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Opinion

Construction of High-Entropy LDH Nanostructures to Promote Alkaline Oxygen Evolution

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Abstract

The development of highly active transition metal-based catalysts is a key challenge for improving the efficiency of the Oxygen Evolution Reaction (OER). In this study, a high-entropy layered double hydroxide (HE-LDH) composed of five metals was successfully designed and synthesized using a hydrothermal method. Electrochemical performance tests comparing different metal combinations in high-entropy LDHs revealed that NiCoCuFeAl LDH exhibited an overpotential of only 389 mV at a current density of 10 mA cm^{-2}. Moreover, it demonstrated a smaller Tafel slope of 124.4 mV dec^{-1}. This superior catalytic performance is attributed to the synergistic interactions among the five metals, which optimize the electronic environment. This study offers a promising strategy for designing efficient electrocatalysts with enhanced OER performance.

Introduction

The Oxygen Evolution Reaction (OER) is a critical half-reaction in electrochemical water splitting, playing a key role in achieving green and efficient hydrogen production [1, 2]. However, the slow kinetics of the four-electron transfer process involved in OER, poses a significant challenge to the large-scale commercial application of electrochemical water splitting [3, 4]. Therefore, the development of highly active OER catalysts to reduce the overpotential and enhance reaction rates is of critical importance. Noble metal oxides, such as RuO_2 and IrO_2, are widely regarded as benchmark OER catalysts [5]. Despite their excellent catalytic activity, their high cost and hinder their feasibility for industrial applications [6]. This has driven urgent efforts to design novel, low-cost, and efficient transition metal-based catalysts to enhance OER performance. Layered Double Hydroxides (LDHs) are a class of typical layered materials that have gained recognition as one of the most representative non-noble metal catalysts for water oxidation [7]. This is attributed to their large specific surface area, abundant active sites, cost-effectiveness, and the tunable composition and ratio of metal elements and interlayer anions [1, 8]. By incorporating three additional metal elements into traditional binary LDHs, high-entropy layered double hydroxides (HE-LDHs) can be synthesized. The synergistic interactions among the five metal elements optimize the electronic environment, significantly increasing the specific surface area and the number of active sites [9-12]. Moreover, the high-entropy effect and slow diffusion characteristics of HE-LDHs enhance structural stability by suppressing phase transitions and mitigating metal leaching [13-15]. These attributes position HE-LDHs as a promising direction for water oxidation electrocatalysts.

In this study, two bulk-phase HE-LDH electrocatalysts, were synthesized using a hydrothermal method and evaluated for OER catalysis. Comprehensive physicochemical characterizations were conducted to analyze their crystalline phases. Electrochemical tests under identical loading conditions demonstrated that NiCoCuFeAl LDH exhibited superior electrocatalytic activity in alkaline electrolyte, along with a smaller Tafel slope. This study provides an effective strategy for designing high-performance HE-LDH catalysts for alkaline water oxidation.

Results and Discussion

To synthesize the HE-LDHs, different metal ion precursors were selected. Urea was used as the precipitating agent. The metal ion precursors and urea were combined in equimolar ratios and transferred to a hydrothermal reaction vessel. The reaction was carried out at 120 °C for 6 hours. This approach successfully resulted in the synthesis of NiCoCuFeAl LDH and CuNiCoFeMn LDH [16]. First, the basic characteristics of the two catalysts were systematically analyzed using various physicochemical characterization techniques. Figure1a shows the powder X-ray diffraction (PXRD) patterns of NiCoCuFeAl LDH and CuNiCoFeMn LDH, which closely match the structure of typical NiFe LDH(JCPDS#40-0215) [17]. The morphology of NiCoCuFeAl LDH and CuNiCoFeMn LDH powders was characterized using scanning electron microscopy (SEM). As shown in Figure 1b, NiCoCuFeAl LDH consists of multi-layered, interlaced nanosheets with relatively small sheet sizes. Elemental mapping via energy dispersive X-ray spectroscopy (EDS) (Figure 1b1 and 1b2) shows that the elements Ni, Co, Cu, Fe, and Al are uniformly distributed across the surface of the material. Figure 1c presents the SEM image of CuNiCoFeMn LDH, which also forms interlaced nanosheets, but with larger sheet sizes compared to NiCoCuFeAl LDH. EDS analysis (Figures 1c1 and 1c2) confirms that the elements Cu, Ni, Co, Fe, and Mn are uniformly distributed on the surface of the material as well.

