Supporting information

The Essence of Electrochemical Prelithiation for Silicon Anode: from Interface to Bulk Phase

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Experimental Section

Electrode preparation

The slurry composed of Si powder with average diameter of ~200 nm (Kejin Co., China), polyvinyl alcohol (PVA, 1799, Sigma Aldrich) binder and carbon black (Super P, Switzerland) at a dry weight ratio of 7:2:1 was homogenized with an emulsifier (Fluko FA25) at a speed of 10,000 rpm for 30 min. The obtained slurry was cast onto a copper foil (10 μm thickness) using a doctor blade. The dried electrode laminate was calendared and punched into 14mm discs. The loading of Si anode was controlled at around 1.0 ± 0.05 mg cm^{-2}. Meanwhile, NCM523 (Tianjin Annuohe Co., Ltd.) cathode was also prepared by casting the homogenous slurry consisting of NCM523 (90 wt%), super P conductive carbon (6% wt) and polyvinylidene fluoride (PVDF, 4% Arkema) in N-methyl pyrrolidone (Aladdin) onto an aluminum foil (13 μm thickness). The dried electrode laminate was calendared and punched into 13mm discs. The loading of NCM was controlled at around 10 mg cm^{-2}. Accordingly, the N/P ratio is controlled at 1: 1.5 in making the full cells. Before use, all the cathode and anode electrodes were further dried at 120 ^{o}C for 12 h under vacuum.

Electrochemical prelithiation

Electrochemical pre-lithiation of Si electrode was conducted using CR2032-type coin cells assembled in a glove box (<0.1 ppm of oxygen and water, OMNILAB, VAC) in which Celgard 2500 was used as the separator and lithium foil as the counter electrode. 1 mol L^{-1} LiPF$_6$ dissolved in EC/EMC/DMC/FEC (3:3:3:1 by volume, Novolyte Technologies) was used as the electrolyte. Galvanostatic electrochemical

pre-lithiation was carried out on a Neware CT-4008 (Neware battery test system, Shenzhen, China) by the lithiation amount of 0.760 mAh (equivalent to 746.6 mAh g^{-1}), corresponding to the total irreversible capacity in the initial 3 electrochemical cycles as discussed in the context.

Electrochemical characterizations

After prelithiation, the Si anodes were harvested from the half cells. Full cells using the raw Si anode and the prelithiated Si anode were fabricated against the fresh NCM523 cathode with the same electrolyte used in prelithiation. The cell formation were done at 0.05 C rate in the voltage range between 2.8 V and 4.3 V on Maccor S4000 (Maccor Instruments, USA) cycler. Cyclic voltammetry (CV) was carried out between 2 V and 4.5 V at scan rate of 0.05 mV/s on Autolab potentiostat(Switzerland). Electrochemical impedance spectroscopy (EIS) was collected at 60% depth of discharge(DOD) on a Zahner Elektrik IM6 electrochemical work station over the frequency range of 10 mHz to 100 kHz with an alternating voltage of 5 mV. The Galvanostatic intermittent titration technique (GITT) test was performed at a low current of 0.05 C on Neware CT-4008 after 100 cycles. The rest period is set to 30 min and 15 min between each pulse. All the tests were conducted at room temperature (25 °C).

GC measurement

To determine the trapped Li within the Si anode, the cycled Si anodes (fully delithiated) after different electrochemical cycles were harvested and sealed in a container with an open-top cap in an argon-filled glovebox. 1 M HNO$_3$ (0.5 mL) was

injected into the container to react with the Li$_x$Si alloy, producing H$_2$ gas. The H$_2$ concentration was measured by a Shimadzu Nexis GC-2030 gas chromatography (GC) system equipped with a thermal conductivity detector (TCD). A gas-tight syringe was used to transfer the resultant gas (50 μL) from the container into the GC system. Three parallel tests were conducted at for each sample and the average value was used to evaluate the trapped Li within the Si anode.

Physical characterizations

SEM observations of the Si electrodes were conducted on Hitachi SV-8010 at 10 kV. Transmission electron microscopy (TEM) images were obtained with FEI Tecnai F20 S-TWIN under 200 kV. The SEI compositions of the Si anodes were identified with X-ray photoelectron spectroscopy measurements (Thermo Fisher ESCALAB 250Xi, USA). For the XPS test, the sample was transferred to the XPS chamber under the protection of argon to avoid any possible oxidation or contamination. TOF-SIMS (TOF-SIMS 5, ION TOF) was used to analyze the surface chemical structure and for depth profiling. X-ray diffraction (XRD, Rint 2000, Rigaku with Cu Kα) was applied to characterize the crystalline structure of the Si anodes. Atomic force microscopy (AFM) is applied to identify the surface evolution and modulus of the Si anodes. Inductively coupled plasma (ICP, PerkinElmer Inc. OPTIMA 8000), was adopted to determine the nickel deposition on Si surface. After DMC washing and drying under vacuum, the Si electrode was immersed into a solution of 20% HNO$_3$ (3.0 mL) and 10% HF (1.0 mL) to dissolve the deposited metal cations.

