Supporting information

A dual-electrolyte system for high efficient Al–air batteries

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Experimental Section

1. Materials preparation

All materials used in this work were of analytical grade, and used without further treatment. Reagents for the electrolyte synthesis, including KOH, acrylic acid (AA), $K_2S_2O_8$, and N, N'-methylene-bisacrylamide cross-linker (MBA), were purchased from Sinopharm Chemical Reagent (Co., Ltd). Al sheet was first polished to remove the oxide layer, followed by cleaning with ethanol. And pure aluminum sheet 99.99% was used as the Al electrode to reduce the influence of aluminum anode performance caused by the uneven distribution of alloying elements. The air electrode was made of a commercial $Mn_xO_y@Ag$ catalyst and gas diffusion layer, which were purchased from Changzhou Yoteco (China). A Cu mesh was used as the cathode current collector.

2. Synthesis of alkaline gel electrolyte

Predetermined amounts of the AA monomer (1.5g), MBA (0.05g), were added to pre-prepared KOH solutions (8M, 9.5g). After all of the solid was completely dissolved under vigorous stirring, the solution was degassed with nitrogen and subsequently centrifuged to remove air bubbles. The resulting translucent solution was added with initiator potassium persulfate (0.05g) under vigorous stirring, and then the final hydrogel electrolyte was obtained.

3. Electrochemical measurements

Electrochemical measurements were carried out in a conventional three-electrode cell. Pure aluminum sheet (10 mm * 10 mm * 0.5 mm) was used as working electrode, the Pt net electrode and Hg/HgO electrodes represent the counter and the reference

electrodes, respectively. The test and analysis equipment was CHI760 Electrochemical Workstation. While in systems containing gels, all gels are synthesized in situ to ensure adequate contact between the gel electrolyte and the electrodes. OCPT techniques were measured for 30 min to record the change of the open circuit potential over time. The potentiodynamic polarization curves were measured from the potential of -0.5 V to 1.5 V vs. the OCP at a scan rate of 1mV s⁻¹ after the OCP stabilizes. Finally, the EIS measurements were performed at OCP in the frequency range of 10^{-2} Hz to 10^{5} Hz with a 5 mV amplitude. The conductivity was measured by sandwiching the electrolyte between two stainless steel sheets using a platinum wire as a reference electrode (Fig S4).

The cathodic electrochemical curve was also measured using a three-electrode system. A commercial $Mn_xO_y@Ag$ catalyst was used as the working electrode, with the catalyst side facing the opposite electrode (platinum net electrode) and Hg/HgO as the reference electrode. But the electrolytes needed to be oxygen-rich before being tested. In particular, ensure that the gel solution is oxygenated for at least 40 minutes before in situ synthesis of the gel. The ORR catalytic activity was evaluated by Taffel plot, cyclic voltammetry (CV), linear sweep voltammetry (LSV) curves on an electrochemical work station (CHI760).

4. Al-air batteries test

The Al-air batteries were assembled with the 3D-printed cell cases made of acrylonitrile butadiene styrene plastic (ABS). The effective reaction area was 1 cm². The dual-electrolyte is composed of cross-linked PAA gel and 4M KOH in half. First, the gel is synthesized in situ in the mold, then the anode is inserted into the gel electrolyte and the electrolyte is injected on the other side. The single hydrogel electrolyte is made entirely of PAA gel. For all full cell tests, the capacity per mass of Al was calculated by dividing the mass difference of Al anode before and after galvanostatic discharge. The completely assembled Al-air batteries prototype was tested to demonstrate its discharge characteristics using a NEWARE BTS-5V3A battery testing system.

5. Characterizations

The morphology of the Al anode surfaces was examined by scanning electron microscopy (SEM, Nova Nano-SEM 230). FTIR spectra of PAA gel were carried out on a Bruker Vertex 70 FTIR spectrophotometer, and the ATR mode was used to detect the PAA gel after freeze-drying directly. The Raman spectra of PAA gel after freeze-drying were performed on confocal laser dispersion Raman Microscope (model-INVIA, laser 532 nm⁻¹, Renishaw Gloucestershire, UK). The self-corrosion of Al anodes was tested by weight-loss method using aluminum sheets of 1cm*1cm*0.05cm in size. The weight-loss method is to compare the corrosion inhibition performances of Al anodes in different solutions by comparing their mass before and after the self-corrosion under open circuit potential for 2 h.



