

# Real-Time Observation of Mechanical Evolution of Micro-Sized Si Anodes by In-Situ Atomic Force Microscopy

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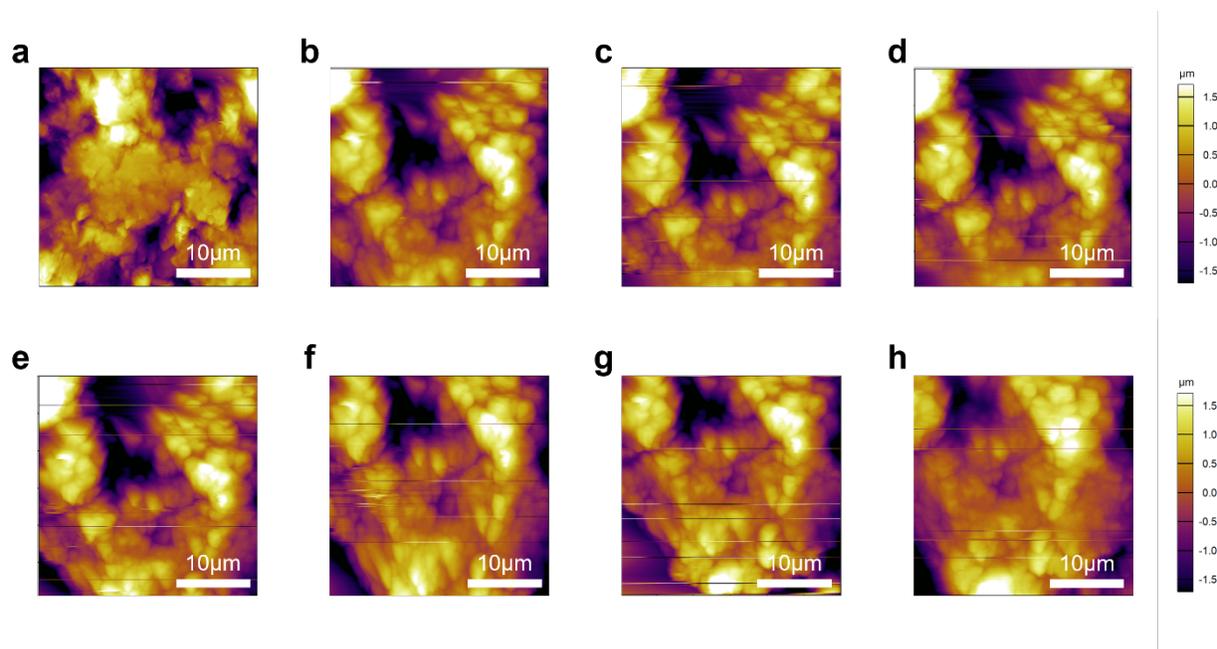
## Experimental Methods

The Si-based anode sample with  $\sim 30$   $\mu\text{m}$  thickness, provided by LG Energy Solution, was firstly calendared with a polymer-coated separator using a roll-press at  $90$   $^{\circ}\text{C}$  to improve adhesion between the separator and the anode. The calendared Si-separator assembly maintained its integrity when it was cut into a  $3$   $\text{mm} \times 10$   $\text{mm}$  rectangle with even and clean edges to make the cross-sectional AFM sample. Then, the Si-separator assembly was moved into an argon-filled glovebox (both moisture and  $\text{O}_2$  at below  $1$  ppm) to make the in-situ AFM battery cell. A piece of Li metal was also cut into a  $3$   $\text{mm} \times 10$   $\text{mm}$  rectangle as the counter electrode. The Si-separator-Li assembly was placed between two pieces of PEEK blocks with Ni foam ( $\sim 3$  mm thickness) as current collectors. The PEEK clamp was fixed by tightening the screws, which provided stable compression forces. The fabricated assembly was placed at the center of an AFM electrochemical cell (EC cell), while stainless steel wires were connected to the Ni foam through the EC cell feedthrough. The cell was then sealed with a clamp – perfluoroelastomer (FFKM) membrane – AFM cantilever holder setup, and the electrolyte was injected in to the gas/liquid-tight EC cell. The electrolyte was  $1\text{M}$   $\text{LiPF}_6$  dissolved into the mixture of ethylene carbonate (EC) and ethyl-methyl carbonate (EMC) (1:1 vol. ratio) with  $5\%$  wt Fluoroethylene carbonate (FEC) additive.

