

Supporting Information

Accurate Prelithiation of Lithium-Ion Batteries SiO_x Anode towards improved Initial Coulombic Efficiency

Cuicui Hu^{a#}, Minghao Zhang^{a#}, Wenbo Zhou^a, Chenyu Liu^{ab*}, and Zhan Lin^{ab}

^aSchool of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510006, China.

E-mail: cy.liu@gdut.edu.cn, zhanlin@gdut.edu.cn

^bGuangdong Provincial Laboratory of Chemistry and Fine Chemical Engineering Jieyang Center, Jieyang 515200, China.

Experimental section

Chemical reagents

Polyacrylic acid (PAA, $M_w = 240,000$, 25 wt.% solution in water), Super P, SiO_x and LiF were purchased from Aladdin Reagent (Shanghai) Co., Ltd.

Preparation of $\text{SiO}_x@LiF$

$\text{SiO}_x@LiF$ composites were fabricated by ball-milling. In brief, SiO_x underwent a pre-treatment process through ball milling with 450 rpm for a duration of 240 minutes. Subsequently, a mixture containing SiO_x , Super P, and LiF was subjected to an additional 120-minute ball milling, carried out at 400 rpm. Two ratios for $\text{SiO}_x@LiF$ composites were prepared (SiO_x : LiF: Super P: PAA = 77:3:10:10 and 75:5:10:10).

The electrodes were prepared by firstly mixing $\text{SiO}_x@LiF$ composites with PAA binder with a mass ratio of 9:1, using water as dispersant. Then the slurry was cast on the Cu collector and dried in a vacuum oven at 80 °C for 12 hours.

Cell Assembly

2032-coin cells were assembled in an argon-filled glove box containing <0.1 ppm water and oxygen. For the half cells, the Li foil was used as the counter electrode and the Celgard 2500 membranes were used as the separator. 1 mol L⁻¹ lithium hexafluorophosphate (LiPF_6) in DEC and EC (1:1 in volume) with 10 wt.% fluoroethylene carbonate (FEC) and 1 wt.% vinylene carbonate (VC) was used as electrolyte.

For the assembled of full cells, $\text{SiO}_x@3\% LiF || Li$ half cells were assembled firstly and discharged to 0.01 V at 0.1 C (1C = 1000 mAh g⁻¹). The diameter of $\text{SiO}_x@3\% LiF$ electrodes are 14 mm. Subsequently, the $\text{SiO}_x@3\% LiF$ electrodes were taken out without any process. The $\text{SiO}_x||\text{NCM622}$ full cells were assembled in the order of NCM622-separator- $\text{SiO}_x@3\%LiF$ with 1.0M LiPF_6 in EC: DMC: EMC=1:1:1 vol% as electrolyte. The thickness of the SiO_x -based electrodes are 15~18 μm and the mass loading of the electrodes are 0.8~1 mg cm⁻² for half cells. These data are the same as the electrodes used in full cells. The current collector of cathode is aluminum foil, and that of anode is copper foil. The N/P ratio of the $\text{SiO}_x||\text{NCM622}$ system is 1.1~1.2. NCM622 cathodes were cut into 10 mm disks.

Characterization

X-ray diffractions (XRD) were obtained at room temperature using a Smartlab 9kw advance powder X-ray Cu Ka radiation diffractometer with Cu Ka radiation ($\lambda = 0.154 \text{ nm}$) in a step of $10^\circ \text{ min}^{-1}$ over a 2θ range of $10^\circ - 80^\circ$. X-ray photoelectron spectroscopy (XPS) was measured with a Thermo Scientific K-Alpha X-ray photoelectron spectrometer operating at an Al K α radiation ($h\nu = 1486.6 \text{ eV}$) source. To evaluate electrochemical performance, galvanostatic charge–discharge cycling tests were carried out between 0.01 and 1.5 V. CV tests were recorded on an electrochemical work station (CHI 660E) between 0.01 and 1.5 V. Electrochemical impedance spectroscopy (EIS) experiments were performed on an electrochemical work station (CHI 660E) within a frequency range from 100 kHz to 0.01 Hz with the amplitude of 5 mV.

