Preparation of $\text{Zn}_{0.65}\text{Ni}_{0.35}\text{O}$ composite from Metal-organic framework as electrode material for
supercapacitor

Feng Yu ^{a,b}, Lei Zhou ^b, Ting You ^a, Li Zhu ^a, Xiang Liu ^b, Zubiao Wen ^{a,*}

Abstract

We have successfully synthesized a Metal-organic framework and then researching its structure and morphology by scanning electron micrographs (SEM) and transmission electron microscopy (TEM). Furthermore, we fabricated $\text{Zn}_{0.65}\text{Ni}_{0.35}\text{O}$ by using the Metal-organic framework as precursor for supercapacitor. The $\text{Zn}_{0.65}\text{Ni}_{0.35}\text{O}$ electrode exhibited a maximum specific capacitance of 471.1 F g^{-1} at the current density of 1 A g^{-1} , which still remained at 81.3% over 1000 cycles

Keywords: metal-organic framework; supercapacitor.

1. Introduction

Supercapacitors are regarded as promising electrochemical energy storage devices because their greater power density with superior cycling ability than conventional rechargeable batteries [1].

Up to now, various of the electrode materials such as carbon-based materials [2] (such as activated carbon, graphene, CNTs), metal oxides/hydroxides [3, 4] (such as NiO/Ni(OH)_2 , MnO_2 , $\text{Co}_3\text{O}_4/\text{Co(OH)}_2$, RuO_2 , V_2O_5), metal sulfides [5], conduction polymers [6] and their composites [7,8] have been used in supercapacitors. Among the explored electrode materials, Nickel oxide (NiO) has been widely researched due to the high theoretical specific capacitance [9] (reaching 2584 F g^{-1}). However, its poor electric conductivity has restricted practical application. ZnO is one of the most

attractive functional semiconductor materials, which can be used as an efficient mechanical support and electron conducting pathway owing to its high chemical stability, conductivity and flexibility [10, 11]. Therefore, there are extensively reports about individual chemical and physical properties of NiO or ZnO, but there are litter study on the design and fabrication of ZnO-NiO composite as a material for supercapacitors. In addition, metal organic frameworks (MOF) are a type of organic-inorganic hybrid functional materials with high porosity and large specific surface area. [12] Recently, [MOF materials are considered to be suitable template](#) for preparing porous carbons and metal oxides by solid-solid transformation process at suitable temperature. [13] However, the process still need to be further studied.

2. Materials and synthesis

The Zn/Ni-MOF was synthesised by a hydrothermal method. All reagents are analytical grade without further treatment. In a typical procedure, 0.2 mmol Nickel (II) acetylacetonate ($\text{Ni}(\text{acac})_2$), 0.12 mmol Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 0.1 mmol 1,4-benzenedicarboxylic acid (H_2BDC) were dissolved in DMAC-Ethanol mixture with ratio in 5:3 under magnetic stirring for 10 minutes at room temperature. The resulting suspension was transferred to a 40 ml Teflon-lined stainless-steel autoclave and kept in a muffle furnace at 150 °C for 3 h. The obtained precipitate was collected by suction filter, washed three times with ultrapure ethanol and deionized water, and dried at 80 °C under vacuum 12 h to get Zn/Ni-MOF. The Zn/Ni-MOF powder was placed in a tube furnace under N_2 atmosphere, and kept at 400 °C for 1h. The obtained black powder was ZnO-NiO-C composite. Then it was putted in a tube furnace in air, and maintained at 380 °C for 1 h to remove the carbon. Finally, the desired product (ZnO-NiO) was obtained by this two-step calcination.

[The working electrode was prepared by ZnO-NiO composite, poly-\(tetrafluoroethylene\) and acetylene](#)

black in a weight ratio of 8: 1: 1. Cyclic voltammogram (CV) curves and electrochemical impedance spectroscopy (EIS) were measured by electrochemical workstation CHI600C in a three-electrode system, which uses a Ni-grid as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The galvanostatic charging and discharging curves and cycle performance of the electrode were performed by LANHE testing system in a three-electrode system.

The specific capacitance C (F g⁻¹) is calculated according to the following equation (1):

$$C = (I \Delta t) / (m \Delta V) \quad (1)$$

Where I (mA) is working current, Δt (s) represents the discharge time, ΔV (V) is the voltage range, and m (mg) is electrode mass.

3. Result and discussion

The morphology of Zn/Ni-MOF and Zn_{0.65}Ni_{0.35}O were characterized by scanning electron microscope and transmission electron microscopy. The obtained sample Zn/Ni-MOF was deemed to be a roughly sphere with an average diameter of 800 nm in the Figure 1a. From TEM image (Figure 1b), we can see that these sphere structure is solid and smooth, which are correspond to the value from SEM image. The Zn_{0.65}Ni_{0.35}O sample presented basically nanospheres aggregate together and the nanospheres were made by nanostructure.

As shown in Fig. 2 (a), the powder X-ray diffraction patterns belonged to ZnO-NiO and ZnO. At the same time, all peaks were well in agreement with the corresponding standard cards, JCPDF 65-3411 and 65-2901, for ZnO and NiO. At the same time, the molar ratio of Zn to Ni in ZnO-NiO nanocomposite was analysis by inductively coupled plasma optical emission spectrometry (ICP), which exhibited that the molar ratio of Zn and Ni were 65% and 35%, respectively. Therefore, the nanocomposite can be described to Zn_{0.65}Ni_{0.35}O. The Brunauer-Emmett-Teller (BET) (Fig. 2(b))

surface area and pore diameter distribution of $\text{Zn}_{0.65}\text{Ni}_{0.35}\text{O}$ were estimated to be $62.0 \text{ m}^2 \text{ g}^{-1}$ and 2 nm, respectively.

