



# Migration behavior, oxidation state of iron and graphitization of carbon nanofibers for enhanced electrochemical performance of composite anodes



Zhiwei Xu\*, Liyuan Wang, Wei Wang, Nan Li, Cheng Chen, Cuiyu Li, Caiyun Yang, Hongjun Fu, Liyun Kuang

State Key Laboratory of Separation Membranes and Membrane Processes, School of Textiles, Tianjin Polytechnic University, Tianjin 300387, China

## ARTICLE INFO

### Article history:

Received 29 August 2016

Received in revised form 28 October 2016

Accepted 28 October 2016

Available online 29 October 2016

### Keywords:

iron oxides

carbon nanofibers

graphitization degree

migration

electrochemical performance

## ABSTRACT

Iron oxide/carbon nanofibers (FeO<sub>x</sub>/CNFs) were prepared by electrospinning FeCl<sub>3</sub>·6H<sub>2</sub>O-polyacrylonitrile (PAN) precursors and heat treating at 400, 600, 800, 1000 °C. As carbonization temperature increased, granular FeO<sub>x</sub> gradually migrated from nanofiber interior with effectual contacts between electrolyte and active materials rising at first and then falling; Oxidation states of iron in FeO<sub>x</sub>/CNFs changed from Fe<sub>2</sub>O<sub>3</sub> to FeO and Fe with an improvement of capacity retention and an extra reversible capacity catalyzed by Fe; Graphitization process of carbon matrices proceed with less defective structures and heteroatom contents, leading to an increase of conductivity and a diminution of irreversible reactions during cycling. As systematically studied and compared in electrochemical performance, FeO<sub>x</sub>/CNFs with FeO, Fe state, highly graphitized carbon matrices and migration structure with FeO and Fe both embedded in and dispersed on carbon matrices presented stable cycling performance with a reversible capacity of ~674 mAhg<sup>-1</sup> after 60 cycles and outstanding rate capability. The above trade-off study of all the cooperative factors that affected the electrochemical property might make an effective guidance for preparation of promising FeO<sub>x</sub>/CNF anodes.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

Rechargeable lithium-ion batteries (LIBs) with great energy density, long cycle life, good safety and environmental friendliness are considered to be a promising technology in the application of portable devices and hybrid electric vehicles (HEV) [1–4]. However, commercial anodes for lithium-ion batteries are currently confined to graphite-based materials, which exhibit relatively low specific capacity (372 mAhg<sup>-1</sup>) and vulnerable safety [5]. Thus, it is necessary to explore new anode materials to meet the demand of high-performance lithium-ion batteries.

Active transition metal oxides have recently attracted tremendous attention as appealing anode materials due to their great theoretical capacities and high reserves abundances [6–11]. Among these alternatives, iron oxide can be one of the most reliable candidates because of its high specific capacity, improved safety, low cost and environmental friendliness. Despite these

advantages, there exist some drawbacks for iron oxides as anode materials. Iron oxides have underwent poor cycling stability, which results from severe volume change and large aggregation of generated Fe metal during lithiation/delithiation reactions. Besides, iron oxide anodes suffer from sharp capacity fading in cycling owing to the generation of unstable solid electrolyte interface (SEI) films and the irreversibility of partial Li<sup>+</sup> in the extraction from Li<sub>2</sub>O. Moreover, low electro conductivity of iron oxide materials induce poor transportation of Li<sup>+</sup> or electrons, leading to an additional performance deterioration in cycling, especially at high current rates [12–15].

Numerous efforts have been exploited to overcome the aforementioned problems of iron oxide anodes, during which designing nanosized iron oxides and integrating them with carbon matrices are believed to be one of the most effective strategies. Here, nanosized iron oxides can buffer the pulverization of electrodes induced by Li<sup>+</sup> insertion/extractions, provide high activity in the redox reactions, and facilitate the transport of ions and electrons. Meanwhile, carbon matrices (such as carbon nanoparticles, nanotubes and graphene) with outstanding conductivity, stable structural property can be beneficial to improve

\* Corresponding author.

E-mail address: [xuzhiwei@tjpu.edu.cn](mailto:xuzhiwei@tjpu.edu.cn) (Z. Xu).

the electrical connections of the whole electrodes and further alleviate the huge volume change during continuous cycling [16–20].

