Electrochemical Performance of Zn-Al Double Layered Hydroxide for Supercapacitor Application

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Abstract. Zn-Al double layered hydroxide (Zn-Al-LDH) was synthesized by a facile coprecipitation method. The morphology and microstructure of samples were characterized by X-ray diffraction (XRD) and Scanning electron microscope (SEM), respectively. The results show that the sample is uniform nanosheet with the diameter of ~400 nm and the thickness of ~80 nm. XRD characterization confirms that it is $Zn_6A_{l2}(OH)_{16}CO_3.4H_2O$ and belongs to Rhombohedral crystallographic system. Electrochemical performances of the sample were investigated by cyclic voltammery (CV) and charge/discharge. The Pure Zn-Al-LDH nanocomposites achieves a specific capacitance of 37.0 F g^{-1} at the current density of 1.0 A/g.

1. Introduction

Worldwide growth in fossil energy consumption need to develop alternative new energy of environment friendly, low cost, compatibility and efficient[1]. The rapid development of various new electronic devices and optoelectronic devices driven by modern technology also calls for more reliable, more energy-dense, longer service life and sustainable power systems, such as batteries and supercapacitors. Unlike a battery, supercapacitor causes a wide interest because of charging speed, infinite long theory of life, no temperature vulnerability, and non-toxic[2,3].

Layered double hydroxide(LDHs), a typical inorganic layered material, its chemical formula can be expressed as general formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{z+}(A^{n-})_{/z/n}.yH_2O$. M^{II} is divalent metal ions, such as Mn^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, and Fe^{2+}. M^{III} is a trivalent metal ion, such as Al^{3+}, Fe^{3+}, Cr^{3+}, Ga^{3+}, etc. A^{n-} is an interlayer anion, which is used to balance the positive charge of the main structure of the layer of hydroxide[4,5]. Due to metal ions and the interlayer anion can be flexible modulation and does not change the main structure, LDHs structure material is widely studied in many applications, such as catalytic, adsorption, biology, and energy storage[6,7]. The high dispersion of active substances in the lattice of the layers, the easy separation and chemical modification of the single layer, provide the possibility of becoming a multi-functional electrochemical electrode material[8].

Among different kinds of LDHs materials, Ni-Co-LDH and Co-Al-LDHs show better elcectrochemical performance[4,9-10]. However, Zn-Al-LDHs are barely researched for their supercapacitor performance[11].

2. Experimental Section

2.1. Preparation of Zn-Al-LDH

Zn-Al-LDH material is prepared by coprecipitation method. 0.21 mol $Zn(NO_3)_2.6H_2O$ and 0.07 mol $Al(NO_3)_3.6H_2O$ are dissolved in 200 ml deionized water (solution I); 0.438 moles of NaOH and 0.113 mol of Na_2CO_3 are dissolved in 200 ml deionized water (solution II). Two solutions are kept in 70 ^{o}C water bath for 30 min under stirring. Solution I is dropped into solution II and react 30 min at 70 °C then aging for 20 h. The sample is washed to neutral and dry overnight[12].

2.2. X-ray Powder Diffraction (XRD)
The XRD experiment is conducted on the X'pert ProSuper ray diffractometer of PAN Analytical (Netherlands). The copper target line is the light source (λ =1.5432 nm), the graphite monochromator, the tube voltage is 40 kV, and the tube current is 100 mA.

2.3. Electrochemical Measurements.
Electrochemical performance test is performed on an Autolab electrochemical workstation (PGSTAT302 N, Ecochemie Co., the Netherlands). in 6 mol/L KOH solution. The electrochemical performance test adopts the classical three-electrode system, in which Zn-Al-LDH is used as working electrode, the Hg_2Cl_2/Hg electrode (SCE, saturated KCl) as reference electrode and Pt as the counter electrode. CV is conducted between 0-0.4 V (vs. SCE) and the constant current charging and discharge test voltage window is 0-0.35 V.

3. Results and Discussion

3.1. SEM Representation of Zn-Al-LDH.
Figure 1a represents SEM image of Zn-Al-LDH samples obtained by coprecipitation method. It can be seen that the Zn-Al-LDH sample is uniform and irregular, and the size of the slices is about 300-500 nm and the thickness is about 50-100 nm, and there is no obvious reunion phenomenon.