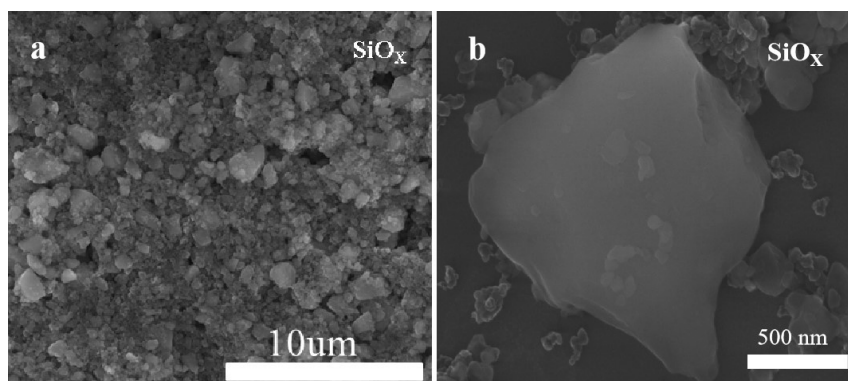


Figure S1. (a-b) SEM images of $\text{SiO}_x/\text{Super P}$ composite.

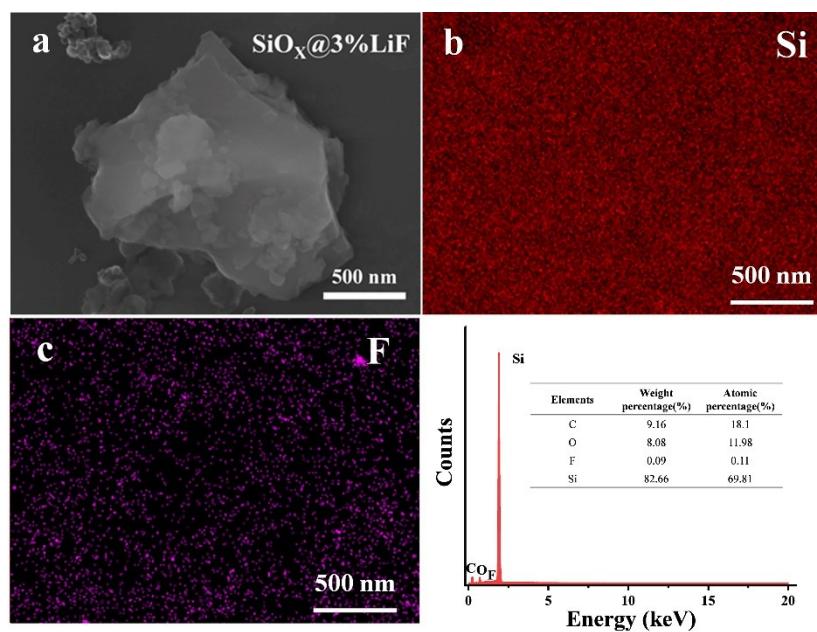


Figure S2. (a) SEM image of $\text{SiO}_x@3\%\text{LiF}$. (b) EDS mapping of Si and (c) F elements of $\text{SiO}_x@3\%\text{LiF}$. (d) EDX spectra of $\text{SiO}_x@3\%\text{LiF}$.

