Electrochemical Properties of Zn–Al–La Layered Double Hydroxides in Zn–Ni Secondary Batteries

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ABSTRACT: Zn–Al–La layered double hydroxides (LDHs) were prepared by the hydrothermal method and used as a new anodic material for Zn–Ni secondary batteries. The morphology and microstructure of Zn–Al–La-LDHs were analyzed by Fourier transform infrared, X-ray diffraction (XRD), and scanning electron microscopy (SEM). The electrochemical properties of Zn–Al–La-LDHs as negative electrode materials for Zn–Ni batteries were studied by the cyclic voltammetry, Tafel polarization curve, and constant current charge–discharge test. XRD and SEM analysis showed that the crystallinity of the prepared Zn–Al–La-LDHs was good and the dispersion was uniform and showed regular hexagonal structures. The results of electrical properties show that Zn–Al–La-LDHs have good cycle reversibility and corrosion resistance when applied to Zn–Ni secondary batteries. The analysis of galvanostatic charge–discharge measurement results shows that the Zn–Al–La-LDH electrode has excellent cycle stability and charge–discharge characteristics. After 150 cycles, the cycle retention rate can reach 91.63%.

INTRODUCTION

In recent years, more and more attention has been paid to the Zn–Ni alkaline secondary battery, which has become a powerful candidate for the next generation of electric vehicles with its unique performance. Compared with other secondary batteries, the Zn–Ni alkaline secondary battery has the advantages of high energy, high power density, high open circuit voltage, excellent low-temperature performance, and low toxicity, and its nickel positive electrode also has the characteristics of long cycle life.1–3 However, the zinc–nickel battery has been greatly limited in commercialization and practical application. Compared with other secondary batteries, such as lithium-ion batteries, zinc–nickel alkaline secondary batteries perform poorly in cycle life, which is also the biggest obstacle to its commercialization. The main reason for the disadvantage of the zinc–nickel battery is the zinc electrode. The deformation, dendrite generation, passivation, self-corrosion, and self-discharge of the zinc anode will occur in the charge–discharge cycle. These problems will lead to the high solubility of the discharge products of the zinc anode in the alkaline electrolyte and the uneven deposition of zinc active substances on the surface of the zinc electrode, which will affect the cycle life of the Zn–Ni battery.4–6 For these problems of zinc electrodes, researchers have carried out a lot of research work, such as adding some additives in the electrolyte or zinc anode, modifying zinc oxide, and using calcium zincate as the negative active material. These research studies have improved the cycle performance of the zinc–nickel battery to some extent but still failed to meet the expectations.7,8 Therefore, it is necessary to find a new type of negative electrode material for the zinc–nickel battery to further improve its cycle life and electrochemical performance.

Layered double hydroxides (LDHs) belong to a class of ionic lamellar compounds which is composed of the positively charged metal hydroxide layer and negatively charged anion or anion group. The metal hydroxide is relatively arranged on the surface, and the anion or anion group is located in the interlayer, and the general formula is \([\text{M}^{II}]_x\cdot\text{M}^{III}_y\cdot(\text{OH})_z\cdot(n\text{H}_2\text{O})\), in which \(\text{M}^{II}\) is a divalent metal cation, \(\text{M}^{III}\) is a trivalent metal cation, and \(A^-\) is an anion or anion group, which is very similar to the structure of brucite \((\text{Mg(OH)}_2)\).9,10 In the past research on LDHs, it has been found that two or three other metal ion radii which are similar to \(\text{Mg}^{2+}\) and \(\text{Al}^{3+}\) can have different functional properties. In addition, different anions or anionic groups between layers can also make it have different properties, so it can be applied in different fields. At present, some special layered hydroxide materials have been used in many aspects,
including catalysts, ion conductivity, adsorbents, and anion exchange. Moreover, hydroxides have good stability in alkaline solution, so there have been some research studies on the electrochemical performance of LDHs in alkaline secondary batteries. Some researchers have applied Zn−Al-LDHs to the zinc electrode of the zinc−nickel battery as a negative material. The research results show that Zn−Al-LDHs, as the negative active material of Zn−Ni batteries, have good reversibility and excellent electrochemical cycle stability. However, Zn−Al-LDHs have low conductivity, and to a large extent, it inhibits the electron transfer rate of electrode reaction. Therefore, in order to improve its electrochemical performance, Zn−Al-LDHs should be further modified.

