

## A highly stable pre-lithiated SiO<sub>x</sub> anode coated with a “salt-in-polymer” layer

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funding

acquisition.

## Experimental

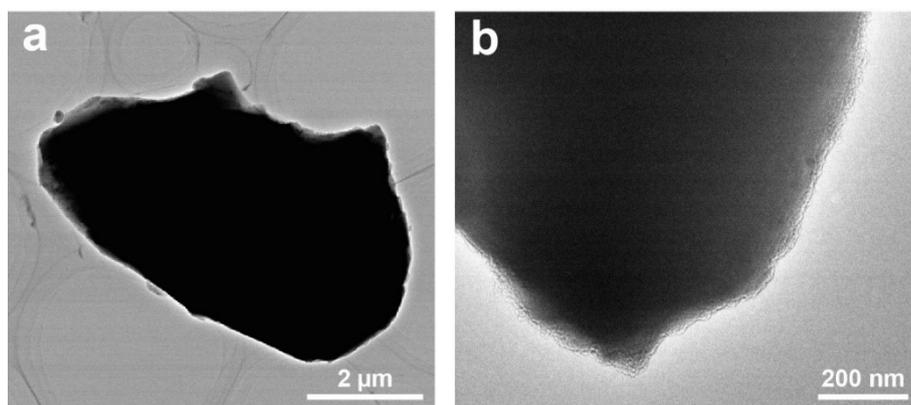
**Chemicals:** Pre-lithiated carbon-coated  $\text{SiO}_x$  microparticles (Li-MSiO<sub>x</sub>, median size D50 = 5  $\mu\text{m}$ ) were obtained from Beijing IAMetal New Energy Technology Co., LTD. Bis(trifluoromethane)sulfonimide lithium salt (LiTFSI) were purchased from Shanghai Aladdin Biochemical Technology Co., LTD. Lithium difluoro(oxalato)borate (LiDFOB) were purchased from Beijing Innochem Science & Technology Co., LTD. 1,3-Dioxolane (DOL) were purchased from Sigma-Aldrich (Shanghai) Trading Co., Ltd. n-Hexane were purchased from Shanghai Aladdin Biochemical Technology Co., LTD.

**Preparation of SP-Li-MSiO<sub>x</sub>:** Firstly, 500 mg Li-MSiO<sub>x</sub> was dispersed in 50 ml n-hexane under stirring for 0.5 h, and then sonicated for 1 h. Secondly, 1 M LiTFSI and 0.5 M LiDFOB in 100  $\mu\text{L}$  DOL was added into the above mixture under stirring and at a temperature of 65  $^\circ\text{C}$  for 10 h. During this process, DOL was polymerized into poly(1,3-dioxolane) (PDOL) via the cation-induced ring-opening polymerization mechanism.<sup>36</sup> Finally, the mixture was separated by centrifugation (10000 rpm) and washed with n-hexane. After drying under vacuum for 24h, the SP-Li-MSiO<sub>x</sub> material was obtained. Since PDOL, LiTFSI and LiDFOB are insoluble in the non-polar n-hexane solvent, a PDOL/LiTFSI/LiDFOB-based SP coating layer would be formed on the surface of Li-MSiO<sub>x</sub> particles.

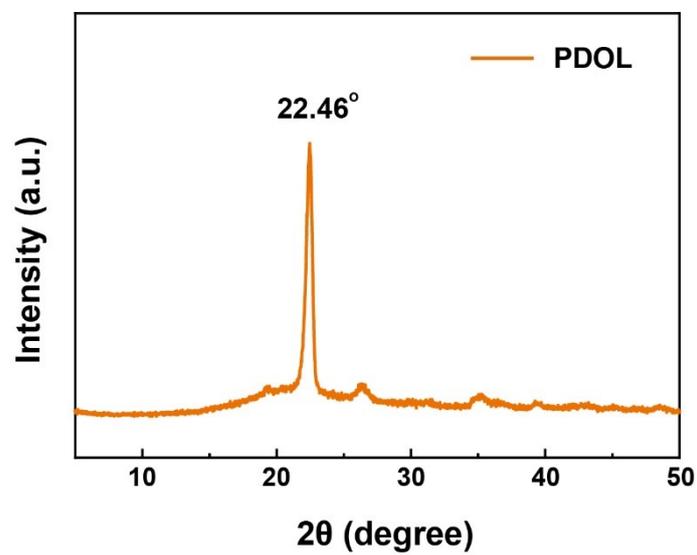
**Structural characterizations:** The microscopic morphologies of samples were investigated by using a field emission scanning electronic microscopy (SEM, Hitachi S-4800) operated at 10 kV and a field emission transmission electronic microscope (TEM, JEOL JEM-2100F) with an energy dispersive spectroscopy (EDS) system. The Fourier transform infrared (FTIR) spectra were performed by a Bruker EQUINOX55 FTIR spectrometer. Thermogravimetric analyses (TGA) were carried out by a TG/DTA6300 thermogravimetric analyzer from 40  $^\circ\text{C}$  to 700  $^\circ\text{C}$  at 10  $^\circ\text{C min}^{-1}$  under  $\text{N}_2$  atmosphere. X-ray photoelectron spectroscopies (XPS) were explored on a Thermo Scientific Escalab 250XI XPS device using 200 W monochromatized Al K $\alpha$