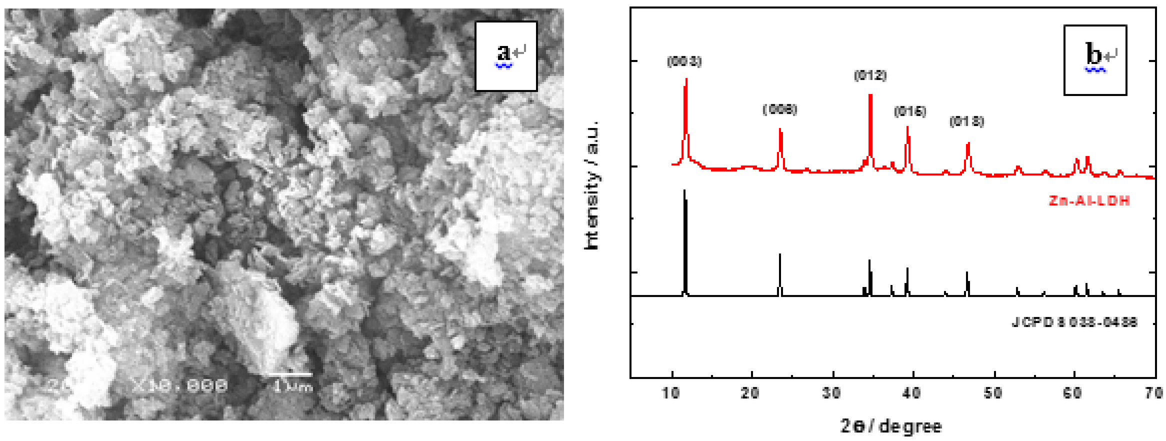

Figure 1. SEM image (a) and XRD patterns (b) for Zn-Al-LDH

3.2. XRD of Zn-Al-LDH.
XRD characterization results in shown in figure 1b. Compared with the JCPDS standard card, the peaks at 2θ=11.64, 23.39, 34.56, 39.15, and 46.64 ° corresponding to the diffraction peaks of (003), (006), (012), (015) and (018) crystal planes for hydrotalcite structure $Zn_6A_{12}(OH)_{16}CO_3.4H_2O$, trigonal system (Rhombohedral), completely consistent with the standard card (JCPDS No. 038-0486)[13]. The sample structure belongs to the space group R-3m, crystal cell parameters for a=b=3.076 Å, c= 22.800 Å,$\alpha=\beta = 90$ °, $\gamma = 120$ °.

3.3. Cyclic Voltampere Curve of Zn-Al-LDH.
The electrochemical properties of Zn-Al-LDH electrode are tested using cyclic voltammetry (CV) technology in 6 mol/L KOH solution under different scanning rates. The voltage window is 0-0.4 V, and the result is shown in figure 2. It can be seen that the curve shows a pair of oxidation-reduction

peaks at about 0.25 V (vs SCE), which means that the electrode presents a typical pseudo-capacitance properties[14]. As the scanning rate increases, the peak value increases, and the peak position moves to high and low potential. These changes related to electrolyte solution ion diffusion ability in the LDH electrode. When lower scanning speed, time for ion diffusion of electrolyte solution is abundant, so polarization voltage is small, and usage of active material is improved.

