

Electronic Supplementary Information (ESI)

A Rechargeable Aqueous Aluminum-Sulfur Battery through Acid Activation in Water-in-Salt Electrolyte

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Supplementary Information including Experimental Section, Figure S1-S5 and Table S1.

Experimental Section

Materials

Preparation of electrolyte: Lithium bis(trifluoromethane)sulfonimide ($\text{LiN}(\text{SO}_2\text{CF}_3)_2$, LiTFSI) (99.95% trace metals basis) and aluminum trifluoromethanesulfonate ($\text{Al}(\text{CF}_3\text{SO}_3)_3$, $\text{Al}(\text{OTF})_3$) (99%) were purchased from Sigma-Aldrich and Alfa Aesar, respectively. The aqueous electrolytes were prepared by mixing the LiTFSI and $\text{Al}(\text{OTF})_3$ in hydrochloric acid (HCl).

Preparation of carbonized-ZIF-67: 1.95 g 2-methylimidazole and 0.86 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sinopharm Chemical) were added into 30 ml methanol and stirred until fully reacted. The resulting purple precipitates were collected by centrifuging and supersonic dispersion followed by vacuum drying overnight. The as prepared ZIF-67 were carbonized by heating at 350 °C for 90 min followed by heating at 700 °C for 210 min in argon atmosphere. Cobalt was removed from the black product by soaking into 10 wt.% HCl for a week. Afterwards the powders were washed with DI water and dried in air.

Preparation of the cathode. Carbonized-ZIF-67 was mixed with sulfur powder at the mass ratio of 4 : 6 under argon protection and then heated at 155 °C for 10 h. The sulfur/carbon composite, Ketjen black, and 10 % PVDF were mixed at a mass ratio of 5:3:2 in an agate mortar using N-methyl-2-pyrrolidone (NMP) as solvent to form a slurry, which was then coated onto Tantalum current collector followed by vacuum drying at 45 °C overnight. The average loading mass density of sulfur per cathode is 0.2 mg cm⁻².

Electrochemical Measurements

The aqueous Al-S batteries were assembled in Swagelok-type cells using Al foil as the anode and Whatman 934 as the separator. The cell assembling was completed under ambient conditions. Galvanostatic charge-discharge were performed in the voltage range between 0.30–1.70 V. The as-prepared battery was measured using a LAND battery system at different current densities and the specific capacity was calculated based on the mass of sulfur. Cyclic voltammetry (CV, Princeton Applied Research Ltd) was carried out at 0.05 mV s⁻¹ for the Swagelok battery. The instrument was also applied to determinate the electrochemical stability window (ESW) at a scan rate of 1 mV s⁻¹ by liner sweeping using a de-oxide (soaked in [EMIM]Cl/ AlCl_3 for a day) aluminum foil as the counter & reference electrode and a glass carbon as the working electrode, which was cleaned with alcohol in ultrasound bath, and then washed three times with high purity water and dried before measurement. In detail, the ESW test was conducted first sweeping from open circuit voltage (OCV) to negative potential. After the lower bound was determined, the system was settled until its potential came back to OCV, then the upper bound was confirmed by a sweep from OCV to positive potential. To measure the stable electrochemical window of the

electrolyte without HCl, the Al foil has to be pretreated with [EMIM]Cl/AlCl₃ in Ar to strip out the passivation layer.

Characterization

Raman spectra were collected using Renishaw inVia equipped with 532 nm incident laser. X-ray photoelectron spectroscopic (XPS) analysis were conducted on the Catalysis and Surface Science Endstation located in National Synchrotron Radiation Laboratory (NSRL), Hefei. To avoid the possible decomposition of the chemicals in cathode due to the exposure to air, the specimen were sealed in a distribution chamber in Ar before loading into the vacuum chamber for XPS analysis. The specimen was retrieved from the full cells at different state of charge, which was soaked in DME for 1 min to remove the electrolyte residuals. Inductively coupled plasma mass spectrometry (ICP-MS) of the cathodes were conducted on a Thermo-Fisher Scientific icap Qc, and the specimen were prepared by collected by dissolving the cathode materials in 0.2 mol L⁻¹ HCl for 2 days. Scanning electron microscopy (SEM) was performed on a JSM-2100F (JEOL Ltd.). The gas mass spectroscopy (MS) was performed on an OminiStar GSD320 Gas Analysis System. In detail, for H₂S tests, 30 mL glass vials were preloaded with 30 mg Al₂S₃ power and sealed in Ar-filled glove-box. Then, 400 μL of aqueous electrolytes, which consisted of 1 m Al(OTF)₃ and 0.02 M HCl yet different concentrations of LiTFSI, were injected into the vials by syringe. The contents of the gas that were sealed in the glass vials were then analyzed by gas mass spectroscopy. For H₂ tests, each of the three samples was sealed into a 30 mL glass vial under Ar atmosphere. Then, 2 mL deionized water was injected into each vial by syringe to react with the metals. The resulting gas inside the vials were analyzed by gas mass spectroscopy.

