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High Performance Hydroxide Zinc Carbonate Composite for Supercapacitors

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Abstract

Energy density and production cost for high-performance electrode materials are the main challenge for the capacitive storage technology. In this paper, novel Hydroxide Zinc Carbonate ($Zn_4CO_3(OH)_6 \cdot H_2O$, HZC) catalyst layers, which are composed of irregular stagger arrangement nanosheets, have been synthesized successfully on foam Ni from inorganic precursors by a feasible *in situ* hydrothermal method. Measured by electrochemical tests as electrode materials for supercapacitors, the HZC@Ni foam show high specific capacitance (1329.2 $F \cdot g^{-1}$ at 1 $A \cdot g^{-1}$ and 882.8 $F \cdot g^{-1}$ at 10 $A \cdot g^{-1}$, respectively). These results show that the HZC@Ni foam could be a potential electrode material for supercapacitors. These encouraging results make these low-cost and eco-friendly materials promising for energy storage application.

Keywords

Hydroxide Zinc Carbonate, *In situ* Hydrothermal Method, Supercapacitor, Specific Capacitance

1. Introduction

Electrochemical capacitors (EC) or supercapacitors are a well-established class of energy storage devices and have been the subject of intense interest due to their high specific power density and fast recharge capabilities. Depending upon the charge transfer mechanisms, supercapacitors are divided into electrical double-layer capacitors (EDLCs) and pseudocapacitors [1] [2] [3]. In EDLCs, the charge storage mechanism is non-faradic and the charges are accumulated in the interface between the electrode and electrolytic solution, while faradic redox reactions take place at the electrode surface in pseudo-capacitors [2]. The fast and the reversible faradic process along with non-faradic electric double layer formation allow pseudocapacitors to store higher energy than that of EDLCs [2].

The performance of pseudocapacitors mainly relies on the properties of the electrode materials [2]. RuO_2 has been considered as one of the best-suited electrode material because of its high quasi-metallic conductivity and high pseudocapacitance [1]. However, the high cost and toxicity of the compound have placed huge obstacles for its large scale production. Therefore, many researchers are looking for various inexpensive transition metal oxides and hydroxides with high energy density as alternative electrode materials, like ZnO, TiO_2, and MnO_2 as electrode materials of pseudocapacitors [3] [4] [5]. Among them, Zn-based materials have drawn great attention because of the low cost and excellent electrochemical properties [6] [7]. For instance, ZnO/graphene nanocomposite exhibited a specific capacitance of 280 at 1 $A \cdot g^{-1}$ [6]. Therefore, ZnO has great potential as the electrode material of supercapacitors. Huang *et al.* [7] synthesized microspherical ZnO which exhibited high specific capacitances of 1017.5 $F \cdot g^{-1}$ at 5 $A \cdot g^{-1}$. However, organic precursors complicate the synthesis process. So it is a challenge to prepare Zn-based materials with feasible methods and enhanced electrochemical performance.

Herein, in this paper, we synthesize Hydroxide Zinc Carbonate (HZC) nanosheets on foam Ni by a feasible in situ hydrothermal method and with inorganic precursors. Electrochemical tests show that the HZC@Ni foam exhibited excellent electrochemical performance.

2. Experimental

All the chemical reagents were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China), which were of analytical purity and used without any further purification. Foam Ni was purchased from Shenyang Research Institute of Nonferrous Metals Co. Ltd. (Shenyang, China).

Nanosheet Hydroxide Zinc Carbonate is directly grown on foam Ni by a hydrothermal synthesis. Typically, Ni foam (10 mm × 10 mm × 1 mm) is ultrasonically washed successively with 3 $mol \cdot L^{-1}$ HCl solution, deionized water, and absolute ethanol in an ultrasound bath for 10 min each to remove NiO layer and residual organics on the surface. An aqueous solution was prepared and stirred thoroughly to form a clear solution with $Zn(NO_3)_2 \cdot 6H_2O$ as precursor, urea as the precipitator, trace $Al(NO_3)_3 \cdot 9H_2O$ as lamellar structure agents. A cleared Ni foam sheet is put into a 50 ml Teflon-lined autoclave containing above homogeneous solution. The autoclave was sealed, maintained at 120˚C for 4 h, and then cooled to room temperature naturally. The final product was thoroughly washed with H_2O and dried at 60˚C for 8 h. The mole ratio of urea/Zinc is 5.

Powder X-ray diffraction (XRD) technique (Cu Kα PW1710, Netherlands) was employed to analyze the crystal structure and phase composition of the samples. The morphological studies of HZC nanosheets were performed using field emission scanning electronic microscope (FESEM, JEOLJEM-6360LV, Japan) and transmission electron microscopy (TEM, H-800, Japan). Fourier transform infrared spectrum spectral (FTIR, TJ270-30A, China) studies were carried out in the frequency region 400 - 4000 cm^{-1}.