### EXPERIMENTAL SECTION

**Preparation of Zn−Al−La-LDHs.** Zn−Al−La-LDHs are prepared by the hydrothermal method. The experiments are as follows: Zn(NO₃)₂ (analytically pure), Al(NO₃)₃ (analytically pure), and La(NO₃)₃ (analytically pure) are dissolved in a reaction kettle at 100 °C which is aged for 24 h; then, it is filtered, put into the drying oven, and dried for 12 h at 60 °C to obtain ZnO. The prepared ZnO negative electrode, nickel positive electrode, and carbon paper separator were put into an ultrasonicator for 10 min. A three-port reaction kettle equipped with a water jacket, a condenser, and a magnetic stirrer was used. In a four-neck reaction kettle, NaOH solution (analytically pure), Al(NO₃)₃ (analytically pure), and La(NO₃)₃ (analytically pure) were used as precipitants, in which the ratio of Al to La is controlled to about 10. After the reaction, we continue to control the pH value of the reaction system to slowly drop the mixed salt solution and the mixed alkali bath temperature is kept at 60 °C. The lower waveband of 400−800 cm⁻¹ belongs to the layered skeleton structure of hydrotalcites, which is attributed to the stretching of Al−OH bonds. The vibration peaks at 1600 cm⁻¹ and 3448 cm⁻¹ are mainly due to the lattice vibration of carbonate (CO₃)²⁻ and the bending vibration of O−H bonds, respectively. The vibration peak near 3448 cm⁻¹ is due to the lattice vibration of hydroxides (OH−) groups.

The Zn−Al−La-LDH working electrodes were prepared by casting a homogeneous slurry of the active material (80 wt %), conductive carbon black (5 wt %), zinc powder (6 wt %), sodium carboxymethyl cellulose (4 wt %), and polytetrafluoroethylene (5 wt %) on copper (Cu) screen. It was dried in a vacuum drying oven at 60 °C for 12 h, pressed into pieces with a tablet press under 30 MPa pressure, and then cut into 8 cm × 8 cm size to obtain zinc negative plates. Each negative plate gains about 4.5 g of the active substance. The preparation method of the Zn−Al-LDHs electrode is the same as above. The prepared zinc negative electrode, nickel positive electrode (size: 12 cm × 10 cm × 0.50 mm), and diaphragm were assembled into a simulated battery. The electrolyte was a saturated ZnO solution of 6 mol/L KOH + 1 mol/L LiOH.

**Characterization and Performance Test of Samples.** Fourier transform infrared (FT-IR) spectroscopy of the samples was conducted on a Nicolet iSS50 FT-IR spectrometer (as KBr discs with a wavenumber of 400−4000 cm⁻¹ and a resolution of 0.09 cm⁻¹). The phase composition and crystal structure of Zn−Al−La-LDH samples were characterized using X-ray diffraction (XRD). XRD patterns of samples were recorded using an X′pert 3 powder diffractometer (40 kV, 40 mA) using Cu Kα radiation at a scanning rate of 2θ = 8° min⁻¹. Moreover, the microstructure of the samples was observed using a HITACHI X-650 scanning electron microscope. Using the CT2001a LAND battery test system to test the assembled simulated battery, we charge it for 10 h at a constant current of 0.1 C, discharge it to 1.4 V cutoff voltage at room temperature two to five times, then charge it for 10 h at 0.1 C, and discharge it to 1.2 V at 0.2 C. The electrochemical performance of the zinc electrode was tested using a PGSTAT302N electrochemical workstation of Vantone, Switzerland. The scanning range of cyclic voltammetry (CV) curve was −1.9 to −0.8 V, and the scanning speed was 1 mV/s. The calomel electrode and platinum electrode were used as the reference electrode and auxiliary electrode, respectively. The electrolyte was 6 mol/L KOH + 1 mol/L LiOH-saturated ZnO solution.

