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# Electrochemical Impedance and Surface Charge Dynamics in Alkaline Oxygen Evolution on NIFE-Based Electrocatalysts

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**Abstract:** *Nickel-based catalysts are widely explored for the oxygen evolution reaction (OER) in alkaline media, yet variations in reported activity and kinetic parameters remain a challenge. This study investigates NiFe-based electrocatalysts synthesized via hydrothermal deposition, assessing their OER performance through electrochemical impedance spectroscopy (EIS) and chronoamperometry under varying alkaline conditions. We demonstrate that the charge transfer resistance ($R_{ct}$) and double-layer capacitance ($C_{dl}$) significantly influence the reaction kinetics, leading to variations in the apparent Tafel slope. At low overpotentials, a near-ideal slope of ~35 mV/dec is observed; however, higher polarization induces deviations due to surface charge accumulation, diffusion limitations, and bubble formation. Unlike conventional Tafel analysis, our approach highlights the role of electrochemical surface area (ECSA) and interfacial charge redistribution in modulating catalytic activity. Additionally, in situ Raman spectroscopy reveals hydroxide adsorption dynamics as a critical factor governing reaction efficiency. Our findings suggest that analyzing impedance behavior alongside conventional kinetic models provides a more comprehensive understanding of OER activity and mitigates misinterpretation arising from non-kinetic effects.*

**Keywords:** *Nickel-iron electrocatalysts, oxygen evolution reaction, electrochemical impedance spectroscopy, chronoamperometry, charge transfer resistance, hydroxide adsorption*

## 1. INTRODUCTION

Currently, growing global energy demand and harsh climate change has become major issues for the world community. It has been reported that by the year 2050, the global energy demand will become double owing to rapid increase in population [1]. Meanwhile, fossil fuel which covers 80% of total energy consumption is slowly depleting and it is also one of the primary contributors to environmental pollution, climate change and various health hazards. Therefore, to meet the energy demand in line with sustainable environment, the modern society is now leading towards clean energy technology. However, ORR and OER are intrinsically sluggish reactions. Platinum (Pt) group metals (PGM) and Ru/Ir oxides are best known electrocatalysts for ORR, and OER respectively [1]. Nevertheless, high cost, less abundance and technical vulnerability in the operating conditions for these electrocatalysts are the factors impinging further development of ORR/OER based renewable technologies [2]. Therefore, in order to overcome the current energy and environmental crisis, designing of advanced electrocatalysts, which could effectively enhance the kinetics of ORR/ OER reactions with performance comparable to that of benchmark catalysts, is the key scientific challenge in this field [3].

The surface of the electrodes is modified using the synthesized materials (Figure 1). The synthesized materials are expected to provide an abundant number of active sites. Drop-casting approach is utilized to get the surface modified electrodes [4]. Suspensions of the synthesized materials are prepared by prolonged sonication of the material in a suitable solvent. The calculated amount of the suspension is drop-casted on vertically mounted electrodes and allowed to dry in the air. The resulting modified electrodes are expected to show an enhanced electrocatalytic response towards the target reactions. Glassy carbon (GC), nickel foam, copper foam, conducting carbon cloth, graphite sheet, etc. can be used as the precursor electrode. Porous/nanostructured carbon materials, mesoporous silica, clay, polymers, zeolites, Mxenes, etc. can be used as the electrode modifiers [5-6].

The ORR is structure-sensitive surface phenomenon. The adsorption of the O2 on the catalyst surface greatly affects the ORR activity. The equilibrium potential of ORR is measured to be 1.23 V (vs. RHE) at pH zero and it is kinetically favourable below thehalf wave potential [7] . However, due to slow kinetics, a large deviation in half wave potential from the equilibrium value is observed and this deviated potential is known as overpotential. Therefore, continuing effort has been made to develop electrocatalysts, which will minimise the loss due to overpotential. Moreover, although both the processes ORR and OER are reversible having same equilibrium potential, in practical situations both the reactions show large variation in onset potential due to high overpotential in both the reactions [8].

