Journal of Power Sources 307 (2016) 649–656

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Amorphous Fe_2O_3 nanoshells coated on carbonized bacterial cellulose nanofibers as a flexible anode for high-performance lithium ion batteries

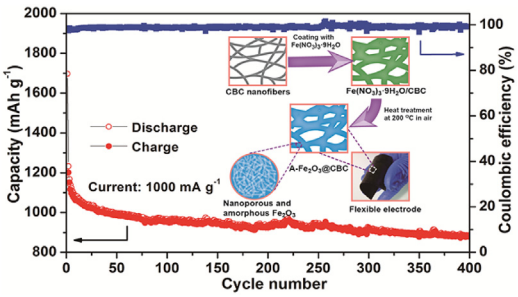
Yang Huang [a], Zixia Lin [b, **], Mingbo Zheng [b], Tianhe Wang [a], Jiazhi Yang [a], Fanshu Yuan [a], Xiaoyu Lu [a], Lin Liu [a], Dongping Sun [a, *]

[a] Chemicobiology and Functional Materials Institute, School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China
[b] Jiangsu Provincial Key Laboratory of Photonic and Electronic Materials Sciences and Technology, School of Electronic Science and Engineering, Nanjing University, Nanjing 210093, China

HIGHLIGHTS

- Flexible anode materials are prepared based on 3D carbonized bacterial cellulose.
- The well-coated Fe_2O_3 nanoshells are formed by a facile heat treating method.
- The hierarchical pores promote ion diffusion and prevent electrode pulverization.
- The amorphous Fe_2O_3 in improving electrochemical performance is fully investigated.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 20 October 2015
Received in revised form
5 January 2016
Accepted 7 January 2016
Available online xxx

Keywords:
Carbonized bacterial cellulose
Aerogel
Li-ion battery
Amorphous Fe_2O_3
Flexible anode

ABSTRACT

A three-dimensional (3D) carbonaceous aerogel derived from biomass bacterial cellulose (BC) is introduced as a flexible framework for iron oxides in Li-ion batteries (LIBs). The 3D carbonized BC (CBC) with highly interconnected nanofibrous structure exhibits good electrical conductivity and mechanical stability. The amorphous Fe_2O_3 is tightly coated on the nanofibers of CBC through a simple *in situ* thermal decomposition method. The obtained amorphous Fe_2O_3 anode (denoted as A-Fe_2O_3@CBC) exhibits stable cycling performance and high rate capability when assembled into a half-cell, which is supposed to benefit from the well-dispersed Fe_2O_3 nanoshells and the hierarchical pores in A-Fe_2O_3@CBC composite. The rational design of the nanostructure could improve the transportation of electrons/ions and effectively alleviate volume changes of Fe_2O_3 during the electrochemical cycling. Meanwhile, the amorphous nature of the Fe_2O_3 in anode provides an enhanced capacitive-like lithium storage and flexible structure of the active materials, resulting in much higher specific capacity and longer cycle life when compared with its crystalline counterpart. This work provides a promising approach to design and construct the flexible metal oxide anode materials based on 3D carbonaceous aerogel for high-performance LIBs.

1. Introduction

Rechargeable Li-ion batteries (LIBs) have now become the

* Corresponding author. Xiao Ling Wei 200, Nanjing, 210094, China.
** Corresponding author. Han Kou Road 22, Nanjing, 210093, China.
E-mail addresses: linzixia@hotmail.com (Z. Lin), sundpe301@163.com (D. Sun).

http://dx.doi.org/10.1016/j.jpowsour.2016.01.026
0378-7753/

dominant energy storage devices in portable electronics and also show great potential in hybrid electric vehicles [1,2]. Nevertheless, the currently most widely used anode material for commercial LIBs, graphite, has a relatively low theoretical capacity (372 mAh g^{-1}), which has hampered the implementation of the emerging large-scale energy applications [3]. In this regard, extensive efforts have been made to seek alternative anode materials with high energy and power density, long cycling life, and good rate capability [4,5]. In contrast to the intercalation reaction for graphite, transition metal oxides (TMOs) are able to interact with Li based on conversion-type reaction ($MO_x + 2xLi \leftrightarrow M + xLi_2O$) [6,7], where M is a transition metal, which can deliver high specific capacities from about 700 to 1000 mAh g^{-1}, much higher than that of graphite [8]. As a typical TMO, iron oxides have long been considered as promising anode materials due to their high theoretical capacities (1005 mAh g^{-1} for Fe_2O_3 and 930 mAh g^{-1} for Fe_3O_4), natural abundance, high corrosion resistance, environmental benignity, and low cost [9,10]. However, the practical application of iron oxides as anode for LIBs is still limited by the unsatisfactory cycling life and poor rate capability [11]. It is mainly attributed to the low electronic and ionic conductivity of iron oxides [12,13]. Furthermore, the dramatic volume changes (~90%) of iron oxides during the repeated charge/discharge processes will cause the agglomeration of active materials, electrode pulverization and finally loss of electrical connectivity, which leads to poor capacity retention [14,15]. In addition, the formation of a thick and unstable solid electrolyte interface (SEI) films on iron oxides surface causes consumption of abundant lithium ions and a large irreversible capacity [16]. Currently, one promising strategy is to employ carbonaceous materials as matrices for active materials to improve the cycle performance of nanostructured electrode materials [17,18]. It is noted that the conductive carbon matrix not only improves the electronic conductivity of active materials and prevents the aggregation and pulverization of nanoparticles, but also overcomes the undesirable side reactions between active materials and electrolyte, due to its intrinsical conductivity and excellent chemical durability [19,20]. Therefore, extensive researches have been focused on developing composite materials with homogeneously dispersed metal oxides on a carbon matrix for advanced LIBs anodes.

