A New Strategy to Improve the Performance of Aluminum-Sulfur Battery

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Abstract. Both aluminum and sulfur are promising materials for future-generation electrochemical energy storage technology owing to their natural abundance, low cost, and high capacity. However, a rechargeable aluminum–sulfur (Al–S) battery with high energy density suffers from poor reversibility and very short cycle life. This paper demonstrates an Al–S battery which comprised of a MWCNT/S cathode, aluminum anode and deep eutectic solvent of AlCl3/acetamide. The Al–S battery delivers an initial capacity of ~453 mAh g\(^{-1}\) and maintains a capacity of up to ~358 mAh g\(^{-1}\) after 200 cycles.

Keywords: Al–S batteries, cycle performance, MWCNT/S composite material.

1. Introduction
In today's society, the rapid increase of energy demand and the environmental pollution caused by fossil fuel consumption are promoting the scientific research on renewable energy and energy storage and utilization [1]. Due to the variability and intermittence of renewable energy output, it is easy to cause the problem of poor grid stability. In order to eliminate the changes in the grid, a more efficient power storage system is needed [2,3]. Electrochemical energy storage system, i.e., battery system, determines the performance and capacity of energy storage system, which is very important for the application of power grid energy storage [4]. In the current electrochemical energy storage system, aluminum ion battery is considered as one of the best substitutes for lithium-ion battery because of its high-cost performance, good safety and environmental friendliness. Aluminum is abundant in the earth's crust (8.3%), which is the most common metal in the earth's crust. Its theoretical specific capacity and volume specific capacity are 2980 mAh g\(^{-1}\) and 8046 mAh cm\(^{-3}\) [5-6], respectively. It is widely used in secondary batteries and it has made substantial progress in the research of energy storage technology. It is an ideal electrode material for batteries [7]. At the same time, the theoretical specific capacity of elemental sulfur is 1675 mAh g\(^{-1}\) and the theoretical specific energy is 2600Wh kg\(^{-1}\) [8]. When sulfur compounds and elemental sulfur are directly used as electrodes, they have many advantages over traditional cathode materials. The specific capacity of 1071 mAh g\(^{-1}\) can be transferred during the electrochemical reaction of sulfur element, and the energy density of the battery can reach 1200wh kg\(^{-1}\) [9], which makes the Al-S battery as a new electrochemical energy storage device showing great potential in the application of power grid energy storage.

Although sulfur as a promising cathode material has been verified, it still faces many challenges. Firstly, elemental sulfur has high insulation. Secondly, as a material based on conversion reaction
mechanism, its volume expansion exceeds 80% during discharge, which easily leads to electrode structure deformation. In addition, dissolved polysulfides shuttle between electrodes will lead to the loss of active substances, this leads to the low coulomb efficiency and the decline of cycle stability [10]. Since 2009, the research on lithium sulfur battery based on carbon materials with high specific surface area and conductivity has developed rapidly. Many novel carbon materials designed by changing the structure can inhibit the occurrence of "shuttle effect", accelerate the electron/ion transmission, and enhance the conductivity and electrochemical activity.

Carbon nanotube (CNT) is considered to be an ideal substrate for high-performance composite materials due to its unique one-dimensional nanostructure, good electrical conductivity, excellent mechanical properties and stable chemical properties, which can be used in Al-S battery system [11]. Electrolyte is a key factor affecting the electrochemical performance and safety performance of aluminum sulfur battery (ASBs). Appropriate electrolyte can give Al-S battery excellent conductivity, wide operating voltage window and fast kinetic reaction rate. In recent years, low-cost urea/acetamide deep eutectic system has also been used in Al-S battery system, becoming a popular electrolyte. In this work, we chose multi walled carbon nanotubes (MWCNT) as the substrate of elemental sulfur and AlCl3/acetamide (AcA) as the electrolyte of Al-S battery to explore higher performance aluminum sulfur battery.

