Research Paper

Zinc Cobalt Layered Double Hydroxide Electrode for High-Performance Supercapacitor

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ABSTRACT

We aim to fabricate a ZnCo layered double hydroxide (LDH) nanostructure through facile one-pot hydrothermal synthesis. ZnCo LDH with interconnected hexagonal sheets having ultrathin thickness with voids are synthesized for the effective penetration of electrolytes to achieve superior electrochemical properties. The as-synthesized ZnCo LDH nanostructure is then subjected to structural, morphological, phase, and electrochemical studies. As an electrode for a supercapacitor, the ZnCo LDH has an areal capacitance of 1964 mFcm⁻² at a 5 mVs⁻¹ scan rate, an energy density of 0.22 mWhcm⁻², and an excellent cycling stability (112 %) after 2000 charge-discharge cycles.

Keywords: ZnCo, Layered double hydroxide, Supercapacitor

1. Introduction

Modern society is technologically advanced and most daily electronic appliances are energy dependent. It is essential to have high-efficiency energy storage systems to fulfill the increasing demand for renewable energy. Supercapacitors, which are also called electrochemical supercapacitors, are gaining considerable attention as a viable energy storage system owing to their long cycle life, high-power density, and rapid recharge ability [1]. There are two types of supercapacitors based on their charge storage mechanisms: electric double layer capacitors (EDLCs) and pseudocapacitors. In EDLCs, the charge is stored at the electrolyte/electrode interface [2]. Various carbon-based materials possessing high surface area are widely used for EDLCs applications, such as graphene, activated carbon, and carbon nanotubes (CNTs) based electrodes [3]. In a pseudocapacitor, the charge is stored due to Faradaic redox reactions at the electrode surface leading to pseudocapacitance. The pseudocapacitance behavior is found in different transition metal oxides (TMOs) and conducting polymers [4].

In pseudocapacitors, various TMOs are widely used because of their high specific capacitance than the carbon-based materials. Unfortunately, the low electronic conductivity of the binary TMOs leads to poor electrochemical activity, which limits their practical application [5]. On the other hand, carbon-based materials have a serious drawback such as poor energy density, which cannot be utilized to meet the requirements of modern electronics, and have limitation related to commercialization. Therefore, it is necessary to develop and synthesize novel low-cost materials possessing high energy density and long cycling stability for efficient energy storage systems.

Recently, layered double hydroxides (LDHs) with nanostructures

have received considerable attention in studies on electrochemical supercapacitors [6]. It has been proved in the literature that LDH electrodes possess richer Faradaic reactions and enhanced capacitances owing to an improvement in pseudocapacitive properties. LDHs are also known as hydrotalcite-like compounds, which are inorganic layered materials whose structure is based on brucite-like layers. The general formula of an LDH is $[M_1^{II}{}_x M_2^{III}{}_y (OH)_2]^{z+} (A^{n-})_{\frac{z}{n}} \cdot \gamma H_2 O$,

where M^{II} and M^{III} are divalent and trivalent metals, respectively, and A^{n-} is the interlayer anion [7]. The beneficial properties of LDHs include their tunable composition, layered structure, highly dispersive cations in host layers, and high specific capacitance. Owing to these properties, LDHs have been widely exploited in supercapacitor studies [8-10].

In this work, we fabricate a ZnCo based LDH for realizing a superior supercapacitor by using facile one-pot hydrothermal synthesis. It is known that Zn resources are abundant in nature, possess outstanding Faradaic pseudocapacitive performance, and are rich in redox reactions of Zn-Co compounds. Hence, bimetallic Zn-Co hydroxides are considered highly suitable for future use in supercapacitors; nanostructures of Zn-Co hydroxides synthesized with an easy route are highly promising. The optimized electrode of ZnCo LDH is subjected to structural, morphological, phase, and electrochemical studies. It is found that the nanostructures of ZnCo LDH show promising electrochemical properties, exhibiting an areal capacitance of 1964 mFcm⁻² at a 5 mVs⁻¹ scan rate, with an excellent capacitance retention of 112 % after 2000 cycles, which is superior than the properties of other metallic LDH nanostructures.

II. Experimental details

Zn-Co hydroxide was grown on Ni foam by a hydrothermal synthesis procedure. Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), and urea ($\text{CO}(\text{NH}_2)_2$) were used as source materials without further purification. In a typical procedure, 0.01 M of ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), 0.02 M of ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), and 0.05 M of ($\text{CO}(\text{NH}_2)_2$) were dissolved in 60 mL of distilled water and kept under constant stirring conditions. The resulting homogeneous solution (60 mL) was then transferred to an 80-mL Teflon lined stainless steel autoclave. A piece of cleaned Ni foam was immersed in the solution by inclining it against the wall of the Teflon liner. Then, the autoclave was sealed and placed in an oven at 140 °C for 8 h. Finally, the Ni foam coated with the resultant product was removed from the autoclave after cooling to room temperature and rinsed thoroughly using distilled water and kept at room temperature for air drying. Thus, the obtained electrode is referred as ZnCo LDH.