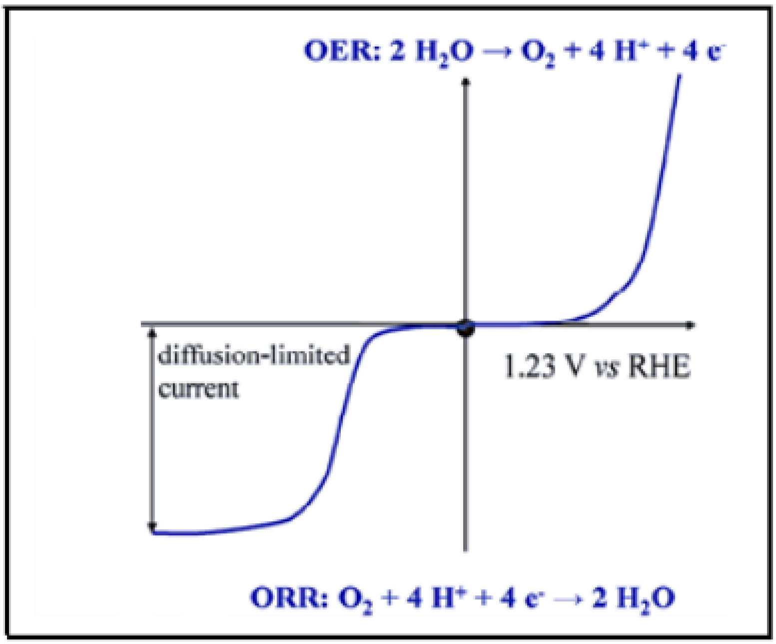


**Figure 1 The polarization curve for evolution reaction and oxygen reduction**

The ORR is a proton-coupled electron transfer process following two different pathways such as 4eand 2epathways; the kinetics of proton/ electron transfer process mostly depends on the pH of the medium in which it is examined [9-10]. Irrespective to the pH of the medium, ORR proceeds through either a 4epathway yielding H2O or OH- ,or a 2epathways producing corrosive H2O2 as product [11]. Therefore extensive research has been done to develop efficient electrocatalysts for alkaline, acidic, and neutral medium. The variation of standard reduction potential for ORR with pH is demonstrated The chemical reactions for 2eand 4epathways with their thermodynamic standard reduction potentials in both alkaline (pH=13) and acidic (pH=0) medium [12].

Developing efficient and low-cost OER electrocatalysts plays a fundamental role in achieving practical green hydrogen production. Precious compounds containing Ir or Ru have been identified as state-of-the-art OER electrocatalysts, especially due to their strong corrosive and oxidative resistance in acidic media [13]. However, knotty obstacles remain in not only the scarcity and prohibitive expense of these noble candidates, but also the severe acidic corrosion that associated with the maintenance and replacement costs of stack components [14]. Noticeably, alkaline OER electrocatalysis eliminates the corrosion issue and broadens the scope of potential electrocatalysts to earthabundant transition metal-based families.

Porous Raney Ni electrodes are widely employed in industrial alkaline electrolyzer, but suffer from insufficient OER activity (≈400 mV overpotential at 400 mA cm−2 even in 30 wt.% KOH electrolyte), which is far from the technical targets raised by U.S. Department of Energy (DOE).[15] It therefore entails mounting concerns for innovation of efficient electrocatalyst. During the recent years, NiFe-based materials including coordination molecules, alloys, oxides, (oxy)hydroxides, layered double hydroxides (LDH), and other derivates have been extensively explored with excellent OER performance comparable to noble references so as to replacing the conventional Raney Ni. However, further efforts on the affordable mass production, catalytic performance upgradation, stability improvement, and mass transfer manipulation of NiFebased materials should be addressed to guarantee the qualification as next-generation industrial OER electrocatalysts.

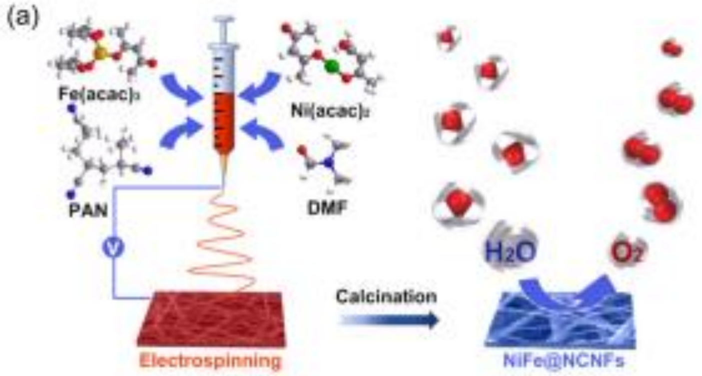
As stability is a fundamental indicator of catalyst performance, a thorough understanding of the degradation mechanism during OER is a key requirement in designing effective practical electrocatalysts. This study explores the critical stability issues associated with NiFe-based electrocatalysts in OER under alkaline conditions. The primary objective is to comprehend the basic relationship between structure, activity, and stability to develop logical recommendations for designing industrially usable catalysts with extended longevity. As summarized in Figure 1, we outline the recent developments of NiFe-based electrocatalysts, including the NiFe alloy, NiFe-based (oxy/layered) hydroxide and oxide, NiFe-based carbides and nitrides, and metal- organic frameworks (MOFs) in this review. Despite the importance of addressing these challenges in the pursuit of stability optimization, solutions remain elusive. Individual strategies for the current problem and prospects are provided to bridge laboratory advancements with practical applications.

