Study on Layered Double Hydroxide and Its Electrochemical Performance

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Abstract. The layered double metal hydroxide can be used as a battery cathode material with the advantages of good stability, easy synthesis and low price. This article mainly studies the electrochemical performance of Ruthenium-containing Fe-Ni layered double metal hydroxide as the cathode material of the battery. The experiment mainly adopts the hydrothermal method to prepare FeNiRu-LDHs, and further calcines them in an argon atmosphere at different temperatures to obtain FeNiRu-LDOs with different Ru concentrations at different temperatures. Through cyclic voltammetry curve and impedance analysis, temperature is used as a variable to determine the electrochemical performance of the material has been tested in groups, and it is found that the 20FeNi-LDO calcined at 450°C shows excellent electrochemical performance. XRD, RAMAN and SEM are further used to study the characterization properties of the sample, and it is found that the shape of Ru20FeNi-LDHs at 450°C is better. Meanwhile, the comprehensive electrochemical performance of Ru20FeNi-LDHs material is best.

Keyword: Layered double hydroxide; Electrochemical performance.

1. Introduction

With the increasing shortage of mineral energy and the severe situation of environmental problems, materials and devices with high-performance energy storage and conversion functions have been widely valued by everyone. In the process of energy development, can we make full use of natural energy: other forms of energy such as wind energy, tidal energy and solar energy are of great significance to whether they can solve environmental problems, but because these energy functions are not continuous in time, we want to large-scale to make full use of these natural energy, it is inseparable from the matching high-efficiency energy storage [1]. The battery, especially the secondary battery [2], is a device that can realize the mutual conversion of chemical energy and electric energy. If you want to use energy reasonably and effectively, you cannot do without the battery as a medium. Layered double hydroxides (LDHs) are new inorganic functional materials composed of two or more metal elements with a layered structure, interlayer ions, and a layered structure with exchangeable properties [3-4]. The chemical composition of layered double hydroxides (LDHs) and the properties of the compounds are very effective in determining its status in various applications [5].

Lithium-air battery has a high theoretical energy density and is environmentally friendly [6-7]. It is an important form of a new generation of secondary batteries and the most likely energy system used as
a power battery. Due to the rapid development of lithium-air battery research in recent years, some problems have been found to be solved, such as poor electrolyte stability, low battery charge and discharge efficiency and short cycle life, unstable positive electrode structure and metal negative electrode corrosion, unitary design of battery structure, etc [8].

In view of the above problems, this article mainly focuses on the research of positive electrodes in lithium-air batteries. The main research contents are: (1) Research status of layered double hydroxides; (2) The specific experimental steps of the NiFeRu-LDH precursor and the method to obtain the LDO of the NiFeRu-LDH calcined product; the influence of LDO as the cathode material of the lithium-air battery on the energy density, charge-discharge performance and cycle life of the battery; (3) Study its basic oxidation-reduction reaction (ORR) and oxygen evolution reaction (OER) characteristics, and use it in the positive electrode of lithium-air battery to improve battery performance [9].

2. Experimental

2.1. Pre-treatment of foamed nickel, carbon cloth, stainless steel mesh
Cut foam nickel, carbon cloth, and stainless steel mesh into a size of 1cm*1.5cm. Place the carbon in a tube furnace at 5°C/min to 800°C and keep it warm for 240min. Wash the foamed nickel, stainless steel mesh, and treated carbon cloth with ethanol, 1mol/L HCl, and deionized water in turn, and dry and weigh. And soak in ethylene glycol for 360min.

2.2. Preparation of LDHs
Add 0.3mmol Ni(NO3)2·6H2O, 0.3mmol Fe(NO3)3·9H2O, 2mmol urea, 15ml deionized water into the PTFE liner and stir for 180min, add ethylene glycol and stir for 30min, then put in the foam The nickel, carbon cloth, and stainless steel mesh were reacted at 120°C for 12 hours, and when cooled to room temperature, they were taken out, washed, dried, and weighed.

2.3. Preparation of LDO
Put the foamed nickel with Ru content of 0%, 10%, 20%, 30% in a tube furnace at a rate of 5°C/min to 350°C, 450°C, 550°C and hold for 240min to obtain the roasting of hydrotalcite The product LDO is weighed.

