



Research Paper

Encapsulating iron oxide@carbon in carbon nanofibers as stable electric conductive network for lithium-ion batteries



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ABSTRACT

To meet the requirements for the quick charge for the hybrid electric vehicles (HEVs) or plug-in hybrid electric vehicles (PHEVs), better rate capability is urgently needed for the lithium ion batteries (LIBs). Here in our work, a new anode with excellent rate capability is developed. In this anode, nanoporous iron oxide nanoparticles coated with carbon (designated as Fe₂O₃@C NPs) are homogeneous distributed in carbon nanofibers (CNFs), which can be designated as Fe₂O₃@C CNFs. The CNF constrains the nanoporous Fe₂O₃@C NPs along the longitudinal direction and the fibers are cross-linked, establishing a three dimensional (3D) stable electric conductive network. The nanoporous Fe₂O₃@C NPs exposed on the surface of CNFs provide more active sites for electrode reactions. The thin carbon shell around the Fe₂O₃ NPs gives the additional protection and improves the conductive connection between the nanofibers, leading to an integral conductive network which links all the Fe₂O₃@C NPs. The Fe₂O₃@C CNFs structure exhibits good capacity retention and excellent rate capacity at high current density.

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1. Introduction

With an increased demand for LIBs, graphite as the commercial anode material with theoretical capacity of 372 mAh/g is far from satisfying people's need [1–7]. Fe₂O₃ with low cost and high specific capacity up to 1007 mAh/g (about three times higher than commercial graphite), is an excellent candidate for anode material [8–12]. However, poor electron transport in electrode, huge volume change (~200%) during lithiation/delithiation and high resistance at the interface of electrode/electrolyte for faster charging/discharging rate severely hamper the practical application of Fe₂O₃ in LIBs [13–18].

One-dimensional (1D) structure can efficiently improve the performance of Fe₂O₃ as anode material due to its excellent electron transport along the lengthways direction and large

surface-volume ratio [19–23]. Electrospinning is now a convenient method to manufacture the 1D structure [24–27], especially for LIBs. On the one hand, the material obtained by electrospinning can take full advantage of 1D architectures. On the other hand, the material can form metal oxide nanoparticles/CNFs after being calcined under an inert atmosphere. Dispersing the metal oxide nanoparticles into CNFs matrix can enhance the conductivity, buffer the large volume change and prevent the agglomerates of nanoparticles [6,28–30].

Recently, our group synthesized nanoporous Fe₂O₃@C NPs with low carbon content of 6.7 wt.% [31]. The nanoporous Fe₂O₃@C anodes exhibit high capacity and good capacity retention at a current density of 500 mA/g due to the protection of thin layer of carbon shell. Unfortunately we found that it is difficult to achieve good capacity retention and high-rate capacity at high current density, such as 2 A/g, 3 A/g and 5 A/g. Better conductivity and faster charge transfer between the nanoparticles are badly in need. To solve these problems, we embedded the nanoporous Fe₂O₃@C NPs into CNFs (designated as Fe₂O₃@C CNFs) to establish a stable electric conductive network in which each Fe₂O₃@C NP is connected with the same conductive matrix. This structure benefits the faster Li ion transport, electrochemical conductivity

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and structural integrity. The thin layer of carbon around Fe_2O_3 nanoparticles, even for those exposing on the fiber surface, can avoid Fe_2O_3 nanoparticles direct contacting with electrolyte which will result in severe structure damage and poor electrochemical performance. Many methods also have been used to give additional protection to the exposed nanoparticles on the surface of fibers [32–35]. Nevertheless, these methods are rather difficult and expensive to scale up or will lead to relatively high content of carbon which will sacrifice the overall anode capacity. In our work, the carbon content of $\text{Fe}_2\text{O}_3@\text{C}$ CNFs is only about 25 wt.%, and the electric conductive network fabricated with $\text{Fe}_2\text{O}_3@\text{C}$ CNFs shows high reversible capacity and excellent rate capacity.

