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Current Development and Practical Thinking of NiFe-based Electrocatalysts for Alkaline Oxygen Evolution Reaction

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Abstract

The oxygen evolution reaction (OER) is the kinetically-limiting half-reaction in alkaline water electrolysis, and is fundamental to the viability of industrial-scale green hydrogen production. NiFe based electrocatalysts represent the most studied class of non-precious metal OER catalysts considering their superior intrinsic activity, earth-abundance and structural variety. In this work, the current progress of NiFe-based electrocatalysts for alkaline OER is summarised from three aspects including mechanistic knowledge, material engineering strategies and stability concerns. The adsorbate evolution mechanism (AEM) and lattice oxygen mechanism (LOM) are critically explored for NiFe layered double hydroxides (NiFe-LDH) and their in-situ regenerated NiFeOOH phases. Systematic reviews on engineering approaches such as heteroatom doping, defect engineering, heterostructure fabrication and substrate integration are offered. The primary obstacles for commercialisation are identified to be stability issues associated with iron segregation, structural degradation and catalyst delamination and potential new mitigation measures are proposed including oxyanion stabilisation and self-healing designs. The review concludes with practical ideas on bridging laboratory performance criteria and industry needs in electrolysis.

Keywords

NiFe-based electrocatalysts; oxygen evolution reaction; alkaline water electrolysis; NiFe-LDH; surface reconstruction; stability; green hydrogen.

1. Introduction

1.1. Research Background

The fast global transition towards renewable energy systems increased the demand for efficient electrochemical water splitting as a route for green hydrogen production. Water splitting consists of two half processes: the hydrogen evolution reaction (HER) at the cathode and the OER at the anode. The OER, while rapid HER kinetics, is a four-electron transfer process with many oxygen-containing intermediates (OH, O, OOH*) and significant intrinsic activation barriers. 8,9 This leads to large overpotentials dominating the efficiency losses of practical electrolysis systems. State-of-the-art precious-metal catalysts, IrO2 and RuO2, are highly active OER catalysts, but their prohibitively high cost and scarcity hinder widespread terawatt-scale deployment. Thus, the creation of earth-abundant, high-performance OER electrocatalysts is a critical materials science challenge with apparent repercussions for the economic sustainability of green hydrogen.

NiFe-based compounds are the most studied non-precious metal catalysts. The nickel and iron exhibit synergistic electrical effects that impart OER activity nearing or reaching precious metal benchmark under alkaline conditions, yet are manufacturable at minimum cost from abundant precursors. The structural diversity of NiFe-based materials, such as layered double hydroxides, oxyhydroxides, oxides, alloys and metal-organic framework (MOF)-derived phases provides a large range of systematic materials engineering to probe . The mechanistic details of the NiFe system have made it an ideal model for fundamental studies of the OER mechanism.

1.2. Research Questions

This review answers three research questions. RQ1: What is the most appropriate mechanistic framework and the genuine catalytically active phase to explain the outstanding OER activity of NiFe-based materials in alkaline media? RQ2: What engineering methods are most beneficial to improve the activity and stability of NiFe-based electrocatalysts? RQ3: What are the major challenges for the practical implementation of NiFe-based catalysts in industrial alkaline electrolysers and what solutions are being developed to overcome them?

2. Reaction Mechanisms and Active Phase Identification

2.1. OER Mechanism in Alkaline Media

The alkaline OER proceeds by a stepwise pathway with four electrons, each step consisting of a proton/electron transfer. The mechanism of the adsorbate evolution (AEM) describes the catalytic cycle as OH→O→OOH→O2. Suen et al. in their extensive investigation of OER electrocatalysis determined that the step O → OOH is the rate-determining step for most transition metal oxides [1]. From the AEM constraint, we can calculate the minimal theoretical overpotential, defined by the scaling relation between the O and OOH* binding energies, to be ~0.37 V, which is a thermodynamic floor that cannot be crossed within the AEM framework by decoupling the scaling relations. A lattice oxygen mechanism (LOM) in which the framework oxygen is a direct participant in O-O bond formation rather than a spectator, provides a way to break the AEM scaling equations and has been proposed to operate in highly oxidised NiFeOOH phases under anodic conditions [3]. The mechanistic difference between AEM and LOM has direct consequences for catalyst design, with AEM optimisation being focused on the electronic structure of the metal active sites to optimise the binding of intermediates, while LOM activation requires the creation of oxygen vacancy sites and the stabilisation of high-valence metal centres. The distinction has direct consequences for catalyst design strategies across the NiFe materials family [2].

