



Polythiophene/graphite fluoride composites cathode for high power and energy densities lithium primary batteries



Xiaodong Yin^a, Yu Li^{a,b,c,d}, Yiyu Feng^{a,b,c,d}, Wei Feng^{a,b,c,d,*}

^a School of Materials Science and Engineering, Tianjin University, Tianjin 300072, PR China

^b Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, PR China

^c Key Laboratory of Advanced Ceramics and Machining Technology, Ministry of Education, Tianjin 300072, PR China

^d Tianjin Key Laboratory of Composite and Functional Materials, Tianjin 300072, PR China

ARTICLE INFO

Article history:

Received 16 March 2016

Received in revised form 23 July 2016

Accepted 27 July 2016

Available online 1 August 2016

Keywords:

Lithium primary battery

Graphite fluorides

Polythiophene

Cathode materials

Rate capability

ABSTRACT

A series of polythiophene/graphite fluoride (PTh/CF_x) composites have been synthesized by in situ polymerization of thiophene monomers on the surface of CF_x. Transmission electron microscopy (TEM) demonstrates that 22.94 wt.% PTh/CF_x is the suitable ratio for the composite due to the uniform and complete PTh coating on the surface of CF_x particles. Electrochemical impedance spectra (EIS) measurements confirm that the coating of PTh decreases the charge transfer resistance of CF_x cathode significantly. Conductive PTh serves as the conducting additive as well as the porous adsorbing agent, so the rate capability of PTh/CF_x composites improves remarkably compared to pure CF_x cathode. The amount of PTh coating affects the electrochemical performances of PTh/CF_x composites, and the one containing 22.94 wt.% PTh can be discharged at high rate up to 4C delivering a maximum power density of 4997 W kg⁻¹, associated with a high 1707 Wh kg⁻¹ energy density.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The use of graphite fluoride (CF_x) as cathode of lithium primary batteries firstly studied by Watanabe [1], which has been commercially developed in Japan in 1970 by the Matsushita Co. As one of cathode materials in lithium primary batteries, CF_x presents many advantages such as high energy density (up to 1500 Wh kg⁻¹), high and flat discharge potential (about 2.2–2.4 V), and broad temperature range of use in the practical batteries (from –40 °C to 170 °C) [2]. CF_x is synthesized by the chemical reaction of fluorine with carbon at high temperature, and the value of *x* can vary from 0 to 1.3, depending on the fluorination temperature [3]. However, because of the covalence of the C–F bond, CF_x shows a very low electrical conductivity, resulting in a low rate capability and an initial potential delay, which hampers its application in high-power devices.

It was an effective method to solve this problem that CF_x with lower fluorination content improved its rate capability [4–6]. For example, sub-fluorinated carbon nanofibres could sustain high discharge rate up to 6C due to the presence of unfluorinated path

within the CF_x [5]. The mixture of CF_x with other cathode materials such as silver vanadium oxide or manganese dioxide to develop a hybrid structure was also utilized to modify the rate capability [7–9]. The addition of some amount of nanostructured conductive additives, such as carbon nanotubes [9] or graphene [10], into the CF_x cathode can significantly improve its rate capability due to the formation of conductive paths for the charges transport. Recently, it was found that substituting nanostructured carbon materials for conventional graphite as the starting materials of CF_x was an effective approach to improve the rate capability thanks to the special nanostructures [5,11].

Besides the methods mentioned above, surface coating was considered as an easy and effective way to enhance the electronic conductivity of CF_x [12,13]. Conducting polymers have received numerous attentions because they can play different roles in improving the cathodes as a result of their good electrochemical stabilities and favorable morphologies [14–16]. For example, the electrodeposition of polypyrrole on CF_x cathode improved its rate capability and the delivered power density achieved to 5235 W kg⁻¹ at 4C rate [13]. Among the various conducting polymers, because polythiophene (PTh) can participate in lithiation and delithiation reactions, contributing to the specific capacity of the composites [17,18], it has been served as the conducting layers in various cathode materials to improve their electrochemical performances [19–21]. In this work, a series of PTh/CF_x composites

* Corresponding author at: School of Materials Science and Engineering, Tianjin University, Tianjin 300072, PR China.

E-mail address: weifeng@tju.edu.cn (W. Feng).

were prepared by in situ polymerization. The influence of the different PTh ratios on the electrochemical performances was studied. PTh particles as a conductive additive were coated on the surface of CF_x powder. The conductivity of CF_x cathode was significantly enhanced by the PTh coating, which decreased the polarization of discharge and hence improves the rate capability.

2. Experimental

2.1. Material preparation

The PTh/ CF_x composites were synthesized by in situ polymerization. At first, 1 g CF_x powders ($x = 1.0$, Alfa Aesar, A Johnson Matthey Company) and some amount of anhydrous FeCl_3 (Tianjin Guangfu Fine Chemical Research Institute) were dispersed in 100 mL CHCl_3 solution to form a homogenous suspension with the help of ultrasonication. Before the polymerization, the suspension was bubbled with argon gas for 30 min to remove the oxygen. While the suspension was magnetically agitated, PTh monomers (0.1, 0.25 and 0.5 g; J&K Scientific Ltd.) dissolved in 50 mL CHCl_3 was slowly added into the suspension in 1 h, and the molar ratio of thiophene to FeCl_3 was kept at 1:4. The polymerization reaction was carried out in ice-bath under a continuous argon flow for 10 h so that thiophene monomers tended to link by α - α position, which could enhance the electrical conductivity of PTh effectively [21]. After the polymerization, 100 mL methanol was added to the mixture to dissolve the remaining FeCl_3 . The mixture was then filtered to remove the iron ions as well as the remained monomers, and the insoluble solid was washed by methanol and deionized water for several times. After this, the solid was poured into the solution of 1 M hydrochloric acid and the mixture was stirred for 2 h at room temperature. Then the solid product was collected by filtration and washed using deionized water until the filtrate being neutral. Finally, the brown product was dried at 80°C for 24 h under vacuum to obtain the PTh/ CF_x composite. The proposed synthesis route of PTh/ CF_x composite is illustrated in Scheme 1.

