Rechargeable Aluminum-Selenium Batteries with High Capacity

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Electronic Supplementary Information

Experimental Procedures

Material Synthesis:

Se nanowires were synthesized by a low temperature hydrothermal treatment method. Typically, selenium dioxide (2 g) and sodium dodecyl sulfate (1 g) were dissolved in deionized water (200 ml) at room temperature. Hydrazine monohydrate (1 ml) was added into the solution with strong stirring. After 2 h stirring, the solution was transferred into Teflon-lined autoclaves and heated at 60 °C for 24 h. Then the suspension was filtered over a ~220 nm track-etched polymer membrane to collect powder products. After rinsing with 3 x 40 mL of deionized water, Se nanowires can be finally obtained. CMK-3 was prepared by a typical hard-templating method reported in ref. 17. Structure Characterizations:

Scanning electron microscopy (SEM) images and element analysis were taken on a JEOL JEM-7800F operated at 5 kV. Transmission electron microscopy (TEM) analyses were conducted on a JEM-2100 microscope operated at 200 kV and a FEI Tecnai F20 FEG-STEM operated at 120 kV. X-ray diffraction (XRD) pattern was obtained from a Bruker X-ray Powder Diffractometer (D8 Advance, $\lambda = 1.5406$ Å). Raman spectroscopy was measured on a Renishaw Raman spectrometer using Ar laser with the wavelength of 514 nm. X-ray photoelectron spectroscopy (XPS) spectrum were measured by a Kratos Axis ULTRA X-ray photoelectron spectrometer. The atomic concentration calculation and peak fitting of XPS results were processed by the Casa XPS version 2.3.14 software. Nitrogen adsorption/desorption measurements were conducted at 77 K on a Micromeritics Tristar 3000 system. Prior to the measurement, the samples were degassed at 180 °C for 12 h. The mesopore size distribution was calculated by Barrett-Joyner-Halenda (BJH) method using both adsorption and desorption branch isotherms. The specific surface area was obtained by the Brunauer-Emmett-Teller (BET) method. The pore volume was estimated from the amount of nitrogen adsorbed at the highest relative pressure.

Electrochemical measurements:

Standard CR2032-type coin cell cases were modified with poly(3,4-ethylenedioxythiophene) for Al-Se battery assembling (ref. 16). Se nanowires (56 wt%), CMK-3 (28 wt%), carbon black (6 wt%) and Nafion binder (10 wt%) were mixed in N-methylpyrrolidone to form the cathode slurry. Then, the slurry was cast on carbon cloth substrates and dried at 80 °C for 12 h to obtain the battery cathodes. The specific Se loading on each cathode was about 3mg cm⁻². Pure Al foil was used as the anode. 1-Ethyl-3-methylimidazolium chloride-aluminum chloride (EMImCl-AlCl₃, 1:1.1 by mole) was used as the electrolyte (~160 μ L per cell). Glass fiber (Filtech) and carbon felt (Sigma-Aldrich) pellet were used as separator and spacer, respectively. The cells were assembled in an Argon-filled glove box. The general structure of an Al-Se battery is schematically illustrated in Figure S2. CV measurements were conducted on a Solartron-Multistat electrochemical workstation. Galvanostatic charge-discharge measurements were performed on Land battery testers. The voltage range for both CV and galvanostatic charge/discharge measurements was 2.3-1.0 V.

Results and Discussion



Figure S1. Visual demonstration of the fast capture of Se₂Cl₂ by CMK-3. (a) Fully charged pure Se nanowire cathode and separator in anhydrous acetonitrile. (b) The reddish oily Se₂Cl₂ leaching after ~10 seconds. (c) The Se₂Cl₂/acetonitrile suspension after ~1 minute immersion of fully charged pure Se cathode and separator. (d) The injection of CMK-3/ acetonitrile suspension. (e, f) The fast adsorption of Se₂Cl₂ within 2-3 seconds.

The Se₂Cl₂ adsorption by CMK-3 nanorods was demonstrated in anhydrous acetonitrile. Pure Se cathode prepared by mixing Se nanowires with carbon black and Nafion binder was charged to 2.3 V in chloroaluminate electrolyte. The charged cell was dissembled to take the cathode and separator out. A brown reddish liquid can be observed in the glass fiber separator (Figure S1a), indicating a severe leaching of the electrode component. After immersing the cathode and separator into an acetonitrile solution, the red liquid diffused rapidly into the solution (Figure S1b and c). The

released reddish liquid can be quickly adsorbed (2-3 seconds) by CMK-3, when injecting a CMK-3/acetonitrile suspension (Figure S1 d-f), demonstrating a promising feasibility of using CMK-3 to capture the cell charge product and confine the subsequent cathode reaction.



Figure S2. (a) SEM and (b) TEM images of Se nanowires.



Figure S3. The corrosion resistant coin-cell configuration for Al-Se batteries and the Se nanowires/CMK-3 composite cathode.



Figure S4. Structure characterizations of CMK-3. (a) Typical TEM images of CMK-3 showing the channel-like mesopores with a hexagonal arrangement. (b) Low-angle XRD pattern presenting three well-resolved peaks that can be indexed as the (100), (110), and (200) reflections of a hexagonal symmetry (p6mm). (c) Nitrogen (N₂) adsorption/desorption isotherms of CMK-3 displaying a type IV shape. (d) The corresponding pore size distribution calculated from both adsorption and desorption branches, giving sharp peaks at 3.4 nm.



