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Sulfur electrode modified by bifunctional nafion/γ-Al_2O_3 membrane for high performance lithium–sulfur batteries

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HIGHLIGHTS

- Sulfur cathode was modified by bifunctional nafion/γ-Al_2O_3 membrane.
- Polysulfides were successfully immobilized in the unique structure of the cathode.
- The effectivity and stability of the nafion/γ-Al_2O_3 membrane was confirmed.
- The modified cathode exhibited high capacity and excellent cycling performance.

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ABSTRACT

Lithium sulfur batteries have brought significant advancement to the current state-of-art battery technologies due to their high theoretical specific energy of 1675 mAh g^{-1}. However, the rapid capacity degradation, mainly caused by polysulfide dissolution, remains a significant challenge prior to practical applications. In this work, a sulfur cathode modified by bifunctional nafion/γ-Al_2O_3 membrane has been successfully prepared, which can remarkably immobilize the polysulfides within the unique cathode structure due to its ions selectivity and absorbent capacity. A high initial discharge capacity of 1448.0 mAh g^{-1} can be achieved at 1C and 788.6 mAh g^{-1} preserved after 200 cycles, indicating a slow degradation. Furthermore, the coulombic efficiency maintains as high as 97% during cycling. The excellent electrochemical properties can be attributed to the bifunctional and stable membrane which can dramatically reduce the shuttle effect and keep integrated even after charging–discharging for 200 cycles.

1. Introduction

Lithium–sulfur batteries, characterized by high theoretical capacity, low cost and natural abundance of the active element, have attracted increasing attention as one of the most promising system to meet the market requirements. Assuming complete reduction of sulfur to form Li_2S, the theoretical specific capacity and energy of Li–S batteries are 1675 Ah kg^{-1} and 2600 Wh kg^{-1}, respectively, substantially higher than those of state-of-the-art lithium ion batteries [1–3]. However, to conquer the marketplace, some hurdles still remains to be cleared, such as the inherently poor electrical conductivity of sulfur (5×10^{-30} S cm^{-1} at 25 °C), significant structure and volumetric changes during the charge–discharge process and the high solubility in organic electrolytes of the polysulfides Li_2S_x ($2 < x \le 8$) [4]. Hence, Li–S battery suffers poor cycle life, low utilization and limited rate capability of sulfur.

In response to these challenges, various strategies have been investigated, including immobilization of sulfur in conducting polymer [3,5–7] and porous carbon matrix [8–11], exploration of different binders [12–14] and optimization of the organic electrolyte [15–17]. Another effective strategy to retrain polysulfides from diffusion is cathode surface modification. Several kinds of carbon or conductive polymer layers has been employed to enhance the cycle performance and capacity retention of lithium sulfur cell, including porous multiwalled carbon nanotube paper [18], microporous carbon paper [19], treated carbon paper [20–22] polydopamine [23], polypyrrole [24] and so on. Nafion, as a well-known perfluoro ionomer, has been adopted in our previous work to enhance electrochemical performance of Li–S batteries by coating nafion membrane on the electrode surface due to its high cation conductivity and anion inconductivity [25]. However, it showed poor cycle capacity at high C rate and the nafion film was about 10 μm in thickness, which increases the cost.

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Herein, we propose a bifunctional nafion/γ-Al_2O_3 membrane to protect the lithium sulfur batteries from shuttle mechanism. Nafion is adopted here as matrix due to its cation selectivity. γ-Al_2O_3 is introduced as sorbent to absorb the polysulfides during charge–discharge process to improve the electrochemical performance of the cells because of its porous structure and absorbent capacity [26–28]. Meanwhile, the porous structure can provide abundant channels for lithium ions to pass through and store electrolyte for redox reaction. Hence, the cation selective nafion and the porous γ-Al_2O_3 are expected to work co-operatively to provide efficient immobilization of sulfur, as a direct consequence to improved electrochemical properties. Furthermore, enhanced electrochemical performance could be obtained by changing the γ-Al_2O_3 content, which indicates that the dual nafion/γ-Al_2O_3 has potential application in advanced lithium sulfur batteries.

2. Experiment

2.1. *Preparation of sulfur carbon materials*

Elemental sulfur (AR, Aladdin, China) (3.5 g) was uniformly mixed with the carbon Bp 2000 (Black pearls 2000, Cabot Corporation) (1 g) by a ball-milling method for 10 h at 300 r min^{-1}. Then the mixture was managed by a traditional thermal melt method. In detail, 1.5 g mixed sulfur–carbon material was firstly heated to 155 °C and kept for 8 h with N_2. At this temperature, the melt sulfur with the lowest viscosity can easily diffuse into the meso/micropores of the carbon Bp 2000. The temperature was then increased to 300 °C and kept for 2 h to vaporize the sulfur covered on the surface of the carbon. The sulfur content is 52.8 wt.% in SC composite, confirmed by thermal gravimetric analyzer (TGA).

2.2. *Preparation of nafion/γ-Al_2O_3 solution*

Nafion solution (wt.% = 5%) was purchased from Dupont Company. The solution was neutralized by LiOH until its pH = 7 to get lithiated nafion solution. Then γ-Al_2O_3 (AR, Aladdin, China) was dispersed in the as-prepared nafion solution under bath sonication for 1 h insuring homo-disperse. For comparison, nafion solutions with 0.5 wt.%, 1 wt.% and 2 wt.% γ-Al_2O_3 were prepared.