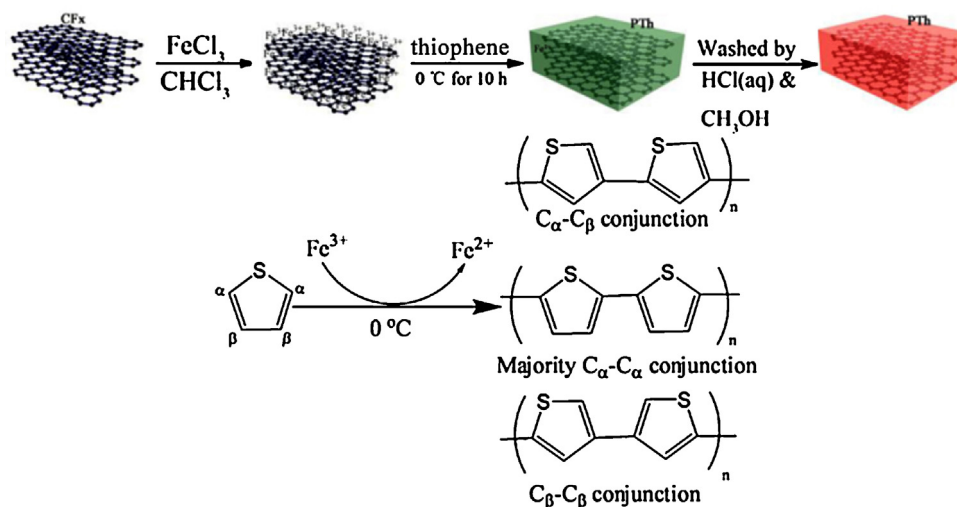
2.2. Materials characterization

The thermal behavior of the samples was examined by thermogravimetry analysis (TGA, Shimadzu DTG-60) from room temperature up to 800°C at a heating rate of 5°C min^{-1} in a dynamic

atmosphere of nitrogen (35 mL min^{-1}). The morphology of CF_x and PTh/ CF_x composites was observed by field-emission scanning electron microscopy (SEM, Hitachi S-4800) and field-emission transmission electron microscopy (TEM, Philips Tecnai G2 F20). Fourier Transform infrared (FTIR) spectroscopy characterized the structure of the synthesized sample. The FTIR spectra were recorded with Perkin-Elmer Spectrum One FTIR Spectrophotometer which used KBr pellets in the region $4000\text{--}500\text{ cm}^{-1}$. X-ray diffraction (XRD) measurements were performed on a Philips diffractometer, which was composed of a quartz monochromator, a $\text{Cu K}\alpha$ radiation source at a scan rate of 10° min^{-1} and a goniometric plate. Four-probe testing instrument (SX1934, Jiangsu) was used to measure the conductivity, and made it on a disc-shaped pellet by four-point direct current method at room temperature.

2.3. Electrochemical measurement

The electrodes were composed of cathode materials (bare CF_x or CF_x /PTh composites), conductive additive (Super P carbon) and binder (polyvinylidene difluoride, PVDF) with a weight ratio of 80:10:10. In order to obtain the homogenous and slightly viscous slurry, *N*-methyl pyrrolidone (NMP) was added. The electrode film was obtained by the means of the slurry coating on an Al foil, and the film was dried at 120°C for 12 h. The electrochemical performances of CF_x /PTh composites were investigated by assembling 2032 coin type batteries, so the diameter of punched electrode disks was about 18 mm, which were further dried at 80°C for 8 h in a vacuum. The mass loading for each cathode was $2\text{--}3\text{ mg cm}^{-2}$. And then, the shaped disks were put into a glove-box filled with argon (Mikrouna Co., Advanced 2440/750) for cell assembly. A metallic lithium disc, a microporous polypropylene/polyethylene/polypropylene film and the solution of 1 M LiPF_6 in ethylene carbonate: dimethyl carbonate (EC:DMC, 1:1, vol%) were used as the anode, separator and electrolyte, respectively. The discharged test of coin cells was operated under constant current densities (Land CT2001A, Wu Han Jin Nuo Electronics Co., China) at room temperature, and the termination potential was 1.5 V (vs Li/Li^+). A three-electrode electrochemical cell included a Li flake as the counter electrode and an extra Li wire as the reference electrode, and the EIS was measured using Advanced Electrochemical System Parstat 2263 over the frequency range from 0.01 to 10 kHz.



Scheme 1. Schematic illustration of the proposed synthesis route of PTh/ CF_x composites.

Download English Version:

<https://daneshyari.com/en/article/1440128>

Download Persian Version:

<https://daneshyari.com/article/1440128>

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