The HZC@foam Ni samples for supercapacitor application were preliminarily explored by constructing the cell involving three electrodes system in 6 mol·L^{-1} KOH solution. In three electrodes, prepared HZC@Ni foam was used as working electrode, Hg/HgO and platium plate were used as the reference and counter electrodes respectively. The cyclic voltammetry (CV) curves were obtained at different scan rates of 5 - 100 mV·s^{-1} using CHI660D electrochemical analyzer.

3. Results and Discussion

3.1. Characterization of HZC

The crystallographic structures of the prepared materials were estimated by X-ray diffraction measurement. XRD pattern of the product is presented in **Figure 1**. The product shows diffraction peaks at 12.8˚, 19.3˚, 34.4˚, etc. corresponding to typical lattice planes of $Zn_4CO_3(OH)_6 \cdot H_2O$ (JCPDS: 011-0287). The diffraction peaks of these planes are especially strong while other peaks have relatively weak intensities, indicating the growth of the crystal along a definite direction. It can be seen from **Figure 1** that $Zn_4CO_3(OH)_6 \cdot H_2O$ has been formed even after 1 h hydrothermal process at 120˚C. With the extension of hydrothermal reaction time, the peak strength of characteristic diffraction peaks of products slightly increases, indicating that the material can be synthesized easily with low energy consumption. And more importantly, the crystal structure and composition of products are stable which is critical to cycle stability.

The FTIR spectrum of the product is given in **Figure 2**, confirming the presence of CO_3^{2-} as well as water molecules intercalated in the interlayer. The absorption band around 3452 cm^{-1} corresponds to the O-H stretching vibration of water molecules in the interlayer, H-bonded hydroxyl group and possible Metal-OH stretching vibration. The band at 1350 - 1550 cm^{-1} assigned to O-C-O

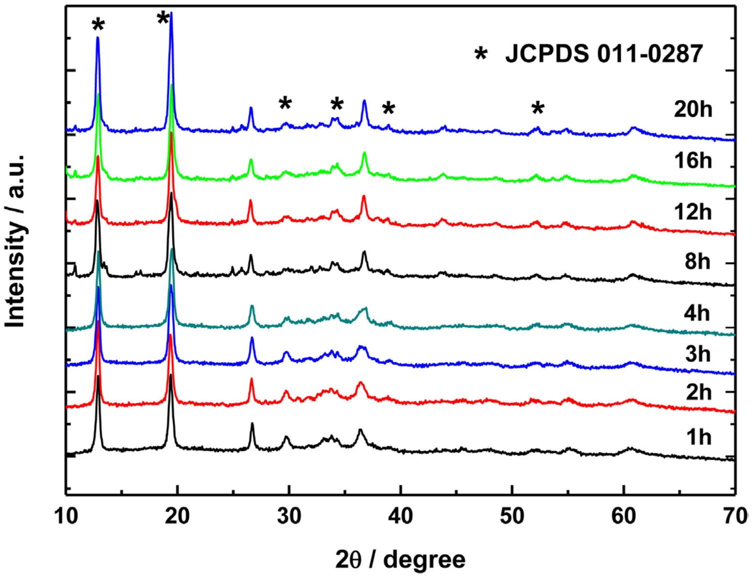


Figure 1. XRD pattern of as-synthesized HZC particles with different hydrothermal time.

groups asymmetric vibration of single-base carbonate group ligand. Other absorption bands at 400 - 700 cm^{-1} are due to attributes to metal-oxygen (M-O) stretching and bending modes, including zinc-O-O, etc. All observations above are in good agreement with the previous reports [8] [9].

Hydrothermal technique over chemical routes is beneficial to control the morphology of products by properly choosing the temperature, time of reaction, solvent used for reaction, with or without the use of any major structure-directing agents and templates. The morphology of the prepared HZC growing on the surface of Ni foam is examined via field-emission scanning electron microscopy (FESEM). **Figure 3(a)** and **Figure 3(b)** show the morphological features of the HZC prepared in the present work at different magnifications. As presented in **Figure 3(a)**, all of the HZC particles display nanosheets that are relatively loosely, irregularly grown on the substrate surface of foam Ni. The morphology of product particles is nearly hexagonal nanosheet with about 1 - 2 μm of diameter and 50 - 100 nm thickness. The interconnected nanosheets form a mesoporous film on foam Ni surface.

