# **Supporting information**

# Tailoring Multilayer Fine-Grained Solid Electrolyte Interphase by Pulse Electrochemical Activation Maneuver for Stable Si/C Anodes

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#### **Experimental section**

#### **Electrolyte preparation**

Materials: The Si/C powder in this work is purchased from Shanghai St-Nano Science and Technology Co., Ltd. According to their product specifications, this Si/C material contains 30% Si and 70% carbon, its specific surface area is only  $3.19 \text{ m}^2 \text{ g}^{-1}$  and the tap density is about 0.89 g cm<sup>-3</sup>. Battery-grade Li salts of lithium bis (fluor sulfonyl) imide (LiFSI, 99.5%) and anhydrous lithium nitrate (LiNO<sub>3</sub>,99.8%) were obtained from Sigma-Aldrich Co., Ltd, and were vacuum-dried at 100°C under Argon overnight. The 1,2-dimethoxyethane (DME), fluoroethylene carbonate (FEC), and 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE) solvents were received from Duoduo Chem Co., Ltd., which were dried with molecular sieves for 2 days. All solvents and lithium salts are transported into an argon-filled glove box as received. The electrolyte and all cell preparation were done in an argon-filled glovebox with both oxygen and water content of < 0.5 ppm and tested under room temperature. The LHCE-FL electrolyte was prepared by dissolving 2.8 mmol LiFSI/0.38mmol LiNO<sub>3</sub> in 0.8 ml DME and 2 ml TTE with 10 vol.% FEC.

Electrodes preparation: Commercialized Si-based materials were purchased from Shenzhen Kejin Star Technology Co., Ltd. China. The Super P (SP) conductive carbon (average diameter = 30 nm) and polyacrylate composite binders (PAA) (99%) (Mw = ~75 kDa) binder was obtained from Shanghai Aladdin Bio-Chem Technology Co., Ltd. with ~99% degree of hydrolysis. The Si/C materials electrodes were prepared with Si/C materials powder, PAA binder, and SP at 7:2:1 wt%. The mixture was then dispersed in deionized water and homogenized using a dispersing emulsifier (Fluko FA25, Shanghai) at a speed of 10,000 rpm for 30 min, followed by casting the asprepared slurry onto Cu foil ( $1.2\sim1.4$  mg cm<sup>-2</sup>) and dried at 60°C for 6 h. The dried laminate was calendared and punched into 13 mm discs, which were further dried at 120°C for 16 h under vacuum. The commercial LFP cathodes were obtained from Pylon Technologies, Co. Ltd. And Tenpower, Co. Ltd., respectively.

## **Structure Characterizations**

The morphologies of Si-based materials anodes were characterized by scanning electron microscopy (SEM; JSM7000 instrument, JEOL). The cryogenic transmission electron microscopy (Cryo-TEM) characterizations were carried out using a Thermo Scientific Themis 300 operated at an accelerating voltage of 300 kV, which was employed to investigate the solid electrolyte interface (SEI) morphologies on Si-based materials surfaces. Sensofar 3D optical profiler (5Mpx: 2442x2048) and AFM tests for Si/C materials electrode surface roughness were tested on VEECO Dimension 3100+ Nanoscope. The SEI films on different electrodes were analyzed by X-ray photoelectron spectroscopy (XPS) was performed on the Thermo Scientific ESCALAB 250Xi using 200 W monochromated Al Ka radiation. All binding energy peaks were calibrated by C 1s at 284.5 eV. In-situ optical tests were conducted on the microscope (YM710TR, YUESCOPE, China) using Li || Si/C symmetric cells with a current of 0.2 mA. All samples collected from the disassembled cells were washed three times using pure DME solvent to clean the surface residual Li salts. After drying in an Ar-filled glove box, all samples were sealed in Ar-filled containers to avoid direct contact with air and moisture for characterization.

#### **Electrochemical test**

All coin-type cells (CR2032) were assembled in an argon-filled glove box. Both the Li||Si/C half cells and the Si/C /LFP full cells were assembled with a Celgard 2500 separator and 50  $\mu$ L of electrolyte. CV was performed at a rate of 0.1 mV s<sup>-1</sup> on the Autolab potentiostat (Autolab Instruments, Netherlands). The cycling performance and rate capability of the cells were evaluated on a Neware battery cycler (CT-4008T-5V 10mA-164, Shenzhen, China). The Li||Si/C materials half-cell was cycled at 0.01–2 V (vs. Li /Li<sup>+</sup>). In terms of Si/C ||LFP full-cell, it was tested at the voltage range of 2.5–3.8 V. The EIS test was performed in different states of charge. A galvanostatic discharge operation was performed on the Li||Si/C materials half-cell and the EIS test was performed every 300 s. The voltage range of the galvanostatic discharge tests was 0.01– 2.0 V, and the current density was 0.1 mA. The frequency range of the EIS test was  $10^{-2}$  to  $10^5$  Hz, and the amplitude was 5 mV. The test method of the charging process was the same as that of the discharging process. Galvanostatic intermittent titration technique (GITT) was performed on Neware CT-4008 to calculate the  $D_{\text{Li}}^+$ . The voltage relaxation time was set to 15 min and the boost time was 15 min between each pulse. All tests were conducted at 25 °C. To assess the practical performance of the fabricated LiFePO<sub>4</sub>-based pouch cell, a flight test was conducted using a commercial quadcopter (L106-DRONE) with four brushless motors for medium-load outdoor use. A custom LiFePO<sub>4</sub> battery pack (3.2 V, 2000 mAh), assembled from pouch cells, was connected to the drone via standard XT60 connectors.

