IN SITU STRAIN MEASUREMENT IN ANODES FOR LITHIUM-ION BATTERIES

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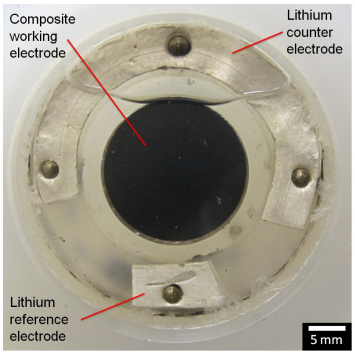
Summary Silicon has garnered much attention as a possible high energy-density anode material for lithium-ion batteries, but poor capacity retention has prevented its use in practical electrodes. In this work, digital image correlation is developed to study the fracture properties of silicon anodes *in situ* during battery charge and discharge cycling with the goal of designing silicon electrodes that have a long lifespan.

BACKGROUND

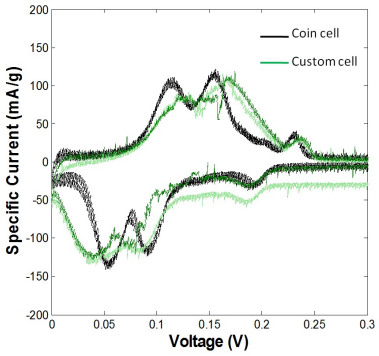
Traditional lithium-ion batteries that employ graphite-based anodes are useful in small, portable electronics, but have a limited charge capacity. Silicon is a promising new anode material for batteries in electric vehicles and for storing renewable energy. It has a theoretical charge capacity (4200 mAh/g [3]) that is more than ten times that of graphite (372 mAh/g [9]). However, upon lithiation, silicon experiences a volume expansion of > 300% [1] and subsequent significant morphological changes that lead to poor capacity retention. The development of new silicon anodes with optimal micro- or nanostructure for improved performance relies on accurate characterization of the anode fracture properties. There are several techniques found in the literature to characterize the degradation of battery anodes, including atomic force microscopy and optical microscopy [1], Raman spectroscopy [6], substrate curvature with the Stoney equation [8], transmission electron microscopy [5] and digital image correlation [7]. Digital image correlation (DIC) has the advantage of being a non-invasive, quantitative, full-field technique that can be used to measure in-plane surface displacements and calculate strains at many different length scales.

EXPERIMENTAL METHOD

A custom cell featuring a working electrode (graphite or silicon composite electrode), lithium metal counter electrode, and lithium reference electrode (Fig. 1(a)) allows optical access to the electrodes during cycling. The cell was assembled and sealed in an argon atmosphere maintaining oxygen and water levels < 2 ppm and brought into normal atmosphere for testing. Composite electrode sheets were fabricated by making a slurry of particulate active material (graphite or silicon), carbon black, and polymer binder (8:1:1 wt. ratio) suspended in water, casting the slurry onto copper foil using a doctor blade, and allowing it to air dry. Electrodes punched from the sheet were 20 mm in diameter and 18 μm thick (excluding the copper foil). The electrolyte consisted of 1M $LiClO_4$ in ethylene carbonate and dimethyl carbonate (1:3 vol. ratio). The cell was cycled using an Arbin cycler, and the electrode was imaged using a Navitar zoom lens and either a Retiga (black and white) or a Basler (color) CCD camera.



(a) Custom cell



(b) Cyclic voltammetry data

Figure 1. (a) Custom battery cell allowing optical access to a composite working electrode, lithium counter electrode, and lithium reference electrode. (b) Slow scan cyclic voltammogram (10 μV/s) of graphite composite electrode and lithium counter electrode in custom cell (green) and coin cell (black). Lighter color indicates the first cycle, while darker color indicates subsequent cycles.

