ISSN: 2710-0723

Application and Development of OER Catalysts in Water Electrolysis for Hydrogen

Baichuan Xi*, Taiyuan Zhang

College of Material, Chemistry and Chemical Engineering, Hangzhou Normal University, Hangzhou, 311121, Zhejiang, China

*Corresponding Author

Abstract

With the growing global energy crisis and environmental pollution, developing sustainable energy technologies is urgent. Hydrogen, a clean energy source with high energy density and water as its only byproduct, is a promising alternative to fossil fuels. Electrolytic water splitting is a green hydrogen production method, but its efficiency is limited by the slow kinetics of the oxygen evolution reaction (OER). Developing efficient OER catalysts is crucial to improving this process. This article reviews the principles of electrolytic water splitting, in-cluding HER and OER mechanisms, and key evaluation parameters such as overpotential, Tafel slope, EIS, ECSA, and stability. It highlights transition met-al-based catalysts, particularly NiFe LDH, which enhances OER performance through the lattice oxygen mechanism (LOM). Future research should focus on optimizing catalyst design to advance electrolytic water splitting technology.

Keywords

Water Splitting; OER; NiFe LDH.

1. Introduction

This Energy drives national development, and the 2015 Paris Agreement aims to limit global temperature rise to below 2°C.[1]To meet 2030 targets, countries must increase emission cuts. The energy crisis and pollution demand more sustainable energy use.[2], [3], [4], [5] Renewable sources like solar and wind are abundant but intermittent, requiring storage or conversion into fuels like hydrogen. Hydrogen, with high energy density and clean combustion (producing only water), is a promising fossil fuel alternative. [6], [7]

Current hydrogen production methods include electrolysis, photolysis, biological decomposition, and thermolysis.[8] Electrocatalytic water splitting, involving HER and OER, is a green approach, but OER's slow kinetics limit efficiency. Developing efficient OER catalysts is key to advancing hydrogen production. [9], [10]

1.1. Water-splitting

1.1.1. Reaction Summary

The process of water electrolysis is described in Equation, where water serves as the reactant. At the cathode, the water reduction reaction occurs, producing hydrogen gas as the product, while at the anode, the water oxidation reaction takes place, yielding oxygen gas as the product. This process is carried out through two half-reactions, known as the Hydrogen Evolution Reaction (HER) and the Oxygen Evolution Reaction (OER), respectively. The specifics are as follows[11]:

Overall: $2H_2O \rightarrow 2H_2 + O_2$

Neutral conditions:

Anode: $2H_2O \rightarrow 4H^+ + O_2 + 4e^-$

ISSN: 2710-0723

Cathode: $2H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$
Acidic conditions:
Anode: $2H_2O \rightarrow 4H^+ + O_2 + 4e^-$
Cathode: $4H^+ + 4e^- \rightarrow H_2$
Alkaline conditions:
Anode: $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$
Cathode: $2H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$

1.2. Evaluation Parameters for Catalytic Activity in Water Electrolysis

To evaluate the catalytic activity of OER (Oxygen Evolution Reaction) and HER (Hydrogen Evolution Reaction) electrocatalysts, key parameters include overpotential, Tafel slope, electrochemical impedance spectroscopy (EIS) analysis, electrochemically active surface area (ECSA), and stability.

(1) Overpotential

In water electrolysis, overpotential (η) refers to the difference between the electrode potential when the electrode reaction deviates from equilibrium to achieve a specific current density and the equilibrium potential of this electrode reaction, which is 1.23 V[12]. For electrocatalytic redox reactions, the applied potential can be expressed by the Nernst equation[13].

$$E = E^0 + \frac{RT}{nF}\ln\left(\frac{C_0}{C_R}\right)$$

Here, E represents the applied potential, E^0 stands for the standard potential, R is the universal gas constant, T is the absolute temperature, F is the Faraday constant, and C_O and C_R are the concentrations of the oxidant and reductant, respectively.

