



## Full Length Article

## In-situ study of surface structure evolution of silicon anodes by electrochemical atomic force microscopy

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## ABSTRACT

Silicon is one of the most promising anode materials for lithium ion batteries because of its extremely high theoretical capacity. However, silicon suffers from mechanical degradation caused by huge volume change and unstable solid electrolyte interphase (SEI) layers. Herein, we report an in situ electrochemical atomic force microscopy (EC-AFM) method to directly visualize the surface topography and analyze Young's modulus of micron-sized (Micron-Si) and nano-sized (Nano-Si) silicon electrodes. Our results show Micron-Si electrodes experienced volume expansion and contraction process which resulted in continuous growth of a thick but soft SEI layer on the surface. In contrast, Nano-Si electrodes demonstrate a thin SEI layer due to absence of volume expansion and contraction process. Young's modulus value shows that the SEI film of Nano-Si electrodes is harder than that of the Micron-Si electrodes. Ex situ XPS analysis reveals that Nano-Si electrodes are composed of mainly inorganic components particularly LiF and carbonate-like species which might contribute to the increased hardness. Results from present study may be helpful to build better SEI layer with good Young's modulus to buffer volume expansion of Si.

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## 1. Introduction

Lithium ion batteries (Li-ion batteries) have been successfully commercialized due to its large energy density and long lifespan. It is now one of the most sought after choices for power source of portable and rechargeable applications [1]. The most frequently used negative electrode in commercial Li-ion batteries is graphite [2]. Graphitic carbon anodes have a theoretical specific capacity of only 372 mAh g<sup>-1</sup> due to the limited number of intercalation sites for Li<sup>+</sup> ions within the host lattice. Thus, developing next-generation anode materials with much higher capacity is essential for improving energy density and prolonging cycle life of high-performance Li-ion batteries.

Among the many currently available anode materials (such as tin-based materials [3,4], metal oxides materials [5–7] and phosphorus-based materials [8,9]), silicon (Si) which is the second most abundant element on earth, is definitely an attractive material as next generation anode material for commercial battery applications [10]. Si processing and fabrication technology has

already been well established for mass production [11]. Other attractive features of Si are the extremely high theoretical specific capacity (4200 mAh g<sup>-1</sup>, Li<sub>4.4</sub>Si) (~ ten times of conventional graphite anode) and relatively low working potential (~ 0.2 V versus Li/Li<sup>+</sup>), which make it possible to fabricate high power batteries [12–14]. However, low cycling stability and electrical conductivity of Si have limited the commercial use of Si in Li-ion batteries [15]. In addition, severe volume change (>300%) during cycling will lead to high internal stress, pulverization of electrode and delamination from current collector [16–21]. Fraction and pulverization of Si electrodes cause continual formation of solid electrolyte interphase (SEI) on the Si surfaces with each lithiation and delithiation process which eventually cause degradation of battery performance [22,23].

Surface structure of electrodes always changes during cycling and it plays important role for cycling performance of Li-ion batteries [24,25]. Stable surface structures (formed by using co-salts/co-solvents electrolyte additives and coating layer [26–32]) can prevent additional electrolyte degradation and enable long-term cycling. To date, many advanced characterization methods have been used to investigate surface structure on Si-based materials, such as electron energy loss spectroscopy (EELS) [33], time of flight-secondary ion mass spectrometry (ToF-SIMS) [34], transmis-

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sion electron microscope (TEM) [35], X-ray photoelectron spectroscopy (XPS) [36], nuclear magnetic resonance (NMR) [37], and atomic force microscopy (AFM) [38–41]. AFM, especially in situ AFM, is one of the most powerful tools to directly investigate the interface reaction of electrodes as a function of applied electrochemical potentials and/or electrolyte compositions/additives. It can also monitor the evolution of surface topography and properties simultaneously at nanoscale resolution [24,42–45].

Herein, we employed electrochemical AFM to investigate the morphological, mechanical (force module analyses) and compositional differences of Si electrodes (micron-sized and nano-sized) surface structure in EC and FEC-based electrolytes. XPS was also employed to evaluate mechanical and chemical composition of the Si electrodes. EC-AFM in combination of XPS and able to provide valuable information about size effect on property and composition of surface structure of Si electrodes and SEI layer formed on Si electrodes.

## 2. Experimental

### 2.1. Preparations of silicon-based electrodes

Silicon electrodes were prepared by mixing Si materials (micron Si  $\sim 1 \mu\text{m}$ , Aladdin; nano Si  $< 150 \text{ nm}$ , Alfa Aesar), conductive carbon black (super P), and binder of sodium carboxymethyl cellulose (CMC) at a weight ratio of 7:2:1. Slurry was formed on copper foil (current collectors) using deionized water as solvent. A vacuum oven was used to dry the obtained circular electrodes (14 mm diameter) at  $100^\circ\text{C}$  for 12 h prior to analysis. Typical mass of Si active materials were in the range of  $0.7\text{--}1.3 \text{ mg/cm}^2$  ( $\sim 10 \mu\text{m}$ ).