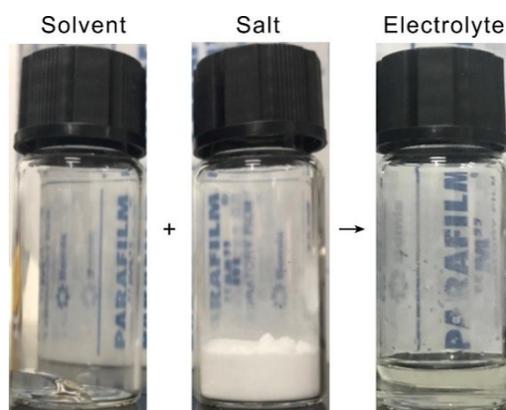


Fig. S1 Photographs of the salt ($\text{LiTFSI}+\text{Al}(\text{OTf})_3$), solvent (H_2O), and the yielded electrolyte.

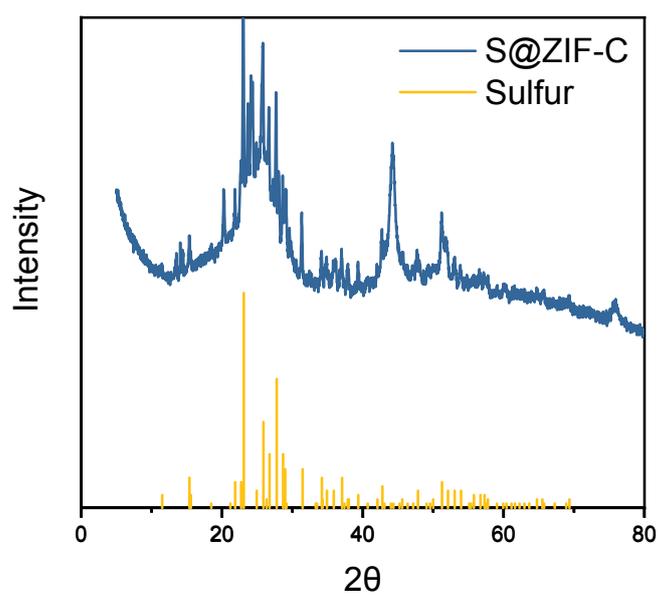


Fig. S2. XRD pattern of the S/C cathode material

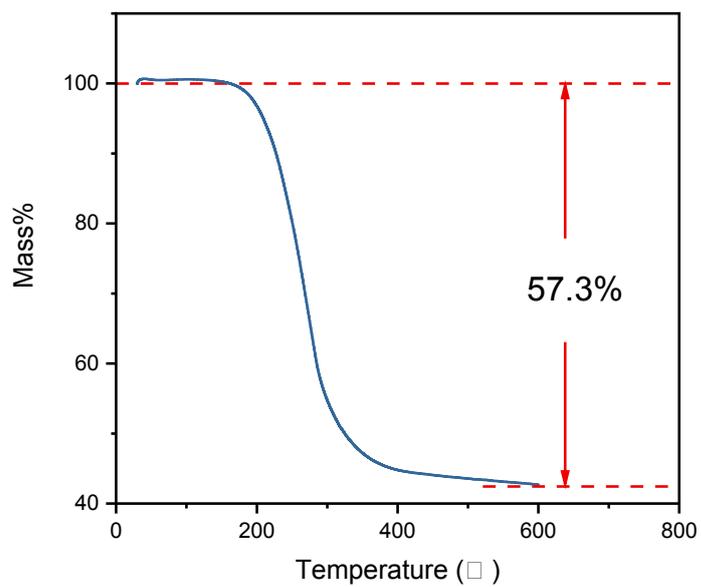


Fig. S3 TGA profile of S/C cathode material in N₂ atmosphere.