### RESULTS AND DISCUSSION

**Infrared Spectrum Analysis of Zn−Al−La-LDHs.** It can be seen from Figure 1 that the FT-IR spectra of Zn−Al−La-LDHs and Zn−Al−La-LDHs with different aluminum−lanthanum ratios: (A): Zn/Al = 3, (B): Al/La = 9, (C): Al/La = 4, and (D): Al/La = 1.5.

[Figure 1. FT-IR spectra of Zn−Al-LDHs and Zn−Al−La-LDHs with different aluminum−lanthanum ratios: (A): Zn/Al = 3, (B): Al/La = 9, (C): Al/La = 4, and (D): Al/La = 1.5.]

LDHs and Zn−Al-LDHs with different Al to La ratios are very similar. In Figure 1, the peak near 3448 cm⁻¹ can be seen that it is caused by the stretching of metal ions connected with OH− groups. The vibration peak of interlayer water appears at 1600 cm⁻¹, and the asymmetric stretching vibration of O−C−O appears at 1300 and 1500 cm⁻¹. Compared with other (such as CaCO₃) CO₃²⁻, the displacement absorption peak at 1365 cm⁻¹ is lower, which indicates that there is a strong hydrogen bond between CO₃²⁻ and H₂O.
basically the same as that of hydrotalcites without the La element. Therefore, it is certain that lanthanum has been successfully introduced into the lattice of hydrotalcites.

**XRD Analysis of Zn–Al–La-LDHs.** Figure 2 shows the XRD patterns of Zn–Al-LDHs and Zn–Al–La-LDHs.

As shown in Figure 2, the diffraction peaks of Zn–Al–La-LDHs (2θ = 11.72, 23.56, 34.56, and 61.2°) correspond to (003), (006), (009), and (110), which can also be seen in the diffraction peaks of Zn–Al-LDHs. At the same time, the diffraction peak is sharp, is narrow, is symmetrical, and has a low baseline, which indicates that the crystallinity of the sample is good, and the highest diffraction peak appears at 2θ = 11.72°, which indicates that the Zn–Al–La-LDH is a kind of highly crystalline hydrotalcite compound with a typical hexagonal crystal structure. The XRD patterns of Zn–Al–La-LDHs with different Al to La ratios are similar to those of Zn–Al-LDHs, which shows that Zn–Al–La-LDHs can be successfully synthesized using different Al to La ratios. The diffraction peaks of C are sharper than those of B and D, which indicates that Zn–Al–La-LDHs with an Al to La ratio of 4 has higher crystallinity and a complete crystal structure.

**SEM Analysis of Zn–Al–La-LDHs.** Figure 3 shows scanning electron microscopy (SEM) images of Zn–Al-LDHs and Zn–Al–La-LDHs with different Al to La ratios. It can be seen from the figure that the samples of Zn–Al-LDHs and Zn–Al–La-LDHs are both hexagonal and lamellar, which is the characteristic structure of hydrotalcites, and the addition of appropriate La does not destroy the original structure of Zn–Al-LDHs. Observing Figure 3b–d, from the dispersion degree, it is found that Figure 3c shows that they are more evenly dispersed without agglomeration, while Figure 3b,d shows that some of them are agglomerated, and the dispersion degree is not as good as Figure 3c, indicating that Zn–Al–La-LDHs with an aluminum to lanthanum ratio of 4 has better crystallinity, and most of the particle size diameter is about 200 nm, and the particle thickness is relatively small.

The SEM images of Zn–Al-LDH and Zn–Al–La-LDH electrodes after 100 charge/discharge cycles are illustrated in Figure 3e,f, respectively. After 100 charge/discharge cycles, obvious shape change and a significant amount of dendrite growth occurred at the electrode/electrolyte interface, originating from the inhomogeneous nucleation and nonuniform polarization. One should note that the irregular impurities, present in Zn–Al-LDHs, prohibit the maintenance of the initial shape and facilitate the dendrite growth (Figure 3f). On the other hand, the Zn–Al–La-LDH electrode maintained the plate-like shape after 100 charge/discharge cycles and did not exhibit a large polarization and dendrite growth, as shown in Figure 3e. Therefore, the Zn–Al–La-LDH electrodes exhibited dendrite-free deposition, outstanding rate capability, and excellent cyclic stability within 150 cycles as compared to the Zn–Al-LDH electrode.