2. Experimental section

2.1. Preparation of Al – MWCNT/S battery

AlCl3 (purity 99.99%) and acetamide (AcA, purity 99%) were purchased from Sigma Aldrich. Aluminum foil (thickness 0.2 mm, purity 99.99%) and nickel foil (thickness 0.2 mm, purity 99.0%) are provided by Beijing Institute of nonferrous metals, China. Acetamide (AcA) was dried in a vacuum oven at 60 °C for 12 hours, and then transferred to an argon atmosphere glove box. AlCl3 was mixed with AcA with molar ratio of 1.3 in an argon atmosphere glove box at room temperature. The aluminum foil (20 mm × 20 mm) was polished with sandpaper and cleaned in ultrasonic bath. The aluminum foil was used as negative electrode after drying. MWCNT was mixed with sulfur powder at the mass ratio of (5:5, 7:3, 85:15) under argon protection and then heated at 155°C for 10h. The sulfur/carbon composite, Super-P, and 15wt.% polyacrylate emulsion adhesive (La132, provided by Chengdu Institute of Organic Chemistry) to form a uniform slurry were mixed at a mass ratio of (8:1:1) which was then coated onto nickel foil current collector followed by vacuum drying at 60 °C overnight. The sulfur loading is 0.5 mg cm⁻².

2.2. Electrochemical measurements

The constant current charge and discharge measurement of the battery was carried by using the NEWARE ct-4008-5V1A-s1 battery test system (Neware, Shenzhen, China). VMP3 potentiostat/galvanostat (Biological Science Instrument, France) was used for cyclic voltammetry measurement. The CV measured a voltage range of 1-2.5 V (vs. Al/Al³⁺) and ascan rate of 1 mv/s.

2.3. Characterization

Scanning electron microscopy (SEM) and Energy dispersive spectroscopy (EDS) were performed on Hitachi s-4800. Transmission electron microscopy (TEM) was performed with jem-2100uhr instrument. Thermogravimetric analysis was performed using a Mettler TGA 2 instrument.
3. Results and discussion

![SEM image of MWCNT/S composite material](image1)

![TEM image of MWCNT/S composite material](image2)

![EDS mapping images of the C and S elements in the MWCNT/S composite material](image3)

**Figure 1** a) SEM image of MWCNT/S composite material. b) TEM image of MWCNT/S composite material. c, d) EDS mapping images of the C and S elements in the MWCNT/S composite material.

Scanning electron microscopy (SEM) analysis (Fig. 1a) and transmission electron microscopy (TEM) (Fig. 1b, 2c, 3d) and found that sulfur has been loaded on carbon nanotubes by hydrothermal method, which indicates the successful preparation of MWCNT/S composite electrode.

![TGA analysis of sulfur (S\textsubscript{8}) and MWCNT/S composite material](image4)

**Figure 2** TGA analysis of sulfur (S\textsubscript{8}) and MWCNT/S composite material.

As shown in Figure. 2, the thermal stability of MWCNT/S composite material was investigated by thermogravimetric analysis (TGA). The rapid weight loss of element S begins at 200 °C and completely loses weight at 350 °C. For MWCNT/S composites, it begins to lose weight rapidly at 250 °C and completely lost weight at 350 °C. The results show that there is about 15% weight loss in MWCNT/S composite material, indicating that the sulfur content is 15 wt.%, which is consistent with the theoretical content of sulfur.
In order to study the electrochemical performance of Al-S battery and AlCl₃/acetamide (1.3 mole ratio) electrolyte, CV and galvanostatic charge discharge measurement were carried out. The redox behavior and kinetics of MWCNT/S cathode in Al-S battery were studied by cyclic voltammetry (CV) (Fig. 3). Figure 3a shows the CV curve of MWCNT/S cathode at the scanning rate of 1 mV/s. The scanning potential window is 1 - 2.5 V. It shows that an anodic peak appears from ~1.9 V and reaches its maximum intensity at ~1.7 and 1.8 V. The corresponding cathodic peak appears from ~1.95 V, forms a shoulder peak at ~2.0 V and reaches its maximum intensity at ~2.1 and 2.25 V. The reversibility of the CV curves is quite good. In Fig. 3b, two discharging plateaus at ~1.7 and 1.8 V is observable, corresponding to the CV anodic peak. The battery delivers a high discharging capacity of the fifth cycle is 493 mA h g⁻¹, and the discharging capacity of the 200th cycle is 358 mA h g⁻¹ at a current density of 1000 mA g⁻¹. The charge/discharge curve in Fig. 3b can well support the data in Fig. 3a.

