Journal of Alloys and Compounds 635 (2015) 225–232

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Enhanced performance of nickel–aluminum layered double hydroxide nanosheets/carbon nanotubes composite for supercapacitor and asymmetric capacitor

Min Li [a], Fu Liu [a], J.P. Cheng [a,*], J. Ying [b], X.B. Zhang [a]

[a] State Key Laboratory of Silicon Materials, Department of Materials Science and Engineering, Key Laboratory of Advanced Materials and Applications for Batteries of Zhejiang Province, Zhejiang University, Hangzhou 310027, China
[b] Department of Mechanical Engineering, Zhejiang University, Hangzhou 310027, China

ARTICLE INFO

Article history:
Received 23 January 2015
Received in revised form 13 February 2015
Accepted 16 February 2015
Available online 23 February 2015

Keywords:
Nickel aluminum-layered double hydroxide
Carbon nanotubes
Supercapacitors
Electrochemical performance

ABSTRACT

Binary composite consisting of nickel aluminum-layered double hydroxides (LDHs) nanosheets and carbon nanotubes (CNTs) is fabricated by a solution method. The CNTs are pre-coated by γ-Al_2O_3. The structural characterization and morphological observation demonstrate that Ni–Al hydroxide crystals with hydrotalcite structure are *in situ* deposited on the surface of CNTs. The as-prepared binary composite combines the pseudo-capacitive of Ni–Al LDHs with double-layer capacitive of carbon nanotubes. CNTs can improve the electrical conductivity and decrease the electrochemical polarization of the composite. Electrochemical measurements of the Ni–Al LDHs/CNTs material show a much better electrochemical performance than pure Ni–Al LDHs. It can yield a high specific capacitance of 1500 F g^{-1} at 1 A g^{-1}, with 70.3% retention at 10 A g^{-1} in 2 M KOH and a good cycling stability. An asymmetric capacitor is assembled with Ni–Al LDHs/CNTs as a positive electrode and activated carbon as the negative electrode. It can cycle reversibly in a potential window of 1.8 V, and exhibits a high specific capacitance of 115 F g^{-1} and a high energy density of 52 W h kg^{-1} at 1 A g^{-1} as well as an excellent cycling stability.

1. Introduction

Electrochemical capacitors, or supercapacitors, are a new kind of energy storage device with high power density and long cycle life. Electrical double-layer capacitors (EDLCs) are using carbon materials (activated carbon, carbon nanotubes, graphene, *etc.*) as electrode materials. Their capacitance arises from charges stored in the electrode/electrolyte interfaces, which makes their capacities limited by the specific surface area of the electrode materials [1–4]. Pseudocapacitors (PCs) with metal oxides/hydroxides [5–14] or conductive polymers [15,16] as the electrode materials can conduct fast surface redox reactions. Their high specific capacitance and fast redox kinetics make them intensively investigated, but they usually have a low conductivity and poor cycle life due to the limited velocity of ion diffusion and electron transfer compared with EDLCs. An efficient solution is to combine highly conductive carbon with pseudo-capacitive materials to form a synergy effect [17–23].

Recently, Ni–Al layered double hydroxides (LDHs) with hydrotalcite-like structure have shown outstanding performances in electrochemical field with their high specific capacitance, low cost and environmental benignity [24–26]. A lot of efforts have been devoted to improve their lifecycle and rate capability. Some work declared that incorporating Ni–Al LDHs with highly conductive carbon materials could greatly improve the rate stability and cycle life. For example, Liu *in situ* grew Ni–Al LDHs on carbon nanoparticles, which displayed excellent pseudo-capacitive behavior and cycling stability in an asymmetric supercapacitor [27]. F. He and his colleagues used an *in situ* method to fabricate Ni–Al LDHs nanosheets on hollow carbon nanofibers and the composite had a specific capacitance of 1613 F g^{-1} and a capacitance retention of 83.4% after 1000 cycles [28]. Yang et al. applied precipitation method to synthesize ternary Ni–Al LDHs/CNTs/GNS composites which exhibited excellent electrochemical stability, only 3.5% deterioration of the initial available capacitance after 1000 cycles [29]. Yang synthesized NiCoAl LDHs/CNTs composites with a specific capacitance of 1035 F g^{-1} and good cycling stability [30]. Our previously synthesized Ni–Al LDHs/rGO composites gained a specific capacitance of 1630 F g^{-1} and good cycling performance [25]. Lei' group reported a Ni–Al LDHs/MWCNT/NF electrode prepared by a facile three-step

