

# Preparation of polypyrrole-coated $\text{CuFe}_2\text{O}_4$ and their improved electrochemical performance as lithium-ion anodes

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## Abstract

$\text{CuFe}_2\text{O}_4$  network, prepared via the electrostatic spray deposition technique, with high reversible capacity and long cycle lifetime for lithium ion battery anode material has been reported. The reversible capacity can be further enhanced by coating high electronic conductive polypyrrole (PPy). At the current density of  $100 \text{ mA}\cdot\text{g}^{-1}$ ,  $\text{Li}/\text{CuFe}_2\text{O}_4$  electrode delivers a reversible capacity of  $842.9 \text{ mAh}\cdot\text{g}^{-1}$  while the reversible capacity of  $\text{Li}/\text{PPy}$ -coated  $\text{CuFe}_2\text{O}_4$  electrode increases up to  $1106.7 \text{ mAh}\cdot\text{g}^{-1}$ . A high capacity of  $640.7 \text{ mAh}\cdot\text{g}^{-1}$  for the  $\text{Li}/\text{PPy}$ -coated  $\text{CuFe}_2\text{O}_4$  electrode is maintained in contrast of  $398.9 \text{ mAh}\cdot\text{g}^{-1}$  for  $\text{Li}/\text{CuFe}_2\text{O}_4$  electrode after 60 cycles, which demonstrates good electrochemical performance of the composite due to the increase of electronic conductivity. The electrochemical impedance spectroscopy (EIS) further reveals that the  $\text{Li}/\text{PPy}$ -coated  $\text{CuFe}_2\text{O}_4$  electrode has a lower charge transfer resistance than the  $\text{Li}/\text{CuFe}_2\text{O}_4$  electrode.

## Key words

$\text{CuFe}_2\text{O}_4$ ; polypyrrole-coated; electrostatic spray deposition; lithium ion batteries

## 1. Introduction

Lithium-ion batteries are attracting extensive attentions for the use in high-power applications such as electric vehicles, plug-in hybrid electric vehicles and hybrid electric vehicles. Graphite is the most widely used material as an anode in commercial LIBs, owing to its low cost and long cycle life [1]. However, a low theoretical capacity of  $372 \text{ mAh}\cdot\text{g}^{-1}$  and an inherent safety risk owing to the possible reaction between lithiated graphite and the electrolyte make graphite unable to fulfill the demands for LIBs with high power and high energy density [2]. Therefore, further research is important to develop novel anode materials combining suitable theoretical capacity and electrochemical stability. In this respect, the cubic spinel structure of transition metal oxides  $\text{MFe}_2\text{O}_4$  ( $\text{M} = \text{Ni}, \text{Co}, \text{Zn}, \text{Cu}$ ) has been proved favorable for lithium-ion stores [3–12]. Among them,  $\text{CuFe}_2\text{O}_4$  has been widely regarded as one of the promising anode materials for LIBs due to its low-cost, high abundance and environmental benignity. Unfortunately, like other transition metal oxides, its huge volume change during the discharge-charge process and poor

electron (and Li-ion) conduction hindered its applications in LIBs.

Minimizing the particle size and coating carbon as a conductive layer on  $\text{CuFe}_2\text{O}_4$  have been regarded as effective strategies to improve their electrochemical properties. Nuli et al. [10] prepared nanocrystalline thin film of  $\text{CuFe}_2\text{O}_4$ , which delivered a reversible capacity of  $452 \text{ mAh}\cdot\text{g}^{-1}$  at  $10 \text{ A}\cdot\text{cm}^{-2}$ . Jin et al. [11] synthesized carbon coated hollow  $\text{CuFe}_2\text{O}_4$  spheres maintaining  $550 \text{ mAh}\cdot\text{g}^{-1}$  at the current density of  $100 \text{ mA}\cdot\text{g}^{-1}$  after 70 cycles. Fu et al. [12] reported that their prepared  $\text{CuFe}_2\text{O}_4$ -graphene showed an initial specific capacity of  $1165 \text{ mAh}\cdot\text{g}^{-1}$  with good cycling stability and rate capability. Most recently, the high electronic conductivity as well as the relative stable SEI layer on conducting polymers surface make polypyrrole a good coating material to enhance the cycling capacity and structure stability for transition metal oxides such as  $\text{Fe}_2\text{O}_3$  [13–16]. Meanwhile, considering the huge volume change during the discharge-charge process, a one-dimensional or network structure of transition metal oxide might be a good choice.