#### Density functional theory (DFT) calculations of theoretical resolution voltage

Density functional theory (DFT) calculations were performed using the VASP code.<sup>1</sup> The exchange-correlation effects were treated with the Perdew-Burke-Ernzerhof (PBE)<sup>2</sup> functional within the generalized gradient approximation (GGA).<sup>3</sup> To describe the electronic eigenfunction expansion, the projector augmented-wave (PAW)<sup>4</sup> pseudopotential was applied with a kinetic energy cut-off of 500 eV. A vacuum thickness of 50 Å was introduced to minimize interlayer interactions. Brillouin-zone integration was carried out using a  $\Gamma$ -centered 1 × 1 × 1 Monkhorst-Pack k-point mesh. All atomic positions were fully relaxed until the energy and force converged to tolerances of 1 × 10<sup>-6</sup> eV and 0.01 eV Å<sup>-1</sup>, respectively. To account for long-range interactions, the dispersion-corrected DFT-D method was employed. <sup>5</sup>

The Gibbs free energy change ( $\Delta G$ ) was calculated by the computational hydrogen electrode (CHE) model as follows:

$$\Delta G = \Delta E + \Delta Z P E - T \Delta S \tag{1}$$

where  $\Delta E$  is the reaction energy obtained by the total energy difference between the reactant and product molecules absorbed on the catalyst surface and  $\Delta S$  is the change in entropy for each reaction,  $\Delta ZPE$  is the zero-point energy correction to the Gibbs free energy.

#### Density Function Theory (DFT) calculation of Li<sup>+</sup> diffusion

First-principles calculations were performed using VASP <sup>6</sup>, with the Generalized

Gradient Approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) functional to describe the exchange-correlation interactions. A plane wave basis set with a cutoff energy of 450 eV was employed, and a  $2\times3\times1$  Gamma-centered k-point mesh was used. Atomic positions were fully relaxed until the residual forces were less than 0.02 eV Å<sup>-1</sup>, with a total energy convergence criterion of  $10^{-5}$  eV. The diffusion barriers for Li<sup>+</sup> on the surfaces of layer 1 and layer 2 were determined using the Climbing Image Nudged Elastic Band (CI-NEB) method 57, ensuring satisfactory energy convergence at  $10^{-6}$  eV and force convergence at 0.02 eV Å<sup>-1</sup>. A  $2\times2\times1$  Gamma-centered mesh was used for this calculation.

#### **COMSOL** simulation method

Finite element simulations were performed using the COMSOL 6.2 AC/DC module. In this model, the stress variation resulting from structural differences between the coating layers of the electrolyte particles is represented by the electric field strength. Specifically, higher electric field strength corresponds to greater stress exerted on the material. A two-dimensional model was constructed based on the collection diagram. The electric field strength within the model is determined by the following equation:

 $j = \sigma E$ 

Where *J* is the current density, in mA cm<sup>-2</sup>,  $\sigma$  is the conductivity, in mS cm<sup>-1</sup>, and E is the electric field strength, in V m<sup>-1</sup>. In this study, *J* is set to 10 mA cm<sup>-2</sup> and  $\sigma$  to 9.91  $\mu$ s m<sup>-1</sup>. In summary, the electrode material itself is selected as the input source term of the current density, the peripheral square calculation domain boundary is set as the output source term of the current density, and all other boundaries are defined as insulation. According to the above boundary conditions and parameters, the model is numerically calculated.

**Supporting Figures** 



Fig. S1 Snapshots of the MD simulation of LHCE-FL electrolyte.



Fig. S2 Theoretical decomposition voltages of DME, FEC, LiFSI, and LiNO<sub>3</sub>.



Fig. S3 LSV curve of Si/C anode in LHCE-FL electrolyte.



**Fig. S4** Initial charge/discharge curves of the Si/C at 0.1 mA, while the constant voltage at 1.3, 1.4, and 1.5 V, respectively.



**Fig. S5** Initial charge/discharge curves of the Si/C at 0.1 mA, while the constant voltage at 0.9, 1.0, and 1.1 V, respectively.



**Fig. S6** Initial charge/discharge curves of the Si/C at 0.1 mA, while the constant voltage at 0.75, 0.8, and 0.85 V, respectively.



Fig. S7 Initial charge/discharge curves of Si/C w/o consSEI at 0.1 mA.



Fig. S8 Initial charge/discharge curves of Si/C with consSEI-10th at 0.1 mA.



Fig. S9 Initial charge/discharge curves of Si/C with consSEI-100th at 0.1 mA.



Fig. S10 Initial charge/discharge curves of Si/C with consSEI-200th at 0.1 mA.



