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Freestanding manganese dioxide nanosheet network grown on nickel/polyvinylidene fluoride coaxial fiber membrane as anode materials for high performance lithium ion batteries

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HIGHLIGHTS

- The Ni/PVDF fiber is obtained by electrospinning and electroless deposition method.
- Novel MnO_2/Ni/PVDF coaxial fiber is prepared for the flexible anode in LIBs.
- High capacity and good cycling stability are achieved for novel composite anodes.

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ABSTRACT

A novel manganese dioxide (MnO_2) nanosheet network grown on nickel/polyvinylidene fluoride (Ni/PVDF) coaxial fiber membrane is successfully fabricated by a three-step route: the polyvinylidene fluoride fiber membrane is prepared by electrospinning method, and then the Ni(shell)/PVDF(core) coaxial fiber membrane with core–shell structure can be obtained by the electroless deposition, and finally the manganese dioxide nanosheet network grown on Ni/PVDF coaxial fiber membrane can be achieved by using a simple hydrothermal treatment. This as-prepared binder-free and flexible composite membrane is directly used as anode for lithium ion batteries. The excellent electrochemical performance of the composite membrane can be attributed to the unique combinative effects of nanosized MnO_2 network and conductive Ni/PVDF fiber matrix as well as the porous structure of composite fiber membrane.

1. Introduction

Lithium ion batteries (LIBs) have been widely applied in many fields as the dominant power sources due to their high power and energy densities, such as cell phones and laptops [1,2]. However, it is the key issue to develop some innovative electrode materials with higher energy density and longer cycling life to meet the requirements of next generation LIBs [3,4]. Until now, nanostructured transition metal oxides are the potential candidates for next generation LIBs anode materials because of their high theoretical specific capacity [5–7]. Among various transition metal oxides, nanostructured manganese dioxide (MnO_2) has been studied as anode material in LIBs with promising excellent electrochemical performance, in addition to its lower cost, environmental friendliness nature, and natural abundance [3,8,9]. However, there are still some challenges for the practical applications of nanosized MnO_2 anode in LIBs, such as poor cycling stability owing to the mechanical instabilities and electrical disconnection caused by the huge volume changes during repeating lithium insertion/extraction process.

Recently, some reports have been carried out to fabricate the nanosized composite by incorporating MnO_2 on the conductive matrix, such as conducting polymer [10,11], carbon fibers [3,9], carbon nanotubes [12–14], grapheme [15,16], which improves the conductivity of MnO_2. More recently, the freestanding composite electrodes with three-dimensional (3D) structure have attracted

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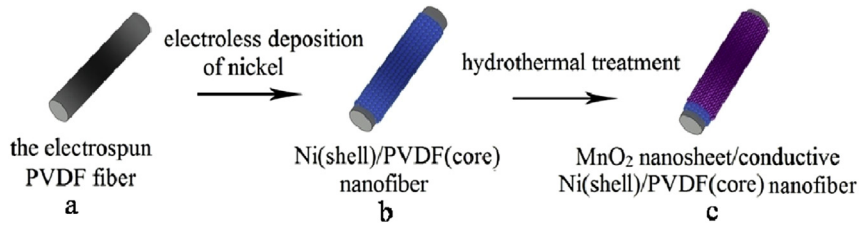

Fig. 1. Schematic representation of the composite fibers. (a) the electrospun PVDF fiber, (b) coating the Ni on the surface of PVDF fiber to form coaxial Ni(shell)/PVDF(core) fiber, (c) the controlled deposition of MnO_2 nanosheet network on the as-prepared conductive Ni/fiber.

greater attention in this field, the 3D structure avoids to use the binder and conductive agent, which can achieve high rate capabilities and good cycle performance because they can combine the advantage of the freestanding matrix and the active nanomaterials [17,18]. The freestanding matrix can provide a highly conductive network in conjunction with a large surface area to support good contact between active nanomaterials. In addition, the freestanding matrix is effective in enhancing and maintaining the mechanical strength of the nanocomposite during volume changes as well as suppressing the aggregation of nanomaterials during Li ion insertion/extraction. In our previous work [19], the 3D Ni/PVDF(Polyvinylidene fluoride) coaxial fiber with silicon membrane can be prepared and used as a flexible free standing composite anode, which exhibit excellent electrochemical performance.

Here, we synthesize the novel MnO_2/Ni/PVDF coaxial fiber membrane by electrospinning, electroless deposition and hydrothermal method (Fig. 1). The Ni was conformably coated on porous PVDF fibers, serving as a conductive 3D framework for subsequent controlled deposition of MnO_2 nanosheet network. The 3D MnO_2/Ni/PVDF coaxial fiber membrane has the following advantages using as anode in LIBs: (i) the electrospun PVDF nanofiber membranes have high porosity (75%), the micropores between the smooth fibers facilitate easy access of electrolyte to the electrodes; (ii) the PVDF fibers with the nickel coating are highly electrical conductivity; (iii) the mesoporous nanosheet MnO_2 network can tightly anchor in the highly conductive Ni/PVDF fiber to form the MnO_2/Ni/PVDF coaxial fiber membrane, the 3D Ni/PVDF fiber framework and the outlayer MnO_2 network can protect it from structural collapsing and breaking. These combined properties enable the coaxial MnO_2/Ni/PVDF fiber composite membrane to have very high charge/discharge capacity and rate capability.

