Journal of Alloys and Compounds 745 (2018) 135–146

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

One-step combustion synthesis of porous CNTs/C/$NiMoO_4$ composites for high-performance asymmetric supercapacitors

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ARTICLE INFO

Article history:
Received 10 September 2017
Received in revised form
17 January 2018
Accepted 13 February 2018

Keywords:
Solution combustion
CNTs/C/$NiMoO_4$
Electrochemical properties
Asymmetric supercapacitor
Energy density

ABSTRACT

A facile and cost-effective one-time solution combustion method is designed for the synthetic of CNTs/C/$NiMoO_4$ and C/$NiMoO_4$ porous composites at 300 °C for 0.5 h in the atmosphere. The characteristics of products are investigated by advanced physical property test and electrochemical analysis. The results reveal that the electrochemical performances of C/$NiMoO_4$ composites are strongly influenced by the molar ratio of oxidizer to fuel and the largest specific capacitance of the optimized sample reaches 859 F g^{-1} at 1 A g^{-1}. Moreover, the capacitance of CNTs/C/$NiMoO_4$ composites has been further enhanced to 1037 F g^{-1} at 1 A g^{-1}, in which added acid-treated CNTs into the precursor mixed solution in the combustion process. Furthermore, an asymmetric supercapacitor CNTs/C/$NiMoO_4$||activated carbon (AC) is assembled, which the CNTs/C/$NiMoO_4$ used as cathode and AC used as anode. Its energy density of 32.6 Wh kg^{-1} at power density of 150.5 W kg^{-1} and even retains 18.2 Wh kg^{-1} at 8509 W kg^{-1}. This asymmetric device exhibits a well cycle stability, which the capacitance retain 96.5% after 1500 cycles. The excellent electrochemical behaviors indicate that CNTs/C/$NiMoO_4$ composites have great potential for application in high capacity energy storage devices.

1. Introduction

With gradual attention to globally environmental issues, the new clean energies and efficient energy storage systems have been established the urgent demand. Supercapacitors (SCs) and Lithium-ion batteries, have been receiving much more attention owing to their influential role in the modern society [1–3]. Compared with Lithium-ion batteries, SCs exhibit distinguished properties of high power density, fast charge/discharge abilities, long cycle life, and environmental friendliness. In the foreseeable future, SCs are one of the most potential energy storage devices [4–6]. SCs are extensive energy storage options and usually classified into electric double layer capacitors (EDLCs) and pseudocapacitors [7–9]. Currently, the electrode materials are mainly carbon-based materials, transition metal oxide, binary transition metal oxide, hydroxide and conducting polymers. The pseudocapacitor is based on the faraday reactions between the electrolyte and surface of the electro-active material, and its energy density is several times larger than EDLCs of carbon-based materials [9]. Therefore, considerable efforts were focused on the pseudocapacitor due to the higher energy density. Now, many less expensive and less toxic transition metal oxides, like Mn_2O_3, NiO, Co_3O_4, MoO, V_2O_5, La_2O_3, Cr_2O_3, have been explored as electrode materials to improve the electrochemical properties [9–17]. Meanwhile, binary transition metal oxides, such as $NiCo_2O_4$, $MnCo_2O_4$, $NiMoO_4$, $MnMoO_4$, have been studied extensively as pseudocapacitor electrode materials owing to its high electrical conductivity, high stability and low cost [1,18–20].

It is reported that binary transition metal oxides include two different metal cations exhibit superior capacitive performance than that of single transition metal oxides. Binary transition metal oxides would show the better electrochemical activities due to their complex chemical composition and the synergic effects of different metal elements [19,21]. Among the metal oxides, metal molybdates, especially $NiMoO_4$, has been extensively studied because of their extraordinary electrochemical performance, which benefits from the high electro-active of the nickel ions. It is also reported that the $NiMoO_4$ exhibited much higher electrical conductivity than that of the single-component metal oxide NiO. Recently, ultrathin mesoporous $NiMoO_4$ nanosheets have been synthesized through a simple hydrothermal method, which exhibited a high specific capacity and outstanding rate capability.

