Polythiophene/Carbon Microsphere Composite as a High-performance Cathode Material for Aluminium-ion Batteries

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Abstract. Due to the high theoretical volume specific capacity and mass specific capacity of aluminum-ion batteries, they can meet the needs of contemporary society for high-performance energy storage devices, and have attracted a lot of research strength. Cathode materials are a key issue limiting the development of aluminum-ion batteries. Herein, polythiophene was prepared on the surface of carbon microspheres by in-situ oxidative polymerization, resulting in polythiophene carbon microsphere composite materials. It exhibits excellent electrochemical performance, as a cathode material for aluminum-ion batteries, in terms of a high specific capacity (106 mAh g⁻¹ at a current density of 1 A g⁻¹), good stability (maintaining 58 % of initial capacity after 10000 cycles) and excellent rate performance (90 mAh g⁻¹ at a high current density of 3.5 A g⁻¹).

1. Introduction
Driven by the demand for electric vehicles and large-scale smart grids, high-energy batteries become a research focus.¹ In recent years, the research on lithium-ion batteries is relatively mature, but there are problems such as low cycle stability, poor safety and high cost.²³ In contrast, aluminum-ion batteries (AIBs) have the advantages of low cost and high safety. Since each aluminum ion can exchange up to three electrons, it has a high theoretical volume capacity of 8056 mAh cm⁻³ and mass capacity of 2042 mAh cm⁻³. Appropriate cathode materials are particularly important for the performance of AIBs. ⁴ So far, the cathode materials for AIBs mainly focus on carbon materials (e.g., defect-free graphene), metal oxides (e.g., VO₂, Co₃O₄ and V₂O₅), metal sulfides (e.g., NiS², SnS₂ and MoS₂) and some recently proposed organic compounds (e.g., polyaniline¹¹). Compared with inorganic materials, organic electrode materials have the advantages of mild synthesis conditions, environmental friendliness, designable structure, and low cost.¹² In our previously work¹¹, polyaniline was used as a cathode material in AIBs, and it showed a high specific capacity of 180 mAh g⁻¹ at a current density of 1 A g⁻¹. Therefore, polythiophene, as one of the three major conductive polymers, is also promising for AIBs cathode materials.

In this work, carbon microspheres used as a substrate material to load polythiophene on its surface by chemical oxidation polymerization, resulting in a polythiophene carbon microsphere composite. The
presence of carbon microspheres can effectively avoid the agglomeration of polythiophene during the polymerization process, benefiting for fully exposing the active sites of polythiophene and enabling the battery to obtain a high specific capacity. On the other hand, the good conductivity of carbon microspheres is also conducive to the battery's good rate performance. In addition, due to the interaction between polythiophene and carbon microspheres, the composite structure has good stability, so that the battery has good cycle stability.

2. Experimental

2.1. Polythiophene Carbon microsphere composite synthesis

Polythiophene was prepared on the surface of carbon microsphere by chemical oxidation polymerization. In a typical synthesis, 100 mg of carbon microsphere was dispersed in 50 mL of chloroform solution and ultrasonic for 30 min. Then, 2.4 g anhydrous FeCl₃ was added to the above carbon microsphere dispersion with magnetic stirring, and cooled to 0℃, resulting in solution A. Afterward, 300 mg thiophene monomer was dispersed in 30 ml chloroform solution, resulting in solution B. Afterwards, solution B was added dropwise to solution A using a peristaltic pump. The reacting solution was kept at 0℃ for 12 h. The product was washed with 1M hydrochloric acid until the supernatant became colorless. Then, the product was washed several times with deionized water until the pH of the solution was close to 7. The solid product was collected and dried under vacuum at 60℃ for 12 h.

2.2. Electrolyte preparation

Before preparation, 1-ethyl-3-methyl-imidazolium chloride ([EMIm]Cl) was degassed under vacuum at 60℃ for 12 h. Then, anhydrous aluminum chloride (AlCl₃) was added to [EMIm]Cl slowly, and the molar ratio of AlCl₃ and [EMIm]Cl was 1.3:1. The entire process was performed in an argon-filled glove box.

2.3. Battery assembly

The as-prepared polythiophene carbon microsphere composite material, acetylene black and polyvinylidene fluoride (PVDF) were mixed and ground at a mass ratio of 8:1:1, and the mixture is ultrasonically dispersed in N-methyl pyrrolidone (NMP), resulting a slurr. The slurry was dip-coated on the Mo sheet, and dried at 60℃ for 6 hours. Glass fiber membrane and aluminum foil were selected as the separator and the anode, respectively. Finally, the battery was assembled using a customized battery mold (Swagelok type).

2.4. Structure characterizations and electrochemical performance

X-ray diffractometer using a Cu Kα radiation (model) was used to characterize the crystal structure of the samples. The microscopic morphology of the samples was observed by scanning electron microscope (model). The battery test system (model) was used to determine the charge and discharge characteristics and cycle stability of the materials.

3. Results and discussion

![Figure 1. Schematic representation for the synthesis of polythiophene carbon microsphere composites.](image)
As shown in Figure 1, we synthesized polythiophene by in-situ polymerization on the surface of carbon microspheres by chemical oxidation polymerization. Fig. 2(a) reveals that the carbon material used in this work was uniform-sized carbon microsphere approximately 1.7 μm in diameter) with relatively smooth surface. After the thiophene polymerization process, the surface of the carbon microspheres was uniformly covered with a thin film, resulting in a rough surface (Figure 2(b)). The elemental mapping of the microsphere (Figure 2(c)) shows that S is uniformly distributed on the surface of the microsphere, indicating that the polythiophene was coated uniformly on the surface of the carbon microsphere. It is reported that the π-π interaction and/or conjugate effect may occur between carbon surface and aromatic Pth rings.13-14 According to XRD spectra analysis (Figure 2(d)), polythiophene carbon microsphere has both the characteristic peaks of carbon microspheres and polythiophene, again indicating the successful preparation of polythiophene carbon microsphere composite.

