



Synthesis and electrochemical performance of hierarchically porous carbon-supported PDMcT–PANI composite for lithium-ion batteries

Ting-yu Chi, Han Li, Xing-wei Li, Hua Bao, Geng-chao Wang*

Shanghai Key Laboratory of Advanced Polymeric Materials, Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, PR China

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ABSTRACT

A novel composite of hierarchically porous carbon (HPC) supported PDMcT–PANI (HPC/PDMcT–PANI) was synthesized through an in situ oxidative polymerization. Field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and Raman spectra showed that a partial amount of PDMcT was parasitized inside of pores of HPC and some other amount of PDMcT formed interpenetrated fibrous electron donor–acceptor PDMcT–PANI adduct with PANI and distributed onto surface of HPC in HPC/PDMcT–PANI composite. X-ray diffraction (XRD) revealed that the interconnected nanoporous structure of HPC and formation of PDMcT–PANI adduct significantly influenced the crystal growth and orientation of PDMcT. As confirmed by the cyclic voltammetry and galvanostatic charge–discharge tests, the incorporation of HPC and PANI had significantly improved the electrochemical performance of PDMcT. It was found that the initial discharge capacity of HPC/PDMcT–PANI composite reached 310 mAh g⁻¹ and its specific capacity remained 150 mAh g⁻¹ after 20 cycles. Moreover, the HPC/PDMcT–PANI composite also showed higher specific capacity and better cycling stability than that of its two binary composites [PDMcT–PANI (291 mAh g⁻¹) or HPC/PDMcT (253 mAh g⁻¹)].

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1. Introduction

In recent years, with the development of renewable energy production and electric vehicles with low CO₂ emission, higher demands were raised on the performance of lithium-ion batteries, and lithium-ion batteries with high energy densities have been become one of the research focuses [1–5]. 2,5-Dimercapto-1,3,4-thiadiazole (DMcT) has attracted considerable attention as active cathode material for lithium-ion batteries due to its high theoretical specific capacity (362 mAh g⁻¹) and environmental benignity [6–10]. Unfortunately, DMcT has several disadvantages in terms of its poor electrical conductivity, low redox rate at room temperature and appreciable solubility in organic electrolytes, which restricts its practical application.

In order to improve the electrochemical activity and stability of DMcT, various approaches, such as blending DMcT with conductive polymers [11–15] or carbonaceous materials [16–18], adding transition metal nanoparticles to DMcT [19–21], intercalating of DMcT to layered inorganics [22–24], have been reported. For examples, Oyama et al. found that the redox behavior of DMcT can be dramatically accelerated by polyaniline (PANI) [11]. Park and

co-workers confirmed that metal–sulfur bonds were formed between DMcT and Pd nanoparticles, and Pd nanoparticles have catalytic effects on electrochemical reactions of DMcT [18]. Recently, our group synthesized sulfonated graphene-supported PDMcT composite using in situ oxidative polymerization, and the composite exhibited improved electrochemical activity and cycling stability [21]. However, for practical application, these composite cathode materials are still unable to meet the demand of electrochemical cyclability.

Hierarchically porous carbon (HPC) has attracted enormous attentions due to its high specific surface area, excellent conductivity, strong adsorption capacity as well as chemical stability [25–28]. Besides, these characteristics are beneficial for the loading of active substances, the diffusion of electrolyte, and the improvement of the charge transport properties, therefore, HPC may be an ideal carrier for electrode material. Nowadays, conductive polymer/HPC composites have attracted significant attention, especially for its application in lithium-ion batteries [29–32] and supercapacitors [33–36]. However, to our knowledge, no publication has reported the research of HPC-supported PDMcT composite.

In this paper, we choose formaldehyde (PF) resin as carbon precursor, nano-CaCO₃ dispersion as double pore-forming agent, by means of calcination and etching to prepare HPC. On the basis, HPC-supported PDMcT–PANI composite (HPC/PDMcT–PANI) was synthesized using in situ oxidative polymerization method with HPC

* Corresponding author. Tel.: +86 21 64253527.

