Supporting Information

Ad hoc Solid Electrolyte on Acidized Carbon Nanotube Paper Improves Cycle Life of Lithium-Sulfur Batteries

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Experimental Procedures

Preparation of ACNTP and the AC/S composite

Carbon nanotubes paper (CNTP) was punched into discs with a diameter of 1.88 cm. Then, the CNTP discs were treated by backflow in 6 mol L^{-1} HNO₃ aqueous solution at 90 °C for 10 h. Then, acidized carbon nanotube paper (ACNTP) was repeatedly washed with water and absolute ethanol. Finally, ACNTP was dried at 60 °C for 12 h.

The AC/S composite was prepared by the mixture of AC (Fuzhou Yihuan Carbon Co. Ltd., China) and sulfur with the mass ratio of 7:3 and heated at 155 °C for 10 h.

Characterization

X-ray diffraction (XRD) patterns were measured on a Bruker-AXS D8 DISCOVER. Copper K α line was used as a radiation source with λ =0.15406 nm. The X-ray photoelectron spectroscopy (XPS) analysis was performed on a Perkin-Elmer PHI 550 spectrometer with Al K α (1486.6 eV) as the X-ray source. Field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) measurements were carried out with JEOL JSM-6380LV FE-SEM and FEI TECNAI-20, respectively. Scanning transmission electronic microscope (STEM) was performed on a Tecnai G2 F30. Thermal gravimetric (TG) analysis was conducted on a TG-DSC instrument (NETZSCH STA 409 PC) under a N₂ atmosphere at a heating rate of 10 °C min⁻¹ from 30 to 500 °C.

Electrochemical characterization

Electrochemical characterization of the AC/S composite electrode, AC/S composite electrode with the CNTP barrier, and AC/S composite electrode with the ACNTP barrier was carried out by galvanostatic cycling using CR2016-type coin cells. The working electrodes were prepared by a slurry coating procedure. The slurry consisted of 70 wt% active material, 20 wt% acetylene black and 10 wt% polyvinylidene fluoride (PVDF) dissolved in N-methyl pyrrolidinone (NMP), and was uniformly spread on an aluminium foil current collector. Finally, the electrode was dried at 70 °C overnight. Each current collector contained ca 2.0 mg cm⁻² active material (with $ca \ 1.0 \text{ mg cm}^{-2} \text{ S}$). Test cells were assembled in an argon-filled glove box using Li foil as the counter electrode and two-layer polypropylene (PP) film as the separator. The CNTP barrier or the ACNTP barrier is placed between the two-layer separator. The electrolyte was 1 mol L⁻¹ LiTFSI and 0.1 mol L⁻¹ LiNO₃ in a mixed solvent of 1, 3dioxolane (DOL) and 1, 2-dimethoxyethane (DME) with a volume ratio of 1:1. The coin cells were galvanostatically charged-discharged at different current densities between 1.7 and 3.0 V (vs. Li/Li⁺) using a CT2001A cell test instrument (LAND Electronic Co.). The cyclic voltammetry (CV) measurement was conducted with a Gamry Reference 3000 electrochemical workstation at a scan rate of 0.2 mV s⁻¹ in the voltage range of 1.7 to 3.0 V

(*vs.* Li/Li⁺). Electrochemical impedance spectroscopy (EIS) was measured in the frequency range of 100 kHz-10 mHz with an amplitude of 5 mV.

Computational Section

The structural optimization was carried out by employing the Vienna ab initio Simulation Package (VASP),^{1, 2} which is based on density functional theory (DFT) and the projected augmented wave (PAW) method. Generalized gradient approximation (GGA) in the form of Perdew-Burke-Ernzerhof (PBE)³ was chosen as exchange correlation potential. The electron wave functions were expanded by a plane wave basis set with a cutoff energy of 400 eV. All structures were fully optimized until none of the forces exceeded 0.02 eV Å⁻¹. The adsorption energy (*E_a*) is defined as the difference between the total energy (*E_{tot}*) of Li₂S_n (*n* = 4, 2 and 1) on substrate and the energy sum of Li₂S_n (*E_{Li₂S_n*) and substrate (*E_{sub}*):}

$$E_a = E_{tot} - (E_{Li_2S_n} + E_{sub})$$

The molecular dynamics (MD) simulation for the lithium salt/polysulfide mixture was created by randomly placing 14 Li⁺, 14 TFSI⁻, and 1 Li₂S₄ molecules in the simulation box to match the F:S atomic ratio in the ACNTP after cycling (**Table S2**). After the structural optimization using conjugate gradient method, a simulation box with the size of $13.2 \times 13.3 \times 13.5$ Å corresponding to 2.9 g cm⁻³ was obtained. The MD was performed at 298 K using velocity Verlet method with a time step of 1 fs. Following 1 ps of equilibration, 9 ps of the molecular dynamics trajectory was used to calculate the mean square displacement of the Li ions in the simulation cell and the S atoms in Li₂S₄.



Figure S1. (a) C 1s X-ray photoelectron spectroscopy (XPS) spectra for CNTP. (b) C 1s and (c) O 1s XPS spectra for ACNTP. (d) Schematic illustration for the chemical structure of ACNTP. The gray, red and white balls in (d) represent C, O and H element, respectively.