Calculation method in GC measurements

In the first cycle, the capacity loss is defined as the difference between lithiation and delithiation (**Equation S1**):

$$Q_{total} = Q_{lith} - Q_{delith} \qquad (1)$$

As we know, SEI is composed of many kinds of Li salts, which does not produce H_2 when react with HNO_3 acid. Therefore, the amount of H_2 determined by GC can be converted into the amount of the trapped atomic Li inside the Si particle, and the trapped Li can be calculated from the amount of the released H_2.

From the amount of H_2 determined, the amount of the trapped Li can be further calculated according to the Faraday's Law (**Equation S2**):

$$Q = nF \qquad (2)$$

The amount of Li loss in SEI formation can be calculated based on charge balance (**Equation S3**):

$$Q_{SEI} = Q_{total} - Q_{trap} \qquad (3)$$
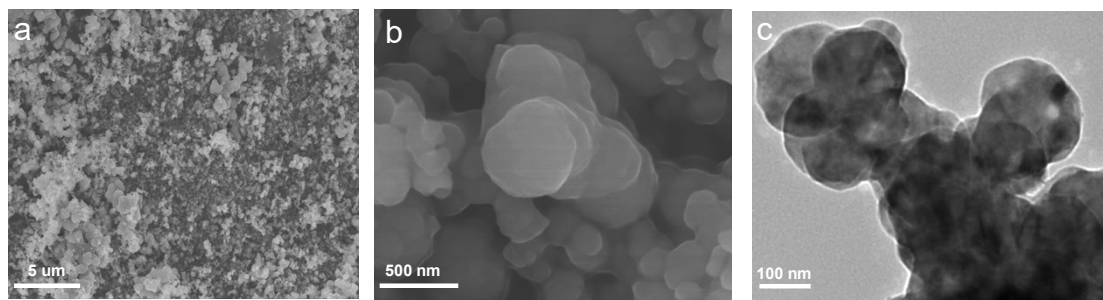
Figure S1. (a, b) SEM and (c) TEM image of the pristine Si nanoparticles.
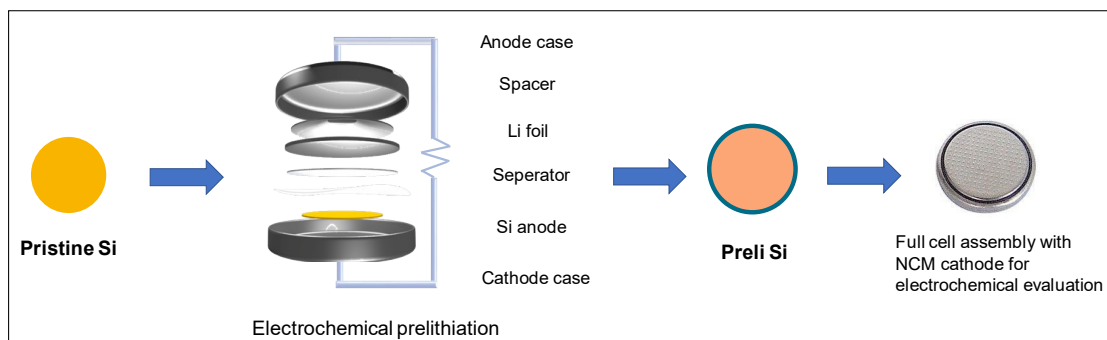
Figure S2. Schematic of electrochemical prelithiation method.
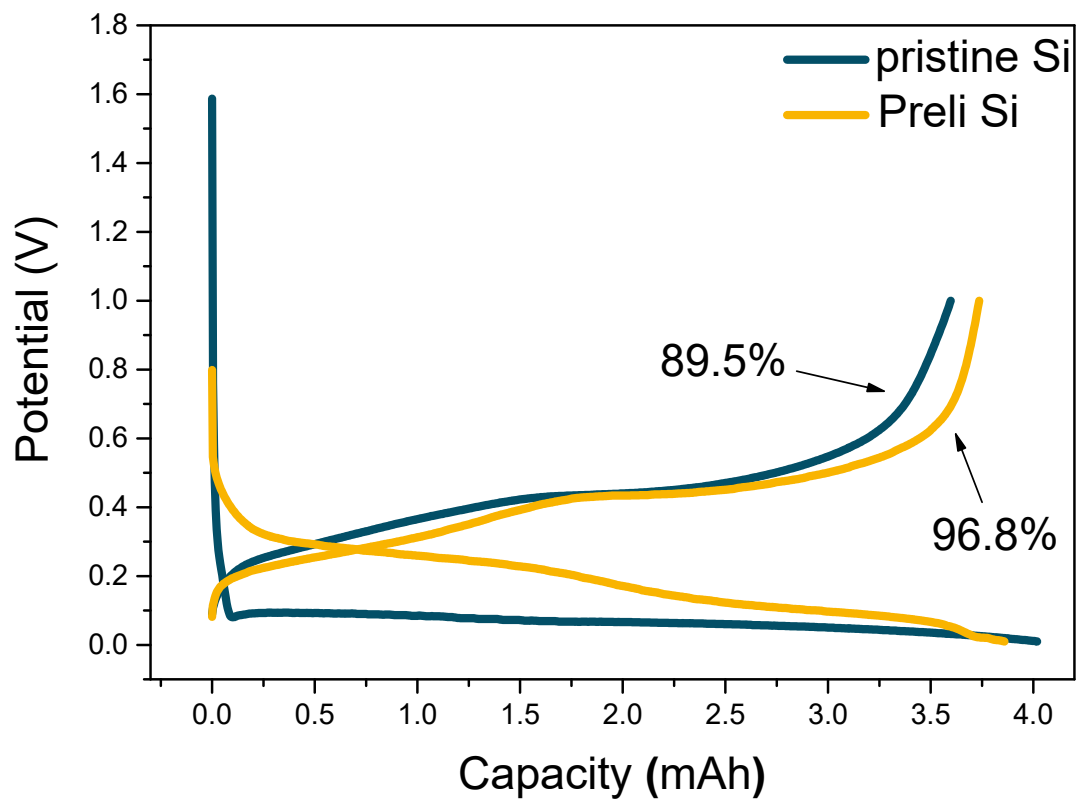
Figure S3. The initial charge/discharge profiles for the pristine Si and the prelithiated Si anodes against Li counter electrode.
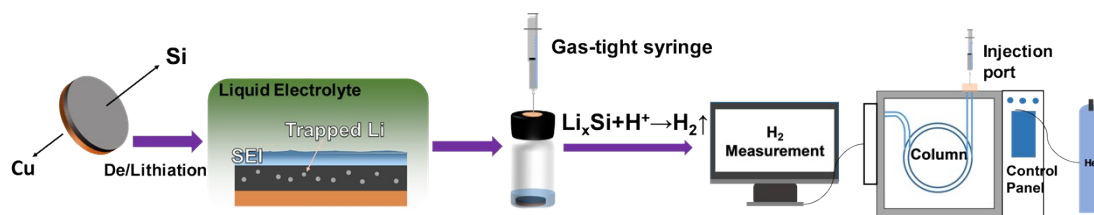
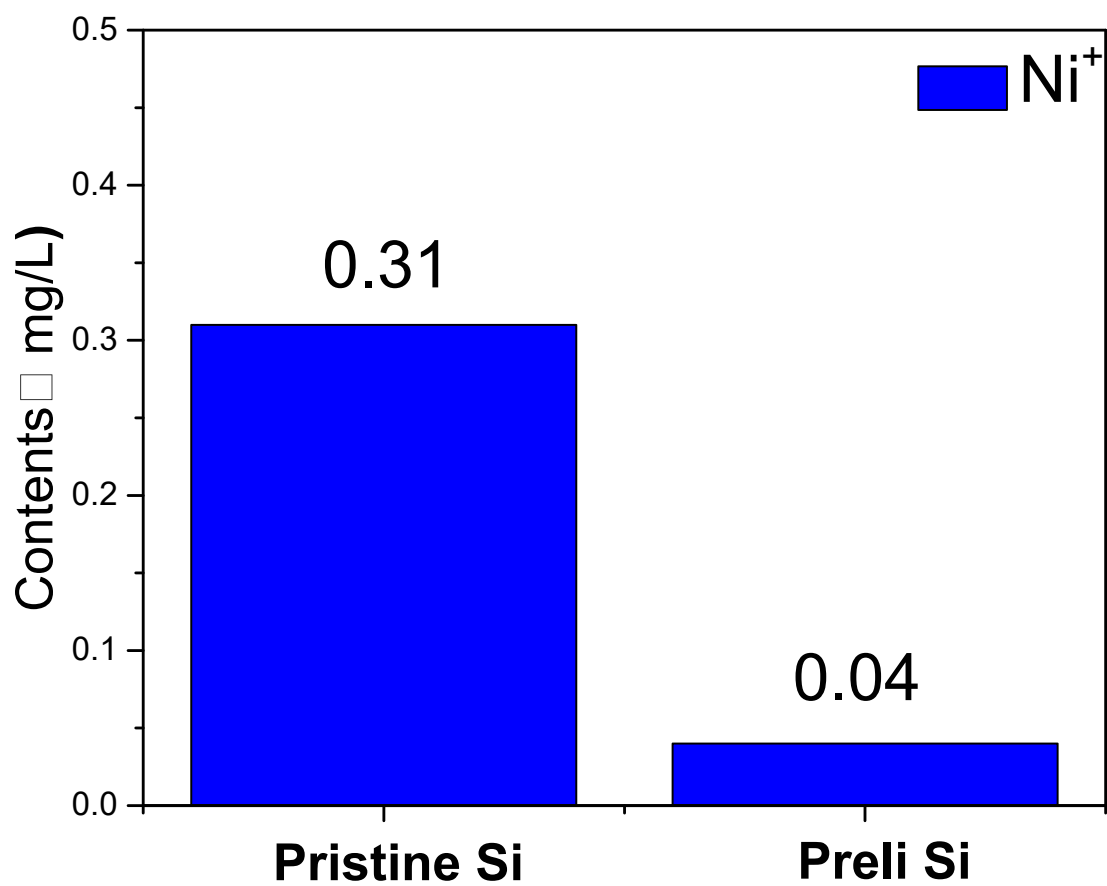**Figure S4.** Schematic of the TGC workflow conducted for the harvested Si anodes.