Figure S5. Electrochemical analysis of Al-Se batteries. (a) CV curves recorded at scan rates of 0.1, 0.2, 0.5, 1.0 and 2.0 mV s⁻¹. (d) The log(i) - log(v) plots of both anodic and cathodic peaks and their linear fittings.



Figure S6. SEM images of Se/CMK-3 composite cathodes during battery charge-discharge. (a) The pristine cathode. (b) Charged to 1.8 V. (c) Fully charged state. (d) Fully discharged state.



Figure S7. SEM characterizations of the Se/CMK-3 composite cathode after 50 cycles at 100 mA g⁻¹. (a) The typical SEM image. (b) The corresponding carbon element mapping. (c) The corresponding selenium element mapping.



Figure S8. The charge voltage change during the 1^{st} and 2^{nd} cycle of Se/CMK-3 cathode at 100 mA g⁻¹. The half-capacity voltage of the 2^{nd} cycle charge branch shows a slight increase of ~0.05 V over that in the 1^{st} cycle.



Figure S9. Electrochemical performance of CMK-3. (a) Charge-discharge profiles at different current rates. (b) The cycling performance.



Figure S10. Electrochemical performance of Se/CMK-3 (3:1 weight ratio) composite cathodes.



Figure S11. Electrochemical performance of pure Se nanowire cathodes. (a) The 2nd cycle chargedischarge profiles at different current rates. (b) The cycling performance.

	Electrochemical performances			
Cathode materials —	first discharge capacity	discharge voltage	cycling capacity	Ref. ^[c]
Al-Se battery: Se nanowires	218 mAh g ⁻¹ at 100 mA g ⁻¹	1.95 to 1.5 V	178 mAh g ⁻¹ over 50 cycles	this work
Metal oxides				
$V_2O_5{}^{[a]}$	305 mAh g ⁻¹ at 125 mA g ⁻¹	~0.55 V	273 mAh g ⁻¹ after 20 cycles	2a
VO2 ^[b]	165 mAh g ⁻¹ at 50 mA g ⁻¹	0.5 V	116 mAh g ⁻¹ after 100 cycles	2b
WO _{3-x}	118.9 mAh g ⁻¹ at 100 mA g ⁻¹	~1.4, 1.0 V, short	64.7 mAh g ⁻¹ over 100 cycles	2c
Metal sulfides				
Ni_2S_3	350 mAh g ⁻¹ at 100 mA g ⁻¹	~1.0 V	~60 mAh g ⁻¹ after 100 cycles	3a
CuS@C sphere	240 mAh g ⁻¹ at 20 mA g ⁻¹	~1.0 V	90 mAh g ⁻¹ after 100 cycles	3b
SnS ₂ /graphen	${\sim}270~mAh~g^{{\scriptscriptstyle -1}}$ at 200 mA $g^{{\scriptscriptstyle -1}}$	< 1.0 V	70 mAh g ⁻¹ after 100 cycles	3c
MXene: V ₂ CT _x	~200 mAh g ⁻¹ at 100 mA g ⁻¹	~1.2 to 0.9 V	~100 mAh g ⁻¹ after 100 cycles	4
Carbon materials				
zeolite-templated microporous carbon	~250 mAh g ⁻¹ at 1 A g ⁻¹ ,	capacitive behaviour, no plateau	178.1 mAh g-1 after 500 cycles	6
graphite foils	~67 mAh g ⁻¹ at 66 mA g ⁻¹	2,25-2.0V, 1.9-1.5 V	~67 mAh g ⁻¹ over 200 cycles	8a, 8b
natural graphite	110 mAh g ⁻¹ at 99 mA g ⁻¹	2,25-2.0V, 1.9-1.5 V	~100 mAh g ⁻¹ over 1000 cycles	8c
graphene foam by CVD growth	~67 mAh g ⁻¹ at 100-5000 mA g ⁻¹	2.25-2.0 V and 1.9- 1.5 V	~67 mAh g ⁻¹ over 7000 cycles	8a
plasma treated graphene foam	148 mAh g ⁻¹ at 2000 mA g ⁻¹	1.9-1.65 V	no decay over 10000 cycles	8d
graphene film	${\sim}120$ mAh g $^{-1}$ at 10-400 A g $^{-1}$	2.3-2.0 V and 2.0- 1.5 V,	no decay over quarter-million cycles	8e
monolithic nanoporous graphene foam	154 mAh g ⁻¹ at 500 mA g ⁻¹	~1.9-1.5 V	151 mAh g ⁻¹ over 100 cycles	17

Al-S batteries

S in activated carbon cloth, 0.8- 1.0 mg cm ⁻²	1320 mAh g ⁻¹ at 50 mA g ⁻¹	0.65 V	~1000 mAh g ⁻¹ over 20 cycles	9a
S in carbon nanofiber film, ~1.0 mg cm ⁻²	~1200 mAh g $^{-1}$ at ~100 mA g $^{-1}$	~0.95 V	~600 mAh g-1 over 10 cycles	9b
S@mesoporous carbon with a 40 wt% S content	~1300 mAh g ⁻¹ at 251 mA g ⁻¹ .	~0.6 V	~400 mAh g ⁻¹ over 20 cycles	9c

^[a] and ^[b] The high capacity and low discharge voltage were found to be ascribed to reactions of electrolyte and coin-cell cases. ^[c] Refs. here are references in main text.