



Water soluble styrene butadiene rubber and sodium carboxyl methyl cellulose binder for ZnFe₂O₄ anode electrodes in lithium ion batteries



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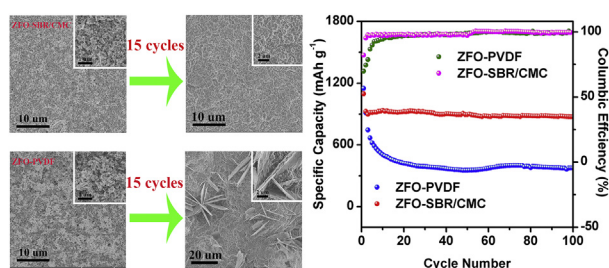
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HIGHLIGHTS

- ZnFe₂O₄ nano particles were prepared by the glycine-nitrate combustion method.
- SBR/CMC water soluble binder was used to prepare ZnFe₂O₄ anode electrode.
- Excellent cycle stability and rate capability were obtained using SBR/CMC.
- SBR/CMC is more promising than PVDF for the ZnFe₂O₄ anode electrode.

GRAPHICAL ABSTRACT



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ABSTRACT

ZnFe₂O₄ nano particles as an anode material for lithium ion batteries are prepared by the glycine-nitrate combustion method. The mixture of styrene butadiene rubber and sodium carboxyl methyl cellulose (SBR/CMC) with the weight ratio of 1:1 is used as the binder for ZnFe₂O₄ electrode. Compared with the conventional polyvinylidene-fluoride (PVDF) binder, the SBR/CMC binder is much cheaper and environment benign. More significantly, this water soluble binder significantly improves the rate capability and cycle stability of ZnFe₂O₄. A discharge capacity of 873.8 mAh g⁻¹ is obtained after 100 cycles at the 0.1C rate, with a very little capacity fading rate of 0.06% per cycle. Studies show that the SBR/CMC binder enhances the adhesion of the electrode film to the current collector, and constructs an effective three-dimensional network for electrons transport. In addition, the SBR/CMC binder helps to form a uniform SEI film thus prohibiting the formation of lithium dendrite. Electrochemical impedance spectroscopy shows that the SBR/CMC binder lowers the ohmic resistance of the electrode, depresses the formation of SEI film and facilitates the charge transfer reactions at the electrode/electrolyte interface. These advantages highlight the potential applications of SBR/CMC binder in lithium ion batteries.

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1. Introduction

Lithium ion batteries (LIBs) have been intensively investigated for promoting the developments of portable electronics, electric vehicles and renewable energy storage. Conventional LIBs use graphite as the anode material which is cheap, abundant and stable

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for cycling. However, both the natural graphite and artificial graphite have hindered further developments of LIBs due to their low specific capacities (theoretically 372 mAh g^{-1}) and serious safety issues. As a consequence, searching for alternative anode materials is strongly required for the development of advanced LIBs. In numerous new anode materials under consideration, recently spinel ternary iron oxides MFe_2O_4 (MFO, $\text{M} = \text{Co}, \text{Cu}, \text{Ni}, \text{Zn}$) have attracted particular attention [1–7]. Especially, ZnFe_2O_4 (ZFO) has been regarded as the most promising one because of its high theoretical capacity (1072 mAh g^{-1}), low toxicity and resource abundance. However, there are still some issues to be solved for ZFO such as low electronic conductivity, high initial irreversible capacity and large volume variations during repeated cycling. In these regards, it has been engineered into many different nanostructures to enhance its electrode performance. For instance, the ZFO nano particles synthesized by the urea combustion method showed a reversible capacity of 615 mAh g^{-1} [8]. The electrochemical performance was further enhanced by either nanostructuring to form hierarchically hollow microspheres ($\sim 900 \text{ mAh g}^{-1}$) [9], nanofibers (730 mAh g^{-1}) [10], nano particles (800 mAh g^{-1}) [11], or by the incorporation of a conductive carbon framework to construct ZFO/carbon hollow spheres (841 mAh g^{-1}) [12] and carbon-coated ZFO nano particles ($\sim 1000 \text{ mAh g}^{-1}$) [13].

In order to enhance the electrochemical performance of LIBs, researchers are not only devoted to searching for new electrode materials, but also to developing new electrode fabrication techniques. Binder is an important component of battery electrodes which acts as an effective dispersion agent to connect the active material and conductive additive together and steadily adhere them to the current collector. The most commonly used binder in LIBs is poly(vinylidene)-fluoride (PVDF) due to its high electrochemical stability and good connection between the electrode films and current collectors. However, PVDF is always dissolved in some organic solvents such as N-methyl-2-pyrrolidone (NMP). It is known NMP is a volatile and combustible solvent which causes safety problems and severe pollution. Moreover, PVDF is readily swollen, gelled, or dissolved by nonaqueous liquid electrolytes to form a viscous fluid or gel polymer electrolyte, which results in desquamation of electrode particles and hence fast capacity fading of the battery after prolonged cycling.

