Effect of Sm-doped Ni-Al layered double hydroxide on electrochemical performance for supercapacitors

Sijing Shen¹, Weimin Guo¹*, Wei Zhuang¹, WenJuan Yang¹, Liping Qin¹,², Xinmei Liu¹ and Zhiwen Yue¹

¹College of Biological and Chemical Engineering, Guangxi University of Science and Technology, Liuzhou, People’s Republic of China
²Department of Graduate Affairs, Guangxi University of Science and Technology, Liuzhou, People’s Republic of China
*Author to whom any correspondence should be addressed.
E-mail: guoweimin8@163.com

Abstract: Sm-doped Ni-Al layered double hydroxides (LDHs) were successfully prepared via hydrothermal-assisted coprecipitation method. The structure and surface morphology of the samples were characterized by X-ray diffractometer (XRD), Fourier transform infrared spectrometer (FT-IR) and scanning electron microscope (SEM). The electrochemical performance of the samples as prepared was measured by cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy (EIS). These results show that Sm-doped Ni-Al LDH exhibit higher specific capacitance 2177 F·g⁻¹ at a current density of 1 A·g⁻¹, compared with pure Ni-Al LDH with a specific capacitance 1312 F·g⁻¹ at same current density.

1. Introduction
With the depletion of fossil fuels and the increasing pollution of the environment, people urgently need to develop green and pollution-free renewable power sources to meet the needs of their life and production [1]. But renewable power sources are not spontaneous, so it is necessary to develop efficient energy storage devices to store it for use [2]. Supercapacitors, a new type of energy storage equipment, receive wide attention due to their significant advantages including high power density, medium energy density and long cycling lifetime [3], etc. Supercapacitors can be classified into two types according to different energy storage mechanisms: electric double-layer capacitors (EDLCs) and Faraday pseudocapacitors. Among them, the energy densities of the pseudocapacitors are better than that of EDLCs, because the pseudocapacitors obtain a high specific capacitance through a fast and reversible Faraday reactions [4].

Transition metal layer double hydroxides (LDHs) are known as one of the most significant pseudocapacitor electrode materials owing to the advantages of excellent anion insertion and exchange capacity, high capacitance, fast redox reaction and environmental friendliness [5]. Among the all LDHs, Ni-Fe LDH, Ni-Al LDH and Ni-Co LDH [6–8] are the most widely studied pseudocapacitor active materials due to the adjustable chemical composition and the high redox activity [9]. But due to the agglomeration phenomenon of LDHs, the intrinsic conductivity is poor, which affects the transmission rate of ions and electrons, resulting in low conductivity and poor stability [5,10,11]. However, the chemical reaction kinetics can be effectively adjusted by doping and hybridizing other
elements to improve the electrochemical performances of the electrode materials [12]. Vanadium-doped nickel-cobalt layered double hydroxide nanosheet arrays (NCV-LDH NSAs) with a high capacitance of 2960 F·g⁻¹ at 1 A·g⁻¹ were successfully synthesized by Wu et al [13]. Compared with Ni-Co LDH (1784 F·g⁻¹ at a current density of 1 A·g⁻¹), it has more excellent electrochemical performances. Rare earth doping has a wide range of applications in the field of advanced energy storage, such as lithium/sodium ion batteries, lithium-sulfur batteries, supercapacitors, nickel-zinc batteries and so on. Facts have proved that the large radius and complex coordination of rare earth ions will cause obvious distortion of the crystal lattice of the electrode materials, forming smaller crystallites [14]. The electrode materials containing rare earth ions can provide higher volumetric energy density because of the reduction of charge transfer resistance and the increase of electrical conductivity [15]. Chuai et al. fabricated cerium doped CuS as supercapacitor electrode via the diffusion control and trapped dopant methods. After doping 0.86% of cerium, the capacitance increased from 956 F·g⁻¹ to 2853 F·g⁻¹ and it has excellent rate performance [16]. Mane et al. prepared lanthanum doped manganese oxide @ graphene oxide composite via facile, inexpensive and binder free successive ionic layer adsorption and reaction. As a high energy density electrode materials, it has 729 F·g⁻¹ electrochemical specific capacitance at the scan rate of 5 mV·s⁻¹ and exhibits 94% capacitive retention over 5000 CV cycles [17].