The expression for overpotential is represented as:

$$\eta = E - E_{eq}$$

Where Eeq is the equilibrium potential (1.23V). To achieve a photoelectrochemical water splitting efficiency of 10%, a current density of 10 mA cm^{-2} needs to be reached, and the overpotential at this point is denoted as η_{10}.[14]

(2) Tafel slop

The Tafel plot illustrates the relationship between the steady-state current density and the overpotential, which is represented by the Butler-Volmer equation. [15]

$$i = i_0\left[\exp\left(\alpha_a n\frac{FE}{RT}\right) + \exp\left(\alpha_c n\frac{F}{RT}\right)\right]$$

Where I0 is the exchange current density, and αa and αc are the symmetry coefficients for the anode and cathode, respectively. The Tafel equation is:

$$\eta = a + b\log|j|$$

Where b is the Tafel slope. From the Tafel equation, we can derive two important parameters, namely the Tafel slope (b) and the exchange current density (j).

ISSN: 2710-0723

(3) EIS

Electrochemical impedance spectroscopy (EIS) is used to analyze the charge resistance during the catalytic reaction process of materials and can also be employed to evaluate the kinetics of the reaction. [16]

(4) ECSA

Electrochemical active surface area (ECSA) is an important criterion for characterizing surface activity.[17]The ECSA is determined from the electrochemical double-layer capacitance (Cdl) of the catalytic surface.[18]In the non-Faradaic region, multiple cyclic voltammetry (CV) scans are recorded at various scan rates (e.g., 10-120 mV s^{-1}) within a certain potential window. The difference in the variation of cathodic and anodic current densities (ΔJ = Ja - Jc) at a given overpotential is plotted against the scan rate, and a linear regression fit is performed on the plot to evaluate the double-layer capacitance (Cdl). A high Cdl value indicates a larger exposure of surface active sites and a higher current density. [19]The calculation of ECSA is expressed as follows [19]:

$$ECSA = C_{dl}/C_s$$

Where Cdl is the double-layer capacitance, and Cs is the specific capacitance of the sample material.[20]

(5) Stability

In practical applications, the long-term stability of a catalyst is also an important indicator for evaluating its quality. Typically, two different testing methods are employed to assess the long-term stability of a catalyst. The first method involves recording the chronopotentiometry curve over an extended period at a constant current density or plotting the change in current density over time at a constant overpotential. The second method involves recording and comparing the linear sweep voltammetry (LSV) curves before and after CV cycling. [21]

1.3. Oxygen Evolution Reaction Catalyst

Among the promising transition metals (such as Ni, Fe, Co, etc.) reported so far, it is a relatively suitable element.[22] Furthermore, with the development of in-situ or operando characterization techniques, transition metal (oxy)hydroxides have been identified as the actual active species reconstructed from most pristine OER catalysts. [23], [24] Meanwhile, it has also been proven that the in-situ generated highly oxidized metal species exhibit superior catalytic activity. By adjusting the orbital hybridization between the metal d-band and O 2p, oxygen species can be activated to trigger the direct O-O coupling translation via the lattice oxygen mechanism (LOM). [25]However, despite the progress made in designing effective electrocatalysts to reduce overpotential, transition metal-based oxides/hydroxides exhibit considerable catalytic activity for oxygen evolution reaction (OER) in alkaline environments. Among them, NiFe layered double hydroxides (NiFe LDH) are considered to be one of the most promising candidates.[26] Due to the interaction between Ni and Fe atoms with the bridging oxygen atoms in NiFe LDH, forming Ni-O-Fe moieties, the electrons in the d-orbitals of the Fe species are more electron-deficient compared to those of the Ni species. This results in partial electron transfer (PET) from Ni to the Fe species in NiFe LDH through the Ni-O-Fe moieties. Consequently, the valence state of the Ni species in NiFe LDH is more prone to increase during the OER process. [27] This mechanism suggests that the involvement of Fe species can enhance the covalency between Ni and O, thereby facilitating electron transfer during the electrocatalytic process.[28] Furthermore, the high valence state of Ni species can induce a downward shift of its d-band, which in turn can penetrate the p-band of oxygen ligands in LDH, enabling lattice oxygen atoms to directly participate in OER. Consequently, the OER process is

ISSN: 2710-0723

more likely to proceed via a favorable lattice oxygen mechanism (LOM), which reduces the large energy barrier (>0.37 V) caused by multiple intermediate adsorption processes in the traditional adsorption-evolution mechanism (AEM).[29] Apart from promoting the pre-oxidation of Ni, previous studies have detected high-valent Fe species during the OER process, suggesting that they can also serve as active sites to directly participate in OER, contributing to the electrocatalytic performance of NiFe LDH. [30]

