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Short communication

A general polymer-assisted solution approach to grow transition metal oxide nanostructures directly on nickel foam as anodes for Li-ion batteries

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HIGHLIGHTS

- Co_3O_4 were grown on nickel foam by polymer-assisted solution method.
- Carbon left from decomposition of polymer is an active binder between Co_3O_4 and nickel foam.
- Co_3O_4 on nickel foam showed much improved battery performance.

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ABSTRACT

Cobalt oxide nanostructures have been successfully grown on nickel foam by a facile polymer-assisted chemical solution method for lithium-ion battery anodes. The carbon left from the decomposition of polymers is an effective binder between the metal oxides and nickel foam. As compared to the metal oxide powder prepared in a conventional way by using polymer binder and carbon black, these one-step direct growth electrodes showed much better Li storage properties with high capacities, stable cyclability, and rate capability: Co_3O_4 on nickel foam gave a capacity of 900 mAh g^{-1} at a current density of 1 A g^{-1} and 600 mAh g^{-1} at 4 A g^{-1}. The good performances of these electrodes could be attributed to intimate contact between the active material and nickel foam, the porosity of the current collector, and the network structure of the active materials. This general method could also be applied to other transition metal oxides.

1. Introduction

Anode materials with both high specific energy densities and good rate capabilities are desirable for lithium-ion batteries intended for use in hybrid electric vehicles (HEVs) and plug-in hybrid electric vehicles (PHEVs). To achieve high power density and energy density, the electrochemical activity and kinetics of the electrodes are the dominant factors. It has been proven that it is effective to enhance the kinetics of ions and electrons transport in electrode–electrolyte and at the electrode–current collector interface [1–3]. Currently, the general preparation method of electrodes involves using an insulating poly(vinylidene difloride) as binder and carbon black as a conductive additive, both of which add extra weight to the electrodes and decrease their overall specific capacity. In addition, the polymer binder greatly decreases the electrical conductivity of the electrode materials, and introduces additional interfaces of active material/polymer binder and active material/active material. By directly growing one-dimensional (1D) or two-dimensional (2D) nanostructures on the current collector substrates, the extra weight of polymer binder and carbon black and their undesirable interfaces are eliminated; therefore, the specific capacity of the electrodes is improved [4–10]. Efficient electron transport and fast Li^+ diffusion are achieved because there is no insulating polymer binder to prevent intimate contact between the active material and current collector. For example, $FeVO_4$ nanosheet arrays directly grown on stainless steel foil delivered a

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stable capacity even at a high current density of 20 A g^{-1} [11]. Iron oxide nanorod arrays grown on the titanium substrate showed a higher reversible capacity compared to the iron oxide powders [7].

Transition metal oxides (TMOs) have been considered as promising anode candidates for their high capacity (e.g. >600 mAh g^{-1}). However, due to poor conductivity, TMOs are always synthesized as nanostructure and coupled with conductive carbon when applied in lithium-ion batteries [4,12–21]. By growing TMOs directly on the surface of nickel foam current collector, the porous structure of nickel foam will promote the diffusion of electrolyte and maximize the utilization of active material. Many efforts have been put on the direct growth of TMOs on nickel foam for energy storage [9,22,23]. Although the performances of these electrodes are impressive, the synthesis processes are always tedious or not able to achieve large-scale production. Compared to those complicated and high cost methods, developing a facile and general strategy to synthesize the binder free electrode is of great importance. In this paper, we report a general polymer-assisted chemical solution method for synthesizing TMOs nanostructure directly on nickel foam (cobalt oxide in this paper, nickel oxide in the supporting information). Polyethylenimine (PEI)/ethylenediaminetetraacetic acid (EDTA) and polyvinylpyrrolidone (PVP) were tried as the polymers to demonstrate the feasibility of this method.

