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A high-performance asymmetric supercapacitor based on a directly grown nickel bicarbonate/nickel foam composite

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ABSTRACT

Three-dimensional (3D) network structure nickel bicarbonate/nickel foam ($Ni(HCO_3)_2$/NF) composite was synthesized by a simple one-pot hydrothermal process. The electrochemical properties of the as-prepared samples were investigated through the cyclic voltammetry and galvanostatic charge/discharge measurements. The results show that the specific capacitance of $Ni(HCO_3)_2$/NF reaches up to 2128.57 F g^{-1} (corresponding to a specific area capacitance of 7.45 F cm^{-2}) at a current density of 2.5 mA cm^{-2}, and the capacitance is still 876.19 F g^{-1} (3.07 F cm^{-2}) even at 50 mA cm^{-2}. Considering the excellent electrochemical performances of $Ni(HCO_3)_2$/NF electrode, an asymmetric supercapacitor based on $Ni(HCO_3)_2$/NF anode and Fe_xC_y/C cathode was assembled, which exhibited high energy density and power density. The maximum energy density of the asymmetric supercapacitor is up to 24.96 Wh kg^{-1} at a power density of 87.75 W kg^{-1}, besides, the power density can reach 1754.37 W kg^{-1} at 6.92 Wh kg^{-1}. Moreover, two such 1 cm^2 devices connected in series could light five LED indicators (40 mW) after charging only 50 s, and power a LED indicator with the same power for half an hour after charging to 3.2 V. The results demonstrate that our asymmetric supercapacitor is a promising device for practical applications.

1. Introduction

Supercapacitors, also called electrochemical capacitors, have aroused considerable attention in recent years due to their higher power density, faster charging/discharging rate capability, longer cycle life than that of secondary batteries as well as their greater energy density compared to those of conventional electrolytic capacitors [1–4]. Very recently, they have been widely applied in portable electronics, hybrid electric vehicles and industrial equipment, where require high power density and long cycle life [5].

As we all know, most commercial supercapacitors are made of carbon-based materials [6]. However, carbon-based symmetric devices have quite low energy density in both aqueous electrolyte and organic electrolyte, which are far from the higher requirements for peak-power assistance in electric vehicles [7–9]. Herein, to obtain a supercapacitor with higher energy density becomes a hot area in electrochemical research. For supercapacitors, according to what we learned, the energy density is calculated following the equation [7,10]: $E = 1/2CV^2$, where *E*,*C*, *V* represent energy density, specific capacitance, and operating voltage, respectively. From the formula, it is clear that the energy density is in direct proportion to capacitance and voltage of supercapacitors. Therefore, it is crucial to increase capacitance and broaden operating voltage of supercapacitors.

To the best of our knowledge, the specific capacitance for supercapacitors has a tight connection with electrode materials [2]. That is to say, the capacitive enhancement of supercapacitors can be implemented by optimizing the capacitance of electrode materials. Currently, it is well-known that pseudocapacitive transition metal oxides/hydroxides have displayed larger capacitance than carbon-based materials owing to Faradic reactions at the surface of active materials [9,11]. Note that nickel-based compounds have been deemed to be promising electrode materials among the numerous pseudocapacitive storage materials [12]. Based on all of the nickel-based compounds, $Ni(HCO_3)_2$ has been widely employed as the precursor for NiO electrode [13–15]. However, there are few researches on the direct application of Ni $(HCO_3)_2$ as active material. Recently, Zhu et al. synthesized $Ni_2(CO_3)(OH)_2$ microspheres with weak crystallinity, showing

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optimal specific capacitance of 1178 F g^{-1} at 0.5 A g^{-1} [16]. Sun et al. prepared $Ni(HCO_3)_2$ particles on graphene nanosheets, which exhibited capacitance of 1200 F g^{-1} at 4 A g^{-1} [15]. Apparently, $Ni(HCO_3)_2$ directly used as active materials have a high specific capacitance. Unfortunately, $Ni(HCO_3)_2$ possesses poor electrical conductivity, restricting the fast electron transport and reducing the electrochemical performance [15]. Nickel foam (NF), a three-dimension (3D) network structure, possesses high electrical conductivity, which has been extensively used as substrate [17]. Such as Huo [18] reported a 3D Ni_3S_2 nanosheet arrays grown on NF and $ZnCo_2O_4$/NF was synthesized by Wang group [19]. Furthermore, NF facilitates interfacial electrochemical reactions because 3D structure is beneficial to the permeation of electrolyte and the transfer of charge and electrolyte ions [8], besides, electrode materials directly grown on NF can avoid introducing the binders which will increase internal resistance of supercapacitors [9]. Therefore, $Ni(HCO_3)_2$ grown on NF can greatly improve the electrochemical performances of $Ni(HCO_3)_2$.

To widen the maximum operation voltage of capacitors is another good way to improve energy density, which can be carried out through assembling asymmetric supercapacitor [10]. For example, Tang [8] and Fan [10] reported asymmetric supercapacitors with broadened operation voltage, which exhibited high energy densities. Herein, assembling asymmetric supercapacitor is a good way to improve energy density. In this work, an additive-free nickel bicarbonate/nickel foam ($Ni(HCO_3)_2$/NF) composite with a 3D network structure was prepared through a simple and facile one-pot hydrothermal method. The specific gravimetric capacitance of Ni $(HCO_3)_2$/NF at 2.5 mA cm^{-2} is as high as 2128.57 F g^{-1} (corresponding to a specific areal capacitance of 7.45 F cm^{-2}), which is superior to most of the NiO-based electrode materials [13,20–23]. On the basis of the $Ni(HCO_3)_2$/NF composite, an asymmetric supercapacitor was assembled with $Ni(HCO_3)_2$/NF as positive electrode and Fe_xC_y/C as negative electrode, which exhibited a high energy density of 24.96 Wh kg^{-1} with a high power density (87.75 W kg^{-1}) at 2.5 mA cm^{-2}. In view of high energy density, two of the asymmetric supercapacitors connected in series could power a LED indicator (40 mW) for 30 min after charging to 3.2 V and light five LED indicators (40 mW) after charging only 50 s. The results prove that our asymmetric supercapacitor can be a promising supercapacitor for practical applications.