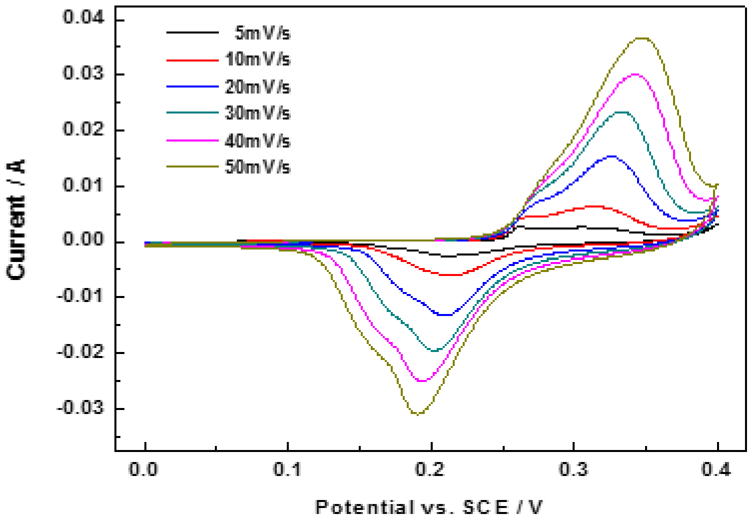

Figure 2. Cyclic voltammetry behavior of Zn-Al-LDH at different scan rates

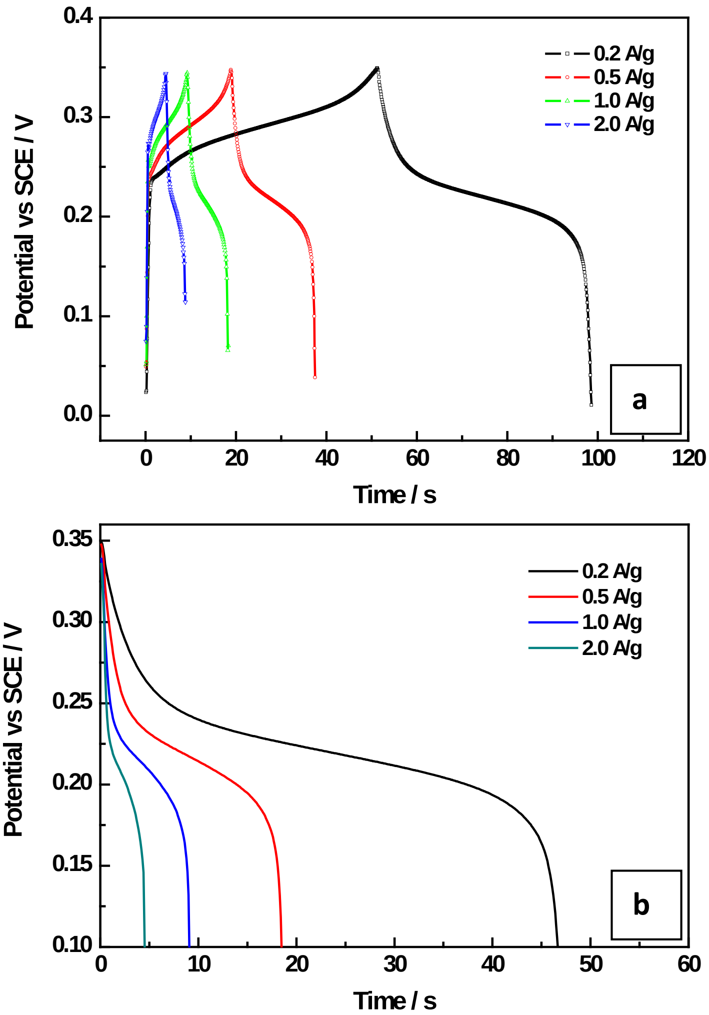

Figure 3. Galvanostatic charge-discharge curves of Zn-Al-LDH at various current densities

3.4. Charge and Discharge Curve of Zn-Al-LDH.

Figure 3 shows charge and discharge curve for Zn-Al-LDH electrode under different current density. It can be seen that the charge and discharge curve is nearly symmetrical hat (Figure 3a), which imply that Zn-Al-LDH electrochemical reaction on the surface of the electrode has a high degree of reversibility[3]. Charge and discharge platform appears near the voltage of 0.25 V. This nonlinear charge-discharge curve and charge and discharge platform is consistent with REDOX peak in CV test that further confirms the capacitance reaction on the electrode surface.

Through the discharge curve (Figure 3b), the ratio capacitance of the electrode is known to be 41.0, 39.7, 37.0, and 33.2 F/g at the current density of 0.2, 0.5, 1.0 and 2.0 A/g, respectively. The capacitance decreases slightly with the current density increasing. When the current increasing, active substances short in a period of time, adsorption of ions of active material and electrolyte interface, ion concentration to the electrolyte ion diffusion velocity cannot meet the transfer of electrode needed to charge and discharge ion number, causes the diffusion polarization between electrode and liquid interface increase.

