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Facile synthesis of nickel-foam-based nano-architectural composites as binder-free anodes for high capacity Li-ion batteries

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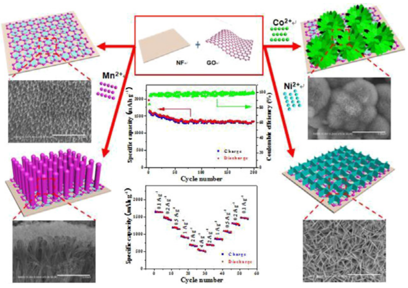
HIGHLIGHTS

- A series of NF-based composites were synthesized *in situ* on nickel foam.
- The composites were directly used as binder-free electrodes for Li-ion batteries.
- The composite electrodes were first designed and fabricated for Li-ion batteries.
- The composite electrodes were prepared by a simple one-step hydrothermal process.
- The NRNN composite electrode exhibited a high reversible capacity.

GRAPHICAL ABSTRACT



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ABSTRACT

A series of nickel foam (NF)-based composites of M_xO_y/RGO/$Ni(OH)_2$ [$M_xO_y = Co_3O_4$, MnO_2, and $Ni(OH)_2$] with diverse multilayer nano-architectures were designed and grown *in situ* on NF through a one-pot hydrothermal process. Based on the redox reaction between the active NF substrate and graphene oxide (GO), along with electrostatic forces between the M^{n+} ions and GO in the solution, strong interactions take place at the interfaces of M_xO_y/RGO, RGO/$Ni(OH)_2$, and $Ni(OH)_2$/Ni, and thus, there is good contact for electron transfer. These M_xO_y/RGO/$Ni(OH)_2$ samples were directly used as conductive-agent- and binder-free anodes for lithium ion batteries (LIBs), and the $Ni(OH)_2$/RGO/$Ni(OH)_2$/NF composite electrode showed a high specific capacity, good rate capability, and excellent cycling stability, especially, it had a high reversible capacity of about 1330 mAh g^{-1} even after 200 cycles at 100 mA g^{-1}. This general strategy presents a promising route for the design and synthesis of various multilayer nano-architectural transition metal oxides (hydroxide)/RGO composites on NF as energy storage materials.

1. Introduction

The development of advanced anode materials with high reversible capacity has drawn intense interest in the field of Li-ion batteries (LIBs) [1–3]. Nanostructured transition metal oxides (TMOs, M: Ni, Co, Fe, Cu, etc.) or the corresponding hydroxides possess a

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significantly high specific capacity based on the multiple electron conversion mechanism, and are considered to be promising anode materials for LIBs [4–6]. Considering their poor intrinsic conductivity, a method for designing and synthesizing nanostructures of electroactive materials on conductive substrates and directly utilizing them as conductive-agent- and binder-free electrodes has been developed [6–10].

Recently, nanostructured $Ni(OH)_2$, directly grown on a three-dimensional porous nickel foam (NF) as binder-free electrode with a high discharge capacity, has been reported, showing its potential for application in LIBs [11,12]. As the electrical conductivity of pure $Ni(OH)_2$ is very low (~10^{-17} S cm^{-1}) [13], however, combining $Ni(OH)_2$ with nano-carbon materials such as graphene will improve the electronic conductivity and thus promote good electrochemical performance, e.g., enhanced discharge capacity and cycling stability [14,15]. Furthermore, a strategy for integrating $Ni(OH)_2$ with another metal oxide (such as Co_3O_4 or MnO_2) has delivered good pseudocapacitor performances due to the synergistic effects of the second metal oxide with $Ni(OH)_2$ in the composites [16,17]. From this point of view, we believed that it was reasonable to directly grow $Ni(OH)_2$/reduced graphene oxide (RGO) or $M_xO_y/Ni(OH)_2$/RGO ($M_xO_y = MnO_2, Co_3O_4, Ni(OH)_2$) composites on NF substrate and use them as electrodes for LIBs, which not only simplifies the electrode preparation process, but also enhances the electrochemical performance. To the best of our knowledge, however, there are still no such reports.

Besides the electrode components, the structure also will play a key role in the electrochemical performance of LIB electrodes. Also, from the viewpoint of synthesis, designing and developing a simple and facile method is necessary as well. In previous work, it was found that graphene oxide (GO) could be reduced and applied as a coating on NF substrate, while the surface Ni at the top of the NF was oxidized *in situ* and transformed into $Ni(OH)_2$ through a hydrothermal process, thus forming a multilayer composite of RGO/$Ni(OH)_2$/NF formed [18]. In addition, positive-charged metal cations (M^{n+}, M: Mn, Co, Ni, etc.) were easily decorated on negative-charged GO sheets due to the electrostatic interaction, where they were converted into M_xO_y/RGO [or $M_x(OH)_y$/RGO] composites [19–21]. These composites indicate that it is possible to anchor M_xO_y [or $M_x(OH)_y$] on the upper surface of the RGO/$Ni(OH)_2$/NF composite by introducing metal cations into the solution during the hydrothermal process. This new route can then be designed and developed to synthesize conductive-agent- and binder-free multilayer M_xO_y [or $M_x(OH)_y$]/RGO/$Ni(OH)_2$/NF composite electrodes for LIBs, which, to the best of our knowledge, have not been previously reported.