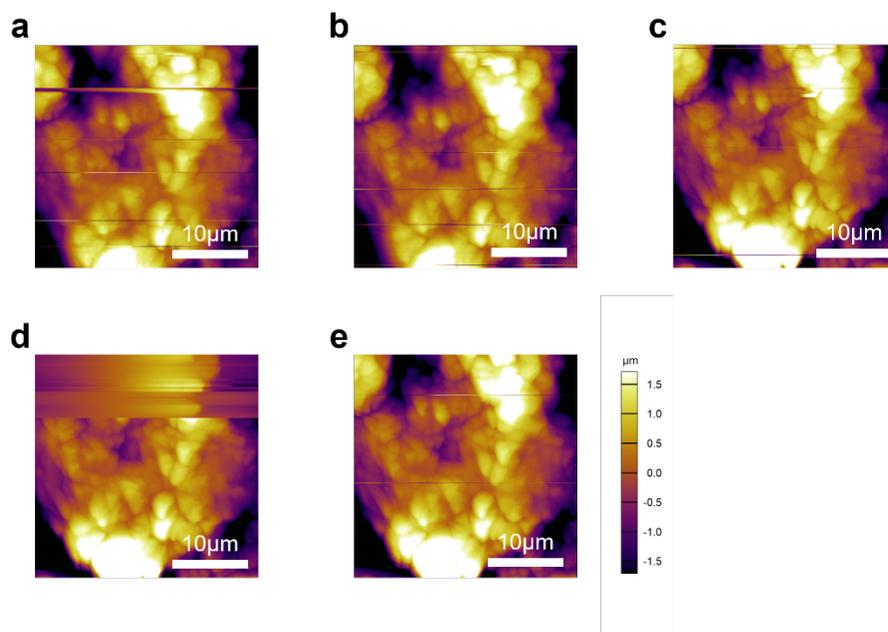
The sealed AFM EC cell was transferred to an MFP-3D Infinity AFM system (Oxford Instrument, Asylum Research) and the tapping mode was applied with a standard commercial AFM cantilever (Olympus AC160-R3, nominal spring constant:  $26$   $\text{nN/nm}$ , nominal resonant frequency:  $300$   $\text{kHz}$ , nominal tip radius:  $7$   $\text{nm}$ ). The EC cell was connected to an external Gamry potentiostat to conduct the electrochemical cycling test.

### **In-Situ AFM Image Processing**

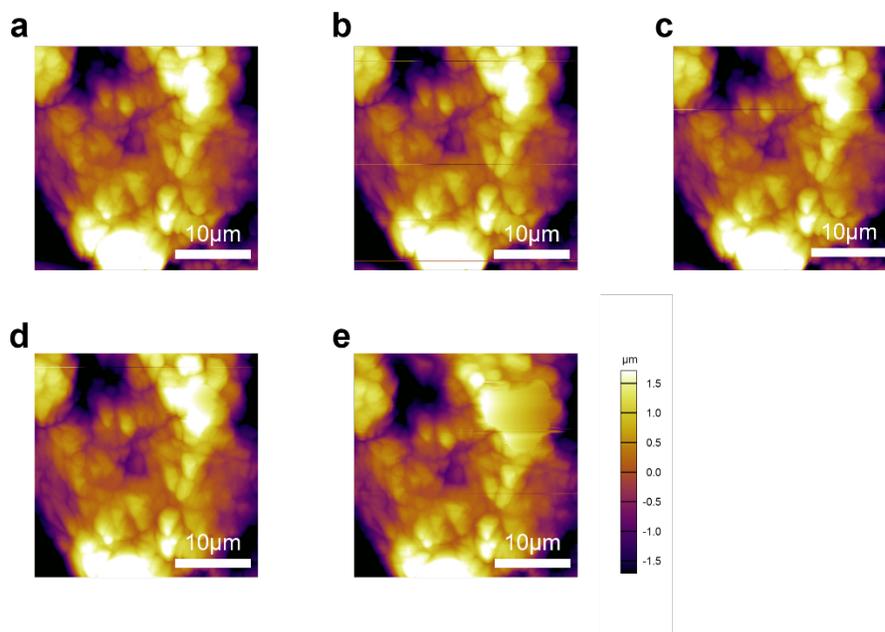
A novel image processing method was developed to quantify the volumetric change of the Si particle from the collected AFM topography. The AFM amplitude data were used to identify the edge of each particle because the AFM amplitude values sharply varied from a pre-set control value when the AFM tip experiences a sudden height change. Firstly an amplitude gradient map was generated, from which the gradient values larger than a threshold value were used to successfully identify the location of grain edges. Then height data at the location of grain edge provided the height threshold to separate the region of a Si particle from its surrounding. The area inside of one closed boundary defined one Si particle. Then, the volume of each Si particle was calculated by the numerical integration of height values within the closed boundary. Our estimation focused on a local area with four Si particles as shown in Figures S5-S8. The same image processing method was applied to each of the in-situ AFM images measured at different SOC moments. Figures S1-S4 show the raw in-situ AFM height maps and Figures S5-S8 shows the maps after image processing with the identified Si grain boundaries and corresponding volumes of Si particles. Complete 3D visualization (the complete version of Figure 2j) of one Si particle is shown in Figure S9.



