

The Effect of Ni/Co Ratio on the Morphology and OER Performance of NiCo-LDH/NF

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Abstract: Electrochemical water splitting is a promising technology for the sustainable conversion, storage and transport of hydrogen energy. Finding earth-abundant, highly active and durable oxygen evolution reaction (OER) electrocatalysts to replace precious metal-based catalysts is of great significance for the large-scale application of water electrolysis. Designing electrodes with a large number of active sites and high specific surface area is an effective strategy to improve electrocatalytic performance. In this paper, a series of NiCo-LDH/NF catalysts with different nanoneedle morphologies were prepared by a simple hydrothermal method on a nickel foam (NF) conductive substrate by adjusting the molar ratio of nickel to copper (2:4, 4:4 and 8:4 mmol). The combination of layered double hydroxide (NiCo-LDH) and NF can ensure a larger active area and provide an effective new way for electron transfer. The formed self-supporting electrode has better OER performance. This work provides new insights into OER under alkaline conditions.

Keywords: Layered double hydroxide; Self-supporting electrode; Electrocatalysis; Oxygen evolution reaction.

1. INTRODUCTION

With the increasing global attention to climate change and energy security issues, the development and utilization of clean energy has become particularly important [1,2]. As a clean energy source, hydrogen has the characteristics of high efficiency and zero carbon emissions, and is considered to be an important direction for future energy transformation [3]. Hydrogen production by electrolysis of water is a process that decomposes water molecules into hydrogen and oxygen, which requires catalysts to accelerate the reaction. The cathodic hydrogen evolution reaction (HER) and the anodic oxygen evolution reaction (OER) are two key half reactions in the process of hydrogen production by electrolysis of water [4,5]. In particular, OER, because it involves a four-electron transfer process, usually requires a higher overpotential, which limits the efficiency of electrolytic water [6]. Although precious metal catalysts with high catalytic activity can effectively reduce the overpotential required for water electrolysis, the scarcity of precious metal materials is the reason for the high cost of water electrolysis technology and the main obstacle to the promotion of the technology [7]. To overcome this challenge, scientists are researching and developing new catalyst materials to improve the efficiency of OER and reduce the required overpotential.

At present, some promising OER catalysts, such as transition metal-based catalyst materials, are not only abundant in reserves and low in cost, but also exhibit diverse structures and excellent OER activity. The research and development of these materials are expected to achieve efficient and low-cost water electrolysis hydrogen production technology in the future, thus promoting the wide application of clean energy [8]. In recent years, transition metal hydroxides have become electrochemical electrode materials due to their excellent electrocatalytic activity and controllable synthesis [9,10]. Among various transition metal hydroxides, nickel hydroxide and copper hydroxide have attracted much attention due to their good stability, low cost and simple preparation [11]. However, it also has the disadvantages of low electronic conductivity and poor electron transfer rate in the electrochemical reaction process [12]. Liu et al. [13] synthesized Ni(OH)₂ nanosheets with a thickness of 20~100 nm by hydrothermal method, which requires an overpotential of 308 mV at a current density of 10 mA cm⁻² in 1.0 M KOH. Ultrathin nickel hydroxide nanosheets, denoted as α-Ni(OH)₂/NF, were synthesized on NF by one-step electrodeposition method [14], which required only 192 and 240 mV low overpotentials at current densities of 10 and 100 mA cm⁻². In addition, it can also maintain excellent OER performance at a large current density and has good stability. These studies indicate that the combination of hydroxides with highly conductive substrates (nickel foam and copper foam, etc.) is a strategy for preparing highly conductive and durable electrolytic hydropower catalysts [15].

In this paper, NiCo-LDH/NF self-supporting electrode was prepared by a simple hydrothermal method. On the nickel foam substrate, a series of NiCo-LDH nanostructures with different nanoneedle morphologies were designed by adjusting the ratio of nickel and copper to provide a richer active area. The nickel foam substrate can not only improve the conductivity, but also the prepared self-supporting electrode is more stable than the powder

catalyst. The combination of bimetallic hydroxides and NF can provide an effective way for electron transfer and further improve the OER performance of the catalyst.

