Carbonyl-based polyimide immobilization on carbon nanotubes for aqueous zinc-ion batteries

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Abstract. The aqueous-based zinc-ion batteries (ZIBs) with higher safety and performance have gained great attention from scientists. Nevertheless, previous electrode materials mainly rely on inorganic metal oxides, and their structure is prone to collapse during charge and discharge, thus resulting in poor cycle stability, which severely limits the development of ZIBs. Here, a novel conjugated polyimide based conjugated microporous polymer (CMP) and multi-walled carbon nanotubes (CNT) hybrid has been gained and used as cathode material for ZIBs. The aromatic carbonyl group as active site can reversibly receive and release zinc ions, thus showing good electrochemical performance. This work provides new view for the design of high-performance ZIBs electrode materials.

1 Introduction:
The rapid development of the scientific and technological revolution has promoted the rapid consumption of fossil fuels and other non-renewable energy sources and has caused serious pollution to the environment. Therefore, the development of renewable resources and new high-performance energy storage technologies (ESTs) has become the main development point for researchers. In recent years, lithium-ion batteries (LIBs), which are recognized as advanced ESTs and conversion equipment and have made great achievements in portable electronic products (laptops, mobile phones, etc.)[1]. However, potential safety and environmental issues, high costs, and limited lithium resources have impeded the development of LIBs in new ESTs[2]. In this case, compared with expensive and unsafe non-aqueous ion batteries, the development of water-based batteries can solve the above-mentioned problems[3].

Owing to the higher theoretical capacity of Zn anode (5854 mAh cm⁻³ and 820 mAh g⁻¹), lower reduction potential (-0.76 V), high stability in aqueous solution, intrinsic safety and low cost, ZIBs have received widespread attention[4]. In order to obtain excellent electrochemical performance, one of the key components of ZIBs: the cathode material, has been extensively studied. However, most of the cathodes of ZIBs reported so far are made of inorganic metal materials (manganese oxide, vanadium oxide, etc.) and Prussian blue analogs, which faces problems such as massive consumption of resources and environmental pollution[5]. In addition, because of the large ion radius of Zn²⁺, inorganic electrode materials with rigid structures will undergo phase change during the reversible insertion of Zn²⁺, thus resulting in poor electrochemical performance.

In recent years, more and more researchers have turned their attention to organic electrode materials because of their structural diversity and abundant resources[6]. The soft crystal lattice and adjustable organic porous structure can adapt to the reversible insertion/extraction of Zn²⁺ and rapid ion diffusion extraction. Among the discovered organic electrode materials, compounds containing
carbonyl groups gained widely studied as electrode materials[7]. Gao et al. [8] successfully synthesized an zinc-organic cathode material, which combining electroactive quinone and pyrazine moieties in one unit, resulting the 86% of the theoretical capacity and outstanding energy density. Sun et al. [7] prepared a carbonyl-containing cathode material bridged by thioether bonds. The introduction of thioether bonds can solve the solubility problem and increase the electrochemical stability. In this work, a novel polyimide based conjugated microporous polymer (CMP) has been prepared from the 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTH) and 4,4',4''-(1,3,5-triazine-2,4,6-triy) trianiline (TA), named TNP, which integrates anhydride and triazine structure. Abundant carbonyl groups can be used as active sites to reversibly react with zinc ions. At the same time, abundant triazine ring is expected to improve the conductivity of the polymer. In order to further improve the conductivity, multi-walled carbon nanotube (CNT) is added in the polymer synthesis process. The obtained composite (TNP@CNT) is used as a ZIBs cathode material, which shows an initial specific capacity of 45.8 mAh g⁻¹ and good cycling stability at 20 mA g⁻¹.

2 Experiment Section

2.1. Material preparations

TNP@CNT composite were prepared according to the previous works [24]. Commercially available raw materials and reagents do not require further purification. Firstly, 54.4 mg CNT, 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTH, 40.2 mg, 0.15 mmol) and 4,4',4''-(1,3,5-triazine-2,4,6-triy) trianiline (TA, 35.4 mg, 0.1 mmol) were mixed and poured into a pyrex tube, subsequently, 1.5 mL NMP, 0.3 mL mesitylene and 0.03 mL isoquinoline were added into the aboved mixture and ultrasonication for 0.5 h. The system containing the mixture is refrigerated and vacuumed to replace the inert gas, sealed and put in oven. After react with 150 °C for 96 h, the obtained product is gained by centrifugation and washed with DMF, THF, EtOH, respectively.

2.2 Material Characterization

Fourier-transform infrared (FTIR) spectra were tested in the wavenumber range of 500-4000 cm⁻¹ with Bruker ALPHA spectrometer. SEM observations were carried out on a JEM-6701F (JEOL Ltd.). XRD measurements were carried out on a XPERT MPD.

2.3 Electrochemical measurements

Combining TNP@CNT composite powder (80%), acetylene black (10%) and carboxymethylcellulose sodium (CMC, 10%) binder to prepare working cathode, then the mixture was ground thoroughly in a mortar with deionized water until homogeneous slurry was got. Then the mud was put on hydrophilic carbon paper and dried at 80°C overnight. The CR2016-type cells were fabricated in air employing Zn foil as the counter electrode. Meanwhile, the working electrolyte is 3 M ZnSO₄ aqueous solution, and the separator is glass fiber. LAND CT2001A battery testing system (Wuhan, China) is employed to test the galvanostatic discharge/charge (GCD) performance. CHI660E electrochemical workstation (Shanghai, China) was used to gain the Cyclic voltammetry (CV) results.