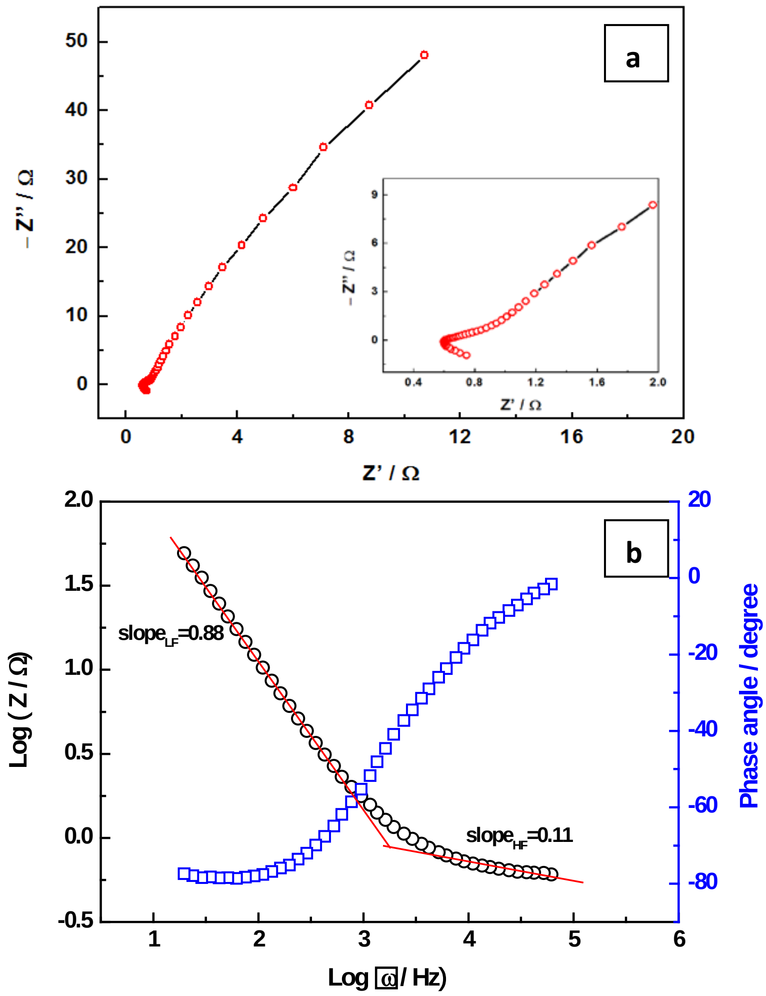

Figure 4. Nyquist (a) and Bode (b) plots of Zn-Al-LDH in 6 M KOH aqueous electrolyte

3.5. Electrochemical Communication Impedance (EIS) Test.

The ion and electron transmission capacity of Zn-Al-LDH electrode system are analyzed by electrochemical communication impedance (EIS) (Figure 4). The power output of the capacitor is closely related to the impedance of the electrode. The curve in the high frequency area forms a half circular, and in low frequency area an approximate linear form, embodies the good capacitance characteristic of electrode. High frequency area half arc curve on the x axis of the intercept the equivalent resistance of Rs is from electrochemical system (including the inherent resistance of substrate, ion resistance of the electrolyte solution and fluid collection and contact resistance of active material, etc.), semicircle diameter represents the interface between the electrodes and the electrolyte solution of the charge transfer resistance Rct. Through the Nyquist graph, the preliminary measure equivalent resistance Rs and the charge transfer resistance Rct about 0.6 and 0.6 Ω, respectively.

4. Conclusions

Zn-Al double layered hydroxide is synthesized by coprecipitation method. The sample is nanosheet-like powder and with about 80 nm thickness. The composition of Zn-Al-LDH is $Zn_6A_{l2}(OH)_{16}CO_3.4H_2O$ and belongs to Rhombohedral crystallographic system. Pure Zn-Al-LDH nanocomposites achieves a specific capacitance of 37.0 F g^{-1} at the current density of 1.0 A/g.

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