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https://doi.org/10.1016/j.jallcom.2018.02.172
0925-8388/

Ghosh et al. obtained a specific capacitance of 367 F g^{-1} at 5 A g^{-1} for the Gr-$NiMoO_4 \cdot H_2O$ composite [22]. Moreover, rationally designed hybrid electrodes with unique chemical composition are proved to possess prominent electrochemical reaction, thus this material can be used as novel electrode materials. Therefore, the metal molybdates are mainly regard as hybrid electrodes material to prepare hybrid capacitors in recent works. For example, Liu et al. reported the $CoMoO_4$-$NiMoO_4 \cdot xH_2O$ bundles, which combine the advantages of $CoMoO_4$ and $NiMoO_4 \cdot xH_2O$, showing excellent electrochemical behavior [23]. The nano-sized β-$NiMoO_4$-$CoMoO_4 \cdot xH_2O$ composites with the weight ratio of 3:1 (Ni:Co) were synthesized and exhibited a maximum specific capacitance of 1472 F g^{-1} at a current density of 5 mA cm^{-2} [24]. Cai et al. reported the unique three-dimensional Co_3O_4@$NiMoO_4$ core/shell nanowires, which exhibited a greatly capacitance of 5.69 F cm^{-2} at the current density of 30 mA cm^{-2} [25].

Conducting carbon materials, such as carbon black, CNTs, and graphene, are the most important electrode materials for EDLCs due to their porous structures, electrical conductivity and well chemical stability [22,26–28]. Nowadays, some researchers reported the hybrid composite material to overcome the drawbacks of single nanoelectrode material, which possess the advantages of both carbon based EDLC and pseudocapacitors [26,29]. Liu et al. have reported the $NiMoO_4$-rGO composites through a microwave-solvothermal method and its specific capacitance reached 1274 F g^{-1} at a current density of 1 A g^{-1}, which is larger than that of pure $NiMoO_4$ [30]. Wei et al. demonstrated that hierarchical C@$NiMoO_4$ electrode materials had a specific capacitance of 268.8 F g^{-1} at 1 A g^{-1} and 88.4% of the initial capacitance was retained after 2000 cycles [31]. Conducting carbon materials in the hybrid electrode materials can offer high porosity and enhance electrical conductivity for electrodes. Hence, rationally designed hybrid electrodes which contain binary transition metal oxides and carbon materials would exhibit high electrochemical performance. However, most of reports about the synthesis of rationally designed hybrid composites are either time-consuming or very tedious, which include multistep process, and sometimes the compound process need the aid of template. In this work, we use a simple, less-timing, and eco-friendly solution combustion method for large scale synthesis of CNTs/C/$NiMoO_4$ nanocomposite. In the composite, *in-situ* formed carbon during the combustion process would increase the electrons transfer efficiency of the active material. Moreover, in order to further increase the electrical conductivity, chemical stability and the electrochemical performance, the appropriate amount of acid-treated CNTs were added before the combustion process. Electrochemical measurements indicated that CNTs/C/$NiMoO_4$ composites show high specific capacitance and attractive rate capability compared with bare C/$NiMoO_4$. The specific capacitance is 1037 F g^{-1} at current densities of 1 A g^{-1}. In addition, CNTs/C/$NiMoO_4$||AC asymmetric supercapacitor (ASC) with a potential of 1.5 V has been fabricated, delivering both high energy density of 32.6 Wh kg^{-1} at a power density of 150.5 W kg^{-1} and power density of 8509 W kg^{-1} at 18.2 Wh kg^{-1}.

