

Oxygen evolution reaction electrocatalysts for efficient hydrogen production in anion
exchange membrane water electrolyzers

By

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AN ABSTRACT OF A DISSERTATION

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DOCTOR OF PHILOSOPHY

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Abstract

Due to the global energy crisis and climate change, developing clean energy sources, such as hydrogen, is becoming urgent. A critical method for hydrogen production is electrochemical water splitting (i.e., water electrolysis), specifically through anion exchange membrane water electrolyzers (AEMWEs), which combine the advantages of both alkaline water electrolyzers (AWEs) and proton exchange membrane water electrolyzers (PEMWEs). AEMWEs with excellent fabrication are a vital way in pursuit of efficient and environmentally hydrogen generation.

However, AEMWEs suffer from low energy efficiency and poor hydrogen production rate, which is ascribed to the sluggish kinetics of the anodic oxygen evolution reaction (OER) in the alkaline media. Therefore, it is crucial to discover an efficient catalyst to increase the reaction rate. Highly active and platinum group metal-free (PGM-free) OER electrocatalysts are essential for producing low-cost and clean hydrogen in AEMWEs.

Thanks to the unique characteristics of perovskite oxides, oxyhydroxide (OOH), and layered double hydroxides (LDH), which include low-cost, tunable electronic structure and cation deficiency, high electronic conductivity, high durability, high specific catalytic activity, and environmental friendliness, they are widely designed and employed as the OER electrocatalysts. This study centers on designing, synthesizing, and characterizing new OER electrocatalysts, including perovskite oxides, oxyhydroxide (OOH), and layered double hydroxides (LDH), which aims to produce green hydrogen in AEMWEs with enhanced energy efficiency.

Ruddlesden–Popper perovskite is one type of perovskite group and also a great OER electrocatalyst. Here, a set of novel hybrid perovskites, $\text{La}_x\text{Sr}_{4-x}\text{Ni}_y\text{Fe}_{3-y}\text{O}_{10-\delta}$ ($\text{L}_x\text{S}_{4-x}\text{N}_y\text{F}_{3-y}$), were demonstrated, which consist of a single-layer perovskite phase (P phase) and two Ruddlesden–Popper perovskite phases (RP phases). These hybrid perovskites synergize the advantages of the P phase and RP phases, which improves the oxygen-ion diffusion rate, leading to enhanced OER activity. Furthermore, the concentration of each phase can be tuned by alternating the compositional stoichiometry. A relatively uniform distribution of the P phase and RP phases can maximize the interfacial area and

achieve the highest oxygen-ion diffusion rate. $\text{L}_3\text{S}_1\text{N}_2\text{F}_1$, $\text{L}_2\text{S}_2\text{N}_1\text{F}_2$, and $\text{L}_2\text{S}_2\text{N}_{1.5}\text{F}_{1.5}$ exhibit outstanding OER activity, which achieve 10 mA/cm^2 at a low overpotential of $<360 \text{ mV}$ in 1.0 M KOH . Additionally, herein, the hybrid perovskites are implemented as the anodes of AEMWEs, which deliver an exceptional current density of $>1.0 \text{ A/cm}^2$ at 1.8 V .

Additionally, we demonstrate unique perovskite oxides, $\text{La}_x\text{Ce}_{1-x}\text{Ni}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ ($\text{L}_x\text{C}_{1-x}\text{N}_y\text{F}_{1-y}$). $\text{L}_{0.9}\text{C}_{0.1}\text{N}_{0.7}\text{F}_{0.3}$ exhibits outstanding OER activity, which achieves 10 mA/cm^2 at a low overpotential of 338 mV in 1.0 M KOH in a half-cell test. Furthermore, $\text{L}_{0.9}\text{C}_{0.1}\text{N}_{0.7}\text{F}_{0.3}$ and $\text{L}_{0.9}\text{C}_{0.1}\text{N}_1$ show the unique feature that the performance tends to increase at the beginning of the stability test.

Moreover, oxyhydroxide (OOH) is also a type of platinum group metal-free (PGM-free) electrocatalysts for oxygen evolution reaction (OER) electrodes in AEMWE, which displays excellent performance. In this study, the OOH electrode is different from perovskite oxides, $\text{L}_x\text{C}_{1-x}\text{N}_y\text{F}_{1-y}$, hybrid RP-perovskite electrode, and $\text{L}_x\text{S}_{4-x}\text{N}_y\text{F}_{3-y}$. Ni-incorporated CoFeOOH on Fe foam (NiCoFeOOH/FF) is a 3-D unified electrode without a binder. Herein, first, we optimize cobalt–iron (oxy)hydroxide (CoFeOOH/FF), which is directly grown on Fe foam via the galvanic corrosion method, with different Co concentrations to achieve great catalyst activity for OER. Then, Ni-incorporated CoFeOOH on Fe foam (NiCoFeOOH/FF) with different Ni concentrations is prepared. CoNiFeOOH with a Co/Ni ratio of 20:10 (NiCoFeOOH/FF 10) exhibits outstanding OER activity, which achieves superior catalytic performance. At a current density of 10 mA/cm^2 , a low overpotential of 234 mV is achieved in 1.0 M KOH at room temperature in half-cell testing. Additionally, NiCoFeOOH/FF 10 is implemented as the anode of AEMWE full cells, which delivers an exceptional current density of 1.6 A/cm^2 at 1.8 V and 50°C . This study shows a new insight into designing OER catalysts in water splitting.

Furthermore, unlike the above water splitting utilizing pure water, this research also explores seawater electrolysis. As an abundant and more environmentally conscientious alternative resource, seawater could be used directly in electrochemical water splitting to generate hydrogen, which is also helpful for seawater desalination. In seawater electrolysis, it is imperative to utilize electrocatalysts that exhibit exceptional activity for the oxygen evolution reaction (OER) and catalyst selectivity.

NiFe LDH is one type of advanced OER electrode in water electrolysis. This thesis investigated the highly active electrocatalyst NiFe LDH with different Ni/Fe ratios half-cell test scale. NiFe LDH with Ni/Fe ratio 75/25 (NiFe LDH 75) expressed outstanding performance, with an overpotential of 282 mV at a current density of 10 mA/cm². In simulated seawater, an overpotential of 378 mV is achieved at a current density of 10 mA/cm², which is higher than that attained in 1M KOH. However, the performance is much better than the previous report catalyst, for example, IrO₂. Additionally, NiFe LDH 75 is studied as the OER electrode of AEMWEs with different configurations for seawater electrolysis. All asymmetric feeds expressed remarkable performance, achieving an exceptional current density of >1 A/cm² at 1.8 V, and a high Faradaic efficiency, close to 100%. Feeding 1M KOH to the anode and 0.5M NaCl to the cathode, an energy conversion efficiency of 77% is achieved, and long-time stability in seawater was demonstrated up to 150 hours. Our NiFe LDH 75 AEM catalyst operated in simulated seawater demonstrated superior performance compared to the previously reported AEM electrolyzer performed in 1.0 M KOH.

In summary, this comprehensive investigation navigates through diverse OER electrocatalytic materials, L_{0.9}C_{0.1}N_{0.7}F_{0.3}, L₃S₁N₂F₁, NiCoFeOOH/FF 10, and NiFe LDH 75, unveiling innovative pathways to enhance energy efficiency and achieve sustainable hydrogen production through electrochemical water splitting and seawater electrolysis in the backdrop of a rapidly evolving energy landscape.

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Major Professor
Chuancheng Duan

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Table of Contents

List of Figures.....	xv
List of Tables.....	xxiv
List of Acronyms and Definitions.....	xxv
Acknowledgments	xxvii
Chapter 1 – Background and Motivations	1
1.1 Anion Exchange Membrane Water Electrolyzers (AEMWEs)	1
1.2 Motivations of Studying Anion Exchange Membrane Water Electrolyzers	2
1.3 Critical Barriers in the Field of Anion Exchange Membrane Water Electrolyzers ...	4
1.4 HER and OER Mechanisms Under Alkaline Conditions.....	5
1.4.1 HER Mechanisms Under Alkaline Conditions.	5
1.4.2 OER Mechanisms Under Alkaline Conditions.....	5
1.5 Electrocatalysts for OER under Alkaline Conditions	7
1.5.1 Platinum Group Metal (PGM)-based electrocatalysts	7
1.5.2 Perovskites	8
1.5.3 Layered Double Hydroxides (LDH)	10
1.5.4 Oxyhydroxide (OOH)	11
1.5.5 Other OER Catalysts under Alkaline Conditions.....	12
1.6 Seawater Electrolysis.....	12
1.6.1 Challenges in Seawater Electrolysis.....	12
1.6.2 Current Studies in Seawater Electrolysis	13
1.6.3 OER Catalyst Design in Seawater Electrolysis	17
Chapter 2 - Fundamentals of the Materials Synthesis and Characterizations	18
2.1 OER Electrocatalysts Synthesis Methods	18
2.1.1 Sol-Gel method.....	18

2.1.2 Co-precipitation Methods for Synthesizing NiFe LDH and NiFeOOH	20
2.1.3 Corrosion Methods for synthesizing unified NiFeOOH on Fe/Ni foam	21
2.1.4 Others	23
2.2 Structural Characterization Methods	24
2.2.1 X-Ray Diffraction.....	24
2.2.2 Scanning Electron Microscopy / Transmission Electron Microscopy	28
2.2.3 X-ray Photoelectron Spectroscopy	29
2.3 Different OER Electrodes for Performance evaluation	30
2.3.1 Rotating Disk Electrode (RDE)	30
2.3.2 Binder-free unified Electrode	32
2.3.3 Catalyst Loading Effect.....	33
2.4 Electrochemical Testing System Setup.....	34
2.4.1 Three Electrode System	34
2.4.2 Membrane Electrode Assemblies	36
2.5 OER Electrochemical Measurement and Data Analysis	37
2.5.1 Cyclic Voltammetry and Linear Sweep Voltammetry	37
2.5.2 Electrochemical Impedance Spectroscopy	39
2.5.3 Electrochemically Active Surface Area Measurement	40
2.5.4 Tafel slope	42
2.5.5 Stability	43
2.5.6 Overpotential Analysis	45
2.5.8 Oxygen-ion Diffusion Coefficient Analysis	46
Chapter 3 - Hybrid Perovskites as Oxygen Evolution Electrocatalysts for High- Performance Anion Exchange Membrane Water Electrolyzers.....	48
3.1 Introduction	48

3.2 Experimental Section	50
3.2.1 Materials Synthesis: Perovskites	50
3.2.2 Structural Characterization	51
3.2.3 Electrochemical Characterization at the Half-cell Level	51
3.2.4 Evaluation of the OER Electrocatalysts at the AEM Water Electrolyzer Level.....	53
3.3 Results and Discussion.....	55
3.3.1 Structural Properties of Hybrid Perovskites	55
3.3.2 Electrochemical Properties of Hybrid Perovskites at the Half-cell Level	58
3.3.3 Correlation of Electrochemical Properties with the Oxygen-ion Diffusion Coefficient and Crystal Structure	64
3.3.4 Electrochemical Performance of AEM Electrolyzers with Hybrid Perovskites as OER Catalysts.	67
3.4 Conclusion	71
Chapter 4 - Designing OER Electrocatalysts for Hydrogen Production via Seawater Electrolysis	
4.1 Introduction	73
4.2 Experimental Section	74
4.2.1 Materials Synthesis: NiFe Layered Double Hydroxides	75
4.2.2. Structural Characterization	75
4.2.3 Electromical Characterization at the Half cell.....	75
4.2.4 Evaluation of the OER Electractlysts at the AEM Water Electrolyzers.....	76
4.2.5 Free chlorine detection	78
4.3 Results and Discussion.....	79
4.3.1 Structural Properties of NiFe LDH	79
4.3.2 Electrochemical Properties of NiFe LDH at the Half-cell Level	80

4.3.3 Electrochemical performance of the AEM Water Electrolyzers Level with NiFe LDH as the OER Catalysts	86
4.4 Conclusions	106
Chapter 5- Optimizing NiCoFeOOH on Iron Foam for Anion Exchange Membrane Water Electrolyzers.....	108
5.1 Introduction	108
5.2 Experimental Section	109
5.2.1 Materials Synthesis: CoFeOOH and CoNiFeOOH on Iron Foam	109
5.2.2 Structural Characterization	111
5.2.2 Electrochemical Characterization at the Half-cell Level	111
5.2.3 Evaluation of the OER Electrocatalysts at the AEM Water Electrolyzer Level	111
5.3 Results and Discussion.....	112
5.3.1 Structural Properties of NiCoFeOOH on Fe Foam.....	112
5.3.2 Electrochemical Properties of NiCoFeOOH on Fe Foam at the Half-cell Level	122
5.2.3 Electrochemical performance of the AEM Water Electrolyzers Level with NiCoFeOOH on Fe Foam as the OER Catalysts	131
5.4 Conclusions	137
Chapter 6 – Perovskites of $\text{La}_x\text{Ce}_{1-x}\text{Ni}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ as Oxygen Evolution Electrocatalysts for High-Performance Anion Exchange Membrane Water Electrolyzers	138
6.1 Introduction	138
6.2 Experimental Section	139
6.2.1 Materials Synthesis: Perovskites	139
6.2.2 Structural Characterization	139
6.2.3 Electrochemical Characterization at the Half-cell Level	140

6.3 Results and Discussion.....	140
6.3.1 Structural Properties of Perovskites.....	140
6.3.2 Electrochemical Properties of Perovskites at the Half-cell Level	141
6.3.3 Special Electrochemical Properties - Stability of Perovskites at the Half-cell Level	144
6.4 Conclusions	147
Chapter 7 - General Conclusion and Future Work	148
References.....	150

List of Figures

Figure 1. Schematic diagram of the anion exchange membrane water electrolyzers [8].	2
Figure 2. Schematic diagram of three types of water electrolysis. (A) AWE; (B) PEMWE; (C) AEMWE [9].	2
Figure 3. Comparison of electrode reactions for acid-based proton exchange membrane water electrolyzers (PEMWEs) and alkaline exchange membrane water electrolyzers (AEMWEs) [21].	6
Figure 4. Oxygen evolution mechanisms under alkaline conditions. (A) AEM [22]; (B) LOM [25].	7
Figure 5. Crystal structure of RuO ₂ [30].	8
Figure 6. The crystal structure of the RP phase ($A_{n+1}B_nO_{3n+1}$ where $n=1,2$, and 3) [39].	9
Figure 7. The structure diagram of NiFe LDH [48].	10
Figure 8. Roubaix diagram of chlorine [57].	13
Figure 9. Schematic illustration of AEM seawater electrolyzers with different configurations. (A) type A: 1M KOH+0.5M NaCl is fed to the anode; (B) type B: 1M KOH+0.5M NaCl is fed to the anode and 0.5 M NaCl solution is fed to the cathode; (C) type C: 0.5 M NaCl solution is fed to the cathode and 1M KOH is fed to anode (D) type D: deionized(DI) water is fed to the cathode and 1M KOH is fed to anode.	14
Figure 10. Schematic of the sol-gel process [83].	19
Figure 11. Schematic diagram of the synthesis route of LNMO [89].	20
Figure 12. Schematic illustrations of the formation and microstructure of the electrodes. These specific reactions happen during the corrosion of iron substrates [93].	21
Figure 13. Schematic illustration of the formation and microstructure of the electrodes. (A) Schematic illustration of the preparation process of Cu–NiFe LDH/NF. (B) The specific reactions occur during the surface oxidation etching of NF [94].	23
Figure 14. Schematic illustration for the synthesis of CCO* on Ni foam. The bottom picture indicates an actual synthesized electrode [102].	24
Figure 15. Schematic diagram of the structure of the X-ray diffractometer and goniometer [103].	24

Figure 16. Schematic of the atomic energy levels and emission of characteristic X-ray radiation [104].	25
Figure 17. Intensity over wavelength distribution of the X-ray radiation produced by a sealed tube showing the continuous and characteristic spectrum [104].	26
Figure 18. Geometrical condition for diffraction from lattice planes [104].	26
Figure 19. The full width at half maximum [104].	27
Figure 20. Refined XRD profile of RP/P-LSCF [42].	28
Figure 21. Schematic of SEM, TEM, and STEM imaging methodology. (A) Serial collection of data points in SEM. (B) Parallel image acquisition in TEM [107].	29
Figure 22. Schematic of a typical X-ray photoelectron spectrometer [109].	30
Figure 23. Solution movement is caused by the rotation of an RDE. a: flow of electrolyte solution; b: vitreous carbon electrode; c: RDE body; d: direction of electrode rotation [110].	30
Figure 24. Representation of the Nernst diffusion layer profile model [110].	31
Figure 25. Schematic of the electrocatalytic OER in alkaline media [114].	32
Figure 26. Conventional and unified electrode with the Stainless steel paper. Schematic diagram of two types of electrodes [51].	33
Figure 27. Catalyst loading effect in electrochemical water splitting [115].	34
Figure 28. Three-electrode system [117].	36
Figure 29. Scheme of AEMWE [96].	36
Figure 30. Schematic of (A) the two-electrode electrolyzer configuration and (B) the three-electrode electrolyte configuration for performance evaluation [118].	37
Figure 31. Cyclic voltammetry of ferricyanide/ferrocyanide [119].	38
Figure 32. Concentration profiles (mM) for Fc^+ (blue) and Fc (green) as a function of the distance from the electrode [119].	39
Figure 33. Schematic of typical Nyquist plots for EDLC electrodes or devices [120].	40
Figure 34. Voltammogram for a Pt electrode in 0.5 M sulphuric acid [124].	41
Figure 35. Cyclic voltammogram recorded on Pt [125].	42
Figure 36. Tafel slope [126].	43
Figure 37. Schematic comparison of aqueous model system (AMS) and membrane electrode assembly (MEA) [129].	44

Figure 38. Applied voltage breakdown for this system [132].	45
Figure 39. A schematic illustration of the AEM and LOM reaction pathways on Si-incorporated strontium cobaltites [133].	46
Figure 40. Perovskite, $L_xS_{4-x}N_yF_{3-y}$, preparation process.	51
Figure 41. Three-electrode system with rotating disk electrode in half-cell test.	52
Figure 42. Single cell test station.	54
Figure 43. XRD patterns of three representative hybrid perovskites and TEM images of $L_3S_1N_2F_1$. XRD pattern and Rietveld refinement results of (A) $L_3S_1N_2F_1$, (B) $L_2S_2N_{1.5}F_{1.5}$, and (C) $L_1S_3N_2F_1$. (D) TEM images of $L_3S_1N_2F_1$, (E) High-resolution TEM image of $L_3S_1N_2F_1$, (F) High-resolution TEM image of $L_3S_1N_2F_1$ with three phases identified, (G) selected area electron diffraction (SAED) image of $L_3S_1N_2F_1$.	57
Figure 44. XRD patterns of (A) $L_2S_2N_1F_2$ and (B) $L_2S_2N_2F_1$.	58
Figure 45. Electrochemical performance of hybrid perovskites at the half-cell level, which is evaluated in 1.0 M KOH solution at room temperature. (A) Ohmic resistance-corrected polarization curves of $L_2S_2N_1F_2$, $L_2S_2N_{1.5}F_{1.5}$, and $L_2S_2N_2F_1$. (B) Electrochemical impedance spectra of $L_2S_2N_1F_2$, $L_2S_2N_{1.5}F_{1.5}$, and $L_2S_2N_2F_1$ at 1.7 V. (C) Tafel plots of $L_2S_2N_1F_2$, $L_2S_2N_{1.5}F_{1.5}$, and $L_2S_2N_2F_1$. (D) Ohmic resistance-corrected polarization curves of $L_3S_1N_2F_1$, $L_2S_2N_2F_1$, and $L_1S_3N_2F_1$. (E) Electrochemical impedance spectra of $L_3S_1N_2F_1$, $L_2S_2N_2F_1$, and $L_1S_3N_2F_1$ at 1.7 V. (F) Tafel plots of $L_3S_1N_2F_1$, $L_2S_2N_2F_1$, and $L_1S_3N_2F_1$.	59
Figure 46. Cyclic voltammetry testing in a non-Faradic current region under various scan rates. (A) $L_2S_2N_1F_2$, (B) $L_2S_2N_{1.5}F_{1.5}$, (C) $L_2S_2N_2F_1$, (D) $L_3S_1N_2F_1$, and (E) $L_1S_3N_2F_1$.	60
Figure 47. Linear fitting curves of the non-Faradaic current as a function of CV scan rates for determining the double-layer capacitance and ECSA. (A) $L_1S_3N_2F_1$, $L_2S_2N_2F_1$, $L_3S_1N_2F_1$, and (B) $L_2S_2N_1F_2$, $L_2S_2N_{1.5}F_{1.5}$, $L_2S_2N_2F_1$.	61
Figure 48. Specific activity normalized to ECSA of hybrid perovskites as a function of potential. (A) $L_1S_3N_2F_1$, $L_2S_2N_2F_1$, $L_3S_1N_2F_1$, and (B) $L_2S_2N_1F_2$, $L_2S_2N_{1.5}F_{1.5}$, $L_2S_2N_2F_1$.	62
Figure 49. Electronic structures of $L_3S_1N_2F_1$, $L_2S_2N_1F_2$, and $L_2S_2N_{1.5}F_{1.5}$. (A) High-resolution XPS spectra of Fe 2p. (B) High-resolution XPS spectra of O 1s.	63
Figure 50. Correlation of OER activity with the oxygen-ion diffusion coefficient and crystal structure. (A) Overpotential at 10 mA/cm ² for these five hybrid perovskites. (B) Oxygen-	

ion diffusion coefficients for these five hybrid perovskites. (C) The correlation of OER activity with oxygen-ion diffusion coefficient. (D) The weight percentage of each phase for these five hybrid perovskites.	65
Figure 51. The chronoamperometry results of five hybrid perovskites, where show the current as a function of $t^{1/2}$	67
Figure 52. OER performance of hybrid perovskites at the AEMWE single-cell level and 60 °C. (A) Schematic illustration of the anion exchange membrane water electrolyzer. (B) Polarization curves of AEM water electrolyzers with $L_3S_1N_2F_1$, $L_2S_2N_{1.5}F_{1.5}$, and $L_2S_2N_1F_2$ as the OER electrocatalysts. (C) The current density achieved at 1.8V in AEMWEs. (D) The ohmic loss as a function of current density. (E) The activation loss as a function of current density. (F) A preliminary stability testing of AEMWE with $L_2S_2N_1F_2$ as the OER electrocatalyst at 60 °C and a current density of 0.5A/cm ²	68
Figure 53. LHV energy efficiency of AEMWEs with three hybrid perovskites as the OER electrocatalysts at a current density of 0.5 A/cm ² and 1.0 A/cm ²	69
Figure 54. (A) Stability testing of $L_2S_2N_1F_2$ at the half-cell level. (B) XRD patterns of fresh, $L_2S_2N_1F_2$ on carbon cloth prior to stability testing, $L_2S_2N_1F_2$ on carbon cloth after stability testing, and carbon cloth.	70
Figure 55. Performance comparison of AEMWE demonstrated in this work with the literature [15,20,49,63,92,96,100,102,148,149,151–188].....	71
Figure 56. A three-electrode system with NiFe LDH in half-cell test.....	76
Figure 57. Single-cell test station in seawater electrolysis.....	77
Figure 58. Single-cell test setting procedures.....	78
Figure 59. XRD patterns of NiFe LDH with different Ni/Fe ratios: 85:15, 80:20, 75:25, 70:30, and 60:40.	80
Figure 60. Electrochemical performance of NiFe LDH of 60, 70, 75, 80, and 85mM at the half-cell level, which was evaluated in 1.0 M KOH solution at room temperature (A) Ohmic resistance-corrected polarization curves (B) Electrochemical impedance spectra at 1.7 V. (C) Tafel plots. (D) Linear fitting curves of the non-Faradaic current as a function of CV scan rates for determining the double-layer capacitance and ECSA.	81
Figure 61. Comparison of overpotential at a current density of 10mA/cm ² using NiFe LDH 60, 70, 75, 80, 85 as the OER electrode in half cell.	82

Figure 62. Electrochemical performance of NiFe LDH with 75mM at the half-cell level, which was evaluated in 1.0 M KOH and 1.0 M KOH+0.5 M NaCl solution at room temperature. (A) Ohmic resistance-corrected polarization curves (B) Electrochemical impedance spectra at 1.6 V. (C) Tafel plots. (D) Linear fitting curves of the non-Faradaic current as a function of CV scan rates for determining the double-layer capacitance and ECSA.	83
Figure 63. Comparison of overpotential at 10mA/cm ² of NiFe LDH 75 in the electrolyte of 1M KOH and 1M KOH+ 0.5M NaCl in half cell.	84
Figure 64. Comparison of redox of NiFe LDH 75 in the electrolyte of 1M KOH and 1M KOH+ 0.5M NaCl.	85
Figure 65. Ro in 1M KOH and 1M KOH+ 0.5M NaCl.....	86
Figure 66. Schemes of AEM electrolyzes using independent electrolyte feeds with different electrolyte compositions (A) type i: 1M KOH is fed to the anode (B) type ii: 1M KOH+0.5 M NaCl is fed to the anode; (C) type iii: 0.5 M NaCl solution is fed to the cathode, and 1M KOH is fed to cathode.	87
Figure 67. Comparison of cell voltage of NiFe LDH 75 with electrolyte feeding with type i, ii, and iii at a current density of 0.5A/cm ² , 1A/cm ² , and 1.5A/cm ²	89
Figure 68. Comparison of the current density of NiFe LDH 75 with electrolyte feeding with type i, ii, and iii at the cell voltage of 1.8V.....	90
Figure 69. Comparison of energy efficiency of H ₂ of NiFe LDH 75 with electrolyte feeding with type i, ii, and iii at the current density of 0.5A/cm ²	91
Figure 70. Electrochemical impedance spectra of NiFe LDH 75 with electrolyte feeding with type i, ii, and iii at (A) 1.7V (B) 1.2A/cm ²	91
Figure 71. The performance of AEM electrolyzer with NiFe LDH 75 as anode catalyst with asymmetric electrolyte feeds of type A, B, C, and D. (A) polarization curves of AEM water electrolyzers (B) electrochemical impedance spectra (C) a preliminary stability testing of AEMWE at 50C and a current density of 0.5A/cm ² [59,63–82].	92
Figure 72. Stepped constant current tests with current holds of 30 min of NiFe LDH 75 as anode catalyst with type i electrolyte feed: asymmetric 1M KOH at the anode and dry at the cathode with (A) cell voltage (B) O ₂ production rate (C) energy efficiency of H ₂ . (D) O ₂ gas concentration.	94

Figure 73. Stepped constant current tests with current holds of 30 min as anode catalyst with type ii electrolyte feed: asymmetric 1M KOH+0.5M NaCl at the anode and dry at the cathode with (A) cell voltage (B) O ₂ production rate (C) energy efficiency of H ₂ (D) O ₂ gas concentration.....	95
Figure 74. Stepped constant current tests with current holds of 20 min as anode catalyst with type iii electrolyte feed: asymmetric 1M KOH at the anode and 0.5M NaCl at the cathode with (A) cell voltage (B) O ₂ production rate (C) energy efficiency of H ₂ (D) O ₂ gas concentration.....	96
Figure 75. Stability test with Faradaic efficiency (FE) of type i at 500 mA/cm ²	97
Figure 76. Stability test with Faradaic efficiency (FE) of type ii at 500 mA/cm ²	98
Figure 77. Stability test with Faradaic efficiency (FE) of type iii at 500 mA/cm ²	99
Figure 78. The ohmic loss as a function of current density.....	99
Figure 79. The activation loss as a function of current density.	100
Figure 80. The concentration loss as a function of current density.....	102
Figure 81. The cell voltage, iR correct voltage and kinetic voltage as a function of current density of type i.	103
Figure 82. The cell voltage, iR correct voltage and kinetic voltage as a function of current density of type ii.	104
Figure 83. The cell voltage, iR correct voltage and kinetic voltage as a function of the current density of type iii.....	104
Figure 84. Intermittent stability test of NiFe LDH 75 with electrolyte feeding with type i.	105
Figure 85. NiFe LDH 75 with electrolyte feeding with type i (A) polarization curves of AEM water electrolyzers at faradic efficiency about 77% (B) electrochemical impedance spectra at 1.6V.	106
Figure 86. Electrode morphology. (A) Fe foam; (B) CoFeOOH with 20mM Co on Fe foam (C) CoNiFeOOH with 20mM Co and 10mM Ni on Fe foam.....	113
Figure 87. XRD of CoFeOOH with different Co concentrations.	114
Figure 88. XRD of NiCoFeOOH with different Ni concentrations.....	115
Figure 89. XRD of CoFeOOH 20 with a preparation time of 24 and 48 hours.	116
Figure 90. XRD of CoFeOOH 20 prepared with Co(NO ₃) ₂ and CoCl ₂	117

Figure 91. SEM images of pure Fe foam of (A)~(D): top view; (E)~(H): cross-section.	118
Figure 92. SEM images of CoFeOOH/FF Co 20mM on Fe foam of (A)~(D): top view; (E)~(H): cross-section.	119
Figure 93. SEM images of NiCoFeOOH/FF Ni10 mM and Co 20 mM on Fe foam of (A)~(D): top view; (E)~(H): cross-section	120
Figure 94. SEM images of NiCoFeOOH/FF Ni 50 mM of (A)~(C): top view; (D)~(F): cross- section view.....	121
Figure 95. (A)~(C): SEM images of NiCoFeOOH/FF Ni 30 mM after the electric test.	121
Figure 96. Electrochemical performance in different Co concentrations of CoFeOOH at half-cell, which is evaluated in 1.0M KOH solution at room temperature. (A) Ohmic resistance-corrected polarization curves and (B) Electrochemical impedance spectra	122
Figure 97. Overpotential of half-cell test at a current density of 10mA/cm ² using CoFeOOH prepared with different Co concentrations.	123
Figure 98. Ohmic resistance-corrected polarization cures of CoFeOOH on Fe foam with different preparation periods.	124
Figure 99. Ohmic resistance-corrected polarization curves of CoFeOOH FF with different salts fabrication.	125
Figure 100. Overpotential of half-cell test with different Co salts at a current density of 10mA/cm ²	125
Figure 101. Stability testing of sample CoNiOOH 20 mM at room temperature and a current density of 10mA/cm ²	126
Figure 102. Electrochemical performance of NiCoFeOOH with different Ni concentrations at half-cell, which are evaluated in 1.0M KOH solution at room temperature. (A) Ohmic resistance-corrected polarization curves and (B) Electrochemical impedance spectra.	127
Figure 103. Ohmic resistance, R_0 , of NiCoFeOOH at different Ni concentrations.	128
Figure 104. Potential at 10mA/cm ² of half-cell test with NiCoFeOOH with different Ni contrations.....	128
Figure 105. Electrochemical performance at the half-cell level, which is evaluated in 1.0 M KOH solution at room temperature. (A) Ohmic resistance-corrected polarization curves	

of CoFeOOH with Co 20mM on Fe foam, CoNiFeOOH with Co 20mM, and Ni 10mM on Fe foam. (B) Electrochemical impedance spectra CoFeOOH with Co 20mM on Fe foam, CoNiFeOOH with Co 20mM, and Ni 10mM on Fe foam at 1.6 V. (C) Tafel plots of CoFeOOH with Co 20mM on Fe foam, and CoNiFeOOH with Co 20mM, and Ni 10mM on Fe foam.	129
Figure 106. Overpotential at the current density of 10 mA/cm ² and 150 mA/cm ²	130
Figure 107. OER performance at the AEMWE single-cell level and 50 °C. (A) Polarization curves of AEM water electrolyzers with CoFeOOH with Co 20mM on Fe foam, CoNiFeOOH with Co 20mM, and Ni 10mM on Fe foam as the OER electrocatalysts. (B) The ohmic loss is a function of current density. (C) The activation loss is a function of current density. (D) performance comparison of AEMWE demonstrated in this work with the oxyhydroxide catalyst literature [51,55,101,199–208].	131
Figure 108. NiCoFeOOH with different Ni concentrations on Fe foam at 60°C.....	132
Figure 109. Stability of CoFeOOH with 20 mM at 0.5mA/cm ² at 60°C.....	133
Figure 110. Stability of CoFeOOH with 20 mM at 60°C at the current density of (A) 500 mA/cm ² ; (B) 900 mA/cm ²	134
Figure 111. Stability of NiCoFeOOH/FF Ni 30 mM at 60°C and a current density of 0.5 A/cm ²	135
Figure 112. Polarization curves of CoFeOOH/FF Co 20 mM at 50 °C in different electrolytes.	136
Figure 113. XRD patterns of (A) L _{0.7} C _{0.3} N _{0.7} F _{0.3} , L _{0.8} C _{0.2} N _{0.7} F _{0.3} , and L _{0.9} C _{0.1} N _{0.7} F _{0.3} (B) L _{0.9} C _{0.1} N _{0.3} F _{0.7} , L _{0.9} C _{0.1} N _{0.7} F _{0.3} , and L _{0.9} C _{0.1} N ₁	141
Figure 114. Electrochemical performance of perovskites at the half-cell level, which is evaluated in 1.0 M KOH solution at room temperature. 1N ₁ (A) Ohmic resistance-corrected polarization curves of perovskites L _{0.7} C _{0.3} N _{0.7} F _{0.3} , L _{0.8} C _{0.2} N _{0.7} F _{0.3} , and L _{0.9} C _{0.1} N _{0.7} F _{0.3} (B) Electrochemical impedance spectra of perovskites L _{0.7} C _{0.3} N _{0.7} F _{0.3} , L _{0.8} C _{0.2} N _{0.7} F _{0.3} , and L _{0.9} C _{0.1} N _{0.7} F _{0.3} (C) Tafel plots of perovskites L _{0.7} C _{0.3} N _{0.7} F _{0.3} , L _{0.8} C _{0.2} N _{0.7} F _{0.3} , and L _{0.9} C _{0.1} N _{0.7} F _{0.3} (D)) Ohmic resistance-corrected polarization curves of L _{0.9} C _{0.1} N _{0.3} F _{0.7} , L _{0.9} C _{0.1} N _{0.7} F _{0.3} , an L _{0.9} C _{0.1} N ₁ (E) Electrochemical impedance spectra of L _{0.9} C _{0.1} N _{0.3} F _{0.7} ,	