2.2. Surface Reconstruction and the True Active Phase

One of the crucial conclusions from the last decade of NiFe OER research is that the as synthesised catalyst is rarely the catalytically active species . In alkaline media, under anodic OER conditions, NiFe-LDH and related precatalysts undergo irreversible surface reconstruction to form amorphous or partially ordered NiFeOOH phases, which are considerably different in structure and content from the precatalyst [4]. Operando X-ray absorption spectroscopy studies have verified that in this reconstruction the oxidation of Ni2+ to Ni3+/4+ and incorporation of Fe3+ into the NiOOH framework occurs, and the resulting Fe-substituted NiOOH (NiFeOOH) exhibits significantly higher OER activity than pure NiOOH or FeOOH [4]. The attribution of the active site in NiFeOOH is currently under discussion, as both density functional theory (DFT) calculations and in-situ spectroscopic studies point towards Ni sites, Fe sites and cooperative Ni-Fe pairs as prominent active centers. Recent work combining synchrotron XAS with electrochemical isotope labelling suggests that Fe is the major OER active site, with Ni providing the electronic framework that keeps Fe in the ideal +3/+4 redox window during catalysis [3][4].

3. Engineering Strategies for Enhanced OER Performance

3.1. Heteroatom Doping and Electronic Structure Tuning

Heteroatom doping of NiFe-LDH frameworks is one of the most widely used strategies for promoting OER activity by tuning the d-band electronic structure at active sites and optimising the binding energies of intermediates. Third-row transition metal dopants such as Co, Mn, V and Mo have been included into the interlayer and framework locations of NiFe-LDH with observed improvements in overpotential and Tafel slope [2]. Special attention has been paid to doping with non-metallic atoms – P, S, Se and N – to tune the charge distribution around the active metal sites without changing the structural framework. Phosphorus incorporation has been shown to promote the reconstruction of NiFe precatalysts into highly active NiFeOOH phases through weakening interlayer bonding and accelerating topochemical conversion [5]. In a recent systematic study of divalent-site doping in NiFe-LDH, Co incorporation at Ni2+ sites led to a CoNiFe-LDH catalyst with an overpotential of 191 mV at 10 mA cm-2 in 1 M KOH, and the improvement was attributed to Co-mediated enhancement of the Fe site accessibility and optimisation of the O* binding energy [6].

3.2. Defect Engineering and Structural Optimisation

OER active sites tend to be located at structural imperfections such vacancies, grain boundaries and coordinatively unsaturated metal sites, as they are distinct from the bulk coordination environment and lead to d-orbital electronic configurations which are favourable for intermediate binding. The vacancy engineering of NiFe-LDH was realised by chemical etching, electrochemical activation and heat treatment. The OER activity has been reported to be enhanced by cation vacancies (particularly Ni vacancies), which increase the density of high-valence Fe sites in the rebuilt NiFeOOH phase [7]. The cavity-rich amorphous NiFeOOH phase from fluoride-induced reconstruction leads to low overpotentials of 152 mV at 10 mA cm-2 and TOF of 1.6 × 10-1 s-1 at 200 mV overpotential for the deeply reconstructed NiFe-F catalysts synthesised by solvothermal fluorination [8]. Consequently, the overpotentials can be suppressed to 235 mV at 100 mA cm-2 and 308 mV at 1000 mA cm-2 in 1 M KOH by incorporating Cr vacancies into NiFeOOH/FeOOH heterostructures, indicating the potential of vacancy-rich heterostructures for high current density operation for industrial electrolysis [9].

3.3. Heterostructure Construction and Substrate Engineering

Heterojunctions of NiFe based active phases with complementary materials can provide the benefits of enhanced charge transfer, increased active site density and improved interfacial stability simultaneously. NiFe-LDH@FeOOH hybrid electrocatalysts composed of FeOOH nanostructures grown on or incorporated with NiFe-LDH nanosheets show synergetic improvement on adsorption of intermediates than individual components, with reported overpotentials of 245 mV at 100 mA cm-2 [10]. The powder catalysts can be assembled into the self-supported electrodes with enhanced mass transfer, reduced interfacial resistance and no activity loss due to binders [2][7] by introducing them into 3D current collectors (nickel foam, iron foam and carbon cloth). A scalable room temperature synthesis of NiFeOOH/FeOOH on iron foam by a corrosion approach provides a viable route to self-supported catalysts for industrial scale-up with overpotentials of 279 mV at 500 mA cm-2 and exceptional chronopotentiometric stability [9].

4. Stability Challenges and Practical Perspectives

4.1. Iron Segregation and Structural Degradation

The major hurdle for the commercialisation of NiFe-based OER catalysts is their long-term durability under the high current density, high temperature and strongly alkaline conditions of industrial alkaline electrolysis. The three degradation processes have been recognised as the main stability limiting factors [11]. Iron segregation, i.e. preferential leaching of Fe from the NiFeOOH framework under extended anodic polarisation, progressively shifts the catalyst composition toward pure NiOOH, which shows much lower OER activity than the Fe-doped phase. The structural deterioration, i.e. loss of the ordered NiFe-LDH or NiFeOOH framework through oxidative dissolution and amorphisation, results in an increase in the charge transfer resistance and a decrease in the active site accessibility with time. A failure scenario most acute at current densities over 500 mA cm-2 is gas evolution pressure induced catalyst delamination from the substrate, volume changes during redox cycling and electrolyte penetration, all of which remove active material from the electrode [11].