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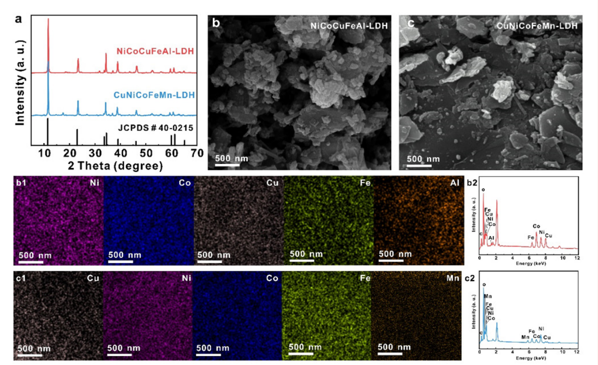
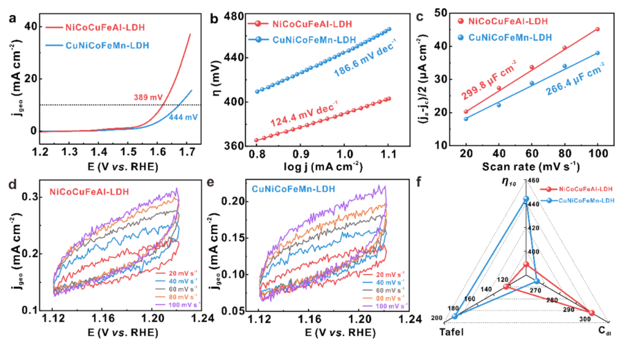
FIgure 1: (a) PXRD patterns. (b) SEM image of NiCoCuFeAl LDH. (c) SEM image of CuNiCoFeMn LDH. (b1-b2) Elemental distribution map and EDS spectrum of NiCoCuFeAl LDH. (c1-c2) Elemental distribution map and EDS spectrum of CuNiCoFeMn LDH.



To investigate the effect of HE-LDHs electrocatalysts on OER performance, electrochemical tests were conducted in 1 M KOH electrolyte saturated with O_2. As shown in Figure 2a, the linear sweep voltammetry (LSV) curves indicate that at a current density of 10 mA cm^{-2}, the overpotential of NiCoCuFeAl LDH is 389 mV, which is significantly lower than that of CuNiCoFeMn LDH (444 mV) by 55 mV. As shown in Figure 2b, NiCoCuFeAl LDH has a Tafel slope of only 124.4 mV de^{c-1}, which is markedly lower than that of CuNiCoFeMn LDH, indicating faster reaction kinetics for NiCoCuFeAl LDH. Since electrochemical active surface area (ECSA) is proportional to the double-layer capacitance (C_{dl}). As shown in Figure 2c, NiCoCuFeAl LDH exhibits a significantly higher C_{dl} value compared to CuNiCoFeMn LDH, suggesting that NiCoCuFeAl LDH has a larger ECSA. Figures 2d and 2e present the cyclic voltammetry (CV) curves of NiCoCuFeAl LDH and CuNiCoFeMn LDH at different scan rates, respectively. The C_{dl} values in Figure 2c were derived by fitting these CV curves. Figure 2f presents a radar chart comparing the performance of NiCoCuFeAl LDH and CuNiCoFeMn LDH. The chart clearly demonstrates that NiCoCuFeAl LDH exhibits superior intrinsic catalytic activity during the OER process, further confirming its potential for performance optimization within high-entropy structures.

FIgure 2: Comparison of OER performance between NiCoCuFeAl LDH and CuNiCoFeMn LDH electrocatalysts: (a) LSV curves; (b) Tafel slope plots; (c) Cdl plots; (d) and (e) cyclic voltammetry curves of NiCoCuFeAl LDH and CuNiCoFeMn LDH, respectively, at scan rates of 20, 40, 60, 80, and 100 mV s-^{1} in 1 M KOH electrolyte; (f) radar chart showing performance comparison.



Conclusion

In summary, we have successfully synthesized bulk-phase HE-LDH electrocatalysts via a hydrothermal method. The NiCoCuFeAl LDH electrocatalyst demonstrated superior OER performance, requiring only a 389 mV overpotential to achieve a current density of 10 mA·cm^{-2}, along with a Tafel slope as low as 124.4 mV·dec^{-1}. Its excellent catalytic activity is primarily attributed to the synergistic effects among the five metal elements, which optimize the electronic environment and enhance the overall catalytic efficiency. This study provides valuable insights and strategies for the design and synthesis of high-activity bulk HE-LDH electrocatalysts, offering a promising approach to improve OER performance.

Declaration of Competing Interest

The authors declare no competing financial interest.

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