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Interconnected Ni_2P nanorods grown on nickel foam for binder free lithium ion batteries

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ABSTRACT

Herein, we report a moderate and simple approach to synthesize nickel phosphide nanorods on nickel foam (Ni_2P/NF), which was employed as anode material for lithium ion batteries (LIBs). In this paper, interconnected Ni_2P nanorods were fabricated through hydrothermal treatment of NF and subsequently by high temperature phosphating. NF is not only regarded as nickel source and metal current collector, but also as a support to grow electro-active material (Ni_2P). Therefore, Ni_2P/NF could act as a self-supported working electrode for LIBs without any extra addition of cohesive binders. Moreover, benefiting from the conductive capacity of Ni_2P/NF, the active compound behaved superior lithium storage performance and cycling reversibility during electrochemical cycling process. The Ni_2P/NF delivered excellent reversibility of 507 mAh g^{-1} at the current density of 50 mA g^{-1} after 100 cycles. This work may provide a potential method for preparation of metal phosphides as promising materials for LIBs, hydrogen evolution reaction (HER) or other fields.

1. Introduction

Lithium ion batteries (LIBs), one of the advance devices for energy storage, are arousing increasing concern in researchers due to its excellent properties of fast recharge ability, excellent rate performance, and high power density, etc [1–3]. To meet the more and more energy demand in the future, the current task is to improve the electrochemical behavior of recyclable LIBs and search more alternative electrode materials [4].

Transition metal phosphides (TMPs), which possess high performance of catalytic and low polarization, have attracted great attentions as electrode materials for hydrogen evolution reaction [5–7], LIBs [8,9], or other fields [10,11]. Up to date, some approaches for preparing TMPs seemed to need hard experimental conditions, including high temperature or expensive reagents [12]. For example, CoP was prepared through organophosphonic acid and $CoCl_2{\cdot}6H_2O$ under the process of calcination at 900 °C [13]. Susan's group utilized metal-PPh_3 as precursors to obtain nanoparticles Ni_2P in a pot reaction [14]. Among the TMPs, nickel phosphides were widely applied in the realm of LIBs. However, nickel phosphides suffered from general volume expansion [14–16] and poor electric capacity [17,18] during the discharge-charge process for LIBs. Therefore, many groups try to seek some feasible ways to mitigate the above mentioned problems, such as coating nickel phosphides with conductive carbon material [19,20]. However, these works involves complex process. Hence, we need to find more simple ways for further improving the performance of Ni_2P as anode materials for LIBs.

Three dimensional nickel foam (NF) is often acted as a self-supported nanostructure used in LIBs [21–23]. The active material combining with NF to form binder-free LIBs, takes advantages of these merits as follows: (1) alleviate volume expansion during cycling process [24,25]; (2) reduce time consumption for fabricating batteries caused by film preparation [26]; (3) speed up the penetration of the electrolyte along active material to NF [27,28]. It's worth mentioned that NF could be combined with metal phosphides to form electro-active compound for LIBs. For example, Ni_5P_4/Ni composite was prepared by reaction of red phosphorus and NF under high temperature [29]. Metal phosphides were electrodeposited on NF to obtain Ni_3P-Ni films [30]. However, these works need to add extra nickel sources. According to the references, there is a possible approach that metal hydroxide can transform into the metal phosphides under high temperature [31]. So in this work, we have synthesized Ni_2P/NF by employing Ni $(OH)_2$ as precursor without adding any additional nickel source.

Herein, we have put forwards a moderate method to obtain Ni_2P nanorods on NF. Ni_2P/NF was fabricated by two step procedures via

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hydrothermal treatment and subsequently phosphating under high temperature. Interconnected Ni_2P nanorods were anchored on NF for self-supported and binder-free LIBs, which exhibited better electrochemical capacity and cycling stability for LIBs. Meanwhile, this mild and simple synthetic approach could possibly be extended to the preparation of other TMPs.

2. Experimental Section

2.1. Synthesis of $Ni(OH)_2$/NF

The hydroxide precursor was prepared by modified reference [32]. The cleaned NF was transferred to autoclave (50 mL) and subsequently the deionized water was added to 60% of the autoclave capacity. Then it was kept at 120 °C for 24 h. Then prepared precursor was dried in air at 70 °C for overnight.

2.2. Synthesis of Ni_2P/NF

$NaH_2PO_2{\cdot}6H_2O$ as phosphorus source, was mixed with $Ni(OH)_2$ by the mass ratio of 5:1. The mass of $Ni(OH)_2$ was calculated as follows, $\Delta m = m_{[Ni(OH)_2/NF]} - m_{[NF]}, m_{[Ni(OH)_2]} = \Delta m \times M_{[Ni(OH)_2]} / [2 \times M_{[OH]}]$. Those materials were treated at 300 °C for 2 h with a heating rate of 2 °C min^{-1} under argon atmosphere. According to the reaction ($2\,Ni + P \rightarrow Ni_2P$), the weight of Ni_2P anchored on NF can be estimated as follows, $\Delta m = m_{[Ni_2P/NF]} - m_{[NF]}$, $m_{[Ni_2P]} = \Delta m \times M_{[Ni_2P]}/M_{[P]}$.