$\text{L}_{0.9}\text{C}_{0.1}\text{N}_{0.7}\text{F}_{0.3}$, an $\text{L}_{0.9}\text{C}_{0.1}\text{N}_1$ (F) Tafel plots of of $\text{L}_{0.9}\text{C}_{0.1}\text{N}_{0.3}\text{F}_{0.7}$, $\text{L}_{0.9}\text{C}_{0.1}\text{N}_{0.7}\text{F}_{0.3}$, an $\text{L}_{0.9}\text{C}_{0.1}\text{N}_1$ 143

Figure 115. (A) Ohmic resistance-corrected polarization curves of $\text{L}_{0.9}\text{C}_{0.1}\text{N}_{0.7}\text{F}_{0.3}$ at different times. (B) stability testing of $\text{L}_{0.9}\text{C}_{0.1}\text{N}_{0.7}\text{F}_{0.3}$. (C) Ohmic resistance-corrected polarization curves of $\text{L}_{0.9}\text{C}_{0.1}\text{N}_1$ at different times. (D) stability testing of $\text{L}_{0.9}\text{C}_{0.1}\text{N}_1$ at room temperature and a current density of 10 mA/cm^2 145

Figure 116. XRD patterns of $\text{L}_{0.9}\text{C}_{0.1}\text{N}_{0.7}\text{F}_{0.3}$, $\text{L}_{0.9}\text{C}_{0.1}\text{N}_{0.7}\text{F}_{0.3}$ on carbon cloth after stability testing, and carbon cloth. 146

List of Tables

Table 1. Comparison of low-temperature water electrolysis technologies [4,16–18].	4
Table 2. Advances and disadvantages of AWEs, PEMWEs, and AEMWEs [16]	5
Table 3. Hypothesized advantages and disadvantages of AEMWEs with different configurations.	15
Table 4. Summary of the recent reports on OER electrocatalysts for seawater electrolysis	16
Table 5. Summary of XRD refinement results.....	56
Table 6. Binding Energy (eV) and atomic percentages (%) of Fe and O elements obtained from XPS spectra of $L_2S_2N_1F_2$, $L_3S_1N_2F_1$, and $L_2S_2N_{1.5}F_{1.5}$	63
Table 7. A summary of the double-layer capacitance and ECSA	66
Table 8. Comparison of different configuration	88
Table 9. CoFeOOH fabrication on Fe foam with different Co concentrations	110
Table 10. NiCoFeOOH fabrication on Fe foam with different Ni concentrations	110

List of Acronyms and Definitions

AEM	Adsorbate evolution mechanism
AEMWEs	Anion exchange membrane water electrolyzers
AWEs	Alkaline water electrolyzers
CE	Counter electrode
CER	Chlorine evolution reaction
CV	Cyclic voltammetry
ECSA	Electrochemically active surface area
EIS	Electrochemical impedance spectroscopy
FE	Faradaic efficiency
FF	Fe foam
DLC	Double layer capacitor
GDL	Gas diffusion layer
HER	Hydrogen evolution reaction
LOM	Lattice-oxygen oxidation
LSV	Linear sweep voltammetry
MEAs	Membrane electrode assemblies
NiFe LDH	NiFe layered double hydroxides
NiFeOOH	NiFe oxyhydroxide
OER	Oxygen evolution reaction
OOH	Oxyhydroxide
PEMWEs	Proton-exchange membrane water electrolyzers
R_o	Ohmic resistance

Rp	Polarization resistance
RE	Reference electrode
RDE	Rotating disk electrode
RHE	Reversible hydrogen electrode
SEM	Scanning electron microscopy
SCE	Saturated calomel electrode
TEM	Transmission electron microscopy
WE	Working electrode
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

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Chapter 1 – Background and Motivations

Recently, the global energy crisis and climate change are two major problems affecting human beings. One of the most effective solutions to address these challenges is to develop sustainable energy technologies with higher energy conversion efficiencies and lower CO₂ emissions. Efficient conversion and storage of solar and wind energy is the “holy grail” for solving the global energy crisis. However, solar and wind energy is intermittent because it depends on the geographic location, season, time, weather, etc. Therefore, technologies that can effectively convert intermittent renewable energy into fuels/chemicals (e.g., H₂) are essential to realize long-term energy storage [1–3]. H₂ is a clean and renewable energy storage media that can be produced via water electrolysis.

1.1 Anion Exchange Membrane Water Electrolyzers (AEMWEs)

Anion exchange membrane water electrolyzers (AEMWEs) are at early-stage technology for producing H₂. As shown in Figure 1, AEMWEs are composed of three main components: the anion exchange membrane, cathode, and anode. The anion exchange membrane is permeable to water and hydroxide ions, separating the anode from the cathode. The anode denotes the electrode where the oxygen evolution reaction (OER) occurs, while the cathode is the hydrogen evolution reaction (HER) electrode. AEMWEs usually operate at 40-70 °C with an alkaline solution, such as 1M KOH, fed to either the anode or cathode sides or both sides [4,5].

Water electrolysis in AEMWEs includes two half-reactions, which are OER and HER. At the cathode, the HER reaction is $2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-$. As shown in Figure 1, the OH⁻ anions produced at the cathode then move to the anode through the anion exchange membrane. At the anode, the OER reaction is $2\text{OH}^- \rightarrow 1/2\text{O}_2(\text{g}) + \text{H}_2\text{O} + 2\text{e}^-$. Compared to HER, which is a two-electron transfer reaction, OER is kinetically slower because OER is a four-electron transfer reaction [6,7]. Therefore, OER determines the overall reaction rate and efficiency, necessitating the development of high-performance OER electrocatalysts.

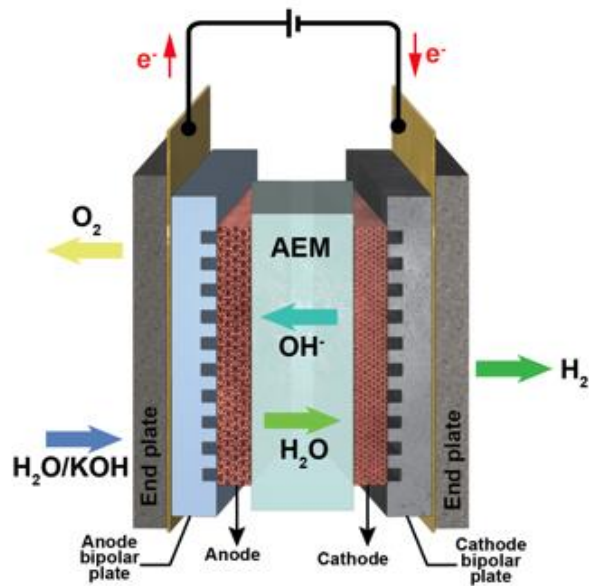


Figure 1. Schematic diagram of the anion exchange membrane water electrolyzers [8].

1.2 Motivations of Studying Anion Exchange Membrane Water Electrolyzers

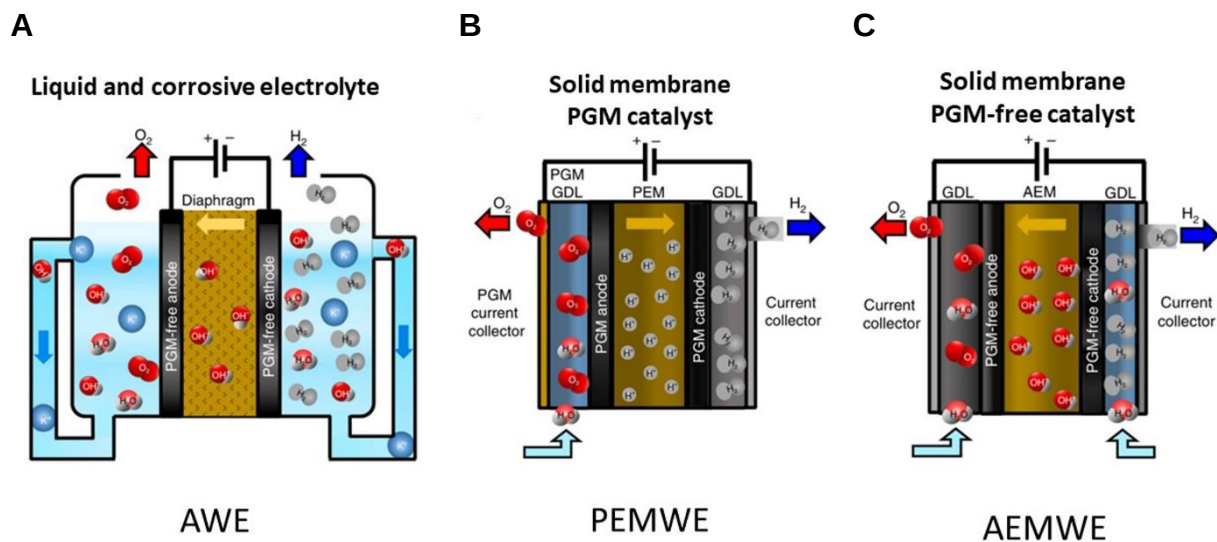


Figure 2. Schematic diagram of three types of water electrolysis. (A) AWE; (B) PEMWE; (C) AEMWE [9].

Anion exchange membrane water electrolyzers (AEMWEs) are emerging as one of the most promising technologies for converting renewable power to hydrogen [10–14]. As shown in Figure 1 and Figure 2, AEMWEs are a new technology compared to relatively mature alkaline water electrolyzers (AWEs) and proton exchange membrane water electrolyzers (PEMWEs), which exhibit the advantages of both AWEs and PEMWEs. Thus, it is expected that AEMWEs could be one of the critical technologies for clean hydrogen production [14].

First, as shown in Table 1, compared to AWEs and PEMWEs, the operating conditions of AEMWEs are milder and more catalysts are available. AWEs employ high-concentration and highly corrosive KOH solution as the electrolyte, while PEMWEs operate in acidic conditions. AWEs can, therefore, use platinum group metal-free (PGM-free) catalysts. Nevertheless, AWEs suffer from corrosive liquid electrolyte and potential leakage. PEMWEs, which run in an acidic media, are equipped with costly noble metal-based catalysts, constraining their further deployment due to the high material cost. In contrast, AEMWEs use diluted KOH solution or distilled water [4,5,15]. Therefore, AEMWEs allow using non-precious metal-based electrocatalysts, such as those based on Ni and Co, as the anode and cathode electrodes.

Second, due to the utilization of a thin solid electrolyte membrane, the electrolyzer size and weight of AEMWEs are smaller than those of AWEs [14]. Figure 2 displays traditional AWEs that are composed of two electrodes separated by a thick and porous diaphragm. However, the anion exchange membrane could be manufactured lightweight, thin, and micro-scale, reducing the space between the anode and cathode, which saves a lot of space [5].

Third, the anion exchange membrane physically separates H_2 and O_2 , which avoids gas crossover, allowing it to produce high-pressure H_2 via electrochemical compression directly. However, in AWEs, as the diaphragm is also permeable to gas molecules, the potential gas crossover limits the high-pressure H_2 production. Additional power is consumed to mechanically compress the H_2 for storage [4]. Therefore, AEMWEs could achieve higher energy efficiency than AWEs. Finally, as shown in Table 1, the AEMWEs can realize a current density that is much higher than AWEs and comparable to PEMWEs.

Table 1. Comparison of low-temperature water electrolysis technologies [4,16–18].

	AWEs	PEMWEs	AEMWEs
Electrolyte	20~40% KOH	Acid solution	1M KOH or distilled water
Operating temperature (°C)	60~100	25~90	50-80
Charge carrier	OH ⁻	H ⁺	OH ⁻
Operating pressure (bar)	1~30	30~80	~30
Current density (mA/cm²)	450~1,250	600~20,000	1000~3,000
Cell voltage (V)	1.7~2.1	1.8~2.2	1.8~2.2
Durability (hour)	100,000	50, 000 – 100,000	NA
Hydrogen purity (vol%)	9.99~99.3	99.9999	99.99
Technology status	mature	Mature for small scale	Early stage

1.3 Critical Barriers in the Field of Anion Exchange Membrane Water Electrolyzers

Although significant progress has been made in the last decade to demonstrate high-performance AEMWEs, the current density, energy efficiency, and stability are still lower than PEMWEs (Table 2). First, its poor performance is ascribed to high ohmic resistance of the anion exchange membrane and sluggish OER catalysts [19,20]. Second, the degradation is due to the aggressive oxidizing agent, hydroxide, and its radical attack on ion exchange polymers. This attack affects the membrane character, which influences long-term stability [21]. This work will focus on developing highly efficient, cost-effective, and highly durable electrocatalysts for OER, which improves the current density and energy efficiency of producing H₂ in AEMWEs.

Table 2. Advances and disadvantages of AWEs, PEMWEs, and AEMWEs [16]

	AWEs	PEMWEs	AEMWEs
Advantages	Mature technology	High performance	Non-noble metal catalyst
	PGM-free catalyst	Rapid system response	Low cost
	Long-term stability	High voltage efficiency	High operating pressure
Disadvantages	Low current density	High cost	Low stability
	Low operating pressure	Noble metal catalyst	Low current density
	Crossover of gas	Acidic and corrosive	Excessive catalyst loading

1.4 HER and OER Mechanisms Under Alkaline Conditions.

1.4.1 HER Mechanisms Under Alkaline Conditions.

The hydrogen evolution reaction (HER) is a two-electron transfer process. The intermediated species, H^* , is either formed or absorbed through the Volmer-Heyrovsky or Volmer-Tafel mechanism [22]. The HER in an alkaline medium is represented as follows.

Volmer steps: $H_2O + e^- \rightarrow H^* + OH^-$

Heyrovsky step: $H_2O + e^- + H^* \rightarrow H_2(g) + OH^-$

Tafel step: $H^* + H^* \rightarrow H_2(g)$

1.4.2 OER Mechanisms Under Alkaline Conditions.

The adsorbate evolution mechanism (AEM) and lattice oxygen-mediated mechanism (LOM) are two primary mechanisms for OER under alkaline conditions. AEM undergoes the four concerted proton electron transfer (CPET) processes shown in Figure 3, which

are shown in equations (1) ~ (4) [6,23,24]. As shown in Figure 4, OH^- is first absorbed and HO^* is formed on the catalyst surface, which is followed by the formation of O^* . O^* will further react with OH^- to form HOO^* . In the final step, O_2 is generated on the catalyst surface.

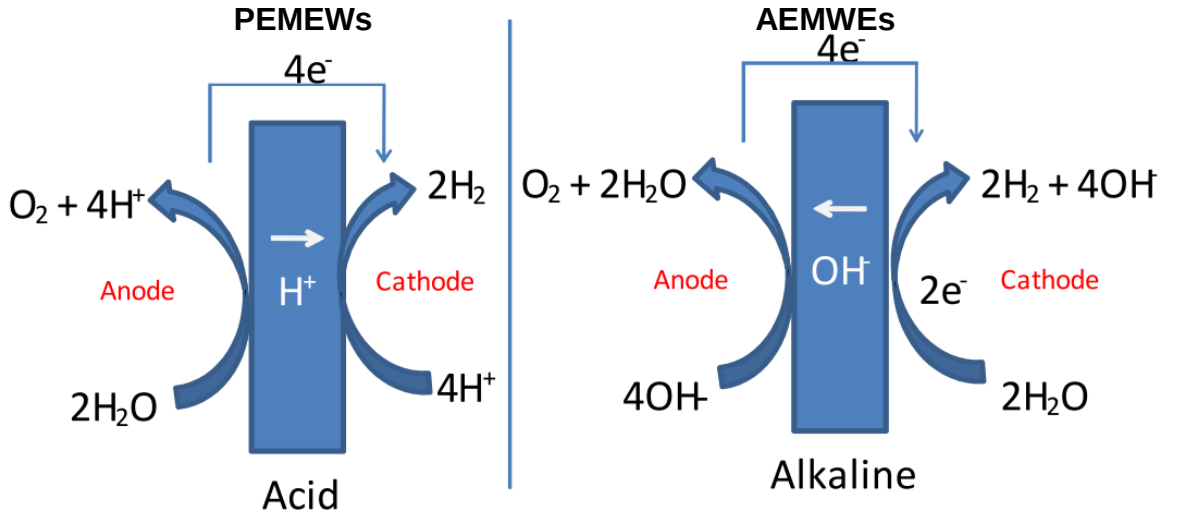
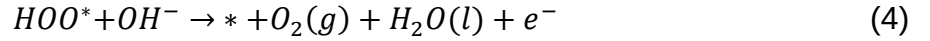
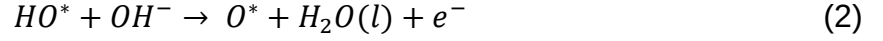
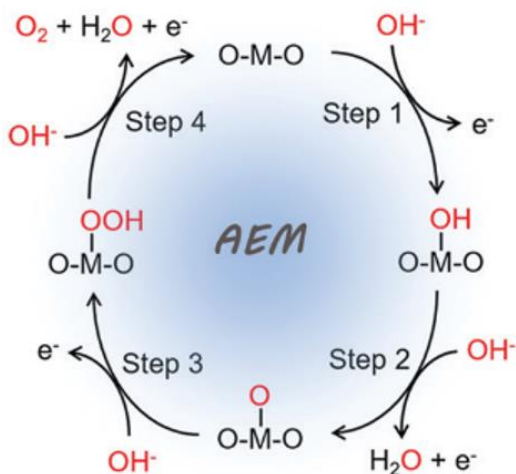


Figure 3. Comparison of electrode reactions for acid-based proton exchange membrane water electrolyzers (PEMWEs) and alkaline exchange membrane water electrolyzers (AEMWEs) [21].

The difference between AEM and LOM is the process regarding O-O bonding formation. In AEM, O-O bonding from HOO^* is formed in step 3, which is shown in equation (3). One oxygen atom originates from O^* that is adsorbed on the catalyst, and the second oxygen atom is from the OH^- in the KOH solution. In contrast, as shown in Figure 4, for the LOM, oxygen atoms from the lattice of the catalyst form O-O bonding [25].

A



B

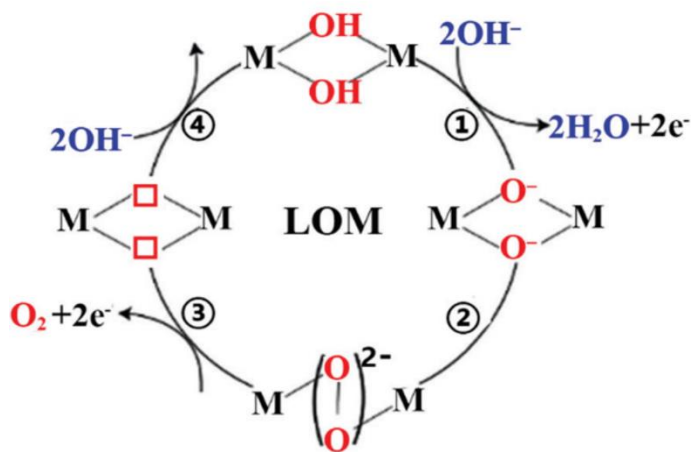


Figure 4. Oxygen evolution mechanisms under alkaline conditions. (A) AEM [23]; (B) LOM [26].

1.5 Electrocatalysts for OER under Alkaline Conditions

OER catalysts are essential for highly efficient AEMWEs. To improve the performance of AEMWEs, platinum group metal-based (PGM) catalysts, such as iridium oxide (IrO_2) and ruthenium oxide (RuO_2), and PGM-free catalysts, including layered double hydroxides (LDHs), oxyhydroxides, perovskites, and other electrocatalysts are studied as OER electrocatalysts for AEMWEs [27–30].

1.5.1 Platinum Group Metal (PGM)-based electrocatalysts

Platinum group metal (PGM)-based OER electrocatalysts primarily include IrO_2 and RuO_2 , which are octahedral (Figure 5) [31]. The oxygen atoms are at the corners, and the Ru or Ir atom is in the center.

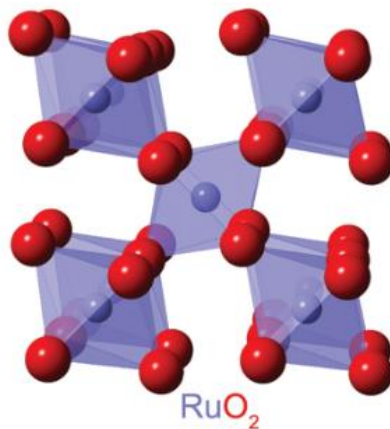


Figure 5. Crystal structure of RuO₂ [31].

IrO₂ and RuO₂ are benchmark OER catalysts, offering the most active and stable OER performance because of the favorable binding energies of oxygen and hydroxyl radicals [32,33]. However, these materials are expensive, and their availability is limited. Additionally, IrO₂ and RuO₂ with high surface area to mass ratios or IrO₂ and RuO₂ doped with other low-cost elements are synthesized to reduce the loading of PGM-based catalysts [32,34]. Alternatively, using catalysts that are made of low-cost materials is another promising option, for example, the perovskites, layered double hydroxides (LDH), and metal oxyhydroxides (MOOH) [35].

1.5.2 Perovskites

Generally, perovskites exhibit a crystal structure with the formula of ABO₃, in which A refers to alkaline or rare-earth metal, and B refers to transition metal [31]. As shown in Figure 5, Ruddlesden-Popper (RP) perovskites are another branch with the formula of A_{n+1}B_nO_{3n+1}. In these perovskites, the B-site ions could be 3d, 4d, and 5d transition metals [36–38]. RP phases are layered perovskites consisting of layers stacked along the c-axis with *n* ABO_{3-δ} perovskite layers, alternating with an AO rock-salt layer. RP 1 phase is denoted as the perovskite has one ABO_{3-δ} perovskite layer. RP 3 phase is the perovskite has three ABO_{3-δ} perovskite layers. Due to the layered structure of RP phases, the

oxygen located between the layered perovskite is easily removable and essential to increasing the efficiency of OER [39].

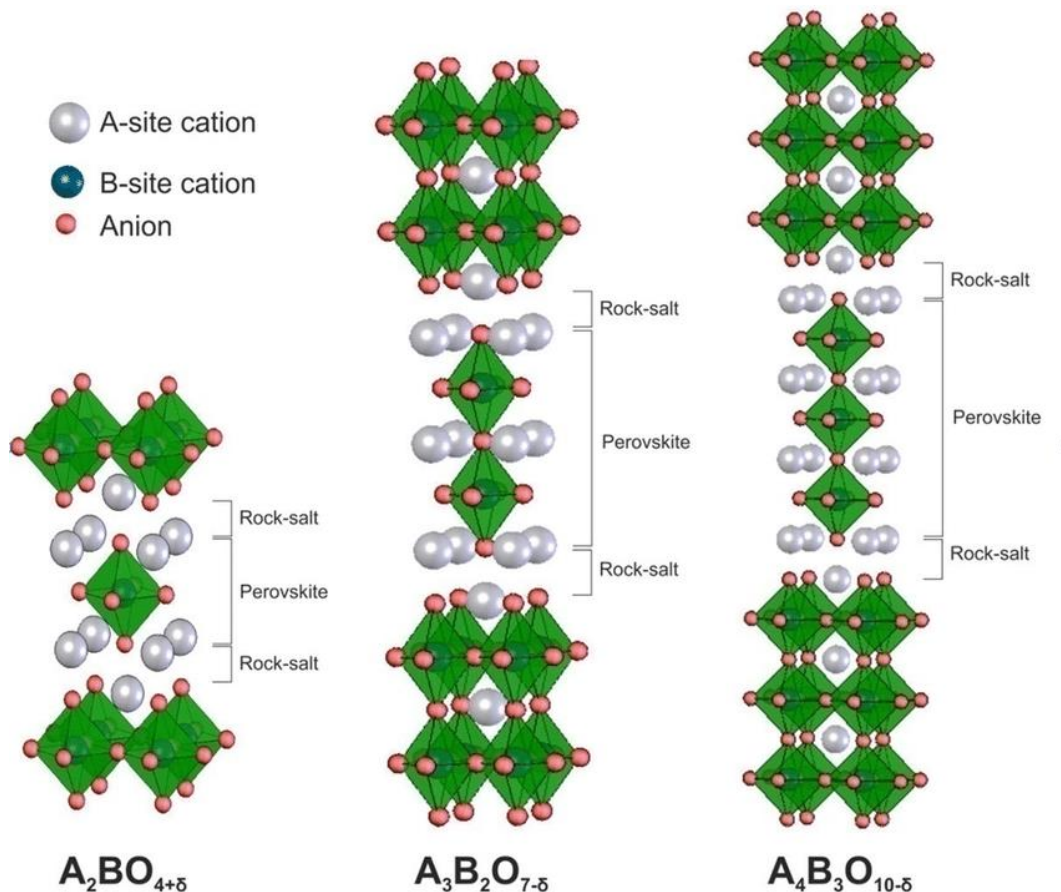


Figure 6. The crystal structure of the RP phase ($A_{n+1}B_nO_{3n+1}$ where $n=1,2, \text{ and } 3$) [40].

Many perovskites increase OER performance. For example, Wang et al. [41] demonstrated $\text{LaNi}_{0.8}\text{Fe}_{0.2}\text{O}_3$ that displays an overpotential of 302 mV at 10 mA/cm². Zhao et al. [42] employed that $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (LSCF) as the OER electrocatalyst, achieving an overpotential of 248mV at 10 mA/cm². Zhu et al. [43] recognized the hybridization between the RP phase, and the perovskite phase increases the metal-oxygen covalency, which accelerates the oxygen-ion diffusion and improves the OER activity. However, the OER performance of perovskites is lower than that of NiFe LDH or NiOOH. Furthermore, the stability of perovskites is not as good as PGM-based catalysts and LDH.

1.5.3 Layered Double Hydroxides (LDH)

One of the state-of-the-art PGM-free OER electrocatalysts under alkaline conditions is Ni-Fe layered double hydroxide (LDH) [44–48], which is shown in Figure 7. LDH is a two-dimensional layered nanosheet composed of a brucite-like layer. The structure of LDH is similar to metal oxyhydroxides ($M(OH)_2$, M is transition metals). $M_{1-x}^{II}M_x^{III}(OH)_2A^{\frac{1-x}{n}} \cdot m H_2O$ is the molecular formula. A is a valence anion [49].

LDH shows excellent electrocatalytic activity. Its outstanding performance is attributed to the open structure, in which exchangeable charge-balancing interlayer anions separate the cationic brucite-like layers. This causes a faster diffusion of reactants and products alongside a rapid proton-coupled electron transfer [35].

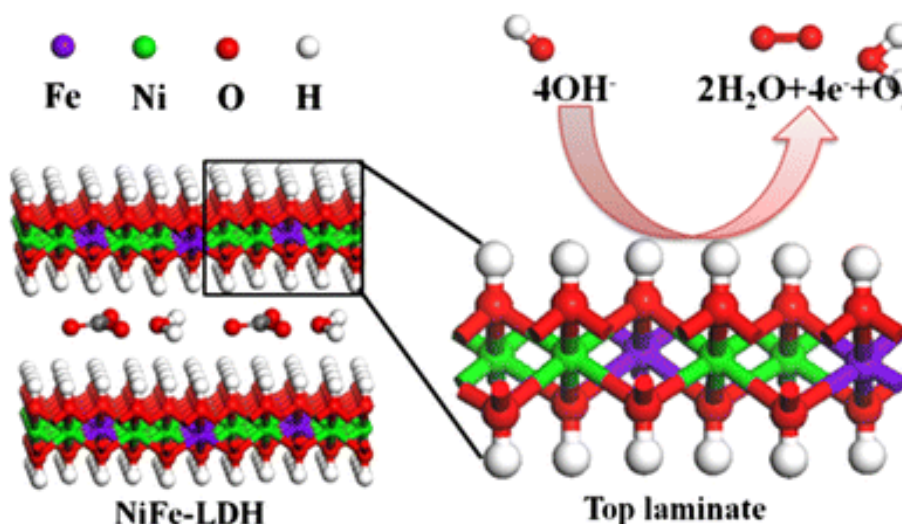


Figure 7. The structure diagram of NiFe LDH [49].

For Ni-based LDH, Fe-doped Ni LDH shows favorable activity in OER because of the synergistic effect between the two elements [33]. To further increase the OER performance, hollow NiFe LDH, micro-, and nanometer sized NiFe LDH less than 10nm can increase the active area between electrode and electrolyte [50]. However, the low conductivity and potential agglomeration are intractable issues. Nevertheless, there are still several bottlenecks in NiFe LDH [33,51]. Its preparation method is complex, limiting

its large-scale synthesis. The mechanism of NiFe LDH doped with other elements is unclear. Furthermore, their electrochemical stability is poor.

In Ni and Fe-based catalysts, with Fe concentration increased, the ionic conductivity increased, causing ohmic resistance to decrease in AEMWE. However, during the half-cell test, the catalyst activity could become lower when Fe increases too much. Therefore, to achieve excellent performance, it is necessary to optimize Fe concentration in the catalyst [52].

1.5.4 Oxyhydroxide (OOH)

Oxyhydroxide (OOH) is another advanced PGM-free OER catalyst. The oxyhydroxide catalysts can be synthesized via simple processes, such as electrodeposition and hydrothermal methods [53]. The metal sources are Non-precious and earth-abundant transition-metal catalysts, such as Fe, Ni, Cu, and Co. In previous studies, Fe, the most abundant metal element on the earth, is the active single-component oxyhydroxide for OER. However, FeOOH is unstable and has low electrical conductivity. Therefore, doping is used to improve its performance. Trotochaud et al. [54] found that the Fe doping of NiOOH on Ni foam can enhance the activity, which is due to the disorder of γ -NiOOH crystal. Yang [55] improved its conductivity and stability by Co doping on FeOOH. Kim [56] studied S-(Co, Fe)OOH as the catalyst to enhance the activity of (Co, Fe)OOH.

Oxyhydroxides are also synthesized on metal substrates, such as Ni foam, and the synthesis method will be mentioned in section 2.3.2 (binder-free electrodes). These electrodes combine the catalyst layer and gas diffusion layer (GDL) as AEMWEs electrodes to reduce contact resistance. Recently, Park et al. [52] demonstrated outstanding AEMWEs performance, with a current density of 3.6 A/cm^2 achieved at 1.9 V and 70°C using NiFeOOH on a stainless steel paper substrate to combine GDL and catalyst layer. Kahnamouei et al. [57] prepared S-(Fe/Ni)OOH on carbon cloth and stainless-steel substrate to further improve the activity.