3 Results and discussions

3.1. Synthesis and characterizations
Fig. 1. The preparation routes of TNP@CNT.

Fig. 1 presents the preparation route of the polyarylimide composite, which was prepared by employing NTH and TA as basic building block, CNT as substrate. The selection of these units can not only form a large number of pores, but also establish more redox active sites within the polymer framework. Simultaneously, CNT as a substrate is expected to increase the conductivity of the polymer, thereby increasing the utilization of active sites of organic cathode materials.

Fig. 2. FT-IR spectra of TA, NTH, CNT and TNP@CNT.

First, FT-IR is conducted to demonstrate the successful condensation of polyarylimide framework (Fig. 2). Obviously, the disappearance of the stretching vibration peaks at 3444 and 3353 cm\(^{-1}\) belong to the -N-H peaks in TA. At the same time, on the FT-IR spectrum of TNP@CNT, the appearance of a new vibration peak at 1333 cm\(^{-1}\) indicates the formation of C-N-C bond in imide functionality. In addition, several vibration peaks around 1714 and 1668 cm\(^{-1}\) ascribed to the asymmetric and symmetric stretching bands of C=O in imide functionality. These phenomena indicate the formation of polymer.

Fig. 3. SEM image of TNP@CNT.
Subsequent, the morphology of the obtained TNP@CNT hybrids are analysed through SEM. As displayed in Fig. 3, the morphology of TNP@CNT hybrids is based on regular-shaped rod structure with a large number of micropores. The addition of CNT builds a porous structure, which can be used as electrolyte storage place and a good conductive network, thus resulting the electrochemical performance of electrode materials improved.

![XRD curves of TNP@CNT and NTH.](image)

Fig. 4. XRD curves of TNP@CNT and NTH.

The XRD results of TNP@CNT and NTH shown in Fig. 4 further confirm the formation of the target complex. From the Fig. 4, we can clearly see that NTCDA has obvious XRD characteristic peaks, but TNP@CNT does not have obvious characteristic peaks. These results in disguise prove the successfully synthesis of the target product.

3.2. Electrochemical characterization of TNP@CNT

![CV curves of TNP@CNT cathode at 0.1 mV s⁻¹.](image)

Fig. 5. CV curves of TNP@CNT cathode at 0.1 mV s⁻¹.

In order to study the unique electrochemical zinc ion storage performance of TNP@CNT cathode materials, a CR2016-type half-cell was assembled, which used zinc sheet as the counter electrode and ZnSO₄ in deionized water (3 M) as the electrolyte. Initially, CV measurement is employed between a voltage window of 0.2-0.9 V (V vs Zn²⁺/Zn), shown in Fig. 5. Obviously, from the CV curves of TNP@CNT, single broad reduction and oxidation peaks around 0.35 and 0.49 V can be observed, which corresponds to a reversible reaction from C=O to C-O-Zn to C=O, respectively. The subsequent CV curves display similar redox peaks, proving the good chemical reversibility of TNP@CNT.
Fig. 6. GCD profiles of TNP@CNT at 20 mA g$^{-1}$.

Fig. 6 presents the representative galvanostatic charge/discharge test at 20 mA g$^{-1}$, there is a tilted platform during charging and discharging progress, which corresponds well to the CV curve.

Fig. 7. Cycle stability of TNP@CNT at 20 mA g$^{-1}$.

For further investigate the long cycling behavior, continuously galvanostatic charge/discharge measurements are conducted. As seen in Fig. 7, TNP@CNT displays pristine discharge and charge specific capacities of 45 and 45.8 mAh g$^{-1}$ at a 20 mA g$^{-1}$, respectively. After 100 cycles continuously galvanostatic charge/discharge measurement, TNP@CNT can also provide a discharge specific capacity of 31 mAh g$^{-1}$. Meanwhile, a coulombic efficiency (CE) approaching ~98% can be acquired, demonstrating the robustness of TNP@CNT as a cathode material in ESTs.

Continuous testing cycle performance under different current densities is an important indicator for testing battery systems. As shown in Fig. 8, TNP@CNT displays a discharge capacity of 34 mAh g$^{-1}$. Until the
current density rises to 500 mA g\(^{-1}\) stepwise, TNP@CNT also can present a discharge capacity of 34 mAh g\(^{-1}\), and the charge and discharge capacities remain almost constant. What is more striking is that when the current density is reduced to 20 mA g\(^{-1}\) again, a specific capacity of 39.5 mAh g\(^{-1}\) can still be obtained.

4 Conclusions
In this work, a novel conjugated polyimide based CMP@CNT hybrid has been prepared. The material with polyimide and CNT has an unparalleled rigid structure and a porous structure that facilitates ion transport. Overall, a good electrochemical performance can be found when TNP@CNT is employed as a cathode material for organic ZIBs. The research results show that the new polyimide we designed is a promising aqueous energy storage material.

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