2.4. Material characterization test
UltimaIV X-ray diffraction (XRD) and DXR-2 Raman spectroscopy (Raman) were used to study the crystal structure and composition of the cathode material. The morphology and microstructure of the cathode were observed through a scanning electron microscope (JEOL 7600F ESEM). HI660E electrochemical workstation was used for impedance and cyclic voltammetry analysis. The impedance is 10000000Hz at high frequency and 0.1Hz at low frequency. Cyclic voltammetry uses a two-electrode method for cyclic voltammetry.

3. Results and discussion
Under hydrothermal conditions, adding urea and amine fluoride to uniformly generate Ru20% FeNiRu-LDHs on carbon cloth, stainless steel mesh and foam nickel respectively. Figure 1 shows the XRD patterns of carbon cloth, stainless steel mesh and foam nickel. It can be seen from the spectrum that the XRD pattern of foamed nickel shows the characteristic diffraction peaks of foamed nickel (at 44.5° and 51.8°) and the characteristic diffraction peaks of Ru (38.5°); there is no obvious characteristic peak on the carbon cloth, combined with the upper part After the analysis of the Raman spectrum on the right, the main component on the carbon cloth is still carbon. The conclusion is that even the treated carbon cloth is still not easy to adhere to the product LDHs; the spectrum of the stainless steel mesh has a weak diffraction peak except 11.8°. There are no characteristic peaks at 44.5° and 51.8°. By SEM shooting, the prepared FeNiRu-LDHs with 20% Ru are densely packed on the surface of the foamed nickel substrate, forming a relatively uniform nanostructure. Combining the SEM image and the Raman
spectrum (Figure 2), it can be seen that the FeNiRu-LDHs on the foamed nickel can grow and are relatively uniform; the main component on the carbon cloth is still carbon; the stainless steel mesh has a small amount of LDHs attached, and the adhesion is uneven.

In summary: Foam nickel is easier to adhere to the product LDHs than carbon cloth and stainless steel mesh, and is more suitable for in-depth research. In order to ensure that LDHs can be attached to the base, the next experiment will mainly use foamed Ni as the base.

![XRD spectra of Ru20FeNi-LDHs on different substrates.](image1)

**Figure 1.** XRD spectra of Ru20FeNi-LDHs on different substrates.

![Raman spectra and SEM pictures of Ru20FeNi-LDHs.](image2)

**Figure 2.** (a) Raman spectra of Ru20FeNi-LDHs on different substrate and (b-c) SEM pictures of Ru20FeNi-LDHs on Ni foam.

![XRD spectra of LDO.](image3)

Figure 3 shows the XRD spectra of LDO with different Ru content uniformly generated on the foamed nickel after calcination at 350°C. It can be seen from the figure that when LDO with different content of Ru is generated with foamed nickel as the base, the foamed nickel still maintains its original structure, and has its own characteristic diffraction peaks at 44.5° and 51.8°. The XRD spectrum of Ru20% has a diffraction peak at 14°, and the XRD spectrum of Ru0% has a diffraction peak at 14° and 17°. After analysis, these two diffraction peaks are the peaks of the glass substrate for measuring XRD. That is to say, there is no obvious difference in the XRD diagram, so I further analyzed the Raman
After comparing the standard diagram and analyzing the surface deposition of the material, it was found that when the Ru was 10% and 30%, the material was obviously uneven, that is, some LDOs fell off. Under the same reaction conditions of 350°C, the best condition is that the Ru content on the foamed nickel is 20%.

![Figure 3](image_url)

Figure 3. (a) XRD spectrum and (b) Raman spectrum of FeNiRu-LDO obtained at 350°C with different Ru content.

Figure 4 shows the XRD spectra of LDO with different Ru content uniformly generated on the foamed nickel after calcination at 450°C in this experiment. It can be seen from the figure that when LDO with different content of Ru is generated on the nickel foam substrate, the nickel foam still maintains the original structure, with its own characteristic diffraction peaks at 44.5° and 51.8°, without other obvious peaks, namely XRD. There is no obvious difference in the graph, so I further analyzed the Raman graph. After comparing the standard graph and analyzing the surface deposition of the material, it was found that when the material was 10RuFeNi-LDO and 30RuFeNi-LDO, the material was obviously uneven, that is, some LDOs fell off; In the case of 0RuFeNi-LDO, the LDO material formed on the surface is relatively uniform.