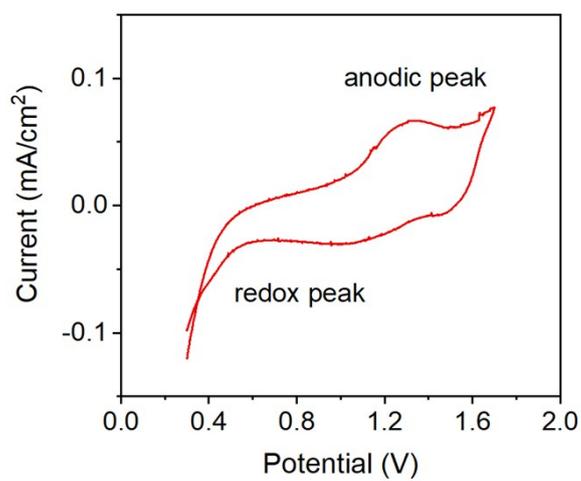


Fig. S4 CV diagram of the Al | Al(OTF)₃+LiTFSI+HCl | S/C cell under sweep rate at 0.1 mV/s

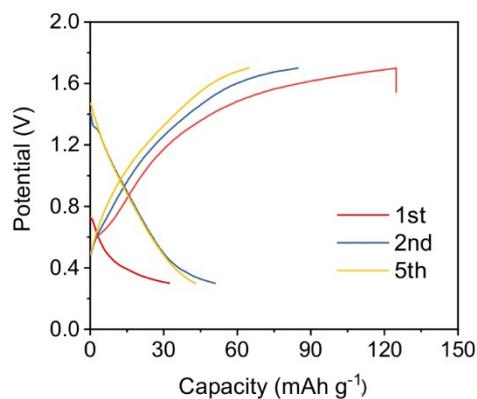


Fig. S5 Galvanostatic discharge curves of the Al || Al(OTF)₃+LiTFSI+HCl || Carbonized -ZIF-67 cell measured at current density of 200 mA g⁻¹.

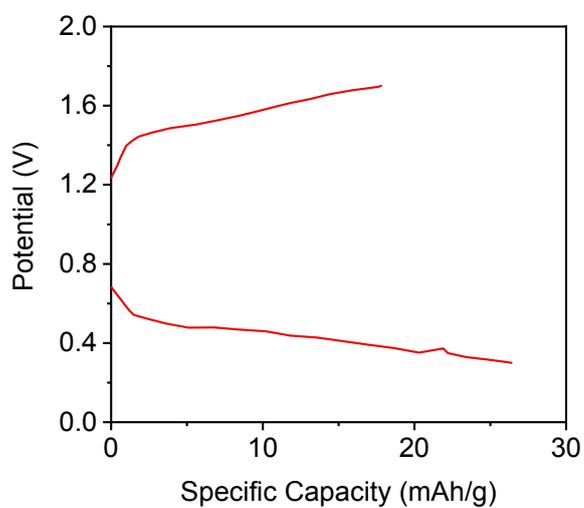


Fig. S6 Galvanostatic discharge curves of the $\text{Al} \parallel \text{Al}(\text{OTF})_3 + \text{LiTFSI} + \text{HCl} \parallel \text{Carbonized -ZIF-67}$ cell measured at current density of 200 mA g^{-1} .

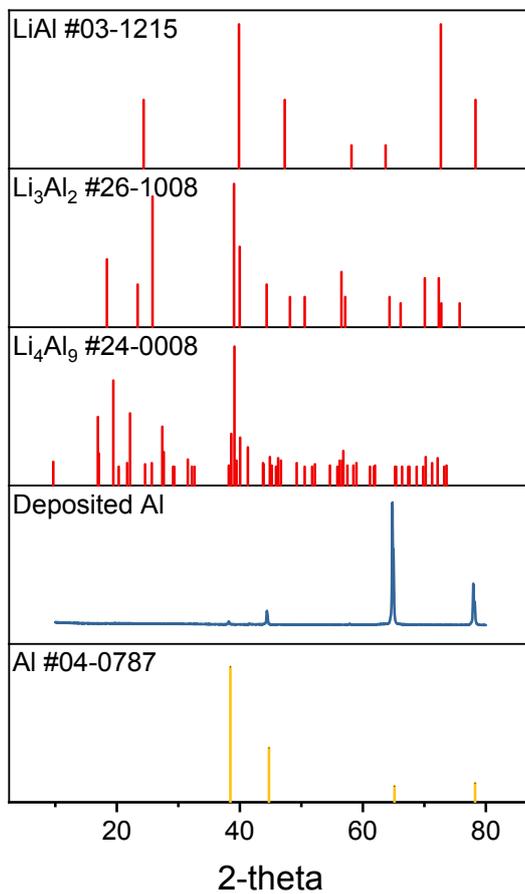


Figure S7. XRD pattern of the anode at discharged state.