E-mail address: gengchaow@ecust.edu.cn (G.-c. Wang).

as substrates. The effects of HPC and PANI on the redox behavior and electrochemical performance of PDMcT were discussed in detail.

2. Experimental

2.1. Materials

Analytical grade aniline (Shanghai Chemical Reagent Corp.) was purified by distillation under reduced pressure prior to use. DMcT (Acros) was purified by recrystallization from ethanol. The nano-CaCO₃ water-dispersion (40–60 nm, Shanghai Huaming Hi-Tech Co. Ltd.) and the carbon precursor PF resin (Beijing Furunda Co. Ltd.) are commercial products. All other reagents were received as analytical grade and were used without further purification.

2.2. Preparation of HPC

HPC was prepared using the modified method as reported in the literature [37]. In this experiment, to overcome aggregation of nano-CaCO₃ powders, water-dispersion of CaCO₃ nanoparticles was adopted. Firstly, water-dispersion of CaCO₃ nanoparticles turned into ethanol dispersion of CaCO₃ nanoparticles by filtration, washing with ethanol, and ultrasonic treatment (Fig. S1). Secondly, 4 g of phenolic resin was dissolved in 16 g ethanol, and 6 g nano-CaCO₃ (25 wt% in ethanol) was added into the above solution with stirring and ultrasonic treatment. Then, the ethanol was removed by evaporation at room temperature for 24 h, and light yellow powders were obtained. Thirdly, carbonization of mixtures of powders were performed in a furnace under an argon atmosphere from room temperature of about 25 to 300 °C at 2 °C min⁻¹, from 300 to 700 °C at 5 °C min⁻¹, and from 700 to 850 °C at 5 °C min⁻¹. During heating, the samples were kept for 90, 60, and 60 min at 300, 700, and 850 °C, respectively (the carbonization condition of CaCO₃/PF composite was determined according to TG results, see Fig. S2). CaO produced during CaCO₃ pyrolysis was removed by 2 M hydrochloric acid solution. Finally, the mixture was filtered, washed with deionized water and dried at 80 °C for 24 h to obtain HPC.

2.3. Preparation of HPC/PDMcT–PANI composite

(1) 0.41 g HPC was vacuumized for 1 h. (2) 0.75 g DMcT and 0.47 g aniline were dissolved in a mixed solution of 200 mL ethanol and 100 mL 2 mol L⁻¹ H₂SO₄, then the mixed solution was added to HPC under vacuum and stirred for 12 h. (3) 2.28 g ammonium persulfate (dissolved in 50 mL 2 mol L⁻¹ H₂SO₄) was added into the above suspension quickly. (4) The reaction was kept at 40 °C for 24 h with continuous stirring. The dark gray product of the reaction was filtered and washed repeatedly with distilled water and ethanol. The resulting product was dried under vacuum at 80 °C for 6 h. The content of PDMcT and PANI in composite was calculated to be 35.1 wt% and 34.2 wt% obtained from elemental analysis, respectively.

For comparison, the PDMcT–PANI adduct was synthesized through the similar procedure above without the presence of HPC. The HPC/PDMcT composite was obtained using 1.5 g of DMcT instead of 0.75 g DMcT and 0.47 g aniline with all other conditions being the same as the process above. The 68.2 wt% of mass load of PDMcT in the HPC/PDMcT composite was evaluated by elemental analysis.