2. EXPERIMENTAL

2.1 Chemicals and Reagents

Nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), cobalt nitrate trihydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and urea ($\text{CO}(\text{NH}_2)_2$) were purchased from China Aladdin Chemical Reagent Co., Ltd. Hydrochloric acid (HCl, 12 mol/L) and absolute ethanol (99.7%) were purchased from China National Pharmaceutical Chemical Reagents Co., Ltd. Nickel foam (NF) was purchased from Suzhou JiaShiDe Metal Foam Co., Ltd.

2.2 Synthesis of NiCu-LDH/NF

Firstly, NF substrate was pretreated. NF was sonicated in acetone, 3 M hydrochloric acid, deionized water and absolute ethanol for 10 min, respectively, to remove the residual oil and oxides on the surface of NF.

4 mmol of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 4 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 15 mmol of urea were transferred to the lining of the high temperature and high pressure reactor, and 30 mL of deionized water was added. The liner was placed on a magnetic stirrer for continuous stirring for 30 min to fully dissolve the drug. After stirring, the pretreated NF was put into the lining, which was sealed in the reactor, and the reactor was put into the blast drying box, and the reaction was carried out at 100°C for 10 h. After the reaction was completed, the reaction kettle was cooled to room temperature, the sample was taken out and repeatedly washed with deionized water and anhydrous ethanol, and dried overnight at 60°C in a vacuum oven. The obtained sample was recorded as $\text{Ni}_4\text{Co}_4\text{-LDH/NF}$. The $\text{Ni}_2\text{Co}_4\text{/NF}$ and $\text{Ni}_8\text{Co}_4\text{/NF}$ catalysts were prepared with Ni/Co molar ratios of 2:4 and 8:4 mmol.

3. RESULTS AND DISCUSSION

As shown in Figure 1, the morphology of $\text{Ni}_2\text{Co}_4\text{-LDH/NF}$, $\text{Ni}_4\text{Co}_4\text{-LDH/NF}$ and $\text{Ni}_8\text{Co}_4\text{-LDH/NF}$ catalysts was observed by scanning electron microscopy (SEM). As shown in Figure 1a and d, the $\text{Ni}_2\text{Co}_4\text{-LDH/NF}$ sample exhibits a loose nanoneedle array structure. Compared with $\text{Ni}_2\text{Co}_4\text{-LDH/NF}$, $\text{Ni}_4\text{Co}_4\text{-LDH/NF}$ (Figure 1b and e) and $\text{Ni}_8\text{Co}_4\text{-LDH/NF}$ (Figure 1c and f) samples also grow nanoneedle arrays, but generally exhibit a three-dimensional cluster structure. With the increase of Ni/Co ratio, the cluster structure is more obvious, which increases the roughness of NF surface and enriches the active area accordingly.