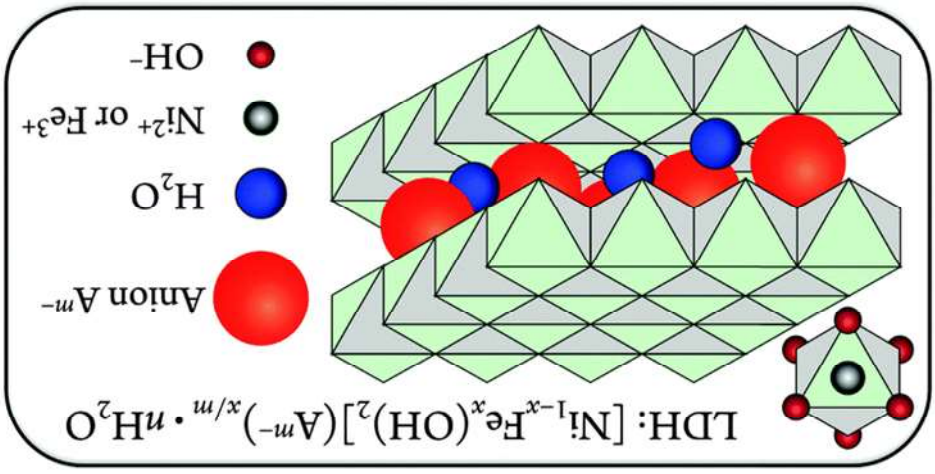

Figure 1. Schematic Diagram of NiFe LDH Structure.[31]

2. Conclusion

Electrolytic water splitting for hydrogen production, as a green and sustainable method, holds significant potential in addressing global energy crises and envi-ronmental pollution. However, its widespread application is limited by the slug-gish kinetics and high overpotential of the oxygen evolution reaction (OER). This article systematically summarizes the reaction mechanisms of electrolytic water splitting and the key parameters for evaluating catalyst performance, including overpotential, Tafel slope, electrochemical impedance spectroscopy (EIS), elec-trochemically active surface area (ECSA), and stability. Research indicates that transition metal-based catalysts, particularly nickel-iron layered double hydrox-ides (NiFe LDH), exhibit excellent OER catalytic activity in alkaline environments. Through electronic modulation of the Ni-O-Fe structure, NiFe LDH can promote the lattice oxygen mechanism (LOM), significantly reducing the reaction energy barrier and enhancing catalytic efficiency. Additionally, the generation of high-valence metal species further enhances catalytic activity. Future research should focus on optimizing catalyst design to further reduce overpotential, im-prove stability, and lower costs, thereby advancing the large-scale application of electrolytic water splitting technology and providing strong support for achieving global energy transition and carbon neutrality goals.

References

[1] C.-F. Schleussner, J. Rogelj, M. Schaeffer, T. Lissner, R. Licker, E.M. Fischer, R. Knutti, A. Levermann, K. Frieler, W. Hare, Science and policy characteristics of the Paris Agreement temperature goal, Nature Climate Change, 6 (2016) 827-835.

[2] T.F. Qahtan, I.O. Alade, M.S. Rahaman, T.A. Saleh, Mapping the research landscape of hydrogen production through electrocatalysis: A decade of progress and key trends, Renewable and Sustainable Energy Reviews, 184 (2023) 113490.

[3] Y. Wang, D. Yan, S. El Hankari, Y. Zou, S. Wang, Recent Progress on Layered Double Hydroxides and Their Derivatives for Electrocatalytic Water Splitting, Advanced Science, 5 (2018) 1800064.

ISSN: 2710-0723

[4] W. Zhang, M. Liu, X. Gu, Y. Shi, Z. Deng, N. Cai, Water Electrolysis toward Elevated Temperature: Advances, Challenges and Frontiers, Chem. Rev., 123 (2023) 7119-7192.

[5] L. Niu, R. Tian, W. Zhang, H. Wang, J. Wang, Y. Liu, Efficient Photoelectrocatalysis of Glycerol to Dihydroxyacetone and Synergistic Hydrogen Generation via Dual Oxidation Pathways Using Co-LDH/Bi2O3/TiO2 Ternary Array, ACS Catalysis, (2025) 2124-2138.

[6] B. Zhu, B. Dong, F. Wang, Q. Yang, Y. He, C. Zhang, P. Jin, L. Feng, Unraveling a bifunctional mechanism for methanol-to-formate electro-oxidation on nickel-based hydroxides, Nat. Commun., 14 (2023) 1686.