Herein, we have prepared a series of NF-based composites in the form of M_xO_y/RGO/$Ni(OH)_2$/NF [$M_xO_y = Co_3O_4$, MnO_2, and $Ni(OH)_2$] with diverse multilayer nano-architectures through a facile and simple hydrothermal process. The nano-architectures of these composites were built up through the redox reactions between the active Ni foam substrate, M^{n+} cations, and GO, in which the upper M_xO_y layer is deposited from M^{n+} and the lower $Ni(OH)_2$ layer is transformed from elemental Ni on the NF. GO plays important roles in controlling the alignment of the M_xO_y nanostructures in the upper layer, as well as connecting the upper M_xO_y and lower $Ni(OH)_2$ layers.

Such a multilayer nano-architectural electrode design has some advantages: (1) the as-prepared composites can be directly used as conductive-agent- and binder-free electrodes for LIBs, rendering the usual conductive agents and binders unnecessary; (2) the synergistic effects of the two metal ions in the composites provide richer redox chemistry than those of the corresponding individual components, which could effectively enhance the specific capacity of the electrode materials; (3) the lower layer of $Ni(OH)_2$ formed *in situ* on the conductive NF substrate with high adhesion, promotes good conductivity, and the upper array of nanostructures can effectively buffer the volume changes induced by the phase transformation of the active materials during charging and discharging.

When directly utilized as electrodes for LIBs, the as-prepared composites delivered high specific capacity, good rate capability, and excellent cycling performance; specifically, the $Ni(OH)_2$/RGO/$Ni(OH)_2$/NF composite electrode had a high reversible capacity of about 1330 mAh g^{-1}, even after 200 cycles at 100 mA g^{-1}. This strategy presents a promising general route for designing and synthesizing multilayer and nano-architectural metal oxide (or hydroxide)/RGO composites on NF as energy storage materials.

2. Experimental section

2.1. Synthesis of NF supported Co_3O_4/RGO/$Ni(OH)_2$, MnO_2/RGO/$Ni(OH)_2$, and $Ni(OH)_2$/RGO/$Ni(OH)_2$ composites

Graphene oxide (GO) was synthesized by a modified Hummers' method [22,23]. The synthesis of composites was carried out through a hydrothermal process, by immersing cleaned Ni foam (NF, Alfa Aesar) in a mixed solution of GO and $M(NO_3)_2 \cdot 6H_2O$ [M = Ni, Co, Mn]. Typically, GO (30 mg) and $M(NO_3)_2 \cdot 6H_2O$ (1 m mol) were added to deionized water (50 ml) and dispersed in an ultrasonication bath for 30 min. The NF (3 × 3 cm^2) substrate was then immersed in this aqueous solution. The substrate and solution were then loaded into a Teflon-lined stainless steel autoclave (100 ml in volume) for hydrothermal reaction at 200 °C for 24 h. The final product was washed with water and ethanol in turn, and then dried in a vacuum oven at 80 °C for 12 h. The Co_3O_4/RGO/$Ni(OH)_2$/NF, MnO_2/RGO/$Ni(OH)_2$/NF, and $Ni(OH)_2$/RGO/$Ni(OH)_2$/NF composite samples were denoted as CRNN, MRNN, and NRNN, respectively. The RGO/$Ni(OH)_2$/NF (RNN) composite was also prepared under identical conditions, except that there was no $M(NO_3)_2 \cdot 6H_2O$ involved.

2.2. Characterization

The crystalline structure of the as-prepared composites was characterized by powder X-ray diffraction (XRD), using an X-ray diffractometer with Cu Kα radiation ($\lambda = 0.15406$ nm). Raman spectra were collected on an INVIA Raman microprobe (Renishaw Instruments, UK) with 514 nm laser excitation. X-ray photoelectron spectroscopy (XPS) was conducted on an ESCALAB 250Xi (Thermo Fisher, U.S.A.) instrument. The morphology and elemental composition of the samples were investigated by field-emission scanning electron microscopy (FESEM, Hitachi S-4800), transmission electron microscopy (TEM, JEOL JEM-2100), and energy dispersive spectroscopy (EDS, Bruker, AXS, Quantax 400–30), respectively.

2.3. Electrochemical measurements

The electrochemical tests were performed via CR2032 coin type cells. All the composite samples were pressed and cut into disks, which were then directly used as working electrodes, with Li foil as the counter and reference electrode, a Celgard 2400 porous polypropylene film as separator, and 1 M $LiPF_6$ in ethylene carbonate-dimethyl carbonate-diethyl carbonate (EC/DMC/DEC, 1:1:1, volume ratio) as the electrolyte. The cells were assembled in an argon-filled glove box. The cells were cycled at different current densities between 0.01 and 3.0 V on a Land CT2001A battery tester. The specific capacity is based on the weight of the composite films supported on NF, which was determined according to the method reported in a previous work [18]. The loading rate of active materials was around 4.5 ± 0.2 mg cm^{-2}. Cyclic voltammetry (CV) measurements were carried out in the voltage range between 0 and 3.0 V at a scan rate of 0.1 mV s^{-1}, and the electrochemical impedance spectroscopy (EIS) measurements were performed by applying an AC voltage with a sinusoidal signal of 5 mV in the frequency range from 0.01 Hz to