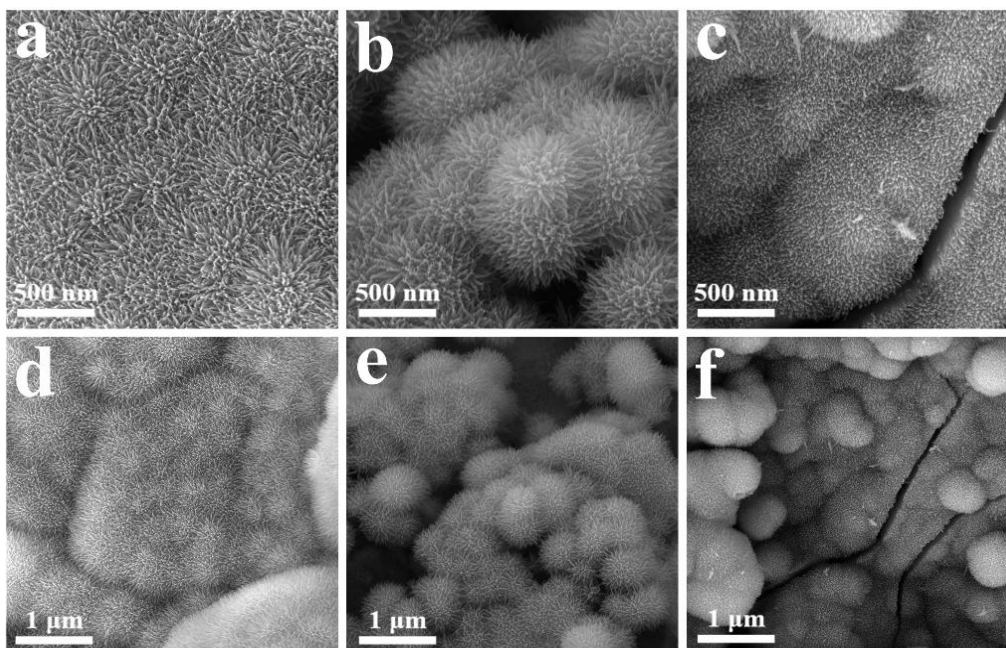


Figure 1: SEM images of (a, d) $\text{Ni}_2\text{Co}_4\text{-LDH/NF}$, (b, e) $\text{Ni}_4\text{Co}_4\text{-LDH/NF}$ and (c, f) $\text{Ni}_8\text{Co}_4\text{-LDH/NF}$ at different resolutions

The OER electrocatalytic properties of NF, Ni₂Co₄-LDH/NF, Ni₄Co₄-LDH/NF and Ni₈Co₄-LDH/NF samples were measured by a three-electrode system under 1M KOH conditions. Figure 2 is the OER polarization curves of each sample after iR compensation. Under the same conditions, Ni₄Co₄-LDH/NF has excellent OER performance. At a current density of 10 mA cm⁻², the overpotential of Ni₄Co₄-LDH/NF is 184 mV, which is lower than Ni₂Co₄-LDH/NF (338 mV), Ni₈Co₄-LDH/NF (235 mV) and NF (379 mV) of other control groups. At a current density of 50 mA·cm⁻², the overpotential of Ni₄Co₄-LDH/NF was 339 mV, which was also lower than that of Ni₂Co₄-LDH/NF (405 mV), Ni₈Co₄-LDH/NF (359 mV) and NF (434 mV) in other control groups. When the current density reaches 100 mA·cm⁻², 200 mA·cm⁻² and 100 mA·cm⁻², the overpotential of Ni₄Co₄-LDH/NF is also the lowest. These results indicate that the combination of NiCo-LDH and NF can significantly improve the OER activity of the catalyst.

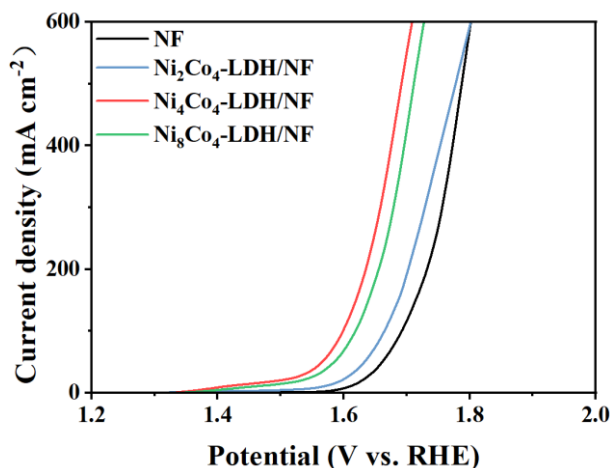


Figure 2: OER polarization curves of NF, Ni₂Co₄-LDH/NF, Ni₄Co₄-LDH/NF and Ni₈Co₄-LDH/NF

4. CONCLUSION

In summary, NiCo-LDH nanoneedle arrays with different morphologies were successfully synthesized on NF by a simple hydrothermal method, and NiCo-LDH/NF self-supporting electrode was prepared. The nickel foam substrate can not only improve the conductivity, but also the prepared self-supporting electrode is more stable than the powder catalyst. The combination of bimetallic hydroxides and NF not only makes it easier to expose abundant unsaturated metal sites, but also improves conductivity and accelerates electron transfer, which is conducive to more efficient OER. The prepared Ni₄Co₄-LDH/NF catalyst has an overpotential of 184 and 339 mV at current densities of 10 and 50 mA cm⁻², respectively. This work provides a simple and effective way to construct efficient and low-cost OER electrocatalysts.

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