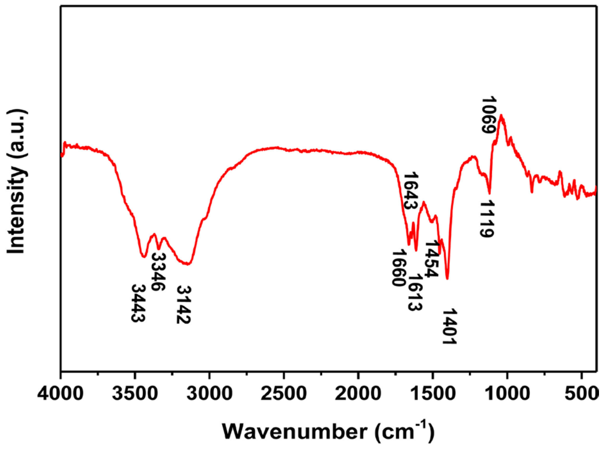
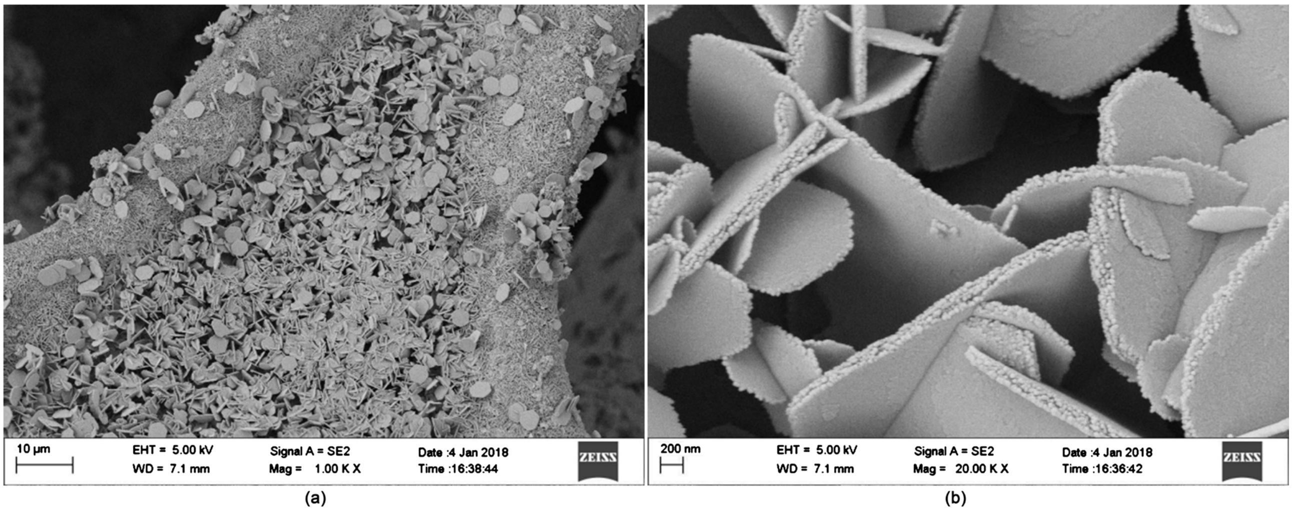


Figure 2. FTIR spectrum of as-synthesized HZC particles.



(a)

(b)

Figure 3. (a) SEM and (b) enlarged images of products.

3.2. Electrochemical Performance

The electrochemical richness of HZC composite electrode has been extensively studied using cyclic voltammetry, galvanostatic charge-discharge studies and electrochemical impedance techniques. The CV traces (**Figure 4**) of HZC shows a pair of redox peaks in the range of 0 - 0.6 V (vs Hg/HgO) of HZC composite electrode in three electrode system, which indicates that HZC composite electrode exhibits typical energy storage mode of Faraday pseudocapacitance [3]. It is generally believed that the pseudocapacitance energy storage mechanism of Zn(II)-based oxide or hydroxide electrode in alkaline electrolyte solution is derived from the redox reaction of Zn(II), which is completed with the assistance of ion insertion and removal in electrolyte solution. Theoretical analysis shows that $E^{\theta}(Zn^{2+}/Zn) = -0.762$ V, so it can be inferred that $E^{\theta}(Zn(OH)_2/Zn) = -1.240$ V. In the experiment, the redox peak of was about 0.45 - 0.5 V (vs Hg/HgO). Based on the literature, it was preliminarily speculated that the redox process of the active component of HZC electrode under the study conditions was between Zn (II) and Zn (III).

Galvanostatic charge-discharge curves (**Figure 5**) of HZC were recorded at different current densities in the potential range of 0 - 0.6 V. From the constant-current charge and discharge curves, it can be seen that the curves are nearly symmetrical, with obvious charging and discharging platforms around 0.45 V. The charging curves with relatively slow voltage change at the range of 0.45 - 0.6 V and the discharging curves at the range of 0.3 - 0.45 V both reflect the typical pseudocapacitive properties of HZC composite electrode, and correspond to the redox peaks in the CV curve of the electrode in **Figure 4**.