1.5.5 Other OER Catalysts under Alkaline Conditions

Other OER catalysts include oxides, metal nitrides/borides/sulfides, metal phosphides/phosphates, and so on. The oxide-based OER catalysts include CoO_x , NiO , MnO_x , and AB_xO_y . Non-precious and earth-abundant transition-metal catalysts, such as Ni, Cu, Co-based catalysts, NiFe LDH, NiOOH , NiFe alloys, and so on, exhibit good OER activity [52]. For these earth-abundant transition metals-based oxides, their multivalent oxidation states, $\text{M}^{+2/+3/+4}$ state, are correlated with the active sites for OER [35]. Compared to oxides, metal phosphides/phosphates are more stable due to the different orientations of phosphate groups [35]. Carbonaceous materials include carbon nanotubes, graphene, and nanocarbon [35]. For Hybrid nanostructures, there are carbon material-based hybrids, Graphene-based hybrids, g-C₃N₄-based hybrids, and other hybrids [35]. NiFeOOH is also an excellent OER catalyst due to the doping of Fe, which creates the disorder of γ -NiOOH crystal, leading to better activity than β -NiOOH [35].

This work focuses on studying perovskites and LDH, which is due to low cost, tunable electronic structure and cation deficiency, high electronic conductivity, high durability, high specific catalytic activity, and environmental friendliness.

1.6 Seawater Electrolysis

Currently, most studies of OER catalysts in water splitting are based on pure water. On the other hand, seawater is an abundant water resource on the earth. It is possible to use seawater splitting as a sustainable and renewable source of hydrogen. As a more environmentally conscientious alternative, seawater could be used in electrochemical water splitting to save water. In addition, seawater splitting could remove salt from seawater. It is helpful in areas lacking of fresh water. Additionally, seawater is cheaper and easier to obtain compared to fresh water.

1.6.1 Challenges in Seawater Electrolysis

Seawater electrolysis could generate hydrogen. However, there are two major challenges due to salts in seawater. First, there is a problem because of Cl erosion, caused by chlorine evolution reaction (CER) [58]. On the OER side, it may generate Cl_2 , and Cl_2 could form ClO^- . These could damage the reactor and make the O_2 product impure. This reaction depends on the electrolyte PH condition. In acid conditions, CER is $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$ $E_0=+1.36\text{V}$, and in alkaline conditions, it is $\text{Cl}^- + 2\text{OH}^- \rightarrow \text{ClO}^- + \text{H}_2\text{O} + 2\text{e}^-$ $E_0=+0.89\text{V}$ [58]. Figure 8 shows the Pourbaix diagram of chlorine. Therefore, OER is more favorable and has a lower potential in alkaline conditions. Another challenging aspect is the reaction with ions such as Na^+ , Mg^{2+} , and Ca^{2+} . In seawater, there is salt, including ions such as Na^+ , Mg^{2+} , and Ca^{2+} . These ions can react with OH^- , and the resulting product could block the catalyst's active sites and decrease the reaction rate [59]. In addition, salts could cause corrosion in the electrodes and other instruments, leading to a decrease in their lifetime.

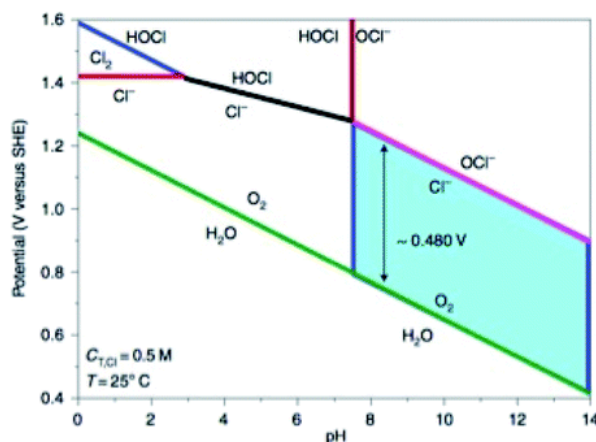


Figure 8. Pourbaix diagram of chlorine [58].

Figure 8 shows the Pourbaix diagram of chlorine. PH is a crucial parameter in OER. Therefore, OER is more favorable in alkaline conditions and has low potential.

1.6.2 Current Studies in Seawater Electrolysis

Soren Dresp et al. [60] studied the NiFe LDH as OER catalysts in AEMWEs with different electrolytes, including seawater, pure water, and KOH solution with different

concentrations. Subsequently, they studied NiFe-LDH for seawater electrolysis with different solutions fed to anode and cathode sides [61]. They found the catalyst performance remains similar in both seawater and KOH solutions. Similarly, Yoo Sei Park et al. [62] observed the same result for Ni-doped FeOOH as the OER catalyst in seawater, showing better performance with a current density of 729 mA/cm² achieved at 1.7 V.

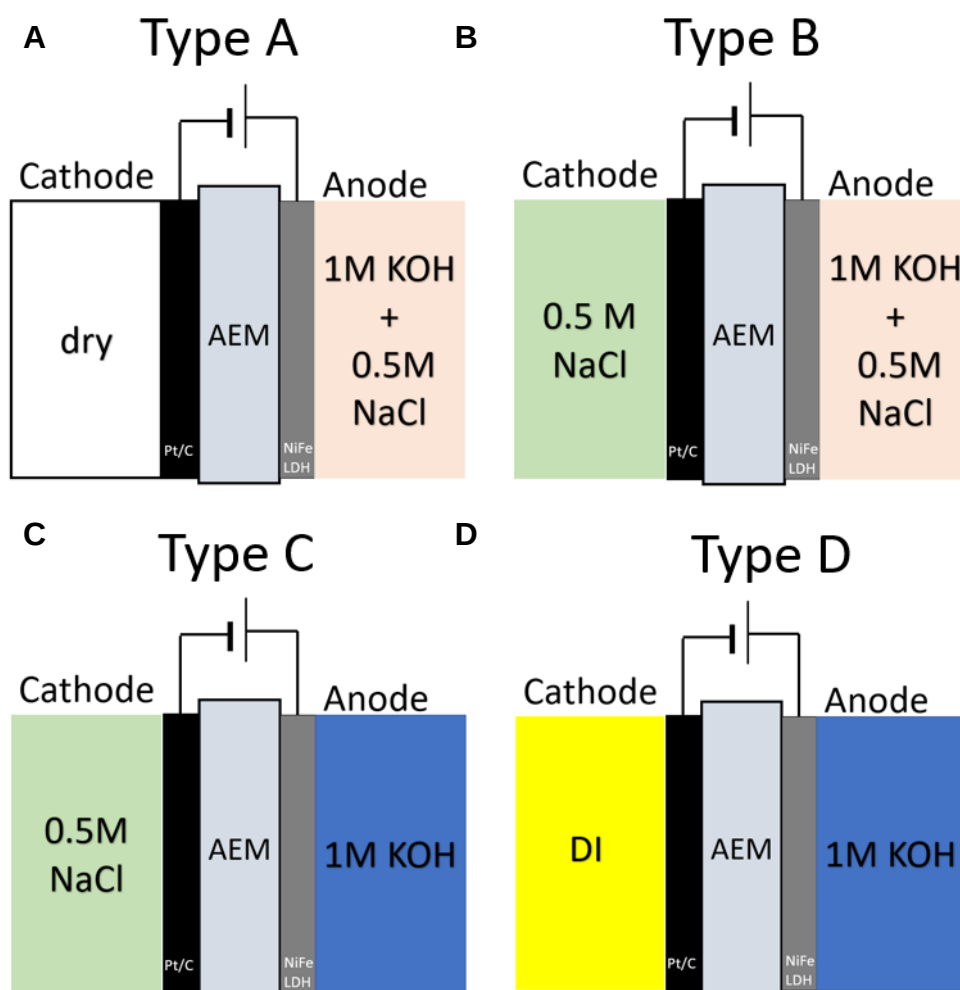


Figure 9. Schematic illustration of AEM seawater electrolyzers with different configurations. (A) type A: 1M KOH+0.5M NaCl is fed to the anode; (B) type B: 1M KOH+0.5M NaCl is fed to the anode and 0.5 M NaCl solution is fed to the cathode; (C) type C: 0.5 M NaCl solution is fed to the cathode and 1M KOH is fed to anode (D) type D: deionized(DI) water is fed to the cathode and 1M KOH is fed to anode.

The hypothesis is that seawater electrolysis performance and durability can be improved by optimizing the AEMWE configurations. Optimized NiFe LDH will be used as the OER catalyst in this work. The chlorine evolution reaction (CER) shown in Figure 8 will be studied in the AEMWEs. Different AEMWE configurations will be designed to minimize the CER and selectively favor OER.

Table 3. Hypothesized advantages and disadvantages of AEMWEs with different configurations.

	Configuration A	Configuration B	Configuration C
Advantages	Dry H ₂ production is feasible, and no separation process is required.	Better performance compared with asymmetric feed [61,63]	Better performance compared with asymmetric feed [61,63]
	Better stability compared with feeding 1M KOH to the cathode [20]		Better stability compared with asymmetric feed [61,63]
Disadvantages	Cl ⁻ oxidation on the OER side.	OER electrolyte becomes dilute as water flows from the cathode to the anode.	OER electrolyte becomes dilute as water flows from the cathode to the anode.

The goal is to identify the NiFe LDH performance in seawater and study which configuration favors OER and minimizes CER in AEMWEs. In this project, to determine the optimal configuration, different configurations shown in Figure 9 will be developed and studied using single-cell testing. These four feed configurations are type A, that 1M KOH + 0.5 M NaCl is fed to the anode; type B, that 0.5 M NaCl solution is fed to the cathode, and 1M KOH+0.5M NaCl is fed to the anode; type C, that 0.5 M NaCl solution is fed to the cathode and 1M KOH is fed to the anode; type D, that deionized water is fed to the cathode, and 1M KOH is fed to the anode.

Their advantages and disadvantages are shown in Table 3. The electrochemical characterization methods are the same as project one. To explore the effect of Cl^- , titration analysis with iodide is used to detect chlorine in the electrolyte on the OER side. GC will be used to determine the Faradaic efficiency of both OER and HER.

Table 4. Summary of the recent reports on OER electrocatalysts for seawater electrolysis

Reference	Cell voltage (V)	Current density (A/cm^2)
[64]	1.7	0.729
[60]	1.6	0.2
[65]	1.8	0.103
[66]	1.8	0.01
[67]	2.1	0.01
[68]	1.57	0.01
[68]	2.02	1
[69]	2.1	0.4
[70]	1.71	0.1
[70]	1.867	0.5
[71]	1.661	0.1
[71]	1.837	0.5
[72]	1.625	0.01
[72]	1.749	0.05
[72]	1.801	0.1
[72]	1.625	0.01
[73]	1.46	0.01
[73]	1.7	0.1
[74]	0.97	0.3
[75]	1.82	0.3

[76]	1.7	0.84
[77]	1.7	0.688
[77]	1.562	1
[78]	1.8	0.275
[79]	1.78	0.5
[79]	1.92	1
[80]	1.861	0.5
[81]	1.58	0.01
[82]	1.5	0.5
[83]	1.7	0.32

Table 4 shows the current studies in seawater electrolysis. Due to corrosion, the performance is worse. To promote performance, different electrolyte configurations, different types of electrodes, and fabrications are researched.

1.6.3 OER Catalyst Design in Seawater Electrolysis

Due to the corrosion, pH effect, and other reasons, designing an OER catalyst in seawater electrolysis is a challenge. It should consider catalyst selection, electrode design, electrolyte choice, and system fabrication. The catalyst should be corrosion-resistant and durable in harsh conditions. For electrode design, it could be with many active areas, and more methods could be introduced in the following chapters. Regarding electrolytes, due to the pH effect, the alkaline condition is better. For system fabrication, there are many studies considering electrolyte configurations and other things. Asymmetric electrolyte configuration is better in AEMWE.

Chapter 2 - Fundamentals of the Materials Synthesis and Characterizations

In the last chapter, the fundamentals of AEMWEs are introduced. This chapter focuses on the fundamentals of experimental methods. The sample preparation and characterization methods will be first introduced. To evaluate the performance of the OER catalysts, electrochemical measurements in half cells and full cells will be mentioned.

2.1 OER Electrocatalysts Synthesis Methods

As mentioned in section 1.5, electrocatalysts for OER are nano- or micro-materials. Several methods, such as sol-gel, co-precipitation, and corrosion methods, are used to synthesize these catalysts.

2.1.1 Sol-Gel method

The sol-gel method is a common and one of the simplest methods for preparing nanocatalysts, and it is primarily used for synthesizing metal oxide catalysts, such as perovskite-based oxides [84,85].

The sol-gel method is more popular than other methods because it has a lot of advantages. First, it is simple and cost-effective. It doesn't require a high-temperature synthesis process compared with other methods. The temperature range is between 70 ~320°C [84]. Therefore, it reduces energy consumption and lowers equipment costs. Second, the products are high-homogeneity and pure at low temperatures, based on the stoichiometry. Third, the catalyst has a large surface area due to its high porosity [84].

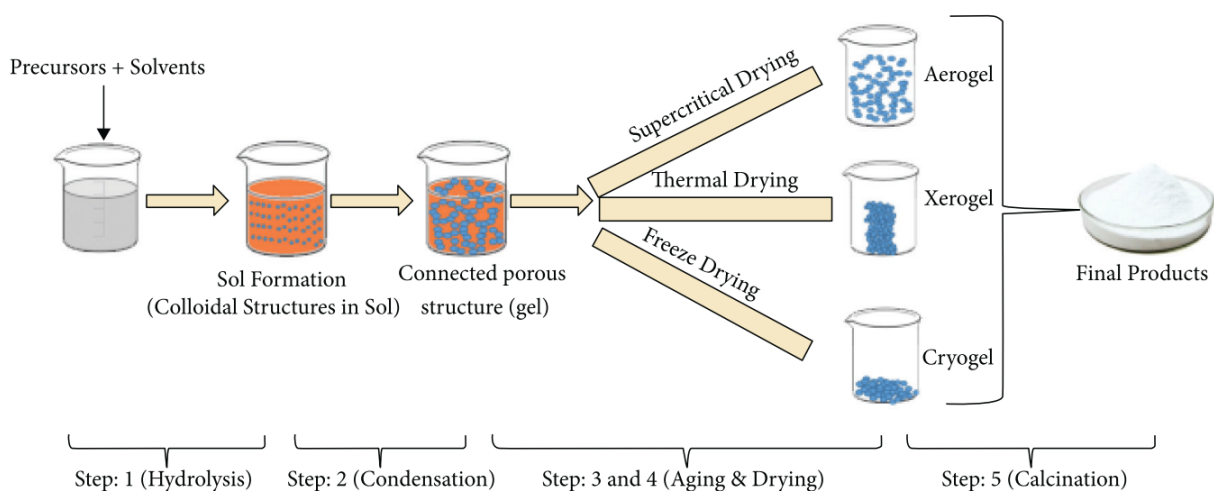
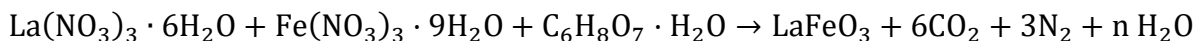


Figure 10. Schematic of the sol-gel process [84].

The sol-gel process is a wet chemistry method, which is shown in Figure 10. It includes hydrolysis, condensation, aging and drying, and calcination. During hydrolysis, different salts at stoichiometry with unique reaction rates form metal hydroxides at various factors. Step 2 forms a gel structure by joining the cavities. After the drying step, a solid structure with nanosized porosity is obtained by supercritical, thermal, or freeze drying [84].

Products from sol-gel methods could be used in many areas, such as membranes and thin film. Membranes could be prepared by casting and molding. The thin film could be generated with a thickness of 50~500nm, which could be used in electronics and chemical industries [84].

Recently, the sol-gel method has been used to prepare nanomaterials, such as perovskite and oxide [85]. It is used to prepare LaFeO_3 [86] and LaSrCoFeO_3 [87]. In this study, the thermal drying method is used to prepare perovskite. Gosavi et al. [86] compare the sol-gel method with the co-precipitation and combustion method for preparing perovskite - LaFeO_3 . The products synthesized via the sol-gel method exhibit a single phase with high surface area and high porosity. The overall reaction to prepare LaFeO_3 is shown as follows [86].



..... Equation 1

2.1.2 Co-precipitation Methods for Synthesizing NiFe LDH and NiFeOOH

The co-precipitation method is another common and low-cost “one pot” technique for synthesizing catalysts, especially layered double hydroxides (LDHs) and related materials [88,89]. It involves the simultaneous precipitation of two or more metal ions from a base solution, resulting in the formation of a solid compound or mixture. In this method, metal precipitates in the form of hydroxide from a salt precursor in the presence of a base in a solvent.

Figure 11 shows the process of the co-precipitation method to prepare LNMO. The co-precipitation method includes preparation of a precursor solution, mixing and precipitation, washing and drying, and calcination or annealing. It is essential to choose appropriately soluble metal salts, as shown in Figure 11 solution A. During the mixing step, the solvent is ethanol or water.

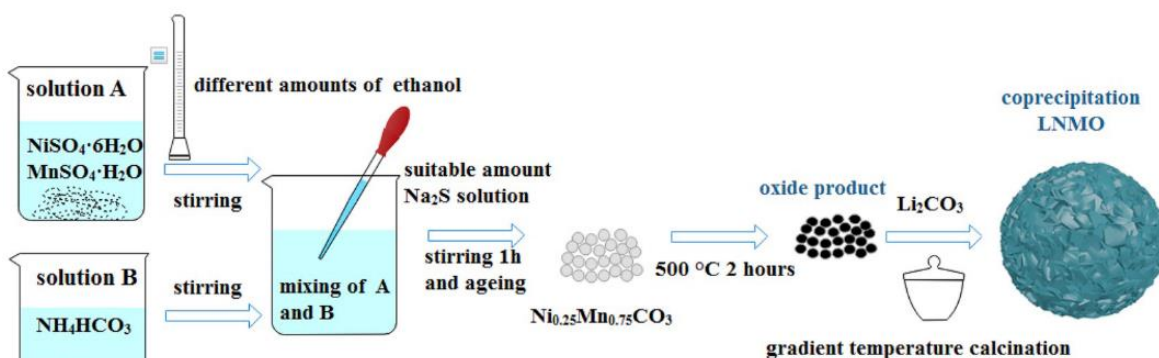


Figure 11. Schematic diagram of the synthesis route of LNMO [90].

The co-precipitation could be used to prepare various catalysts, including metal oxides, hydroxides, or mixed metal compounds. It is a simple and relatively low-cost method. Shen et al. [90] used this method to prepare $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ for batteries. Wei et al. [91] prepared LDHs using this method to control morphology.

2.1.3 Corrosion Methods for synthesizing unified NiFeOOH on Fe/Ni foam

Corrosion is a natural undesirable process of deterioration and gradual destruction of materials, typically metallic materials, due to chemical, electrochemical, or other reactions at the interface with the material surface and the environment [92]. It is a common phenomenon that affects a wide range of materials, including iron, nickel, aluminum, copper, and more. Many studies discuss the methods to prevent corrosion to avoid metal damage or failure due to chemical transformation reactions caused by corrosion. However, recently, corrosion has been used to produce nanostructures with an unconventional morphology or composition that cannot be achieved otherwise [93].

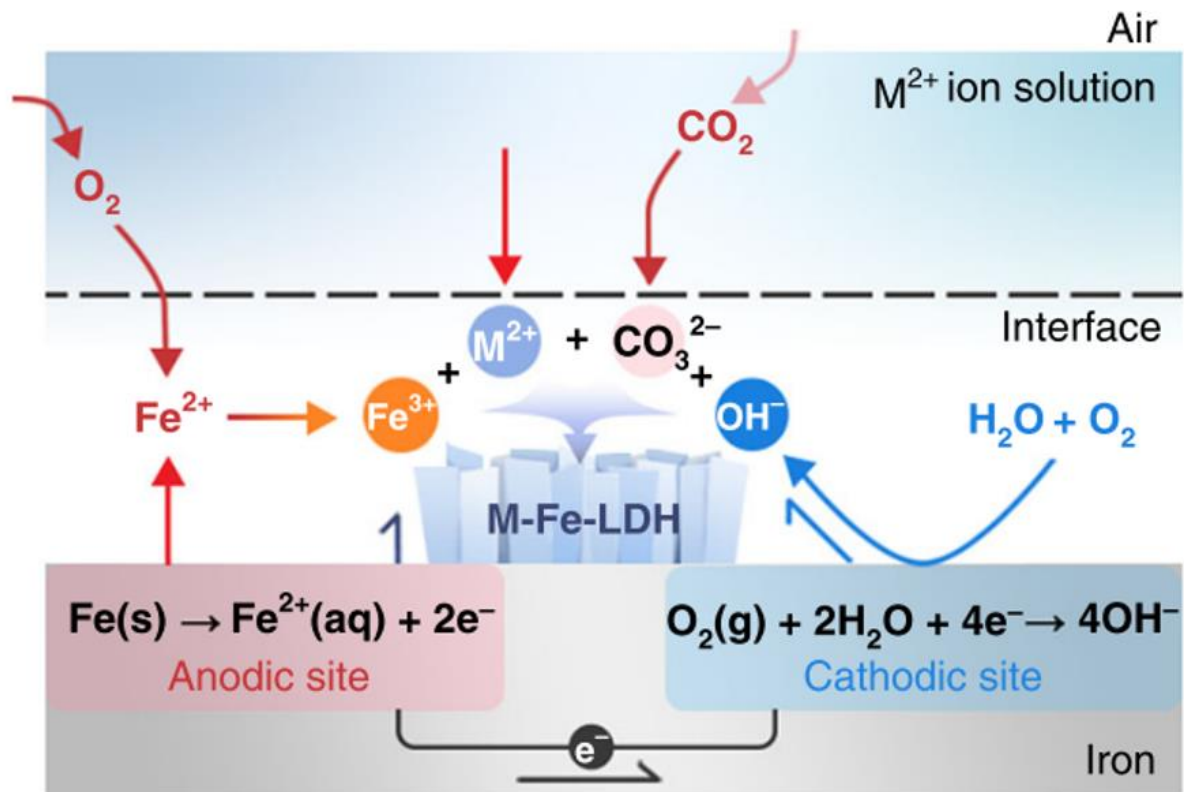
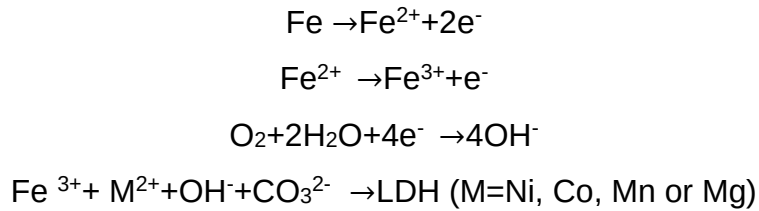


Figure 12. Schematic illustrations of the formation and microstructure of the electrodes. These specific reactions happen during the corrosion of iron substrates [94].

Iron corrosion, often named rusting, is one of the most well-known and common corrosion phenomena. It occurs when iron substrate contacts oxygen and water in the presence of the environment, leading to the formation of iron oxide, commonly known as rust. Even though it causes function deterioration of the materials and significant economic losses, it is used to fabricate OER electrode, which exhibits excellent catalyst activity, such as iron-containing LDHs [94]. To manufacture it, as shown in Figure 12, the iron substrate, such as Fe foam, is immersed in an aqueous solution containing divalent cations, e.g., Ni^{2+} , at room temperature. The well-oriented grain boundary-enriched nanosheet Fe-bearing LDHs are spontaneously produced on the Fe surface. Different divalent metal cations, M^{2+} , could be used to synthesize LDH, such as Ni^{2+} , Co^{2+} , Mn^{2+} , or Mg^{2+} . The electrochemical reactions show the following equations [94].



Similar to Fe substrate, it is also common to synthesize LDH on Ni foam, and the process is shown in Figure 13 [95]. For example, Ni foams (NF) were corroded in aqueous solutions with Fe^{3+} and Co^{2+} cations to obtain OER electrodes composed of double hydroxide (LDH) nanosheets with a ternary NiFeCo layer supported by NF." [93].

It is popular to synthesize LDH and OOH via corrosion on metal substrates, such as Ni or Fe foam as a substrate [96]. Lee et al. [97] used it to prepare NiFeV LDH by corroding Ni foam, leading to a current density of $2.1\text{A}/\text{cm}^2$ at $1.8\text{V}_{\text{cell}}$. Similar to Lee's method, NiFeV LDH [98], $\text{Ni}(\text{OH})_2$ [99], and NiFeCo LDH [93] are also prepared on substrate foam as OER electrodes. These electrodes are binder-free on the metal substrate.

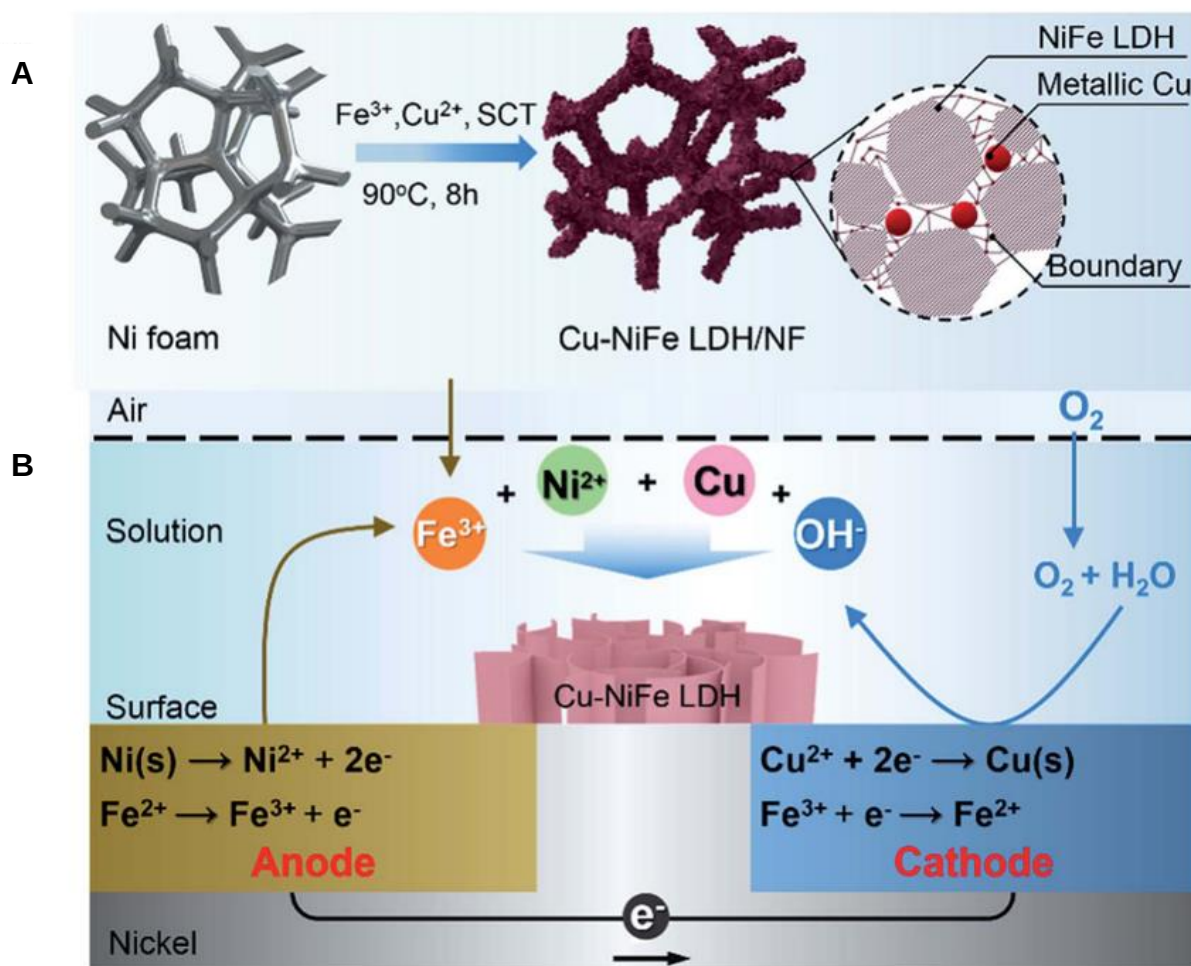


Figure 13. Schematic illustration of the formation and microstructure of the electrodes. (A) Schematic illustration of the preparation process of Cu–NiFe LDH/NF. (B) The specific reactions occur during the surface oxidation etching of NF [95].

2.1.4 Others

There are several methods to prepare catalysts. For powder catalysts, spray coating is the most common method to prepare electrodes on the substrate. For example, Wang et al. [15] used a plasma-sprayed method to coat electrodes. For uniform electrodes, there are electrodeposition method [100,101], one-step hydrothermal method [102], and galvanic corrosion reactions [56]. Park et al. [103] used a hydrothermal process

and heat treatment to synthesize CuCo_2O_4 on Ni foam, which is shown in Figure 14. Jiang et al. used the electrodeposition method to synthesize NiFe LDH/FeOOH on Ni-Fe foam.

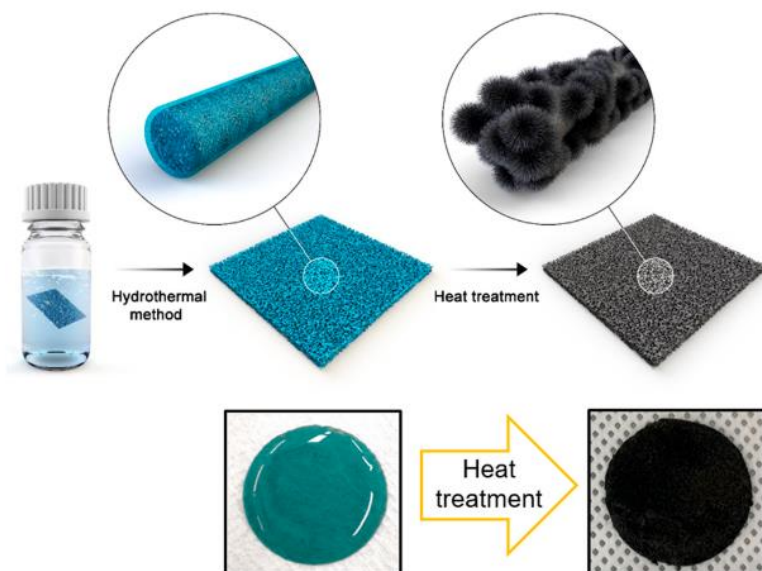


Figure 14. Schematic illustration for the synthesis of CCO* on Ni foam. The bottom picture indicates an actual synthesized electrode [103].

2.2 Structural Characterization Methods

2.2.1 X-Ray Diffraction

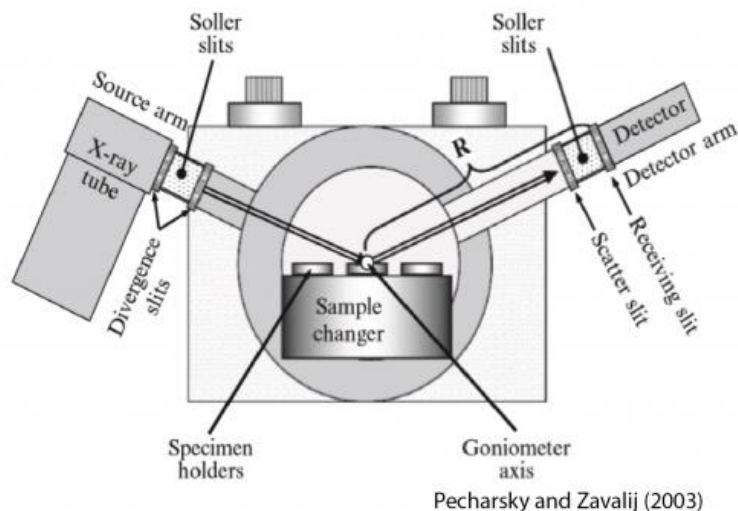


Figure 15. Schematic diagram of the structure of the X-ray diffractometer and goniometer [104].

