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# Self-healing of cracks formed in Silicon-Aluminum anodes electrochemically cycled at high lithiation rates



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## HIGHLIGHTS

- Healing of cracks in Si particles of composite Si-Al anode at high lithiation rate.
- Crevices formed in Si acted as stress concentrators that aided crack initiation.
- Ductile Al matrix with higher fracture toughness stopped crack propagation in Si.
- Step 1 of self-healing: Arrest of lithiation-induced cracks at the Si/Al interface.
- Step 2: Crack-closure by compressive stresses applied by localized amorphous zones.

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## ABSTRACT

Lithiation-induced volume changes in Si result in fracture and fragmentation of Si anodes in Li-ion batteries. This paper reports the self-healing behaviour of cracks observed in micron-sized Si particles dispersed in a ductile Al matrix of a Si-Al electrode electrochemically cycled vs. Li/Li<sup>+</sup> using a high lithiation rate of 15.6 C. Cross-sectional high-resolution transmission electron microscopy and Raman spectroscopy revealed that an amorphous layer with a depth up to ~100 nm was formed at the surface of Si particles. In-situ optical microscopy performed during electrochemical experiments revealed development of cracks in Si particles as the voltage decreased to 0.02 V during lithiation. Self-healing of cracks in Si particles occurred in two steps: i) arresting of the crack growth at the Si/Al interface as the surrounding Al matrix had a higher fracture toughness and thus acted as a barrier to crack propagation, and ii) closure of cracks due to compressive stresses applied to the crack faces by the amorphous zones formed on each side of the crack paths.

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## 1. Introduction

Lithium-ion battery technology is geared towards meeting the ever-increasing power requirements for large-scale applications, including pure and hybrid electric vehicles. This demand has spurred intense interest for developing high gravimetric and volumetric capacity battery electrodes capable of sustaining high power rates [1–6]. In search of high capacity anodes, Si has attracted attention as it has the highest known theoretical specific charge capacity (4200 mAhg<sup>-1</sup> for Li<sub>4.2</sub>Si). Although the theoretical specific capacity of Si is about four times higher than Sn (991 mAhg<sup>-1</sup> for Li<sub>4.4</sub>Sn) and ten times higher than graphite

(372 mAhg<sup>-1</sup> for LiC<sub>6</sub>), the use of Si electrodes presents a significant challenge as volume expansion induced fracture of Si during charge/discharge cycles lead into capacity loss [7]. Electrochemical tests have revealed that the battery's capacity decreases abruptly and irreversibly during the initial few cycles [8], with the first cycle being the most detrimental, because of rapid surface damage and sometimes fragmentation of electrodes [9–11]; a phenomenon referred to as electrochemical shock [12]. Once a stable solid electrolyte interphase (SEI) layer is established and covers the anode surface, the rate of electro-mechanical damage starts to decrease but the capacity still continues to decline albeit much gradually [2,11]. Using x-ray diffraction (XRD) [13] and in-situ transmission electron microscopy (TEM) [14] studies, it was observed that the first lithiation step could cause transformation of crystalline Si to an amorphous structure. In-situ TEM studies provided evidence for lithiation-induced amorphization in Si and orientation-dependent

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displacement of the interface between crystalline and amorphous phases [15]. Stress measurements performed in a 250 nm thick amorphous Si film electrode suggested that the thin Si films would yield and show plastic deformation at a stress above 1 GPa [16,17]. Micro-crack formation in Si single crystal has been studied by applying current densities in the range of 100–500  $\mu\text{Acm}^{-2}$  [18,19] and formation of an amorphous Si layer on the top of the Si was observed. It was stated that compressive stresses would develop in the amorphous layer formed at the surface due to Li insertion and would cause outward expansion of the layer, while the unlithiated Si in the interior would constrain the amorphous layer preventing it from free expansion [18]. This mismatch could create stresses that would lead to crack formations. Crack growth was explained using a fracture mechanics criterion i.e., cracks were formed when the strain energy release rate,  $G$ , reached a critical value,  $G_c$  [18]. It was also suggested that once the cracks were formed in the Si wafers, they would create preferential diffusion paths for lithium-ions [19].

Some researchers have proposed practical ways to alleviate detrimental effects of fracture, and pulverization events observed in Si anodes by designing Si/C composite electrodes [20–23]. Electrode configurations that used three-dimensional architectures involving thin films and nano-crystalline coatings [24–27], nano-wires and nanotubes [2,3,28–31], and nanoparticles [4,32,33] have been also explored. In all these efforts, the common goal has been to reduce the Si electrode fragmentation and hence the prevent the capacity loss. Si electrodes with nano-scale morphologies would have high surface area-to-volume ratios. This kind of electrode design was found beneficial in volumetric expansion during lithiation. Pores or voids were also deliberately incorporated to accommodate the large internal lithiation-induced stresses [34].