III. Results and discussion

The ZnCo LDH electrode fabricated by the 8-h hydrothermal reaction was characterized to assess the properties of the material. X-ray diffraction (XRD) was used to study the phase and crystal structure of the ZnCo LDH sample. Figure 1 shows the XRD pattern of the ZnCo LDH electrode coated on nickel (Ni) foam. The

Figure 1. (Color online) XRD pattern of ZnCo-LDH.

diffraction peaks located at 2θ values of 14.73°, 19.39°, 28.65°, 29.45°, 32.99°, 36.31°, 37.75°, 42.09°, 47.51°, and 49.67° were assigned to the (002), (011), (013), (111), (-113), (020), (113), (200), (024), and (-124) planes of the ZnCo LDH nanostructure, respectively. These diffracted peaks are in accordance with the standard data file JCPDS no. 21-1477 [11]. Along with these diffraction peaks, the peaks located at 44.55°, 51.91°, and 76.47° were caused by the substrate Ni foam.

To obtain information on the chemical state and valency of a material, X-ray photoelectron spectroscopy (XPS) measurement was performed. Figures 2(a)–(c) show the high resolution XPS of a sample ZnCo LDH nanostructure consisting of Zn 2p, Co 2p, and O 1s spectra. In the Zn 2p spectrum, the binding energy peaks located at 1024.08 and 1047.28 eV correspond to Zn $2p_{3/2}$ and Zn $2p_{1/2}$, respectively. The characteristic binding energy peak at ~1024 eV is caused by Zn^{2+} in the metal hydroxide, and it confirms that the valency of Zn is +2 [12]. Similarly, the Co 2p XPS spectra consists of two main peaks Co $2p_{3/2}$ and Co $2p_{1/2}$ located at 783.28 and 799.38 eV, which can be attributed to Co^{3+} and Co^{2+} , respectively. The O 1s XPS spectrum consists of three peaks located at 529.58, 531.28, and 534.38 eV, which are caused by Co-O, M-OH bonding (where M= Zn, Co), and surface contamination, respectively [13]. From the XPS analysis, it is observed that the ZnCo LDH material is composed of Zn, Co, and OH without any impurities, thus affirming the purity of our sample.

The surface morphological features of the sample ZnCo LDH were determined through field emission scanning electron microscopy (FESEM). Figures 3(a)–(f) show the FESEM images of ZnCo LDH at different magnifications. It is clearly observed that the entire Ni foam is coated uniformly with the ZnCo LDH nanostructures, as seen in Fig. 3(a). After viewing the morphology at further higher magnifications [Figs. 3(b) and 3(c)], it is interesting to note that the ZnCo LDH nanostructure is composed of hexagonal sheets interconnected with each other. This interconnected network of hexagonal sheets has resulted in various valley points resembling voids that are highly beneficial for the effective penetration of the liquid electrolyte leading to enhanced electrochemical activity. FESEM images at magnifications of $\times 25$, $\times 50$, and $\times 100$ K [Figs. 3(d)–(f)] show that the hexagonal sheets of ZnCo LDH are stacked upon each other and the thickness of each hexagonal sheet is ~60 nm.

To investigate the electrochemical performance of the as prepared ZnCo-LDH, electrochemical measurements are performed through conventional three electrodes configurations in 2 M KOH. Figure 4(a) shows a CV curve of ZnCo-LDH at a scan rate of 5 mVs^{-1} within the

Figure 2. (Color online) High-resolution XPS of ZnCo-LDH: (a) Zn 2p, (b) Co 2p, (c) O 1s.

Figure 3. SEM images of ZnCo-LDH at different magnifications.

Figure 4. (Color online) (a) CV curves at a scan rate of 5 mVs^{-1} , Inset: at different scan rate, (b) charge-discharge at different applied current, (c) areal capacitance versus scan rate, (d) Nyquist plot, Inset: magnified Nyquist plots of ZnCo-LDH.

potential range between -0.1 and 0.6 V vs. Saturated Calomel Electrode (SCE). From the CV curve, two strong redox peaks can be clearly seen, which are attributed to faradaic reactions occurring between the active

material and the electrolyte. This signifies the pseudo-capacitive charge storage mechanism of the synthesized electrode. The inset of Fig. 4(a) exhibits the CV curves of ZnCo-LDH recorded at different

scan rates. As the scan rate increases, the area under the CV curves increases, and this is correlated with the linear variation of the peak current with the square root of the scan rate. The areal capacitance of the electrode was calculated from the CV curve integrals by

$$C_A = \frac{\int i dV}{2A \times \Delta V \times S} \quad (1)$$

where C_A is the areal capacitance, $\int i dV$ is the integrated area of the CV curve, A is the area of the electrode, ΔV is the potential range, and S is the scan rate.