In the present work, Ni-Al LDH and different ratio Sm doped Ni-Al LDH electrodes are prepared via hydrothermal-assisted coprecipitation method. The effects of Sm doping on the structure, morphology and electrochemical properties of Ni-Al LDH were studied.

2. Experimental

2.1. Synthesis of Ni-Al-Sm LDH

All the reagents in this work were of analytical grade and used without further purification. Water used in the synthesis and washing was deionized. Ni-Al-Sm LDH compounds were prepared by a method of hydrothermal-assisted coprecipitation. In a typical procedure, 100 mL of the nitrate salts (Ni(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O and Sm(NO₃)₃·6H₂O) solution were prepared with a total cationic concentration of 0.1 mol·L⁻¹, Ni/(Al+Sm) mole ratio keep a constant 3. The mole ratio of Sm/Al were 0, 0.05, 0.1, 0.2, and 0.3, respectively. An aqueous solution of NaOH was added dropwise into the above solution with vigorous stirring to adjust the pH≈9.0. The suspension was magnetically stirred for 60 min at room temperature, then transferred to an autoclave and heated at 120 °C for 10 h. The resulting products were filtered and washed with deionized water and ethyl alcohol, dried at 50 °C to a constant weight. The samples obtained were labeled as the SA0, SA0.05, SA0.1, SA0.2 and SA0.3, respectively.

2.2. Structure characterization

The crystal structure of the powders were characterized by a X-ray diffractometer (XRD, DX-2700) with Cu Kα radiation (λ=1.5418 Å). The scans were performed in the 2θ ranging from 10–90° with a step of 0.03° and a scanning rate of 4°·min⁻¹. Fourier-transform infrared (FT–IR) spectroscopy of the materials as prepared was performed on a Nicolet 5700 spectrophotometer in the range 400–4000 cm⁻¹ using KBr pellets as standards. The morphology of the synthesized powders and the microstructure of the electrodes were performed using a Zeiss SIGMA field emission scanning electron microscopy (SEM).

2.3. Preparation of the electrodes and electrochemical tests

The working electrodes were prepared as follows: 75 wt% LDH powder, 10 wt.% graphite, 10 wt.% acetylene black and 5 wt% Polytetrafluoroethylene (PTFE) were well mixed and several drops of deionized water were added to make a homogeneous paste, Then the paste were coated on nickel foam (1 cm×1 cm). The electrodes were dried at 50°C and pressed under a pressure of 10 MPa. The LDH loaded on each electrode was about 10 mg.
All the electrochemical measurements were carried out using the CHI660D electrochemical workstation in a three-electrode system. 6 mol·L⁻¹ KOH as the electrolyte, Pt wire as the counter electrode (CE), SCE as the reference electrode (RE) and the prepared electrode as the working electrode (WE), respectively. The cell potential ranges of cyclic voltammetry (CV) tests were from −0.2 to 0.6 V. Galvanostatic charge/discharge (GCD) tests were carried out with different current densities in a voltage range of 0 to 0.4 V (vs.SCE). Electrochemical impedance spectroscopy (EIS) tests were made at open circuit potential with 5 mV amplitude in the frequency range of 0.1 Hz to 100 kHz.

3. Results and discussion
XRD patterns of Ni-Al LDH and Ni-Al LDH with different Sm doping levels are shown in Figure 1. All samples presented a typical layered structure that can be indexed to hexagonal Ni-Al LDH (PDF 22-0452). The characteristic diffraction peaks at 2θ=11.2°, 22.8° and 33.9° correspond to the (001), (002) and (100) planes, respectively. The d-spacing values of (001) plane and lattice parameters of the samples are summarized in Table 1. With the incorporation of Sm in the Ni-Al LDH, the values of d-spacing increased and lattice parameters changed. The results indicated that the Sm doped into the metal hydroxide layers. Moreover, the crystallinity of samples show that Sm doping in small quantity can improve the crystallinity of LDH.

The FT-IR of Ni-Al LDH and NI-Al LDH with different Sm doping levels are shown in Figure 2. These spectra show typical features of LDH. The absorption peaks obtained of all samples were similar. The broad peak around 3500 cm⁻¹ can be ascribed to the stretching vibration of O–H. The weak absorption peak near 1630 cm⁻¹ is due to the bending vibration of interlayer water [18]. The band at 1380 cm⁻¹ observed in all the samples is due to N–O stretching vibrations of nitrate ions [19]. Wide absorption bands at 450 to 800 cm⁻¹ belong to the O–M–O, M–O and M–O–M related vibrational modes of LDH [20].

