Supporting Information

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

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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® AluC130 (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. 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$_2$O$_3$ (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 M-Al2O3 (upper) and unmodified Al2O3 (lower); (d) F 1s spectrum of the Li anode in the M-Al2O3 electrolyte.

Reference