Figure S5. Ni content obtained with ICP-MS determination for the Si anodes without
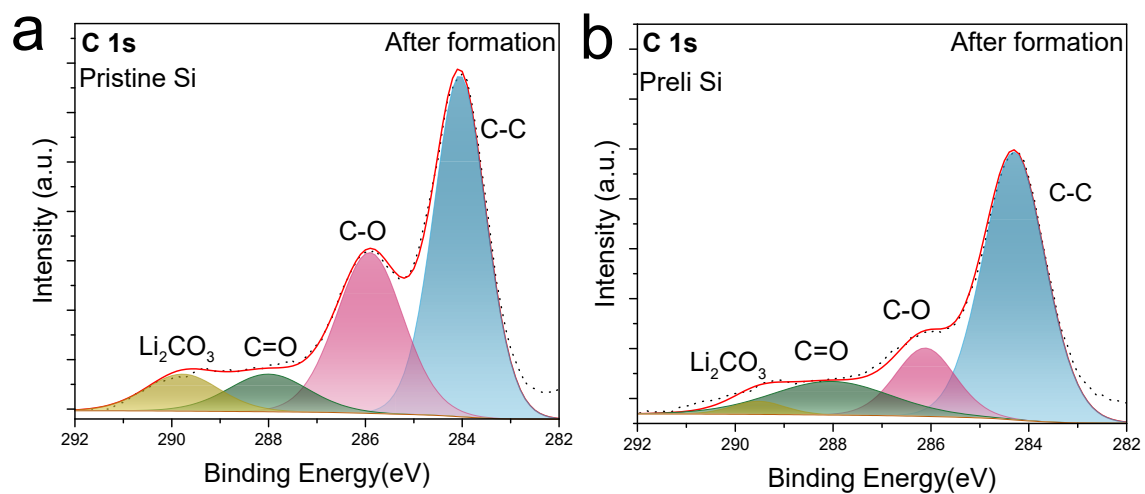
and with prelithiation after 3 formation cycles against NCM523 cathode.