![Figure 1. XRD patterns of the Ni-Al-Sm LDH.](image)

**Table 1. d(001) data and lattice parameters of Ni-Al-Sm LDH.**

| Samples  | d(001) (Å) | a=b (Å) | c (Å) | Crystallinity |
|----------|------------|---------|-------|--------------|
| SA0      | 7.875      | 3.044   | 7.850 | 72.7%        |
| SA0.05   | 7.878      | 3.044   | 7.852 | 73.1%        |
| SA0.1    | 7.881      | 3.045   | 7.865 | 73.5%        |
| SA0.2    | 7.908      | 3.048   | 7.908 | 70.6%        |
| SA0.3    | 8.006      | 3.053   | 7.972 | 70.4%        |
The SEM images of Ni-Al LDH and Ni-Al LDH with different Sm doping levels are shown in Figure 3 (a-e). From the SEM images, it can be seen that all samples display similar morphological features. It exhibits many small particles with layer-like structure agglomerated to form irregular shape particles. There is no obvious changes of the samples with the increasing Sm-doped. In order to investigate the situation of doping Sm in the LDH, energy dispersive spectroscopy (EDS) was applied to element analysis. Table 2 shows the atomic percentages of the Ni, Al and Sm element in Ni-Al-Sm LDH.

![Figure 2. FT-IR spectra of the Ni-Al-Sm LDH.](image)

![Figure 3. SEM images of the samples (a) SA0, (b) SA0.05, (c) SA0.1, (d) SA0.2, (e) SA0.3.](image)

| Samples | Ni/(Al+Sm) molar ratio | Sm/Al molar ratio |
|---------|------------------------|------------------|
|         | Initial | Experimental | Initial | Experimental |
| SA0     | 3.00    | 2.917        | 0       | 0             |
| SA0.05  | 3.00    | 3.227        | 0.05    | 0.034         |
| SA0.1   | 3.00    | 2.447        | 0.1     | 0.057         |
| SA0.2   | 3.00    | 3.199        | 0.2     | 0.166         |
| SA0.3   | 3.00    | 2.845        | 0.3     | 0.215         |
The electrochemical properties evaluation of the Sm-doped Ni-Al LDH electrode materials were performed by CV, GCD and EIS in a three-electrode system with 6 mol L\(^{-1}\) KOH aqueous electrolyte. The CV curves at a scan rate of 1 mV s\(^{-1}\) of Ni-Al-Sm LDH electrodes are shown in Figure 4. Each CV curves of Ni-Al-Sm LDH materials exhibits a pair of well-defined redox peaks, which come from the redox reactions as known as pseudocapacitance. The redox reactions during charge/discharge progresses correspond to the conversion between different oxidation states of Ni as follows:

\[
2\text{Ni(OH)}_2 + \text{OH}^- \leftrightarrow \text{NiOOH} + \text{H}_2\text{O} + e^-
\]  

(1)

From the CV curves in Figure 4, it is evident that the shape of all the samples is similar at 1 mV s\(^{-1}\). Moreover, the integral areas of CV curves can use to evaluate the capacitance performance [21]. A comparison of the pure electrode was made with the doped electrodes which are plotted where it can be seen that the largest integral area is obtained for SA0.1, indicating SA0.1 has the highest value of capacitance.

![Figure 4. CV curves of the Ni-Al-Sm LDH at a scan rate of 1 mV s\(^{-1}\) in 6 mol L\(^{-1}\) KOH.](image)

In order to further evaluate the electrochemical performance of the Ni-Al-Sm LDH, GCD tests were carried out in the potential window of 0−0.4 V (vs.SCE) at a current density of 1 A g\(^{-1}\) and the first discharge curves are shown in Figure 5a. It can be seen that the discharge curves of the Ni-Al-Sm LDH are divided into two parts: a fast potential drop (0.4 V−0.2 V) and a nonlinear potential drop (0.2 V−0 V). The initial drop results from internal resistance, and the latter represents the pseudocapacitance of the electrodes [22]. The specific capacitances of the active materials were calculated according to the equation:

\[
C_m = \frac{I \times \Delta t}{m \times \Delta V}
\]