The specific capacitance of HZC composite electrode can be estimated from the discharge current using the following equation [3]:

$$C = I \times t \big/ \left(m \times \Delta V \right) \tag{1}$$

where, C (F·g^{-1}) is the specific capacitance of the electrode. I (A) is charge and

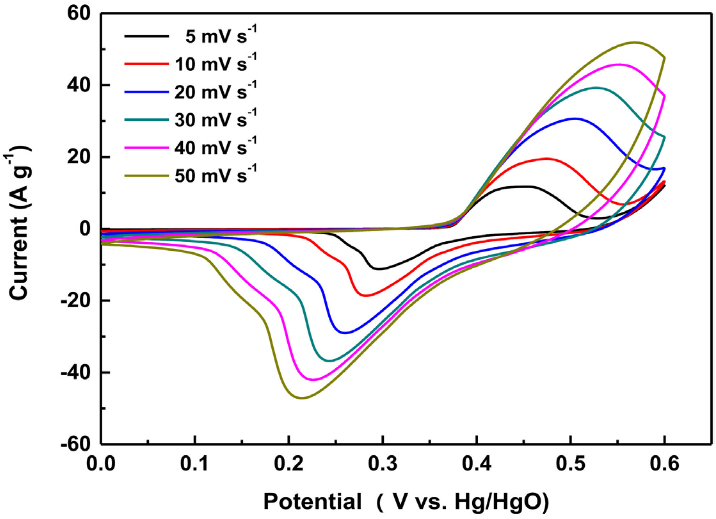


Figure 4. CV curves of electrode at different scan rate in 6 mol·L^{-1} KOH.

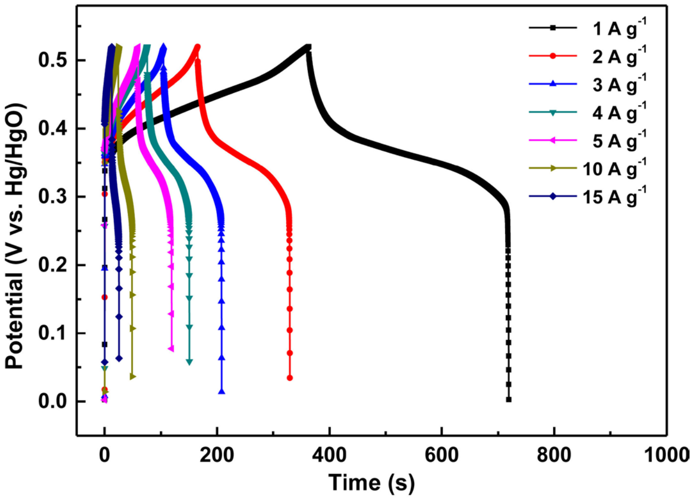


Figure 5. Galvanostatic charge and discharge curves of HZC electrode.

discharge current. T (s) is discharge time and ΔV (V) for charging and discharging voltage window, m (g) as electroactive material quality. The estimated specific capacitance of HZC composite electrode is 1329.2 F·g^{-1} at a current density of 1 A·g^{-1} and 882.8 F·g^{-1} at 10 A·g^{-1}, respectively. HZC in situ grown on foam Ni exhibits 40 fold enhancement in the capacity to store charges, when compared to HZC powders coated on foam Ni under the same test condition (32.7 F·g^{-1} at 1 A·g^{-1}). By comparing the research progress and electrochemical performance results of Zn-based electrode materials in recent years, it can be seen that a one-step hydrothermal process using inorganic precursors in this experiment is facile, and the synthesized HZC electrode materials show superior electrochemical activities [10] [11].

More advantageous crystal structure and the nanosheet morphology of HZC on foam Ni are the possible reasons for the excellent charge storage characteristics. Thin nanosheet arrays of uniform lamellar provide both large active surface area and good electrical conduction for fast redox kinetics. The layed structure of HZC can increase the rate of active centers participate in electrochemical reaction. This result shows that the ordered electrode material has a significant influence on the electrochemical performance of the HZC electrode. It is calculated that the energy density can reach 38.9 Wh·kg^{-1} when the power density is 2000 W.

4. Conclusion

$Zn_4CO_3(OH)_6 \cdot H_2O$ composite electrode material was synthesized by a feasible in situ hydrothermal method with inorganic precursor. HZC particles on foam Ni were regular multi-layer nanosheets. The synthesized HZC electrode shows novel electrochemical activity in three electrode system. The specific capacitance of the electrode can reach about 1359 F·g^{-1} at the current density of 1 A·g^{-1}. The next work will further refine the process of synthesis, analysis mechanism, and improve the cycle stability of the electrode materials.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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