

Supporting Information for

Regulating the Solvation Structure of Li⁺ Enables Chemical Prelithiation of Silicon-Based Anodes Toward High-Energy Lithium-Ion Batteries

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S1 Experimental Section

S1.1 Half-Cell Assembly and Electrochemical Measurements

The electrochemical performances were characterized by assembling CR2032 coin cells with lithium foil as the counter electrode and (prelithiated) anode as working electrode. 1M LiPF₆ EC/DEC (1:1 v/v) electrolyte with 5 vol% FEC was used as the electrolyte. Galvanostatic charge/discharge measurements were performed in a potential range of 0.01-2.0 V using a multichannel battery testing system (LAND CT2001A). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were tested with electrochemical workstation system (Biologic Science Instruments, Claix, France).

S1.2 Full-Cell Assembly and Electrochemical Measurements

SiO/C and p-SiO/C were used as anodes and high voltage LiCoO₂ (LCO) were used as cathode. The mass ratio of cathode to anode was around 3:1, and the weight ratio of LCO: carbon black: PVDF was 8:1:1 in the cathode. The full-cells were galvanostatic charged/discharged at 0.1 A g⁻¹ in the electrochemical window of 3-4.35 V.

S1.3 Test of LAC redox potential

The electrolyte used in CV tests was 1 M LiPF₆ in THF/2-MTHF solvent containing 0.1 M Li-arene. The Cu foil and lithium metal were used as the counter electrode and as working electrode, respectively. CV curves were recorded at a scanning rate of 20 mV s⁻¹ at room temperature.

S1.4 Computational Details

Molecular dynamics (MD) simulations are performed with Gromacs, version 2019.6 (*SoftwareX* 1, 19–25, (2015)). Quantum chemical calculations (including desolvation energy and electrostatic potential mapping), are carried out with Gaussian 16, Multiwfn (*J. Comput. Chem.*, 33, 580 (2012)), and VMD program (*J. Mol. Graph* 14, 33–38 (1996)). The MD simulation systems consist of 100 lithium cations, 100 BP/MBP anions and 300 THF/MTHF solvent molecules. All species during MD simulations are modelled by GAFF force field (*J. Comput. Chem.* 25, 1157–1174, (2004)), with the RESP atomic charges derived by Multiwfn program by fitting to electrostatic potential calculated at the B3LYP-D3/6-31+G* level of theory. Lennard-Jones (LJ) potential truncated at 1.2 nm is used to calculate van der Waals interactions. LJ parameters between unlike atoms are derived by Lorentz–Berthelot mixing rules. Coulombic interactions are calculated with the particle-mesh Ewald method. Initial conformations are energy minimized by steepest descent algorithm, followed by 20-ns production runs at 298.15 K and 1 bar, with v-rescale thermostat and Berendsen barostat. The time step is 1 fs. Three dimensional periodic boundary conditions are considered during simulations.

The average solvation structure around a lithium cation is determined by the integrated radial distribution function analysis (coordination number) of a MD trajectory. On that basis, the solvation structures are extracted from the three MD simulations. Subsequently, the structures are optimized at the B3LYP-D3/6-31+G* level of theory, and further calculated at the B3LYP-D3/6-311G** level of theory. The electrostatic potential as well as the molecular isosurface are analyzed by Multiwfn and visualized by VMD program.

