# **Supporting Information**

# Sulfur-Doped Carbon Interface Modification for high-performance silicon Anodes in Lithium-Ion Batteries<sup>+</sup>

Jingyan Li,<sup>a,b</sup> Shuqi Wang,<sup>a,b</sup> Fei Wang,<sup>c</sup>\* Zhendong Liu,<sup>b</sup> Chengzhi Zhang,<sup>b</sup>\* Weidong Zhang,<sup>c</sup> Quanbing Liu,<sup>a</sup> and Dai Dang<sup>a</sup>\*

<sup>a</sup>School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou, Guangdong, 510006, China <sup>b</sup>Ji Hua Laboratory, Foshan, Guangdong, 528000, China <sup>c</sup>Department of Materials Science and Engineering, National University of Singapore, Singapore 117574, Republic of Singapore

## \*Corresponding authors.

Fei Wang, Department of Materials Science and Engineering, National University of Singapore, Singapore 117574, Republic of Singapore.

Email: feiwang@nus.edu.sg

Chengzhi Zhang, Ji Hua Laboratory, Foshan, Guangdong, 528000, China.

Email: zhangchz@jihualab.ac.cn

Dai Dang, School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou, Guangdong, 510006, China Email: dangdai@gdut.edu.cn

#### **Experimental Section**

#### Materials

The silicon particles were purchased from Shanghai Maclean's Biochemical Technology Co., Ltd.; the lithium-ion battery-grade electrolyte formulation of 4 M  $LiPF_6$  in EMC = 100Vol.% with 2%VC was purchased from Suzhou Duoduo Chemical Technology Co., Ltd.; the pp separator and copper foil from Shenzhen Youyan Technology Co., Ltd.; and the battery case from Dongguan Krud Experimental Equipment Technology Co., Ltd.

#### **Preparation of the Si–SDCL**

First, we prepared a hydrochloric Acid-Tris buffer solution with a pH comprised between 7 and 7.5. Next, we added 300 mg of nanosilicon particles to the solution, stirred for 30 minutes, and then ultrasonically dispersed the mixture for 20 minutes. Subsequently, we added dopamine hydrochloride powder to the solution at weight ratios of 15%, 25%, and 35%. Next we maintained the solution in a water bath at a constant temperature of 30°C, and stirred for 48 hours to allow the dopamine to undergo self-polymerization and fully coat the surface of the silicon particles. Afterward, we centrifuged and washed the material repeatedly until it reached a 7 pH. The material was then placed in a forced-air drying oven at 80°C for 12 hours, then further dryed in a vacuum oven at 80°C for another 12 hours. Next, we used a tube furnace to heat the dried material at a rate of 1°C per minute to 500°C under an argon atmosphere, before the temperature was kept constant for two hours to obtain the Si-CL material. Finally, we placed the Si-CL material along with an alumina crucible containing CS<sub>2</sub> solution into the tube furnace. Under an argon atmosphere, we heated the system at a rate of 5°C per minute to 600°C, and we held the temperature for two hours to complete the sulfurization process. The resulting material was named Si-SDCL. Depending on the dopamine addition amounts of 15%, 25%, and 35%, the materials were designated as Si-SDCL-15%, Si-SDCL-25%, and Si-SDCL-35%, respectively.

## **Preparation of Anode**

Si-SDCL-15%, Si-SDCL-25%, Si-SDCL-35%, Si-CL-25%, and pristine silicon were used as active materials. Electrode slurries were prepared by mixing the active material, conductive agent, and binder in a weight ratio of 8:1:1, and the slurries were coated onto the copper current collectors. After the slurries had been fully dried, the electrodes were cut into 12 mm diameter circular disks using a mold. The batteries were then assembled in an argon-filled glove box, with lithium metal for the counter electrode. The assembly of lithium-ion half-cells was conducted in an argon-filled glove box.

#### **Preparation of Cathode**

Firstly, the slurry of LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> (NCM811), Super P Conductive Carbon Black (Super-P), and Polyvinylidene Fluoride (PVDF) in N-Methyl-2-pyrrolidone (NMP) with a mass ratio of 8:1:1 was uniformly coated on an aluminum foil. After being dried in a vacuum oven at 60 °C overnight, NVP electrodes were collected by cutting the above-dried aluminum foils into discs with a diameter of 13 mm. The N/P ratio of the full battery is 1.1.