radiation. The X-ray diffraction (XRD) patterns of samples were carried out by using a Rigaku D/max 2500 X-ray diffractometer with Cu K $\alpha$  radiation. The atomic force microscopy (AFM) system (Bruker Corp., Dimension Icon) was employed to collect the topography and modulus images by using an insulating silicon AFM tip (Bruker Corp.) to scan the sample surface in the mode of peak force QNM (Quantitative Nano Mechanics). The surface and cross-sectional morphology analyses of the particles were performed by dual-beam focused ion beam (FEI Helios 600i).

***Electrochemical measurements:*** Electrochemical measurements were performed using 2032-type coin cells which were assembled in an argon-filled glove box with water and oxygen concentration less than 0.1 ppm. The electrode slurry consisting of 80 wt% active materials, 9 wt% super-P, 1 wt% CNT and 10 wt% binder (CMC/SBR) was mixed in a planetary mixer, and then coated on the copper foils by a doctor-blade process. After drying at 60 °C for 12 h under vacuum, the electrodes were punched into discs with a diameter of 10 mm for cell assembling. The areal mass loadings of active materials are 1.2 $\pm$ 0.1 mg cm<sup>-2</sup>. For the half-cell tests, the prepared electrodes, Li foils and Celgard 2500 polypropylene membranes were used as working electrodes, counter electrodes and separators, respectively. 1 M LiPF<sub>6</sub> dissolved in ethylene carbonate/dimethyl carbonate/diethyl carbonate (EC/DMC/DEC, 1:1:1 by volume) with 5% fluoroethylene carbonate (FEC) was employed as electrolyte. The charge-discharge measurements were taken under the current density of 0.05C (1C = 1400 mA g<sup>-1</sup>) for first three cycles and 0.2C for subsequent cycles in the voltage range between 0.005 and 1.5 V. The cyclic voltammetry (CV) measurements were carried out in the voltage window of 0.005–1.5 V (vs. Li<sup>+</sup>/Li) at the scan rate of 0.1 mV s<sup>-1</sup>. The electrochemical impedance spectral (EIS) measurements were obtained within a frequency range between 100 kHz and 0.1 Hz.



**Fig. S1** TEM images of SP-Li-MSiO<sub>x</sub> particles at different magnifications.



**Fig. S2** XRD pattern of pure PDOL.

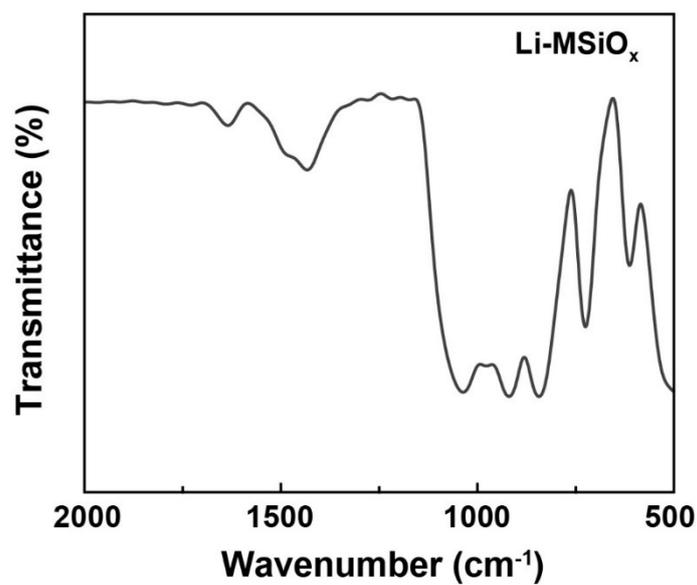


Fig. S3 FTIR spectrum of Li-MSiO<sub>x</sub>.

