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Graphene Supported Ni-based Nanocomposites as Electrode Materials with High Capacitance

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ABSTRACT

The Ni-based/graphene materials were synthesized by a simple hydrothermal method, using the graphene oxide as the support precursor. The textural and structural properties of the as-prepared Ni-based/graphene samples were fully characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, thermalgravimetric analysis and Fourier transform infrared spectroscopy, respectively. Electrochemical properties were examined by cyclic voltammetry, electrochemical impedance spectroscopy and cyclic charge-discharge tests. The results showed that the 15%-β-$Ni(OH)_2$/graphene had the high specific capacity of 2077 F g^{-1} at 5 mV s^{-1} in the range of 0.0–0.7 V (vs. Ag/AgCl) and had a good cycle life with 965 F g^{-1} after 500 cycles at 50 mV s^{-1}.

1. Introduction

With the consumption of fossil fuels and environment changes, it is urgent to find new energy and efficient energy storage devices. Electrochemical supercapacitors (ESs) are regarded as promising candidates for energy storage due to fast charge time, long cycle life, and high power density [1,2]. Based on the charge conversion/storage mechanism, ESs can be classified as electrical double-layer capacitors (EDLCs) and the redox electrochemical capacitors (pseudocapacitors). The electrical charge of EDLCs based on carbon materials is stored at the electrode/electrolyte interface, while the metal oxides/hydroxides and conducting polymers have the nature properties of the pseudocapacitors by utilizing the capacitance trimming from reversible faradaic reaction occurring at the electrode surface [3,4].

Great efforts have been made to study the materials based on the carbons and metal oxides/hydroxides for ESs. Carbon materials such as activated carbon [5], carbon aerogels [6], porous carbons [7,8], and carbon nanotubes (CNTs) [9] are usually utilized as electrode materials in supercapacitors due to their excellent conductivity, high surface area and stable chemical property, but the small double layer capacitance limits its application. For pseudocapacitors, the transition metal oxides/hydroxides have relatively higher capacitance and faster redox kinetics than EDLCs, while a relative lower capacitance stability and a shorter cycle life are major limitations of ESs. To utilize the good electrochemical properties of both carbon materials and metal oxides/hydroxides, one possible route is to integrate these two kinds of materials into the electrodes for ESs.

Recently, graphene, consisting of a single layer of carbon atoms in a two-dimensional (2D) lattice, has been emerging as a fascinating material with its large surface, high electron mobility, and chemical stability [10]. Therefore, the graphene materials used in various electrical devices, such as electromechanical resonators [11], dye-sensitized solar cells [12], and supercapacitors [13] are in prospect. Compared with costly and toxic Ru [14], the inexpensive and eco-friendly nickel metal [15], oxides [16] and hydroxides [17] as the pseudocapacitors electrode materials with good capacitive characteristic for ESs have been widely studied. However, the nickel oxides/hydroxides have poor electrical conductivity, which results in a decreased capacitive performance after long cycle and slow electron transport at high electrical rates, limiting its practical applications [18,19]. To resolve the issue, we can incorporate graphene into the nickel compounds to maximize the electrochemical properties of the pseudocapacitive material.

In this work, we proposed an application of the graphene as support for Ni-based materials in supercapacitors. The graphene oxide (GO) was employed as a precursor for preparation of the electrode materials. The plenty of the oxygen-containing functional groups (carboxyl, hydroxyl, carbonyl and epoxy group) on

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GO sheets can provide a large amount of uniform anchor sites for the nickel species [20]. The textural and structural properties of the as-prepared Ni-based/graphene electrode materials were characterized. The effect of the graphene support, Ni loading, the cyclic voltammetric window and the Ni phase of the Ni-based/graphene for supercapacitors were investigated. As a result, the 15%-β-Ni$(OH)_2$/graphene showed a high specific capacity of 2077 F g^{-1} at 5 mV s^{-1} in the range of 0.0–0.7 V(vs. Ag/AgCl) and had a good cycle life.

2. Experimental

2.1. Synthesis of materials

2.1.1. preparation of GO

GO was produced by natural graphite according to a solvothermal synthesis method [21]. All chemicals in our experimental were of analytical grade and used without any further purification. Graphite powder (1 g) was stirred in 23 mL of H_2SO_4 solution (98 wt%) at 0 °C for 1 h. Then, $KMnO_4$ (5 g) was gradually added into the above-mentioned solution in two hours under vigorous magnetic agitation. Continuing vigorous stirring for 3 hours at room temperature, the final suspension was transferred to a 50 mL of Teflon-lined autoclave and heated in an oven at 70 °C for 15 h, and then cooled down to room temperature naturally. 20 mL of H_2O_2 (30 wt%) was added into the mixture to remove the residual $KMnO_4$. After the H_2O_2 adding into the mixture, it released a large amount of bubbles and the color of the mixture changed into brilliant yellow. Then, the mixture was filtered and washed with 50 mL 5 wt% HCl aqueous solution to remove the metal ions and then deionized water was used to remove the acid. Finally, the dark brown solution of GO with ca. 6.2 mg mL^{-1} was obtained.