---

* Corresponding author. Tel./fax: +86 571 87951411.
E-mail address: chengjp@zju.edu.cn (J.P. Cheng).

http://dx.doi.org/10.1016/j.jallcom.2015.02.130
0925-8388/

fabrication method with a specific capacitance of 1293 F g^{-1} [31]. Above literatures imply that the synergy effect between carbon materials and Ni–Al LDHs has taken advantages of them both. However, there are few reports on the fabrication of Ni–Al LDHs/CNTs composites. So, we will fabricate Ni–Al LDHs/CNTs composite as electrode material of supercapacitor in this contribution. Duan's [32,33] and Yang's groups [34–36] reported a simple way to *in situ* grow Ni–Al LDHs on carbon materials by a mediate process of depositing AlOOH on the carbon base. But Li et al. made a comparison between γ-Al_2O_3 and AlOOH as the Al source to fabricate LDHs [37]. They found that it was easier to form LDHs precipitates on γ-Al_2O_3 than on AlOOH because of their different surface dissolution constants (γ-Al_2O_3 > AlOOH). So we will use γ-Al_2O_3-coated CNTs as a support to grow Ni–Al LDHs. The small Ni–Al LDHs nanosheets can directly grow on the surface of CNTs to form a three-dimensional structure. These elongated CNTs can facilitate the fast electron transfer and decrease electrochemical polarization of electrode material. It also shows a promising property as a positive electrode of asymmetric capacitor.

2. Experimental

2.1. Pre-treatment of CNTs

The pristine CNTs were treated with nitric acid by refluxing in a round-bottom flask at 120 °C for 6 h. Then the modified CNTs were filtered and washed with water until pH = 7 [38]. Finally, the collected powder was dried at 70 °C for 12 h. As a result, a number of negatively charged oxygen-containing functional groups were introduced onto the surface of CNTs.

2.2. Synthesis of Ni–Al LDHs/CNTs composite

Firstly, boehmite primer (AlOOH) sol as the precursor of γ-Al_2O_3 was prepared by hydrolysis process. 1.02 g aluminum isopropoxide was added into 200 mL water, followed by heating for 3 h at 90 °C. After that, 1 mL 5% HNO_3 solution was added into the above solution to reflux for 4 more hours to obtain hydrolyzate (boehmite primer sol). Then 50 mL CNTs suspension containing 200 mg CNTs dispersed by ultrasonication was mixed with AlOOH sol to form an AlOOH shell on CNTs. Subsequently, the mixture was refluxed at 100 °C for 6 h followed by filtration, and then washed thoroughly with water and ethanol for several times. After being dried at 70 °C in vacuum, AlOOH/CNTs composite was obtained. Annealing treatment transformed the AlOOH/CNTs into Al_2O_3/CNTs in a tube furnace at 700 °C for 1 h in N_2.

Preparation of Ni–Al LDHs/CNTs composite was carried out through a solution method. Above fabricated CNTs–Al_2O_3 core–shell composite was directly used as a substrate for the following growth of Ni–Al LDHs. 0.2 g Al_2O_3/CNTs powder was dispersed in 150 mL water for 1 h by sonication to form a suspension. Then 1.5 g $Ni(NO_3)_2 \cdot 6H_2O$ and 50 mL 6% NH_4NO_3 solution were added into above suspension. Aqueous ammonia solution (1%) was added dropwisely into the reaction solution until pH = 7. Then the mixture was heated and refluxed at 100 °C for 2 h in a microwave reactor. Finally, the resulting Ni–Al LDHs/CNTs composite was separated by filtration, rinsed with water and dried at 70 °C. Scheme 1 shows the fabrication process of the composite. Pure Ni–Al LDHs composite as a control sample was also synthesized by a microwave-assisted reflux method as our previous report [25].