## 2. MATERIALS AND METHODS

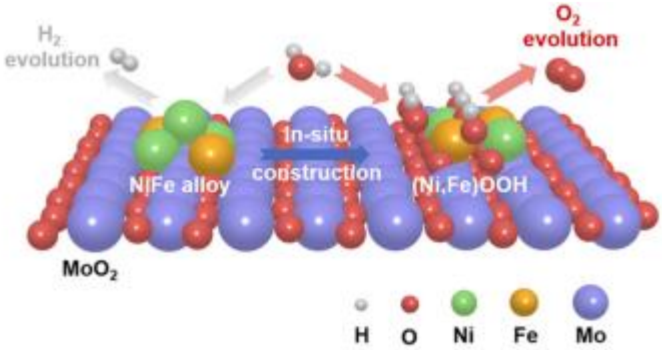
### 2.1. Materials Synthesis

#### 2.1.1. NiFe-Based Electrocatalysts

NiFe-based electrocatalysts were synthesized using a hydrothermal deposition method to ensure uniform composition and high surface area. Nickel and iron precursors were dissolved in deionized water containing ammonium hydroxide as a pH regulator to facilitate controlled nucleation. Upon cooling, the precipitate was gathered, washed several times with ethanol and deionized water, and dried at a temperature of 80°C (figure 2). The resulting powder was then subjected to calcination at 350°C in an inert atmosphere to enhance crystallinity and phase purity. The structural and morphological properties of the synthesized catalysts were characterized using XRD and SEM to confirm phase composition and surface topography.



(a)



(b)

**FIGURE 2 (a) The synthesis procedure of NiFe@NCNFs. (b) Schematic depiction illustrating NiFe alloy/MoO2 and hydrogen evolution reaction/OER for the catalyst.**

### 2.1.2. Electrode Preparation and Ink Formulation

To prepare the working electrodes, the synthesized NiFe catalyst powder was dispersed in a solution of isopropanol and Nafion as a binding agent to ensure stable adhesion to the electrode surface. The homogeneous ink was sonicated for 30 minutes to ensure uniform dispersion of catalyst particles. The loading of the catalyst was optimized at 0.5 mg/cm$^2$ to balance mass transport and catalytic efficiency. Prior to electrochemical testing, the electrodes were subjected to CV in 1.0 M KOH to stabilize the electroactive surface and remove any residual organic impurities from the synthesis process (figure 3).The catalyst ink was applied via drop casting onto a GCE and allowed to dry at ambient temperature, achieving a loading of 0.5 mg/cm$^2$ in order to reconcile mass transport with catalytic efficiency. Cyclic voltammetry was applied to the electrodes in 1.0 M KOH to stabilize the electroactive surface.

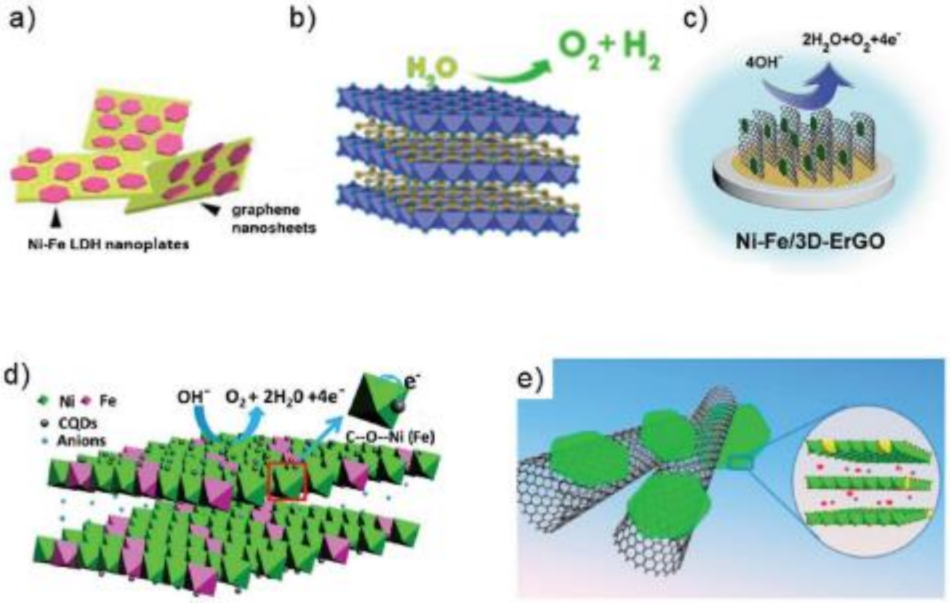


**Figure 3. a) NiFe LDH nanoplates supported on graphene nanosheets. b) NiFe LDH nanosheets and graphene stacked alternately. c) NiFe LDH nanoplates deposited on a three-dimensional graphene electrode. d) NiFe LDH/carbon quantum dot composite. e) NiFe LDH nanoplates on carbon nanotubes**