X-ray Diffraction (XRD) is used to determine the microstructure of a material, including its crystal phase and lattice constants. XRD uses the diffraction phenomenon of X-rays in the crystal to obtain the characteristics of the X-ray signal after diffraction. Then, after processing, the diffraction pattern spectrum is obtained. The use of spectrum information can not only realize the determination of the phase, but also to see whether there are defects and lattice defects inside the crystal.

X-ray is a high frequency electromagnetic wavelength. This is because its penetrating power is extreme, and its propagation direction in the magnetic field is not affected. However, X-rays have a certain amount of radiation and have specific side effects on the human body. Currently, lead glass is mainly used for shielding.

X-rays are produced by a stream of high-speed electrons or other high-energy radiation streams (γ -rays, neutron streams, etc.) that suddenly decelerate when they collide with other substances and interact with inner electrons in the substance. In general, K_{α} radiation with the highest intensity is used in XRD methods. Another radiation is removed by appropriate filters or monochromators [105]. For different target materials in the X-ray tube, the radiation wavelength changes with the target materials.

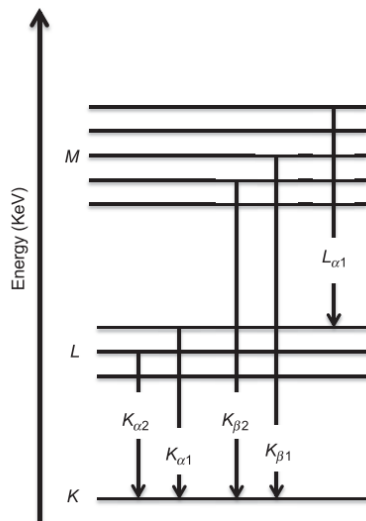


Figure 16. Schematic of the atomic energy levels and emission of characteristic X-ray radiation [105].

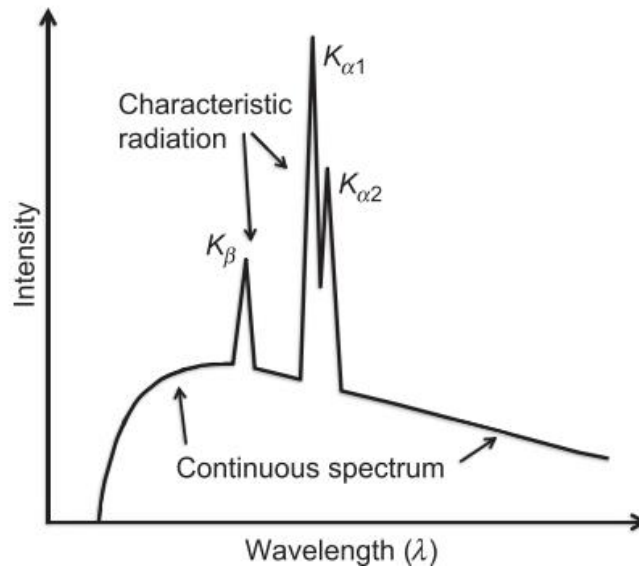


Figure 17. Intensity over wavelength distribution of the X-ray radiation produced by a sealed tube showing the continuous and characteristic spectrum [105].

The Bragg equation is a fundamental condition that X-rays need to meet to produce diffraction in a crystal, and it reflects the relationship between the direction of the diffraction line and the crystal structure.

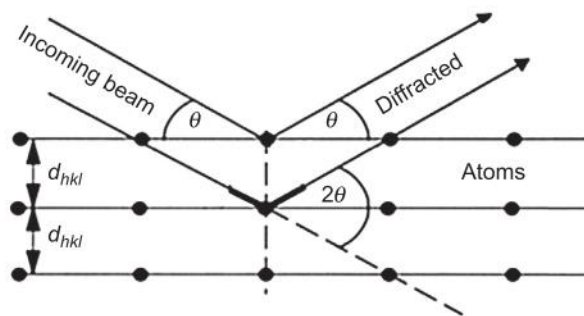


Figure 18. Geometrical condition for diffraction from lattice planes [105].

In XRD, the reflection angle of X-rays is different from the reflection angle of visible light, and the angle between the incident angle and the reflection angle of X-rays is always 2θ .

XRD patterns relate the diffraction angle to the Miller index, which is a geometric function of the size and shape of the lattice parameter.

The degree of broadening of the X-ray diffraction band is related to the size of the crystal grains. The smaller the crystal grains, the diffraction lines will become diffuse and broadened. The Scherrer formula, also known as the Scherrer formula, describes the relationship between the grain size and the half-width of the diffraction peak shown in the following.

$$FWHM = \frac{K\lambda}{L\cos\theta} \dots\dots\dots \text{Equation 2}$$

K: shape factor

L: grain size

λ : X-ray wavelength

θ : Bragg angle

FWHM: full width at half maximum

The Scherrer equation is used to calculate the average particle size. In the equation, FWHM, is the full width at half maximum in Figure 19, the width at which the diffraction intensity is half of the maximum value. This equation is used to measure the lattice range with 3-200 nm [106].

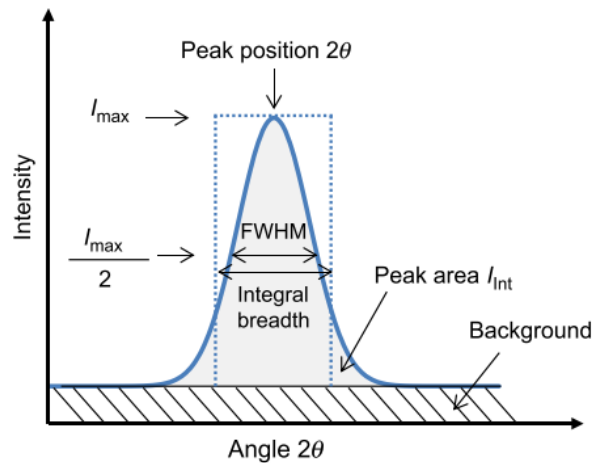


Figure 19. The full width at half maximum [105].

XRD analysis is helpful for identifying single-phase crystal characterization. However, the amount percentage of each phase in polycrystalline is hard to identify. The spectrum peaks overlap seriously, which causes a large amount of material structure information loss. To solve this problem, in 1967, Rietveld proposed a fitting method for diffraction data

to analyze polycrystalline diffraction. After that, the Rietveld method is used to refine XRD data to obtain various structural information of polycrystalline materials, such as mass fraction.

In Figure 20, by performing XRD refinement, three phases, P(perovskite), RP1 (Ruddlesden-Popper, $n=1$), and RP3 (Ruddlesden-Popper, $n=3$) are distinguished in the sample. Multiple phase information, including composition, space group ($I4/mmm$, $Pm/3m$), and lattice parameters, are shown after refinement.

However, the XRD refinement results should be carefully used. This Rietveld method is fitted by the least square method in statistics.

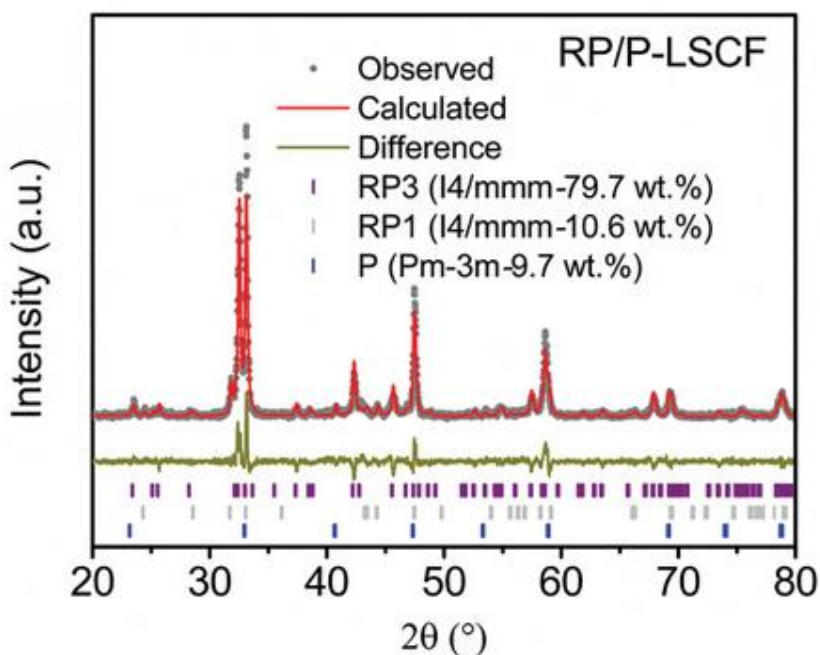


Figure 20. Refined XRD profile of RP/P-LSCF [43].

2.2.2 Scanning Electron Microscopy / Transmission Electron Microscopy

Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) are powerful imaging techniques in materials characterization used to obtain high-resolution images. In SEM, a focused beam of electrons is scanned across the material surface and detects the signals generated by the interaction between the electrons and the material shown in Figure 21. It works on a nanometer to micrometer (μm) scale [107].

TEM is used to examine materials at the nanoscale level. A high energy beam of electrons is transmitted through a very thin sample, and the interactions between the electrons and the atoms can be used to observe the internal structure of a material, such as the crystal structure and features in the structure.

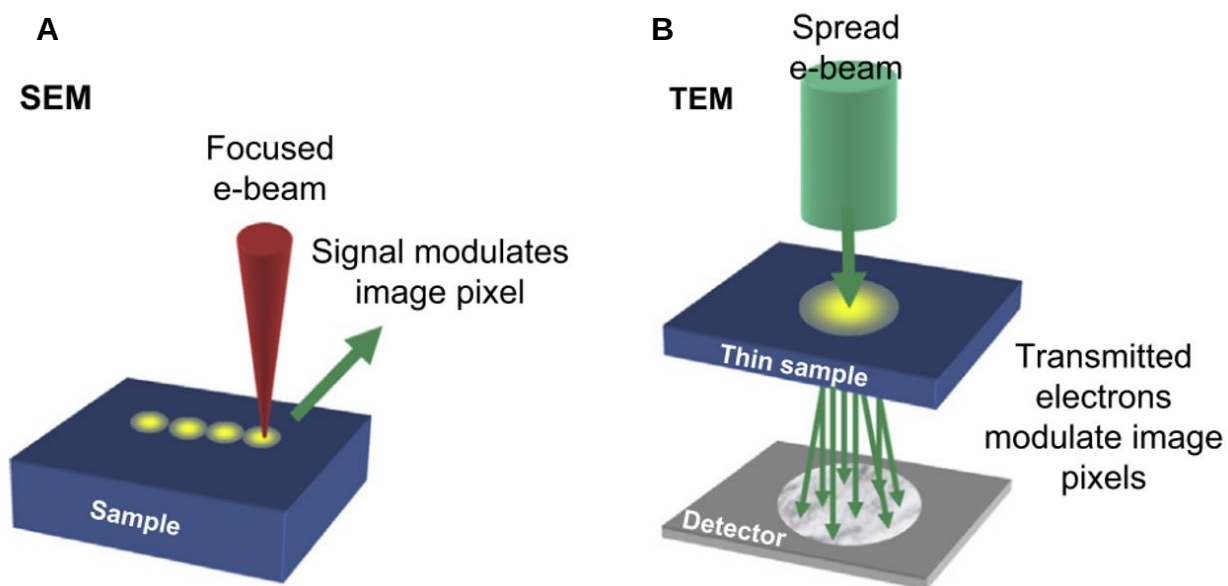


Figure 21. Schematic of SEM, TEM, and STEM imaging methodology. (A) Serial collection of data points in SEM. (B) Parallel image acquisition in TEM [108].

2.2.3 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) measures the elemental composition, and the chemical and electronic state of the atoms. When X-rays illuminate atoms, electrons are excited from all populated orbitals, where electrons are bound at energies lower than the photon energy as shown in Figure 22. The relationship among kinetic energy (E_k), which the electrons leave the surface, the X-ray photon energy ($h\nu$), the energy that bound the electron (E_B), and the work function of the material (ϕ) is shown in the following equation [109].

$$h\nu = E_k + E_B + \phi \dots\dots\dots \text{Equation 3}$$

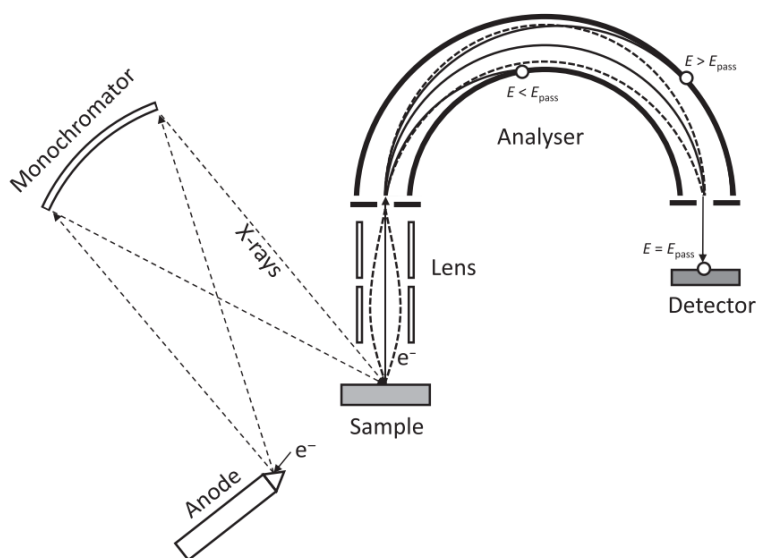


Figure 22. Schematic of a typical X-ray photoelectron spectrometer [110].

2.3 Different OER Electrodes for Performance evaluation

2.3.1 Rotating Disk Electrode (RDE)

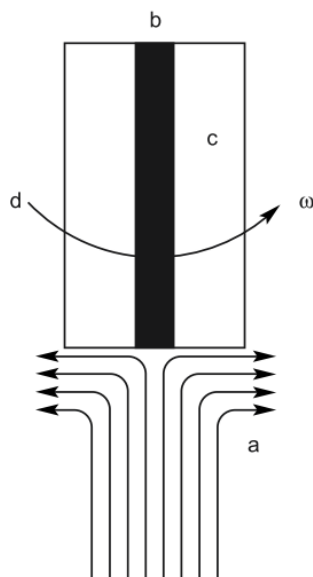


Figure 23. Solution movement is caused by the rotation of an RDE. a: flow of electrolyte solution; b: vitreous carbon electrode; c: RDE body; d: direction of electrode rotation [111].

A rotating disk electrode (RDE) is a type of electrochemical cell used in electroanalytical chemistry and electrocatalysis studies, as shown in Figure 25. It is used as a working electrode in a three-electrode system. It consists of a disk-shaped electrode that is rotated at a controlled speed in a solution containing the analyte. The rotation of the electrode creates hydrodynamic conditions that enhance mass transport to and from the electrode surface, allowing for more efficient and reliable electrochemical measurements.

The rotation of the disk electrode produces a convective flow of the solution near the electrode surface, as shown in Figure 23. This flow helps to maintain a fresh supply of analyte to the electrode surface, acting as a pump, and removes any reaction products that may hinder the electrode kinetics [111]. The electrolyte follows the Nernst diffusion layer model shown in Figure 24. There is a diffusion zone close to the surface and a convection zone away from the surface outside of the diffusion zones. As a result, RDE measurements can provide more accurate kinetic information and allow for the determination of electrochemical reaction mechanisms. However, the gas accumulation on the disk surface still affects the catalyst performance during experiments [112].

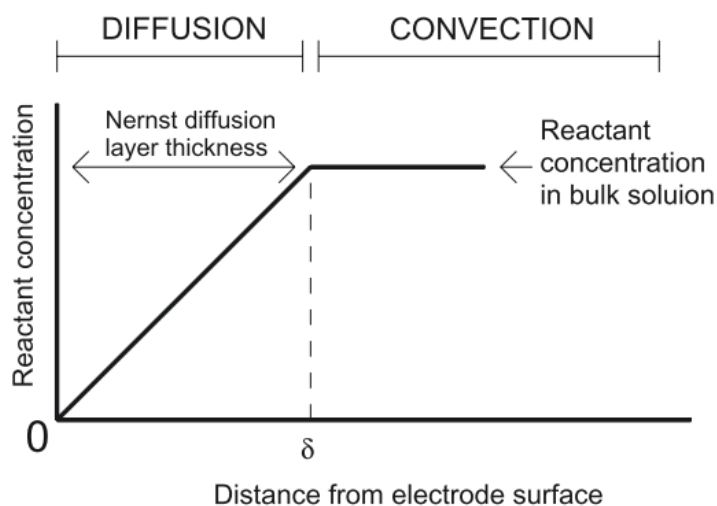


Figure 24. Representation of the Nernst diffusion layer profile model [111].

The RDE technique is widely used in electrochemical studies, including to investigate reaction kinetics, determine electrode reaction mechanisms, measure electrochemical parameters (such as diffusion coefficients and rate constants), and

evaluate the electrocatalytic activity of materials. It is particularly useful for studying fast electrode reactions or systems with low electrolyte concentrations. H. Yu et al. [113] used the RDE technology in OER with a perovskite catalyst. It is also used in lithium batteries [114].

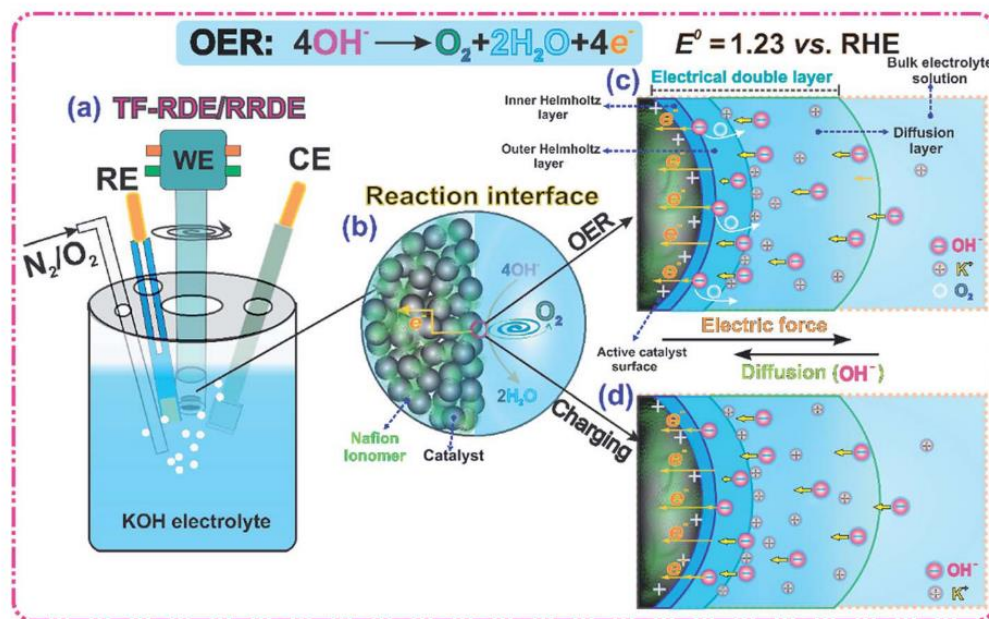


Figure 25. Schematic of the electrocatalytic OER in alkaline media [115].

2.3.2 Binder-free unified Electrode

Section 2.4 introduces the configuration of cell testing. For powder catalysts, to prepare electrodes, it is common to apply a binder, such as an ionomer, through spraying to enhance the binding. However, this could increase the ohmic resistance due to the non-conductive ionomer. What's more, there are two layers in conventional AEMWE electrodes, including the catalyst layer and the gas diffusion layer (GDL). These two separated assemblies cause lower electron transfer kinetics, which could increase contact resistance. Moreover, during the preparation process, the catalyst layer is dense and thick. Therefore, it could hinder catalyst utilization, and this dense and thick dispersion could block the active area. They could reduce mass transfer between reactants and products.

Recently, binder-free electrodes that combine the catalyst layer and gas diffusion layer (GDL) as AEMWE electrodes have been studied to achieve high efficiency. Park et al. [52] demonstrated excellent performance, with a current density of 3.6 A/cm^2 achieved at 1.9 V and 70°C using NiFeOOH on stainless steel paper (SUS) substrate by combining GDL and catalyst layer, which is shown in Figure 26. Kahnemouei et al. [57] prepared S-(Fe/Ni)OOH on carbon cloth and stainless-steel substrate to improve the activity.

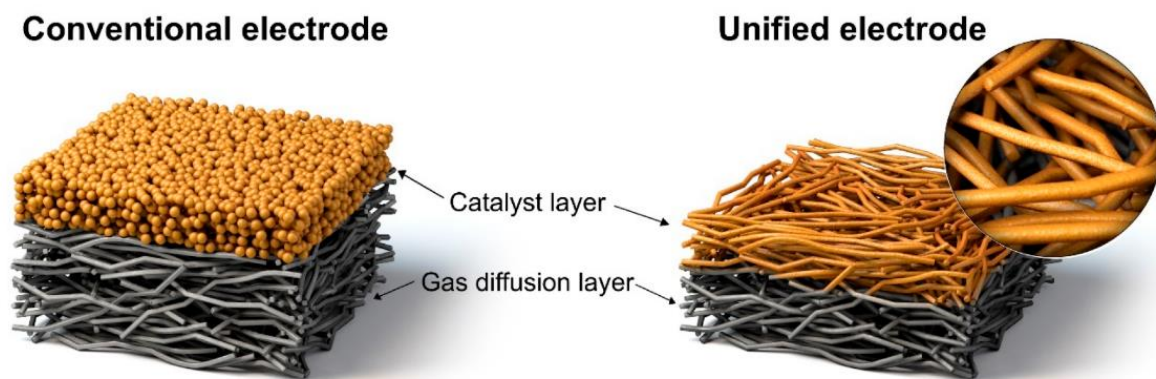


Figure 26. Conventional and unified electrode with the Stainless steel paper. Schematic diagram of two types of electrodes [52].

2.3.3 Catalyst Loading Effect

Based on the preparation method, the catalyst products are powder or nanosheets. When the catalyst is powder, they are deposited on the substrate surface as electrodes, such as carbon cloth, Ni foam, and so on. The quantity of catalyst amount is essential in comparing electrochemical performance. As mentioned in Chapter 1, The catalyst is crucial in facilitating the electrochemical reactions and improving their efficiency. In AEMWEs, the oxygen evolution reaction at the anode is often a rate-limiting step. Catalysts enhance the kinetics of the oxygen evolution reaction, reduce overpotentials, and improve the overall performance of the electrolysis process.

Higher catalyst mass loading generally increases electrochemical activity, as more active sites are available for the oxygen evolution reaction. This can result in higher current densities, improved reaction kinetics, and enhanced efficiency of oxygen evolution. However, excessively high catalyst mass loading can also increase ohmic

resistance and limit mass transport, negatively affecting the performance of the AEMWE system.

Therefore, the catalyst mass loading optimization is vital in OER testing. It is essential to balance the maximum active surface area and minimize resistance and transport limitations. The optimal catalyst loading depends on several factors, including the specific catalyst material, electrode design, operating conditions, and desired performance metrics.

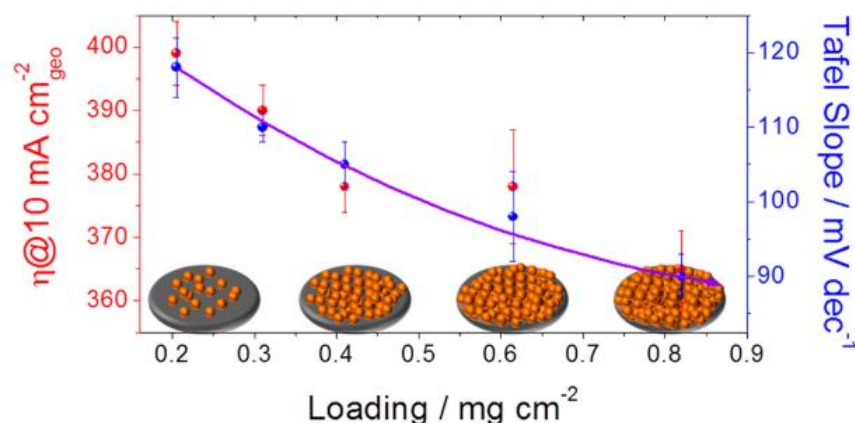


Figure 27. Catalyst loading effect in electrochemical water splitting [116].

By carefully controlling and optimizing the catalyst mass loading in AEMWE, it is possible to improve the efficiency and performance of the oxygen evolution reaction, leading to a more effective water electrolysis processes for hydrogen production. S. Anantharaj and S. Kundu reported that the Tafel slope depends on the mass of catalyst loading [116]. Figure 27 also shows the catalyst loading effect on electrochemical water splitting performance.

2.4 Electrochemical Testing System Setup

2.4.1 Three Electrode System

To better control and measure the current and potential going through the cell during the electricity-driven chemical reaction, it is better to use the three-electrode

system to reduce and compensate for the potential changes caused by large currents passing through the working and counter electrodes.

A three-electrode system is a typical setup used in electrochemical measurements and experiments [117]. It consists of three electrodes: a working electrode (WE), a reference electrode (RE), and a counter electrode (CE) as shown in Figure 28. Each electrode plays a specific role in the electrochemical cell, allowing for accurate and controlled measurements. The working electrode is where the electrochemical reaction of interest occurs. It is where the analyte is oxidized or reduced, and it is the electrode where the current is measured. It is typically made of a conductive material, such as platinum, gold, glassy carbon, or other materials, depending on the application. In this study, the catalyst electrodes, such as perovskite coated on carbon cloth, is working electrode. The reference electrode provides a stable reference potential against which the potential of the working electrode is measured without passing any current. It has a known and constant potential that remains unchanged during the experiment. Commonly used reference electrodes include the silver/silver chloride (Ag/AgCl) electrode and the saturated calomel electrode (SCE). In this study, both of those are used. The counter electrode completes the electrical circuit in the cell. It is responsible for ensuring that the current flow in the cell is maintained by providing a pathway for the flow of electrons. The counter electrode is typically made of an inert material, such as platinum or graphite, that does not participate in the electrochemical reaction.

Three-electrode setups have a distinct experimental advantage over two-electrode designs, which measure only one-half of the cell. That is, the potential changes of the working electrode are measured independently of changes that may occur at the counter electrode. In addition, the three-electrode system allows for precise control and measurement of the electrochemical processes. The reference electrode provides a stable reference potential, ensuring accurate measurements of the working electrode potential. The counter electrode ensures that the current flow is maintained, preventing any polarization effects that could interfere with the measurement.

This setup is commonly used in various electrochemical techniques, including cyclic voltammetry, chronoamperometry, and impedance spectroscopy, among others, in half-cell testing. The three-electrode system provides a reliable and well-defined

electrochemical environment, making it an essential tool for studying electrochemical reactions, determining reaction kinetics, and characterizing electrochemical systems.

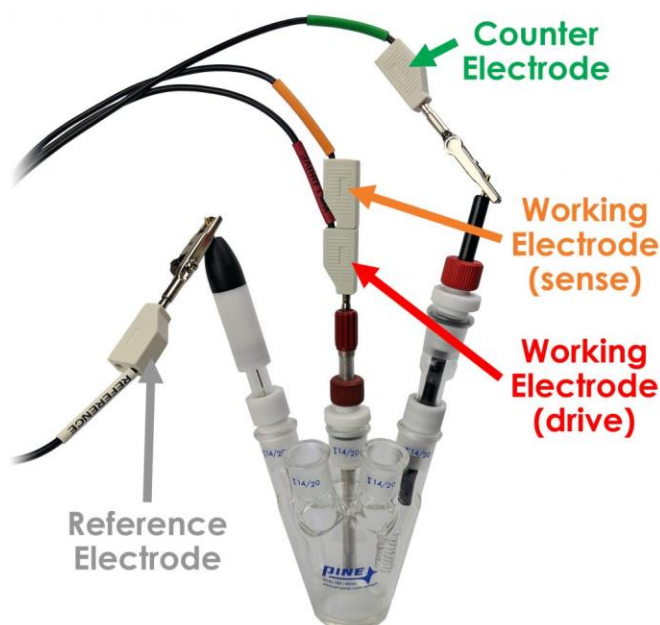


Figure 28. Three-electrode system [118].

2.4.2 Membrane Electrode Assemblies

Membrane electrode assemblies (MEAs) are a crucial component in cell testing. There are several layers that work together to facilitate the electrochemical reactions that produce electricity.

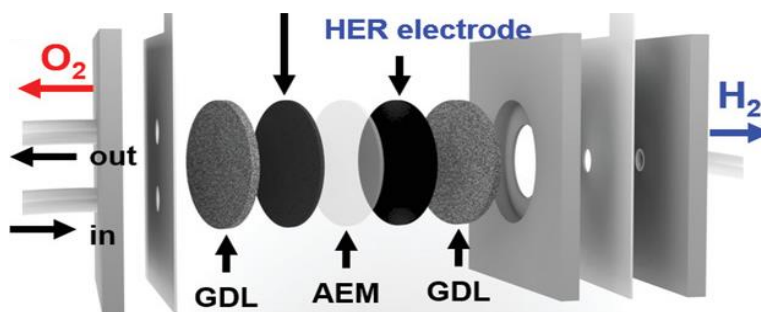


Figure 29. Scheme of AEMWE [97].

The main components of a membrane electrode assembly include an anion exchange membrane, a catalyst layer, and a gas diffusion layer (GDL), as shown in Figure

29. Powder catalysts are dispersed on the substrate, such as carbon cloth, Ni foam, and so on. The GDLs are porous materials that provide a conductive pathway for electrolytes to reach the catalyst layers. GDLs are typically composed of carbon fibers, carbon cloth, Ni foam, and so on. The cell acts as sandwiched between the anode and cathode catalyst layers, with GDLs on either side.

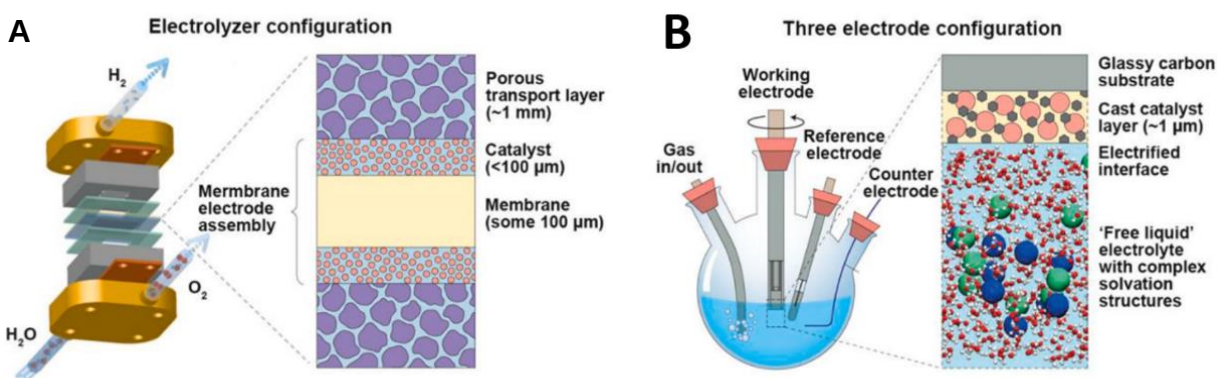


Figure 30. Schematic of (A) the two-electrode electrolyzer configuration and (B) the three-electrode electrolyte configuration for performance evaluation [119].

Xu compares the AEMWE and three electrode configurations shown in Figure 30. The sandwiched AEMWE structure can achieve a higher operating current density ($\sim 2 \text{ A/cm}^2$) than that of a three-electrode configuration ($\sim 0.2 \text{ A/cm}^2$), because of the porous transport layer promoting the mass transport of water to the catalyst layer and faster gas release [119].

2.5 OER Electrochemical Measurement and Data Analysis

2.5.1 Cyclic Voltammetry and Linear Sweep Voltammetry

Cyclic voltammetry (CV) is a powerful electrochemical technique used to study the redox behavior of chemicals in electrolytes. It is widely employed in various fields, including analytical chemistry, electrochemistry, material science, and biochemistry. CV involves applying a controlled potential sweep to an electrochemical cell containing the analyte of interest, typically between two working electrodes (often made of inert

materials like platinum, gold, or glassy carbon) [117]. As the potential is swept linearly versus time, the current passing through the cell of a redox active solution is measured. The potential is swept back and forth in a repetitive manner, forming a cyclic curve shown in Figure 31.