In this work, we successfully synthesized  $\text{CuFe}_2\text{O}_4$  via

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the electrostatic spray deposition technique. The following coating of PPy produces  $\text{CuFe}_2\text{O}_4/\text{PPy}$  composite. The reversible capacity of  $640.7 \text{ mAh}\cdot\text{g}^{-1}$  is obtained after 60 cycles for PPy coated  $\text{CuFe}_2\text{O}_4$  network. The electrochemical impedance spectra (EIS) demonstrate the decrease of charge transfer impedance with PPy coating on  $\text{CuFe}_2\text{O}_4$  network.

## 2. Experimental

### 2.1. Synthesis of $\text{CuFe}_2\text{O}_4$ and PPy-coated $\text{CuFe}_2\text{O}_4$

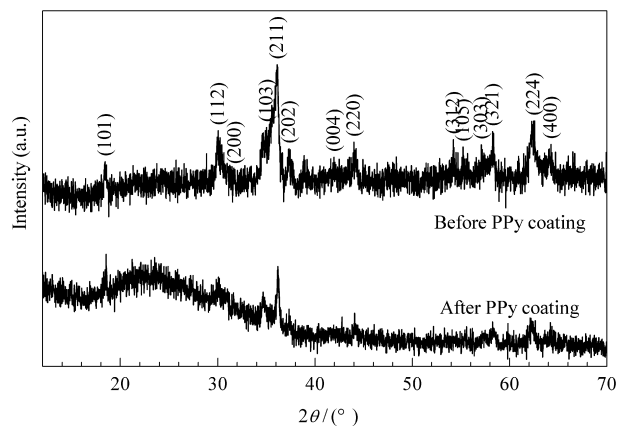
$\text{CuFe}_2\text{O}_4$  powders were prepared by the electrostatic spray deposition technique. The ESD equipment details and working principle were described by Chen et al. [17]. The stoichiometric  $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$  and  $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$  solutions were first dissolved in ethylene glycol to obtain the precursor solution. Then, the precursor solution was pumped through the metal capillary nozzle at a rate of  $4 \text{ mL}\cdot\text{h}^{-1}$ . Thin Ni foams (12 mm in diameter) heated at  $220^\circ\text{C}$  were used as a network substrate. A distance of about 3.5 cm was kept between the nozzle and the substrate, and a DC voltage of 18 kV was applied. Finally, the deposited networks were annealed at  $700^\circ\text{C}$  in air for 2 h to form the spinel phase and the obtained sample was coated by PPy as introduced by Zhou et al. [18].

### 2.2. Characterization and electrochemical measurements

The characteristics of the as-prepared powders after being stripped from Ni foams were identified by X-ray powder diffraction (XRD,  $\text{Cu } K_\alpha$  radiation,  $\lambda = 1.5418 \text{ \AA}$ ). The network of  $\text{CuFe}_2\text{O}_4$  and  $\text{CuFe}_2\text{O}_4/\text{PPy}$  composite were further characterized by scanning electron microscopy (SEM) with a JEOL JSM-7600F field emission instrument.  $\text{CuFe}_2\text{O}_4$  and  $\text{CuFe}_2\text{O}_4/\text{PPy}$  powders were also characterized by transmission electron microscopy (TEM) using JEOL-1011 microscope. The coin electrodes comprised of the prepared networks as a cathode, a lithium foil as an anode, and a mixture of 1 mol/L  $\text{LiPF}_6$  in an ethylene carbonate (EC)-diethyl carbonate (DEC)-ethyl methyl carbonate (EMC) mixture (1 : 11 : 1 in volume). The electrode preparation was carried out in an Ar-filled dry box. The charge-discharge cycles for assembled electrodes were measured in a 2032-coin electrode and characterized on Land-CT2001A battery cyler (Xinnuo, Wuhan China) at room temperature. Electrochemical impedance spectroscopy (EIS) was measured on an FRA-520 (MaterialsMates, Italia) connected to a Potentiostat-510 (MaterialsMates) over the frequency range of 100 kHz to 0.01 Hz.