### 2.1.3. EIS Measurements

Using electrochemical impedance spectroscopy (EIS), the study examined how a material behaved under various applied voltages in a 1.0 M KOH electrolyte. Impedance spectra were obtained for frequencies from 100 kHz to 0.1 Hz, using an amplitude of 10 mV. Ancorresponding circuit model was used to analyze the Nyquist plots (figure 4). The extracted Rct values were correlated with reaction kinetics to assess the effect of charge transfer dynamics on OER activity.

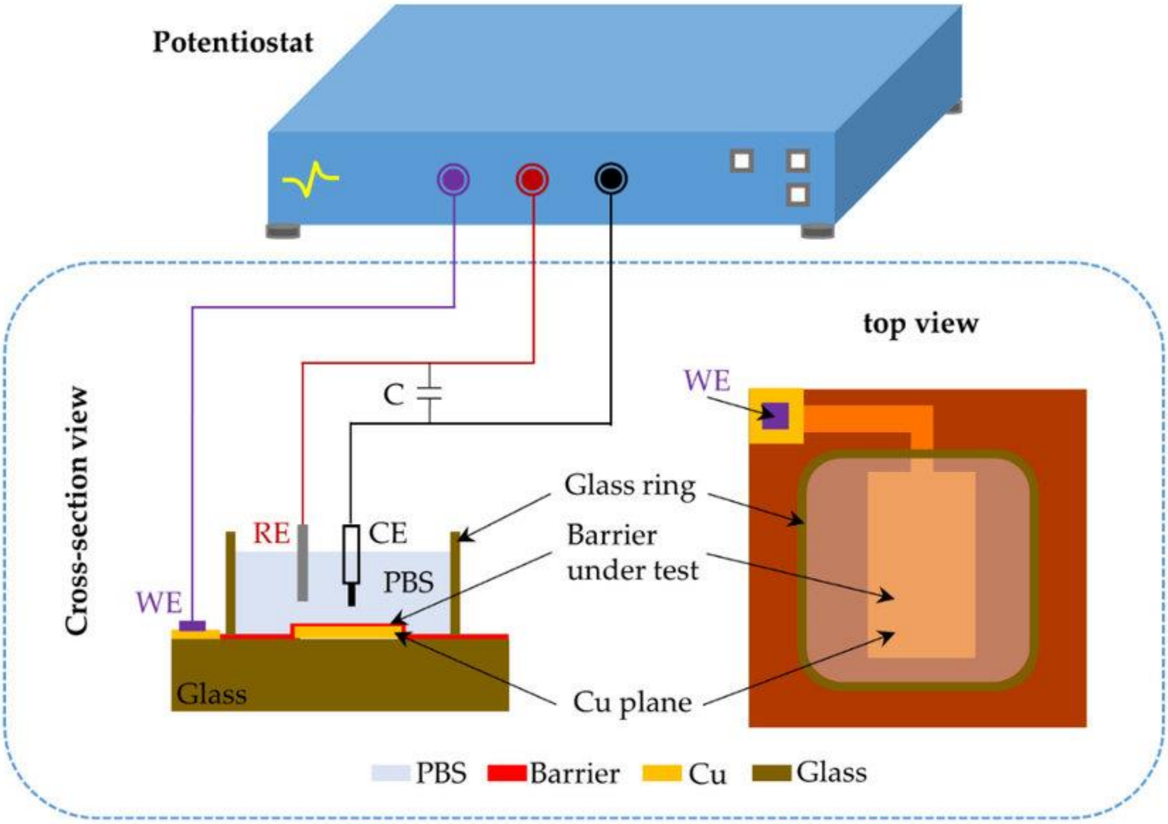


**Figure4 Electrochemical impedance spectroscopy (EIS) test setup.**

### 2.1.4. Chronoamperometric Stability Testing

Using chronoamperometry at a constant potential of 1.6 V vs. RHE for 10 hours in 1.0 M KOH, the electrochemical stability of NiFe-based electrocatalysts was evaluated. The current density was continuously monitored to assess degradation and stability trends. Post-stability analysis was conducted via XPS to investigate surface oxidation states before and after prolonged electrolysis. Structural integrity was also examined using transmission electron microscopy (TEM) to determine morphological changes due to electrochemical cycling.