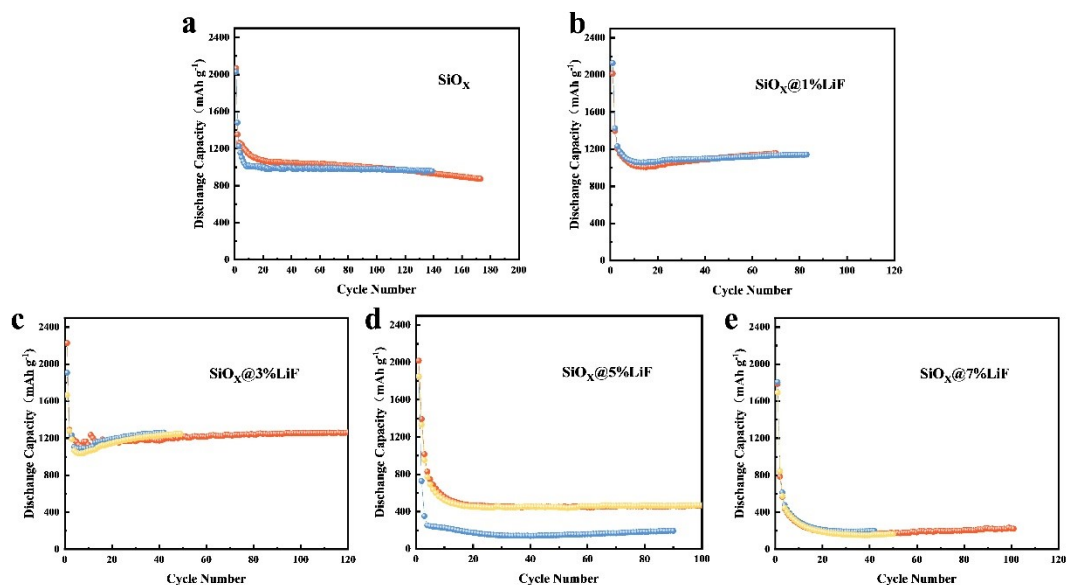


Figure S3. (a-e) The 4 groups of cyclic performance for SiO_x and SiO_x with 1%, 3%, 5% and 7% LiF prelithation.

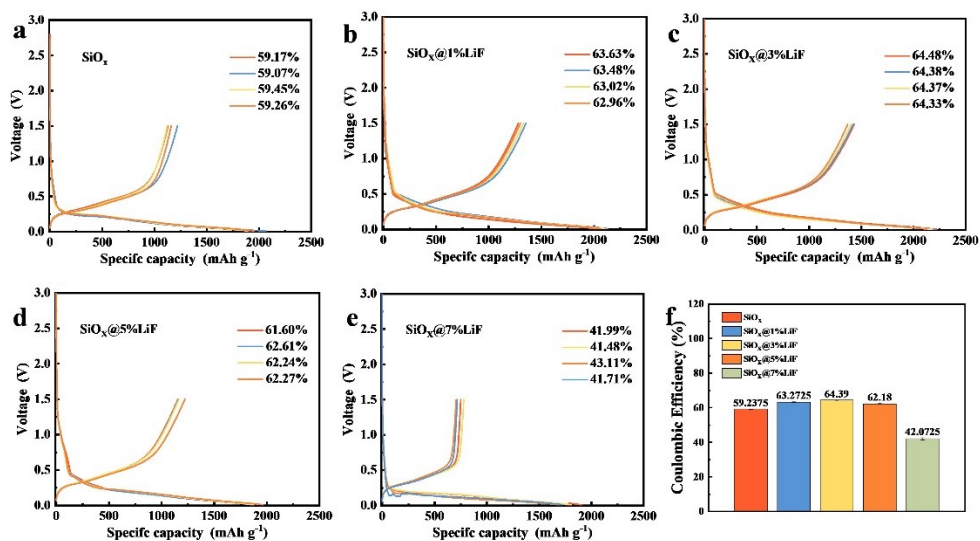


Figure S4. (a-e) The 4 groups of charge-discharge curves for SiO_x and SiO_x with 1%, 3%, 5% and 7% LiF prelithation at 1st cycle. (f) The average values of ICE for SiO_x and SiO_x with 1%, 3%, 5% and 7% LiF.

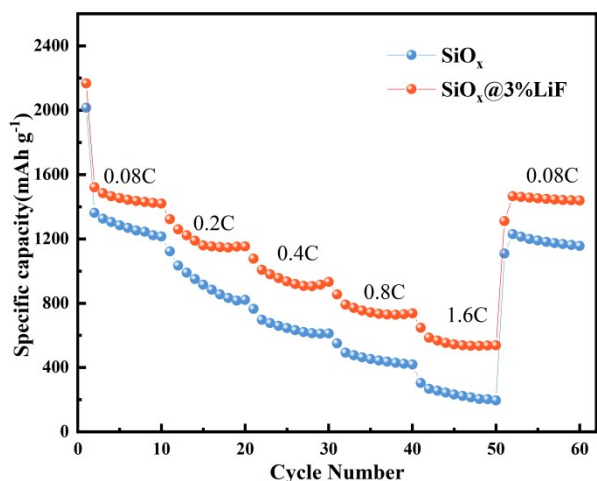


Figure S5. The rate performance of SiO_x and SiO_x@3%LiF.