2. Experimental section

2.1. Materials synthesis

Polyacrylonitrile (PAN) ($M_w \approx 150\,000$, Macklin), N,N-Dimethylformamide (DMF) ($\geq 99.9\%$, Aladdin), Iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) ($\geq 99.0\%$, Sinopharm Chemical Reagent Co. Ltd) and glucose (Sinopharm Chemical Reagent Co. Ltd) are used without purification. Nanoporous $\text{Fe}_2\text{O}_3@\text{C}$ NPs were prepared according to our previous work [31]. In a typical process, 40 mL of buffer solution with 1.6 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 1 g glucose was transferred to and sealed in a Teflon-lined autoclave (50 mL), kept at 160°C for 24 h, and finally cooled to room temperature. The product was freeze-dried after centrifugation and washing. For the electrospinning process, 500 mg $\text{Fe}_2\text{O}_3@\text{C}$ NPs were dispersed in a

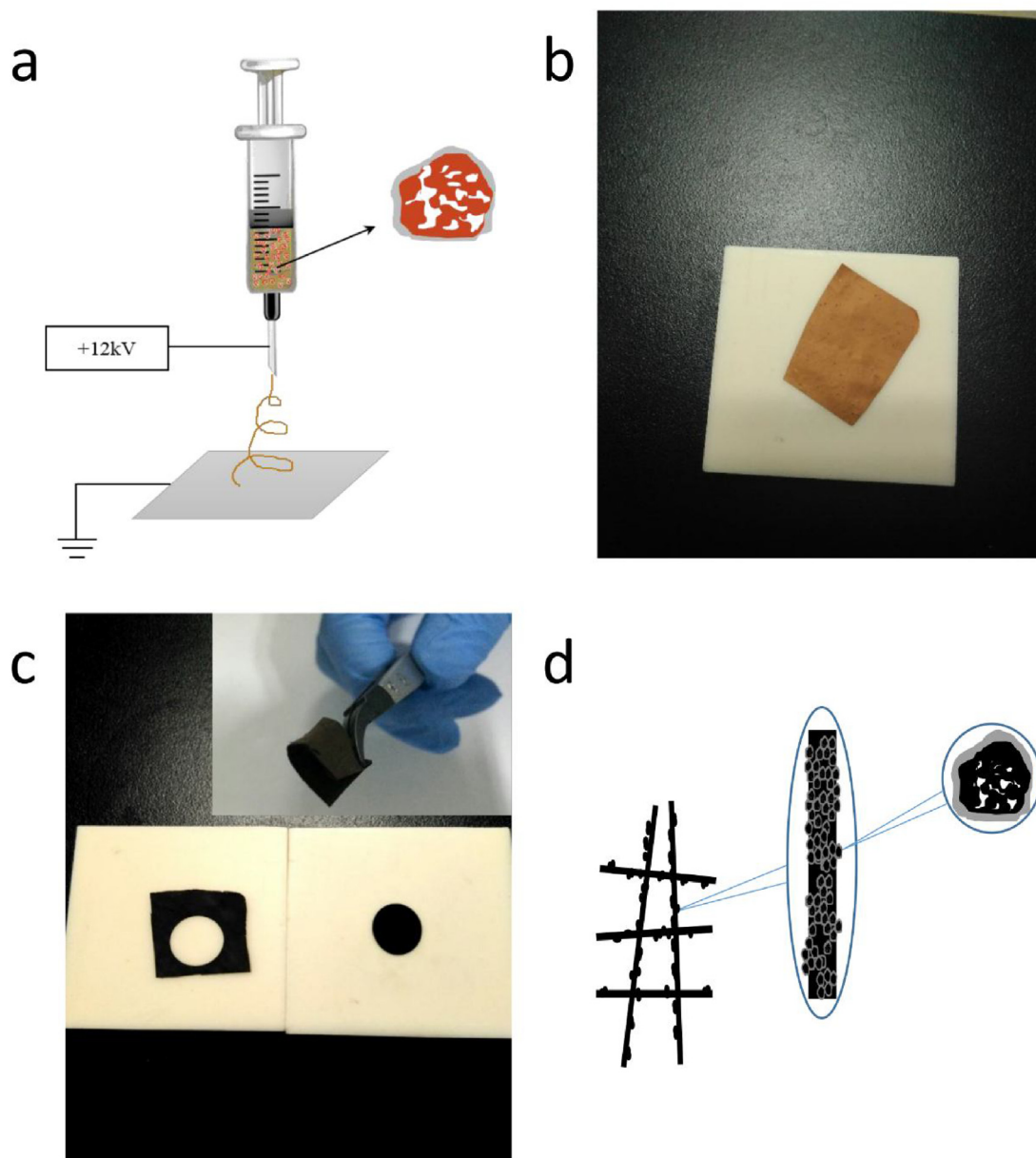


Fig. 1. (a) Illustration of electrospinning process. (b) Photograph of the electrospinning film before calcination. (c) Photographs of $\text{Fe}_2\text{O}_3@\text{C}$ CNFs film after calcination. (d) Structure of $\text{Fe}_2\text{O}_3@\text{C}$ CNFs.

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