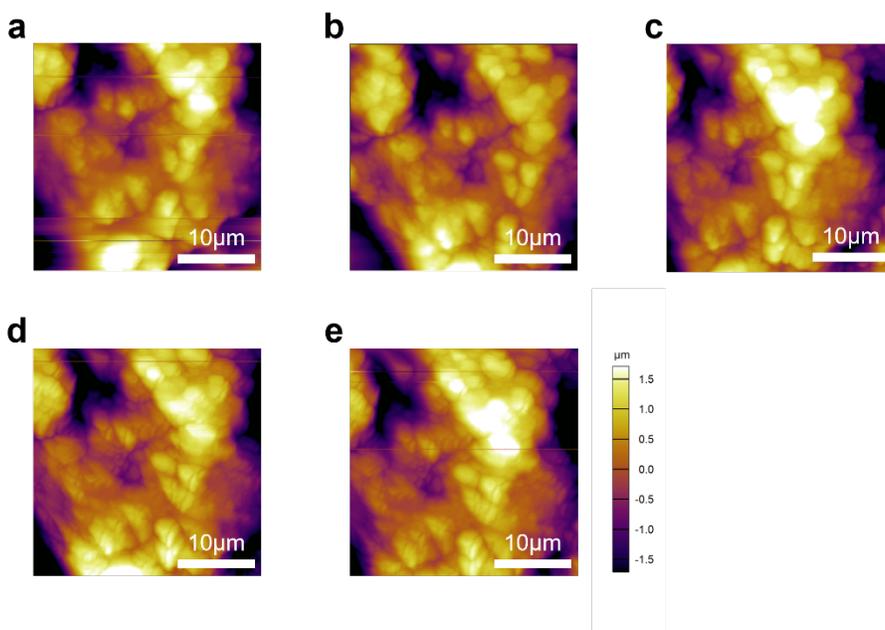
**Figure S1.** In-situ AFM images recorded during the first lithiation process at various EC cell potentials: (a) 40 mV, (b) 36 mV, (c) 31 mV, (d) 26 mV, (e) 18 mV, (f) 10 mV, (g) 5 mV.