### 2.1.5. In Situ Raman Spectroscopy for Hydroxide Adsorption Analysis

In situ Raman spectroscopy was conducted to investigate hydroxide adsorption dynamics during OER. A custom-built electrochemical Raman cell with a quartz window was used to enable real-time spectral acquisition. Raman spectra were recorded at different applied potentials (1.4 V to 1.8 V vs. RHE) using a 532 nm excitation laser. The intensity and shift of vibrational modes corresponding to Ni-OH and Fe-OH species were analyzed to determine the potential-dependent evolution of active hydroxide species. These insights were used to establish a direct correlation between surface charge redistribution and catalytic efficiency.

## 3. RESULT AND DISCUSSION

### 3.1. Chronoamperometric Stability Testing

The NiFe-LDH HMS demonstrates stability under the tested conditions, with a 4.5% rise in decomposition current density after 40,000 seconds. However, current densities decline within 20,000 seconds. The LSV curve coincides with the fresh sample, validating its durability. During successive inclination at anodic current density for 2000 s, the electrode exhibits comparable activity, signifying a stable potentiometry response for NiFe-LDH HMS.

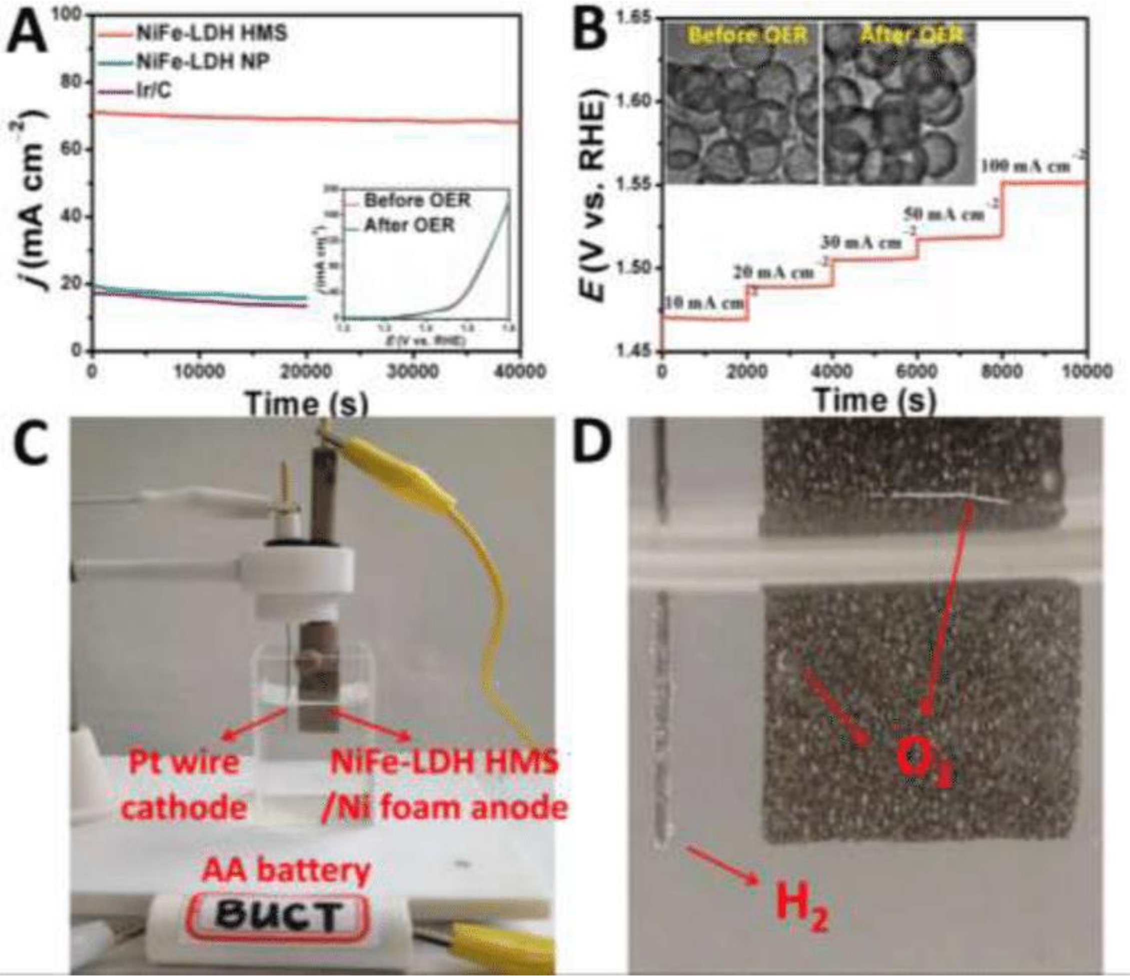


**Figure 5 chronoamperometric results of (a) NiFe-LDH HMS and (b)Ir/C electrocatalyst in 1 M KOH solution, chronopotentiometry response at different currents(c) (j = 10, 20, 30, 50, and 100 mA cm −2), and the (d)corresponding enlarged image of a water-splitting system powered by a battery.**