In order to further determine the electrochemical behavior of $\text{Zn}_{0.65}\text{Ni}_{0.35}\text{O}$ electrode, cyclic voltammetry curves in the range from 0 to 0.5 V (vs. SCE) are performed in 2 M KOH electrolyte solution. As displayed in Fig 3a, it shows the CV curves of $\text{Zn}_{0.65}\text{Ni}_{0.35}\text{O}$ electrode. The shapes are different from that of electric double layer capacitance, suggesting that the capacity mainly dominated by battery-type capacitance. In addition, the electrode of $\text{Zn}_{0.65}\text{Ni}_{0.35}\text{O}$ still have obviously redox peaks when the scan rate increased from 20 to 500 mV s^{-1} , and this phenomenon indicate that this structure of nanocomposite material of $\text{Zn}_{0.65}\text{Ni}_{0.35}\text{O}$ can not only lead fast electron conduction but also enhance the rate performance. Furthermore, the galvanostatic charge-discharge (GCD) of $\text{Zn}_{0.65}\text{Ni}_{0.35}\text{O}$ electrode is measured in 2 M KOH electrolyte at different current densities, as the potential-time curves shown in Fig. 3b. The nonlinear line curves of $\text{Zn}_{0.65}\text{Ni}_{0.35}\text{O}$ electrode material support the battery-type performance, because the double layer capacitor is a triangular wave-like curve at the charge-discharge process.

The specific capacitance derived from the discharging curves at current densities of 1-10 A g^{-1} and these shown in Fig. 4c. The specific capacitances of the $\text{Zn}_{0.65}\text{Ni}_{0.35}\text{O}$ electrode were 471.1, 465.7, 456.0, 444.4, 431.1, 426.6, 416.8, 412.4, 408.0, 400.0 F g^{-1} at current densities 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 A g^{-1} , respectively. However, the virginal ZnO electrode was only about 20 F g^{-1} (which is given in the inset of in Fig. 3c) at the same current density.

The electrochemical impedance spectroscopies of $\text{Zn}_{0.65}\text{Ni}_{0.35}\text{O}$ and NiO electrode are further conducted to elucidate the fast electron conduction. As shown in Fig. 3d, the $\text{Zn}_{0.65}\text{Ni}_{0.35}\text{O}$ electrode has a nearly straight line together with an ultrasmall ESR (1.5Ω), which is less than this of NiO

electrode. The above result suggests that $\text{Zn}_{0.65}\text{Ni}_{0.35}\text{O}$ has good electron conduction, corresponding to some previous reports. [10, 14] We conclude that the functional conductor material of ZnO plays a key role in electron transfer that it can support electron conducting pathway due to its high chemical stability, conductivity and flexibility properties. At the process of electrochemical reaction, the ZnO has novel interfaces which enhance the electron transfer.

The cycling performance of $\text{Zn}_{0.65}\text{Ni}_{0.35}\text{O}$ electrode at current density 1 A g^{-1} is shown in Fig. 4. We find that the $\text{Zn}_{0.65}\text{Ni}_{0.35}\text{O}$ electrode has outstanding cycling performance, the coulombic efficiency of the $\text{Zn}_{0.65}\text{Ni}_{0.35}\text{O}$ electrode is close to 100%. Although ZnO-NiO composite has been researched extensively in the field of supercapacitors in recent years, our fabrication $\text{Zn}_{0.65}\text{Ni}_{0.35}\text{O}$ electrode reveals better cycle performance than these of ZnO-NiO composite electrodes, which still maintains more than capacitance of 81.3% after 1000 charge-discharge cycles. [10, 15] The very slight decline of the specific capacitance of $\text{Zn}_{0.65}\text{Ni}_{0.35}\text{O}$ electrode possibly results from only the slight collapse of the $\text{Zn}_{0.65}\text{Ni}_{0.35}\text{O}$ structures due to the ZnO, which has an efficient mechanical support for the ZnO-NiO structures.

4. Conclusion

In summary, we have prepared a $\text{Zn}_{0.65}\text{Ni}_{0.35}\text{O}$ composite by two step annealing Zn/Ni-MOF. And evaluated this material as electrode material for supercapacitor, the $\text{Zn}_{0.65}\text{Ni}_{0.35}\text{O}$ electrode exhibited large specific capacitance and excellent cycling performance. The reasons are that ZnO improves the speed of charge-transfer and the stability at the electrode reaction surface, and NiO increases the capacitance of composite.

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Captions of Figures:

Fig.1 (a) SEM of prepared Zn/Ni-MOF, (b) TEM of prepared Zn/Ni-MOF and (c) SEM of prepared

Fig. 2 (a) XRD patterns of ZnO and $\text{Zn}_{0.65}\text{Ni}_{0.35}\text{O}$, (b) Nitrogen adsorption isotherm for the $\text{Zn}_{0.65}\text{Ni}_{0.35}\text{O}$ sample.

Fig. 3 (a) Cyclic voltammograms of $\text{Zn}_{0.65}\text{Ni}_{0.35}\text{O}$ electrode at scan rate 20-500 mV s^{-1} , (b) Galvanostatic charge-discharge curve of $\text{Zn}_{0.65}\text{Ni}_{0.35}\text{O}$, and (c) variation of specific capacitance with different discharge current density for $\text{Zn}_{0.65}\text{Ni}_{0.35}\text{O}$, (d) Electrochemical impedance spectroscopies of $\text{Zn}_{0.65}\text{Ni}_{0.35}\text{O}$ and NiO electrode.

Fig. 4 The cycling behavior of $\text{Zn}_{0.65}\text{Ni}_{0.35}\text{O}$ electrode at the current density of 1 A g^{-1} .

Fig.1

Fig. 2

Fig. 3

Fig. 4