**Cyclic Voltammetric Analysis of the Zinc Electrode.** In order to further study the electrochemical reaction of Zn–Al-LDHs and Zn–Al–La-LDHs with different Al to La ratios in charge–discharge cycle, 10 CV tests were carried out on the prepared zinc electrode, and the test results are shown in Figure 4. The 10th cyclic voltammetric curve of Zn–Al-LDHs and Zn–Al–La-LDHs with different Al to La ratios is shown in the figure. It can be seen from the figure that the current response occurs between −1.9 and −0.8 V. In the cathode area, the peak potential of the electrode successively appears at −1.693, −1.642, −1.591, and −1.624 V, corresponding to Zn–Al-LDHs (code A, with a molar ratio of Zn/Al = 3), Zn–Al–La-LDHs (code B, with a molar ratio of Al/La = 9), Zn–Al–La-LDHs (code C, with a molar ratio of Al/La = 4), and Zn–Al–La-LDHs (code D, with a molar ratio of Al/La = 1.5). Compared with the peak potential of the Zn–Al-LDH electrode, the peak potential correction of the Zn–Al–La-LDH electrode, and the fact that the more positive the peak potential means the higher the electrochemical kinetics in the reduction process, we can obtain that the performance of Zn–Al–La-LDHs in the electrochemical kinetics is better and the
charging process efficiency is higher, in which the peak potential corrosion of B and D and the gap between them are very small, almost negligible. In the anode region, the peak value of the C electrode appears at −1.173 V, while that of B and D electrodes appears at −1.082 and −1.095 V, respectively, and it can be seen that the difference between B and D is not big, while the anode peak of the A electrode appears at −1.116 V, and the anode peak of A, B, and D electrodes is larger than that of the C electrode. Generally, the lower anode peak means that the zinc electrode has higher electrochemical activity, so it can be seen that the electrochemical activity of the Zn−Al−La-LDH electrode is larger than that of Zn−Al-LDHs. The potential difference between the cathode peak value and the anode peak value of C and D electrodes is smaller among the four electrodes. The smaller the difference between the cathode peak value and the anode peak value, the greater the reversibility of the electrodes. Therefore, in the reversibility of the electrode materials, C is undoubtedly better. That is to say, the Zn−Al−La-LDH electrode with an aluminum to lanthanum ratio of 4 has better cycle reversibility.

**Tafel Curve Analysis of the Zinc Electrode.** In order to understand the influence of Zn−Al−La-LDHs on the polarization and corrosion behavior of the zinc electrode, the Tafel curve of the prepared zinc electrode was tested. The test results are shown in Figure 5. The electrochemical dynamic parameters obtained from the Tafel curve of the zinc electrode are listed in Table 1, including corrosion potential $E_{corr}$ and corrosion current density $j_{corr}$.

![Figure 4](https://example.com/figure4.png) **Figure 4.** CV curves of Zn−Al-LDH and Zn−Al−La-LDH electrodes with different aluminum−lanthanum ratios: (A): Zn/Al = 3, (B): Al/La = 9, (C): Al/La = 4, and (D): Al/La = 1.5.