2.4. Characterization

Fourier transform infrared spectra (FT-IR) were obtained through a Nicolet 5700 spectrometer using KBr sample pellets. Raman spectra were recorded with Renishaw in Via + Reflex using a 50 mW He–Ne laser operated at 785 nm wavelength. A Rigaku D/Max 2550 VB/PC X-ray diffractometer using the Cu-K α radiation

served as the instrument in the study of X-ray diffraction (XRD) patterns, which were recorded from 3° to 50° (2 θ -angle). The morphology and energy dispersive spectroscopy (EDS) mapping of the samples were obtained with a transmission electron microscopy (TEM, JEOL JEM-2100 at the accelerating voltage of 200 kV) and a field-emission scanning electron microscopy (FE-SEM, Hitachi S-4800), respectively. Nitrogen adsorption–desorption isotherms were performed using a Micromeritics ASAP 2020 analyzer at 77 K. Before measurements, the samples were degassed in vacuum at 393 K for 8 h. The electrical conductivity of the samples was determined using a SX 1934 four-probe instrument.

2.5. Battery assembled and electrochemical measurements

The positive electrodes were fabricated by mixing active materials (80 wt%), acetylene black (10 wt%) and binder (10 wt% polyvinylidene fluoride dissolved in N-methyl-2-pyrrolidone) to form slurries. The mixed slurries were homogeneously coated onto aluminum current collectors. The electrodes were dried under vacuum at 80 °C for 48 h. Subsequently, the electrodes were cut into disks with a diameter of 12 mm. 0.15 mL 1 M LiPF₆ in a mixture of ethylene carbonate (EC), diethyl carbonate (DMC) and ethyl methyl carbonate (EMC) (1:1:1 by volume) was used as electrolyte. Coin-type (CR 2016) cells were assembled in an argon atmosphere glove box.

The galvanostatic charge/discharge tests were carried out on a LAND CT2001A battery tester at a current density of 20 mA g⁻¹ between 1.8 and 3.8 V vs. Li/Li⁺. The cyclic voltammetry (CV) (scan rate: 0.1 mV s⁻¹; cut-off voltage: 1.8–3.8 V) and electrochemical impedance measurements (frequency range: 0.01–100,000 Hz; amplitude: 5 mV) were conducted on a CHI 660D electrochemical workstation using fresh cells, respectively.

3. Results and discussion

The FT-IR spectra of PDMcT, HPC/PDMcT, HPC/PDMcT–PANI, and PDMcT–PANI are shown in Fig. 1. IR spectrum of HPC/PDMcT (Fig. 1b) composite is similar to pure PDMcT (Fig. 1a), and the bands at 1381 and 1049 cm⁻¹ are assigned to C=N stretching and thiadiazole ring stretching band, respectively [23,38]. For the PDMcT–PANI, the characteristic bands of PANI ($\nu_{\text{C=Cofquinoidring}}$ at 1568 cm⁻¹ and $\nu_{\text{C=Cofbenzenering}}$ at 1495 cm⁻¹) and PDMcT

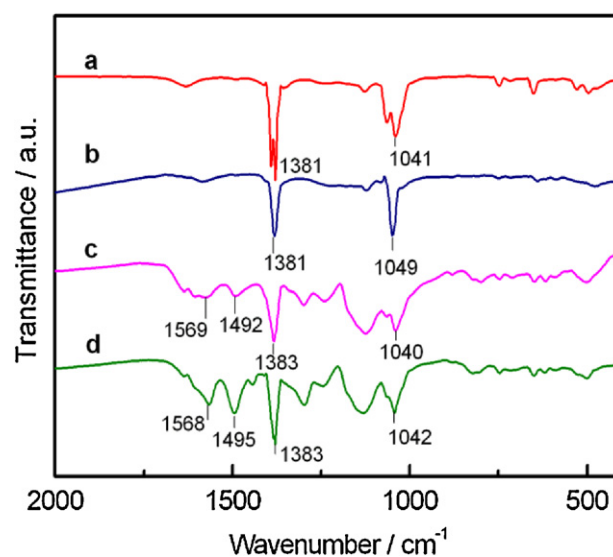


Fig. 1. FT-IR spectra of (a) PDMcT, (b) HPC/PDMcT, (c) HPC/PDMcT–PANI, and (d) PDMcT–PANI.

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