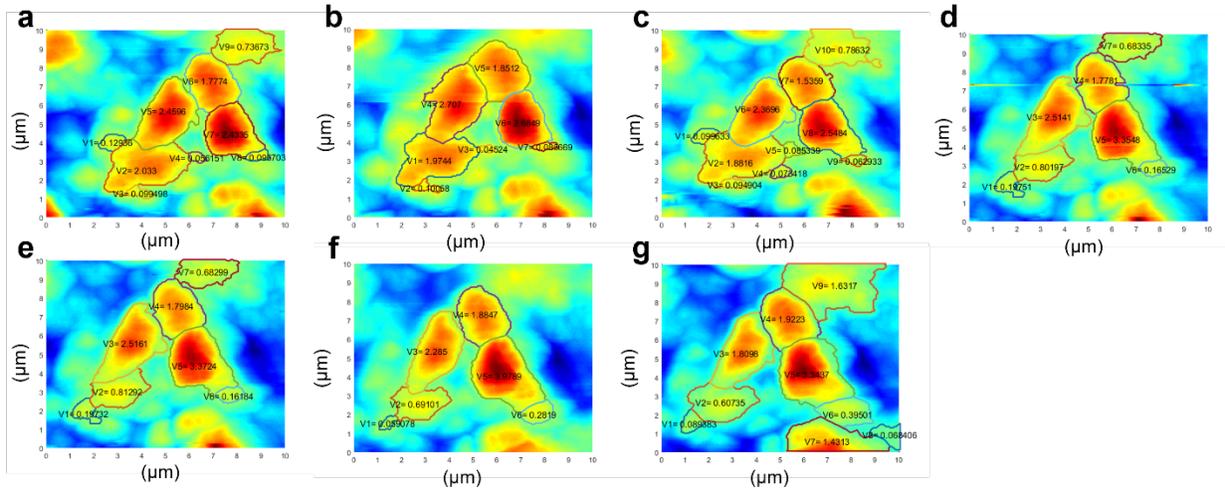
**Figure S2.** In-situ AFM images recorded during the first delithiation process at various EC cell potentials: (a) 438 mV, (b) 443 mV, (c) 454 mV, (d) 470 mV, (e) 503 mV.



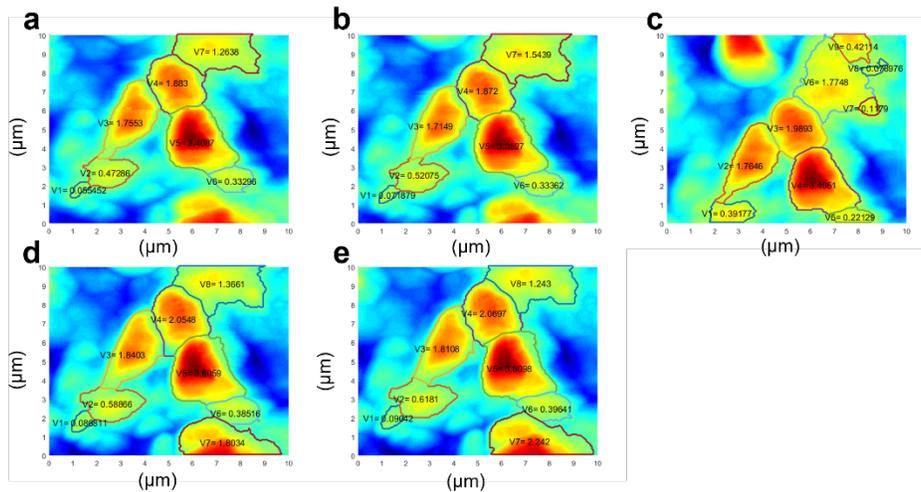
**Figure S3** In-situ AFM images recorded during the second lithiation process at various EC cell potentials: (a) 190 mV, (b) 138 mV, (c) 86 mV, (d) 50 mV, (e) 5 mV.



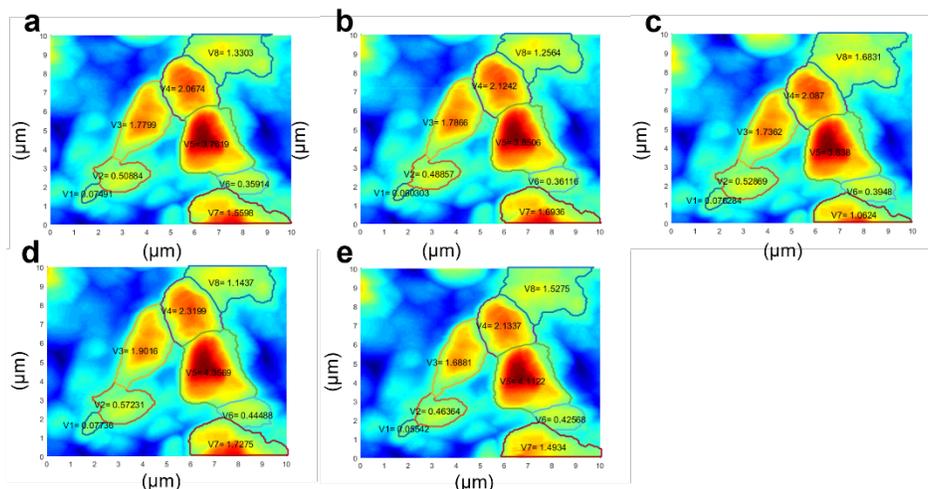
**Figure S4.** In-situ AFM images recorded during the second delithiation process at various EC cell potentials: (a) 363mV, (b) 436mV, (c) 490mV, (d) 701mV, (e) 995mV.