Elgrishi explains the fundamentals shown in Figure 32. The cyclic voltammogram is a plot of the current (y-axis) versus the applied potential (x-axis). It displays peaks and valleys representing the redox reactions of the analyte. The peaks correspond to the oxidization (anodic peak) and reduction (cathodic peak) processes. The peak potentials and the peak currents provide valuable information about the analyte's electrochemical properties, such as its oxidation and reduction potentials, electron transfer kinetics, and analyte concentration.

The polarization curves are tested by the linear sweep voltammetry (LSV) method. LSV is a plot of current density (i) versus electrode potential (E) for a specific electrode-electrolyte combination. It involves sweeping the potential of the working electrode linearly with time while measuring the resulting current. At the same current density, a lower potential means better catalyst performance in OER.

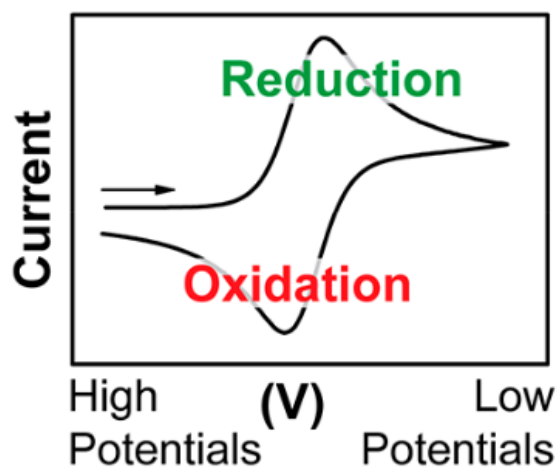


Figure 31. Cyclic voltammetry of ferricyanide/ferrocyanide [120].

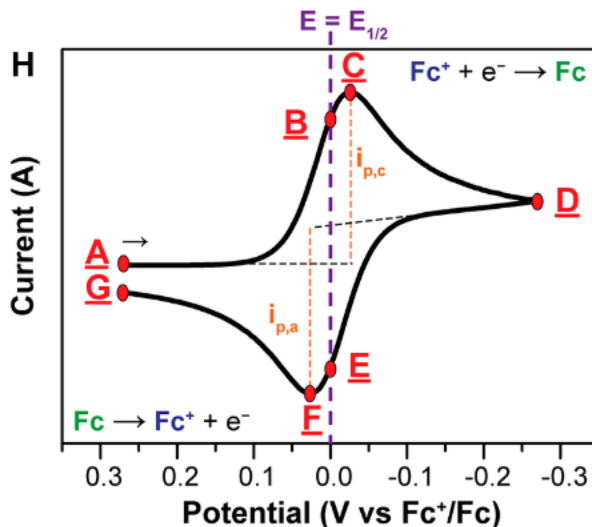


Figure 32. Concentration profiles (mM) for Fc^+ (blue) and Fc (green) as a function of the distance from the electrode [120].

2.5.2 Electrochemical Impedance Spectroscopy

EIS is electrochemical impedance spectroscopy. The ohmic resistance and electrode polarization resistance can be determined by conducting EIS and analysis. Nyquist plots tested by EIS represent a negative of the imaginary versus the real parts of the complex impedance of individual electrodes or electrochemical cells shown in Figure 33.

EIS is a multifrequency AC electrochemical measurement technique that measures the electrical resistance (impedance) of a metal/solution interface over a wide range of frequencies (from 1 mHz to 10 kHz).

EIS spectra were performed to better understand the AEMWEs equipped with a catalyst as the anode. The intercept of EIS spectra with the real impedance axis at the high frequency in the Nyquist plots corresponds to the ohmic loss of the AEMWE.

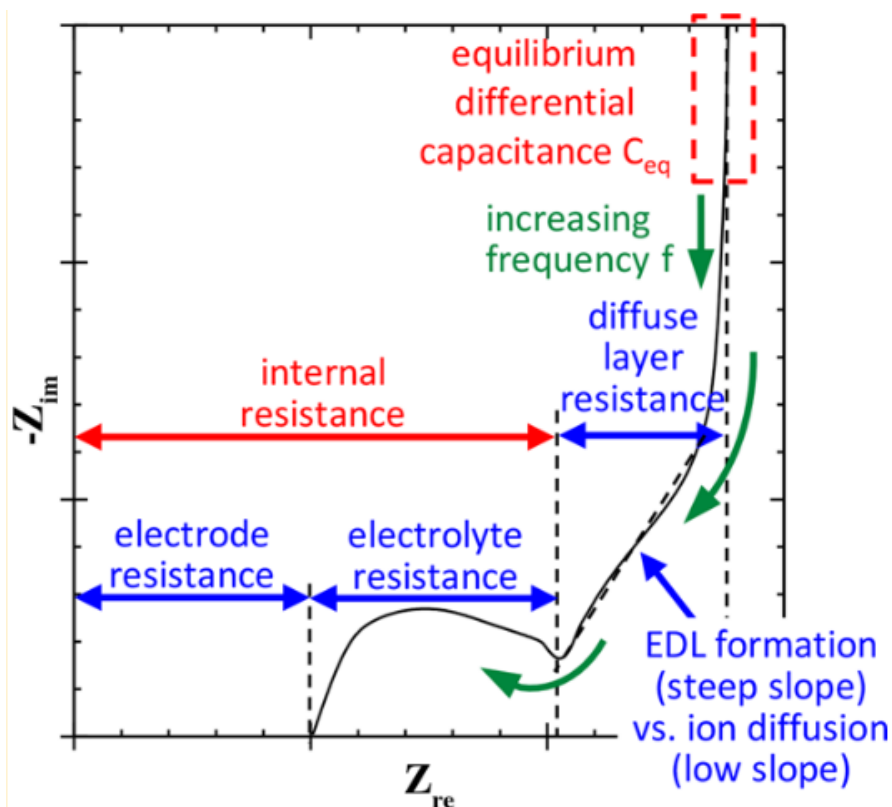


Figure 33. Schematic of typical Nyquist plots for EDLC electrodes or devices [121].

Recently, EIS has also been used to explain the kinetic by EIS model fitting [122]. Anatharaj et al. [123] studied different EIS tested effects, such as at 0V vs. OCP and constant potential (0.5V vs. Hg/HgO), and found that the best condition is at constant potentials to achieve correct R_{ct} .

2.5.3 Electrochemically Active Surface Area Measurement

The electrochemically active surface area (ECSA) is a key parameter of cell electrodes to determine the kinetic parameter of electrochemical reactions [124]. Measuring the ECSA allows for comparing the specific catalytic activity of different catalyst materials and investigating the catalyst utilization and degradation in different conditions and electrode architectures.

One often used approach is to determine the surface area with an electrochemical measurement of the double layer capacitance (DLC). A double layer (DL, also called an electrical double layer, EDL) is a structure that appears on the surface of an object when it is exposed to a fluid, as shown in Figure 25. The DL refers to two parallel layers of charge surrounding the object. The first layer, the surface charge (either positive or negative), consists of ions adsorbed onto the object due to chemical interactions. The second layer is composed of ions attracted to the surface charge via the Coulomb force, electrically screening the first layer.

There is no electrochemical reaction. So, it is a non-Faradaic reaction area, as shown in Figure 34, the flat area. The double-layer capacitances are determined by linearly fitting the non-Faradaic current as a function of the cyclic voltammetry (CV) scan rate. If this measurement is in a range with no Faradaic reaction, the resulting differential capacitance equals the double layer capacitance (C_{DL}).

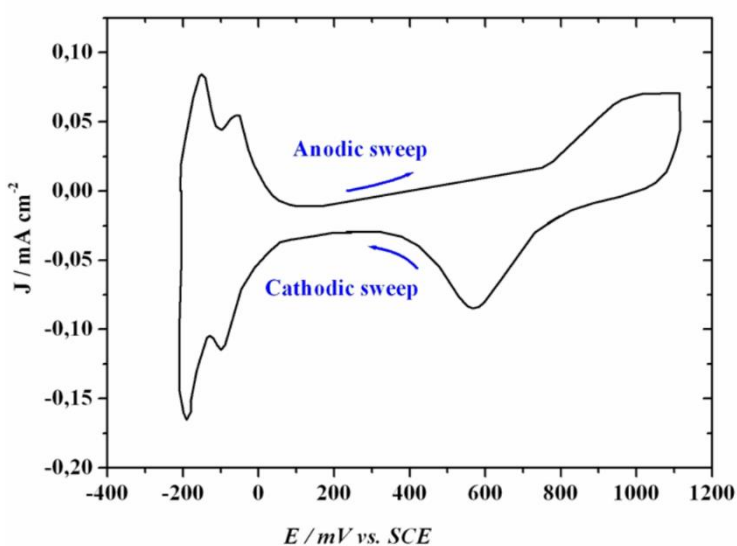


Figure 34. Voltammogram for a Pt electrode in 0.5 M sulphuric acid [125].

At each scan rate, the average different current between the anode and cathode is calculated. The slope of the scan rate of the average current difference is the C_{dl} . The higher C_{dl} means a larger active surface area, which could be with high catalyst performance.

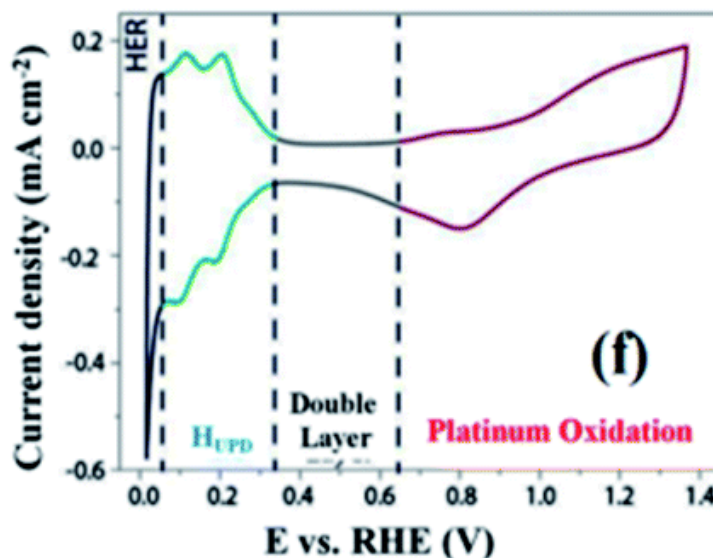


Figure 35. Cyclic voltammogram recorded on Pt [126].

2.5.4 Tafel slope

Tafel analysis is used to understand the reaction kinetics and mechanism and to compare the catalytic activity of different catalysts. The Tafel equation, which serves as a linearized representation of the Butler–Volmer expression, permits the extraction of fundamental parameters of electrochemical systems, such as exchange current densities and Tafel slopes. It is used to define the rate-determining step by examining the sensitivity of the current response to the given voltage by using the Tafel equation as follows [35].

$$\eta = \frac{RT}{\alpha nF} \ln j = \frac{2.303RT}{\alpha nF} \log j \dots\dots\dots \text{Equation 4}$$

It could be measured by LSV methods. It is the Tafel slope in the log current density and potential curve shown in Figure 36. The above equation expresses the Tafel behaviors in a half-cell reaction. In the equation, it shows the relationship between the overpotential and $\log j$, and j is the current density. Figure 36 shows how to get the Tafel slope in CV/LSV.

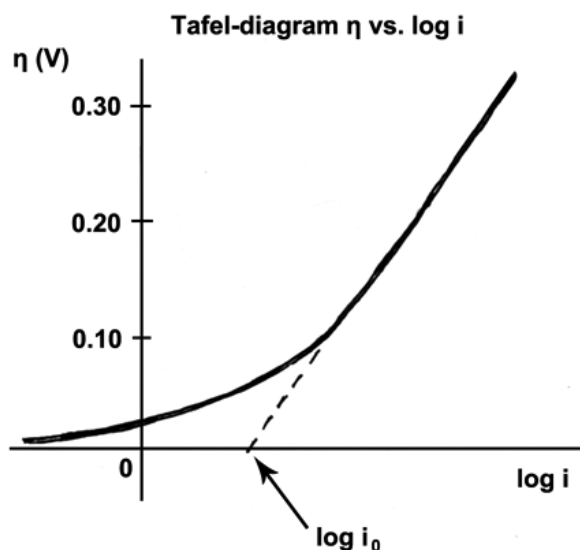


Figure 36. Tafel slope [127].

In addition, Anantharaj et al. [128] suggested the dynamic CV/LSV method should be replaced by potentiostatic or galvanostatic due to the misleading irrespective of the scan rate.

2.5.5 Stability

Stability is a crucial factor in the long-term performance and durability of electrochemical systems, such as batteries, fuel cells, and supercapacitors. It could be affected by several parameters, such as electrolytes and catalysts [35].

Chronopotentiometry at a constant potential or current density is used to evaluate the stability. It is hard to figure out the catalyst structure and composition change during electrocatalysis [35].

Hartig-Weiss and their team summarized the literature to understand the stability degradation in half cell tests by four distinct decay hypotheses [112]. Their degradation hypotheses are: additional resistance due to catalyst passivation; depletion of OER catalyst; loss of active site due to structure change; and blocking of the active site due to bubbles or other factors.

Ehelebe et al. [129] studied the stability in different systems, which are shown in Figure 37. They find AMS could be used in fundamental studies, but it is hard to explain the complexity. Ei-Sayed et al. [130] evaluated why the RDE technique presents a low stability compared to PEMWE. They found that the degradation is not only due to the catalyst but also the bubbles formed during the experiment within the pores of the catalyst layer. Because bubbles cannot be entirely removed via electrode rotation, they accumulate and block the catalyst active sites from the electrolyte, increasing the potential, which is mistakenly interpreted as catalyst degradation in previous literature. Subsequently, Hartig-Weiss et al.'s [112] research brought another finding that by removing gas from the surface of the disk by sonication, the rate of performance decay saw a significant amplification. Li et al. [131] studied the three different electrolyte effects on stability. The degradation in pure water is much lowered compared to the electrodes with ionomer binder in K_2CO_3 electrolyte.

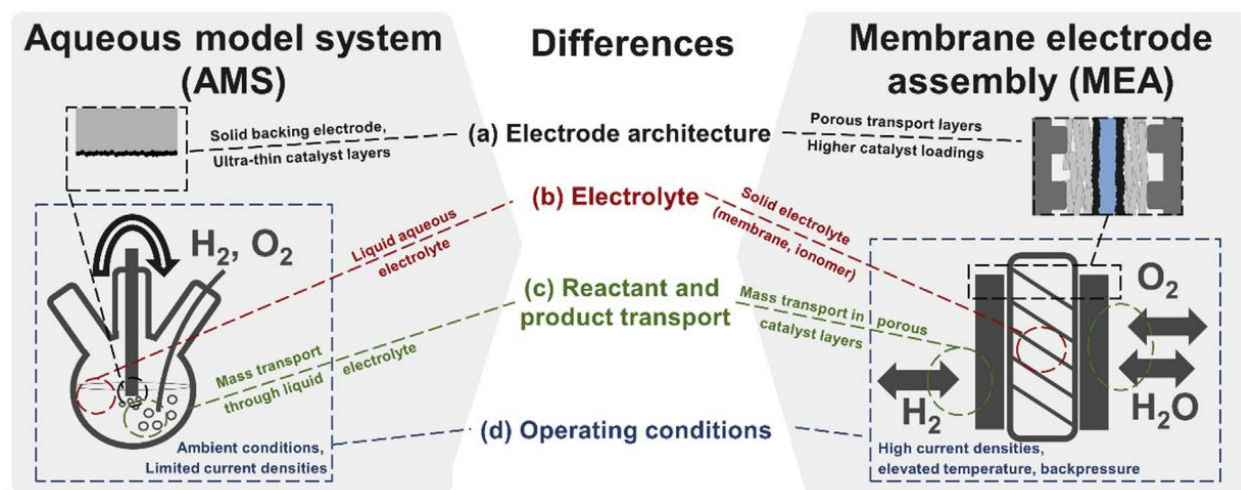


Figure 37. Schematic comparison of aqueous model system (AMS) and membrane electrode assembly (MEA) [129].

However, currently, stability is still a significant challenge in the development of OER catalysts, as many of the materials that exhibit good catalytic activity may suffer from degradation or corrosion over time, leading to decreased performance and efficiency.

2.5.6 Overpotential Analysis

The overpotential is the difference between RHE potential and 1.23V. In most studies, the overpotential at a current density of 10mA/cm² is used to compare with different materials.

Figure 38 illustrates potential loss. The most considerable voltage losses include the OER kinetics, the ohmic resistance of the membrane, and the mass-transport loss through the anode catalyst layers [132].

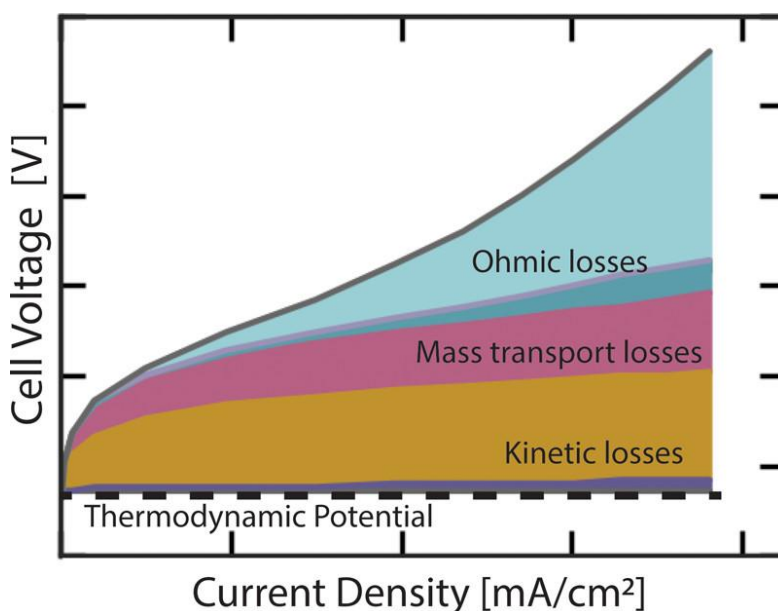


Figure 38. Applied voltage breakdown for this system [132].

The potential loss due to the OER kinetics is a characteristic of the catalyst. Due to the slower kinetics of OER, the OER overpotential is more significant than that for the HER. The activation loss (kinetic) is plotted using the difference between a linear approximation in the Tafel region (Tafel slope) and equilibrium potential.

The ohmic loss in the membrane increases rapidly with current density and is a function of water activity within the membrane phase. The ohmic loss is ascribed to the sum of the electrical and ionic resistance of the AEMWE. It represents the voltage drop due to the transfer of electrons in the electric circuit and the movement of ions through the electrolyte and membrane.

The mass-transport loss within the anode catalyst layer corresponds to the influence of changes in the reactant water concentration between the gas pathways, reaction sites, and ionomer. The origin of these mass-transport losses is caused by a combination of catalyst layer underutilization and local temperature rise [132].

2.5.8 Oxygen-ion Diffusion Coefficient Analysis

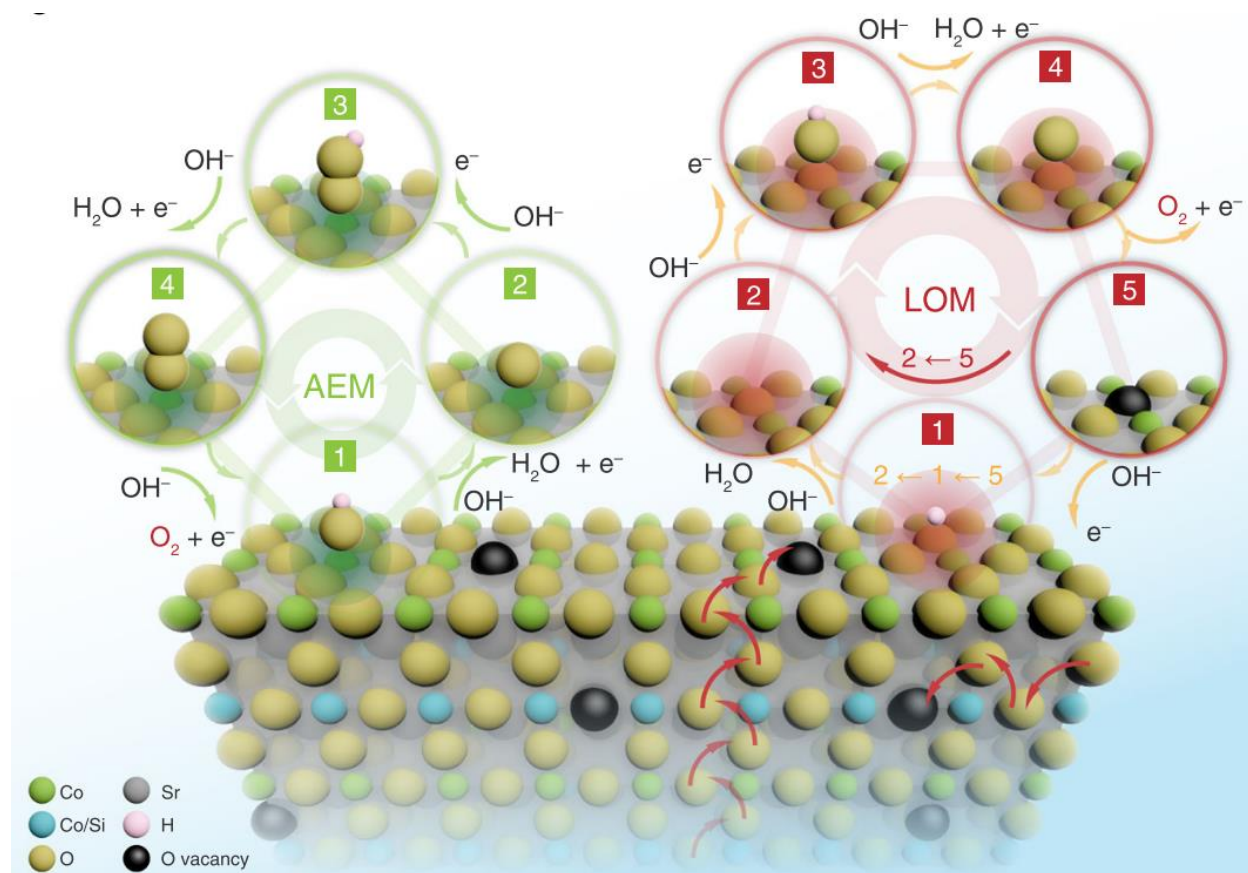


Figure 39. A schematic illustration of the AEM and LOM reaction pathways on Si-incorporated strontium cobaltites [133].

As mentioned in section 1.4, there are LOM and AEM of the oxygen evolution mechanism, and the oxygen ions (O²⁻) mobility is shown in Figure 39 [133]. The diffusion of oxygen ions through the catalyst material is one of the rate-limiting steps in the overall OER process. AEM shows the redox activity on the transition metal site. The lattice oxygen-mediated mechanism (LOM) occurs in perovskite-based OER catalysts under

alkaline conditions. Zhu et al. [43] studied the oxygen-ion diffusion in hybrid RP/perovskite , and they determined oxygen-ion diffusion coefficients by conducting CV and chronoamperometry measurements, and the equation is the following, where the current is plotted as a function of $t^{-1/2}$.

$$\lambda = \alpha((D_0 t)^{-1/2}) \dots\dots\dots \text{Equation 5}$$

- λ : dimensionless shape factor, 2;
- α : radius of the particle, $1.72 \mu m$;
- D_0 : oxygen-ion diffusion coefficient

Chapter 3 - Hybrid Perovskites as Oxygen Evolution Electrocatalysts for High-Performance Anion Exchange Membrane Water Electrolyzers

3.1 Introduction

One of the most effective solutions to the global energy crisis and climate change is developing sustainable clean energy through technologies with higher energy conversion efficiency and lower emission. Efficient conversion and storage of solar and wind energy is the “holy grail” for solving the global energy crisis. However, solar and wind energy is intermittent because it is affected by geographic location, season, time, weather, etc. Therefore, technologies that can effectively convert intermittent renewable energy into fuels/chemicals (e.g., H_2) are essential for long-term renewable energy storage [1–3].

Anion exchange membrane water electrolyzers (AEMWEs) are emerging as one of the most promising technologies for the conversion of renewable power to hydrogen [10–14]. AEMWEs exhibit the advantages of both alkaline water electrolyzers (AWEs) and proton-exchange membrane water electrolyzers (PEMWEs). AEMWEs operate in a basic media, allowing the use of non-precious metal-based electrocatalysts as the anode and cathode. However, PEMWEs, which run in an acidic media, are equipped with costly noble metal-based catalysts, constraining their further deployment due to the high material cost. Additionally, AEMWEs employ a solid-state membrane as the electrolyte, which eliminates the use of aqueous and corrosive alkaline electrolytes, reducing electrolyzer size and weight. Thus, AEMWEs could be one of the key technologies for clean hydrogen production [14,134,135].

However, AEMWEs suffer from low efficiency and poor hydrogen production rate, which are hampered by the sluggish kinetics of the anodic oxygen evolution reaction (OER) in the alkaline media [19,20]. Therefore, highly efficient, cost-effective, and highly durable electrocatalysts for OER are critical for the commercial viability of AEMWEs. Currently, IrO_2 , RuO_4 , Rh_2O_3 , layered double hydroxides (LDHs), oxyhydroxides, perovskites, and other non-PGM electrocatalysts are used as OER electrocatalysts for AEMWEs [27–30,34,136,137]. One of the state-of-the-art non-PGM electrocatalysts for

OER in alkaline media is Ni-Fe layered double hydroxide (LDH) [[44–47]. Alternatively, perovskite-based electrocatalysts have attracted significant attention [37,38,45,138–140]. Single layered perovskites ($\text{ABO}_{3-\delta}$) or perovskites with Ruddlesden – Popper (RP) phases ($\text{A}_{n+2}\text{B}_n\text{O}_{3n+1}$) or double-layered perovskites ($\text{A}_2\text{B}_2\text{O}_{6-\delta}$), where larger A-site cation is a rare-earth or alkaline earth element and smaller B-site cation is a transition metal element, have demonstrated promising performance as efficient electrocatalysts for OER. In these perovskites, the B-site ions could be 3d, 4d, and 5d transition metal elements [36–38]. RP phases are layered perovskites consisting of layers stacked along the c-axis with n $\text{ABO}_{3-\delta}$ perovskite layers, alternating with AO rock-salt layer. RP 1 phase is denoted as the perovskite has one $\text{ABO}_{3-\delta}$ perovskite layer. RP 3 phase is the perovskite has three $\text{ABO}_{3-\delta}$ perovskite layers. Due to the layered structure of RP phases, the oxygen that is located in between the layered perovskite is easily removable and is essential to increase the efficiency of OER [39].

The RP perovskites display strong metal–oxygen covalency and the single-layer perovskites exhibit fast oxygen-ion diffusion kinetics; thus, hybrid perovskites consist of a RP perovskite (e.g., $\text{LaSr}_3\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_{10-\delta}$) and a single-layered perovskite (e.g., $\text{La}_{0.25}\text{Sr}_{0.75}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$) create interfaces that can synergize their properties to promote the activation of surface lattice oxygen. Wang et al. [43] demonstrated that the hybrid perovskites significantly enhance OER activity and achieve higher activity than that of either the pure RP perovskite or the single-layer perovskite. However, this concept has not been validated for other hybrid perovskites, for example, $\text{La}_x\text{Sr}_{4-x}\text{Ni}_y\text{Fe}_{3-y}\text{O}_{10-\delta}$. Additionally, there is a lack of well-established approaches to modulating the hybridization between RP perovskites and single-layered perovskites by altering the concentration of each phase. Furthermore, the OER activity of hybrid perovskites at the AEMWE single-cell level for clean hydrogen production has not been demonstrated yet.

Here, we demonstrated a new set of hybrid perovskites, $\text{La}_x\text{Sr}_{4-x}\text{Ni}_y\text{Fe}_{3-y}\text{O}_{10-\delta}$ ($\text{L}_x\text{S}_{4-x}\text{N}_y\text{F}_{3-y}$), which are constituted of single-layered perovskites and perovskites with RP phases, as efficient OER electrocatalyst. The phase structure of $\text{L}_x\text{S}_{4-x}\text{N}_y\text{F}_{3-y}$ can be tuned by alternating its stoichiometry, which consequently affects the hybridization of single-layered perovskites and RP perovskites. $\text{L}_3\text{S}_1\text{N}_2\text{F}_1$, $\text{L}_2\text{S}_2\text{N}_1\text{F}_2$, and $\text{L}_2\text{S}_2\text{N}_{1.5}\text{F}_{1.5}$ are composed of > 40 wt% of a single-layered perovskite, ~20–30 wt% of a RP1 perovskite,

and ~ 20–30 wt% of a RP3 perovskite, leading to a higher oxygen-ion diffusion rate than that of $\text{L}_1\text{S}_3\text{N}_2\text{F}_1$, which mainly contains RP1 perovskite. Additionally, the OER activity of $\text{L}_x\text{S}_{4-x}\text{N}_y\text{F}_{3-y}$ is highly correlated with the oxygen-ion diffusion coefficient, while $\text{L}_3\text{S}_1\text{N}_2\text{F}_1$, $\text{L}_2\text{S}_2\text{N}_1\text{F}_2$, and $\text{L}_2\text{S}_2\text{N}_{1.5}\text{F}_{1.5}$ possess relatively high oxygen-ion diffusion rate. Therefore, $\text{L}_3\text{S}_1\text{N}_2\text{F}_1$, $\text{L}_2\text{S}_2\text{N}_1\text{F}_2$, and $\text{L}_2\text{S}_2\text{N}_{1.5}\text{F}_{1.5}$ are identified as potential OER electrocatalysts, which are subsequently applied as the anode for AEMWEs. At 1.8 V, the AEMWE equipped with $\text{L}_2\text{S}_2\text{N}_1\text{F}_2$ achieves a current density of $1.16\text{A}/\text{cm}^2$, which represents the highest performance among these three catalysts. Additionally, this work first demonstrates the OER performance of $\text{L}_x\text{S}_{4-x}\text{N}_y\text{F}_{3-y}$ at the AEMWE single-cell level, validating those perovskites can be employed as the anode of AEMWEs for low-cost and clean hydrogen production.

3.2 Experimental Section

3.2.1 Materials Synthesis: Perovskites

$\text{La}_x\text{Sr}_{4-x}\text{Ni}_y\text{Fe}_{3-y}\text{O}_{10-\delta}$ ($\text{L}_x\text{S}_{4-x}\text{N}_y\text{F}_{3-y}$) were synthesized via the Pechini process [141,142]. A stoichiometry amount of La_2O_3 was first dissolved into a nitric acid solution to make $\text{La}(\text{NO}_3)_3$ solution, which was then mixed with strontium nitrate ($\text{Sr}(\text{NO}_3)_2$), nickel(II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), and iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$). This mixture was then dissolved in deionized water (DI water). The chelating agents (i.e., citric acid and ethylenediaminetetraacetic acid (EDTA)) with chelating agents-to-total metal cations ratios (C/I ratios) of 1.5 were added to the above solution, which was followed by the addition of ammonium hydroxide solution to adjust its pH to ~10. This solution was subsequently stirred at $250\text{ }^\circ\text{C}$ until a gel was formed. The gel was immediately transferred to a drying oven at $175\text{ }^\circ\text{C}$ for 24 h, followed by calcination under air at $900\text{ }^\circ\text{C}$ for three hours to obtain the as-fired hybrid perovskites. The whole process is shown in Figure 40.