![Figure 3](image1.png)

**Figure. 3** a) CV curves of the Al-S battery with a MWCNT/S cathode. b) Discharging/charging profiles at different cycles recorded at 1000 mA g⁻¹.

![Figure 4](image2.png)

**Figure. 4** Cyclability of the Al-S battery at a current density of 1000 mAg⁻¹. a) Capacities and Coulombic efficiencies of MWCNT without element S as a control experiment. b) Coulomb efficiencies of Al-S cell with a sulphur content of 50 wt%. c) Coulomb efficiencies of Al-S cell with a sulphur content of 30 wt%. c) Coulomb efficiencies of Al-S cell with a sulphur content of 15 wt%.
The influence of sulfur content in MWCNT/S composite material and the proportion of MWCNT/S composite material in slurry mixing on electrochemical performance was investigated. As a control, MWCNT and MWCNT/S composite material were treated by the same process. As shown in Fig. 3.4a, the long-term charging/discharging performance of Al-MWCNT battery was studied at a current density of 100 mA g\(^{-1}\) with a cut-off voltage between 2.48 and 1V. The initial specific capacity is 14.4 mAh g\(^{-1}\), after 100 cycles, the specific capacity is maintained at about 14.4 mA h\(^{-1}\), the discharge specific capacity is maintained at about 10.6 mAh g\(^{-1}\), and the coulomb efficiency is about 73%. The results show that the specific capacity of MWCNT contribution can be ignored. On the contrary, the batteries assembled with sulfur-containing cathode materials obtained relatively excellent specific capacity, which can be attributed to the contribution of elemental sulfur. The influence of MWCNT/S composite material with sulfur content of 50 wt%, 30 wt% and 15 wt% on the electrochemical performance was also studied. Figure 3.4b shows the performance of the Al-S battery with sulfur content of 50 wt% at a current density of 1000 mA g\(^{-1}\). The initial discharge specific capacity is 256 mAh g\(^{-1}\). After 20 cycles, the specific discharge capacity decreases to 96 mAh g\(^{-1}\), and after 200 cycles, the discharge specific capacity is 65 mAh g\(^{-1}\), and the sulfur utilization rate is more than 82%. Figure 3.4c shows the performance of the Al-S battery with 30 wt% sulfur content at a current density of 1000 mA g\(^{-1}\). The initial discharge specific capacity is 356 mAh g\(^{-1}\). After 20 cycles, the specific discharge capacity decreases to 102 mAh g\(^{-1}\), and after 200 cycles, the discharge specific capacity is 88 mAh g\(^{-1}\), and the sulfur utilization rate is about 80%. Figure 3.4d shows the performance of the Al-S battery with 15 wt% sulfur content at a current density of 1000 mA g\(^{-1}\). The initial discharge specific capacity is 453 mAh g\(^{-1}\). After 200 cycles, the discharge specific capacity can still be maintained at 358 mAh g\(^{-1}\), which is superior to the previous reports. Therefore, the performance advantages of the Al-S battery with 15 wt% sulfur content are obvious. The lower the sulfur content, the higher the discharge specific capacity may be due to the high resistance state of sulfur, the "shuttle effect" to a certain extent, and the difficulty of carbon nanotubes as one-dimensional nano materials to load more sulfur, which makes sulfur agglomerate together and cannot be used effectively, and it is difficult to transport ions.

4. Conclusions
In conclusion, the highly reversible Al-S cells with AlCl\(_3\)/acetamide electrolyte have been demonstrated at room temperature. The performance of Al-S cells with 15 wt% sulfur content in the composite material was more outstanding. At the current density of 1000 mA g\(^{-1}\), the initial specific capacity of the Al-S battery is 453 mAh g\(^{-1}\), and maintains a specific capacity of about 358 mAh g\(^{-1}\) after 200 charge/discharge cycles. Our findings show a battery system capable of harvesting electricity from a naturally abundant, low price, high energy source materials, which contributes to the improve cycle performance of stationery energy storage.

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