Fig S1. The dual-electrolyte Al-air battery consists of PAA gel and 4MKOH.



Scheme S1. Illustration of the polymerization process from AA monomers to a PAA matrix.



Fig S2. (a) Optical image of the prepared PAA gel; (b) PAA gel with good bending resistance.



Fig S3. SEM image of porous PAA gel.



Fig S4. Schematic illustration of ionic conductivity test.



Fig S5. EIS of different electrolytes.

Equation S1 $\theta_2 + 2H_2\theta + 4e^- \rightarrow 4\theta H^-$ (4e process)



Fig S6. The Al anode is immersed in (a) 4M KOH and (b) PAA gel.



Fig S7. Mass change of PAA gel in KOH solution upon time



Fig S8. SEM images and four times magnification in an optical microscope of untreated aluminum anode surface (a), (d); and Al anode surfaces after 2 h exposure under OCP in (b), (e) 4 M KOH and (c), (f) single PAA gel.



Fig S9. Time versus voltage curve of Al-air batteries with commercial platinum-carbon catalyst at 20 mA cm⁻².

(a)



Fig S10. Time versus voltage curve of Al-air batteries with commercial $Mn_xO_y@Ag$ catalyst at 20 mA cm⁻².

Table S1. Comparison of the discharge current density, cathode catalyst, specific capacity, operation voltage, reaction area of our dual-electrolyte with the performance of other solid or quasi solid Al-air batteries air batteries.

Electrolyte	Discharge current density	Cathode catalyst	Specific capacity	Operation voltage	Reaction area	Ref
Dual- electrolyte	20 mA cm ⁻²	Pt-carbon	1769 mAh g- 1	~1.28V	1 cm ²	This work
Dual- electrolyte	20 mA cm ⁻²	Mn _x O _y @Ag	1563 mAh g ⁻ 1	~1.26V	1 cm ²	This work
AGE	3 mA cm ⁻²	N-Graphene	2148.5 mAh g ⁻¹	~1.3V	10 cm ²	1
AGE	20 mA cm ⁻²	N-Graphene	875 mAh g ⁻¹	~0.6V	10 cm ²	1
Alkaline PAA hydrogel	1 mA cm ⁻²	HCA-Co	N/A	~1.3V	0.75 cm^2	2
Alkaline paper-based sodium- polyacrylate gel	1 mA cm ⁻²	MnO ₂ -CNT	900.8 mAh g- 1	~1.18V	1 cm ²	3
NaOH solution in paper	5 mA cm ⁻²	MnO ₂ -CNT	1087 mAh g ⁻¹	~1.25	5 cm ²	4
NaOH solution in paper	10 mA cm ⁻²	Blank carbon paper	1273 mAh g ⁻¹	~1.05	5 cm ²	5
Alkaline PVA hydrogel	12.5 mA cm ⁻²	Co-N/CNs	N/A	~1.1V	N/A	6
Alkaline PAA hydrogel	1 mA cm ⁻²	Fe ₃ C@N-CFs	g ⁻¹ 1287.3 mAh	~1.6V	0.75 cm^2	7
Alkaline chitosan hydrogel	1 mA cm ⁻²	Mn ₃ O ₄ /C	288.5 mAh g- 1	~1.1V	1 cm ²	8
NaCl solution in paper	0.005 mA cm ⁻²	Carbon black	153 mAh g ⁻¹	~0.6V	4 cm^2	9
Alkaline k- carrageenan gel	10 mA cm ⁻²	Pt/C	400 mAh g ⁻¹	~1.1V	1.33 cm ²	10

Alkaline PVA-PEO hydrogel	0.5 mA cm ⁻²	CNT/Ag	935 mAh g ⁻¹	~1.4V	N/A	11
Alkaline PAA hydrogel	4.4 mA cm ⁻²	MnO ₂ /C	426 mAh g ⁻¹	~1.3V	3 cm ²	12
Alkaline PAA hydrogel	52 mA cm ⁻²	La ₂ O ₃ +SrO+MnO ₂	1166 mAh g ⁻¹	~1.1V	0.12 cm^2	13



Fig S11. The photographs of the discharged Al anodes after discharging test in (a) single gel electrolyte and (b) dual-electrolyte.



Fig S12. Discharging profiles of Al-air batteries with commercial $Mn_xO_y@Ag$ catalyst at 10mAcm⁻², (a) Specific capacity curve versus voltage; (b) Time versus voltage curve.

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