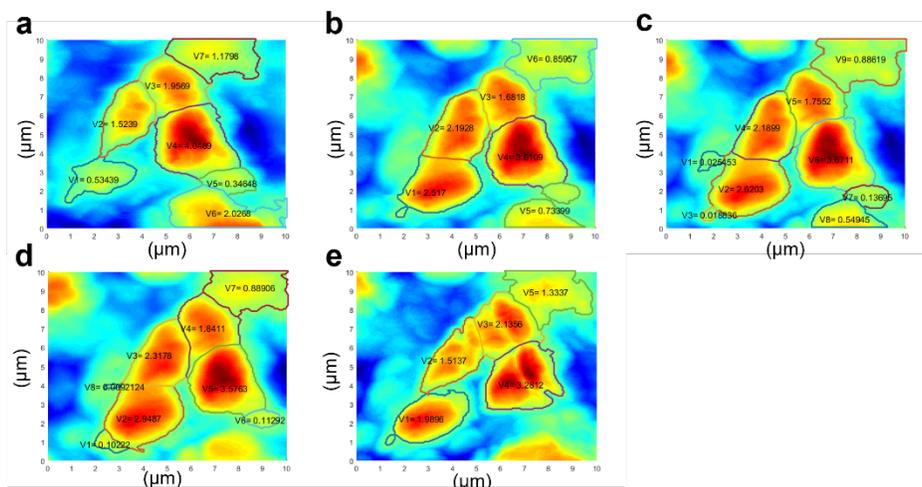
**Figure S5.** Processed in-situ AFM data via Si grain boundary identification and volume estimation recorded during the first lithiation process at various EC cell potentials: (a) 40 mV, (b) 36 mV, (c) 31 mV, (d) 26 mV, (e) 18 mV, (f) 10 mV, (g) 5 mV.



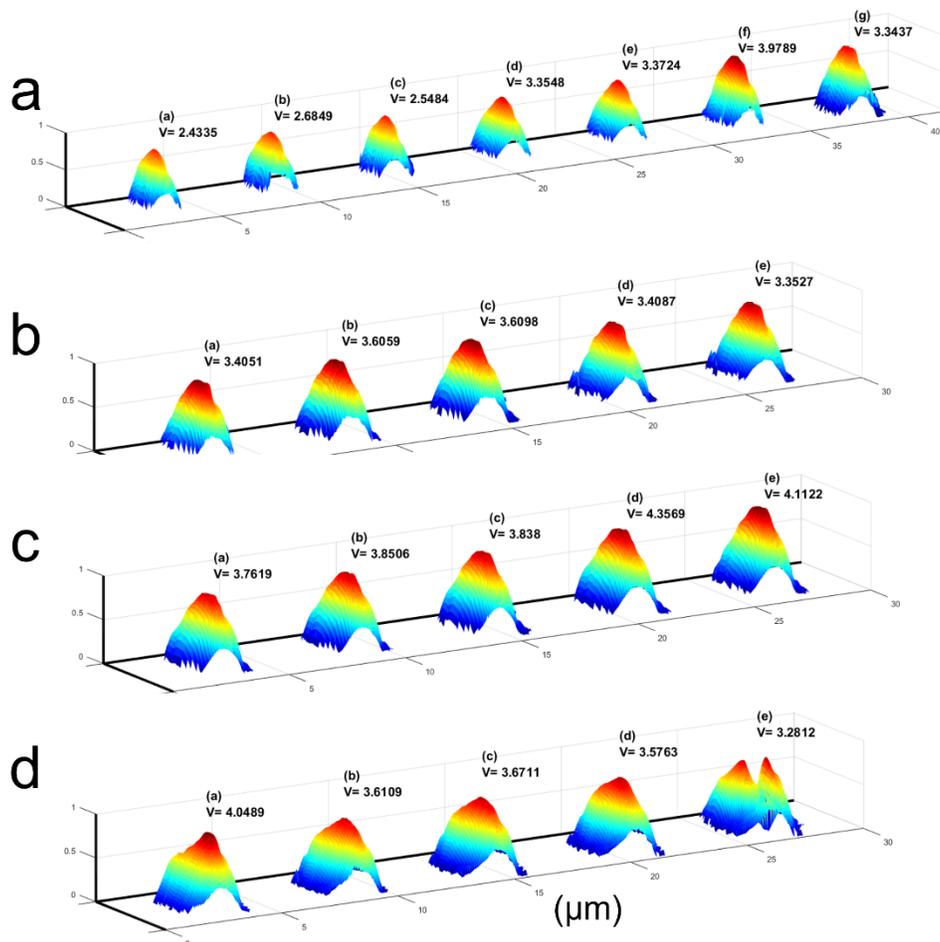
**Figure S6.** Processed in-situ AFM data via Si grain boundary identification and volume estimation recorded during the first delithiation process at various EC cell potentials: (a) 438 mV, (b) 443 mV, (c) 454 mV, (d) 470 mV, (e) 503 mV.