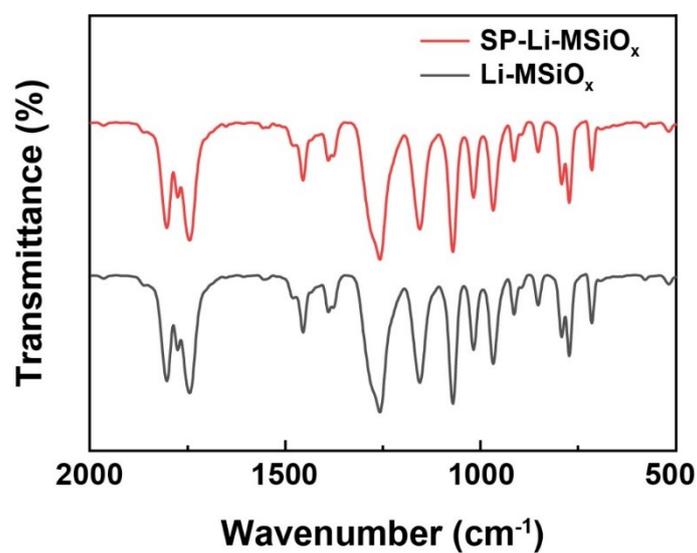
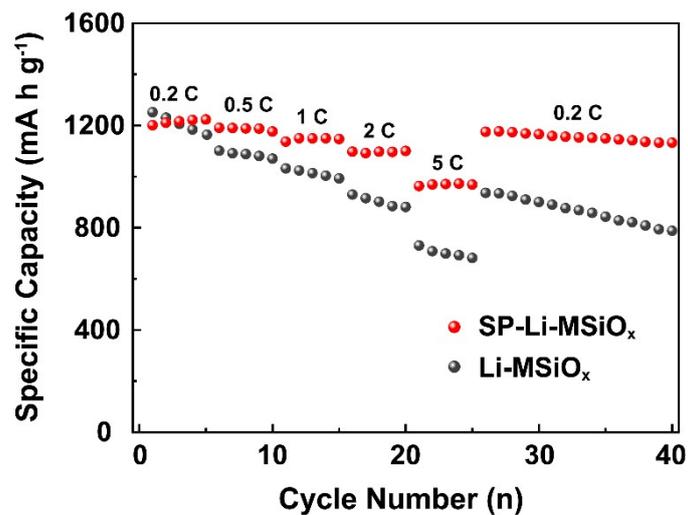
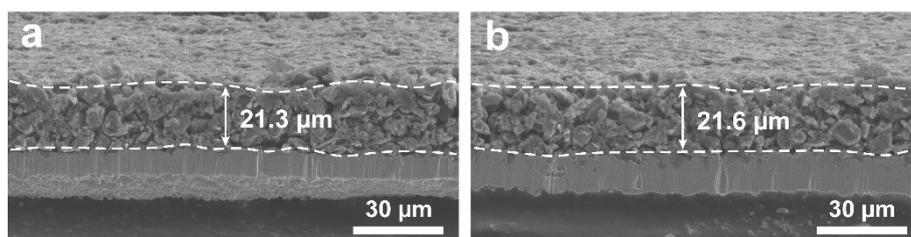


Fig. S4 FTIR spectra of Li-MSiO<sub>x</sub> and SP-Li-MSiO<sub>x</sub> soaked electrolyte.

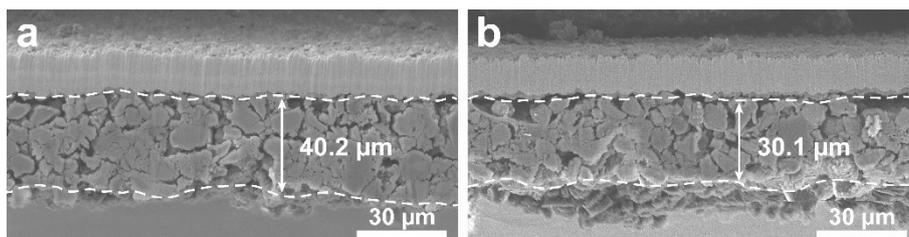
As shown in Fig. S4, no obvious difference was observed for the soaked electrolyte and control electrolyte, implying that the SP layer on the surface of SP-Li-MSiO<sub>x</sub> is stable in the liquid electrolyte.



**Fig. S5** The rate capabilities of Li-MSiO<sub>x</sub> and SP-Li-MSiO<sub>x</sub> under various current densities.

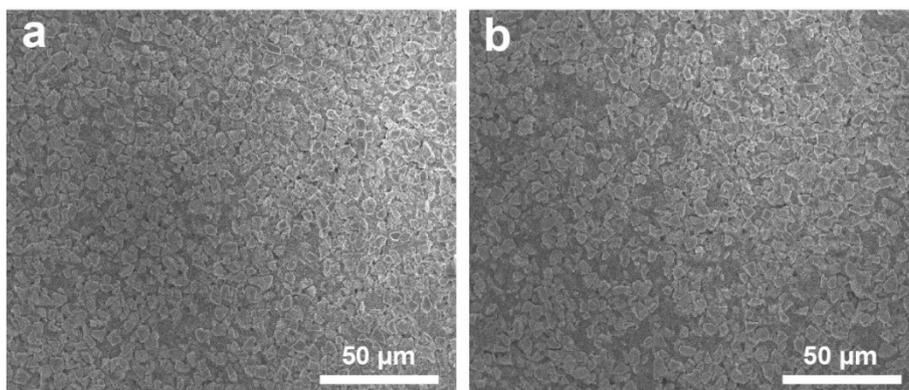


**Fig. S6** Cross-sectional SEM images of (a) Li-MSiO<sub>x</sub> and (b) SP-Li-MSiO<sub>x</sub> electrodes before cycling.

