

Chloride ion-doped polyaniline/carbon nanotube nanocomposite materials as new cathodes for chloride ion battery

Zhigang Zhao^a, Tingting Yu^a, Yingchun Miao^b, Xiangyu Zhao^{a, c, *}

^a College of Materials Science and Engineering, Nanjing Tech University, 5 Xinmofan Road, 210009 Nanjing, China

^b Advanced Analysis and Testing Center, Nanjing Forestry University, 159 Lonpan Road, 210037 Nanjing, China

^c Jiangsu Collaborative Innovation Center for Advanced Inorganic Functional Composites, Nanjing Tech University, 210009 Nanjing, China



ARTICLE INFO

Article history:

Received 5 February 2018

Received in revised form

1 March 2018

Accepted 11 March 2018

Available online 13 March 2018

Keywords:

Polyaniline

Chloride ion

Rechargeable batteries

Cathode materials

Electrochemistry

ABSTRACT

Finding and optimizing the appropriate cathode materials in the electrolyte are critical to the development of chloride ion batteries. Herein, chloride ion-doped polyaniline/carbon nanotubes (PANI/CNTs) composite materials, which were prepared by an in situ chemical oxidative polymerization method using $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as the oxidant, have been developed as new cathodes for chloride ion battery. The PANI/CNTs cathode showed reversible electrochemical energy storage through redox reactions of nitrogen species and chloride ion transfer, as confirmed by the results of the electrochemical testing and X-ray photoelectron spectroscopy. The structural configuration of PANI by the incorporation of conductive CNT carrier contributed to significant improvement in the electrochemical properties. More than 80 mAh g^{-1} stable capacity and a high Coulombic efficiency of about 99% were delivered. This work offers a promising strategy for designing chloride ion storage electrode and novel electrochemical systems.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Alternative battery chemistries such as Na^+ , K^+ , Mg^{2+} , Zn^{2+} or Al^{3+} beyond lithium ion and using abundant electrode materials have been developed [1–6]. Besides cation systems, new battery chemistries allowing anion transfer such as F^- and Cl^- have been recently reported [7–11]. The room temperature rechargeable battery system was firstly realized for the chloride ion system in the non-aqueous or aqueous electrolyte [10–17]. This battery system can theoretically deliver high energy density and shows abundant chloride-containing materials available worldwide. The detailed advantages were listed in the recent excellent review work by Gschwind et al. [18]. Finding and optimizing the appropriate cathode materials in the electrolyte are critical to the development of chloride ion batteries (CIBs). Metal oxychlorides such as layered BiOCl , FeOCl and VOCl were proposed as new cathode materials for CIBs in the Lewis base ionic liquid electrolyte [11,14,15]. It is interesting that the BiOCl material was further applied as the chloride ion Faradaic electrode in the seawater desalination system and showed high electric charge efficiency of above 95% for chloride ion

desorption/absorption [19]. Besides the inorganic cathode materials, organic conjugated polymer polypyrrole chloride (PPyCl) with high chemical stability has also been developed [16]. This cathode showed dominant electrochemical reactions by the chloride ion deintercalation/intercalation during cycling. Most research on the conjugated polymers has focused on polypyrrole (PPy), polyaniline (PANI) and polythiophene (PTH) due to their ease of synthesis, high electrical conductivity, high Coulombic efficiency and attractive mechanical properties towards the flexible electrochemical energy storage (EES) devices [20,21]. One of the successful electrochemical active materials is polyaniline, which was firstly developed in commercial batteries, had high oxidative stability and exhibited interesting redox chemistry and doping mechanisms [22,23]. Many studies have been performed using polyaniline as active materials or functional composite components in the electrodes of rechargeable batteries and supercapacitors [20,22–27]. Furthermore, both p-doping and n-doping polyaniline electrode materials have been developed for EES based on cation transfer [24,28].

Herein, we focus on anion transfer of polyaniline as cathode material in the CIB system. The nanostructured chloride ion-doped polyaniline (PANI) materials were prepared by chemical oxidative polymerization with the incorporation of carbon nanotubes (CNTs). The PANI/CNTs cathode showed reversible redox reactions based on Cl^- transfer. More than 80 mAh g^{-1} capacity and a high Coulombic

* Corresponding author. College of Materials Science and Engineering, Nanjing Tech University, 5 Xinmofan Road, 210009 Nanjing, China.

E-mail address: xiangyu.zhao@njtech.edu.cn (X. Zhao).

efficiency of 99% were delivered.

2. Experimental

The composite of a chloride ion-doped PANI with multiwalled carbon nanotubes (MWCNTs) were synthesized via in situ chemical oxidative polymerization. Multiwalled carbon nanotubes (Aladdin, >95%) were purified and oxidized in a mixture of concentrated $\text{H}_2\text{SO}_4/\text{HNO}_3$ with a 3:1 ratio at 70°C for 2 h under an ultrasonic condition. Aniline monomer (Alfa Aesar, >98%) was purified before use by vacuum distillation at 453 K using a rotary evaporator. A schematic fabrication process of the PANI/CNTs nanocomposite material was shown in Fig. 1a. The as-prepared carbon nanotubes were dispersed in 1 M HCl solution by ultrasonication for 2 h, in order to obtain well-dispersed suspensions. Then the purified aniline monomer was added via a syringe. After fifteen minutes, the oxidant $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (Aladdin, 99%) aqueous solution was added dropwise. The dark suspension became green. The polymerization was allowed to proceed for 24 h. All the procedures were carried out with stirring and Ar atmosphere protection at 0°C . The resulting precipitate was filtered and rinsed with distilled water and ethanol several times until the washings were clear and neutral, followed by 24 h vacuum drying at 333 K. The as-prepared PANI/CNTs composites including 10, 30 and 50 wt% CNTs are denoted as PANT/10CNTs, PANI/30CNTs and PANI/50CNTs, respectively. Pure chloride ion-doped PANI with greenish black in color was prepared by the same procedures without the addition of carbon nanotubes. In addition, the chemically dedoped PANI was

obtained by soaking the pure chloride ion-doped PANI in 1.5 M $\text{NH}_3 \cdot \text{H}_2\text{O}$ and deprotonating for 24 h at room temperature. The product was washed with deionized water until the filtrate had a pH of 7 and then dried in vacuum at 333 K for 24 h. The blue-black dedoped PANI was obtained.

