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Hierarchically structured mesoporous bimetallic oxides as a potential anode material for rechargeable lithium batteries

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ABSTRACT

Transition metal oxides have been considered as a promising class of electrode materials in electrochemical energy storage devices and possess better capacities than mono-metal oxides. For the development of lithium-ion energy storage systems, the architecture of the electrode material plays a vital role. Herein, we have synthesized one-dimensional (1D) mesoporous $NiCo_2O_4$ hollow nanofibers (HNFs) with the flaky architecture of its surface using the lab waste filter paper as a template during the hydrothermal process. The $NiCo_2O_4$ HNFs show good electrochemical properties such as initial discharge capacity of 1702 mAh g^{-1} with the coulombic efficiency of 82% at a current density of 100 mA g^{-1}, in comparison to $NiCo_2O_4$ nanospheres (NSs) delivering an initial discharge capacity of 1204 mAh g^{-1} with the coulombic efficiency of 74%. The HNFs with interconnected flaky surface provides a large number of lithium storage sites and also shortens the diffusion path for both the lithium ions and electrons and thereby enhancing the performance of Li-ion batteries.

1. Introduction

In lithium ion batteries (LIBs), the need of environmentally friendly electrode materials with high energy densities and long life cycles is very important for the practical application like portable devices, electric vehicles, hybrids, and plug-in hybrids [1–5]. Currently, carbon based materials are using as a negative electrode material for LIBs due to its environment friendliness, low cost, long life cycle, relatively low potential, and non-toxicity [6]. Therefore, the demand for high specific capacity anode materials for LIBs has become an urgent task. Nowadays the researchers focused predominantly on metal oxides. In order to identify new negative electrode materials for LIBs, binary transition metal oxides (BTMOs) are being studied as a possible alternative negative electrode material due to their higher theoretical capacity (<1000 mAh g^{-1}) [7].

The morphologies of the electrode materials used in energy storage devices play a significant role in determining their electrochemical performance [8]. Morphologies, such as nanoflakes, nanobelts, nanofibers, nanospheres, and nanotubes, have been widely studied for application in energy storage devices [5,9–20]. However, very few efforts have been devoted to the synthesis of hollow structures with mesoporous in nature hardly been studied. With regard to the anode materials used in the most attractive energy storage devices (i.e., Li-ion batteries), only a few hollow architectures have been reported. For example, $ZnMn_2O_4$ [21], $MnCo_2O_4$ [22], and Co_3O_4 [23] were synthesized and analyzed as anodes for Li-ion batteries by G. Wang et al., L. Shen et al. [24], and J. Wang et al., respectively. For other applications, metals and metal oxides (e.g., Ga_2O_3, GaN, Cu_2O, Fe_2O_3, CoO, Ni/NiO, etc.) have been synthesized with hollow architectures. In comparison to particles with solid architectures, hollow particles have several benefits in Li-ion batteries. These benefits include a larger surface area that provides excess area for electrode-electrolyte interaction, the hollow space provides excess space to accommodate the enlargement of particles during lithiation and delithiation processes, and the hollow architecture of the material provides additional lithium storage sites. These benefits have a significant positive influence on the electrochemical behavior of Li-ion batteries [25–31].

To date, the synthesis of these beneficial hollow structures with flaky architectures has been a tedious task. The reported metal oxides $NiCo_2O_4$ and Co_3O_4, used in Li-ion batteries, followed two different strategies. The metal oxide Co_3O_4 is synthesized using the

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hard-template method, where carbonaceous microspheres are used as sacrificial templates. Alternatively, the metal oxide $NiCo_2O_4$ was synthesized using the self-template strategy to obtain a hollow, complex architecture [24]. It should be noted that both of these hollow architectures were reported to possess spherical morphologies and were superior to solid architectures made of similar compositions in Li-ion batteries.

Here, we report a more complex architecture of $NiCo_2O_4$ HNFs with flaky surface synthesized using recyclable waste filter paper as a template [32]; this is a comparatively facile process compared to previous approaches. In addition, we also synthesized $NiCo_2O_4$ (NSs) with flaky surfaces, i.e., without using a template. We chose $NiCo_2O_4$ as the active material of our anode due to its promising characteristics, such as its good electronic conductivity, low diffusion resistance to protons/cations, and easy electrolyte penetration, in comparison to other transition metal oxides (e.g., $ZnCo_2O_4$, $CuCo_2O_4$, and $ZnMn_2O_4$) [24]. For transition metal oxides, the electrochemical behavior largely depends on the physical characteristics of the material such as its structure, morphology, size, and surface area [33,34]. Hence, we demonstrated our obtained electrochemical properties (e.g., the capacity, stable cycling behavior, and impedance) by analyzing the structural properties using X-ray diffractometry (XRD). We also studied the morphology using field emission scanning electron microscopy (FE-SEM) and high resolution transmission electron microscopy (HR-TEM). The pore size and surface area were investigated using Brunauer-Emmett-Teller (BET) analysis.