![Figure 2](image-url)

**Figure 2.** (a) SEM image of carbon microspheres; (b) SEM image of polythiophene carbon microsphere composite; (c) the element maps of S element in polythiophene carbon microsphere composite and (d) XRD spectra of polythiophene, carbon microspheres and polythiophene carbon microsphere composites.

The as-prepared polythiophene carbon microsphere composite material was used as the cathode material of aluminium ion battery, and its electrochemical performance was investigated. We first optimized the cut-off voltage of the battery through the galvanostatic charge-discharge test. As illustrated in Figure 3 (a), when the voltage is higher than 2.4 V, the coulombic efficiency of the battery will be significantly decreased. This may be due to side reactions such as the decomposition of the electrolyte under high voltage. Considering both the specific discharge capacity and coulomb efficiency, 2.3 V was selected as the cut-off voltage for the charge-discharge process. In the voltage range of 0.1-2.3 V, the rate performance of the polythiophene carbon microsphere composite material was tested (Figure 3(b)). The battery can achieve specific capacities of 104, 100, 97, 94, 91, and 90 mAh/g, at the current densities of 1, 1.5, 2, 2.5, 3, and 3.5 A/g, respectively, and the capacity retention ratio at 3.5 A/g reaches about 86.5% of that at 1 A/g, indicating that the battery has a good rate performance. Polythiophene carbon microspheres provided a specific capacity of 106 mAh/g in the first cycle (at a current density of 1 A g⁻¹), and maintained 63 mAh g⁻¹ after 10000 cycles with coulombic efficiencies as high as 99.3–100%. This excellent electrochemical performance was closely related to its structural characteristics. First, the uniform dispersion of polythiophene on the surface of carbon microspheres is conducive to the full exposure of the active sites of polythiophene, leading to high capacity. Secondly,
the high conductivity of carbon microspheres and the interaction between polythiophene and carbon microspheres are benefit to the rate performance of the material. Third, the interaction between polythiophene and carbon microspheres makes the structure of the composite material stable. This makes the composite material withstand the repeated doping/dedoping of active ions during the charge and discharge process, thereby improving the cycle stability of the material.

![Figure 3](image)

**Figure 3.** Electrochemical performance of polythiophene carbon microsphere composite materials as a cathode material for aluminium ion batteries (a) constant current charge and discharge under different cut-off voltages; (b) rate performance and (c) cycle performance.

In order to further analyze the electrochemical kinetics of polythiophene carbon microspheres cathode, we analysed the CV curves of different scan rates (0.5–10 mV s\(^{-1}\)) shown in Figure 4(a). With the scanning rate increasing, the shape of the CV curve changed slightly, showing weak polarization. In general, the peak current (i) and scan rate (v) obey \(i = av^b\), where a and b are two coefficients. When b=0.5, it represents the solid diffusion-control process, and b=1 represents the surface-control process. Figure 4(b) shows that the b values corresponding to the oxidation peak (Peak 1) and reduction peak (Peak 2) are 0.987 and 0.919, respectively, indicating surface-controlled capacitive energy storage. The formula \(i(v) = k_1v + k_2v^{1/2}\) can quantitatively analyze the capacity contribution, where \(k_1v\) is the capacitance contribution part of surface-controlled, and \(k_2v^{1/2}\) is the diffusion-controlled part. Figure 4(c) shows the contribution ratio of the surface-controlled capacity of the polythiophene carbon microsphere composite electrode at 1 mV/s, taking up 71% of the total capacity. In addition, with the increase of the scan rate, the contribution ratio of the capacitive contribution gradually increases (Figure 4(d)), also indicating that the capacitive contribution is dominant.
Figure 4. Electrode process analysis of the polythiophene@carbon microsphere composite. (a) CV curves of Pth@GO-3 at scan rates of 0.5, 1, 2, 5 and 10 mV s$^{-1}$; (b) determination of the b-value according to the relationship between peak current and scan rate; (c) the capacitance contribution ratio of surface-controlled contribution at 1 mV s$^{-1}$ and (d) the normalized contribution of the diffusion-controlled and surface-controlled at different scan rates.

4. Conclusion

In this work, polythiophene carbon microsphere composite was synthesized through in-situ polymerized polythiophene on the surface of carbon microspheres. Due to the combination of polythiophene and carbon microspheres, the problem of easy agglomeration of polythiophene is overcome, so that its active sites can be fully exposed. In addition, the interaction between carbon microspheres and polythiophene is also conducive to the structural stability of the composite material, making the composite material withstand the repeated doping/dedoping of active ions. Furthermore, the good electrical conductivity of carbon microspheres and polythiophene make the composite material have good electrical conductivity, which is favorable to its rate performance. As the cathode material for the aluminum ion battery, the polythiophene carbon microsphere composite material showed excellent electrochemical performance in terms of high specific capacity, excellent rate performance and cycling stability. This study shows that polythiophene carbon microsphere composite material is a promising cathode material for aluminum ion batteries.

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