XPS was carried out to analyze the carbon and oxygen bonds in CNTP and ACNTP. In the C 1s spectra of CNTP, the peak at 284.8 eV is attributed to the C-C bond (**Figure S1a**). The peak at 285.7 eV corresponds to the C-O bond, which may result from the absorbed oxygen on the surface of CNTP. As shown in the C 1s spectra of ACNTP, the peaks at 289.1, 287.0, 285.7, 284.8 eV correspond to the O-C=O, C=O, C-O and C-C bonds, respectively (**Figure S1b**).^{4, 5} In the O 1s spectra of ACNTP, the peaks at 533.8 and 532.5 eV are attributed to C-OH and C=O bonds (**Figure S1c**).⁶ The results indicate the O–H and –COOH groups were successfully grafted onto ACNTP (**Figure S1d**).



Figure S2. X-ray diffraction (XRD) patterns of CNTP and ACNTP. The peak intensity of ACNTP at about 26° and 42° decreased compared to that of CNTP in XRD patterns because the acid treatment broke the hexagonal symmetry of graphite lattice.⁷



Figure S3. Digital photographs of (a) CNTP, (b) ACNTP and (c) ACNTP after 250 cycles at 0.5 C. The flexibility of ACNTP remained after the nitric acid treatment.



Figure S4. Scanning electron microscopy (SEM) images of (a) CNTP after dipped into the electrolyte, (b) CNTP after washing, (c) ACNTP after dipped into the electrolyte, and (d) ACNTP after washing.

The electrolyte can deposit on the surface of CNTP (**Figure S4a**). However, the electrolyte disappears after washed using absolute methanol (**Figure S4b**). The trapped electrolyte still deposits on the surface of ACNTP (**Figure S4c, d**), indicating the strong interaction between solvent molecules and the polar groups on ACNTP.



Figure S5. (a) Digital photograph of H-type cell. (b) Impedance plots of the H-type cell with different membranes in the electrolyte. The electrolyte is 1 mol L⁻¹ LiTFSI and 0.1 mol L⁻¹ LiNO₃ in a mixed solvent of 1, 3-dioxolane (DOL) and 1, 2-dimethoxyethane (DME) with a volume ratio of 1:1. The membranes are two-layer polypropylene separator (PP+PP), with the ACNTP barrier or the cycled ACNTP barrier placed in between (PP+ACNTP+PP, PP+Cycled ACNTP+PP).



Figure S6. Transmission electron microscopy (TEM) image of (a) AC, (b) AC/S and the corresponding elemental mapping images for (c) carbon and (d) sulfur.



Figure S7. TG curve of the AC/S composite.



Figure S8. Rate capability of AC/S composite electrode with the ACNTP barrier.



Figure S9. (a) Scanning electron microscopy (SEM) image of ACNTP and corresponding energy-dispersive X-ray spectroscopy (EDS) elemental maps of (b) carbon, (c) oxygen. SEM and EDS characterization of ACNTP after 50 cycles at 0.5 C (charged state): (d) SEM images of the cycled ACNTP. (e-h) EDS elemental maps for the region shown in (d): (e) carbon, (f) oxygen, (g) sulfur and (h) fluorine.



Figure S10. Typical cyclic voltammetry (CV) curves of (a) the CNTP barrier and (b) the ACNTP barrier as cathode after 50 cycles at 0.5 C.



Figure S11. (a) Scanning electron microscopy (SEM) image of CNTP cross-section. SEM and EDS characterization of CNTP cross-section after 50 cycles at 0.5 C (charged state): (b) SEM images of the cycled CNTP cross-section. (c-f) EDS elemental maps for the region shown in (b): (c) carbon, (d) oxygen, (e) sulfur and (f) fluorine.



Figure S12. (a) C 1s, (b) O 1s, and (c) S 2p XPS spectra for ACNTP after 50 cycles at 0.5 C.



Figure S13. The representative geometries after fully optimized show the interactions between (a) the CNTP surface and (b-d) the Li_2S_n (n=4, 2, 1) molecules.



Figure S14. XRD patterns of cycled ACNTP and LiTFSI.

	Ι	II	III
С	98.04 %	97.27 %	97.89 %
О	1.01 %	1.48 %	0.77 %
F	0.63 %	0.92 %	0.98 %
S	0.33 %	0.33 %	0.35 %

Table S1. The composition of cycled CNTP in **Figure S9**. The amounts of C, O, F, S (at. %) are estimated from EDS.

	Ι	II	III	IV
С	75.89 %	75.97 %	70.69 %	71.05 %
0	10.13 %	10.22 %	7.76 %	10.90 %
F	9.78 %	8.56 %	6.49 %	12.05 %
S	4.21 %	5.25 %	15.06 %	6.01 %

Table S2. The composition of cycled ACNTP in **Figure 4**. The amounts of C, O, F, S (at. %) are estimated from EDS.

Video S1 and 2. The tension of the cycled ACNTP after 50 cycles at 0.5 C (Played at x5 original speed).

Video S3. The molecular dynamics simulation of the LiTFSI/Li₂S₄ mixture.

References

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