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Cobalt–carbon derived from zeolitic imidazolate framework on Ni foam as high-performance supercapacitor electrode material

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ABSTRACT

ZIF-67 (Co(MeIM)$_2$, MeIM = 2-methylimidazole) was selected as a precursor to synthesize the metallic cobalt/carbon composites on Ni foam directly and intimately. The results show that ZIF-67 forms a uniform membrane and densely covers the Ni foam substrate. Besides, the cobalt/carbon composites obtained are composed of cobalt nanoparticles with a diameter up to around 2.6 nm, which are anchored on carbon homogeneously. The specific capacitance of the composites material is up to 512 F g^{-1} at a current density of 1 A g^{-1} in 1.0 M KOH electrolyte. Furthermore, the specific capacitance loss is ~46.4% with increase at the current density from 1 to 20 A g^{-1}. More significantly, the specific capacitance retention rate is 87.5% at a current density of 5 A g^{-1} after 1000 cycles. These results suggest that the electrochemical performance can be greatly enhanced by the well-controlled size and distribution of the cobalt nanoparticles, which is mainly attributed to the unique structure and composition of ZIF-67.

1. Introduction

Nowadays, it is an urgent task to develop renewable and clean energy sources because of the fast consumption of traditional fossil fuels, such as coal and petroleum and nature gas. Supercapacitors, as a novel energy storage device, have attracted much attention for their high power capabilities, good reversibility, and long cycle life [1,2]. Nonetheless, at about 5 W h/kg, the energy density of supercapacitors is lower than that of batteries, which has limited their wider application [1]. Therefore, it is significant to enhance the energy density for such applications, which demands the development of advanced electrodes with high capacitance.

On one hand, cobalt metal and its oxides have been heavily studied for applications such as supercapacitors [3–8], which showed a good pseudocapacitor behavior. On the other hand, porous carbons, which have the characteristics of large surface area, high conductivity, superior electrochemical stability, good processing ability, controlled pore structure and relatively low cost [9,10], are considered as candidates of electrode materials for supercapacitor. Meanwhile, it is notable that recently the development of new hybrid porous nanostructures has made great progress due to the advances in nanoscience and nanotechnology. These hybrid porous composites have been known as their unique properties including well-controlled pore structures, high surface areas, and large and tunable pore sizes [11]. As regards the applications of porous carbon-based composites, joint efforts have been made, which have achieved great success in electrodes [12,13], catalysts [14], and adsorbents [15]. Therefore, combining them with carbon can be a good choice in strategies for enhancement of performance in energy conversion based on cobalt metal and its oxides.

What is more, metal–organic frameworks (MOFs) have had a rapid development in the past decade, which are a relatively new class of microporous and crystalline materials that consist of inorganic clusters bridged by organic moieties in tridimensional arrangements [16]. As one of the most representative MOFs, ZIF-8 (Zn(MeIM)$_2$, MeIM = 2-methylimidazole) is formed by bridging 2-methylimidazolate anions and zinc cations resulting in a sodalite (SOD) topology and possesses a high carbon content, high chemical and thermal stability, and large Brunauer–Emmett–Teller (BET) surface area. All of this make it a novel and promising template for porous carbon synthesis [17,18]. Jun et al. succeeded in growing ZIF-8 on the Ni foam by one-step hydrothermal crystallization technique [19]. The only drawback is that zinc has little effect on improving the electrochemical performance. ZIF-67 (Co(MeIM)$_2$, MeIM = 2-methylimidazole), which is the same as ZIF-8 in structure, contains cobalt cations instead of zinc ones. Herein, ZIF-67 can be chosen as precursor to synthesize the cobalt/carbon composites. Wei et al. had successfully developed the metallic cobalt/carbon composites via a one-step thermal decomposition process [20], which manifests excellent capacitive performance.

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In this work, due to the advantages of a comparatively high surface area, high electron conductivity, and low costs [21–23], Ni foam was chosen to serve as a template, support, as well as current collector. A method of direct intimate growth of electrode materials on current collectors was adopted to grow ZIF-67 on Ni foam and Ni foam/cobalt/carbon electrode was obtained ultimately, which would avoid the addition of organic insulating binder, not only increasing the conductivity, but simplifying the electrode manufacture. Indeed, the binder-free method of directly growing active materials on conductive substrates had been adopted by Zhang et al., which performs well in improving the electrochemical performance [24–26]. From the above, the high specific capacitance of the Ni foam/cobalt/carbon material could be expected for the synergistic electrochemical result of the combination of metallic cobalt and porous carbon in alkaline electrolyte.

2. Experimental

2.1. Preparation of the Ni foam/ZIF-67

The Ni foam (1 cm × 2 cm) was pretreated with 20 mL of HCl solution (2 M) containing Polyvinylpyrrolidone (PVP) (0.5 g) to clean its surface and enhance the affinity of the surface. After 30 min, the Ni foam was washed with deionized water and methanol in order to remove the remaining PVP. Then, the Ni foam was immersed in methanol (50 mL) containing $Co(NO_3)_2{\cdot}6H_2O$ (260 mM) and 2-methylimidazole (780 mM) without disturbance for about 5 h. The sample was washed with deionized water and methanol for three times successively. At last, the sample was dried in a freezer dryer 24 h to obtain Ni foam/ZIF-67.