![Figure 4](image_url)

Figure 4. (a) XRD spectrum and (b) Raman spectrum of FeNiRu-LDO obtained at 450°C with different Ru content.
Figure 5 shows the XRD spectra of LDO with different Ru content generated on the foam Ni after calcination at 550°C. It can be seen from the figure that 44.5° and 51.8° of the XRD spectrum are the characteristic diffraction peaks of Ni foam without other obvious peaks. After further analysis of the Raman diagram, after comparing the standard patterns and analyzing the surface deposition of the material, it is found that 0RuFeNi-LDO, 10RuFeNi-LDO and 30, the material is obviously uneven, some of the LDO falls off and the material is not uniformly formed on the surface of the foamed Ni, that is, part of the foamed Ni is still exposed.

Based on the above analysis, it is concluded that the 20RuFeNi-LDO obtained at 450°C has the best material structure, and the formed LDO can be uniformly attached to the foam Ni.

![Figure 5. (a) XRD spectrum and (b) Raman spectrum of FeNiRu-LDO obtained at 550°C with different Ru content.](image)

Figure 6 shows the cyclic voltammetry curve (CV) of LDHs with different Ru contents at 450°C. It is found from the figure that the RuFeNi-LDO calcined at 450°C all have redox peaks, and the reduction peaks are located at 2.1-2.5V. The oxidation peaks are all located at 4.2-4.4V, indicating that RuFeNi-LDO with 10% and 20% Ru at 450°C have better ORR and OER performance. Since the electric capacity of the battery mainly comes from the oxidation-reduction reaction on the surface of the material, and the specific electric capacity of the electrode material is proportional to the closed area of the CV curve, since the curves of Ru30FeNi-LDO and Ru0FeNi-LDO are not closed, the comparison curve shows that Ru20FeNi- The curve of the LDO has a larger closed area, so the Ru20FeNi-LDO material has a higher specific capacitance at 450°C.

![Figure 6. CV diagram of RuFeNi-LDO with different Ru content at 450°C](image)
The semicircle in the high-frequency region of the EIS curve corresponds to the charge transfer impedance of the battery. The charge transfer impedance represents the ability to transfer electrons during the electrochemical reaction process, that is, the smaller the charge transfer impedance, the better the battery's conductivity. According to Figure 7 from the enlarged view of the semicircular area, it can be seen that Ru20FeNi-LDO has the smallest load transfer impedance at 450°C.

![Figure 7. EIS diagram of RuFeNi-LDO with different Ru content at 450°C](image)

4. Conclusion
In this paper, stainless steel mesh, carbon cloth and Ni foam are used as the substrates to attach LDHs with different Ru content, and then the products attached to the substrate are obtained by comparison. It is found that the products grown in situ on the Ni foam are uniform and moderate in thickness. Then the samples are appropriately cut and tested. First, through CV, EIS and other electrochemical performance tests, then selected suitable samples for XRD and RAMAN tests, and finally combined CV, EIS, XRD, RAMAN spectra to select a part of the samples for SEM testing. This experiment mainly studies the best material composition and electrochemical performance of LDOs with different temperatures and different Ru contents. The following conclusions are obtained through experiments and tests:

1) Nickel foam, carbon cloth and stainless steel mesh are used as the substrate of this experiment, and LDHs are attached under the same experimental conditions. Then, through the comparison of test results, it is found that more and even products are attached to Ni foam, that is, foam Ni is the substrate with good performance in this experiment.

2) Comparing the characterization results of LDOs obtained at different temperatures, it is found that the material structure of Ru20FeNi -LDO obtained at 450°C is reasonable, and the morphological characteristics are stable.

3) The electrochemical performance of the LDOs obtained at different temperatures are further compared. Through EIS, CV, it is found that the electrochemical performance of Ru20FeFei-LDOs obtained at 450°C is the best. Considering the material structure and electrochemical properties, Ru20FeNi-LDO obtained at 450°C is the best product obtained in this experiment.

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