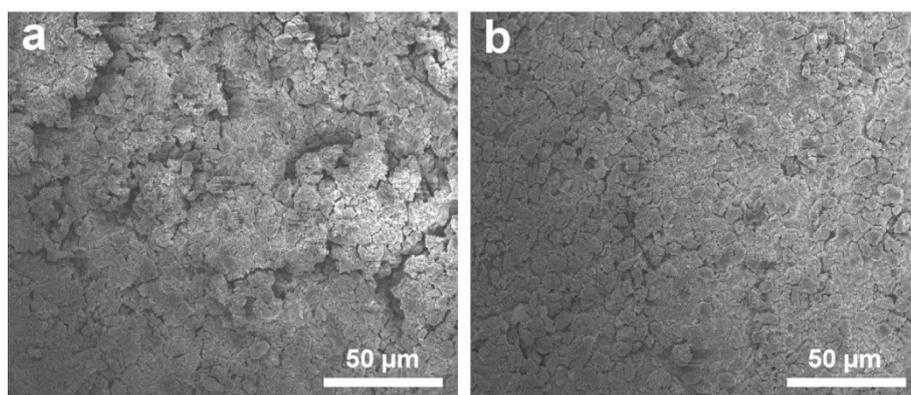


**Fig. S7** Cross-sectional SEM images of (a) Li-MSiO<sub>x</sub> and (b) SP-Li-MSiO<sub>x</sub> electrodes after 100 cycles.

After 100 cycles, the thickness of the Li-MSiO<sub>x</sub> electrode expanded to 40.2 μm, corresponding to an expansion of 88.7% (Fig. S6a and S7a). For the SP-Li-MSiO<sub>x</sub> electrode, the thickness expanded to 30.1 μm after 100 cycles, corresponding to an expansion of 39.3% (Fig. S6b and S7b).

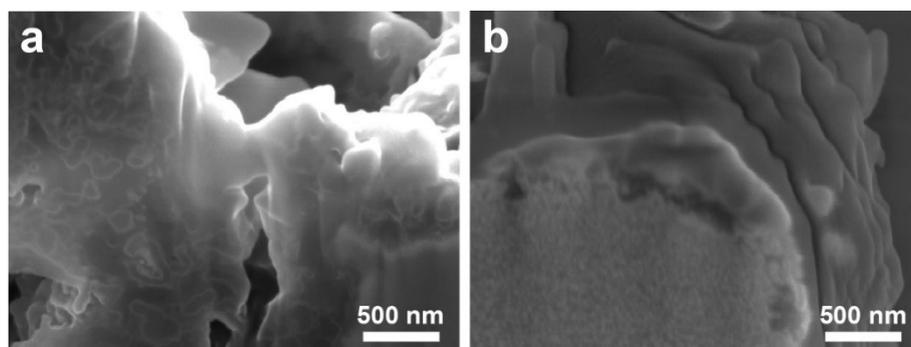


**Fig. S8** Top-view SEM images of (a) Li-MSiO<sub>x</sub> and (b) SP-Li-MSiO<sub>x</sub> electrodes before cycling.



**Fig. S9** Top-view SEM images of (a) Li-MSiO<sub>x</sub> and (b) SP-Li-MSiO<sub>x</sub> electrodes after 100 cycles.

From the top-view SEM images (Fig. S8 and S9), due to the huge and repeated volume expansion/contraction during cycling, serious delamination and cracks could be observed for the cycled Li-MSiO<sub>x</sub> electrode.



**Fig. S10** Cross-sectional SEM images of (a) Li-MSiO<sub>x</sub> and (b) SP-Li-MSiO<sub>x</sub> particles after 100 cycles.

**Table S1** The assignments of FTIR spectra of PDOL, LiTFSI, LiDFOB and SiO<sub>x</sub>.

Description of bands	Wavenumber (cm <sup>-1</sup> )
C=O of LiDFOB	1765
B-F of LiDFOB	1637
-SO <sub>2</sub> of LiTFSI	1353
-CF <sub>3</sub> of LiTFSI	1196
long-chain vibration of PDOL	921
Si-O-Si	1037