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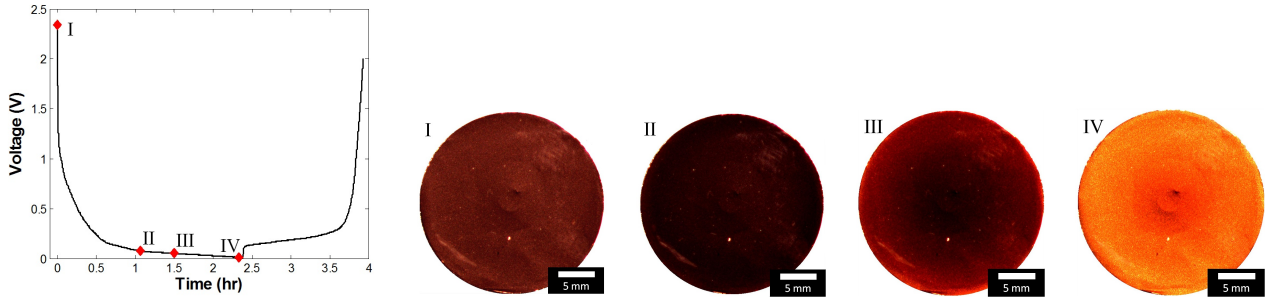
RESULTS AND DISCUSSION

Composite electrodes have a natural speckle pattern at increased magnification. By imaging the electrode in the custom cell before and after applying a known rigid translation to the cell, the resolution of the natural speckle pattern was determined to be +/- 1 μm for three different magnifications (fields of view ranging from 3.4 x 2.7 mm to 500 x 400 μm). However, due to the color change in graphite and the large morphological changes in silicon that occur during cycling, it was found that the speckles appear, disappear, and change size and shape during cycling, leading to an inconsistent and poorly-correlated speckle pattern. Berfield *et. al.* utilized a novel speckle pattern for DIC, generated by fluorescent silica nanoparticles, and showed that it has a resolution of +/- 20 nm [2]. Therefore, fluorescent particles were spincoated on the composite electrode, excited with a 75 mW, 532 nm laser, and imaged through a 620 nm filter, generating a consistent speckle pattern during cycling that is expected to have a similar resolution as in [2].

In order to confirm that the custom cell was operating properly, we carried out slow scan cyclic voltammetry (10 μV/s sweep rate) of a graphite composite electrode in both the custom cell and a standard coin cell (Fig. 1(b)). There is a larger hysteresis between the charge and discharge current peaks in the custom cell compared to the coin cell, which is expected from the different electrode geometry. Otherwise, the data from the two different cells agrees qualitatively. Additionally, galvanostatic cycling of a graphite composite electrode was performed in the custom cell (Fig. 2). The color change of graphite as a function of its lithium content has been documented in the literature [4], and was observed in the custom cell (Figs. 2(b) - 2(e)), further confirming that the working electrode can be lithiated and delithiated in the custom cell.



(a) Galvanostatic cycling data

(b) Fully delithiated (black) stage, C

(c) Blue stage, LiC_{18}

(d) Red stage, LiC_{12}

(e) Fully lithiated (gold) stage, LiC_6

Figure 2. Galvanostatic cycling (C/2 rate, 1st cycle) of a graphite composite electrode and lithium counter electrode. As the voltage decreases, lithium is being inserted into the electrode, with each stage of lithiation distinguished by a distinct color.

CONCLUSIONS

The use of silicon as an anode material in high-capacity lithium-ion batteries for use in electric vehicles and for storing renewable energy is currently limited by silicon's huge volume expansion upon lithiation and its consequent fracture. The application of digital image correlation is being developed in this work to characterize the fracture properties of silicon during lithiation and delithiation, with the goal of developing new micro- and nanostructures that can accommodate the expansion without fracturing. Towards this goal, a custom cell has been designed and fabricated that allows optical access to the electrodes, and a consistent, well-correlated speckle pattern has been generated using fluorescent silica nanoparticles spincoated on the electrode. Additionally, it has been shown that working electrodes can be lithiated and delithiated in the custom cell through both cyclic voltammetry and galvanostatic cycling.

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