![Figure 5](https://example.com/figure5.png) **Figure 5.** Tafel polarization curves of Zn−Al-LDHs and Zn−Al−La-LDHs with different aluminum−lanthanum ratios: (A): Zn/Al = 3, (B): Al/La = 9, (C): Al/La = 4, and (D): Al/La = 1.5.

| $E_{corr}$ (V) | $j_{corr}$ (mA cm$^{-2}$) |
|---------------|--------------------------|
| A             | $-1.42$                   | $4.71 \times 10^{-2}$ |
| B             | $-1.41$                   | $3.15 \times 10^{-2}$ |
| C             | $-1.38$                   | $2.21 \times 10^{-2}$ |
| D             | $-1.39$                   | $2.94 \times 10^{-2}$ |

Table 1. Zn−Al-LDH and Zn−Al−La-LDH Tafel Polarization Curve Data of Different Aluminum−Lanthanum Ratios: A: Zn/Al = 3, B: Al/La = 9, C: Al/La = 4, and D: Al/La = 1.5.

Obviously, the corrosion potential of the Zn−Al−La-LDH zinc electrode in Figure 5 is significantly positive compared to that of the Zn−Al-LDH zinc electrode: Zn−Al-LDHs (code A, with the molar ratio of Zn/Al = 3), Zn−Al−La-LDHs (code B, with the molar ratio of Al/La = 9), Zn−Al-LDHs (code C, with the molar ratio of Al/La = 4), and Zn−Al−La-LDHs (code D, with the molar ratio of Al/La = 1.5). The $E_{corr}$ of the sample appears at −1.42, −1.41, −1.38, and −1.39 V, and among them, the C electrode has the most positive corrosion potential, as can also be seen from Table 1. Among the four, it has the lowest corrosion current, that is, it has the best corrosion resistance. In the principle of electrochemical corrosion, the corrosion potential $E_{corr}$ plays a vital role in electrode corrosion. The more negative the corrosion potential $E_{corr}$, the greater the corrosion degree, and the other data $j_{corr}$ indicate the corrosion rate, and the larger the value, the faster the corrosion rate and the smaller the value of $j_{corr}$, which means better corrosion resistance. Therefore, it can be concluded that the C electrode has the best corrosion resistance among the four.

The relationship between corrosion current density $j_{corr}$ and electrode potential can be expressed as follows

$$j_{corr} = j_{0,c} \exp \left( \frac{E_{c,c} - E_{c,a}}{\beta_c + \beta_e} \right)$$

When other parameters are the same or similar, $E_{c,c} - E_{c,a}$ decreases, the value of $j_{corr}$ will also decrease, $E_{c,c} - E_{c,a}$. When the value of $j_{corr}$ increases, the value of $E_{c,c}$, will also increase. Therefore, the lower $j_{corr}$ will improve the corrosion resistance. These data show that the Zn−Al-LDHs doped with La can improve the corrosion resistance of the zinc electrode. The addition of La will make the polarization of the electrode smaller, resulting in the positive movement of the corrosion potential $E_{corr}$, which is consistent with the Tafel curve test results in Figure 5.

**Analysis of the Cycling Performance of the Zn−Al−La-LDH Electrode.** In Figure 6, the discharge capacity of the Zn−Al-LDH electrode and Zn−Al−La-LDH electrode with different Al to La ratios changes with the number of cycles. The prepared zinc electrode has been tested for 150 charge−discharge cycles. It can be seen from the figure that in the previous cycles, the capacity of the electrode is low because the...
active substance in the zinc electrode is not fully activated. With the charge−discharge cycle, the active substance in the zinc electrode is gradually fully activated, and the discharge capacity of the zinc electrode returns to the normal value. Although the initial discharge capacity of the Zn−Al-LDH electrode is very high (code A, 399.8 mA h g\(^{-1}\)), after 35 cycles, the discharge capacity of the Zn−Al-LDH electrode began to decline rapidly and after 150 cycles, the discharge capacity has dropped to 314.86 mA h g\(^{-1}\) and the capacity retention rate (discharge capacity/initial discharge capacity) is 78.75%. Zn−Al−La-LDH electrodes with different Al to La ratios show relatively stable cycle stability in 150 cycles. The initial discharge capacity of Zn−Al−La-LDH electrodes with Al to La ratios of 9 (code B), 4 (code C), and 1.5 (code D) is 391.55, 390, and 391.23 mA h g\(^{-1}\), respectively, and the initial discharge capacity of Zn−Al−La-LDHs is slightly lower after the rare earth element La partially replaces the metal element Al because the molar mass of the rare earth element La is larger than that of the metal element. After 150 charge−discharge cycles, the discharge capacities of B, C, and D electrodes are 348.87, 357.34, and 344.26 mA h g\(^{-1}\), respectively. The cycle retention is 89.10, 91.63, and 87.99, respectively. It can be seen from the figure that the cycle stability of Zn−Al−La-LDHs with the rare earth element La partly replacing metal element Al can be improved obviously, and the effect of Zn−Al−La-LDHs with an aluminum to lanthanum ratio of 4 is the best.