2.3. Synthesis of NiO/NF

NiO/NF was synthesized similarly as Ni_2P/NF for making a comparison. Firstly, $Ni(OH)_2$/NF was prepared under the same condition in the above mentioned. Nextly, NiO/NF was obtained by the calcinations procedure without $NaH_2PO_2{\cdot}6H_2O$ under 300 °C (Scheme 1).

2.4. Material characterization

The phase structures of the products were obtained by powder X-ray diffractometer (XRD, MAXima-7000, Japan) with Cu Kα radiation. The morphologies and microstructure of different samples were characterized by scanning electron microscope (SEM, S-4800, Hitachi, Japan), transmission electron microscope (TEM, Tecnai G2 F20 S-Twin, USA). Special surface area and pore size were analyzed by Brunauer-Emmett-Teller measurement (BET, ASAP 2020, USA).

2.5. Electrochemical measurements

Interconnected Ni_2P nanorods supported on the nickel foam were regarded as binder-free working electrode. Celgard (2300) played the role of separator and metal lithium acted as counter electrode. Electrolyte was formed by a solution of $LiPF_6$ (1 mol/L) containing diethyl carbon and ethylene carbonate, (volume ratio = 1/1). We randomly selected five nickel foams to calculate the loading weight of Ni_2P supported on NF and the average value for loading weight of active material is nearly 2.21 mg. Batteries were packaged in glove box (LS800S, China) to measure the electrochemical properties of the active material. These batteries with galvanostatic cycling were detected at the battery test system (LAND CT2001A, China) with 0.005-3.0 V (*vs.* Li^+/Li) [32]. Electrochemical impedance spectroscopy (EIS, CHI 660D, China) was conducted in a electrochemical workstation from 0.1 Hz to 1.0×10^5 Hz. Cyclic voltammograms (CV, CHI 660B, China) were detected at a sweep speed of 0.1 mV s^{-1} in continuous voltage from 0.005 to 3.0 V (*vs.* Li^+/Li).

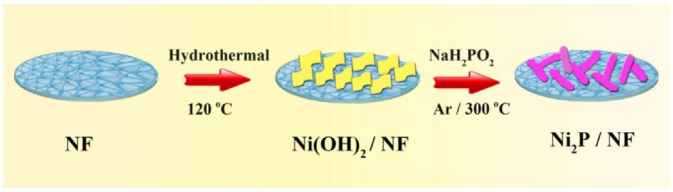
3. Results and discussion

Herein, nickel phosphide supported on nickel foam (Ni_2P/NF) was fabricated by a two-step process as shown in Scheme 1. First, nickel foam (NF) directly acted as nickel sources and transformed into the $Ni(OH)_2$/NF precursor through hydrothermal treatment. Then $NaH_2PO_2{\cdot}6H_2O$ as phosphorus source was mixed with $Ni(OH)_2$/NF to generate Ni_2P/NF under high temperature. The chemical process under high temperature can be expressed by the reaction: $Ni(OH)_2 + NaH_2PO_2 \rightarrow Ni_2P + Na_2HPO_4$ [33,34].

In order to affirm the products which were anchored on nickel foam (NF) through phosphating, nickel phosphide supported on nickel foam (Ni_2P/NF) were tested by powder X-ray diffractometer (XRD). The XRD pattern of Ni_2P supported on NF was shown in Fig. 1. The diffraction peaks at 40.7°, 47.4° and 54.2° were corresponded with the {111}, {210} and {300} planes of the cubic phase Ni_2P (JCPDS No.74-1385), marked as "●". In addition, the diffraction peaks at 44.5°, 51.8° and 76.4° are owing to the {111}, {200}, and {220} planes of the cubic phase nickel (JCPDS No. 187-0712), marked as "■".

The morphologies of the samples were investigated through scanning electron microscopy (SEM). The image of NF at low magnification was shown Fig. 2A, indicating that NF possessed a reticular-like morphology. Fig. 2B demonstrated that NF owned a clear surface at high magnification. Fig. 2C showed the SEM image of $Ni(OH)_2$/NF. It was observed that the surface of NF was covered with nanoflakes. In Fig. 2D, Ni_2P nanorods were anomalously anchored on the surface of NF. To our surprise, after high-temperature phosphating, nanoflakes of hydroxides have transformed into nanorods. We suspected that the nanoflakes were cleaved into nanorod-like structure after phosphating at high temperature.

To verify more detailed microstructure information of the as-prepared Ni_2P/NF, the composites were tested through



Scheme 1. Schematic illustration of the fabrication procedure of nanorods Ni_2P/NF.

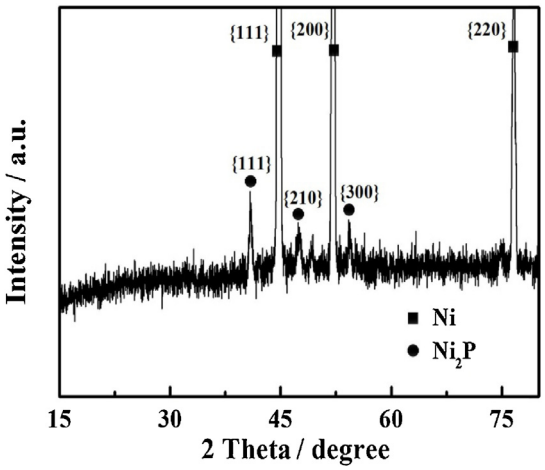


Fig. 1. The XRD pattern of Ni_2P/NF, Ni_2P marked as "●" and Ni marked as "■".