### 3.2. Raman Spectroscopy for Hydroxide Adsorption Analysis

The below figure presents in situ Raman spectroscopy measurements of NiFe-LDH and d-NiFe-LDH during the oxygen evolution reaction (OER). Figure 6 (a) and (b) display Raman spectra of pristine NiFe-LDH and d-NiFe-LDH, respectively, at different applied potentials, highlighting key vibrational modes such as $\beta$-Ni(OH)$_2$ (528 cm$^{-1}$) and Ni$^{2+}$-O (457 cm$^{-1}$) with potential-dependent shifts. Panel (c) illustrates the evolution of the intensity ratio $I_{528}/I_{457}$ as a function of applied potential, indicating structural transformations relevant to catalytic activity. Panel (d) compares $\Delta I_{528}/I_{457}$ values for NiFe-LDH and d-NiFe-LDH, showing a higher ratio for d-NiFe-LDH, suggesting enhanced catalytic properties.

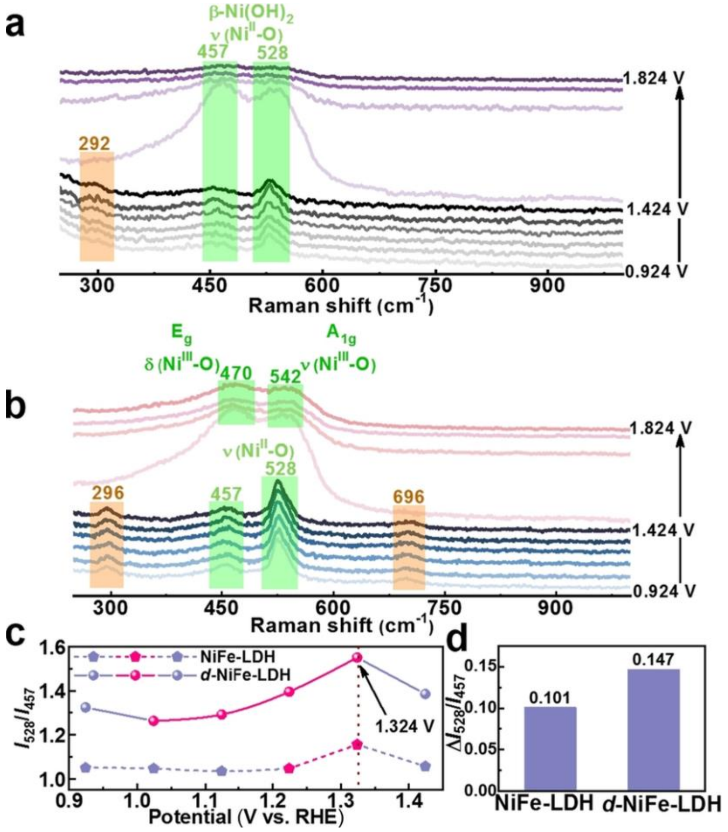
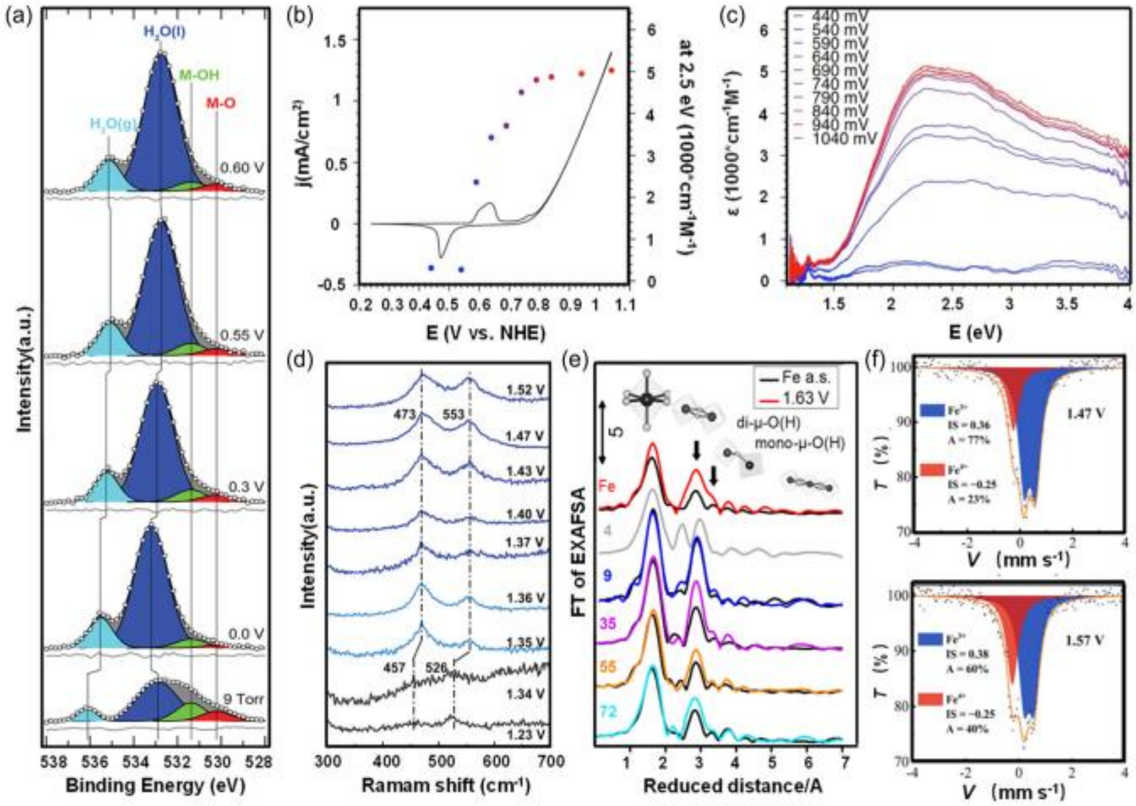