### 2.2. Electrochemical performance and image scanning using EC-AFM

In situ AFM (Bruker Icon) experiments were conducted in an argon-filled glovebox (MBRAUN,  $\text{H}_2\text{O} \leq 0.1 \text{ ppm}$ ,  $\text{O}_2 \leq 0.1 \text{ ppm}$ ) at ambient temperature. The Li-Si cell was composed of Si electrode as working electrode (WE) and Li wire as reference and counter electrodes (RE and CE). Electrolyte solutions used were 1 M  $\text{LiPF}_6$  dissolved either in a mixture of fluoroethylene carbonate/dimethyl carbonate or ethylene carbonate/dimethyl carbonate (FEC/DMC or EC/DMC, 1:1 V:V) (Zhangjiagang Guotai-Huarong New Chemical Material Corporation). SEI layer was formed by cycling the Li-Si cell at a scanning rate of  $0.6 \text{ mV/s}$  between 1.5 and 0 V. AFM topography was collected simultaneously in ScanAsyst mode using SCANNASYST-FLUID+ tip (Bruker Corporation). Contact mode was performed to scratch the surface using SCANNASYST-AIR tip (Bruker Corporation). Ex situ quantitative nanomechanics (QNM) experiment was applied to compare and analyze the Young's modulus of SEI films formed on Si electrodes of different sizes (tip model: TAP525A, Bruker Corporation). An AC signal of 10 mV in amplitude was used as the perturbation for EIS measurements using A Solartron 1470E Electrochemical Interface (Solartron Analytical, U.K.) electrochemical workstation, and the frequency range was from 0.01 to 1 MHz.

### 2.3. X-ray photoelectron spectroscopy characterization

KratosAxis Ultra X-ray photoelectron spectrometer was used to perform ex situ XPS analysis using  $1486.6 \text{ eV}$  Al  $\text{K}\alpha$  X-rays. We removed samples from the Li-Si cells and cleaned residual solvent and salt by rinsing with dimethyl carbonate (DMC) in an glovebox (argon-filled). All samples were dried under vacuum and then transported to XPS facility in sealed bags to avoid oxygen and water. Hydrocarbon C1s peak at  $284.8 \text{ eV}$  was used to reference the binding energies.

## 3. Results and discussion

### 3.1. Cyclic voltammetry curves of Li-Si cell with EC/DMC and FEC/DMC electrolytes

Fig. 1a and b show the cyclic voltammogram of Micron-Si and Nano-Si electrodes between 1.5 and 0 V in 1 M  $\text{LiPF}_6/\text{EC/DMC}$ . A single cathodic peak can be observed at 1.24 V for Micron-Si electrode (inset in Fig. 1a); and at 1.21 V for Nano-Si electrode (inset in Fig. 1b) which disappeared in the subsequent cycles (Fig. S1a and S1b). These peaks can be attributed to the irreversible reduction of electrolyte and formation of SEI. In addition, two additional peaks can also be observed for Micron-Si electrode (Fig. 1a). The broad peak at around 0.2 V can be attributed to formation of Li-Si alloy ( $\text{Li}_x\text{Si}$ ); meanwhile, the sharp peak below 0.1 V might due to phase transition of  $\text{Li}_x\text{Si}$  to  $\text{Li}_{15}\text{Si}_4$  [46]. A single sharp peak below 0.1 V can be observed for Nano-Si electrode which corresponded to formation of amorphous  $\text{Li}_x\text{Si}$  during insertion of Li into crystalline Si (Fig. 1b) [47]. Two anodic peaks can also be observed for Micron-Si (0.35 V and 0.51 V) and Nano-Si (0.33 V and 0.49 V) during oxidation state which can be attributed to extraction of Li ions from Si [44,46,48].

CV curves of Micron-Si and Nano-Si electrodes between 1.5 and 0 V in 1 M  $\text{LiPF}_6/\text{FEC/DMC}$  were similar to those observed in  $\text{LiPF}_6/\text{EC/DMC}$  electrolyte (Fig. 1c and d). The obvious difference was presence of two small cathodic peaks (1.24 and 0.82 V for Micron-Si, 1.21 and 0.87 V for Nano-Si) when Si electrodes were cycled in FEC-based electrolyte. These peaks can be ascribed to formation of SEI films as they were not present in the subsequent cycles (Fig. S1c and S1d). It has been demonstrated that the reduction peak at a potential of  $\sim 1.3 \text{ V}$  (vs Li/Li+) corresponds to the reduction of FEC, so we think the first reductive decomposition peak at 1.2–1.3 V in FEC based electrolyte is more likely to be the reduction of FEC; furthermore, the reduction product of the FEC can be VC and the VC might react again to form the poly(VC) or PC as following reactions:  $\text{FEC} + \text{R-O Li}^+ \rightarrow \text{VC} + \text{R-OH} + \text{LiF}$ ;  $n\text{VC} + n\text{e}^- \rightarrow \text{PC/poly(VC)}$  [49–51]. The SEI film rapidly formed at around 0.2 V when  $\text{Li}^+$  insert into the Si, which was marked by the arrows in Fig. S5c. This is in consistent with previously reported findings [52].

### 3.2. In situ AFM imaging of surface structure change during the first cycle

Peak force tapping mode was used to directly investigate the evolution of surface morphology of Si electrodes under potential control. Peak force tapping mode performs a fast force curve at every pixel in the image, which can effectively minimize damage of the sample surface during scanning. Peak force tapping mode operates at force even lower than tapping mode; hence are able to protect the soft and sticky surface structure. Besides that, cantilever tuning does not resonate during peak force tapping mode which is particularly advantageous in fluids [42,44]. A home-made AFM fluid cell was used to hold the sample and a plastic-ringing was used to prevent the leakage of electrolyte. A rubber seal was used as a protective skirt to protect the AFM scanner tube from liquids. Fig. 2 shows the surface structural evolution of Micron-Si electrode during the first lithiation-delithiation cycle in 1 M  $\text{LiPF}_6/\text{EC/DMC}$ . The scan rate for the AFM measurement was 1 Hz. And the measurement performed was in-situ; arrows we used in the images indicated the AFM scanning direction while the number was the potential window. There was no significant change in primary morphology of Micron-Si electrode at 1.5–1.31 V (Fig. 2a). Compared with Fig. 2a, as we can see, the clear outline of the particles in the Fig. 2b has disappeared and the arrows indicate the

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