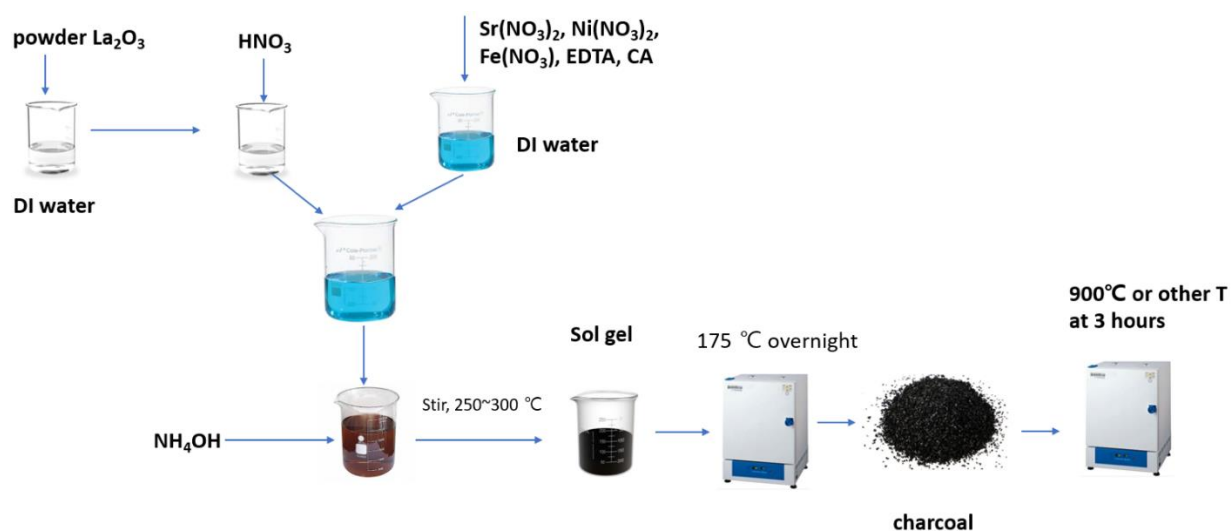


Figure 40. Perovskite, $L_xS_{4-x}N_yF_{3-y}$, preparation process.

3.2.2 Structural Characterization

The X-ray diffraction (XRD) patterns of all samples were collected using a Rigaku MiniFlex diffractometer with a Cu K α radiation source operated at 30 kV and 15 mA (2 θ : 5.1-90°, scanning speed: 1°/min). The Rietveld refinements were performed using the open-source GSAS software [143]. Transmission electron microscopy (TEM) was performed with an FEI Talos F200X TEM/STEM using a 200 keV accelerating voltage. X-ray photoelectron spectroscopy (XPS) was performed by PHI 5000 Versa Probe II (Physical Electronics, Inc).

3.2.3 Electrochemical Characterization at the Half-cell Level

All electrochemical measurements at the half-cell level were carried out using a Gamry Reference 3000, shown in Figure 41, A rotating disk electrode (RDE, 0.198 cm² of glassy carbon electrode, Pine instrument) was tested in a three-electrode cell with 1 M KOH solution as the electrolyte. The counter and reference electrodes were a graphite rod and Hg/HgO, respectively. All potentials versus the reference electrode were converted into potentials versus the reversible hydrogen electrode (RHE) using the Nernst equation. The OER ink solution was prepared by mixing the hybrid perovskites

(20 mg) with 5 wt.% Nafion solution (100 μ L) and ethanol (900 μ L). The polarization curves for OER were recorded at a scan rate of 5 mV/s, and iR was corrected. The double-layer capacitance (C_{dl}) was calculated by cyclic voltammetry (CV) with different scan rates in the non-Faradaic region in 1 M KOH. The electrochemical impedance spectroscopy (EIS) was conducted at 1.63 V (vs. RHE) from 200 kHz to 10 Hz with an AC voltage of 10.0 mV. All electrochemical characterizations at the half-cell level were conducted at room temperature.

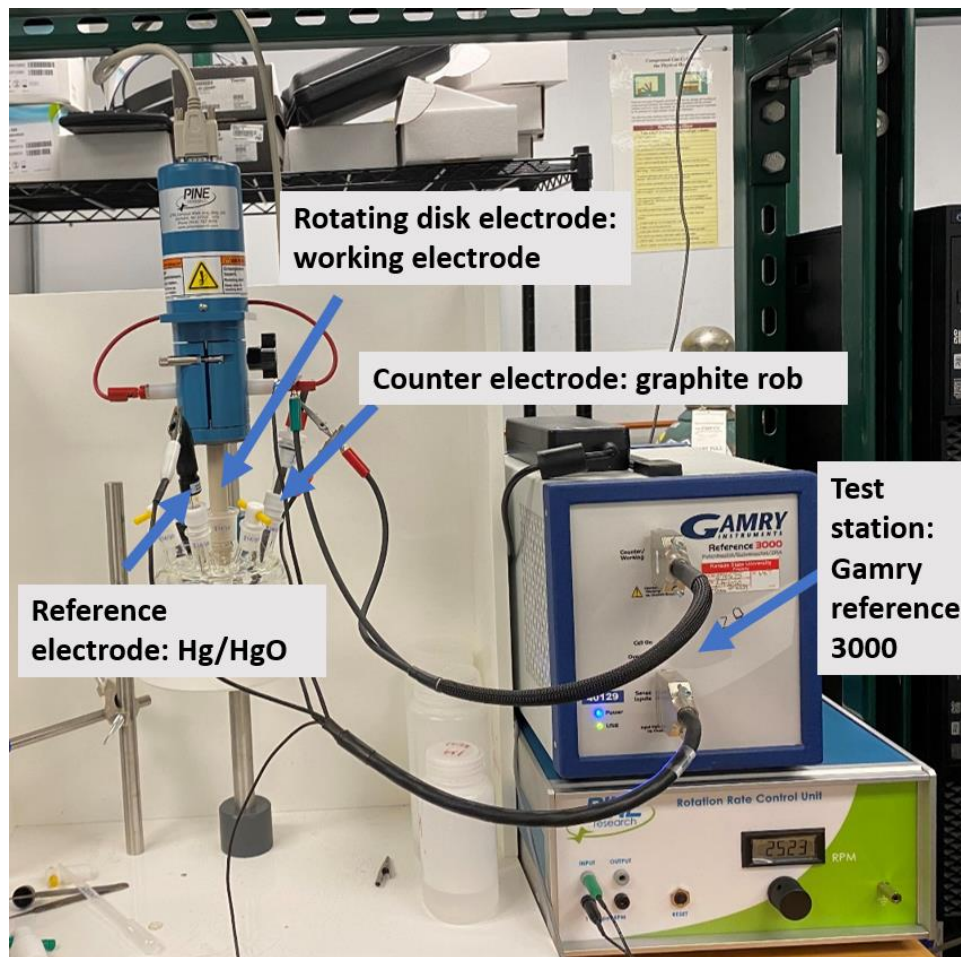


Figure 41. Three-electrode system with rotating disk electrode in half-cell test.

Oxygen-ion diffusion coefficients of hybrid perovskites are determined by conducting chronoamperometry measurements [43]. RDE coated with the hybrid perovskite is employed in this measurement. The experimental setup is the same as evaluating hybrid perovskites at the half-cell level. Chronoamperometry was performed

by applying a potential of 1.627V with a RDE rotating speed of 2500 rpm. The corresponding current was then plotted as a function of the inverse square root of time (i vs. $t^{1/2}$). The linear portion of this plot was subsequently fitted to determine the intercept with $t^{1/2}$, where the current is 0. According to the three-dimension solid state diffusion model established for oxide materials, the oxygen-ion diffusion coefficient can be calculated using the equation $\lambda = a(D_O t)^{-1/2}$, where λ is a dimensionless shape factor, a is the radius of the particle, and D_O is the oxygen-ion diffusion coefficient. Here, λ was assumed to be 2. The radius a was estimated as 1.72 μm by a particle size analyzer.

3.2.4 Evaluation of the OER Electrocatalysts at the AEM Water Electrolyzer Level

The hardware for testing AEMWE single cell was purchased from Fuel Cell Technologies, Inc. The single cell test station is shown in Figure 42. A titanium plate with the flow pattern was used as the anode flow channel, and the graphite plate with the flow pattern was used as the cathode flow channel. The gold-plated connectors were used as the current collector. The anion exchange membrane (AEM, X37-50) was purchased from Dioxide materials. The anode was prepared by spray coating the electrode ink solution on commercial nickel foam. The ink solution for the anode was prepared by mixing the catalysts, deionized (DI) water, isopropyl alcohol, ethanol, and ionomer (Fumion, FAA-3-solut-10). The loading mass of anode catalysts was approximately $5.0 \pm 0.1 \text{ mg/cm}^2$. The cathode ink solution was prepared by mixing Pt/C (40 wt.%, HISPEC 4000, Johnson Matthey) with a Nafion binder on carbon cloth with a microporous layer. The loading amount of HER catalysts was approximately $1.0 \pm 0.05 \text{ mg}_{\text{Pt}}/\text{cm}^2$. 1 M KOH solution was used as the electrolyte media, which was supplied to the AEM electrolyzer at a flow rate of 50 mL/min. A hot plate and a heater embedded in the single-cell hardware were used to control the operating temperature. All electrochemical characterizations at the single-cell level were performed at 60 °C. The active electrode area of all AEM electrolyzers is 3.8 cm^2 . The electrochemical performance of the AEM electrolyzers was evaluated using a Gamry Interface 5000 and a DC power supply (Keysight Technologies E36313A). The single-cell polarization curves were measured by recording the voltage at a constant

current mode. The durability of AEM electrolyzers was tested at a constant current of 0.5 A/cm².

The AEMWE energy efficiency on a lower heating value of H₂ basis (LHV) is calculated using the following equation.

$$\text{AEMWE energy efficiency (\%)} = \frac{\Delta H_{H_2, LHV} \times n_{H_2, \text{measured}}}{I \times V} \times 100 \% \dots \text{Equation 6}$$

where $\Delta H_{H_2, LHV}$ is the LHV reaction enthalpy for water electrolysis (241.8 kJ/mol).

$n_{H_2, \text{measured}}$ is the measured hydrogen production rate (mol/s). I is the current applied (A).

V is the voltage applied (V).

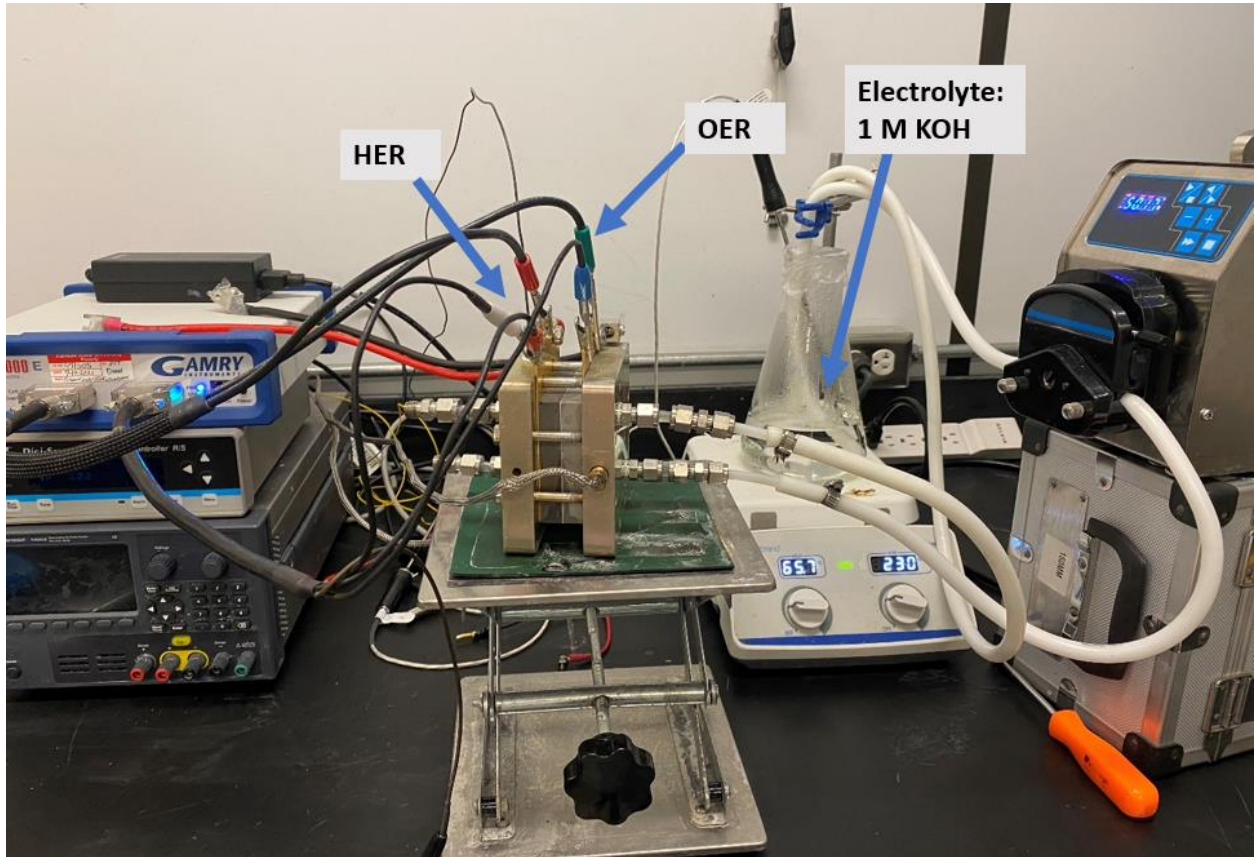


Figure 42. Single cell test station.

The ohmic overpotential (η_{ohmic}) is determined by measuring the ohmic resistance of AEMWEs under various currents and timing the corresponding current, which leads to the iR drop or ohmic overpotential [38]. The iR -corrected potential of AEMWEs could be plotted. The activation loss (kinetic overpotentials) (η_{act}) is then

plotted using a linear approximation in the Tafel region and subtracting it by the thermodynamic equilibrium potential (E_{Nernst}) at 60 °C. Additionally, the overpotential ascribed to mass transport can be calculated by determining the difference between total overpotential and the sum of ohmic overpotential and activation overpotential. In this work, the current density of AEMWEs is relatively low, leading to negligible mass transport overpotential. Therefore, the mass transport overpotential of AEMWEs is not considered in this work.

3.3 Results and Discussion

3.3.1 Structural Properties of Hybrid Perovskites

The hybrid perovskites were synthesized via the one-pot wet-chemistry approach. The ions will self-assemble to generate a mixture of a single-layered perovskite (P phase), a perovskite with RP1 phase, and a perovskite with RP3 phase. Figure 43 and Figure 44 display the structural properties of five hybrid perovskites demonstrated in this work, which include $\text{L}_3\text{S}_1\text{N}_2\text{F}_1$, $\text{L}_2\text{S}_2\text{N}_{1.5}\text{F}_{1.5}$, $\text{L}_1\text{S}_3\text{N}_2\text{F}_1$, $\text{L}_2\text{S}_2\text{N}_1\text{F}_2$, and $\text{L}_2\text{S}_2\text{N}_2\text{F}_1$. All these hybrid perovskites are composed of three perovskite phases. The detailed Rietveld refinement results shown in Figure 43, Figure 44, and Table 5 indicate the primary phase of $\text{L}_3\text{S}_1\text{N}_2\text{F}_1$, $\text{L}_2\text{S}_2\text{N}_{1.5}\text{F}_{1.5}$, $\text{L}_2\text{S}_2\text{N}_1\text{F}_2$, and $\text{L}_2\text{S}_2\text{N}_2\text{F}_1$ is a single-layered perovskite with a chemical formula of $\text{ABO}_{3-\delta}$ that possesses a cubic structure with the space group of Pm-3m , which accounts for 40-50wt.%. However, $\text{L}_2\text{S}_2\text{N}_2\text{F}_1$ has a relatively lower amount of the single-layered perovskite while $\text{L}_1\text{S}_3\text{N}_2\text{F}_1$ has only ~0.16 wt. % of single-layered perovskite. Additionally, the phase compositions of these perovskites are highly correlated with the stoichiometry of $\text{L}_x\text{S}_{4-x}\text{N}_y\text{F}_{3-y}$. Two additional kinds of RP phases are observed in all these five hybrid perovskites, which include the RP1 phase and RP3 phase. RP1 phase is a tetragonal structure that consists of one rock-salt layer and one perovskite layer, which has a space group of I4/mmm and general chemical formula of $\text{A}_2\text{BO}_{4-\delta}$. RP3 phase also has a tetragonal structure and a space group of I4/mmm , while has layers stacked along the c -axis with three perovskite layers, alternating with a rock-salt layer. RP3 phase has a chemical formula of $\text{A}_4\text{B}_3\text{O}_{10-\delta}$. The RP n phase, where n denotes the number of

perovskite layers sandwiched between the rock-salt layer, has the general chemical formula of $A_{n+1}B_nO_{3n+1-\delta}$.

Table 5. Summary of XRD refinement results.

sample	P	RP1	RP3	Reliability factors
L₃S₁N₂F₁	41.17 wt. %	23.16 wt. %	35.67 wt. %	Rwp=16.73%
	a=b=c=3.87 Å	a=b=3.84 Å c=12.73 Å	a=b=3.87 Å c=27.64 Å	Rp=12.94% $\chi^2=2.737$
L₂S₂N₁F₂	45.9 wt. %	31.9 wt. %	22.2 wt. %	Rwp=16.59%
	a=b=c=3.88 Å	a=b=3.85 Å c=12.63 Å	a=b=3.90 Å c=27.80 Å	Rp=13.16% $\chi^2=2.551$
L₂S₂N_{1.5}F_{1.5}	47.19 wt. %	25.04 wt. %	27.77 wt. %	Rwp=18.08 %
	a=b=c=3.90 Å	a=b= 3.6 Å; c=12.65 Å	a=b=3.84 Å; c= 29.42 Å	Rp=13.68 % $\chi^2=2.990$
L₂S₂N₂F₁	26.02 wt. %	64.04 wt. %	9.94 wt. %	Rwp=16.46%
	a=b=c=3.88 Å	a=b=3.88 Å c=12.57 Å	a=b=3.89 Å c=27.00 Å	Rp=12.29% $\chi^2=3.02$
L₁S₃N₂F₁	0.16 wt. %	90.98 wt. %	8.88 wt. %	Rwp=15.74%
	a=b=c=3.83 Å	a=b=3.83 Å c=12.47 Å	a=b=3.84 Å c= 28.59 Å	Rp=11.7% $\chi^2=3.057$

Table 5 comprehensively summarizes the refinement results of hybrid perovskites studied in this work. The refinement of XRD patterns shows that L₃S₁N₂F₁, L₂S₂N₁F₂, and L₂S₂N_{1.5}F_{1.5} have >40 wt. % of a single-layered perovskite, ~20-30 wt. % of a RP1 perovskite, and ~20-30 wt. % of a RP3 perovskite. However, both L₁S₃N₂F₁ or L₂S₂N₂F₁ has one phase that is less than 10 wt. %. For example, L₂S₂N₂F₁ has ~9.94 wt. % of RP3 while L₁S₃N₂F₁ has ~0.16 wt. % of single-layered perovskite. The hybridization of a perovskite phase with a RP3 phase enhances the OER activity of RP/P-LSCF [43].

Therefore, it is expected that the hybridization of these perovskites can tune the OER activity of $L_xS_{4-x}N_yF_{3-y}$. As shown in Figure 43A, Figure 43B, and Figure 44A, three perovskite phases are relatively uniformly distributed in $L_3S_1N_2F_1$, $L_2S_2N_1F_2$, and $L_2S_2N_{1.5}F_{1.5}$, which is expected to enhance synergistic effects between different phases, promoting the OER activity. However, $L_1S_3N_2F_1$ has the RP1 phase as the dominant phase and it lacks the RP3 phase and single-layer phase. Additionally, single-layer perovskite is the dominant phase in $L_2S_2N_2F_1$, while the RP3 concentration is relatively low. Therefore, the effective interfacial area between RP perovskites and single-layer perovskites is low in $L_1S_3N_2F_1$ and $L_2S_2N_2F_1$, which might not be able to promote OER activity.

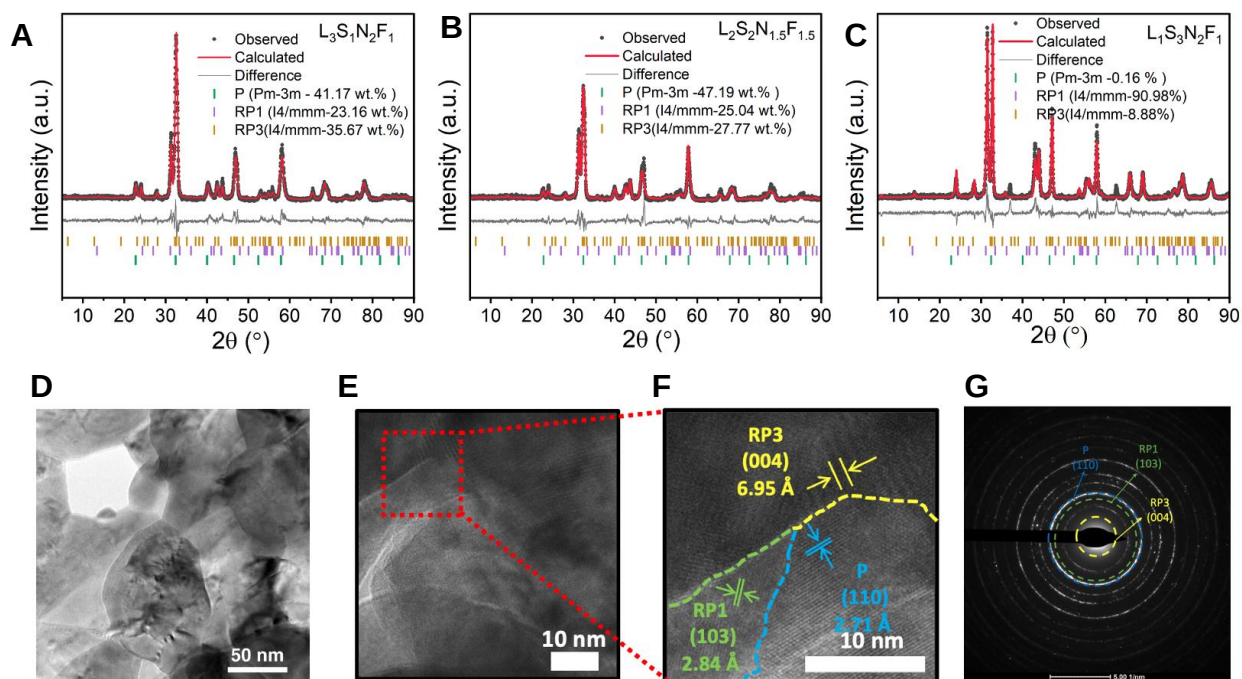


Figure 43. XRD patterns of three representative hybrid perovskites and TEM images of $L_3S_1N_2F_1$. XRD pattern and Rietveld refinement results of (A) $L_3S_1N_2F_1$, (B) $L_2S_2N_{1.5}F_{1.5}$, and (C) $L_1S_3N_2F_1$. (D) TEM images of $L_3S_1N_2F_1$, (E) High-resolution TEM image of $L_3S_1N_2F_1$, (F) High-resolution TEM image of $L_3S_1N_2F_1$ with three phases identified, (G) selected area electron diffraction (SAED) image of $L_3S_1N_2F_1$.

Transmission electron microscopy (TEM) was performed to study the morphology and microstructure of a representative hybrid perovskite (i.e., $L_3S_1N_2F_1$). Figure 43D shows the particle size is 50-100 nm. As shown in Figure 43E-Figure 43G, the high-resolution TEM images of $L_3S_1N_2F_1$ further confirm that it is constituted of three perovskite phases, creating interfaces between two phases among them. Figure 43F displays three interplanar distances of 2.71 Å, 2.84 Å, and 6.95 Å, which correspond to the (110) plane of the single-layer perovskite phase, (103) plane of RP1 phase, and (004) plane of RP1 phase, respectively. According to the XRD refinement results shown in Table 5, the (110) plane distance of P phase should be 2.73 Å, which is similar to that shown in the TEM image (2.71 Å). The XRD refinement results show the (103) plane distance of the RP1 phase is 2.84 Å, which is consistent with the TEM image (2.84 Å). Furthermore, the (004) plane distance of the RP3 phase is wider than other phases. According to the XRD refinement results, the (004) plane distance is 6.91 Å, which is also consistent with the TEM image (6.95 Å). Additionally, the SAED image shown in Figure 43G further confirms these three phases, implying the materials demonstrated in this work are hybrid perovskites.

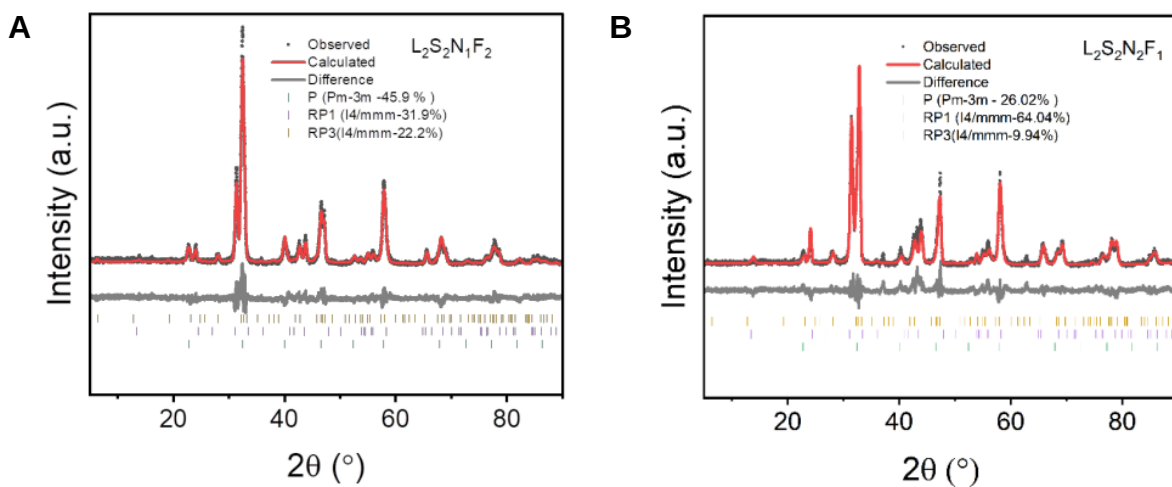


Figure 44. XRD patterns of (A) $L_2S_2N_1F_2$ and (B) $L_2S_2N_2F_1$.

3.3.2 Electrochemical Properties of Hybrid Perovskites at the Half-cell Level

The OER electrocatalytic performance of hybrid perovskites was first evaluated using the conventional three-electrodes setup by drop coating the OER catalyst ink on the glassy carbon rotating disk electrode. Figure 45 summarizes the OER electrocatalytic performance normalized by the disk electrode area. The linear scan voltammetry (LSV) curves shown in Figure 45 are corrected to a reversible hydrogen electrode (RHE). Additionally, the LSV curves are also iR corrected.

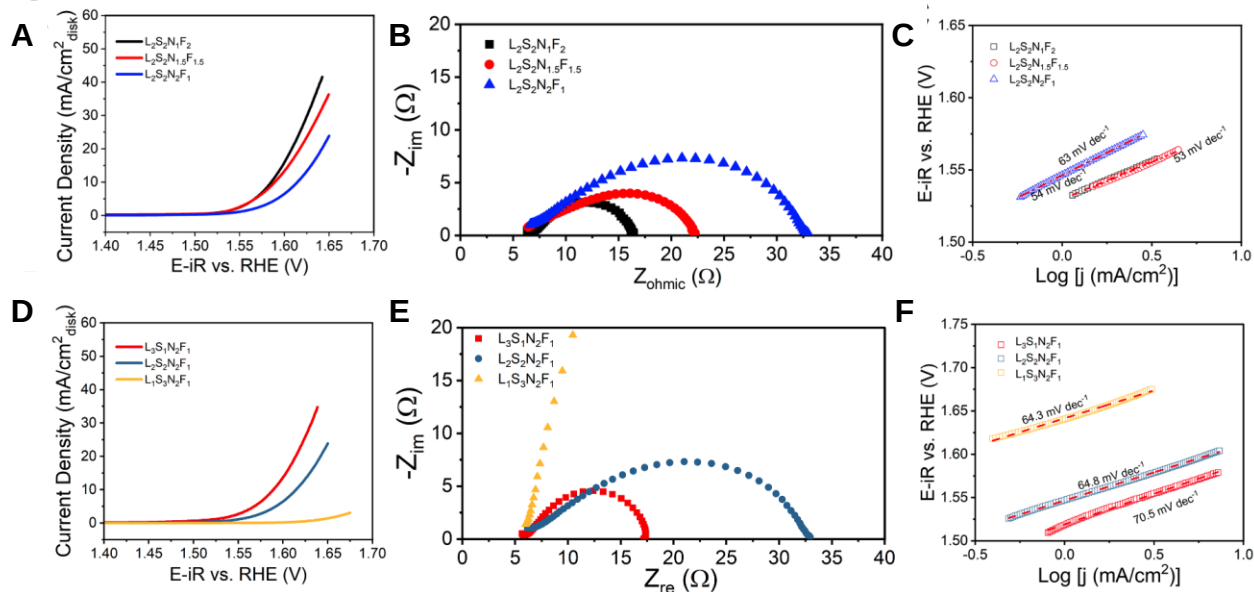


Figure 45. Electrochemical performance of hybrid perovskites at the half-cell level, which is evaluated in 1.0 M KOH solution at room temperature. (A) Ohmic resistance-corrected polarization curves of $L_2S_2N_1F_2$, $L_2S_2N_{1.5}F_{1.5}$, and $L_2S_2N_2F_1$. (B) Electrochemical impedance spectra of $L_2S_2N_1F_2$, $L_2S_2N_{1.5}F_{1.5}$, and $L_2S_2N_2F_1$ at 1.7 V. (C) Tafel plots of $L_2S_2N_1F_2$, $L_2S_2N_{1.5}F_{1.5}$, and $L_2S_2N_2F_1$. (D) Ohmic resistance-corrected polarization curves of $L_3S_1N_2F_1$, $L_2S_2N_2F_1$, and $L_1S_3N_2F_1$. (E) Electrochemical impedance spectra of $L_3S_1N_2F_1$, $L_2S_2N_2F_1$, and $L_1S_3N_2F_1$ at 1.7 V. (F) Tafel plots of $L_3S_1N_2F_1$, $L_2S_2N_2F_1$, and $L_1S_3N_2F_1$.

Figure 45A presents the LSV curves of $L_2S_2N_1F_2$, $L_2S_2N_{1.5}F_{1.5}$, and $L_2S_2N_2F_1$, which possess the same A-site stoichiometry. The OER performance tends to be improved by increasing the Fe/Ni ratio. As shown in Table 5, $L_2S_2N_1F_2$ and $L_2S_2N_{1.5}F_{1.5}$ consist of three perovskite phases that are relatively uniformly distributed and are expected to possess facilitated OER activity. The LSV curves shown in Figure 45A are

correlated with their phase structures. The EIS spectra shown in Figure 45B also clearly indicate the $\text{L}_2\text{S}_2\text{N}_1\text{F}_2$ exhibits the lowest OER activation loss.