(2)

where \(C_m\) (F g\(^{-1}\)) is the specific capacitance, \(I\) (A) is the discharge current, \(m\) (g) is the mass of the active materials, \(\Delta t\) (s) is the discharge time and \(\Delta V\) (V) is the total potential deviation, respectively. The calculated specific capacitances of SA0, SA0.05, SA0.1, SA0.2, and SA0.3 electrodes were 1312, 1672, 2177, 1588, and 785 F g\(^{-1}\), respectively. SA0.1 electrode exhibited the maximum specific capacitance at 1 A g\(^{-1}\). The results are consistent with CV tests. It can be attributed to the high proton diffusion rate through the lattice caused by Sm doping [23,24]. Figure 5b exhibits the calculated specific capacitances of the samples at different current density. It can be seen that all samples have higher specific capacitance at low current density. This is because that at low current density, more of the active surface area of electrodes can contact well with the electrolyte ions, leading to complete use of the active materials [25,26]. Figure 5c shows the cycling life tests of SA0 electrode and SA0.1 electrode at a current density of 1 A g\(^{-1}\) in 6 mol L\(^{-1}\) KOH electrolyte. It can be seen that each electrodes have an obviously activation process before reach the highest specific capacitance, and the specific capacitance of electrodes began to degrade after the maximum. At the beginning of the cycle test, the capacitance increasment of the electrode is attributed to the activation of active materials, and the following the capacitance degradation of the electrode material may be attributed to the
transformation from LDH to $\beta$-Ni(OH)$_2$ during the charge/discharge process [27]. In the first 90 cycles, the specific capacitance of each electrodes degraded obviously. After that, the values gradually stabilized at a slant plateau. After 300 cycles, the specific capacitance of SA0 electrode and SA0.1 electrode maintains 35.1% and 51.7%, respectively. It is worth mentioning that the low cycle life may cause by redox kinetics and limited by the rate of mass diffusion and electron transfer [24,28‒30].

Figure 5d shows the discharge curves with the highest specific capacitances of SA0 and SA0.1 at 1 A·g$^{-1}$. The calculated specific capacitances were 1800 and 2260 F·g$^{-1}$ respectively, which corresponds to the cycling life tests exhibited in Figure 5c.

The Nyquist plots as obtained by EIS studies are shown in Figure 6 in which the first panel plots the imaginary part of the impedance against its real part for both the undoped and different Sm doped electrodes. In the Nyquist plots, the electrodes represent a similar straight line at lower frequency, which represents the similar electrolyte diffusion impedance [31]. Five small semicircles can be observed at high frequency region, the diameter of semicircle stood for the charge-transfer resistance caused by the faradic reaction and the double-layer capacitance on the electrode surface [32]. In addition, the intercept at real part ($Z$) is a combinational resistance of ionic resistance of electrolyte, intrinsic resistance of substrate and contact resistance at the active materials/current collector interface [33]. The results indicat that SA0.1 electrode showed the best electrochemical capacitive performance than other electrodes.

Figure 5. The first discharge curves of Ni-Al-Sm LDH electrodes in 6 mol·L$^{-1}$ KOH at 1 A·g$^{-1}$ (a), specific capacitances of Ni-Al-Sm LDH electrodes at different current density (b), charge/discharge cycling performance of SA0 and SA0.1 at 1 A·g$^{-1}$ (c), and GCD curves for SA0 and SA0.1 at 1 A·g$^{-1}$ (d).
4. Conclusion
Ni-Al-Sm LDHs were prepared by a method of hydrothermal-assisted coprecipitation. The electrochemical effect of the contents of Sm has also been investigated. Ni-Al LDH with Sm doping in small quantity have better electrochemical performance than pure Ni-Al LDH. The SA0.1 electrode exhibited highest specific capacitance of 2260 F·g⁻¹ at 1 A·g⁻¹ current density after an activation process. The enhancement of electrochemical performance is due to the high proton diffusion rate through the lattice and a low charge transfer resistance caused by Sm doping. This study demonstrates rare earth elements doped LDH have a promising future as electrode materials for supercapacitors.

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