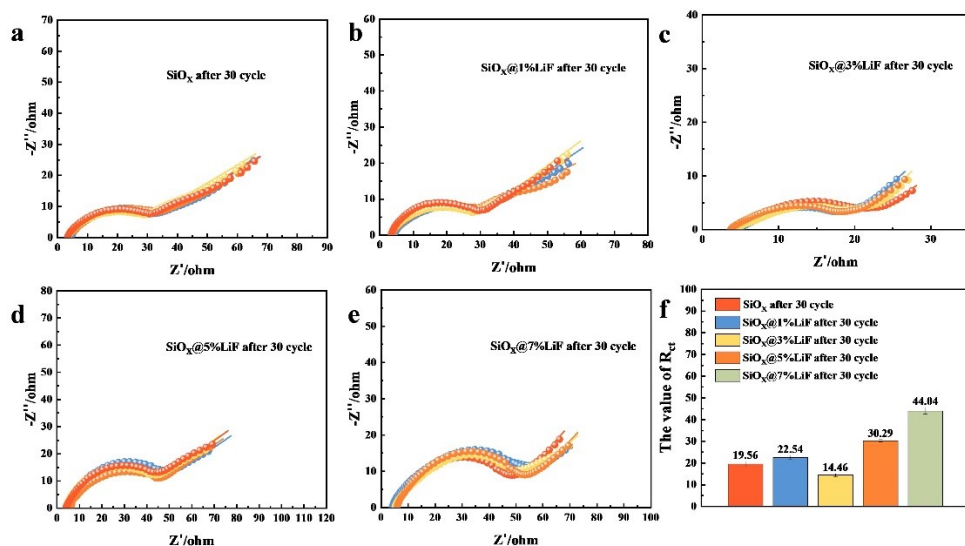


Figure S6. (a-e) The 4 groups of EIS spectra for SiO_x and SiO_x with 1%, 3%, 5% and 7% LiF pre-lithiation after 30 cycles. (f) The average values of R_{ct} for SiO_x and SiO_x with 1%, 3%, 5% and 7% LiF pre-lithiation after 30 cycles.

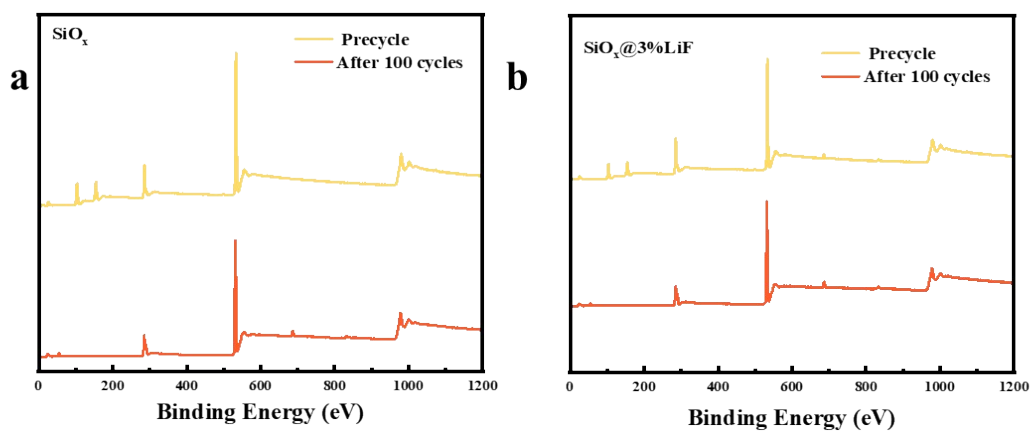


Figure S7. The full spectra of (a) SiO_x and (b) $\text{SiO}_x@3\%\text{LiF}$ after precycle and 100 cycles.

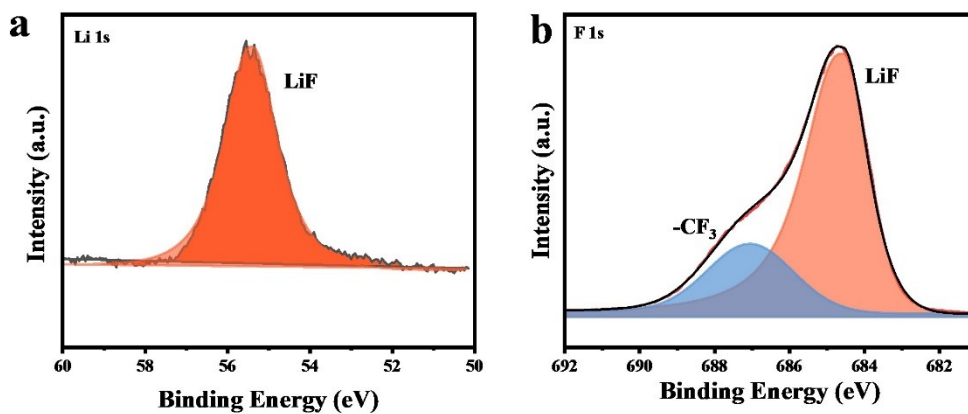


Figure S8. XPS spectra of LiF (a) $\text{Li } 1s$, (b) $\text{F } 1s$.