In the last few years, the mixture of sodium carboxyl methyl cellulose (CMC) and styrene butadiene rubber (SBR) has attracted great attention as a new binder for LIBs. Fig. 1 shows the molecular structures of PVDF, CMC and SBR, respectively. CMC is a typical polymeric derivative of cellulose containing carboxylate anion and hydroxyl functional groups. The existing of these two groups makes CMC a water-soluble binder and an effective thickening agent. SBR as an elastomer has higher flexibility, stronger binding force and better heat resistance than PVDF. In addition, it is very attractive that the prices of CMC ($1\text{--}2 \text{ EUR kg}^{-1}$) and SBR ($0.2\text{--}1 \text{ EUR kg}^{-1}$) are much cheaper than that of PVDF ($15\text{--}18 \text{ EUR kg}^{-1}$) [14]. To date, the SBR/CMC binder has shown much effectiveness for a number of electrode materials including graphite [15–17], transition metal

oxides [18–20], sulfur [21,22], and silicon based materials [23–25]. But to the best of our knowledge, most of the studies on the ZFO anode still used PVDF as the binder. The electrodes thus prepared showed unsatisfying cycle stability and rate capability especially for those of ordinary ZFO particles without novel nanostructures and conductive carbon framework. Herein in this work, we synthesized ZFO nano particles by the glycine-nitrate combustion method. Then we prepared ZFO electrode using SBR/CMC as the binder. The electrode showed much better electrochemical properties compared to the traditional PVDF-based ZFO electrode.

2. Experimental section

The ZFO nano particles were prepared by the glycine-nitrate combustion method. The chemicals used in the synthesis process were zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Aladdin), ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Aladdin) and glycine (Aladdin). The ratio of glycine (fuel) to metal nitrates (oxidizer) was fixed at 3:5 to allow completion of the combustion reactions. The above mixture was dissolved in 30 mL of deionized water under continuous stirring. Ammonia water was dropped slowly to keep the pH value of the solution at 9–10. Then, the solution was transformed into oven. At a critical temperature of $\sim 200 \text{ }^\circ\text{C}$, a spark was generated due to enormous heat creation in the solution. This caused an exhaustive heat release through the foam, yielding a brown voluminous fluffy powder in the container. The obtained powder was then calcinated at $350 \text{ }^\circ\text{C}$ for 3 h in air to remove the un-reacted fuel and nitrates. Subsequently, the decomposed powder was grinded and calcined at $700 \text{ }^\circ\text{C}$ for 2 h. The ZnFe_2O_4 nano particles were obtained after being cooled to room temperature.

The crystal structure of the material was studied by X-ray diffraction (XRD) on a Bruker AXS D8 X-ray diffractometer with $\text{Cu K}\alpha$ radiation. The morphologies of the material and the electrodes were studied by JSM-6700F field emission scanning electron microscope (SEM). Transmission electron microscope (TEM) was performed on FEI Tecnai G2 F20 S-TWIN. X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB spectrometer using $\text{Mg-K}\alpha$ light source. The binding energy was corrected using the C 1s peak at 284.6 eV . The resistance of the electrodes were measured by the two-point-probe method.

Electrochemical experiments were conducted with CR2032 coin cells between 0.01 V and 3.0 V using metallic lithium foil as the anode. The ZFO electrodes were prepared by mixing 70 wt% of active material, 20 wt% of super P conductive additive and 10 wt% of PVDF (or SBR/CMC) binder. The PVDF binder was dissolved in NMP solvent. The CMC/SBR binder was a mixture of CMC and SBR in an empirically optimized weight ratio of 1:1, which was dissolved in deionized water. Hereafter the electrodes were denoted as ZFO-PVDF and ZFO-SBR/CMC accordingly. The slurries were pasted onto a Cu current collector and dried in vacuum oven at $120 \text{ }^\circ\text{C}$ for 12 h. The dried electrodes were cut into $8 \times 8 \text{ mm}^2$ for use. The loading density of the ZFO active material in the electrodes is about 3.0 mg/cm^2 . The electrolyte was a 1 M LiPF_6 solution dissolving in

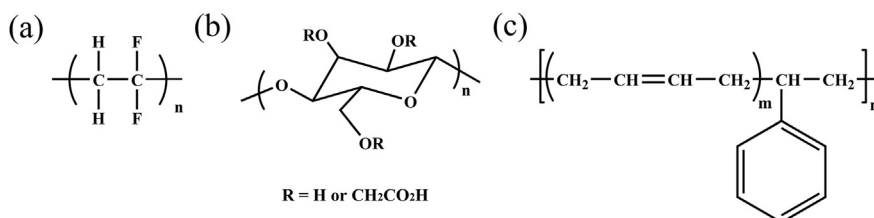


Fig. 1. Molecular structures of (a) PVDF, (b) CMC and (c) SBR.

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