S2 Supplementary Figures

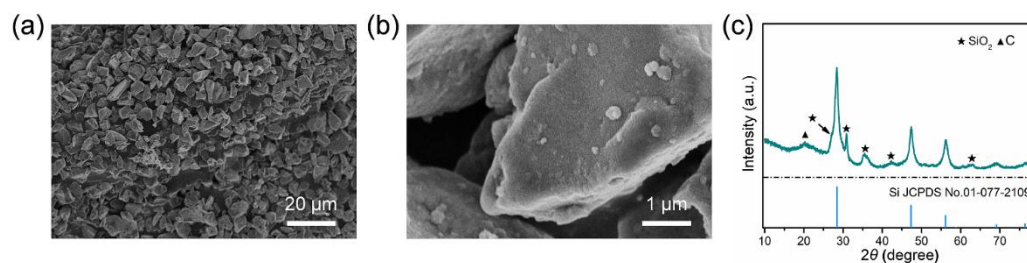


Fig. S1 (a-b) SEM images and (c) XRD pattern of the SiO/C particles

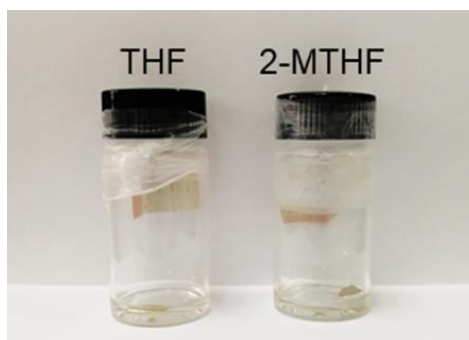


Fig. S2 Digital photograph of lithium metals immersed in THF or 2-MTHF solvents for 24 h

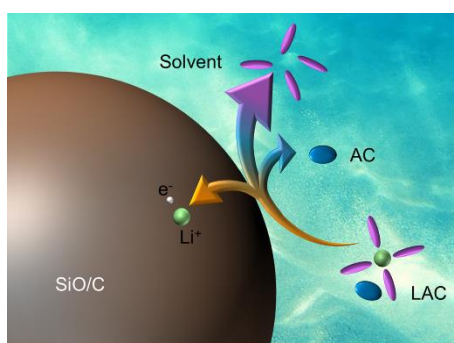


Fig. S3 The schematic diagram of Li^+ desolvation process in LAC reagents

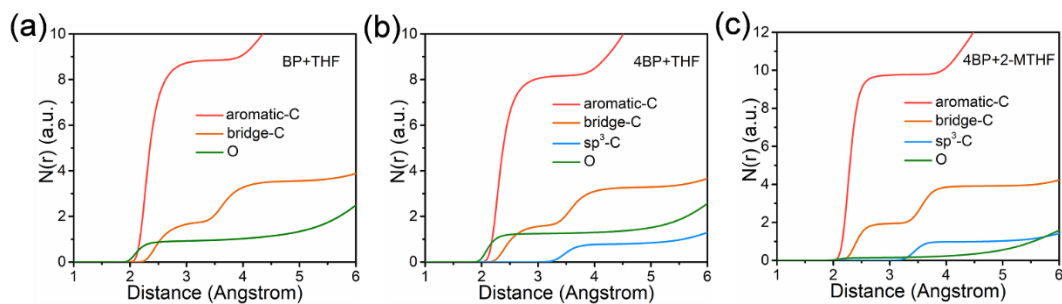


Fig. S4 The corresponding integrals of calculated radial distribution functions

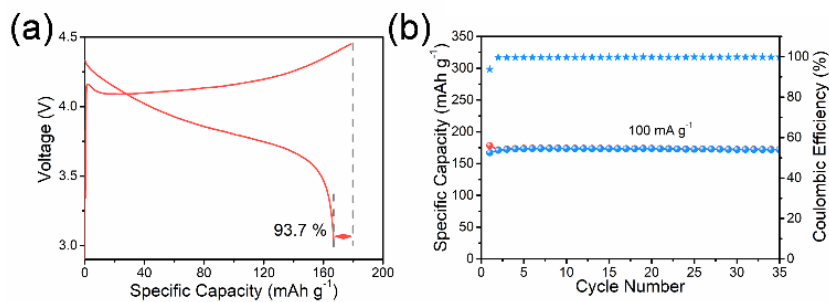


Fig. S5 (a) Initial discharge-charge profiles and (b) the cycling performance of LCO