**Figure S7.** Processed in-situ AFM data via Si grain boundary identification and volume estimation recorded during the second lithiation process at various EC cell potentials: (a) 190 mV, (b) 138 mV, (c) 86 mV, (d) 50 mV, (e) 5 mV.



**Figure S8.** Processed in-situ AFM data via Si grain boundary identification and volume estimation recorded during the second delithiation process at various EC cell potentials: (a) 363 mV, (b) 436 mV, (c) 490 mV, (d) 701 mV, (e) 995 mV.



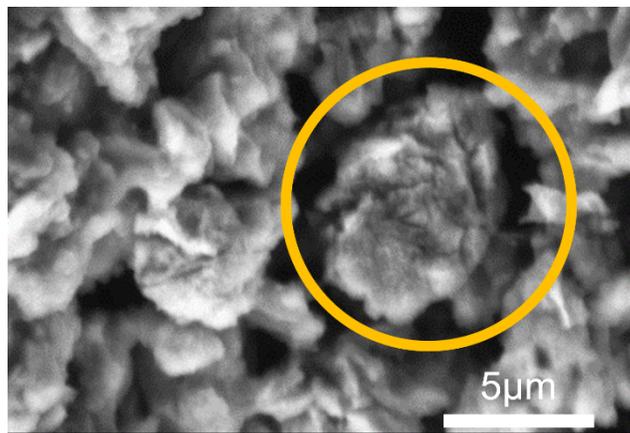
**Figure S9.** 3-D visualization of single Si particle extracted from in-situ AFM images during the (a) first lithiation, (b) first delithiation, (c) second lithiation, (d) second delithiation.

### Ex-situ Scanning Electron Microscopy (SEM) characterization

To confirm the generations of  $\mu$ Si surface fracture during electrochemical cycling, we conducted ex-situ SEM characterization of cycled  $\mu$ Si electrodes. The electrode was cycled in a coin half-cell using the same electrochemical conditions employed for the AFM In-situ cell operation:

- 1<sup>st</sup> cycle: lithiation by 1/20C-rate, CCCV at 5 mV, delithiation by 1/20C-rate up to 1.5V
- 2<sup>nd</sup> cycle: lithiation by 1/10C-rate, CCCV at 5mV, delithiation by 1/10C-rate up tp 1.0V

Then the  $\mu\text{Si}$  electrode was taken apart from the coin cell and washed by DMC to remove the deposited salts residue. The electrode was then characterized by a Hitachi S-3000H SEM. As shown in Figure S10, the surface fractures on  $\mu\text{Si}$  were consistent with what we observed from in-situ AFM experiments.



**Figure S10.** Scanning electron microscopy (SEM) image of  $\mu\text{Si}$  anode revealing the surface fractures after cycling in a coin-half cell following the same electrochemical testing protocols as the AFM in-situ EC cell.