in loss of electrical contact and rapid capacity fading within the battery.

Numerous strategies have been proposed to mitigate these failure mechanisms in Si electrodes; for example: nanostructured Si materials, such as nanowires [7–10] and carbon-coated nanocomposites [11–14]; conductive and self-healing polymer binders [15,16]; modified cycling protocols [6]. Although nano-sized Si materials have been shown to mitigate the severe fracturing associated with lithiation-induced volume expansion, their high production cost, poor first- and later-cycle Coulombic efficiency, and significant solid electrolyte interphase (SEI) formation still remain major drawbacks to their use in commercial battery applications. Therefore, the use of low cost, more readily available Si microparticles (SiMPs) as electrode materials appears promising. However, a clear understanding of the degradation and failure of SiMPs during battery operation is crucial.

Visualization of morphological changes that occur in Si, as well as other alloying-type electrode materials, during electrochemical cycling have previously been carried out *in situ* using two-dimensional (2D) imaging techniques; for example, using *in situ* transmission electron microscopy [17–20], and *in situ* atomic force microscopy [21–23]. However, recent advances in tomography techniques have provided unprecedented insight into the microstructural evolution in Li-ion battery electrode materials in three-

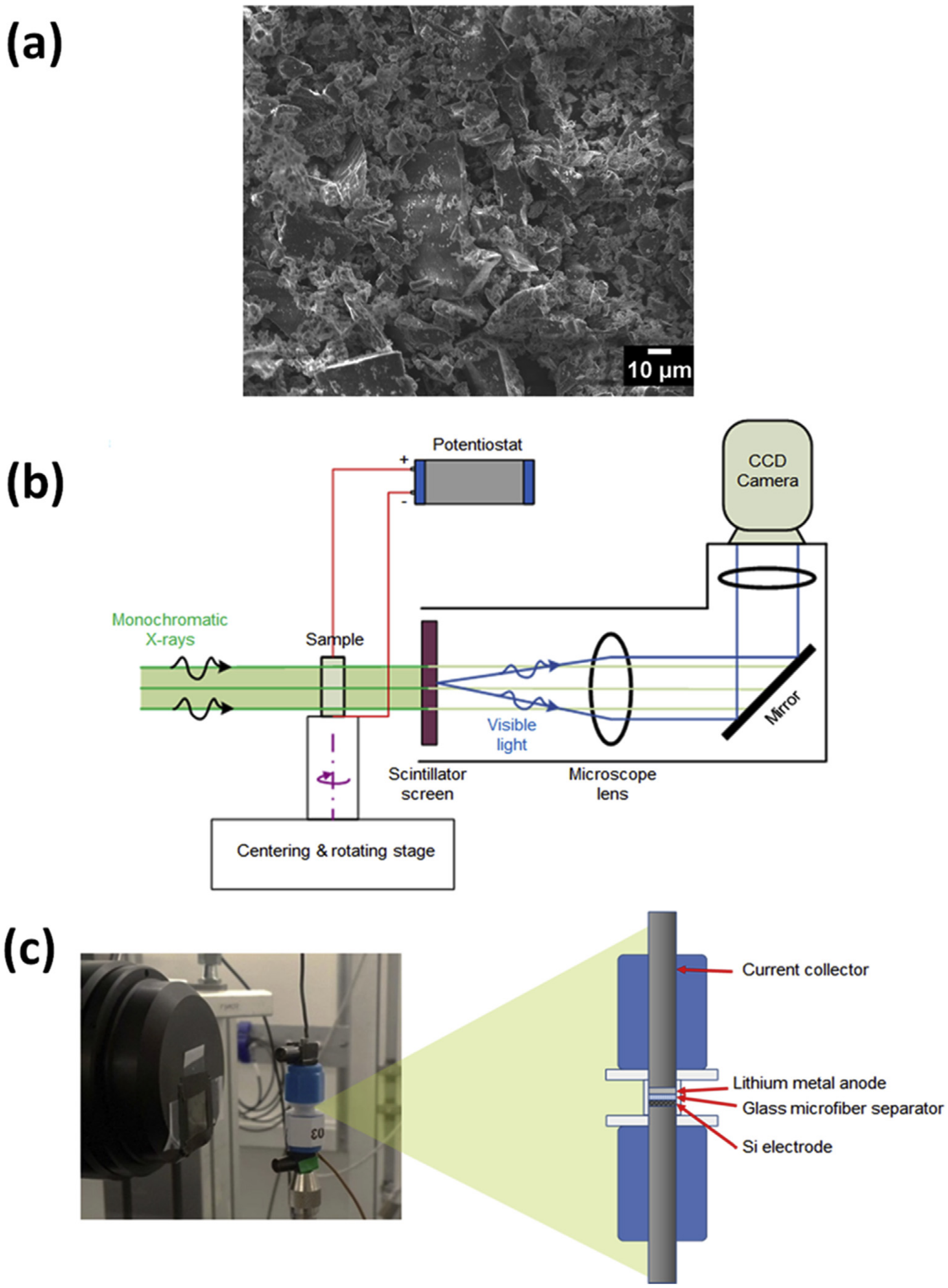

Fig. 1. (a) Scanning electron micrograph of the micron-sized Si particles. (b) Schematic illustration of the experimental setup at the TOMCAT beamline. (c) Assembled battery cell made from PFA Swagelok tube fitting and designed to enable operando X-ray CT.