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Investigation of cycling-induced microstructural degradation in silicon-based electrodes in lithium-ion batteries using X-ray nanotomography

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ABSTRACT

The microstructural degradation of a composite silicon electrode at different stages in its cycle life was investigated in 3D using X-ray nano-computed tomography. A reconstructed volume of 36 μm × 27 μm × 26 μm from the composite electrode was imaged in its pristine state and after 1, 10 and 100 cycles. Particle fracturing and phase transformation was observed within the electrode with increased cycling. In addition, a distinct, lower X-ray attenuating phase was clearly resolved, which can be associated with surface film formation resulting from electrolyte breakdown and with silicon particle phase transformation. Changes in quantified microstructural properties such as phase volume fraction and particle specific surface area were tracked. Electrode performance loss is associated with loss of active silicon. These imaging results further highlight the capability of high resolution X-ray tomography to investigate the role of electrode microstructure in battery degradation and failure.

1. Introduction

The increasing demand for more energy-dense lithium-ion batteries (LIBs), particularly in large scale applications such as grid-scale energy storage and electric vehicles, has led to the exploration of the use of alternative electrode materials. With a theoretical specific capacity ten times higher than that of conventional graphite electrodes – 3579 mAh/g –, silicon (Si) is a promising electrode material [1]. However, silicon suffers rapid capacity fade and short cycle life mainly as a result of the significant volume changes (up to 280% [1]) that it experiences upon lithiation, causing cracking and pulverisation within the electrode, which leads to loss of electrical contacts [2,3].

In an attempt to improve the performance and lifetime of silicon electrodes, significant research effort has been devoted towards the use of nanostructured silicon materials [4–8]. However, issues such as significant solid electrolyte interphase (SEI) formation, as well as the difficulty and high cost of manufacturing scale-up prevent their application in commercial lithium ion batteries [8,9]. These drawbacks show micron-sized silicon particles to still be a favourable option as electrode materials, since they are low-cost, commercially available and can be used to create electrodes with higher volumetric energy density compared with nano-sized silicon-alloy particles.

To overcome this challenge of designing a commercially-viable silicon electrode, an improved understanding of the influence of silicon microstructure on battery performance is required. X-ray computed tomography (CT) is a powerful, non-invasive diagnostic tool that has been used to elucidate the three-dimensional microstructure of a wide variety of materials, including lithium-ion battery electrodes [10–15], and the rapid proliferation of X-ray imaging techniques over the past decade has enabled characterisation of material microstructures with unprecedented resolution at multiple length and time scales using both laboratory and synchrotron sources [16–20].

Recently, X-ray CT has been used to study the lithiation-induced evolution of Si electrodes, and has enabled investigation of electrode delamination [21], bulk electrode volume expansion and phase changes [22,23], and particle cracking and pulverisation [24–27]. However, these 3D X-ray imaging studies on silicon electrodes were performed at the early stages of electrode cycle life (first half cycle or first full cycle), with spatial resolutions down to

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ca. 2 μm being achieved [23,27]. Recent advances in laboratory X-ray tomography have enabled even higher spatial resolutions to be achieved, down to 50 nm [17]. Here for the first time, we study the 3D morphological transformation of a Si electrode over several charge-discharge cycles using high resolution laboratory X-ray nano-CT at a spatial resolution of 150 nm.

2. Experimental

2.1. Electrode preparation and cell fabrication

Powdered Si (Elkem Silgrain e-Si, d_{50} 3.1 μm, 99.7% purity) was used as active material. Carbon black (Alfa Aesar, Acetylene Black, purity, 99.9+ %) and graphite (TIMREX SF56, purity 99.93%) were used as conductive agents and a sodium salt of polyacrylic acid (Na-PAA) as binder. The binder was prepared by dissolving PAA in de-ionised water and then partially neutralizing the solution with sodium carbonate; details of the binder preparation can be found in [28].

The powdered Si, carbon additives and the partially neutralized Na-PAA solution (in a percentage weight ratio of 70:16:14, respectively) were mixed with de-ionised water, and stirred using a high shear mixer (Primix Homodisper Model 2.5) for 30 mins. Electrode laminates were then created by casting the resulting electrode slurry onto 10 μm thick Cu foil (Oak Mitsui, electro-deposited) using a film applicator (RK PrintCoat Instruments, UK), with partial vacuum applied to the Cu foil and a doctor blade gap set to 100 μm. Slurry-coated Cu foils were dried on a hot plate at 80 °C for 2 mins followed by vacuum drying (7 mbar) at 70 °C for 12 h. The dried electrode laminates were cut into 10 mm diameter discs, each of which was weighed in order to obtain the mass loading of Si.