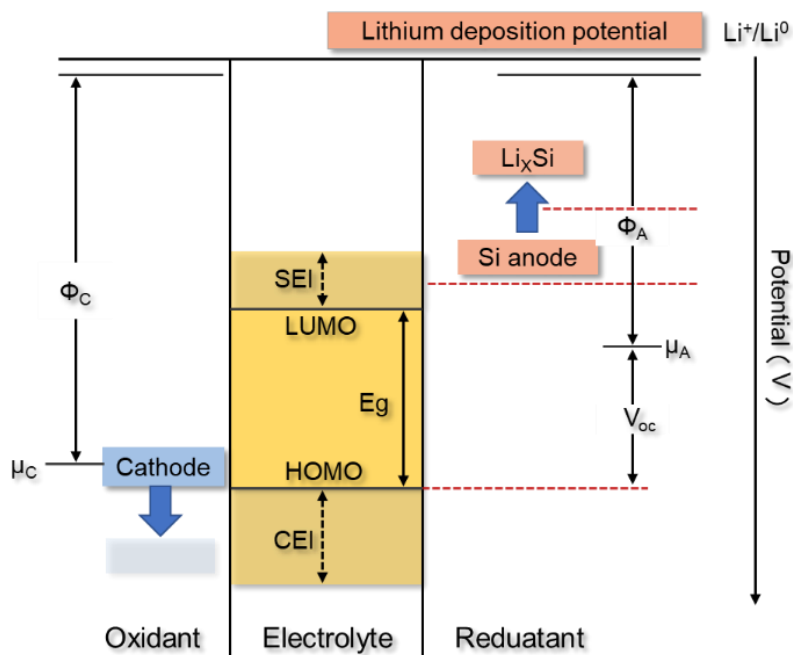


Fig. S6 The thermodynamic stability of the solid-liquid interface

The construction of SEI film during the prelithiation process can compensate for Li^+ loss and solve the solid-liquid interface problem, which is an effective means to achieve stable cycle and high capacity retention. As shown in **Fig. S6**, the thermodynamic stability of the solid-liquid interface depends on the energy difference between the Fermi level of anode and the electrolyte LUMO level. When the LUMO energy level of the electrolyte is lower than the electrochemical potential (μ_A) of the negative electrode, the electrolyte will spontaneously reduce and consume Li^+ , resulting in the passivation of the electrode surface to form a SEI film.

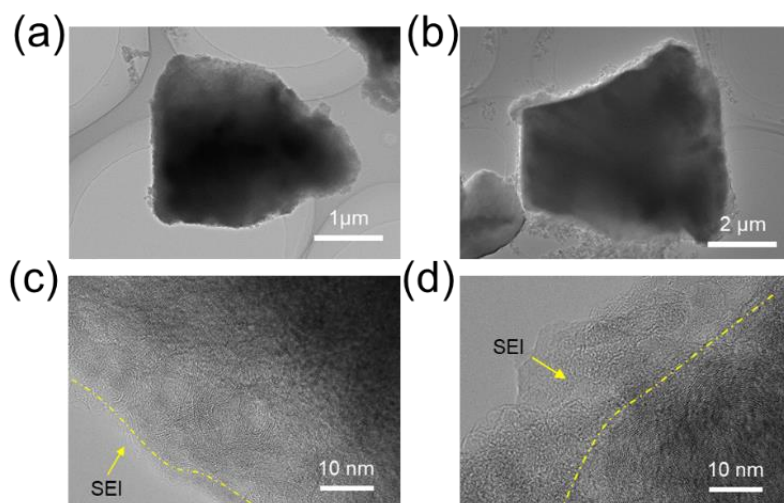


Fig. S7 TEM images of p-SiO/C anodes (a, c) before and (b, d) after 100 cycles

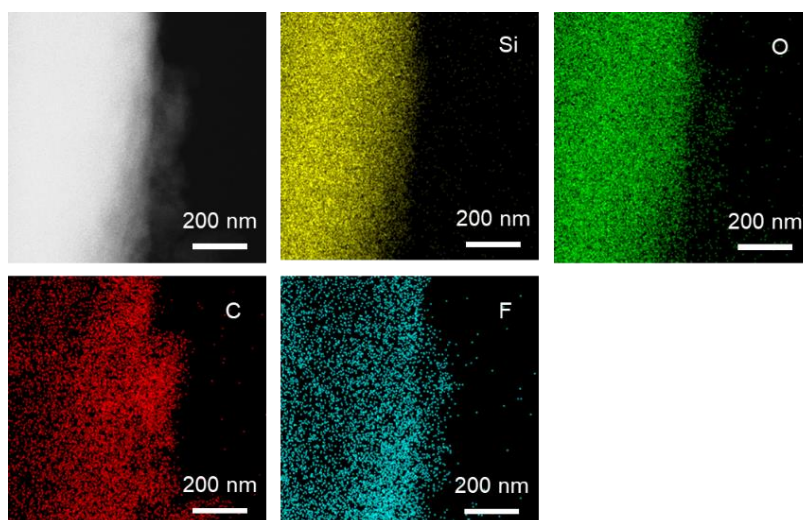


Fig. S8 The corresponding STEM image and elemental mappings of p-SiO/C anodes after 100 cycles