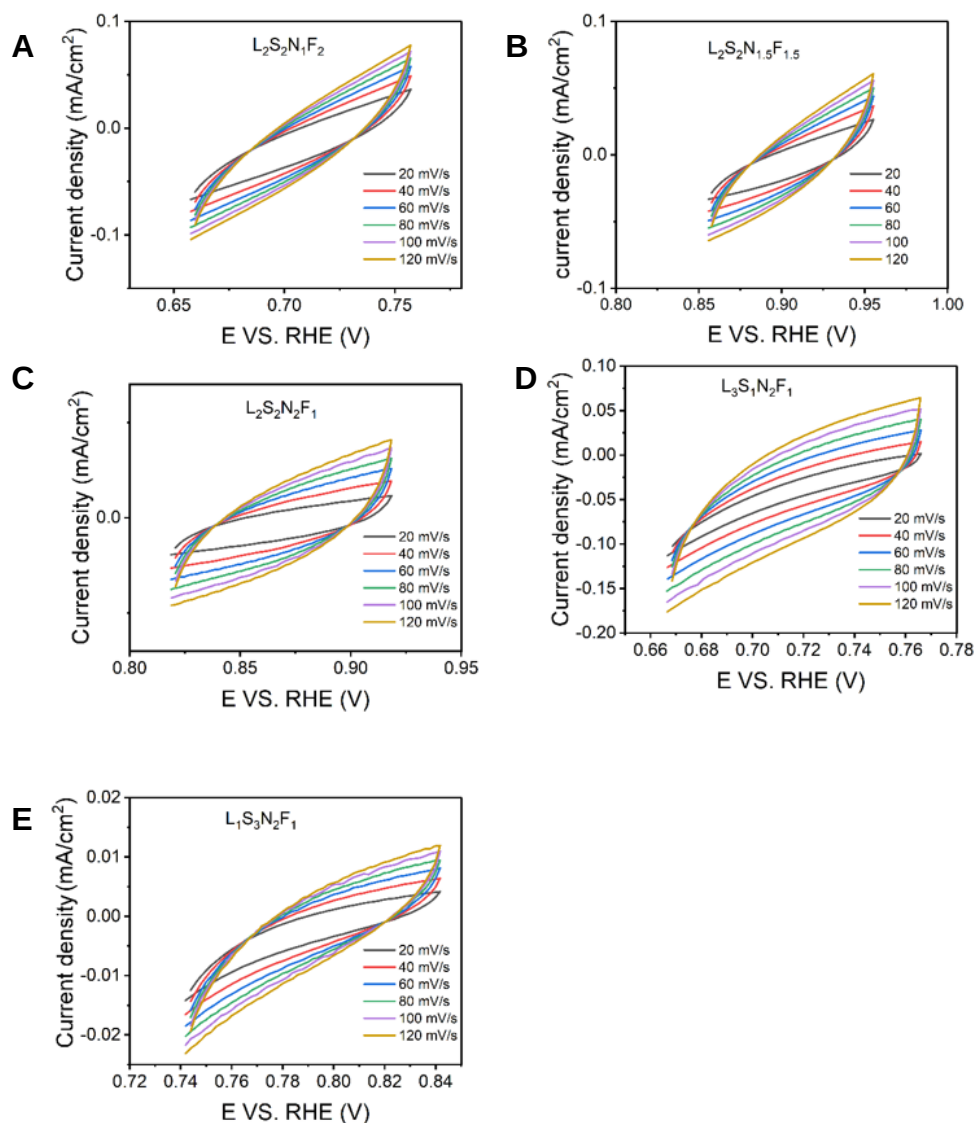


Figure 46. Cyclic voltammetry testing in a non-Faradic current region under various scan rates. (A) $\text{L}_2\text{S}_2\text{N}_1\text{F}_2$, (B) $\text{L}_2\text{S}_2\text{N}_{1.5}\text{F}_{1.5}$, (C) $\text{L}_2\text{S}_2\text{N}_2\text{F}_1$, (D) $\text{L}_3\text{S}_1\text{N}_2\text{F}_1$, and (E) $\text{L}_1\text{S}_3\text{N}_2\text{F}_1$.

To further investigate the OER kinetic over these hybrid perovskites, Figure 45C presents the Tafel plots, which show the Tafel slope of $\text{L}_2\text{S}_2\text{N}_1\text{F}_2$ (53.5 mV dec⁻¹) is similar to $\text{L}_2\text{S}_2\text{N}_{1.5}\text{F}_{1.5}$ (52.7 mV dec⁻¹) while it is smaller than that of $\text{L}_2\text{S}_2\text{N}_2\text{F}_1$ (62.5 mV dec⁻¹), affirming that increasing the Fe/Ni ratio can slightly enhance the OER electrocatalytic

activity. Additionally, as shown in Figure 46 and Figure 47, the double-layer capacitances of these three hybrid perovskites are determined by linearly fitting the non-Faradaic current as a function of cyclic voltammetry (CV) scan rate, which is subsequently used to estimate electrochemically active surface area (ECSA). The ECSA is highly correlated with the number of active sites. As shown in Table 6, among the three catalysts shown in Figure 45A, $L_2S_2N_1F_2$ has the highest ECSA, suggesting the hybridization in $L_2S_2N_1F_2$ is more effective for creating electrochemically active sites, which contributes to the highest OER activity. Furthermore, Figure 48 shows the specific OER activity, which is calculated by normalizing the LSV curves to the ECSA (Figure 48). The specific OER activity corresponds to the intrinsic OER active per active site. Figure 48 shows that $L_2S_2N_1F_2$ also exhibits the highest specific activity.

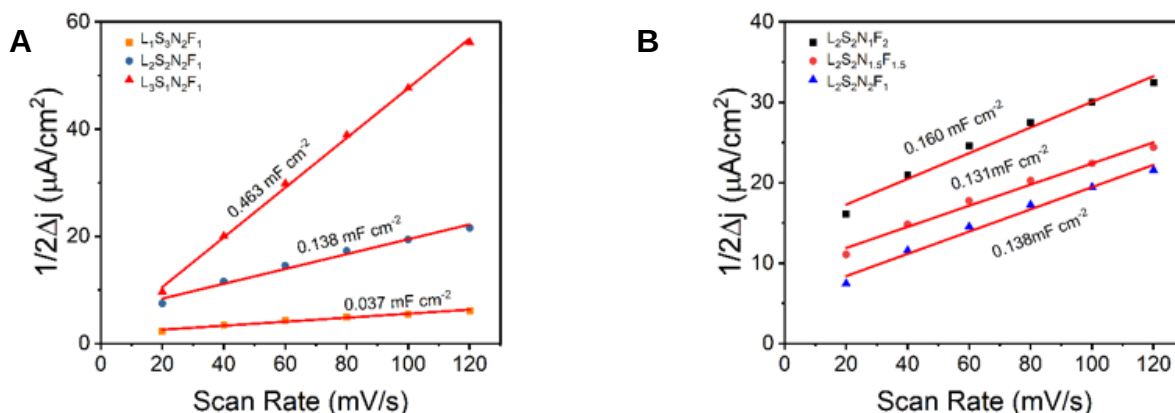


Figure 47. Linear fitting curves of the non-Faradaic current as a function of CV scan rates for determining the double-layer capacitance and ECSA. (A) $L_1S_3N_2F_1$, $L_2S_2N_2F_1$, $L_3S_1N_2F_1$, and (B) $L_2S_2N_1F_2$, $L_2S_2N_{1.5}F_{1.5}$, $L_2S_2N_2F_1$

Figure 45D- Figure 45F present the OER activity of $L_xS_{4-x}N_yF_{3-y}$ that exhibits a constant Ni/Fe ratio of 2. As summarized in Table 5, the concentration of the single-layer perovskite phase shows the trend of $L_3S_1N_2F_1 > L_2S_2N_2F_1 > L_1S_3N_2F_1$. Furthermore, $L_2S_2N_2F_1$ has a relatively low concentration of the RP3 phase while $L_1S_3N_2F_1$ is mainly composed of RP1 and RP3 phases. Thus, $L_3S_1N_2F_1$ creates the highest effective hybridization while $L_1S_3N_2F_1$ exhibits the weakest hybridization. Figure 45D shows the

OER activity of $\text{L}_3\text{S}_1\text{N}_2\text{F}_1$ is higher than that of $\text{L}_2\text{S}_2\text{N}_2\text{F}_1$, while $\text{L}_1\text{S}_3\text{N}_2\text{F}_1$ has poor OER activity, which is consistent with the hybridization predicted according to the crystal structure summarized in Table 5. The EIS spectra of these three materials under OER conditions clearly show $\text{L}_1\text{S}_3\text{N}_2\text{F}_1$ is not active for OER, although its Tafel slope is small in Figure 45F.

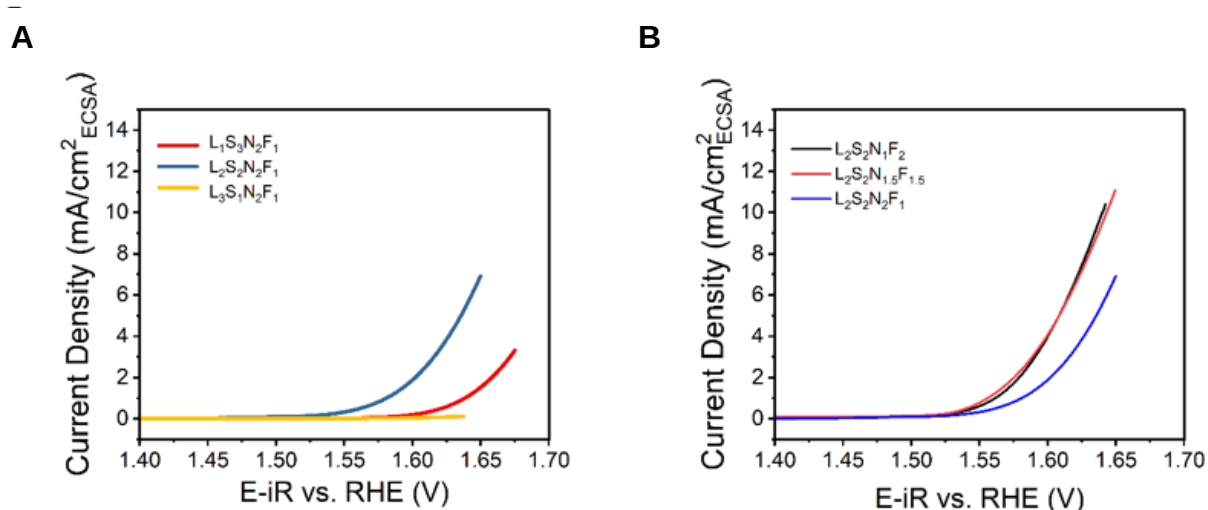


Figure 48. Specific activity normalized to ECSA of hybrid perovskites as a function of potential. (A) $\text{L}_1\text{S}_3\text{N}_2\text{F}_1$, $\text{L}_2\text{S}_2\text{N}_2\text{F}_1$, $\text{L}_3\text{S}_1\text{N}_2\text{F}_1$, and (B) $\text{L}_2\text{S}_2\text{N}_1\text{F}_2$, $\text{L}_2\text{S}_2\text{N}_{1.5}\text{F}_{1.5}$, $\text{L}_2\text{S}_2\text{N}_2\text{F}_1$.

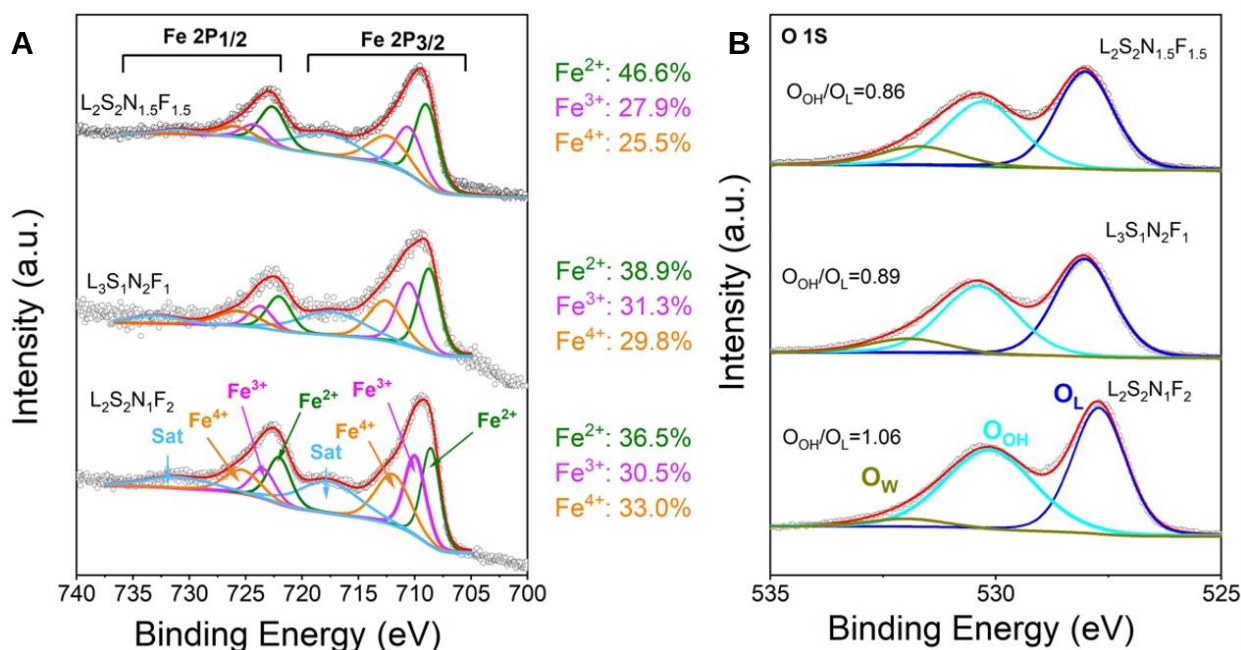


Figure 49. Electronic structures of $\text{L}_3\text{S}_1\text{N}_2\text{F}_1$, $\text{L}_2\text{S}_2\text{N}_1\text{F}_2$, and $\text{L}_2\text{S}_2\text{N}_{1.5}\text{F}_{1.5}$. (A) High-resolution XPS spectra of Fe 2p. (B) High-resolution XPS spectra of O 1s.

The valence state and atomic ratio of Fe and O species vary with the surrounding nearest neighbors and environment, and are closely related to the oxygen non-stoichiometry and the OER catalytic activity. The surface electronic structure of $\text{L}_2\text{S}_2\text{N}_1\text{F}_2$, $\text{L}_2\text{S}_2\text{N}_{1.5}\text{F}_{1.5}$, and $\text{L}_3\text{S}_1\text{N}_2\text{F}_1$ was investigated by using X-ray photoelectron spectroscopy (XPS) (Figure 49 and Table 6). As shown in Figure 49, a mixture of Fe^{4+} , Fe^{3+} , and Fe^{2+} oxidation states were fit to two characteristic Fe 2p peaks, which have been also reported in the literature for the ferrite-based perovskite [144–146]. Table 6 contains the binding energies for each Fe valence state. According to the intergration of the peak area, the ratios of $\text{Fe}^{4+} : \text{Fe}^{3+} : \text{Fe}^{2+}$ are 33.0% : 30.5% : 36.5%, 29.8% : 31.3% : 38.9%, and 25.5% : 27.9% : 46.4%, for $\text{L}_2\text{S}_2\text{N}_1\text{F}_2$, $\text{L}_3\text{S}_1\text{N}_2\text{F}_1$, and $\text{L}_2\text{S}_2\text{N}_{1.5}\text{F}_{1.5}$, respectively. Accordingly, $\text{L}_2\text{S}_2\text{N}_1\text{F}_2$ exhibits the highest average valency of Fe (2.965). The $\text{Fe}^{4+}/\text{Fe}^{3+}$ redox couples in lanthanum ferrite perovskites (LSFs) act as p-type charge carriers, which might be beneficial for the electronic conductivity of OER catalysts [144,147]. The O 1s XPS spectrum was deconvoluted into three characteristic peaks, assigned to the lattice oxygen (O_L), hydroxyl oxygen (O_OH), and water absorbed oxygen (O_w) [148]. The ratio of $\text{O}_\text{OH}/\text{O}_\text{L}$ was 1.06 for $\text{L}_2\text{S}_2\text{N}_1\text{F}_2$, which was 20% and 23% higher than that of $\text{L}_3\text{S}_1\text{N}_2\text{F}_1$ and $\text{L}_2\text{S}_2\text{N}_{1.5}\text{F}_{1.5}$, indicating more oxygen vacancies were generated in the $\text{L}_2\text{S}_2\text{N}_{1.5}\text{F}_{1.5}$. The oxygen vacancies are crucial for the bulk diffusion of oxygen ions in perovskite oxides, thus a higher concentration of oxygen vacancies can lead to higher surface electrocatalytic activities [149]. The high oxygen vacancies in $\text{L}_2\text{S}_2\text{N}_1\text{F}_2$ might be beneficial for the prominent OER performance.

Table 6. Binding Energy (eV) and atomic percentages (%) of Fe and O elements obtained from XPS spectra of $\text{L}_2\text{S}_2\text{N}_1\text{F}_2$, $\text{L}_3\text{S}_1\text{N}_2\text{F}_1$, and $\text{L}_2\text{S}_2\text{N}_{1.5}\text{F}_{1.5}$.

		$\text{L}_2\text{S}_2\text{N}_1\text{F}_2$	$\text{L}_3\text{S}_1\text{N}_2\text{F}_1$	$\text{L}_2\text{S}_2\text{N}_{1.5}\text{F}_{1.5}$
Fe 2P_{1/2}, eV	Fe^{2+}	708.58	708.75	708.98
	Fe^{3+}	709.98	710.52	710.51

	Fe ⁴⁺	711.94	712.6	712.29
	Satellite	717.57	717.42	717.9
Fe 2P_{3/2}, eV	Fe ²⁺	722.03	722.05	722.6
	Fe ³⁺	723.47	723.69	724.17
	Fe ⁴⁺	725.29	725.63	725.92
	Satellite	730.97	732.95	730.88
Partial ratio (%)	Fe ²⁺	36.5	38.9	46.6
	Fe ³⁺	30.5	31.3	27.9
	Fe ⁴⁺	33	29.8	25.5

3.3.3 Correlation of Electrochemical Properties with the Oxygen-ion Diffusion Coefficient and Crystal Structure

Figure 50A presents the overpotentials at 10 mA/cm² for these five hybrid perovskites. The overpotentials for L₃S₁N₂F₁, L₂S₂N_{1.5}F_{1.5}, and L₂S₂N₁F₂ are similar, while L₂S₂N₂F₁ and L₁S₃N₂F₁ display significantly higher overpotentials.

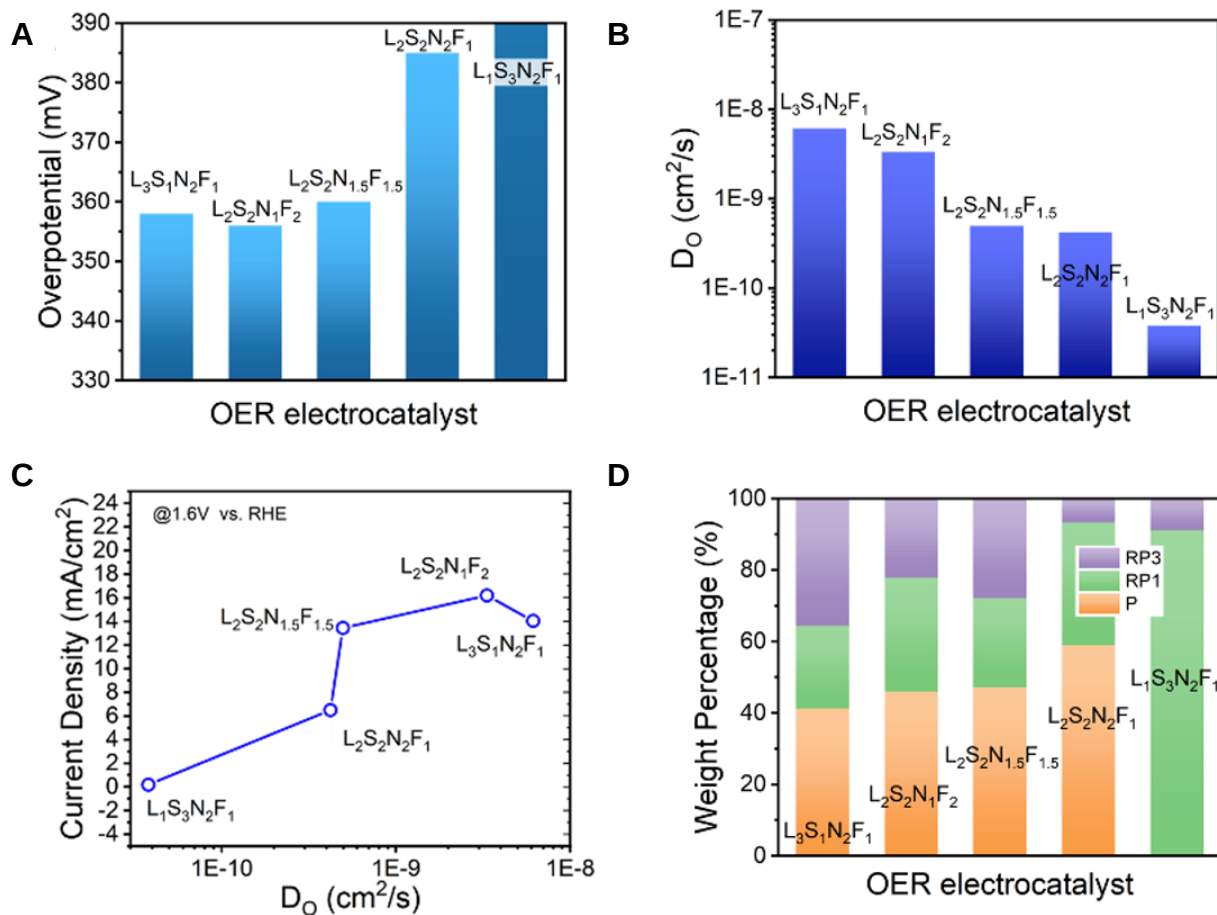


Figure 50. Correlation of OER activity with the oxygen-ion diffusion coefficient and crystal structure. (A) Overpotential at 10 mA/cm² for these five hybrid perovskites. (B) Oxygen-ion diffusion coefficients for these five hybrid perovskites. (C) The correlation of OER activity with oxygen-ion diffusion coefficient. (D) The weight percentage of each phase for these five hybrid perovskites.

As mentioned in section 1.4, the lattice oxygen-mediated mechanism (LOM) has been recognized as the main OER pathway that occurs over perovskite-based OER catalysts under alkaline conditions, where the lattice oxygen of perovskites involves in the OER process [37,38,150]. Therefore, the oxygen-ion diffusion coefficient is intimately correlated with the LOM. That said, a relatively high oxygen-ion diffusion coefficient indicates the fast consumption and refilling rate of surface lattice oxygen, consequently leading to enhanced OER activity. Wang et al. [43] have identified that the single-layered

perovskite can synergize with RP3 perovskite to improve the oxygen-ion diffusion coefficient and OER activity. The oxygen-ion diffusion coefficients of these five hybrid perovskites were measured using the chronoamperometry method. The chronoamperometry results were then fitted based on the previously established 3D solid-state diffusion model [43]. Figure 51 presents the chronoamperometry results of these five perovskites, where the current is plotted as a function of $t^{-1/2}$. Accordingly, the oxygen-ion diffusion coefficients are estimated, which are shown in Figure 50B. $L_3S_1N_2F_1$ exhibits the fastest oxygen-ion diffusion rate, leading to high OER activity. Additionally, as shown in Figure 50A and B, it is obvious the OER activity is highly correlated with the oxygen-ion diffusion coefficient. The oxygen-ion diffusion coefficient of $L_3S_1N_2F_1$ is more than ten times higher than that of $L_2S_2N_2F_1$. Moreover, $L_1S_3N_2F_1$ has an extremely low oxygen-ion diffusion rate, leading to the poor OER activity shown in Figure 45D and Figure 45E.

Table 7. A summary of the double-layer capacitance and ECSA

sample	Double –layer capacitance: Cdl [mF dec-1]	ECSA [m ² /(g* dec)]
$L_2S_2N_1F_2$	0.160	0.785
$L_3S_1N_2F_1$	0.463	2.272
$L_2S_2N_{1.5}F_{1.5}$	0.131	0.643
$L_2S_2N_2F_1$	0.138	0.677
$L_1S_3N_2F_1$	0.037	0.182

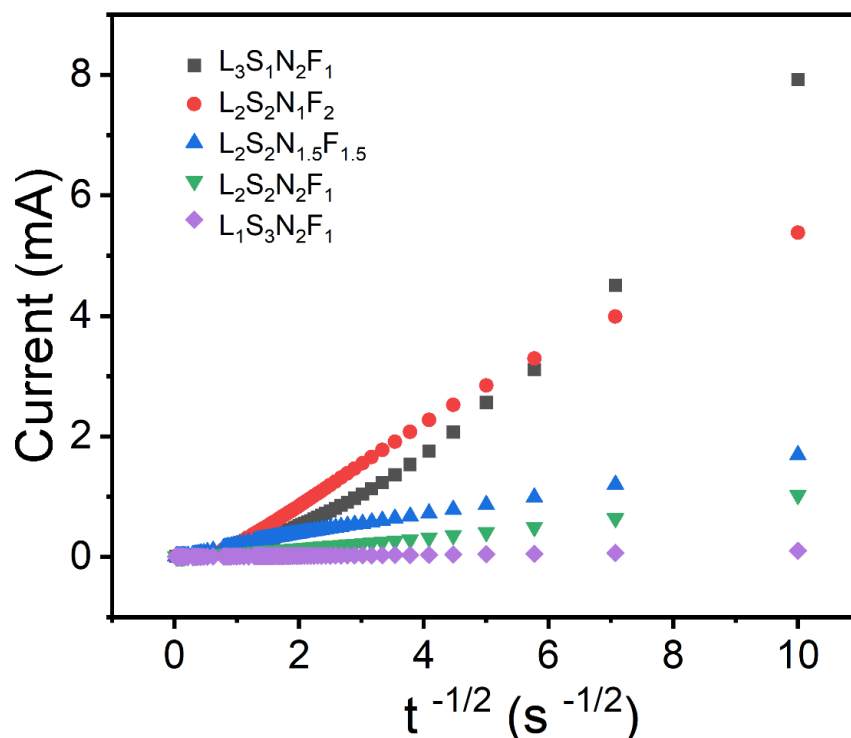


Figure 51. The chronoamperometry results of five hybrid perovskites, where show the current as a function of $t^{-1/2}$.

Figure 50C shows the OER activity as a function of the oxygen-ion diffusion coefficient, which further strengthens the strong correlation between OER activity and the oxygen-ion diffusion rate. Figure 50D shows the compositions for these perovskites. $L_3S_1N_2F_1$, $L_2S_2N_{1.5}F_{1.5}$, and $L_2S_2N_1F_2$ have three perovskite phases that are uniformly distributed. $L_2S_2N_2F_1$ is lack single-layer perovskite while $L_1S_3N_2F_1$ is dominated by RP1 phase. Therefore, the hybridization between different perovskite phases in $L_3S_1N_2F_1$, $L_2S_2N_{1.5}F_{1.5}$, and $L_2S_2N_1F_2$ accelerates the oxygen diffusion coefficient, which consequently promotes the OER activity.

3.3.4 Electrochemical Performance of AEM Electrolyzers with Hybrid Perovskites as OER Catalysts.

Extensive perovskite-based OER electrocatalysts have been developed, aiming to achieve highly efficient water electrolysis under alkaline conditions [37,38,43,150].

However, there is little work that implements perovskites as the OER catalysts for AEMWEs, which is ascribed to the lack of knowledge for fabricating high-quality membrane electrode assembly (AEM).

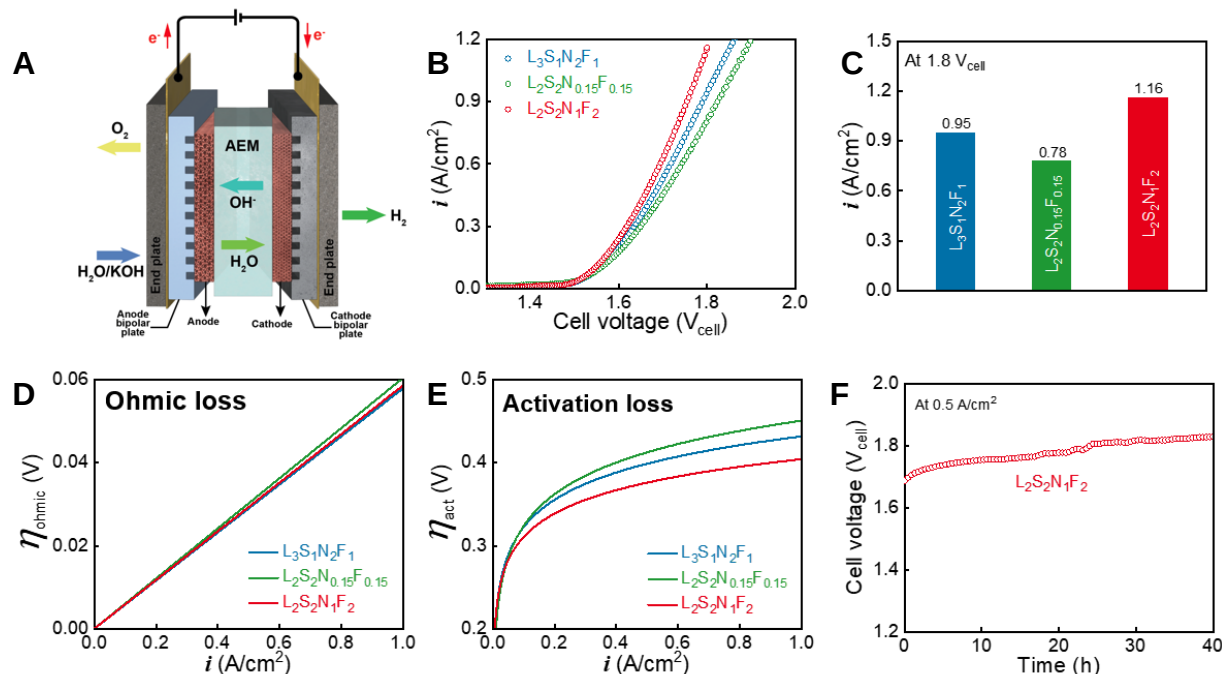


Figure 52. OER performance of hybrid perovskites at the AEMWE single-cell level and 60 °C. (A) Schematic illustration of the anion exchange membrane water electrolyzer. (B) Polarization curves of AEM water electrolyzers with $\text{L}_3\text{S}_1\text{N}_2\text{F}_1$, $\text{L}_2\text{S}_2\text{N}_{0.15}\text{F}_{0.15}$, and $\text{L}_2\text{S}_2\text{N}_1\text{F}_2$ as the OER electrocatalysts. (C) The current density achieved at 1.8V in AEMWEs. (D) The ohmic loss as a function of current density. (E) The activation loss as a function of current density. (F) A preliminary stability testing of AEMWE with $\text{L}_2\text{S}_2\text{N}_1\text{F}_2$ as the OER electrocatalyst at 60 °C and a current density of 0.5A/cm².

To evaluate the performance of the hybrid perovskites and investigate their applicability to anion exchange membrane water electrolyzers, lab-scale AEMWEs single-cells were constructed and tested. Figure 52A displays the architecture of the AEMWEs. $\text{L}_3\text{S}_1\text{N}_2\text{F}_1$, $\text{L}_2\text{S}_2\text{N}_{0.15}\text{F}_{0.15}$, and $\text{L}_2\text{S}_2\text{N}_1\text{F}_2$ have been identified as promising OER electrocatalysts, which are then employed as the anodes for AEMWEs. As this work centers on understanding the electrochemical properties of the anode, Pt/C, one of the best HER electrocatalysts, was used as the cathode to minimize the polarization loss due

to HER. Figure 52B shows polarization curves of AEMWEs at 60 °C, which is the general operating temperature of AEMWEs. The performance of $\text{L}_3\text{S}_1\text{N}_2\text{F}_1$, $\text{L}_2\text{S}_2\text{N}_{1.5}\text{F}_{1.5}$, and $\text{L}_2\text{S}_2\text{N}_1\text{F}_2$ at the AEMWEs single-cell level shows the same trend with the performance evaluated at the half-cell level: $\text{L}_2\text{S}_2\text{N}_1\text{F}_2 > \text{L}_3\text{S}_1\text{N}_2\text{F}_1 > \text{L}_2\text{S}_2\text{N}_{1.5}\text{F}_{1.5}$.

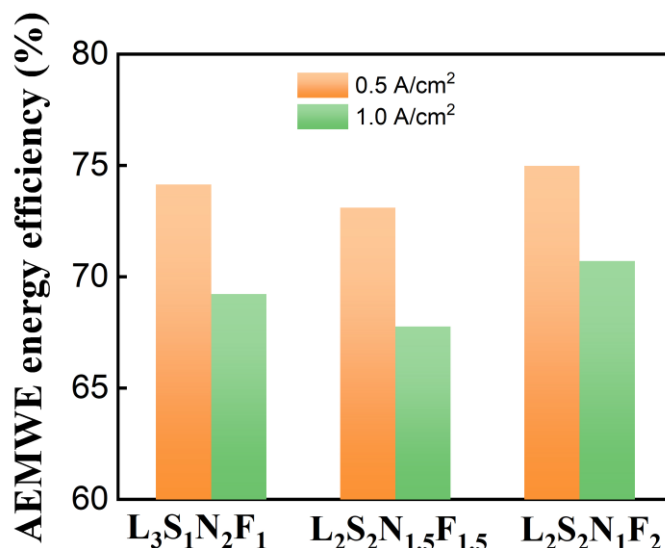


Figure 53. LHV energy efficiency of AEMWEs with three hybrid perovskites as the OER electrocatalysts at a current density of 0.5 A/cm² and 1.0 A/cm².