2. Experimental

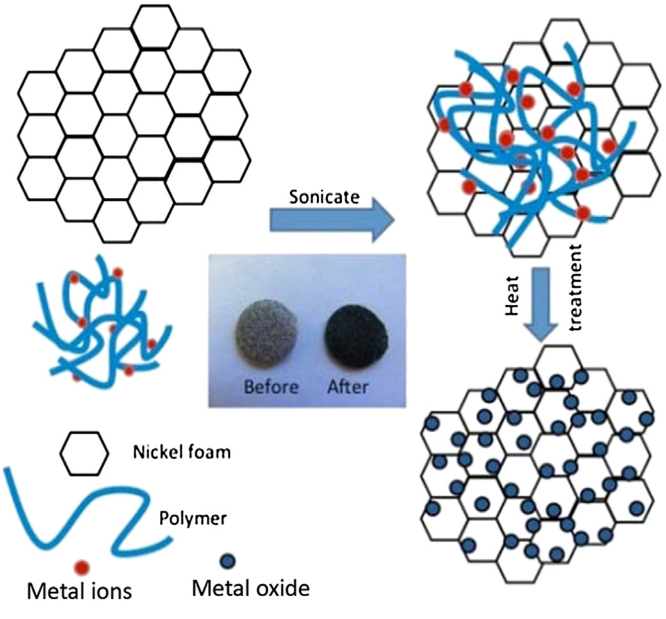
The simple polymer-assisted chemical solution synthesis process is described as following. A viscous cobalt-polymer solution was prepared by dissolving cobalt nitrate (1 g), PEI (2 g, 50 wt% PEI in water), and EDTA (1 g) in 10 mL deionized water, or cobalt nitrate (1 g) and PVP (1 g) were dissolved in 10 mL deionized water. The polymers function as binding agents to metal ions and increase the viscosity of the solution. The nickel foam was sonicated in the mixture solution for 2 min to make sure that all the skeleton of nickel foam was covered by precursor solution, then taken out and transferred to a crucible boat in a box furnace. The nickel foam with cobalt-polymer solution was heated at 150 °C for 1 h and 450 °C for 3 h. Cobalt oxide directly grown on nickel foam was used as anodes after sonication to remove extra oxide powders from the surface of nickel foam.

3. Results and discussion

3.1. Structure and morphology characterization

The structure and morphology of the as-prepared samples were characterized by X-ray diffraction (XRD; MMA GBC, Cu Kα, radiation), field emission scanning electron microscopy (FESEM; JEOL-7500, 2 keV), and transmission electron microscopy (TEM; FEI Tecnai, 300 keV). Thermogravimetric analysis was performed Pyris 1 TGA thermogravimetric analyser (Perkin Elmer). Electrochemical measurements were carried out using CR-2032 coin cells. For the preparation of the working electrode, cobalt oxide on nickel foam was directly used as electrode. A lithium foil was used as the counter electrode. A solution of 1 M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 in volume) was used as the electrolyte. Galvanostatic cycling was performed using a Land battery testing system. In a control experiment, Co_3O_4 powder (without nickel foam) was prepared by heating the cobalt nitrate with EDTA and PEI mixture solution at 150 °C for 1 h and 450 °C for 3 h. Co_3O_4 powder was used to prepare the electrode in a conventional way, which employs polymer binder and carbon black with active material/polymer binder/carbon mass ratio of 70:10:20.

The growth mechanism of TMOs on nickel foam is presented in Scheme 1. The polymers here serve as a binder in the synthesis process. During the immersing process, the long polymer chains tangle the nickel foam and fixed the metal ions on the skeleton. The polymers not only help connect the metal ions stick to the nickel foam but also determine the nanostructure of the metal oxide formed after annealing process as discussed later in this paper. Due to the incomplete decomposition of polymer at 450 °C, residual carbon acts as an effective binder between the metal oxides and nickel foam.



Scheme 1. Schematic mechanism for the growth process of TMOs on nickel foam. The original nickel foam (before) and Co_3O_4 covered on nickel foam (after) are photographed.

XRD was employed to confirm the formation of TMOs. A typical XRD pattern of the Co_3O_4 is shown in Fig. 1. The XRD pattern matches well with the standard crystallgraphic spectrum of spinel Co_3O_4 (JCPDS No.43-1003), indicating a successful growth of Co_3O_4. It is noted that the XRD pattern for Co_3O_4 has no difference from two different polymers.

SEM images of Co_3O_4 prepared from PEI and EDTA are presented in Fig. 2a and b (a higher magnification of the square area in red in Fig. 2a). As compared with the original nickel foam (inset of Fig. 2b), we found that the Co_3O_4 sheet on nickel foam keeps the same skeleton shape as the nickel foam, and the skeleton of nickel

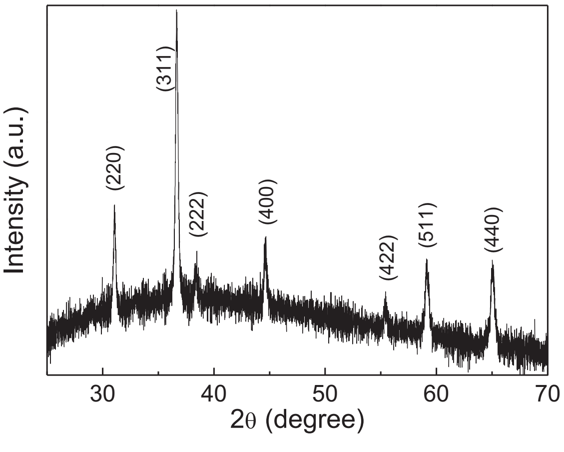


Fig. 1. XRD patterns of Co_3O_4.