The maximum areal capacitance of 1964 mFcm⁻² is obtained for ZnCo-LDH at a scan rate of 5 mVs⁻¹. The variation of areal capacitance with respect to scan rate is as shown in Fig. 4(b). It is well known that the capacitance decreases with an increasing scan rate. At low scan rates, there is sufficient time for ions to penetrate into pores to produce high charges and higher capacitance whereas at high scan rates, the electrolyte can hardly enter the pores, which reduces the capacitance. The areal capacitance of ZnCo-LDH decreased from 1964 to 527 mFcm⁻², with an increasing scan rate from 5 to 100 mVs⁻¹.

Figure 4(c) shows the galvanostatic charge discharge curves of ZnCo-LDH recorded over -0.1 to 0.5 V vs. SCE at different applied currents. The small deviation of the triangular shape of the charge discharge curves from the straight line further confirms that the capacitance of ZnCo-LDH originated from the faradaic redox reversible reactions. With increasing applied currents, the voltage rapidly decreases; as a result, the discharge time reduces. The areal energy density (ED) and power density (PD) of the electrode were calculated from the Galvanostatic Charge-discharge (GCD) curves using the following equations:

$$ED = \frac{It \Delta V}{A} \quad (2)$$

$$PD = \frac{I \Delta V}{A} \quad (3)$$

where I is the applied current, t is the discharge time, ΔV is the potential range, and A is the area of the electrode.

The maximum energy density of 0.22 mWhcm⁻² and power density of 9 mWcm⁻² are achieved for ZnCo-LDH, at an applied current of 15 mA.

The Electrochemical Impedance Spectroscopy measurement was performed to analyze the charge transfer and ion transport performance of the ZnCo-LDH electrode. Figure 4(d) displays the Nyquist plot of the ZnCo-LDH electrode measured in the frequency range from 0.1 to 1 × 10⁵ Hz. The Nyquist plot is composed of two regions: a high frequency region (semi-circle) and a low frequency region (a straight line); this confirms the faradaic charge storage mechanism of the ZnCo-LDH electrode [14]. The intercept with the real axis at very high frequencies indicates the equivalent series resistance and the diameter of the semicircle is equal to the charge transfer resistance of the electrode [15]. From Fig. 4(d), an equivalent series resistance of 0.4 Ω was obtained for ZnCo-LDH. The very small arc diameter was attributed to the fast ion diffusion and low charge transfer resistance of the ZnCo-LDH [13]. The impedance phase angle vs. the frequency plot for the ZnCo-LDH electrode is shown in the

Figure 5. (Color online) Capacitance retention and areal capacitance versus cycle number. Inset: CV curves obtained at 1st and 2001st cycles at 5 mVs⁻¹.

inset of Fig. 4(d). The impedance phase angle for ZnCo-LDH was found to be ~66.5° at low frequency.

To evaluate the cycling performance of the ZnCo-LDH electrode, the electrode was subjected to 2000 cycles at a scan rate of 5 mVs⁻¹. Figure 5 represents the change in the capacitance retention and areal capacitance with the number of cycles. The inset in Fig. 5 denotes the CVs of the 1st and 2001st cycles recorded at 5 mVs⁻¹ for ZnCo-LDH. An increase in the current was observed in the CV after performing 2000 cycles, which indicated the rise in electrochemical performance upon cycling. With an increase in the number of cycles, the areal capacitance reached a maximum of 2318 mFcm⁻², with 118 % capacitance retention, after 500 electrochemical cycles. Furthermore, a 4.7 % loss was observed in the capacitance for the next 500 cycles. Next, only a 1.1 % loss was found for the next 1000 cycles, which indicates an almost stable electrochemical behavior of the electrode. That is, a total of 112.2 % capacitance retention with 2202 mFcm⁻² areal capacitance was achieved after 2000 cycles, suggesting the stable and excellent performance of the ZnCo-LDH electrode. This is attributed to the improved surface wetting and electrochemical activation of the ZnCo-LDH during the insertion and extraction of ions.

IV. Conclusions

We fabricated ZnCo LDH nanostructures using a facile one pot hydrothermal synthesis. The interconnected hexagonal sheets having ultrathin thicknesses of ZnCo LDH with voids are highly beneficial for the effective penetration of electrolytes leading to superior electrochemical properties. The as-synthesized ZnCo LDH nanostructure produced an areal capacitance of 1964 mFcm⁻² at 5 mVs⁻¹ scan rate, energy density of 0.22 mWhcm⁻², and excellent cycling stability (112 %) after 2000 charge discharge cycles. This study provides LDH ZnCo bimetallic hydroxide as a promising electrode for efficient pseudocapacitors, and it opens an avenue for the use of different bimetallic LDHs as an electrode material for electrochemical supercapacitors.

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