Figure S6. Fitted-C1s XPS spectra of (a) pristine and (b) prelithiated Si anodes after 3 formation cycles against NCM523 cathode.
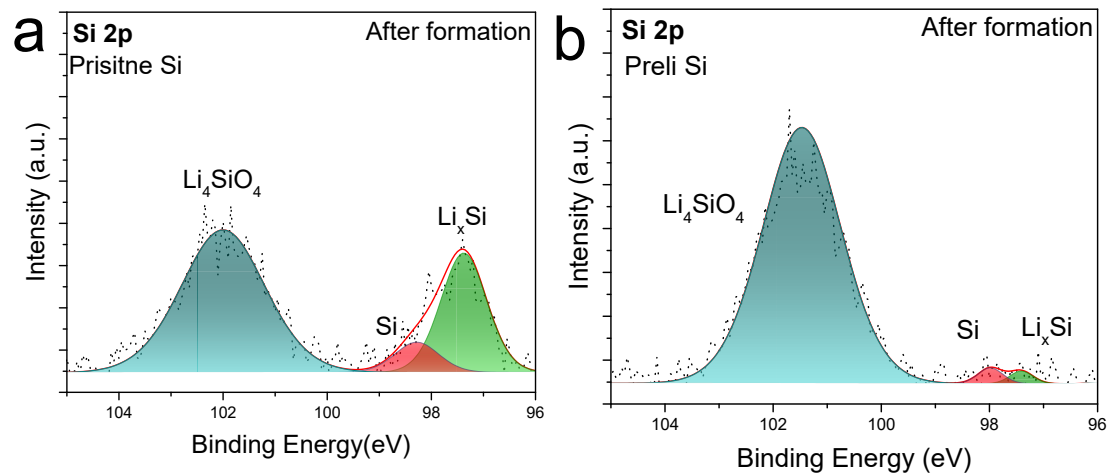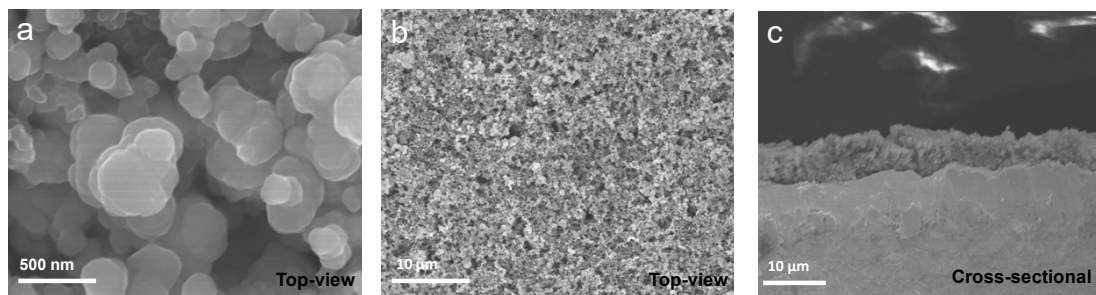
Figure S7. Fitted-Si2p XPS spectra of the (a) pristine and (b) prelithiated Si anodes

after 3 formation cycles against NCM523 cathode..

Pristine Si

Preli Si

a

2 1/nm

b

LiF $_{(220,111)}$

Li$_4$SiO$_{4\,(211)}$

5 1/nm
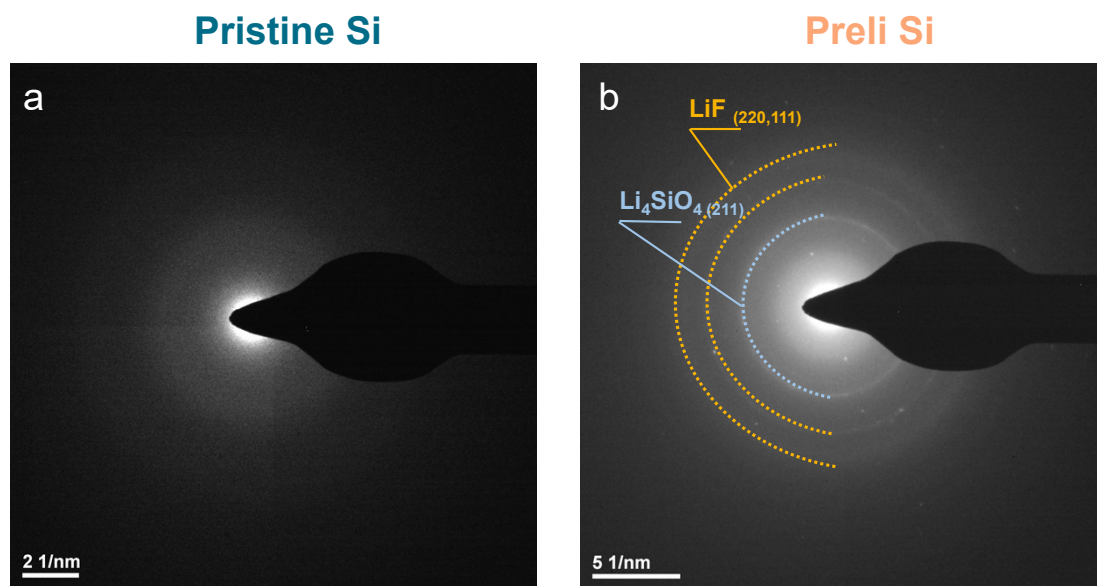
Figure S8. FFT patterns of (a) pristine and (b) prelithiated Si anodes after 3 formation cycles against NCM523 cathode..