2.2. Preparation of Ni foam/cobalt/carbon

The obtained Ni foam/ZIF-67 was calcinated in a flow of argon gas. The specific steps are as follows: The sample was exposed to a flow of argon ($\sim$45 mL min^{-1}) at room temperature half an hour and afterward the furnace was heated to the targeted carbonation temperature with a heating rate of 3 °C min^{-1}. After reaching the targeted temperature, it was heated for 5 h and then cooled down to room temperature. Ni foam/cobalt/carbon was obtained ultimately.

2.3. Materials characterization and electrochemical testing

Morphologies of Ni foam/cobalt/carbon were investigated by a scanning electron microscopy (SEM, JEOL-7600F) and a transmission electron microscopy (TEM, JEOL JEM-1200EX). The sample was immersed in methanol to get the cobalt/carbon composites for TEM. X-ray photoelectron spectroscopy with Al Ka radiation (XPS, ESCALAB 250Xi*) was used to establish the valence states of cobalt in the composites. All electrochemical measurements were performed in an electrochemical workstation according to three-electrode system. A saturated calomel electrode (SCE) was used as the reference electrode, the Pt electrode as counter electrode, and the Ni foam/cobalt/carbon electrode as the working electrode. 1 M KOH solution was adopted as electrolyte in the study.

3. Results and discussion

Considering that the carbonation temperature has great effect on the porous structure and the texture of the samples [27,28], we prepared samples in different temperatures. Fig. 1 shows the TEM images of metallic cobalt/carbon composites obtained in different temperatures, including 600 °C, 800 °C and 1000 °C, respectively. It is obvious that the cobalt nanoparticles of the sample calcinated at 800 °C have formed in the smallest size among the three samples, which are anchored on carbon homogeneously without obvious agglomeration. Metallic cobalt, used as one kind of pseudo-capacitor electrodes, have high superficial areas beneficial for collecting more charge during the surface redox reactions. As is known to us all, the smaller the particle is, the larger the superficial area is. Besides, avoiding agglomeration can also increase the superficial area effectively. Hence, compared to the other two samples, the sample obtained at 800 °C should have better electrochemical performance and the sample was studied in detail.

The morphology of the prepared sample was characterized by scanning electron microscopy (SEM). Fig. 2 shows the low magnified SEM images of the Ni foam/ZIF-67 and Ni foam/cobalt/carbon. To observe the morphology of the sample more clearly, the high magnified SEM images were provided. As shown in Fig. 3a, the surfaces of Ni foam are covered with ordered ZIF-67 membrane. The detailed morphology of the as-synthesized membrane is shown in Fig. 3b and c. The materials are interconnected with each other and interlaced like petals. The thickness of the membrane is uniform with an average size of about 3.4 μm. In reality, the morphology of the Ni foam/cobalt/carbon membrane is greatly changed in contrast to Ni foam/ZIF-67, wherein the surface of carbon membrane has a ladderlike morphology, as can be seen in Fig. 3d and e. Besides, the thickness of the carbon membrane is reduced to around 1.5 μm because of the shrink of the ZIF-67 membrane during the carbonation process (Fig. 3f).

In order to verify the composition and the purity of the obtained composites, XPS analysis was performed. Fig. 4 shows two peaks with binding energy at 285 and 778.3 eV, which are characteristics of C1s and Co2p3 orbital, respectively, indicating the presence of C and Co elementals in the composites.

To further characterize the morphology and microstructure of the synthesized Ni foam/cobalt/carbon sample, TEM inspection was conducted. Fig. 1b shows the TEM image of the sample. The spherical cobalt nanoparticles in shape with a diameter size of around 2.6 nm are distributed on carbon homogeneously without obvious agglomeration, which displays a high superficial area of the cobalt particles. What is more, the cobalt particles take up a rough weight percent of 34.05 wt% [20].

In order to reflect the electrochemical properties of the cobalt/carbon composites, cyclic voltammetry (CV) curve was measured at a scanning rate of 200 mV s^{-1}, and the results are shown in Fig. 5a. With cobalt loading, the CV curve shows clear redox peaks within a potential range of 0.5 to 1.1 V. The shape represents the response of cobalt active sites. Two redox reaction peaks are visible, which is related to the following redox reaction [29]: $Co(OH)_2 + 2e^- \leftrightarrow Co + 2OH^-$. However, the reduction peak of metallic cobalt is weak in comparison with the oxidation peak due to slow reduction reaction rate of $Co(OH)_2$ caused by its diffusion process [29]. In addition, CV curves of the composites electrode for various scan rates are shown in Fig. 5b. The current density increases linearly with the scan rate, indicating the capacitance behavior of the sample. The shape of the CV curve changes with the scan rate [30], which indicates that the capacitance is mainly based on the redox mechanism.

The galvanostatic discharge of the cobalt/carbon composites between 0.4 and 1.0 V at a set of current densities show hat-like shapes further verify the pseudocapacitance characteristic from Faradic redox reaction, as shown in Fig. 6a. The discharge specific capacitance of the composites electrode can be calculated to be 512.0, 500.6, 438.9, 404.6, 374.9 and 354.3 F g^{-1} at current densities of 1, 2, 4, 6, 8 and 10 A g^{-1}, respectively. The relationship between