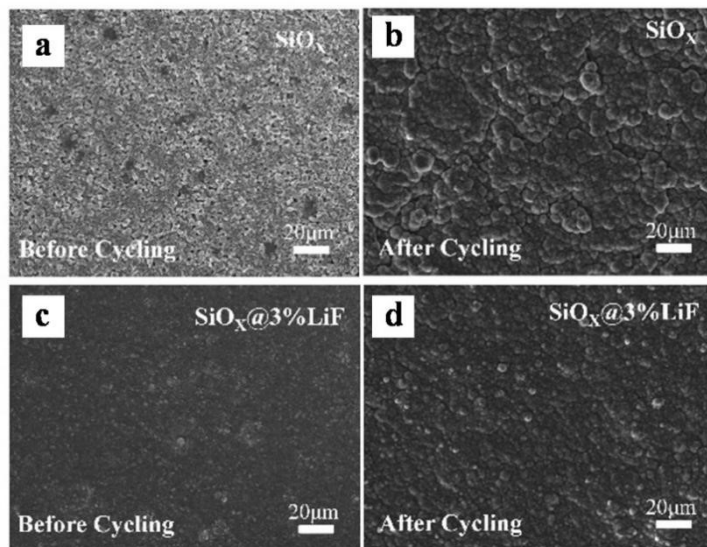


Figure S9. SEM images of (a-b) the surface of SiO_x anode before cycling and after 100 cycles; (c-d) the surface of SiO_x@3% LiF anode before cycling and after 100 cycles.

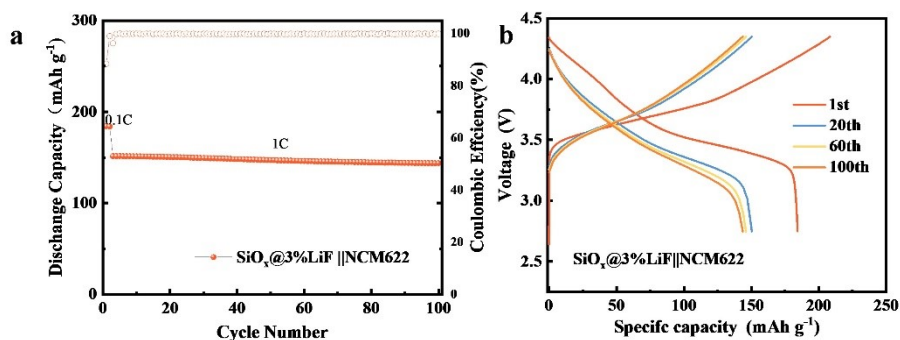


Figure S10. (a) The cyclic performance and (b) charge-discharge curves of SiO_x@3%LiF||NCM622 full cells at 1 C.

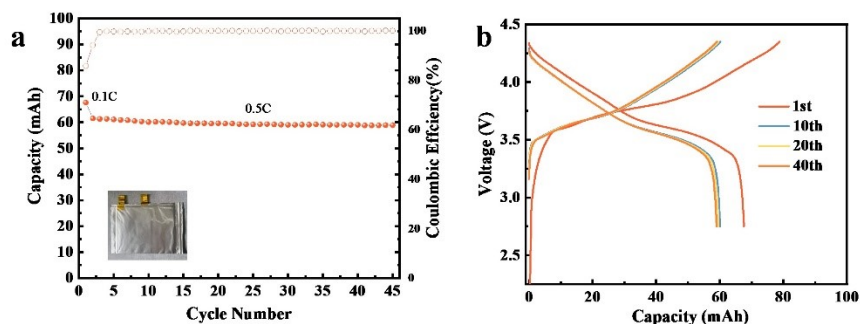


Figure S11. (a) The cyclic performance and (b) charge-discharge curves of SiO_x@3%LiF||NCM622 pouch cells at 0.5 C.

Table S1. Resistance values of SiO_x and SiO_x@3%LiF half cells after different cycles

Cycle Number	Anode	R _s	R _{SEI}	R _{ct}
After	SiO _x	3.77	161.80	602.90
precycle	SiO _x @3%LiF	2.14	62.22	280.10
After 100	SiO _x	4.15	23.46	2.14
cycles	SiO _x @3%LiF	3.43	1.394	5.39