[7] J. Liu, M. Zhang, Q. Tang, Y. Zhao, J. Zhang, Y. Zhu, Y. Liu, X. Hu, L. Li, Supra Hydrolytic Catalysis of Ni3Fe/rGO for Hydrogen Generation, Advanced Science, 9 (2022) 2201428.

[8] F. Dawood, M. Anda, G.M. Shafiullah, Hydrogen production for energy: An overview, Int. J. Hydrogen Energy, 45 (2020) 3847-3869.

[9] L. Yao, X. Wu, Z. Geng, Y. Zhang, Y. Fang, Q. Zhu, N. Liang, M. Cai, H. Sai, J. Cheng, S. Li, Y. Wang, M. Han, K. Huang, S. Feng, Oxygen Evolution Reaction of Amorphous/Crystalline Composites of NiFe(OH)x/NiFe2O4, ACS Nano, 19 (2025) 5851-5859.

[10] Y. Yuan, Y. Yang, G. Liu, M. Chang, Z. Liu, K. Gao, H. Zheng, M. Ye, J. Shen, "One Stone, Two Birds": Multi-Element Doping Induced Crystallinity Modulation for Large Current Density Oxygen Evolution Reaction, Adv. Funct. Mater., n/a (2025) 2422889.

[11] J. Chen, H. Chen, T. Yu, R. Li, Y. Wang, Z. Shao, S. Song, Recent Advances in the Understanding of the Surface Reconstruction of Oxygen Evolution Electrocatalysts and Materials Development, Electrochemical Energy Reviews, 4 (2021) 566-600.

[12] B.M. Stratakes, J.L. Dempsey, A.J.M. Miller, Determining the Overpotential of Electrochemical Fuel Synthesis Mediated by Molecular Catalysts: Recommended Practices, Standard Reduction Potentials, and Challenges, ChemElectroChem, 8 (2021) 4161-4180.

[13] A.J. Bard, L.R. Faulkner, H.S. White, Electrochemical methods: fundamentals and applications., Wiley, 1983.

[14] C.C.L. McCrory, S. Jung, I.M. Ferrer, S.M. Chatman, J.C. Peters, T.F. Jaramillo, Benchmarking Hydrogen Evolving Reaction and Oxygen Evolving Reaction Electrocatalysts for Solar Water Splitting Devices, J. Am. Chem. Soc., 137 (2015) 4347-4357.

[15] P.M. Bodhankar, P.B. Sarawade, G. Singh, A. Vinu, D.S. Dhawale, Recent advances in highly active nanostructured NiFe LDH catalyst for electrochemical water splitting, J. Mater. Chem. A, 9 (2021) 3180-3208.

[16] J. Jiang, C. Xi, Y. Zhao, Y. Zhu, K. Hu, Y. Wang, S. Wang, Z. Zhang, S. Han, MXene-Based Hierarchical Electron Coupling Engineering of F-Doped NiFe LDH/MOF-74 Electrocatalysts for Efficient Overall Water Splitting, ACS Catalysis, (2025) 2561-2575.

[17] H. Yin, M. Huang, L. Wang, S. Muhammad, T.T. Isimjan, J. Guo, D. Cai, B. Wang, X. Yang, Lattice-mismatched MOF-on-MOF nanosheets with rich oxygen vacancies show fast oxygen evolution kinetics for large-current water splitting, Appl. Catal. B, 367 (2025) 125105.

[18] Y. Qin, T. Yu, S. Deng, X.-Y. Zhou, D. Lin, Q. Zhang, Z. Jin, D. Zhang, Y.-B. He, H.-J. Qiu, L. He, F. Kang, K. Li, T.-Y. Zhang, RuO2 electronic structure and lattice strain dual engineering for enhanced acidic oxygen evolution reaction performance, Nat. Commun., 13 (2022) 3784.

[19] C.C.L. McCrory, S. Jung, J.C. Peters, T.F. Jaramillo, Benchmarking Heterogeneous Electrocatalysts for the Oxygen Evolution Reaction, J. Am. Chem. Soc., 135 (2013) 16977-16987.