Another approach that can be made in order to alleviate capacity loss in Si anodes would consist of using Si in the form of small particles dispersed in a ductile and inert phase, having higher fracture toughness, which would arrest the growth of lithiation-induced cracks in Si and thus reduce the propensity for electrode fragmentation. In this work, Si-Al alloy anodes consisting of micron-sized Si particles dispersed in a ductile Al matrix were used to test this hypothesis. By electrochemically cycling these electrodes vs. Li/Li<sup>+</sup>, crack formation and growth in Si particles during the lithiation/de-lithiation cycles were monitored using analytical microscopy and surface characterization techniques. An interesting self-healing process occurred and consisted of arresting of cracks formed in Si particles by the Al matrix, and closure of cracks during de-lithiation. The paper describes the experiments conducted to understand the microstructural and morphological changes in Si leading to the observed self-healing phenomenon in the Si particles of Si-Al anodes. Using in-situ optical microscopy and micro-Raman spectroscopy, it was revealed that self-healing of cracks in Si-Al electrodes occurred in two steps; by arresting of micro-cracks at the Si/Al interfaces and closure of the cracks at the end of the electrochemical cycle. The results are significant for the Li-ion battery technology as “composite electrodes” consisting of high capacity Si particles and a ductile phase around them could, provide extended durability and enhance the capacity retention capability.

## 2. Experimental

### 2.1. Si-Al anodes and electrochemical experiments

Cylindrical electrodes of 5 mm diameter machined from a cast Al-Si alloy, consisting of Si particles, with an average length of  $68 \pm 32 \mu\text{m}$  and width of  $36 \pm 16 \mu\text{m}$ , solidified from an Al-Si alloy melt were used. The volume percent of Si in the electrode was 18.5% [35]. Si particles had a polygonal-shaped morphology with an aspect ratio of  $1.9 \pm 0.4$  and were uniformly dispersed in a ductile Al

matrix. Electrode surfaces were polished using metallographic techniques to a final polish by means of 0.1  $\mu\text{m}$  diamond suspension. The electrodes were etched in a solution of 10% NaOH and cleaned ultrasonically using ethanol in order to ensure proper cleaning of the Si surfaces to be exposed to electrolytes.

The electrodes were then mounted in an electrochemical cell in an Ar-filled (MBraun LABstar) glovebox where H<sub>2</sub>O and O<sub>2</sub> levels were maintained below 1 ppm. A 99.99% pure Li wire with a resistivity of 9.446  $\mu\Omega\text{-cm}$  (at 20 °C) was used as both the counter electrode and the reference electrode. The electrochemical cell is described in Ref. [36]. The electrolyte solution was prepared using 1 M LiClO<sub>4</sub> (99%) in a 1:1 (by vol.) mixture of ethylene carbonate (EC, 99%) and 1,2-dimethoxy ethane (DME, 99%).

Galvanostatic experiments were conducted by initially applying a voltage of 4.00 V and reducing it to 0.02 V (vs. Li/Li<sup>+</sup>) at a constant current density of 5.0  $\text{mAcm}^{-2}$  using a Potentiostat/Galvanostat system (Solartron Modulab System with a data acquisition rate of up to 1.0  $\text{MSs}^{-1}$ ). In the first step, a negative current density ( $-5.0 \text{mAcm}^{-2}$ ) was applied that reduced the potential of the Li-ion cell to 0.02 V. Once the voltage reached 0.02 V, a positive constant current density ( $+5.0 \text{mAcm}^{-2}$ ) was applied, which increased the cell potential to 4.00 V. The current density of 5.0  $\text{mAcm}^{-2}$  was calculated considering the entire electrode surface area, 19.62  $\text{mm}^2$ . The surface area of the Si particles was determined by quantitative metallography where optical microstructures obtained from 10 different locations on the electrode surface, each of area  $234 \times 312 \mu\text{m}^2$ , were analyzed. The area of the Si particles present at each location was determined by a Java-based image processing and analysis program (ImageJ Version 1.45s). The optical microstructures were converted to 8-bit grayscale images and thresholding was performed in the black-and-white channel, which enabled outlining of the particles. The area of the particles calculated using the measuring function ‘Analyze Particles’ was 9.37  $\text{mm}^2$ . Therefore, the current density estimated by considering the Si particles’ surface area was 10.6  $\text{mAcm}^{-2}$ .

### 2.2. ‘In-situ’ observations by optical microscopy and Raman spectroscopy

The electrode surfaces were continuously observed (in-situ) during the course of the electrochemical cycling using an optical microscope with a large depth-of-field. In this way, microscopic features of the electrode surface such as the cracks, having lengths as small as 1  $\mu\text{m}$ , that were formed on Si particles could be detected and recorded in the time scale of the experiments. In addition, the 1000 × magnification objective of the optical microscope was used interchangeably with a 50 × objective of a Raman spectrometer to collect data showing changes in the crystal structure at the Si surface during the tests. Detailed description of the experimental setup including details of the in-situ Raman studies of electrodes was provided in Ref. [37]. Briefly, a 50 mW Nd-YAG solid-state laser diode emitting a continuous wave laser at the 532 nm excitation line was used to obtain Raman spectra by means of a Horiba spectrometer equipped with a CCD detector. The diameter of the laser spot on the specimen surface was 1  $\mu\text{m}$ .

### 2.3. Scanning (SEM) and transmission electron microscopy (TEM) of cracks in Si particles

TEM observations were performed on the electrochemically cycled Si-Al electrodes by taking cross-sections excised by means of focused-ion beam (FIB) milling. A Zeiss NVision 40 cross-beam system comprising of a FIB column and a Schottky field emission gun filament SEM (dual beam FIB/SEM system) was employed. The surface of the sample was protected from beam damage by

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