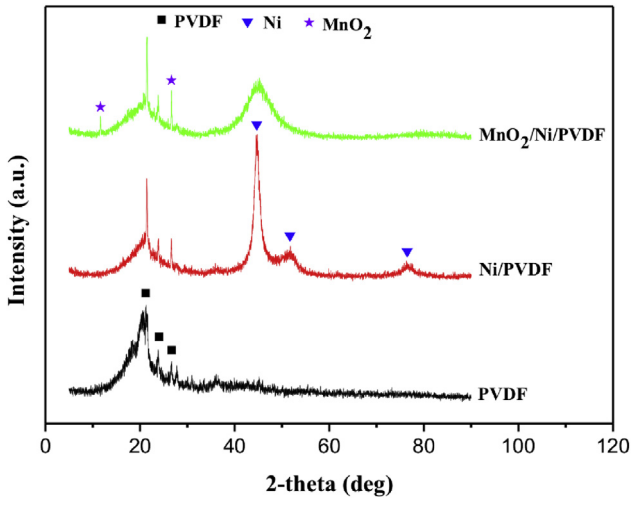

Fig. 2. The XRD patterns of the PVDF fiber membrane, the Ni/PVDF coaxial fiber membrane and the MnO_2/Ni/PVDF coaxial fiber membrane.

2. Experimental section

2.1. Preparation of the freestanding MnO_2/Ni/PVDF coaxial fiber composite membrane

The freestanding MnO_2/Ni/PVDF coaxial fiber composite membrane was synthesized via three steps as described in a schematic representation (Fig. 1). The first step was to prepare the PVDF fiber membrane using the electrospinning technique [20]. A known amount of PVDF (M = 500,000, KnyarFlex 2704 from Atofina Chem.) powder was dissolved in a mixed solvent (acetone/DMAc = 7/3 by weight) to form homogeneous solution with concentrations of 12%, and then a PVDF fiber membrane with thickness of about 40 um was deposited on the collector plate by electrospinning of PVDF solution under high voltage of 18 KV. The second step was to coat PVDF fibers with Ni via the electroless deposition method [21]. The piece of 2 cm × 2 cm PVDF fiber membrane was completely sensitized by immersing into a 0.1 g L^{-1} $SnCl_2$ and 0.1 M HCl mixed aqueous solution, and then was activated in an aqueous solution containing 0.1 g L^{-1} $PdCl_2$ and 0.1 M HCl for 20 min. Ultrasonic treatment was accompanied during the sensitizing and activating process. The surface activated fiber membrane was then immersed into the 28.5 g L^{-1} $NiCl_2 \cdot 6H_2O$, 10.5 g L^{-1} $NaH_2PO_2 \cdot H_2O$, 43.5 g L^{-1} $NaC_6H_5O_7 \cdot 2H_2O$ and 25 g L^{-1} NH_4Cl mixed aqueous solution for Ni electroless plating at 70 °C for about 10 min. The Ni coated fiber membrane was rinsed with distilled water and dried in vacuum. The plating time could be adjusted to control the thickness of coated nickel shell. The third step was the controlled deposition of MnO_2 nanosheet network on the as-prepared conductive fiber membrane by a hydrothermal treatment. The as-prepared conductive Ni/PVDF coaxial fiber membrane was immersed into 50 ml 0.3 M $KMnO_4$ solution under magnetic stirring for 30 min. Subsequently, 0.25 mL ethanol was rapidly added into the above solution, and the mixture was heated to 80 °C and kept for 60 min in the Teflon-line autoclave. After deposition, the as-prepared brown thin film was washed with de-ionized water, and then dried in a vacuum oven at 50 °C for 12 h. The mass loading of MnO_2 on the Ni/PVDF composite fiber membrane was measured by a microbalance before and after the loading. The heterogeneous reaction that occurred on the surface of the Ni/PVDF composite fiber membrane could be represented as follows:

$$4KMnO_4 + 2CH_3CH_2OH \rightarrow 4MnO_2 + 2CH_3COOK + 2KOH + 2H_2O + O_2\uparrow$$

2.2. Material characterization

The porosity (P) was calculated from the density of membrane (ρ_m) and the density of pure PVDF (ρ_p = 1.79 g cm^{-3}): $P = 1 - (\rho_m/\rho_p)$. The membrane density was determined by measuring the volume and the weight of membrane [22]. The morphologies and