**Figure6 Results of Raman spectroscopy (a) NiFe-LDH and (b) d-NiFe-LDH in OER electrocatalysis,(c) I528/I457 evolution versus potential, and (d) ΔI528/I457 of NiFe-LDH and d-NiFe-LDH.**

As displayed in Figure 7a, in situ ambient pressure XPS allows for in situ investigation of surface chemistry characteristics and tracking electrochemical reactions. Another in situ method that can be used to track the process of metal oxidation is in situ Ultraviolet Visible spectroscopy (UV/Vis). By employing in situ UV/Vis, it is feasible to monitor the metal oxidation process taking place in NiFe-based catalysts, as depicted in Figure 7 b,c. Raman spectroscopy is a valuable technique in the chemical and materials sciences due to its rich feedback information. It can characterize the chemical structure of the sample at the molecular level by detecting the vibration of chemical bonds. Raman spectroscopy can be used to characterize the composition of materials, and can also be used for rapid qualitative analysis of unknown materials, which has important application value in the field of electrochemistry. Therefore, in situ Raman spectroscopy (Figure 7d) can be used to detect the catalytic intermediate and track the phase transformation during the OER process.



**F I G U R E 7 In situ methods for detecting the oxygen evolution reaction process of NiFe-based electrocatalysts. (a) In situ APXPS. Reproduced with permission: (b, c) In situ UV/Vis spectroscopy. (d) In situ Raman spectroscopy. (e) In situ XAS. (f) In situ Mössbauer Spectroscopy tests.**

In addition, Fe Mössbauer spectroscopy is a highly effective method for discerning the electron spin configuration, oxidation state, magnetic field, and symmetry of Fe centers.Researchers group synthesized a highly efficient NiFem-OxHy OER catalyst through topological transformation and used in situ electrochemical Mossbauer spectroscopy to investigate the reaction mechanism, as demonstrated in Figure 7f. They found that around the OER starting potential, a significant quantity of Fe4+ (the content of 12%) was already formed and that when the voltage grew, its content might approach 40%. They also discovered a positive correlation between the content of Fe4+ and the current density of OER. These results contribute to a deeper understanding of the Ni–Fe hydroxyl oxide OER catalyst mechanism

### 3.3.SEM analysis

The limited interlayer spacing of NiFe LDHs hinders the diffusion of proton acceptors into the interlayers, consequently resulting in the dissolution of the catalyst. As depicted in Figure 8a, NiFe LDHs exhibit a vertical and uniform arrangement of nanosheets. However, following the durability test in alkaline seawater, no discernible sheet structure is evident on the NiFe–LDH, indicating structural degradation (Figure 8b). Therefore, NiFe LDHs demonstrate a swift decrease in current density, retaining only 21% of the initial value (Figure 8c)

