

Supporting Information

Fumed alumina induced gel-like electrolyte for great performance improvement of lithium-sulfur battery

Bin Lei, Jun Yang*, Zhixin Xu, Shasha Su, Dong Wang, Jinhua Jiang, Jing Feng

Preparation of the gel-like electrolytes. Fumed alumina nanoparticles with or without surface groups (AEROXIDE® Alu 130, primary particle size of 10 nm, B.E.T surface area of 130 m² g⁻¹; AEROXIDE® Alu C805, primary particle size of 13 nm and B.E.T surface area of 100 m² g⁻¹) were obtained from Evonik Specialty Chemicals (Shanghai) Co. Ltd. AEROXIDE® Alu C130 (hydrophilic) fumed alumina contains native surface hydroxyl groups while AEROXIDE® C805 (hydrophobic) fumed alumina was modified with some Alkyl surface groups (abbreviated as M-Al₂O₃). Both fumed alumina powders were pretreated with vacuum suction at 150°C for 24 h before use to remove the residual water. Electrolyte solution, lithium hexafluorophosphate (LiPF₆) in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, v/v), was purchased from Capchem. Co. Ltd. The proposed electrolytes were prepared by the dispersion of a given amount of fumed alumina into above liquid electrolyte with ultrasonic processing. For the 8 wt.% fumed alumina electrolyte, it finally behaved as a stable, uniform and white gel. All operations were carried out inside an Argon-filled glove box (MB-10 compact, MBRAUN).

Preparation of the electrode. S@pPAN composite with 40.3 wt. % S was prepared according to the previous report and served as cathode material in lithium-sulfur cells.¹ S@pPAN composite was ball-milled with carbonyl-β-cyclodextrin (C-β-CD) binder and super P in the ratio of 8:1:1 for 2 h, then the obtained slurry was coated onto an aluminum foil. After the solvent (NMP) was evaporated, the coated foil was cut to disks with a diameter of 12 mm and dried at 70°C under vacuum for 12 h. The final cathode loading was about 1.4 mg cm⁻² and the specific capacity was calculated according to the mass of sulfur.

Characterizations. The ionic conductivity of the electrolytes was measured by the DDS-307A conductivity meter at room temperature. The surface morphologies of the lithium metal were observed by FEI Nova Nano-scanning electron microscope (SEM). Specifically, cells were disassembled in a glove box and the lithium metal electrodes were washed with DMC. Then the dried samples should be transferred quickly in a container filled with purified argon to avoid air contamination. The composition of the SEI layer was analyzed through X-ray photoelectron spectrometer (XPS), using a Kratos Axis UltraDLD spectrometer (Kratos Analytical-A Shimadzu Group Company) with monochromatic Al Ka source (1486.6 eV) under ultra-high vacuum. The sample pretreatment of the XPS measurement is the same as the SEM measurement.

Electrochemical tests. The CR2016-type coin cells were assembled in a glove box with the as-prepared S@pPAN electrode, Celgard 2400 separator and lithium foil (thickness of 250 μm and area of ca. 2 cm²). Different gel-like electrolytes were sandwiched between the anode and the cathode with a blade. The charge/discharge tests at room temperature were carried out at 1C on a LAND-CT 2001A Cell Test System (Wuhan, China) with a cut-off voltage limit of 1.0~3V. Li | Li symmetric cells were assembled with Li metal as both working and counter electrodes. Different current densities (0.25 mA cm⁻², 0.5 mA cm⁻² and 1 mA cm⁻²) were applied for 1.5 h to the plating/stripping of Li metal during each cycle. Electrochemical impedance spectroscopy (EIS) of Li | Li symmetric cells and Li-S@pPAN cells was measured on an AUTOLAB PGSTAT302N (Metrohm) in the frequency range from 1 MHz to 0.01 Hz.