### **Electrochemical characterization**

The electrochemical performance of the different anodes was tested using CR-2032 coin cells. The cycling performance of the cells was evaluated at a current density of 0.2 A  $g^{-1}$ . cyclic voltammetry (CV) curves were obtained using an electrochemical workstation (Bio-Logic) within a voltage range of 1.5 to 0.01 V. Electrochemical impedance spectroscopy (EIS) curves were obtained in the frequency range of 0.01Hz~100kHz

#### Characterization

The crystal structure of Si-SDCL powder was analyzed using an X-ray diffractometer (XRD, Bruker D8 DISCOVER). The morphology of the electrodes was characterized using a field emission scanning electron microscope (SEM, Thermo Fisher Verios 5 UC). The microstructure of the Si-SDCL powder was examined using

a field emission transmission electron microscope (TEM, Thermo Fisher Talos F200X G2). The properties and composition of the solid electrolyte interphase (SEI) were investigated using an X-ray photoelectron spectrometer (XPS, Thermo Fisher Escalab Xi+), and a time-of-flight secondary ion mass spectrometer (TOF-SIMs, IONTOF GmbH M6).

#### **Computational methods**

In this work, the simulations are based on density-functional theory (DFT) and the PBE generalized gradient approximation (GGA) function to describe the exchangecorrelation energy. The Graphite and S doped structures were firstly established on graphite, respectively, and the stable structural configurations were obtained by structural relaxation. The energy cut-off and Monkhorst-Pack k-point grid settings are 450 eV and  $5 \times 5 \times 1$ , respectively. During the geometry optimization process, the convergence tolerance is set to an energy of 1E-5eV per atom and a maximum force of 0.03 eV Å<sup>-1</sup>. For the construction of the surface model, a vacuum of 15 Å is used to eliminate interactions between the periodic images.

The differential charge density formula used in this study is  $\Delta \rho = \rho AB - \rho A - \rho B$ , where  $\rho AB$  is the optimized structural charge density of the interface,  $\rho A$  is the charge density of material A (Graphite), and  $\rho B$  are the charge densities of the doped material B(S). By subtracting  $\rho A$  and  $\rho B$  from  $\rho AB$ , the change in charge density after the formation of the AB interface can be analyzed, including properties like the charge motion.

The CI-NEB method is used to explore the transition state and enhanced the accuracy of force calculations by conducting structural relaxation to 1E–7. Additionally, an optimization algorithm embedded in VASP is used to interpolated the points at three different positions. To validate the obtained transition state, its frequency was confirmed and the presence of only one imaginary frequency.

# **Supporting Figures**



Supporting Fig. 1 Raman spectrum of Si-CL-25% particles.



Supporting Fig. 2 The N 1s spectrum of Si-SDCL-35% (a) and Si-CL-25% (b) particles.



**Supporting Fig. 3** Nyquist plots of the experimental impedances for the Si–SDCL–25%, Si–CL–25% and Pristine-silicon (a) before cycling, and after (b) one, (c) five, and (d) 50 cycles.



**Supporting Fig. 4** GITT voltage plateau titration diagram of Si-SDCL-25%, Si-CL-25%, and Pristine-Si.

GITT provides a clear way to measure the lithium-ion diffusion ability of materials in a battery. The diffusion coefficient,  $D_{Li}^{+}$ , can be calculated using the following formula:

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

where  $\tau$  is the relaxation time,  $n_m$  is the molar number,  $V_m$  is the molar volume of the electrode material, S is the effective contact area between the electrode and electrolyte,  $\Delta E_s$  is the voltage change induced by the pulse, and  $\Delta E_t$  is the voltage change during the constant current charge/discharge process.<sup>1</sup>



**Supporting Fig. 5** CV plots of the first five turns of (a) Si-CL-25% and (b) pristine-silicon. The CV plots of (c) Si-SDCL-25%, (d) Si-CL-25%, and (e) pristine-silicon at different scan rates are also shown.



Supporting Fig. 6 Changes in surface charge density of the carbon layer after sulfur doping.



**Supporting Fig. 7** The SEM images of (a) Si-SDCL-25%, (b) Si-CL-25%, and (c) pristine silicon anodes before (upper photo) and after (lower photo) cycling.



Supporting Fig. 8 Cycling performance (a) and rate performance (b) of Si-SDCL-15%, Si-SDCL-25%, Si-SDCL-35%.



Supporting Fig. 9 (a)-(b) The charge and discharge curves of Si-SDCL and Si-CL with different cycles, and (c) Pristine-Si for the first cycle.

# References

 Y. Yu, C. Yang, Y. Jiang, Z. Shang, J. Zhu, J. Zhang and M. Jiang, *Adv. Energy Mater.*, 2025, 15, 2403086.