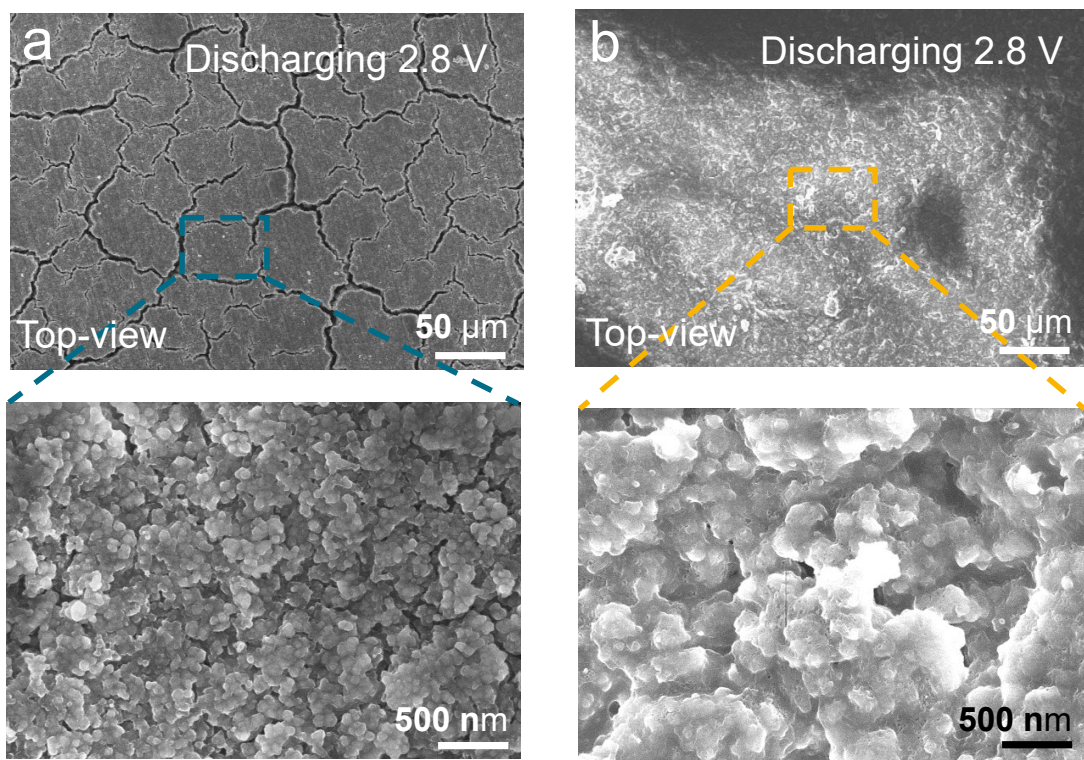**Figure S9**. (a, b) The top-view SEM images and (c) the cross-sectional SEM images of the pristine Si electrode.