Recently there is growing interest for the synthesis of carbon materials derived from biomass precursors owing to their low cost, easy fabrication and environmental compatibility [21–23]. Bacterial cellulose (BC), a typical biomass material, is composed of interconnected networks of cellulose nanofibers, and can be produced in large amounts in a microbial fermentation process [24]. Carbonized BC (CBC) aerogel with highly conductivity and superior structural features has recently attracted researchers' attention and showed promising properties in electrochemical energy storage systems. Yu et al. [25] fabricated a free-standing supercapacitor with heteroatom-doped CBC. The as-prepared CBC based supercapacitor with the introduction of nitrogen/phosphorus heteroatoms exhibits high power density and excellent cycling stability within 4000 cycles. Chen et al. [26] constructed a “vein-leaf” type metal-free electrocatalyst with CBC as the skeleton and nitrogen-doped graphene as the leaf. The resulting catalyst exhibits superior activity comparable to that of Pt/C in the oxygen reduction reaction. Moreover, the prepared metal-free catalyst performs a much better stability and methanol tolerance when compared with Pt/C catalyst. Recently, our group [27] presented a design and fabrication of flexible cathode and multifunctional interlayer based on CBC for advanced Li–S batteries. The electrochemical test results show that the prepared Li–S system with a high sulfur content of 81 wt% exhibits stable cycling, good rate performance, and a high capacity of 1134 mAh g^{-1} at 200 mA g^{-1} current density.

In this paper, a composite material consisting of the continuous CBC nanofibers coated with amorphous Fe_2O_3 (denoted as A-Fe_2O_3@CBC) was properly designed and used as a flexible anode for advanced LIBs. The macroporous architecture of three-dimensional (3D) CBC aerogel can facilitate good contact of the internal active materials with the electrolyte and effectively alleviate the volume variation during the lithium ions insertion and extraction [28,29]. The conductive carbon nanofibers interconnected within the 3D CBC matrix not only maintain electron fast transportation throughout the electrode in a timely way [11], but also provide sufficient surface area for the uniformly dispersed active materials. Meanwhile, the free-standing anode without insulating polymer binder and heavy metal current collectors could enhance the electrochemical performance [30] and achieve a higher energy density of battery [31]. More importantly, the amorphous nature of porous iron oxide in A-Fe_2O_3@CBC might be more favorable for the insertion and extraction of lithium ions, which is quite beneficial for the integrity of the electrode. When compared with its crystalline counterpart, the A-Fe_2O_3@CBC electrode exhibits much higher capacity and more stable cycling performance at relative high current density.

2. Experimental section

2.1. Materials synthesis

The 3D CBC aerogel matrix was prepared by carbonization of the freeze-dried BC precursor at 1000 °C under flowing H_2/Ar mixed atmosphere, as described in our previous report [27]. The preparation processes of the CBC aerogel are explicitly illustrated in Fig. S1, and the electrical conductivity of the obtained CBC is 2.24 S cm^{-1}. The free-standing A-Fe_2O_3@CBC composite was fabricated via impregnation and direct thermal treatment processes. Typically, $Fe(NO_3)_3 \cdot 9H_2O$ (2.6 g) was first dissolved in ethanol (20 mL), into which the flexible CBC membranes were immersed, and kept sealed for 1 h. Following removal from the solution, the membranes were left undisturbed under ambient conditions for 20 min for the evaporation of ethanol. Afterwards, the sample was treated at 40 °C for 24 h in a blast drying oven. The dried $Fe(NO_3)_3 \cdot 9H_2O$/CBC composite was subsequently treated in air at 200 °C for 10 h to obtain the final amorphous A-Fe_2O_3@CBC sample. The overall fabrication process and the micro/macroscopic characteristics of the A-Fe_2O_3@CBC composite are illustrated in Fig. 1. For comparison, crystalline Fe_3O_4/CBC composite was obtained by the annealing treatment of the as-prepared $Fe(NO_3)_3 \cdot 9H_2O$/CBC composite at 600 °C for 6 h in Ar. The obtained crystalline product was denoted as C–Fe_3O_4@CBC. Both of the amorphous and crystalline iron oxide anodes are approximately 1.0 mg–1.4 mg in weight. The as-prepared paper-like anodes can be directly applied as electrodes in LIBs without using a binder, conductive additives, or an extra current collector.

2.2. Materials characterization

The X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 Advance X-ray diffractometer (Germany) using Cu-Kα radiation (λ = 0.15418 nm) at a scanning rate of 4° min^{-1} in the 2θ range of 10°–90°. Raman spectra were collected using a confocal Raman microscope (HORIBA Jobin Yvon, France) with excitation at 532 nm from an Ar-ion laser. The iron oxides contents in the A-Fe_2O_3@CBC and C–Fe_3O_4@CBC composites were determined by thermal gravimetric analysis, TGA (Pyris 1 DSC) performed under air atmosphere with a heating rate of 5 °C min^{-1} from room temperature to 700 °C. The pore-size distribution and Brunauer–Emmett–Teller (BET) specific surface area of A-