## 3. Results and discussion

Figure 1 shows the XRD patterns of  $\text{CuFe}_2\text{O}_4$  powders with or without PPy coating. Both of the XRD diffractions can be basically indexed to the tetragonal  $\text{CuFe}_2\text{O}_4$  (JCPDS Card, No. 34-0425) structure. The broaden peak around  $25^\circ\text{C}$  for the PPy-coated  $\text{CuFe}_2\text{O}_4$  sample can be attributed to the amorphous carbon introduced by PPy.



**Figure 1.** XRD patterns of  $\text{CuFe}_2\text{O}_4$  and PPy-coated  $\text{CuFe}_2\text{O}_4$  powders

The morphology of the as-prepared  $\text{CuFe}_2\text{O}_4$  and PPy-coated  $\text{CuFe}_2\text{O}_4$  samples were characterized by SEM. Figure 2(a) gives the image of  $\text{CuFe}_2\text{O}_4$  grown on Ni network, which shows a coarse surface composed by micro-scale particles. After PPy coating (Figure 2b),  $\text{CuFe}_2\text{O}_4$  particles are adhered and wrapped into larger unit. A loose PPy layer is spreading on bulk  $\text{CuFe}_2\text{O}_4$ . The results indicate that PPy are well coated on the surface of  $\text{CuFe}_2\text{O}_4$ . TEM images of  $\text{CuFe}_2\text{O}_4$  and PPy-coated  $\text{CuFe}_2\text{O}_4$  samples are presented in Figure 2(c) and 2(d). It is found that there appear smooth surfaces for  $\text{CuFe}_2\text{O}_4$  powders without PPy coating. In contract, PPy coated  $\text{CuFe}_2\text{O}_4$  powders develop a rather porous surface film, which is in accordance with SEM result (Figure 2b).

The electrochemical property as anode material for lithium ion batteries of  $\text{Li}/\text{CuFe}_2\text{O}_4$  and  $\text{Li}/\text{PPy}$ -coated  $\text{CuFe}_2\text{O}_4$  electrodes were performed at a current density of  $100 \text{ mA}\cdot\text{g}^{-1}$ . The initial charge-discharge profiles are shown in Figure 3. Both charge and discharge curves show clear voltage plateaus at around 0.8–0.9 V, which could be attributed to the reduction of  $\text{Cu}(\text{II})$  and  $\text{Fe}(\text{III})$ . The sloping curve after the conversion is due to the electrolyte decomposition and interfacial storage [19]. The pristine  $\text{CuFe}_2\text{O}_4$  network delivers the initial discharge and charge capacities of 1150.2 and  $842.9 \text{ mAh}\cdot\text{g}^{-1}$ , respectively. Accordingly, higher capacity of 1484.8 and  $1106.7 \text{ mAh}\cdot\text{g}^{-1}$  are obtained for the PPy-coated  $\text{CuFe}_2\text{O}_4$  network. Though the reversible capacity is not the best data compared with the published results [12], it is the first time that  $\text{CuFe}_2\text{O}_4$  has been successfully prepared by electrostatic spray deposition technique and then coated PPy as a conductive layer. Meanwhile, our active material is free of extra binder and any other conductive matters during assembling the electrode.

Figure 3 shows the cycling performance of pristine and modified samples at the current density of  $100 \text{ mA}\cdot\text{g}^{-1}$ . It can be seen that the reversible capacity of  $640.7 \text{ mAh}\cdot\text{g}^{-1}$  is maintained even after 60 cycles for  $\text{Li}/\text{PPy}$ -coated  $\text{CuFe}_2\text{O}_4$  electrode. But only  $398.9 \text{ mAh}\cdot\text{g}^{-1}$  is left over 60 cycles for pristine  $\text{CuFe}_2\text{O}_4$  sample. The capacity retention from the second cycle up to 60 cycles for  $\text{Li}/\text{PPy}$ -coated  $\text{CuFe}_2\text{O}_4$  electrode is 57.9%, while only 47.2% is obtained for  $\text{Li}/\text{CuFe}_2\text{O}_4$  electrode.

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