Figure S10. The top-view SEM images of the harvested (a) unprelithiated Si and (b) prelithiated Si anode laminates after fully discharged to 2.8V.
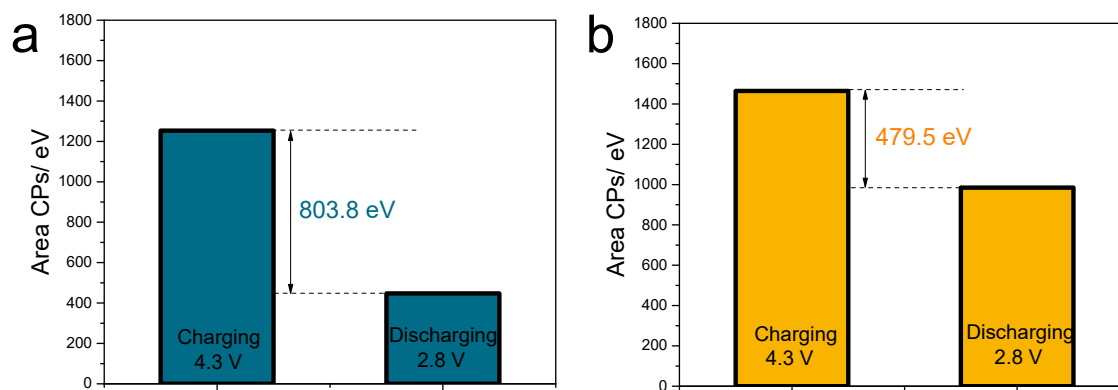
Figure S11. The calculated peak areas at fully charged and fully discharged states for the (a) unprelithiated and (b) prelithiated Si anodes, respectively.
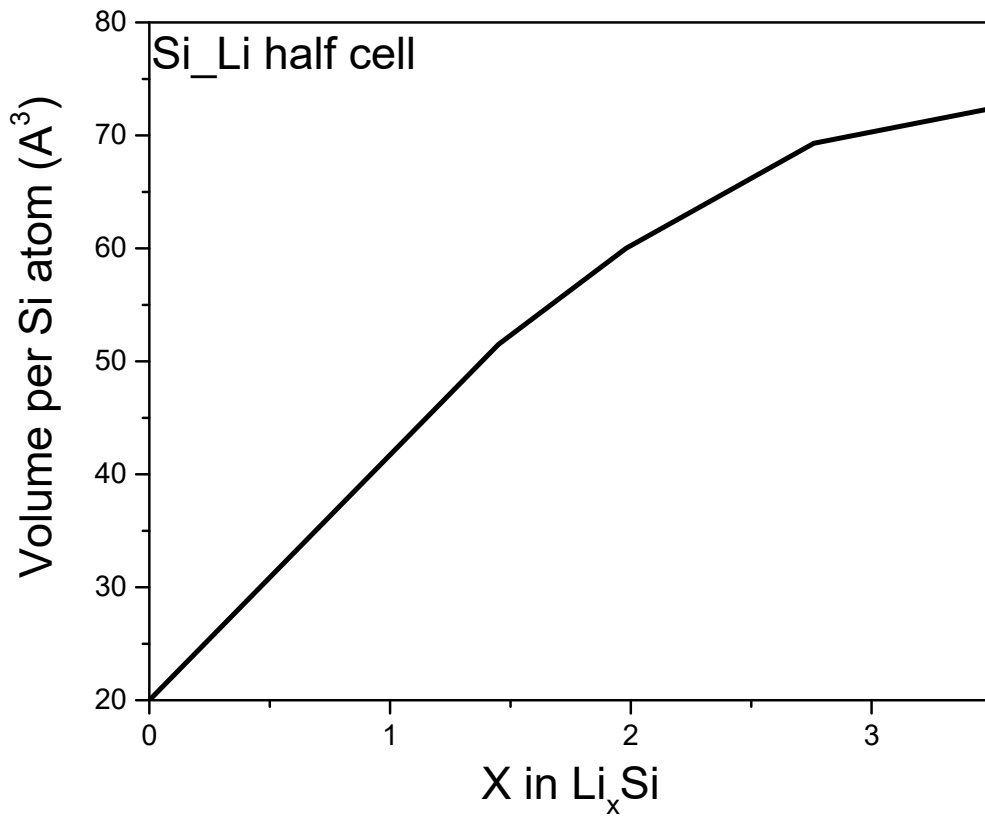
Figure S12. Variation curve of the volume of silicon atoms in crystalline lattice with the amount of embedded Li.
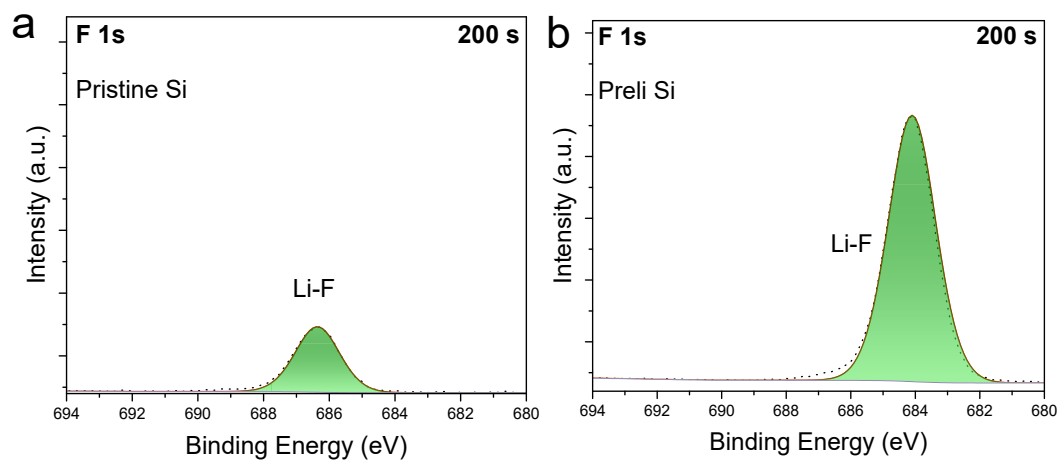
Figure S13. Fitted-F1s in-depth XPS spectra of the harvested (a) unprelithiated and (b) prelithiated Si anodes after 3 formation cycles against NCM cathode.
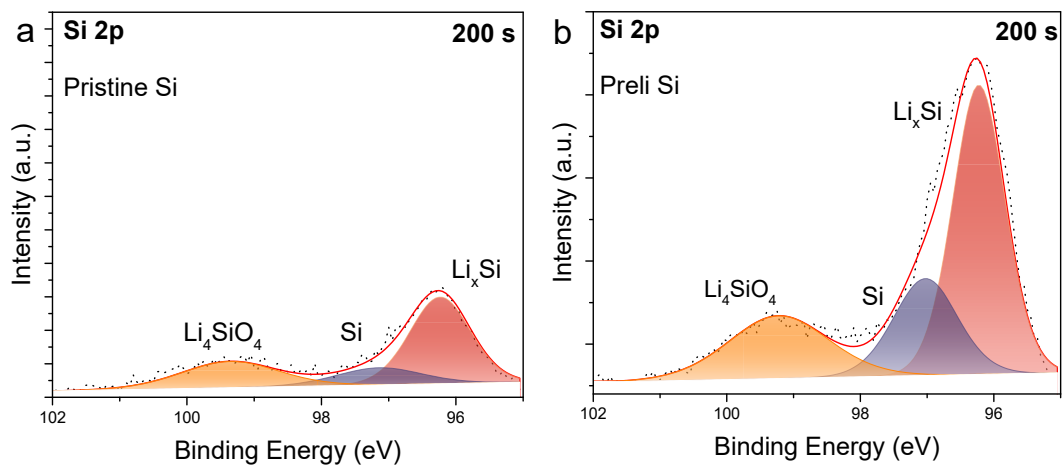
Figure S14. Fitted-Si2p in-depth XPS spectra of the harvested (a) unprelithiated and (b) prelithiated Si anodes after 3 formation cycles against NCM cathode.
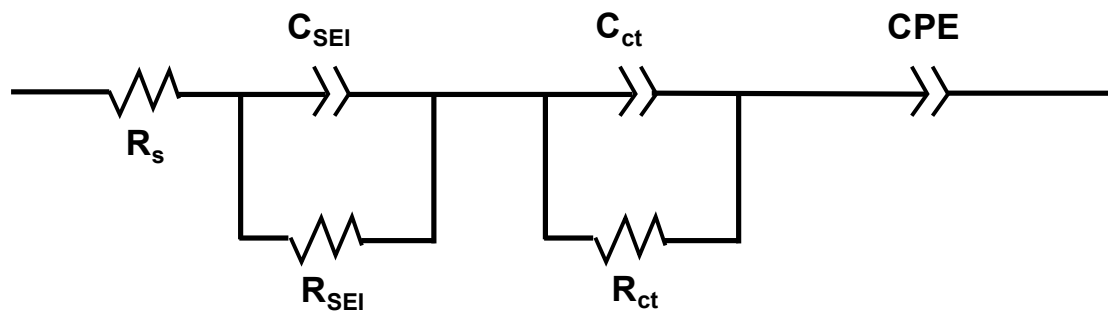