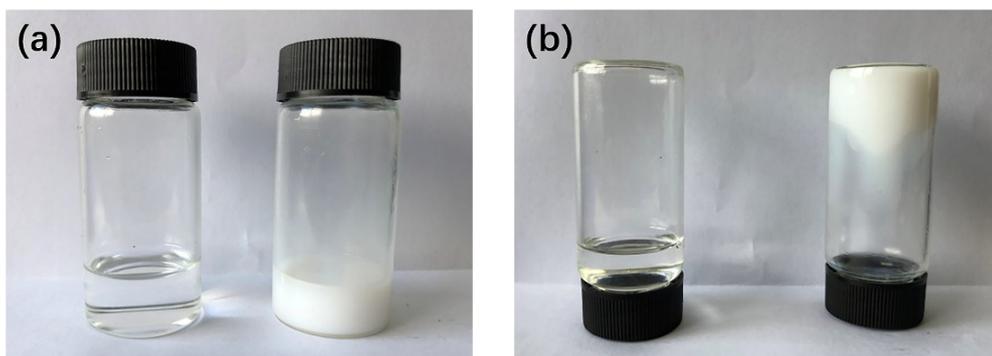


Fig. S1 the photographic images of liquid electrolyte (left) and gel-like electrolyte with 8 wt. % fumed Al_2O_3 (right) at the state of (a) uprightness and (b) inversion.

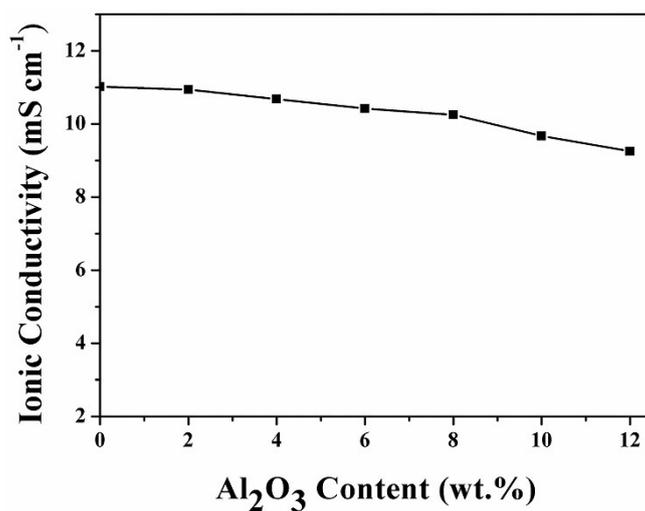


Fig. S2 Ionic conductivity of the electrolytes with different fumed alumina contents.

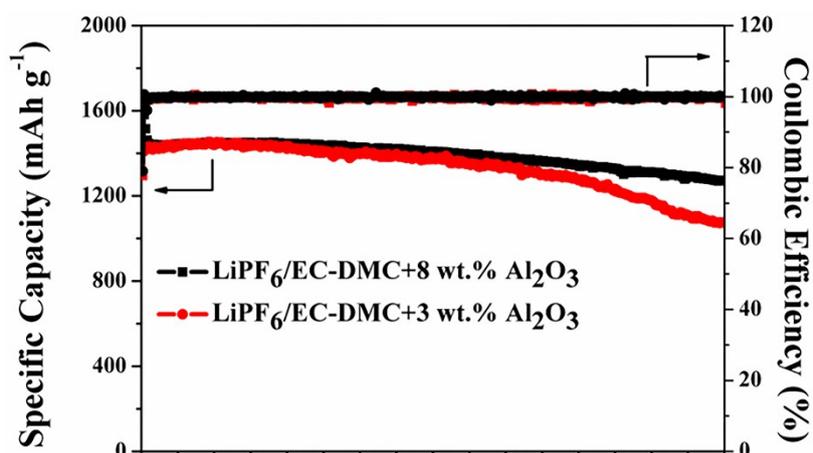


Fig. S3 Comparisons of the cycling performances and coulombic efficiencies of Li-S@pPAN cells in the proposed electrolytes with different fumed alumina contents at 1C (i.e. 1672 mA g^{-1}).