2.1.2. synthesis of electrode materials

200 mL of GO was sonicated for 30 min to exfoliate the GO sheets. Then, a certain amount of $Ni(NO_3)_2 \cdot 6H_2O$ solution (10 mL) was added gradually and was sonicated further for 30 min to produce uniform dispersion. $NH_3 \cdot H_2O$ (25 wt%) was added drop by drop into the solution which resulted in a brownish-black suspension with a pH value of 10. 1 mL of hydrazine was added after stirred the suspension for 30 minutes. The mixture was then transferred to a Teflon-lined autoclave (50 mL of Volume) and heated for 12 h at 180 °C. Then the as-synthesized black product was isolated by filtration, washed for several times with distilled water and 95% of ethanol, and finally dried in a vacuum oven at 70 °C for 24 h to get the β-Ni$(OH)_2$/graphene solid powder, named as x%-β-Ni$(OH)_2$/graphene, where x is the mass rate of Ni metal. The obtained x%-β-Ni$(OH)_2$/graphene materials were calcined in a tube resistance furnace at 300 °C and 500 °C for 2 h to get the x %-NiO/graphene and x%-Ni/graphene with a heating rate of 2 °Cmin^{-1} and with a nitrogen flow rate of 20 mL min^{-1}. As a comparison, the β-Ni$(OH)_2$ was obtained in the same conditions without adding graphene and graphene materials were prepared in the absence of the nickel precursors.

2.2. Characterization of materials

Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer with Cu-Kα radiation (λ≈0.154 nm) at 40 kV and 40 mA in a scanning range of 10–80° (2θ). The morphologies of as-obtained products were observed by scanning electron microscopy (SEM, JSM-6490LV) with the sample dispersed on the Al pan. The images of Transmission electron microscopy (TEM) was taken on a FEI Tecnai G20 microscope, operating at 200 kV. The thermogravimetric analysis (TGA) was performed on a TA SDT Q600 instrument from room temperature to 800 °C with a heating rate of 10 °C min^{-1} in air and with α-Al_2O_3 as the reference. Fourier transform infrared spectroscopy (FT-IR) of electrode materials were recorded by Bruker Vector 22 infrared spectroscopy in the range of 400 to 4000 cm^{-1} by using the KBr pellet technique.

2.3. Electrochemical tests

The working electrodes for electrochemical capacitors were prepared by the following processes. 0.25 g of as-prepared material was mixed with acetylene black and polytetrafluoroethylene (PTFE), and their mass ratio was 75:20:5. The above slurry was made using ethanol as a solvent and coated onto nickel foam. After dried at 70 °C for 12 h, the coated nickel foam was pressed under the pressure of 10 MPa for 10 min as the electrode material.

The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) of electrodes were performed on a IM6 & ZENNIUM electrochemical workstation in three-electrode system. The working electrode (2cm × 2 cm) with the active-material mass around 50 mg was tested in 6 M KOH solution using Ag/AgCl as a reference electrode and a platinum wire as counter electrode. The pure graphene electrode was prepared as the same method mentioned above with the active-material mass of ca. 64 mg. The CV tests were at the scans rate value of 5, 10, 20, 50 and 100 mV s^{-1}, respectively. EIS measurements were recorded in a frequency range of 100 k to 1 m Hz with AC oscillation of 5 mV. The cycle charge-discharge was performed on the Land-CT2001A (100 mA) cell in a symmetric two-electrode system with the cell potential ranges from 0.0 to 1.0 V for 1000 cycle. The button shaped electrode has a diameter about 2 cm with the active-material mass around 18 mg.

3. Results and Discussion

3.1. Characterization of materials

The phase structure and purity of the as-prepared samples were examined by XRD as represented in Fig. 1. The discernible diffraction peaks at 2θ = 19.2°, 33.2°, 38.5°, 52.2°, 59.3°, 62.8°, 69.6° and 72.9° are matched to the standard data card JCPDS 14-0117, which is β-Ni$(OH)_2$ with a hexagonal crystalline structure. The typical peak of GO is disappear after the hydrothermal treatment, suggesting the GO are reduced to graphene [22]. With the loading of β-Ni$(OH)_2$ increased, the intensity of the diffraction peaks becomes slightly strong. Calcinations at 300 °C lead to the phase transition of β-Ni$(OH)_2$ to NiO. As observed, the peaks of

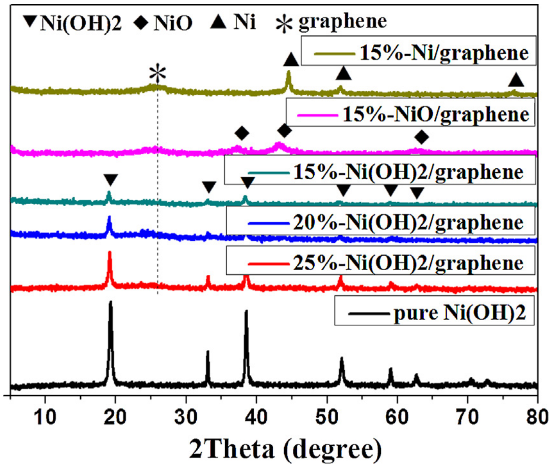

Fig. 1. XRD patterns of all prepared materials.