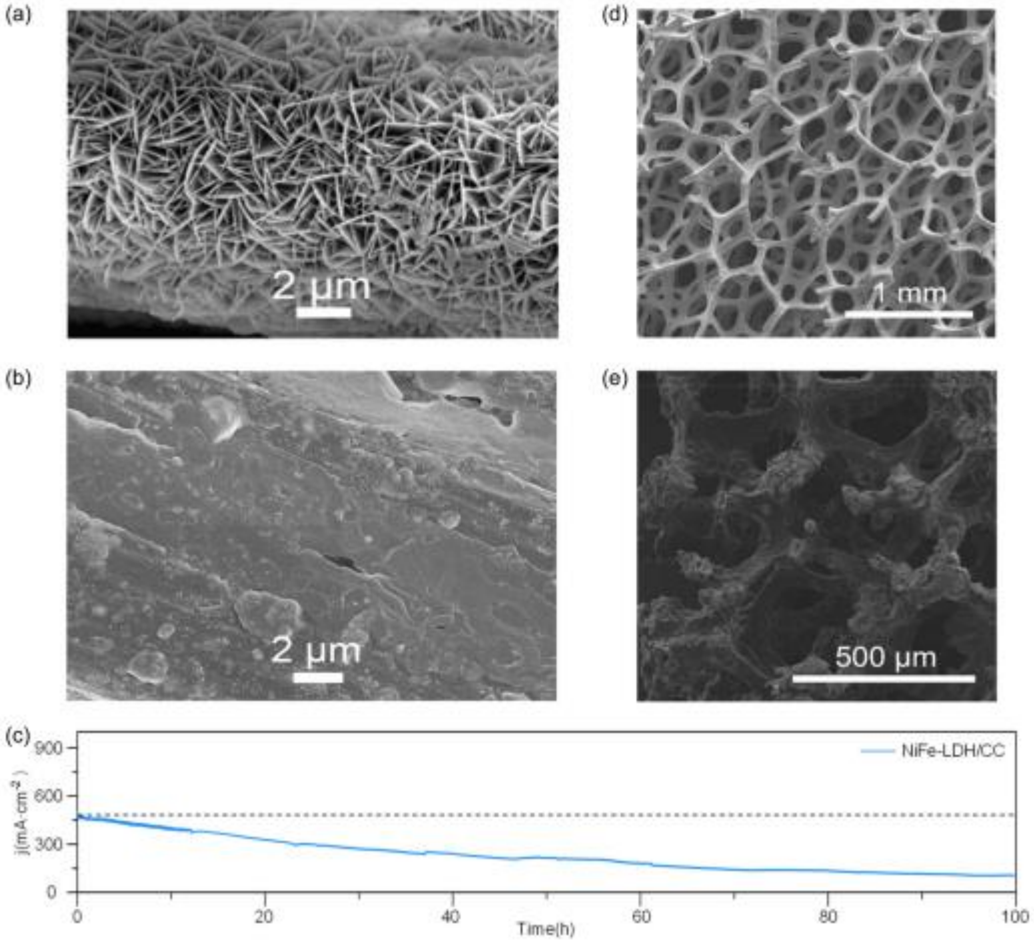


**FIGURE 8 (a) The scanning electron microscope (SEM) images depict NiFe–LDH before and (b) after the durability test in alkaline seawater, (c) Chronoamperometry curves of NiFe–LDH at fixed potentials of 2.41 V in alkaline seawater.**

## 4. CONCLUSION

This research provided an in-depth investigation of NiFe-based electrocatalysts for the oxygen evolution reaction (OER) in alkaline media, emphasizing the role of electrochemical impedance and surface charge dynamics. The findings highlight the significant influence of charge transfer resistance (Rct), double-layer capacitance (Cdl), and electrochemical surface area (ECSA) on catalytic activity, offering a more nuanced understanding of OER kinetics beyond conventional Tafel analysis. Through a combination of electrochemical impedance spectroscopy (EIS), chronoamperometric stability testing, and in situ Raman spectroscopy, we have demonstrated the intricate relationship between hydroxide adsorption dynamics and interfacial charge redistribution, which dictate the long-term stability and efficiency of NiFe-based electrocatalysts. The study further underscores the challenges associated with structural degradation, iron segregation, and substrate peeling, while suggesting strategies to enhance the durability of NiFe-based catalysts for practical applications. By integrating insights from morphological characterization techniques like SEM and XPS, as well as in situ spectroscopic analyses, this work bridges the gap between fundamental electrochemical behavior and real-world applications, paving the way for the development of cost-effective, high-performance OER electrocatalysts suitable for large-scale green hydrogen production.

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