Half-cells were fabricated using PFA-type Swagelok hardware (PFA-820-6, 0.5 inch diameter, Swagelok, USA) in an argon-filled glove-box (oxygen and moisture levels in the glove-box were both maintained at <0.5 ppm) with a metallic lithium foil counter electrode (Pi-KEM Ltd, cut to 11 mm diameter), a borosilicate glass fibre separator (Whatmann GF-D grade, GE, cut to 12 mm diameter), and electrolyte containing 1 M $LiPF_6$ in mixture of ethylene carbonate (EC): ethyl methyl carbonate (EMC) in the ratio 3:7 by volume.

2.2. Electrochemical characterisation

Electrochemical cycling of assembled Swagelok cells was performed between 1–0.005 V (vs. Li/Li^+) at room temperature using a Maccor 4300 series battery cycler. Cells were selected to be cycled for 1, 10 and 100 cycles. A C/5 rate was used for Si electrodes cycled for 1 and 10 cycles. For electrodes cycled for 100 cycles, the first cycle was performed at a C/5 rate to promote SEI formation, and subsequent cycles were performed at a C/2 rate. The C-rates were calculated based on the theoretical capacity of Si at room temperature ($Q = 3579\ mAhg^{-1}$).

After charge cycling, electrochemical impedance spectroscopy (EIS) measurements were performed on each cell using an Ivium CompactStat.e electrochemical workstation (Ivium Technologies, Netherlands). Impedance spectra were acquired with the Si electrodes in the de-lithiated state after 1, 10 and 100 cycles over a frequency range of 100 kHz to 1 mHz, with an AC signal amplitude of 5 mV.

2.3. Scanning electron microscopy (SEM) and X-ray nanotomography

After electrochemical testing, the cycled cells were then carefully disassembled in an argon-filled glove box. The Si electrodes (in de-lithiated state) were carefully extracted from the disassembled cells and then thoroughly rinsed in pure diethyl carbonate (DEC) solution for 6 h to remove traces of electrolyte. The washed electrode was dried by storing it in the evacuated antechamber of the glove box at room temperature to remove any DEC present.

Both the pristine (uncycled) and the washed, cycled versions of the Si electrode sample were then dissected under a visible light microscope (into smaller sample sizes suitable for nanoscale X-ray CT imaging (<500 μm length) and mounted onto the tip of stainless steel needles using epoxy resin. Remaining portions of the pristine and cycled electrodes were reserved for SEM characterisation. Scanning electron micrographs of electrode sample in its pristine and cycled states were captured with the aid of a ZEISS EVO MA 10 microscope.

The electrode samples were then imaged in a laboratory-based nano-scale X-ray microscope (ZEISS Xradia 810 Ultra, Carl Zeiss Microscopy, Pleasanton, CA) using an absorption contrast tomography setting [29]. For each investigated sample, X-ray radiographs were acquired over a 180° sample rotation; details of the tomographic imaging parameters for each sample are presented in Table 1. The acquired radiograph images were then reconstructed into a 3D volume using ZEISS XMReconstructor software (Carl Zeiss X-ray Microscopy Inc., Pleasanton) which employs a filtered-back projection algorithm [30].

2.4. 3D image analysis and quantification

Image processing and volume rendering of each of the reconstructed electrode datasets was carried out using the Avizo software package (v9.1, FEI VSG, France). From within each 3D electrode dataset, a volume of interest (36 μm × 27 μm × 26 μm) was extracted for further analysis. An anisotropic diffusion filter [31] was applied to the cropped 3D greyscale image datasets to minimize random image noise while preserving significant image features, after which a segmentation procedure combining thresholding and 3D region growing was implemented to distinguish between the solid and pore phases based on their greyscale intensity values.

3D quantification of the segmented datasets was also performed in Avizo software; phase volume fraction and volume-specific surface area values, which are important morphological parameters that determine electrode performance, were calculated. Phase volume fraction was calculated using a voxel counting approach as the ratio of the total number of voxels in a particular phase to the total number of voxels in the analysed volume. For surface area calculations, triangulated surface meshes were generated from the segmented image datasets using a marching cubes algorithm [32], and then subsequently smoothed using sub-voxel weights.

3. Results and Discussion

The discharge capacity and Coulombic efficiency profiles of the Si electrode over a 100 cycle period are shown in Fig. 1. At a C/5 rate, a discharge capacity of *ca.* $2700\ mAhg^{-1}$ was obtained in the first

Table 1
X-ray CT image acquisition parameters.

	Pristine	1st cycle	10th cycle	100th cycle
No. of radiographs recorded	1601	2001	2001	2001
Radiograph exposure time (s)	23	15	20	14
Effective voxel size (nm)	63.1			
Photon energy (keV)	5.4			
Field of view dimensions	65 μm × 65 μm			
Detector binning	1			