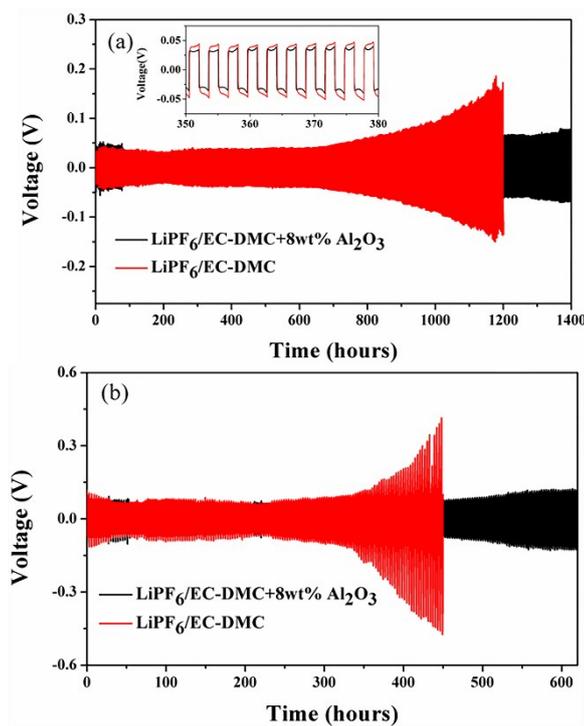


Fig. S4 Galvanostatic voltage-time curves for symmetric Li | Li cells at a current density of (a) 0.25 mA cm⁻² and (b) 0.5 mA cm⁻². The inset plot is the enlarged view.

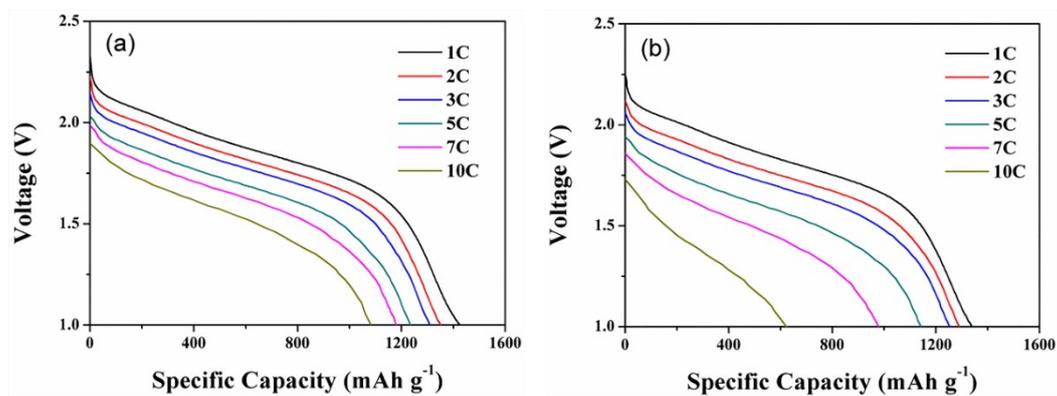


Fig. S5 Discharge profiles of Li-S@pPAN cells at different current rates for the proposed electrolyte (a) and blank electrolyte (b).