2. Experimental section

2.1. Materials synthesis

All of the chemicals used were of analytical grade and used without any further purification. The waste filter papers collected from the laboratory were cut into a small pieces and washed several times with ethanol and de-ionized (DI) water to remove the dust particles. In a typical preparation process of the porous $NiCo_2O_4$ HNFs, 1 mM of Ni $(NO_3)_2 \cdot 6H_2O$ and 2 mM of Co $(NO_3)_2 \cdot 6H_2O$ were dissolved in 60 ml of DI water at room temperature while stirring. This was followed by the addition of 0.516 g of glycine and stirring for 30 more min. The dried pieces of filter paper were immersed into the above prepared precursor solution and stirred for 30 min at 80 °C. The prepared mixture was then transferred into a 100 ml Teflon-lined stainless steel autoclave and maintained at 180 °C for 8 h. After cooling to room temperature, the product was collected by centrifugation and washed several times with deionized water and ethanol. The washed products were dried in a vacuum oven at 60 °C for 12 h. Finally, the dried products were calcined at 500 °C for 3 h under air to produce the porous $NiCo_2O_4$ HNFs material. As a comparison, bulk $NiCo_2O_4$ NSs were obtained in the same way, but without the addition of filter paper.

2.2. Material characterization techniques

X-ray diffractometry (XRD) was used to study the crystal structure and phase purity of the obtained samples (XRD, M18XHF-SRA, Mac Science Ltd.) with Cu Kα radiation ($\lambda = 0.15406$ nm). The morphological features of the as-prepared samples were examined using a field emission scanning electron microscope (FE-SEM, Carl Zeiss, LEO SUPRA 55). A high-resolution transmission electron microscope (HR-TEM, JEOL JEM-2010), equipped with energy dispersive X-ray spectroscopy (EDS) was used to measure the internal microstructure, crystallographic intrinsic properties and elemental analysis of the as-prepared materials. X-ray photoelectron spectroscopy (XPS, MultiLab2000, Thermo VG Scientific System) was used to study the surface analysis of the as-prepared samples with a monochromatic Al X-ray source (Al-Kα line: 1486.6 eV). The porosity of the prepared samples was determined by N_2 adsorption-desorption in BET measurements using an ASAP-2010 surface area analyzer.

2.3. Electrochemical analysis

The working electrode was prepared by mixing 80 wt% active material, 10 wt% carbon black (Super P) as a conductive additive, and 10 wt% polyvinylidene difluoride (PVDF) as a binder in N-methyl-2-pyrrolidone (NMP) to make a viscous slurry. The well-mixed slurry was then coated onto a Cu foil and dried at 120 °C under vacuum for 10 h in order to vaporize the NMP solvent. The dried sheet was punched into electrode disks with a diameter of 14 mm. The loading mass of active material was calculated by subtracting the mass of copper foil measured before and after the coating of slurry. The average mass of active material for all the electrodes were ~1.2 mg CR2032-type coin cells were assembled in an argon-filled glovebox, in which both the oxygen and water contents were less than 1 ppm. A solution of 1 M $LiPF_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 by volume) was used as the electrolyte. Lithium foil and Celgard membrane acted as the counter/reference electrode and separator, respectively. The galvanostatic charge and discharge of the fabricated coin cells were determined with an electrochemical cycler (Arbin Instruments) over the potential range of 0.01–3.0 V at a constant current-constant voltage (CC-CV) with a current density between 100 mA g^{-1} and 1600 mA g^{-1}. Both cyclic voltammetry (CV) and electrochemical impedance spectrometry (EIS) measurements were conducted using an electrochemical analyzer (Iviumstat, Ivium Technologies) between 0.01 and 3.0 V at a scan rate of 0.1 mV s^{-1} and over a frequency range of 1 mHz–100 kHz with an amplitude of 10 mV.

3. Results and discussion

The schematic diagram shown in Fig. 1 illustrates the step-by-step process followed for the fabrication of $NiCo_2O_4$ HNFs. In a typical synthesis, waste cellulose fiber was used as a template/substrate for the growth of $NiCo_2O_4$ by a facile and simple hydrothermal method. XRD analysis was carried out to reveal the phase purity and the crystalline structure of the $NiCo_2O_4$ HNFs and NSs. Fig. 2(a and b), shows the XRD patterns of the hydrothermally-synthesized porous $NiCo_2O_4$ NSs and HNFs. For both mesoporous $NiCo_2O_4$ HNFs and NSs, diffraction peaks are observed at the 2θ values of (18.88), (31.32), (37.12), (43.35), (59.45), (63.936), (75.25), and (79.46). These can be indexed to the (111), (220), (222), (440), (511), (400), (620), and (622) crystal planes, respectively, and ascribed to the cubic crystal system of $NiCo_2O_4$. This material has a well-defined spinel crystalline structure [space group Fd-3m (227), JCPDS card no. 20-0781] [9,13]. There are no impurity peaks observed in the $NiCo_2O_4$ HNFs and NSs, thereby confirming the purity of the prepared samples. In the XRD pattern, the peaks observed for the porous $NiCo_2O_4$ HNFs are comparatively broader than the $NiCo_2O_4$ NSs, which confirms that the porous $NiCo_2O_4$ HNFs crystals are smaller and/or less crystalline than the $NiCo_2O_4$ NSs.

The morphologies of the as-synthesized $NiCo_2O_4$ HNFs and NSs were examined using FE-SEM. Fig. 2c-f, shows the uniform distribution of the $NiCo_2O_4$ HNFs and NSs in low- and high-magnification FE-SEM images. HNFs and NSs are formed via the assembly of nanoflakes. The formation of nanoflakes is influenced by the concentration of precursor, the presence of glycine during the hydrothermal process (which generates excess OH^- ions in the