X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS, Thermo Scientific), transition electron microscopy (TEM, FEI Philips CM300UT/FEG) and field-emission scanning electron microscopy were performed to characterize the structure, composition and morphology. XPS curve fitting was carried out using the standard nonlinear background subtraction and a Gaussian–Lorentzian ratio of 85:15. The specific surface area (SSA) was measured by Brunauer-Emmett-Teller (BET) method at 77 K using a BELSORP-Mini instrument. Fourier transform infrared spectroscopy (FTIR) was recorded on a Bruker Tensor 27 Infrared spectroscopy instrument.

Electrochemical measurements were conducted using coin cells (CR2032) with lithium metal (Alfa Aesar) as anode [10,15], which has a diameter of 16 mm. The PANI and PANI/CNTs electrodes were prepared by a simple slurry coating method. The active material (80 wt%), conductive carbon black (10 wt%) and PTFE (Aladdin, 60% in water) binder (10 wt%) were ground in H_2O to form a uniform slurry. After that, the slurry was coated on stainless steel (SS) current collectors by a scraper, pressed at 6 MPa and dried under vacuum at 333 K for 24 h. A mixture of anhydrous 0.5 M 1-Butyl-1-methylpiperidinium chloride (PP_{14}Cl , 99%, IoLiTech) in 1-Butyl-1-methylpiperidinium bis(trifluoromethylsulfonyl)imide ($\text{PP}_{14}\text{TFSI}$, 99%, IoLiTech) was used as electrolyte. Celgard 2400 film was used

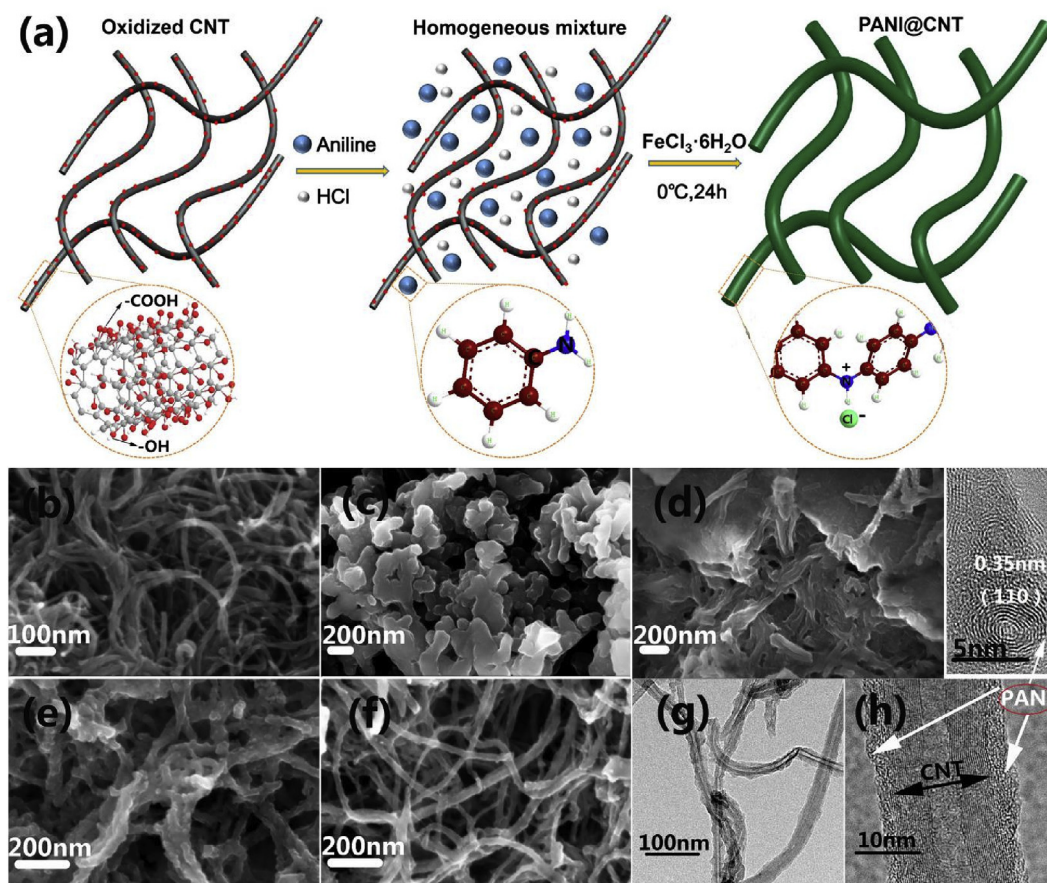


Fig. 1. (a) Schematic fabrication process of the PANI/CNTs nanocomposite. SEM images of the (b) CNTs, (c) PANI, (d) PANI/10CNTs, (e) PANI/30CNTs and (f) PANI/50CNTs materials. (g–h) TEM and HRTEM images of the as-prepared PANI/50CNTs nanocomposite.

Download English Version:

<https://daneshyari.com/en/article/6603376>

Download Persian Version:

<https://daneshyari.com/article/6603376>

[Daneshyari.com](https://daneshyari.com)