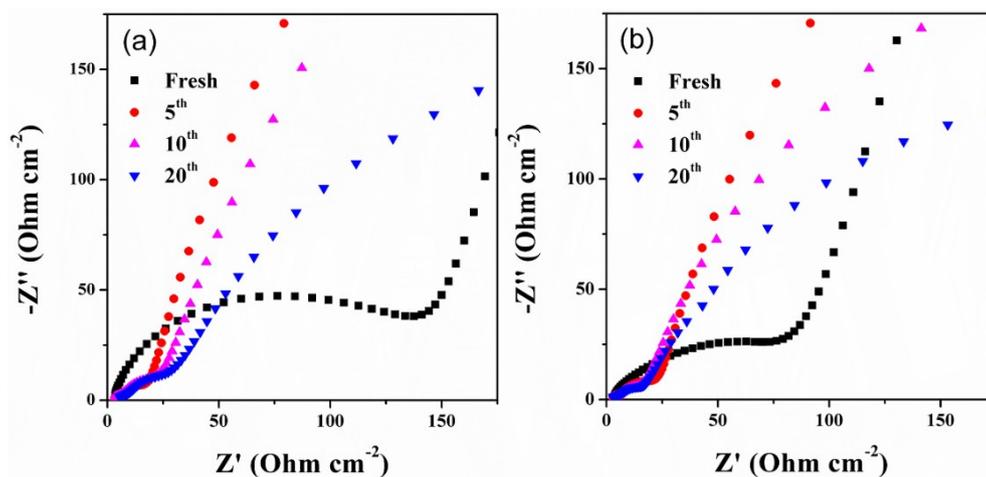


Fig. S6 EIS evolution of Li-S@pPAN cells during cycling at a current density of 1C with (a) blank electrolyte; (b) proposed electrolyte.

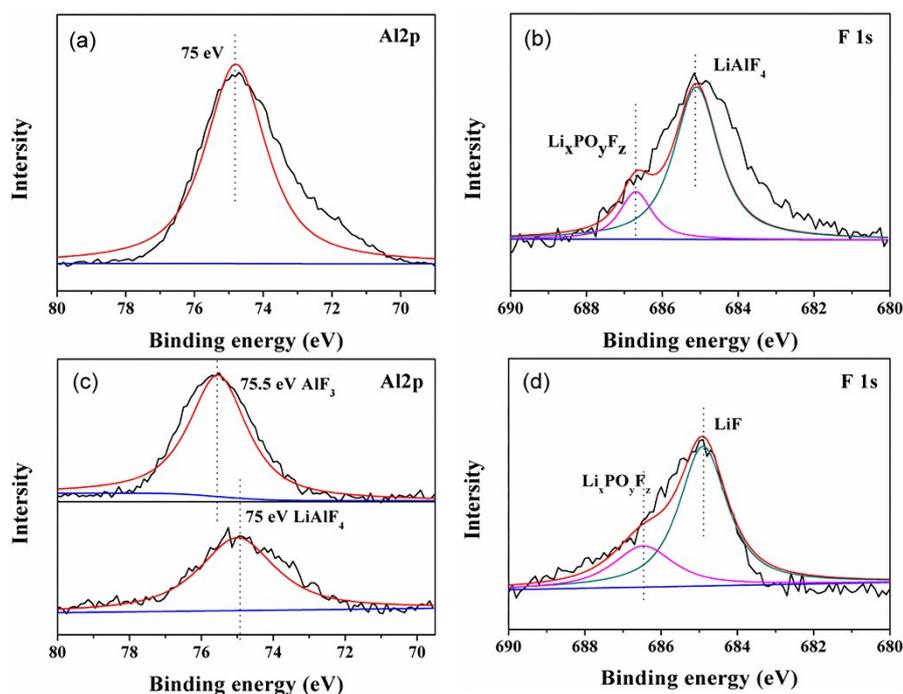


Fig. S7 XPS spectra of the electrodes in the Li-S@pPAN cells after 50 cycles. (a) Al 2p and (b) F 1s spectra of the S@pPAN cathode using the proposed electrolyte; (c) Al 2p spectra of the Li anodes using the electrolyte with $\text{M-Al}_2\text{O}_3$ (upper) and unmodified Al_2O_3 (lower); (d) F 1s spectrum of the Li anode in the $\text{M-Al}_2\text{O}_3$

Reference

1. W. J, Y. J, X. J. and X. N, *Adv Mater*, 2002, **14**, 963-965.