2.3. Characterization

The phase structure and morphology of the samples were characterized by powder X-ray diffractometer (XRD, Shimadzu, LabX XRD-6000) with a secondary graphite monochromator, scanning electron microscope (SEM, Hitachi S-4800), and transmission electron microscope (TEM, JEM-2100). Fourier transformed infrared spectroscopy (FT-IR, Bruker spectrometer, Tensor 27) was obtained by dispersing the sample in KBr and pressing it into transparent pellets. X-ray photoelectron spectroscopy (XPS, Thermo, Escalab 250Xi) was also measured to evaluate the chemical composition. The specific surface area was determined with a Tri-Star II 3020 (Micromeritics Instrument Corporation) analyzer by Brunauer–Emmett–Teller (BET) method. Thermogravimetric (TG) measurement was carried out using a SDT Q600 instrument in a temperature range of 25–800 °C with a heating rate of 10 °C min^{-1} in air.

2.4. Electrochemical measurements

The electrode was prepared by mixing electrode material, acetylene black, polyvinylidene fluoride (PVDF) in a mass ratio of 8:1.5:0.5 and pasting the mixture onto a 1.5 cm × 1.5 cm Ni foam. A series of electrochemical measurements were carried out under a three-electrode system using 2 M KOH aqueous solution as electrolyte. The Ni foam loaded with active material, Ni plate and Ag/AgCl electrode were used as working electrode, counter electrode and reference electrode, respectively. Both the positive and the negative electrodes were pressed individually and assembled into an asymmetric supercapacitor. The asymmetric supercapacitor was fabricated using a Ni–Al LDHs/CNTs composite positive electrode and an activated carbon (AC)-based negative electrode. Cyclic voltammograms (CV), galvanostatic charge–discharge curves and electrochemical impedance spectroscopy (EIS) were measured by a CHI660D electrochemical workstation. The cycle life was conducted on a LAND CT2001A test system by galvanostatic charge–discharge techniques. The specific capacitance (Cs) can be calculated from CV curves according to the following equation:

$$Cs = \int I\,dU/(\upsilon \times m \times \Delta U) \tag{1}$$

or from the discharge curves according to the equation:

$$Cs = I \times t/(\Delta U \times m) \tag{2}$$

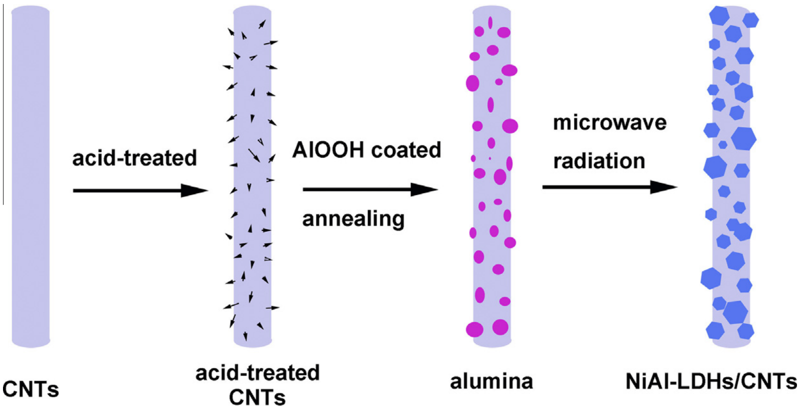
The energy density (E) of ECs can be calculated from Cs according to the following equations:

$$E = 1/2Cs\Delta U^2 \tag{3}$$

where I is the current (A), U is the potential (V vs. Ag/AgCl), ΔU is the voltage difference (V), υ is the potential scan rate (V s^{-1}), m is the mass of total electro-active material of electrodes including positive electrode and negative electrode (g), and t is the discharge time (s).

3. Results and discussion

Fig. 1 shows the XRD patterns of (a) acid-treated CNTs, (b) AlOOH/CNTs, (c) Al_2O_3/CNTs, and (d) Ni–Al LDHs/CNTs composites. As shown in curve *a*, the diffraction pattern of CNTs has a strong peak at 26.1° of (002) planes, featuring a basal spacing of 0.34 nm and a good crystallization. In pattern *b*, all characteristic peaks of CNTs and boehmite (AlOOH, JCPDS NO. 21-1307) can be



Scheme 1. Illustration of the preparation process for Ni–Al LDHs/CNTs composite.