[20] Z.-Y. Wu, F.-Y. Chen, B. Li, S.-W. Yu, Y.Z. Finfrock, D.M. Meira, Q.-Q. Yan, P. Zhu, M.-X. Chen, T.-W. Song, Z. Yin, H.-W. Liang, S. Zhang, G. Wang, H. Wang, Non-iridium-based electrocatalyst for durable acidic oxygen evolution reaction in proton exchange membrane water electrolysis, Nat. Mater., 22 (2023) 100-108.

[21] Y. Shi, B. Zhang, Recent advances in transition metal phosphide nanomaterials: synthesis and applications in hydrogen evolution reaction, Chem. Soc. Rev., 45 (2016) 1529-1541.

[22] D. Zhou, P. Li, X. Lin, A. McKinley, Y. Kuang, W. Liu, W.-F. Lin, X. Sun, X. Duan, Layered double hydroxide-based electrocatalysts for the oxygen evolution reaction: identification and tailoring of

ISSN: 2710-0723

active sites, and superaerophobic nanoarray electrode assembly, Chem. Soc. Rev., 50 (2021) 8790-8817.

[23] Y. Huang, A.G.A. Mohamed, J. Xie, Y. Wang, Surface evolution of electrocatalysts in energy conversion reactions, Nano Energy, 82 (2021) 105745.

[24] X. Liu, J. Meng, K. Ni, R. Guo, F. Xia, J. Xie, X. Li, B. Wen, P. Wu, M. Li, J. Wu, X. Wu, L. Mai, D. Zhao, Complete Reconstruction of Hydrate Pre-Catalysts for Ultrastable Water Electrolysis in Industrial-Concentration Alkali Media, Cell Reports Physical Science, 1 (2020) 100241.

[25] N. Zhang, X. Feng, D. Rao, X. Deng, L. Cai, B. Qiu, R. Long, Y. Xiong, Y. Lu, Y. Chai, Lattice oxygen activation enabled by high-valence metal sites for enhanced water oxidation, Nat. Commun., 11 (2020) 4066.

[26] K. Yin, Y. Chao, F. Lv, L. Tao, W. Zhang, S. Lu, M. Li, Q. Zhang, L. Gu, H. Li, S. Guo, One Nanometer PtIr Nanowires as High-Efficiency Bifunctional Catalysts for Electrosynthesis of Ethanol into High Value-Added Multicarbon Compound Coupled with Hydrogen Production, J. Am. Chem. Soc., 143 (2021) 10822-10827.

[27] J.Y.C. Chen, L. Dang, H. Liang, W. Bi, J.B. Gerken, S. Jin, E.E. Alp, S.S. Stahl, Operando Analysis of NiFe and Fe Oxyhydroxide Electrocatalysts for Water Oxidation: Detection of Fe4+ by Mössbauer Spectroscopy, J. Am. Chem. Soc., 137 (2015) 15090-15093.

[28] F. Dionigi, Z. Zeng, I. Sinev, T. Merzdorf, S. Deshpande, M.B. Lopez, S. Kunze, I. Zegkinoglou, H. Sarodnik, D. Fan, A. Bergmann, J. Drnec, J.F.d. Araujo, M. Gliech, D. Teschner, J. Zhu, W.-X. Li, J. Greeley, B.R. Cuenya, P. Strasser, In-situ structure and catalytic mechanism of NiFe and CoFe layered double hydroxides during oxygen evolution, Nat. Commun., 11 (2020) 2522.

[29] C. Wang, P. Zhai, M. Xia, Y. Wu, B. Zhang, Z. Li, L. Ran, J. Gao, X. Zhang, Z. Fan, L. Sun, J. Hou, Engineering Lattice Oxygen Activation of Iridium Clusters Stabilized on Amorphous Bimetal Borides Array for Oxygen Evolution Reaction, Angew. Chem. Int. Ed., 60 (2021) 27126-27134.

[30] X. Li, Y. Liu, Q. Sun, Z. Huangfu, W.-H. Huang, Z. Wang, C.-C. Chueh, C.-L. Chen, Z. Zhu, Effects of Cationic and Anionic Defects on NiFe LDH in Electrocatalytic Oxygen Evolution, ACS Sustainable Chemistry & Engineering, 10 (2022) 14474-14485.

[31] B.M. Hunter, W. Hieringer, J.R. Winkler, H.B. Gray, A.M. Müller, Effect of interlayer anions on [NiFe]-LDH nanosheet water oxidation activity, Energy Environ. Sci., 9 (2016) 1734-1743.