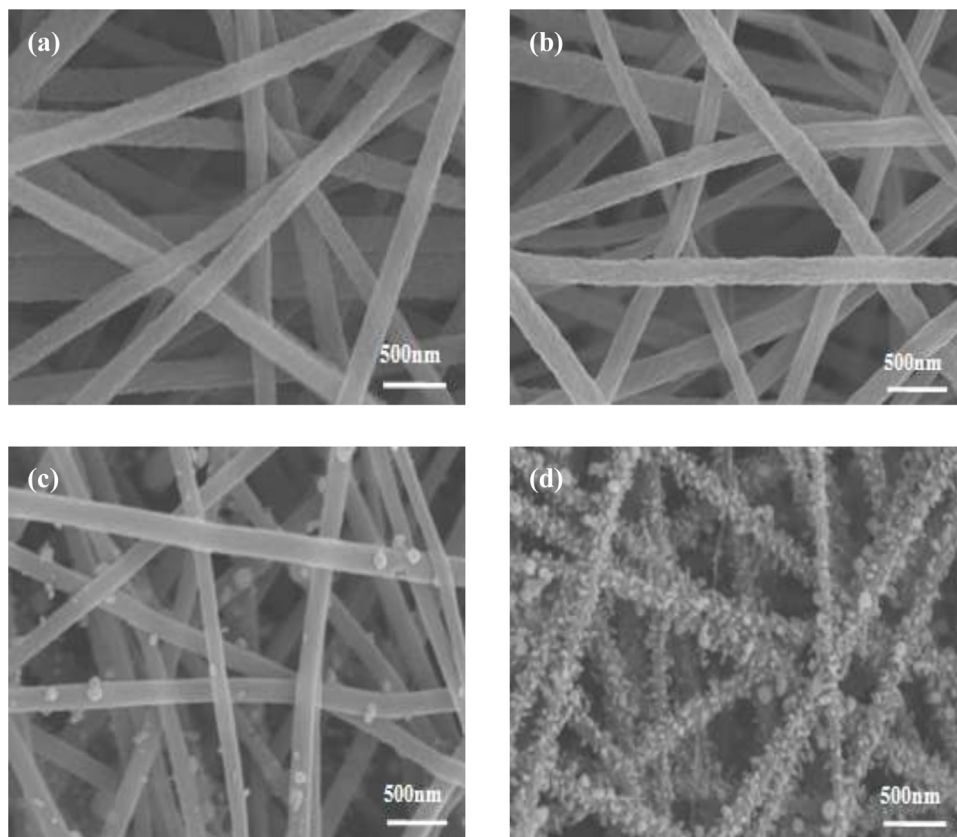
In recent years, it has been proved that carbon nanofibers (CNFs) as matrix for iron oxide composites possess electrochemically kinetic properties due to their good interconnectivity, preferable electrical conductivity and high specific surface area. Electrospinning technique has been lately emerged as a facile and efficient method to fabricate iron oxide/carbon nanofibrous anodes with superior electrochemical performance [21–26]. Zhang et al. [24] have successfully dispersed nanosized  $\alpha$ - $\text{Fe}_2\text{O}_3$  particles into CNFs by electrospinning and subsequent heat treatment (stabilization and carbonization). The  $\alpha$ - $\text{Fe}_2\text{O}_3$ /CNF anodes showed excellent electrochemical characteristics: a capacity of about  $604 \text{ mAhg}^{-1}$  was maintained at  $50 \text{ mAg}^{-1}$ , an enhanced capacity was retained for 100 cycles, and improved rate performance was obtained at high current density of  $500 \text{ mAg}^{-1}$ . Currently, nanosized  $\text{Fe}_3\text{O}_4$  particles dispersed in porous carbon nanofibers ( $\text{Fe}_3\text{O}_4$ @PCNFs) were synthesized via electrospinning strategy by Qin et al. [26]. The acquired  $\text{Fe}_3\text{O}_4$ @PCNF electrodes exhibited a superior cycling performance and outstanding rate capability. On the whole, numerous literatures have been focused on iron oxide/carbon nanofiber composites as anodes for LIBs with outstanding electrochemical performance. However, cooperative mechanisms that variations in oxidation state, migration behavior of iron oxides and graphitization degree of carbon matrices affected the electrochemical performance of iron oxide/carbon nanofibers were rarely reported in current studies and optimizations of above variations to enhance the electrochemical properties of iron oxide/carbon nanofiber anodes were required.

Herein, we prepared iron oxide/carbon nanofiber ( $\text{FeO}_x$ /CNFs) composites by electrospinning  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ -polyacrylonitrile (PAN) precursors and heat treating with different carbonization temperature in  $\text{N}_2$ . By adjusting temperature at 400, 600, 800 and  $1000^\circ\text{C}$ , structure with nano- $\text{FeO}_x$  migration on fiber surface, iron with different oxidation states ( $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{FeO}$ ,  $\text{Fe}$ ) and carbon matrices with variational graphitization degrees were obtained. Furthermore, systematical investigations and comparisons in electrochemical performance have been carried out to clarify the cooperative mechanisms of improving electrochemical properties of  $\text{FeO}_x$ /CNF anodes via weighing the variations in migration behavior, oxidation state of iron and graphitization degree of carbon matrices, which might make an effective guidance for the preparation of  $\text{FeO}_x$ /CNF anodes with high retention capacity and outstanding cycling property.

## 2. Experimental

### 2.1. Materials and preparation of $\text{FeO}_x$ /CNFs

Polyacrylonitrile (PAN,  $M_w = 150,000$ ) was provided by Shaoxing Gimel Advanced Materials Co. Ltd.  $N,N$ -dimethylformamide (DMF) and Ferric chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) were purchased from Tianjin Kemiou Chemical Reagent Co. Ltd. All these chemicals were used as received. The spinning solution was prepared as followed: PAN and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  with optimized concentrations of 12 wt% and 7 wt% were dissolved in DMF, respectively. With magnetic stirring in water bath at  $60^\circ\text{C}$  for 48 h, a homogeneously dispersed solution was obtained. The apparatus used for electrospinning were recommended in our previous work



**Fig. 1.** FESEM images of  $\text{FeO}_x$ /CNFs carbonized at (a)  $400^\circ\text{C}$ , (b)  $600^\circ\text{C}$ , (c)  $800^\circ\text{C}$  and (d)  $1000^\circ\text{C}$ .

Download English Version:

<https://daneshyari.com/en/article/6472588>

Download Persian Version:

<https://daneshyari.com/article/6472588>

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