Fig. S11 Initial charge/discharge curves of Si/C with consSEI-500th at 0.1 mA.



Fig. S12 Cyro-TEM of SEI in w/o consSEI.



**Fig. S13** (a) Cyro-TEM of SEI in consSEI-10th; (b) magnified HRTEM images and corresponding FFT images of SEI in consSEI-10th.



Fig. S14 Cyro-TEM of SEI in consSEI-100th.



**Fig. S15** (a) F 1s and (d) N 1s XPS of the Si/C anode at 1.4 V of the initial cycle, (b) F 1s and (e) N 1s XPS of the Si/C anode at 1.0 V of the initial cycle, (c) F 1s and (f) N 1s XPS of the Si/C anode at 0.8 V of the initial cycle.



**Fig. S16** (a) F 1s and (d) N 1s XPS of the Si/C anode in Stage 1, (b) F 1s and (e) N 1s XPS of the Si/C anode in Stage 1 to 2, (c) F 1s and (f) N 1s XPS of the Si/C anode in Stage 1 to 2 to 3.



Fig. S17 2D TOF-SIMS sputtering images and the selected secondary ion fragments (a)  $\text{LiF}_2^-$ , (b)  $\text{LiN}^-$ , (c)  $\text{CHO}_2^-$ , and (d)  $\text{CH}_3\text{O}^-$ .



Fig. S18 The lattice plane of (a)  $Li_3N$  and (b) LiF.



**Fig. S19** In-situ EIS plots of Li || Si/C half cells with (a) w/o consSEI and (b) consSEI-100th.



Fig. S20 DRT analysis of the EIS data of Si/C with consSEI-100th.<sup>7</sup>



**Fig. S21** The GITT curves of Li || Si/C half cells with various SEI structures. (a) w/o consSEI, (b) consSEI-100th.



Fig. S22 The original SEI structure of w/o consSEI and consSEI-100th.



Fig. S23 AFM image of pristine Si/C.



**Fig. S24** Height sensor AFM images of (a) pristine Si/C and after cycling with (b) w/o consSEI, and (c) consSEI-100th.



**Fig. S25** 2D and 3D images of 3D surface optical profiler. (a) Stage 1, (b) Stage 1 to 2, (c) Stage 1 to 2 to 3.



**Fig. S26** 2D images of 3D surface optical profiler. (a) Pristine, (b) w/o consSEI, (c) consSEI-100th.



Fig. S27 Initial charge/discharge curves of Si/C at 0.1 A  $g^{-1}$  with w/o consSEI and consSEI-100th.



Fig. S28 The self-made three-electrode (Si/C-Li-LiFePO<sub>4</sub>) setup.



Fig. S29 The pulse voltage-time curve of Si/C  $\parallel$  LiFePO\_4.



**Fig. S30** Initial charge/discharge curve at 0.1 A  $g^{-1}$  of Si/C || LiFePO<sub>4</sub> with consSEI-100th.



Fig. S31 Charge/discharge curves of the Si/C  $\parallel$  LiFePO<sub>4</sub> cell with consSEI-100th at different cycling numbers.



Fig. S32 The structural diagram of the Si/C  $\parallel$  LiFePO4 pouch cell.



Fig. S33 Initial charge/discharge curve at 0.1 A of the Si/C  $\parallel$  LiFePO<sub>4</sub> pouch cell with consSEI-100th.



Fig. S34 Charge/discharge curves of the Si/C  $\parallel$  LiFePO<sub>4</sub> pouch cell with consSEI-100th at different cycling numbers.



Fig. S35 Cross-sectional SEM images of the Si/C electrodes in (a) pristine, (b) w/o consSEI, and (c) consSEI-100th.



**Fig. S36** In-situ optical images of Li  $\parallel$  Si symmetric cells for cycling at a current of 0.2 mA with w/o consSEI (a) before and (b) after cycling 12 h.



**Fig. S37** In-situ optical images of Li || Si half cells for cycling at a current of 0.2 mA with consSEI-100th (a) before and (b) after cycling for 12h.



Fig. S38 SEM images of (a) pristine, (b) w/o consSEI, and (c) consSEI-100th.

Parameters					
Areal capacity (mAh cm <sup>-2</sup> )	Temperature (°C)	Electrolyte-to- active-material (E/A) ratio	Cycle number	Cell format	References
1.1	25	$23 \ \mu L/mAh$	200	Si/C  LiNCM	[51]
1.7	25	21 µL/mAh	200	SiO <sub>x</sub> /C   NCM811	[52]
0.6	25	N.G	150	Si/C   NCM811	[53]
1.5	25	17 μL/mAh	60	Si/C   NCM532	[54]
0.5	25	N.G	500	Si/C  LiFePO <sub>4</sub>	[55]
1.8	25	$27 \ \mu L/mAh$	600	Si/C  LiFePO <sub>4</sub>	[56]
1.9	25	14 µL/mAh	100	Si  NCM532	[57]
2.6	25	N.G	100	Si/C   NCM811	[58]
2.9	25	10 µL/mAh	583	Si/C  LiFePO <sub>4</sub>	This work

 Table S1. The parameter comparison of those works in Figure 5e.

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