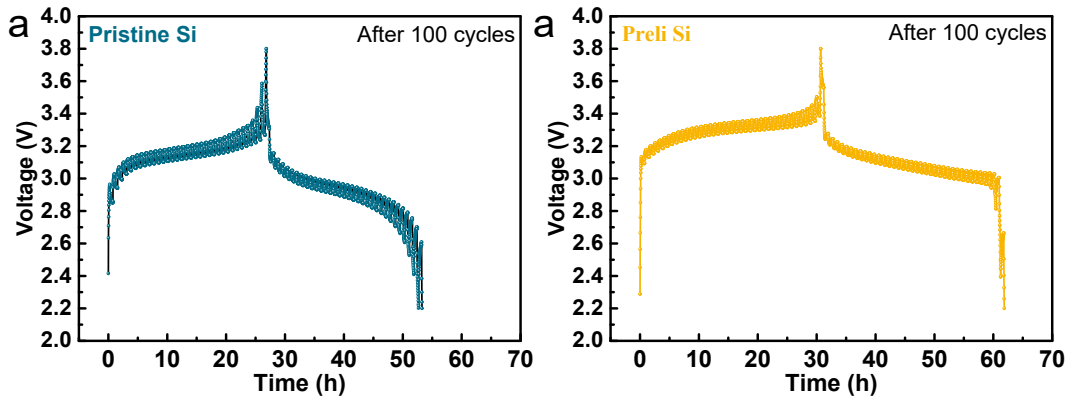**Figure S15.** Analog circuit of the Nyquist plots.

Figure S16. The GITT curves of the (a) unprelithiated and (b) prelithiated Si anode in full cell with NCM cathode after 100 cycles.

The Li$^+$ diffusion coefficients of pristine and prelithiated Si at varying states are calculated based on the following equation:

$$D = \frac{4}{\pi\tau}\left(\frac{n_m V_m}{S}\right)^2\left(\frac{\Delta E_s}{\Delta E_t}\right)^2$$

Here, the duration of the current pulse (τ) is 600 s; the number of moles (n_m) is 0.155 mmol; the molar volume of the electrode (V_m) is 6.834 cm^3 mol^{-1} and the electrode/electrolyte contact area (S) is 1.327 cm^2. Through the GITT test, the steady-state voltage change due to the current pulse (ΔE_s) and the voltage change during the constant current pulse eliminating the iR drop (ΔE_t) can be obtained. Therefore, the corresponding lithium ion diffusion coefficient can be calculated by the equation above.