Galvanostatic Current Charge−Discharge Characteristics of the Zinc Electrode. Figure 7 shows the charge−discharge cycle test curve of the 40th Zn−Al−LDH electrode and Zn−Al−La-LDH electrode with different Al to La ratios. In a complete charge−discharge cycle of the zinc electrode, the charge−discharge process can be expressed by the following two chemical formulas

charge process: \( \text{Zn(OH)}_4^{2-} + 2e \rightarrow \text{Zn} + 4\text{OH}^- \)

discharge process: \( \text{Zn} + 4\text{OH}^- \rightarrow \text{Zn(OH)}_4^{2-} + 2e \)

The curve in Figure 7 shows that compared with the Zn−Al−LDH electrode, the charge platform voltage of the Zn−Al−La-LDH electrode with different Al to La ratios is lower, and its discharge platform voltage is higher. It shows that the Zn−Al−La-LDHs with the rare earth element La partly replacing metal element Al can effectively improve the charge and discharge performance of Zn−Ni secondary batteries because La\(^{3+}\) tends to be reduced to La metal during activation. The uniform distribution of La between the layers helps to improve the contact between the active material and the collector and electrolyte, and the La metal can no longer be oxidized to La\(^{3+}\) during the cycle. Moreover, Al\(^{3+}\) cannot be reduced to Al, but stably. It exists in the zinc electrode and forms a stable layered frame structure. When La\(^{3+}\) is reduced to La, the La metal can be attached to the skeleton. The conductive system is formed in the layered structure, and the conductive network helps to improve the electricity and reduce the internal resistance of the zinc electrode. In addition, the charge platform voltage and discharge platform voltage of the Zn−Al−La-LDH electrode with different Al to La ratios are also different. It can be seen from the figure that the charge platform voltages of the Zn−Al−La-LDH electrode with Al to La ratios of 9 (code B), 4 (code C), and 1.5 (code D) are not different, and the lowest is the C electrode, and the C electrode has the highest discharge voltage in the discharge platform voltage. In the charge platform voltage and discharge platform voltage of the battery, the lower the charge platform voltage is, the more favorable it is to inhibit the generation of hydrogen, which can effectively improve the charge efficiency of the zinc−nickel secondary battery. The higher the discharge platform voltage, the better the discharge performance of the zinc−nickel secondary battery. Therefore, Zn−Al−La-LDHs with rare earth element La partly replacing metal element Al have better charge−discharge characteristics in Zn−Ni secondary batteries, in which Zn−Al−La-LDHs with an Al to La ratio of 4 have the best charge−discharge characteristics.

CONCLUSIONS

Zn−Al−La-LDHs prepared by the hydrothermal method have a hexagonal sheet structure and even dispersion. As the anodic material of the Zn−Ni secondary battery, its electrochemical performance is better than that of Zn−Al-LDHs. The results of CV and Tafel curves show that La doping can effectively improve the electrochemical activity and discharge voltage of Zn−Al-LDHs and reduce the polarization and charge voltage.
of Zn–Al-LDHs. Compared with Zn–Al-LDHs, Zn–Al–La-LDHs with different Al to La ratios, especially Zn–Al–La-LDHs with an Al to La ratio of 4, have better electrochemical performance. After 150 charge–discharge cycles, the specific capacity of Zn–Al–La-LDHs is 357.34 mA h g⁻¹, and the cycle retention rate can reach 91.63%. The research results of this work can provide some reference value for the later development of high-capacity and high-stability zinc–nickel secondary battery anode materials.

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