2.3. *Cell assemble*

The cathode electrode was fabricated with heat treated S/C composite, acetylene black and polyvinylidene fluoride in a weight ratio of 70:20:10, followed by adding a certain amount of *N*-methyl-2-pyrrolidinone to form a homogeneously slurry. The slurry was casted onto carbon coated aluminum foil via doctor-blade coating technique and dried at 50 °C for 22 h under vacuum. After that, a certain amount of nafion solution or nafion/γ-Al_2O_3 solution was casted on the surface of the cathode and finally dried for another 2 h to get a membrane coated electrode. Electrodes were punched into round disks with a diameter of 14 mm. CR2032 coin cells were assembled in a glove box filled with argon. A microporous polypropylene film (Celgard 2000) was used as a separator, and lithium metal as the counter and reference anode. Meanwhile, 0.1 M anhydrous lithium nitrate and 1 M lithium bis(trifluoromethane sulfonyl)imide ($Li(SO_2CF_3)_2$, LiTFSI) in 1,3-dioxolane (DOL) and dimethyl ether (DME) (1:1 by volume) (AR, Guotai-Huarong New Materials, China) was used as the electrolyte.

2.4. *Characterization and electrochemical measurements*

The morphologies of the electrodes were characterized by scanning electron microscopy (SEM, HITACHI, S-4800). Corresponding EDS line scanning and mapping were performed. Nitrogen adsorption and desorption isotherms were obtained using a Quantsorb at 77 K; the γ-Al_2O_3 was degassed on a vacuum line at 250 °C. The specific surface area, pore size distribution and pore volumes were determined by Brunauer–Emmett–Teller (BET) theory and the Barrett–Joyner–Halenda (BJH) model adsorption branch of the isotherms. ^1H NMR spectra were obtained at 25 °C on a VARIAN INOVA 500 MHz spectrometer (America) using $CDCl_3$ as solvent. The chemical shift values reported here are calibrated using $CDCl_3$ as a reference. The morphologies of γ-Al_2O_3 were observed by transmission electron microscopy (TEM, Hitachi JEM-2100F, Japan). Cyclic voltammetry (CV) measurements were carried out at a scan rate of 0.1 mV s^{-1} within the voltage of 1.5–3.0 V (CHI600D electrochemical workstation, Chenhua, China). Galvanostatic charge–discharge tests were performed between 1.5 V and 3 V on a Land test system (LAND-CT2001A, Wuhan Xinnuo, China) at different C rates. Electrochemical impedance spectroscopies (EIS) were measured on Zahner IM6e electrochemical workstation (Germany) in the frequency range of 1 MHz–100 mHz at a disturbance amplitude of ±5 mV.

The electrode modified by nafion membrane and nafion with 0.5 wt.%, 1 wt.%, 2 wt.% γ-Al_2O_3 were marked as NSC, NASC-0.5, NASC-1, NASC-2, respectively. As comparison, electrode without membrane, named as SC, was prepared in the same method and tested under same condition.

3. Result and discussion

Nafion and γ-Al_2O_3 work together in NASC during charge–discharge process. As illustrated in Fig. 1, during discharging process lithium ions diffuse through the nafion/γ-Al_2O_3 membrane to the cathode to react with the sulfur or polysulfides. Meanwhile, soluble polysulfides can be effectively retrained inside the membrane, which guarantees good electrochemical performance. This is not only because nafion can prevent high-order lithium polysulfide from diffusing to lithium electrode due to its ionic selectivity but also γ-Al_2O_3 can absorb and adhere the lithium polysulfide due to its porous structure (Fig. 2) and absorbent capacity [26]. It is similar in the charging process during which the lithium ions diffuse away through the bifunctional membrane while polysulfides can be reserved. Hence, the shuttle effect can be effectively prevented. In addition, the space between the active material and modified film can accommodate the volume expansion during cycling. Therefore, improved electrochemical performance is certainly forecasted.

The pore structure of γ-Al_2O_3 is characterized by N_2 adsorption/desorption isotherms with a high specific surface area of 144.3 m^2 g^{-1}. The total pore volume is 0.716 cm^3 g^{-1} calculated by

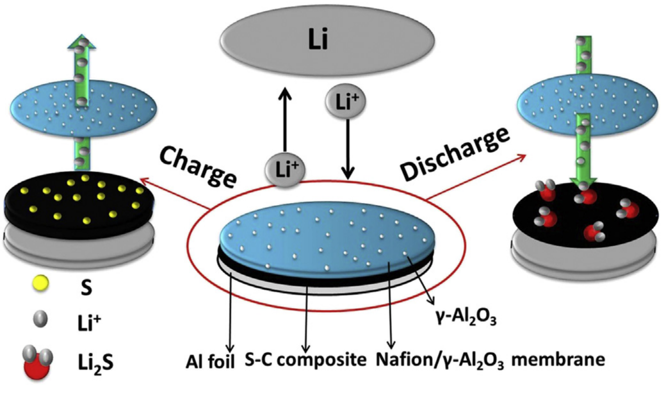

Fig. 1. Schematic illustration of electrode modified by nafion/γ-Al_2O_3 membrane during charge–discharge process.