2. Experimental

2.1. Synthesis of the C/NiMoO4 composites

All the reagents were analytical grade with no further purification in the experimentation. In the synthesis processes, nickel nitrate hydrate ($Ni(NO_3)_2 \cdot 6H_2O$) and ammonium molybdate ($(NH_4)_6MoO_{24} \cdot 4H_2O$) were used as oxidizer, citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$) was used as fuel, respectively. Assumption that the gaseous products are CO_2, N_2 and H_2O, the reaction formula in the combustion reaction can be possibly conducted as below:

$$7Ni(NO_3)_2 + (NH_4)_6Mo_7O_{24} + \phi C_6H_8O_7 + \left(\left(\frac{9}{2}\right)\phi - 13\right)O_2 \rightarrow 7NiMoO_4 + 6\phi CO_2\uparrow + 10N_2\uparrow + (12\phi + 4)H_2O\uparrow \tag{1}$$

According to equation (1), φ = 26/9 means that the initial reaction process could smoothly finish without oxygen. However, the products of the reaction can be influenced by the amount of citric acid (fuel). For studying the influence of the fuel consumption on the samples microstructure and electrochemical property in the precursor mixed solution, the values of φ were adjusted to be 6.5/9, 13/9, 26/9, 39/9 and 52/9 (corresponding products are denoted as Sample I-V, respectively, as shown in Table 1). During the typical course of the experiment, 7 mmol $Ni(NO_3)_2 \cdot 6H_2O$, 1 mmol $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and a certain amount of $C_6H_8O_7 \cdot H_2O$ were dissolved in 20 ml deionized water of a heat-proof glass beaker. With 0.5 h magnetic stirring, the precursor solution was placed in a preheated muffle furnace at 300 °C for 0.5 h in the atmosphere. Initially, the mixed solution was boiled and underwent dehydration after a few seconds at 300 °C. Then, the viscous liquids swelled and autoignited followed by decomposition with the rapid release of a large amount of gases. Finally, the powders were collected in indoor temperature. The ingredients of precursor solutions have been displayed in Table 1.

2.2. Synthesis of the CNTs/C/NiMoO4 composites

The CNTs/C/$NiMoO_4$ composites were obtained by adding an appreciable quantity of acid-treated CNTs (25 mg, 50 mg, and 100 mg denoted as 25-CNTs/C/$NiMoO_4$, 50-CNTs/C/$NiMoO_4$ and 100-CNTs/C/$NiMoO_4$, respectively, as shown in Table 1) into the optimized fuel-to-oxidant ratio precursor solution (Sample II) via an ultrasound for 20 min. Then, putting the fully mixed solution into muffle furnace remains at 300 °C for 30 min in the atmosphere. The other experimental conditions are as same as the samples I-V. The acid-treated CNTs were obtained by refluxing in 10 wt % nitric acid for 10 h. Subsequently, it were dried in an oven at 60 °C overnight after washing with deionized water by filtration.

2.3. Material characterization

The crystalline structure were characterized by Powder X-ray diffraction (XRD) on Bruker D8 Advance diffractometer with Cu Kα radiation (λ = 1.5417 Å) in the 2 theta range between 20° and 80°, and X-ray photoelectron spectroscopy (XPS) using Al Kα source. Scanning electron microscopy (SEM) micrographs and energy dispersive spectrometry (EDS) images were obtained on a Mira3 field emission SEM equipped with an Oxford Inca X-Max spectrometer. Nitrogen sorption isotherms were measured at 77.3 K on an automatic N_2 adsorption/desorption instrument (Quantachrome Autosurb Automated Gas Sorption System), and the samples were out gassed in vacuum at 300 °C for 3 h before testing.

2.4. Electrochemical measurements

The working electrodes were manufactured by coating method. The coating slurry consists of synthesized active material (samples), acetylene black and polyvinyldifluoride (PVDF, dissolved in N-methylpyrrolidone solvent with a concentration of 10 g L^{-1}) with a weight percent of 80:10:10, which the PVDF was dissolved in N-methylpyrrolidone solvent with a concentration of 10 g L^{-1}. Then the slurry was cast onto the as-prepared Ni foam (1.5 × 1.5 cm^2), after this it was placed at 80 °C oven for 10 h, lastly pressed in