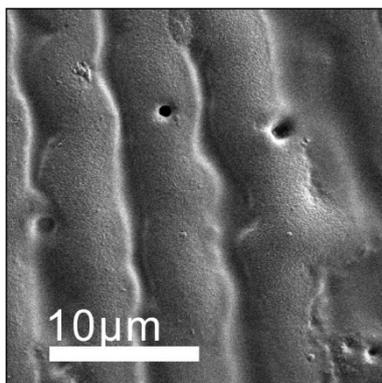


Fig. S8 SEM image of Al foil after soaking in [EMIM]Cl/AlCl₃ electrolyte for a day

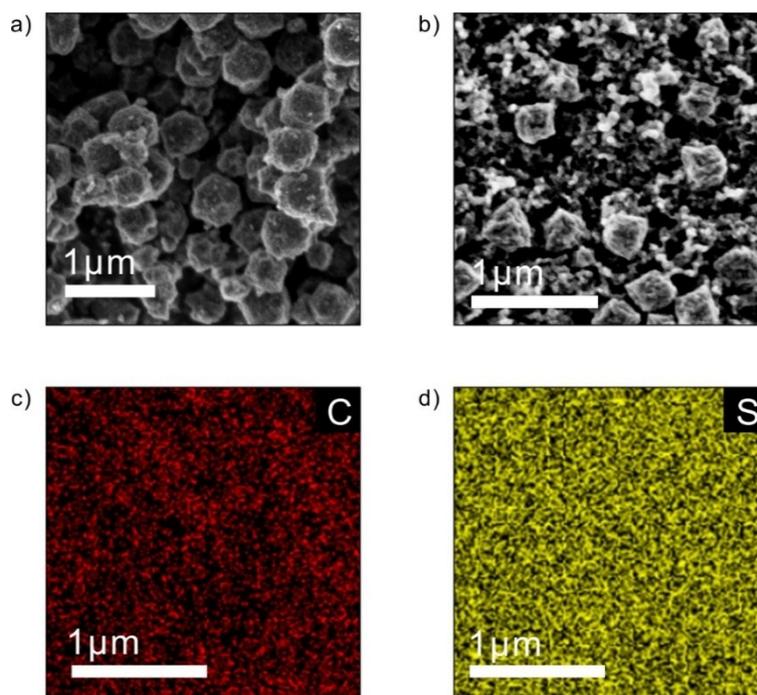


Fig. S9 SEM images of a) carbonized-ZIF-67 and that after loading with sulfur b). c) and d) EDX elemental mapping of carbon and sulfur acquired in the area shown in panel b).

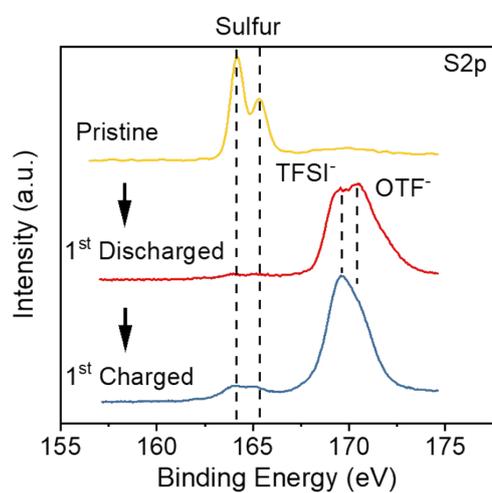


Fig. S10 Ex-situ Raman spectra of the cathode at different SOCs.

Table. S1 Comparison of the reversible gravimetric capacity based on the mass of the active cathode materials of various aqueous aluminum ion batteries

Cathode Material	Electrolyte	Discharge capacity (mAh g ⁻¹)	Current density (mA g ⁻¹)	Ref
	17 m LiTFSI+1 m			
Sulfur@Carbonized MOF	Al(OTF) ₃ +0.02 M HCl	1450(initial)/800(cycle)	200	This work
Bir-MnO ₂	2 m Al(OTF) ₃	550	100	1
Al _x MnO ₂ ·nH ₂ O	5 m Al(OTF) ₃	467	30	2
α-MnO ₂	2 m Al(OTF) ₃	390	100	3
TiO ₂ nanospheres	1 M AlCl ₃	183	50	4
Na ₃ V ₂ (PO ₄) ₃	0.1 M AlCl ₃	100	60	5
Xero-V ₂ O ₅	1 M AlCl ₃	120	60	6
TiO ₂ /CNT nanocomposite	1 M AlCl ₃	170	335	7
Exfoliated graphite	Al ₂ (SO ₄) ₃ / Zn(CHCOO) ₂	80	500	8

m is molality (mol kg⁻¹); M is mol L⁻¹

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