The vast majority of laboratory studies report stability at 10 mA cm-2 for 10-12 hours but industrial alkaline electrolysers operate at 200-500 mA cm-2 for thousands of hours which is a difference of many orders of magnitude between laboratory validation and operational needs [2][11]. To address this there is a need for protocols for the assessment of stability that are explicitly targeted at industry-relevant conditions including galvanostatic testing at high current density, accelerated stress tests to mimic start stop cycling and post-mortem characterisation to relate compositional changes to performance decay.

4.2. Emerging Stability Strategies

The study of Fe segregation has been a significant research frontier. The stability of the Ni-Fe bond was shown to be enhanced by the incorporation of oxyanions (NO3-, PO43-, SO42- or SeO42-) into the NiFeOOH framework (i.e. oxyanion incorporation) by allowing for the coordination of the metal with the oxyanions. The activity decay of unmodified NiFeOOH was 13.19% over 100 hours at 1 A cm-2 but this was reduced to 3.33% for NiFeOOH-NO3- which showed a fourfold improvement in long-term stability by inhibiting Fe dissolution [12]. In AEM electrolyser architectures with a near-neutral pH in the catalyst microenvironment while keeping an alkaline electrolyte composition, the thermodynamic driving force for Fe leaching is minimised, offering a system-level approach to stability enhancement, complementing strategies for materials-level stabilisation [11]. It has been shown that self-healing catalyst architectures exist for NiFe thin films, where dissolved catalyst species readsorb onto the electrode surface from solution, indicating that partial catalyst dissolution does not necessarily lead to irreversible activity loss if the redeposition equilibrium is maintained [13].

To answer RQ2: the most effective engineering strategies combine defect engineering and heteroatom doping to boost intrinsic activity with substrate integration and oxyanion stabilisation to overcome the stability limitations that impede their practical application.

5. Discussion: Bridging Laboratory Performance and Industrial Requirements

5.1. Metrics Gap and Benchmarking Standards

A recurring problem in the lab OER literature for NiFe-based catalysts is the difference in reported performance settings and circumstances of industrial significance. The traditional comparison metric overpotentials at 10 mA cm-2 are related to the lit regions of photoelectrochemical cells rather than to the industrial current densities. Activity rankings at 10 mA cm-2 are not always predictive of performance at 500–1000 mA cm-2 because to mass transfer restrictions and Ohmic losses [2]. Standardised reporting including overpotentials at industrially relevant current densities (100 mAcm-2), electrochemical active surface area normalised turnover frequencies for mechanistic comparison and stability protocols beyond 500 hours under galvanostatic conditions would be beneficial for the field.

5.2. Theoretical Guidance and Mechanistic Integration

The answer to RQ1 is that the true active phase for NiFe-based OER catalysis is the in-situ reconstructed NiFeOOH phase and Fe is identified as the primary active site with Ni providing the electronic environment that stabilises Fe in the catalytically optimal high-valent state. DFT-guided design has been successful in identifying dopant combinations that optimise Fe site activity while maintaining Ni scaffold stability, using d-band centre and oxygen p-band centre as activity descriptors, and represents the most theoretically consistent approach to rational catalyst design [3][4].

In response to RQ3: the main practical limits are the long-term stability requirements in Section 4, and the metrics gap in Section 5.1. For example, practical paths to advancement include embedding oxyanion-stabilised NiFeOOH catalysts in AEM electrolysers and evaluating their performance under conventional high current density conditions.

6. Conclusion

Here we report NiFe-based electrocatalysts as the most promising earth-abundant OER catalysts for alkaline water electrolysis, owing to the combination of excellent intrinsic activity, resulting from Fe active sites in the reconstructed NiFeOOH phase, and structural versatility, enabling systematic performance optimisation by doping, defect engineering and heterostructure construction. The remaining major challenge is long term stability under industrial operating conditions: iron segregation, structural degradation, and catalyst delamination all limit the operational lifetime of current NiFe catalysts to a small fraction of the thousands of hours required for viable commercial deployment. Potential avenues to address these stability restrictions are emerging technologies of oxyanion stabilisation, integration of AEM electrolyser and self-healing systems. Achieving the full potential of NiFe-based catalysts for industrial green hydrogen production demands convergent advances in mechanistic understanding, materials engineering and evaluation methodology – and alignment of laboratory benchmarking with the performance requirements of practical electrolysis systems.

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