2. Experimental

2.1. Preparation of 3D network structure $Ni(HCO_3)_2$/NF composite

All the chemicals are analytical grade and used as received without further purification. Firstly, 10 mmol $Ni(NO_3)_2{\cdot}6H_2O$ and 20 mmol hexamethylene tetramine (HMT) were sequentially dissolved in 60 mL mixed solvent consisting of deionized water (DI) and absolute ethanol (molar ratio is 5:1). Subsequently, the above solution and NF were transferred to a 100 mL Teflon stainless-steel autoclave, heated in an oven at 180 °C for 8 h, then cooled to room temperature naturally. Finally, the samples were rinsed with DI and absolute ethanol, respectively, and then dried at 70 °C for 5 h in air to obtain the $Ni(HCO_3)_2$/NF electrode. For comparison, a parallel experiment was carried out to prepare powder $Ni(HCO_3)_2$ without adding NF. And NiO/nickel foam (NiO/NF) electrode was obtained by annealing $Ni(HCO_3)_2$/NF 2 h at 500 °C in the air.

2.2. Physicochemical characterizations of $Ni(HCO_3)_2$/NF composite

The structure of the samples was characterized by X-ray diffraction (XRD, RIGAKU D/Max-2550 with Cu Kα radiation). The composition and the surface electronic state of the as-prepared composite materials were investigated by X-ray photoelectron spectroscopy (XPS; AXIS ULTRA Kratos Analytical Ltd.). The morphology and microstructure of the products were examined with field emission scanning electron microscope (FESEM, HITACHI S-4800, Japan) with energy-dispersive X-ray spectroscopy (EDX) and field emission transmission electron microscopy (FETEM, Tecnai G2 F20 S-TWIN, USA).

2.3. Electrode preparation and electrochemical measurements

The as-synthesized $Ni(HCO_3)_2$/NF composite (1cm × 1 cm) was directly used as working electrode. The mass of active material is about 3.5 mg through the weight difference before and after hydrothermal process. The Fe_xC_y/C cathodic material was synthesized as our previous reported method [24]. And the cathode was prepared by mixing 80 wt% active material (Fe_xC_y/C), 10 wt% conductive material (acetylene black), and 10 wt% binder (polyvinylidene fluoride, PVDF) and coating the mixture paste onto a NF (1cm × 1 cm). Then, the electrode was dried at 70 °C overnight. The mass of cathode active material is about 20 mg. The AC electrode was prepared similarly to the Fe_xC_y/C cathode. The NiO/NF electrode (1cm × 1 cm) was also directly used as working electrode. Powder $Ni(HCO_3)_2$ (3.5 mg) was prepared as working electrode (1cm × 1 cm) by the slurry-coating technique, which was analogous to the preparation of Fe_xC_y/C cathode. The only difference was that the electrode was prepared by mixing 90 wt% active material ($Ni(HCO_3)_2$) and 10 wt% PVDF. A platinum foil (1.5cm × 1.5 cm) and a Ag/AgCl electrode were used as the counter and reference electrode, respectively.

The electrochemical properties of the as-obtained samples were valuated by cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS) tests in a three-electrode system on an electrochemical workstation (CHI660E, Shanghai, Chenhua Co., Ltd, China) with 2 M KOH aqueous solution used as electrolyte. The CV measurements of as-prepared electrodes were performed in the potential range of 0-0.6 V (vs Ag/AgCl) at different scan rates of 5, 10, 20, 30, 40, 50, 100 mV s^{-1}. The GCD experiments were performed at various current densities of 2.5, 5, 10, 20, 30, 40, 50 mA cm^{-2}. And the EIS technique was employed at open circuit potential in the frequency range of 10^5 to 0.01 Hz.

2.4. The assembly of asymmetric supercapacitors and electrochemical measurements

A two-electrode asymmetric supercapacitor was assembled using integrated $Ni(HCO_3)_2$/NF as anode and Fe_xC_y/C as cathode. The active material loadings in anode and cathode are 3.5 and 20 mg, namely, the total mass of active materials is 23.5 mg. The asymmetric supercapacitor, denoted as $Ni(HCO_3)_2$//Fe_xC_y/C for convenience, was fabricated with non-woven fabrics as separator and 2 M aqueous KOH as electrolyte. The specific assembly steps of the supercapacitor are as follows: Firstly, we immersed the anode and cathode in the 2 M KOH for 12 h, respectively, to make the electrolyte better penetration. Then, according to the sequence (current collector, anode, separator, cathode and current collector), we successfully assembled the asymmetric supercapacitor and dropwise added the electrolyte from the side in the non-woven until the separator is wetted completely. In addition, a series of electrochemical measurements for $Ni(HCO_3)_2$//Fe_xC_y/C supercapacitor, consisting of CV and GCD measurements, were curried out on a CHI660E electrochemical station to evaluate the electrochemical properties of the asymmetric supercapacitor. And the scan rates and current densities of $Ni(HCO_3)_2$//Fe_xC_y/C asymmetric device are similar to single electrode.