The AEM water electrolyzers equipped with $\text{L}_2\text{S}_2\text{N}_1\text{F}_2$ as the anode delivers the best electrolysis performance. As shown in Figure 52C, at a voltage of 1.8V applied on the single cell (V_{cell}), the AEM electrolyzers can achieve an electrolysis current of 1.16 A/cm² ($\text{L}_2\text{S}_2\text{N}_1\text{F}_2$), 0.95 A/cm² ($\text{L}_3\text{S}_1\text{N}_2\text{F}_1$), and 0.78 A/cm² ($\text{L}_2\text{S}_2\text{N}_{1.5}\text{F}_{1.5}$). As shown in Figure 53, the AEM electrolyzers with $\text{L}_2\text{S}_2\text{N}_1\text{F}_2$ also display the highest cell efficiency, 75.0% and 70.7 % at a current density of 0.5 A/cm² and 1.0 A/cm², respectively. This work has for the first time demonstrated the hybrid perovskites for clean hydrogen production in the AEM water electrolyzer single cells. Although the single cell equipped with the hybrid perovskites does not deliver world-record performance (Figure 55), this work validates the feasibility of employing hybrid perovskites for clean hydrogen production in AEMWEs.

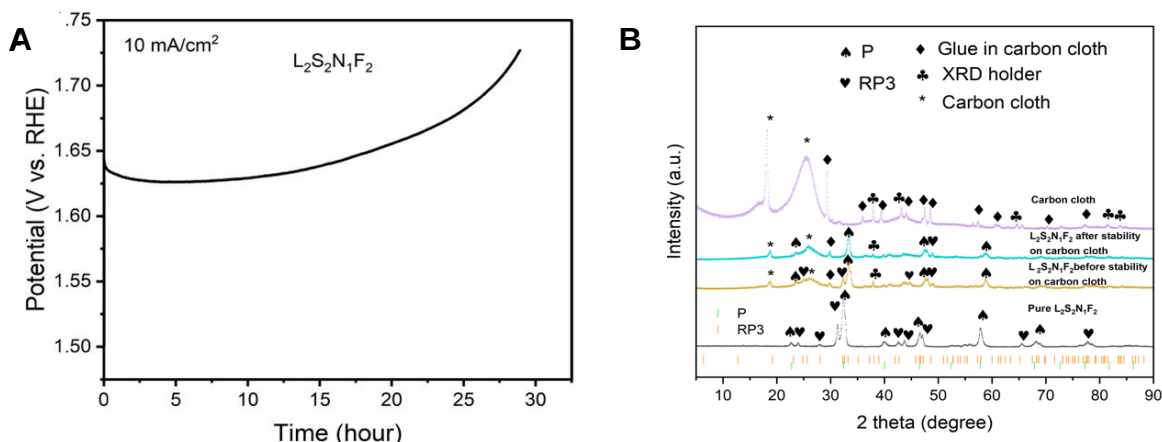


Figure 54. (A) Stability testing of $L_2S_2N_1F_2$ at the half-cell level. (B) XRD patterns of fresh, $L_2S_2N_1F_2$ on carbon cloth prior to stability testing, $L_2S_2N_1F_2$ on carbon cloth after stability testing, and carbon cloth.

EIS spectra were performed to better understand the AEMWEs equipped with hybrid perovskites as the anode. The intercept of EIS spectra with the real impedance axis at the high frequency in the Nyquist plots corresponds to the ohmic loss (η_{ohm}) of the AEM water electrolyzers. The ohmic loss is ascribed to the sum of the electrical and ionic resistance of the AEM water electrolyzers. In this study, the change in η_{ohm} is ascribed to the OER electrocatalysts because the AEM water electrolyzers are identical except for the OER electrocatalyst. Figure 52D shows the η_{ohm} of these three AEM water electrolyzers are quite similar, indicating the electrical conductivities of $L_3S_1N_2F_1$, $L_2S_2N_{1.5}F_{1.5}$, and $L_2S_2N_1F_2$ are similar.

The polarization resistance of AEM electrolyzers also depends on the OER electrocatalyst. The semicircles at a relatively high-frequency area related to both HER and the first charge transfer of the 4-electron process of OER. The semicircles at an intermediate frequency are associated with OER processes. The semicircles at a low frequency are associated with mass transport. To further analyze the impacts of the OER electrocatalyst on electrode activation loss of the AEM water electrolyzers, the activation loss of the AEM water electrolyzers were calculated. Figure 52E shows the kinetic overpotentials ($\eta_{kinetic}$) of AEM water electrolyzers. $L_2S_2N_1F_2$ exhibits the lowest kinetic overvoltage among these three hybrid perovskites, which is consistent with the

polarization curves shown in Figure 52B. The durability of the AEM water electrolyzer catalyzed by $\text{L}_2\text{S}_2\text{N}_1\text{F}_2$ was tested at a current density of 0.5 A/cm^2 for 40 h. As shown in Figure 52F, the AEM water electrolyzer has a degradation rate of 3 mV/h , which suggests that future work should also focus on improving the stability of the AEM water electrolyzer single cell.

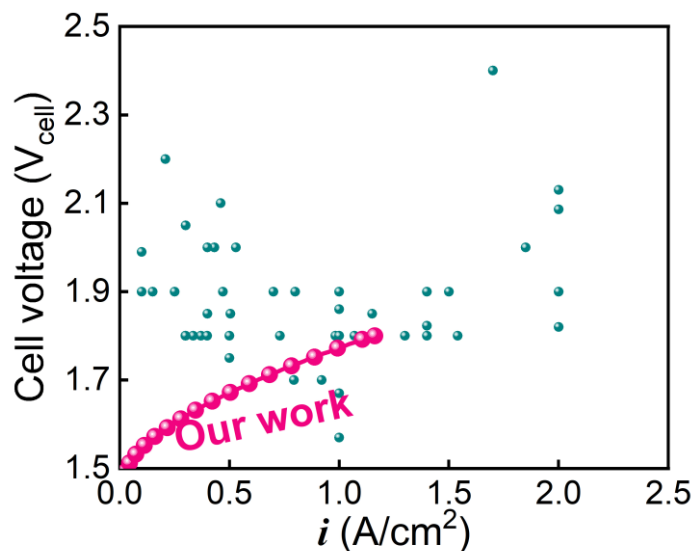


Figure 55. Performance comparison of AEMWE demonstrated in this work with the literature [15,20,50,64,93,97,101,103,148,149,151–188].

To better understand the crystal structure after electrochemical stability testing, we have performed the XRD. Figure 54A shows the XRD patterns of $\text{L}_2\text{S}_2\text{N}_1\text{F}_2$ after stability testing at the half-cell level by coating the catalyst on carbon cloth. Figure 54B shows the XRD patterns of $\text{L}_2\text{S}_2\text{N}_1\text{F}_2$, which indicates the hybrid perovskites, especially the RP phase, can decompose under OER conditions. The degradation of the AEM water electrolyzer single cell could be ascribed to the decomposition of the RP phase.

Based on the above analysis, as shown in Figure 55, our catalyst, LSCF, shows advanced performance as an OER catalyst and is competitive comparing recent reports in water splitting.

3.4 Conclusion

In summary, a set of novel hybrid perovskites, $L_xS_{4-x}N_yF_{3-y}$, were demonstrated for the first time as the OER electrocatalysts of AEMWEs. The crystal structure can be tuned by alternating their composition stoichiometry, which can modulate the hybridization between single-layer perovskite and RP perovskites. This hybridization improves the oxygen-ion diffusion rate and OER activity. $L_3S_1N_2F_1$, $L_2S_2N_{1.5}F_{1.5}$, and $L_2S_2N_1F_2$ are identified as outstanding OER electrocatalysts at the half-cell level. Among these three hybrid perovskites, $L_2S_2N_1F_2$ displays the best performance at the AEMWE single-cell level. An exceptional energy conversion efficiency of 75% is achieved at a current density of 0.5 A/cm^2 . This work has for the first time demonstrated the hybrid perovskites for clean hydrogen production in the AEM water electrolyzers single cell.

Chapter 4 - Designing OER Electrocatalysts for Hydrogen Production via Seawater Electrolysis

4.1 Introduction

Recently, due to the ongoing energy crisis and climate change, developing clean, renewable energy has become exceedingly urgent. Hydrogen, as a type of noble renewable energy, offers excellent versatility without geographical, time, and weather limitations compared to solar, wind, and hydropower energy. Even though it currently constitutes only a tiny portion of renewable energy sources, hydrogen production is still important in renewable energy sources. Electrolysis is a zero-carbon emission method for hydrogen production, and is witnessing an increasing share compared to prevailing coal, oil, and natural gas methods.

Currently, most investigations into water splitting focus on pure freshwater. However, some obstacles exist, such as water distribution issues [64]. On the other hand, seawater is an abundant resource. Exploring seawater as an alternative for electrochemical water splitting presents an environmentally conscious option that conserves purified water. This approach is precious within the context of seawater desalination endeavors.

However, there are two major challenges due to salts in seawater. First, there is the problem of Cl erosion due to the chlorine evolution reaction (CER) [58]. On the OER side, it may generate Cl_2 , which can form ClO^- , which could damage the reactor. In addition, these reactions could contaminate the O_2 product with impurities. To avoid these issues, high OER selectivity compared to CER is required in seawater electrolysis [64]. At alkaline conditions, when voltage is under $1.72V_{\text{RHE}}$, OER selectivity is high because this reaction depends on the electrolyte pH. In alkaline conditions, it is $\text{Cl}^- + 2\text{OH}^- \rightarrow \text{ClO}^- + \text{H}_2\text{O} + 2\text{e}^-$ $E^0 = +1.72V_{\text{RHE}}$. The second challenging is the reaction with ions. In seawater, there are many dissolved salts, with Na^+ , Mg^{2+} , and Ca^{2+} ions. They could react with OH^- , and the product could block the catalyst's active site and decrease the reaction rate [59].

NiFe LDH shows excellent electrocatalytic activity due to its open structure, in which exchangeable charge-balancing interlayer anions separate the cationic brucite-like layers. Consequently, the reactants to diffuse faster and products alongside a rapid

proton-coupled electron transfer [35]. NiFe LDH shows favorable activity for OER because of the synergistic effects between Ni and Fe [33]. In particular, NiFe LDH exhibits exceptional catalytic activity for OER and demonstrates excellent resistance to chlorine corrosion.

There are some studies about AEM seawater electrolysis. Soren Dresp et al. [60] studied the NiFe LDH as the OER catalyst for both seawater and pure water electrolysis. Subsequently, they compared the seawater electrolyzers with different solutions fed to the anode and cathode [61]. They found the catalyst performance is similar in seawater and KOH solution. For other catalysts, Ni-doped FeOOH, Yoo Sei Park et al. [62] got identical results in seawater and found better performance, with a current density of 729mA/cm² achieved at 1.7V.

This work aims to achieve high seawater electrolysis performance and identify the configuration that favors OER and minimizes CER in AEM seawater electrolyzers. First, in a half-cell test, we investigated the highly active electrocatalyst NiFe LDH with different Ni/Fe ratios, determining the optimal Ni/Fe ratio. Then, the performance of NiFe LDH with Ni/Fe ratio 75/25 (NiFe LDH 75) was measured in simulated seawater, leading to an overpotential of 378 mV at a current density 10 mA/cm², which is slightly lower than that in 1 M KOH solution but is much better than the previously reported results. Additionally, the configurations shown in Figure 66 will be optimized and studied using a single-cell test in anion exchange membrane (AEM) seawater electrolyzer. The asymmetric feeds showed remarkable performance, achieving an exceptional current density of >1A/cm² at 1.8V, and a high Faradaic efficiency of close to 100% in all electrolyte configurations. With 1M KOH fed to the anode, and 0.5 M NaCl fed to the cathode, an energy conversion efficiency of 77% is achieved, and a long-time stability, up to 150 hours in seawater is demonstrated. Our NiFe LDH 75 AEM catalyst operated in simulated seawater demonstrated superior performance compared to the previously reported AEM seawater electrolyzers conducted in 1.0 M KOH.

4.2 Experimental Section

4.2.1 Materials Synthesis: NiFe Layered Double Hydroxides

NiFe LDH is synthesized by the co-precipitation method [88]. First, a stoichiometry amount of nickel(II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) are dissolved in 100 mL deionized water (DI water). Second, 5 mmol potassium carbonate (K_2CO_3) and 50 mmol potassium hydroxide are dissolved in 100 mL deionized water (DI water) to prepare the alkaline solution. Then, the alkaline solution is added to nickel nitrate and iron nitrate solution until the pH of the mixture is 8.5. This mixture is stirred at room temperature for 24 hours. After aging, the mixture is washed by centrifugation and dried in an oven at 24 hours, 80°C.

4.2.2. Structural Characterization

The crystal structure of NiFe LDH was examined by X-ray diffraction (XRD) using a Rigaku MiniFlex diffractometer with a Cu K α radiation source operated at 30 kV and 15 mA (2θ : 5.1-90°, scanning speed: 1°/min).

4.2.3 Electromical Characterization at the Half cell

The Gamry Reference 3000 was employed to perform all electrochemical measurements at the half-cell level in a three-electrode cell with an alkaline electrolyte, 1 M KOH solution, and simulated alkaline seawater electrolyte, 1 M KOH + 0.5 M NaCl, at room temperature as shown in Figure 56. The working electrode was OER ink coated on a 1*1cm² carbon cloth. The OER ink was prepared by mixing the 100 μL of 5 wt.% Nafion solution, 900 μL of ethanol, with 20 mg of NiFe LDH. The counter electrode was a graphite rod, and the reference electrode was Hg/HgO. Based on the Nernst equation, all potentials versus the reference electrode were changed to potentials versus the reversible hydrogen electrode (RHE). At a scan rate of 5 mV/s, the polarization curves for OER were captured, and iR was adjusted. The double-layer capacitance (C_{dl}) was determined using cyclic voltammetry (CV) with various scan rates in the non-Faradaic zone in 1 M KOH and 1 M KOH + 0.5 M NaCl. The electrochemical impedance spectroscopy (EIS) was carried out at 1.63 V (vs. RHE) between 500 kHz and 0.2 Hz with

an AC voltage of 10.0 mV. All electrochemical characterizations at the half-cell level were conducted at ambient temperature.

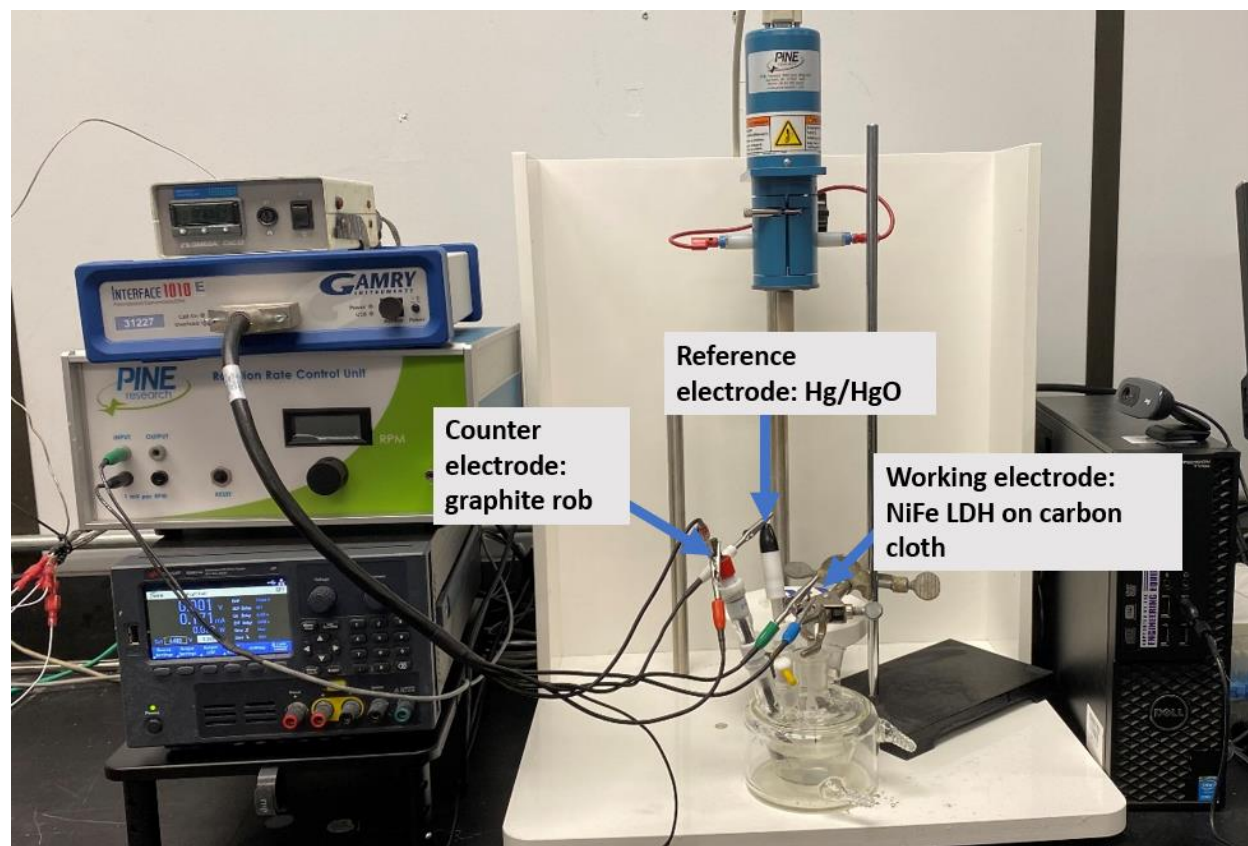


Figure 56. A three-electrode system with NiFe LDH in half-cell test.

4.2.4 Evaluation of the OER Electractlysts at the AEM Water Electrolyzers

Fuel Cell Technologies, Inc. supplied the hardware for AEMWEs single-cell testing. The anode flow channel was a titanium plate with a flow pattern, and the cathode flow channel was a graphite plate with a flow pattern, as shown in Figure 57. The current collector was made of gold-plated connectors. The anion exchange membrane (AEM, X37-50) was obtained from Dioxide materials. The anode was prepared by spray coating the electrode ink solution on commercial nickel foam. The ink solution for the anode was prepared by mixing the catalysts, deionized (DI) water, isopropyl alcohol, ethanol, and ionomer (Fumion, FAA-3-solut-10). The loading mass of anode catalysts, NiFe LDH, was approximately $5.0 \pm 0.1 \text{ mg/cm}^2$. The cathode ink solution was prepared by mixing Pt/C

(40 wt.%, HISPEC 4000, Johnson Matthey) with a Nafion binder on carbon cloth with a microporous layer. The loading amount of HER catalysts was approximately $1.0 \pm 0.05 \text{ mg}_{\text{Pt}}/\text{cm}^2$. The electrolyte media feed in four different types, as shown in Figure 66, which was supplied to the AEMWEs at a 50 mL/min flow rate. A hot plate controlled the electrolyte's operating temperature, and the heater embedded in the system controlled the single-cell hardware. All electrochemical characterizations at the single-cell level were performed at 50 °C. The active electrode area of all AEMWEs is 3.8 cm^2 . The electrochemical performance of the AEMWEs was evaluated using a Gamry Interface 5000 and a DC power supply (Keysight Technologies E36313A). The single-cell polarization curves were measured by recording the voltage at a constant current mode. The durability of AEM electrolyzers was tested at a constant current of $0.5 \text{ A}/\text{cm}^2$.

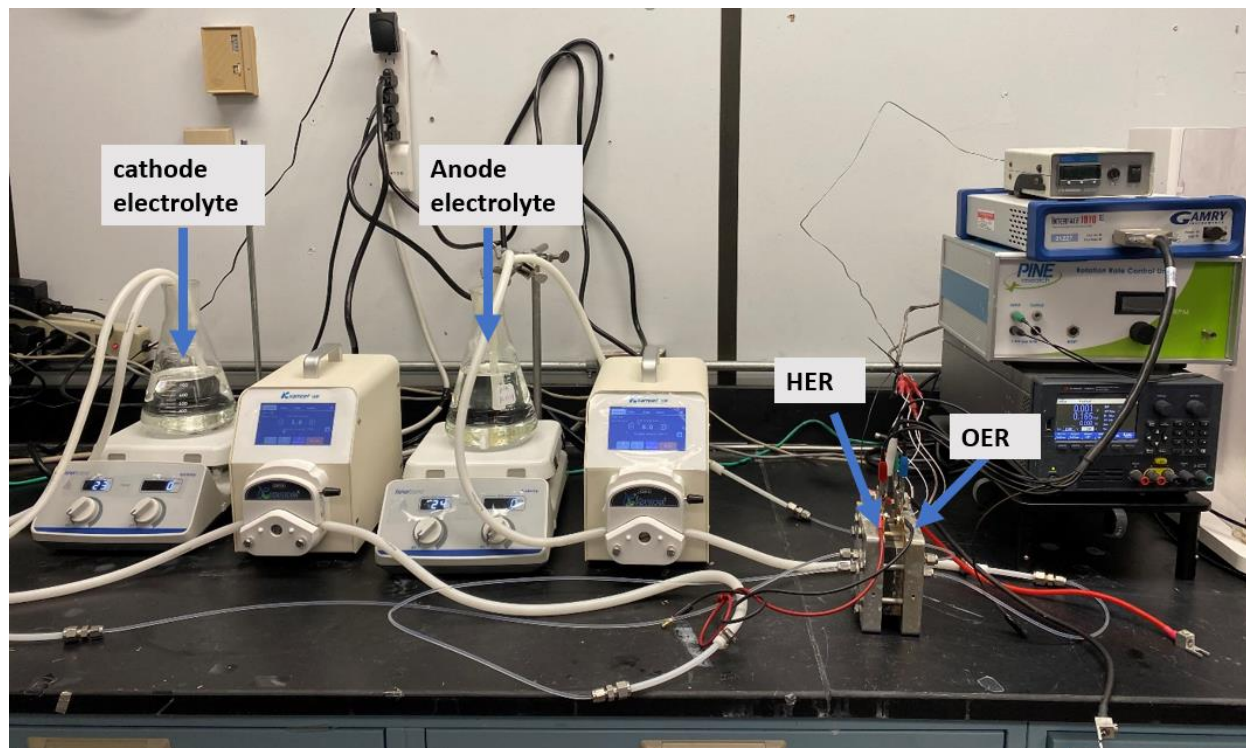


Figure 57. Single-cell test station in seawater electrolysis.

The AEMWE energy efficiency based on a lower heating value of H_2 (LHV) is calculated using the following equation.

$$\text{AEMWE energy efficiency (\%)} = \frac{\Delta H_{\text{H}_2, \text{LHV}} \times n_{\text{H}_2, \text{measured}}}{I \times V} \times 100 \% \dots \text{Equation 7}$$

$\Delta H_{\text{H}_2, \text{LHV}} = 241.8 \text{ kJ/mol}$. the lower heating value of hydrogen

$n_{H_2, \text{measured}}$ = the measured hydrogen production rate (mol/s)

I = the applied current (A)

V = the applied voltage (V)

The concentration of O_2 was measured using a gas chromatography (GC, 3000 Micro GC from INFICON). The carry-on gas is Ar, and the flow rate is 50 sccm.

The single-cell test setting process is shown in Figure 58.

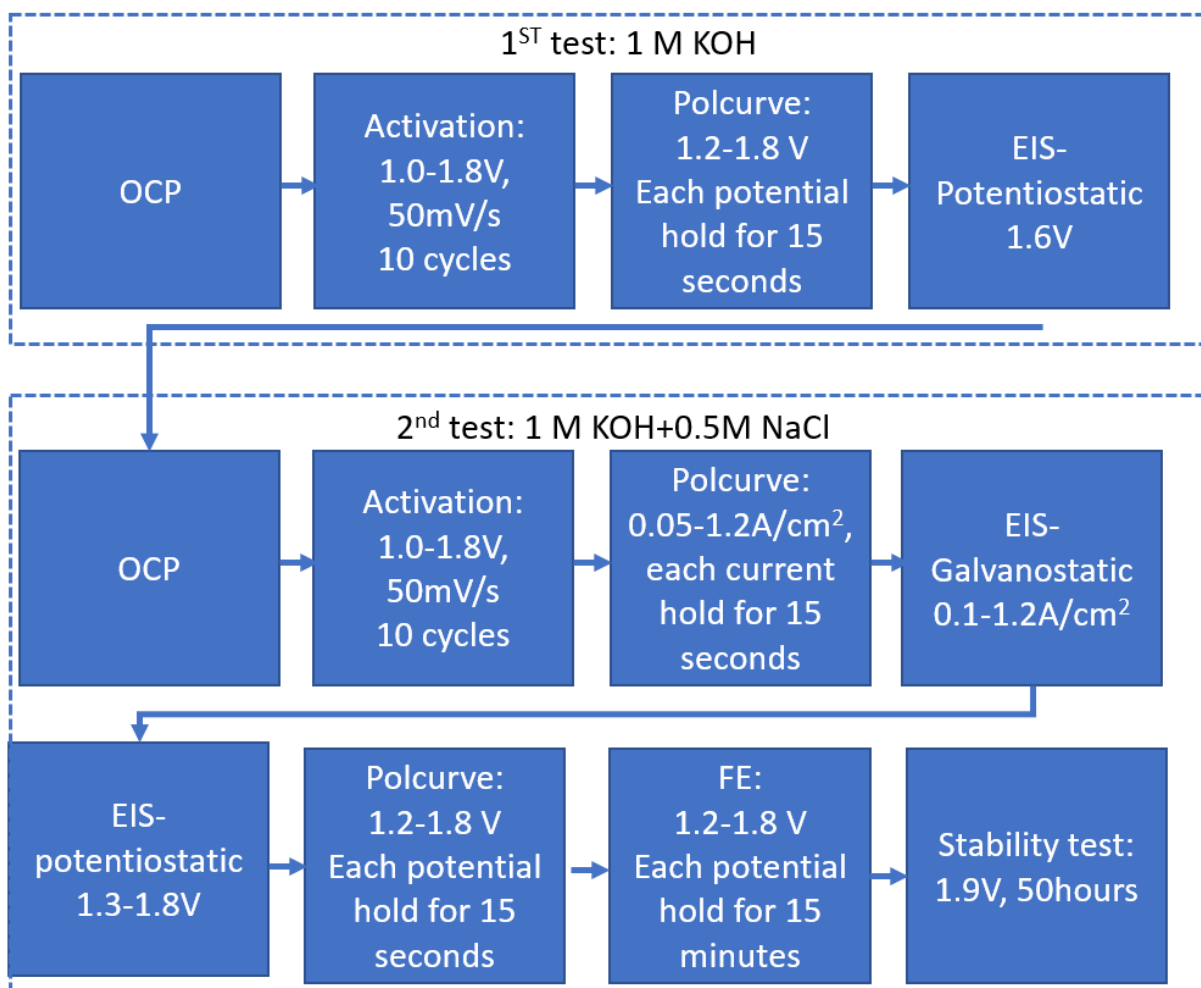


Figure 58. Single-cell test setting procedures.

4.2.5 Free chlorine detection

The hypochlorite was detected via a titration method [61]. The electrolytes from the single-cell tests of types i, ii, and iii after the stability test in the anode side were collected for the experiment. First, a 10mL sample from the electrolyte was mixed with 15mL of 0.5M potassium iodide (KI) in a flask. Then, 1mL of the starch solution was added to the flask, and the color changed to blue. Then, the 0.02 M thiosulfate solution was added to the flask through the burette until the color changed to light yellow. The concentration of chlorine could be calculated by the following equation.

$$\text{Concentration of free chlorine (M)} = \frac{V_{\text{thiosulfate solution used (L)}} * C_{\text{thiosulfate (M)}}}{\text{sample volume (L)}} \dots\dots \text{Equation 8}$$

V: consumed volume

C: thiosulfate concentration – 0.02M

4.3 Results and Discussion

4.3.1 Structural Properties of NiFe LDH

The highly active electrocatalyst, NiFe LDH powder for OER was synthesis via co-precipitation with a Ni/Fe ratio of 60/40 (NiFe LDH 60), 70/30(NiFe LDH 70), 75/25(NiFe LDH 75), 80/20(NiFe LDH 80), and 85/15(NiFe LDH 85) [88]. Five samples were prepared for half cell test.

The X-ray diffraction (XRD) patterns confirmed the crystal structure of NiFe LDH in Figure 59, with peaks at 11.32 (003), 22.34 (006), 34.24 (009), 38.7 (015,), 46.48 (018,), 60.06 (110), and 61.04 (113) [88] [189]. They matched with the peaks corresponding to the rhombohedral structure of NiFe LDH. The plane (003), (006), and (009) +(012) are expressed as the layered structure of the 3R polytype [50,88,190]. The patterns of peaks from 35° to 60° correspond to the reflections of the interlayer. There were no recognizable XRD peaks of NiFe in any of the samples.

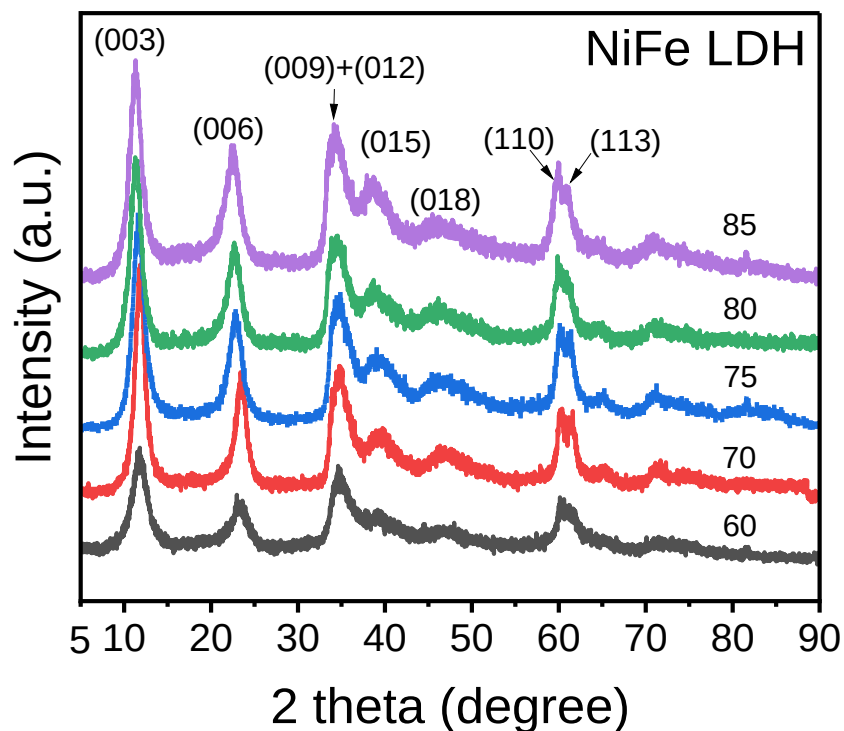


Figure 59. XRD patterns of NiFe LDH with different Ni/Fe ratios: 85:15, 80:20, 75:25, 70:30, and 60:40.

4.3.2 Electrochemical Properties of NiFe LDH at the Half-cell Level

Through the process of drop coating, the OER catalyst ink with NiFe LDH is applied onto the carbon cloth substrate. This method ensures a uniform and controlled deposition of the catalyst material, which is crucial for consistent and accurate assessment of its electrocatalytic performance. The conventional three-electrodes method employed for performance evaluation is a well-established approach in electrochemical studies, allowing for precise measurements of current and potential under controlled conditions.

The Ni/Fe ratio's impact on performance is a crucial aspect of interest. Previous investigations have highlighted that a Ni/Fe ratio ranging from 1.5 to 3 yields the most favorable results [191][192]. This ratio is pivotal in determining the activity of the NiFe LDH. A balanced Ni/Fe ratio is thought to promote synergistic effects between the two metals, leading to enhanced catalytic activity for the OER. This cooperative interaction is

attributed to the distinct properties of Ni and Fe, which complement each other in facilitating the catalytic process. The intriguing performance of NiFe LDH can be attributed to the formation of oxygen-bridge metal structures, such as Fe-O-Fe and Ni/Fe-O-Fe. These structures play a crucial role in facilitating charge transfer and stabilizing reaction intermediates during the OER process. The presence of these unique structures underscores the significance of the Ni/Fe ratio, as it directly influences the prevalence and effectiveness of such structures.

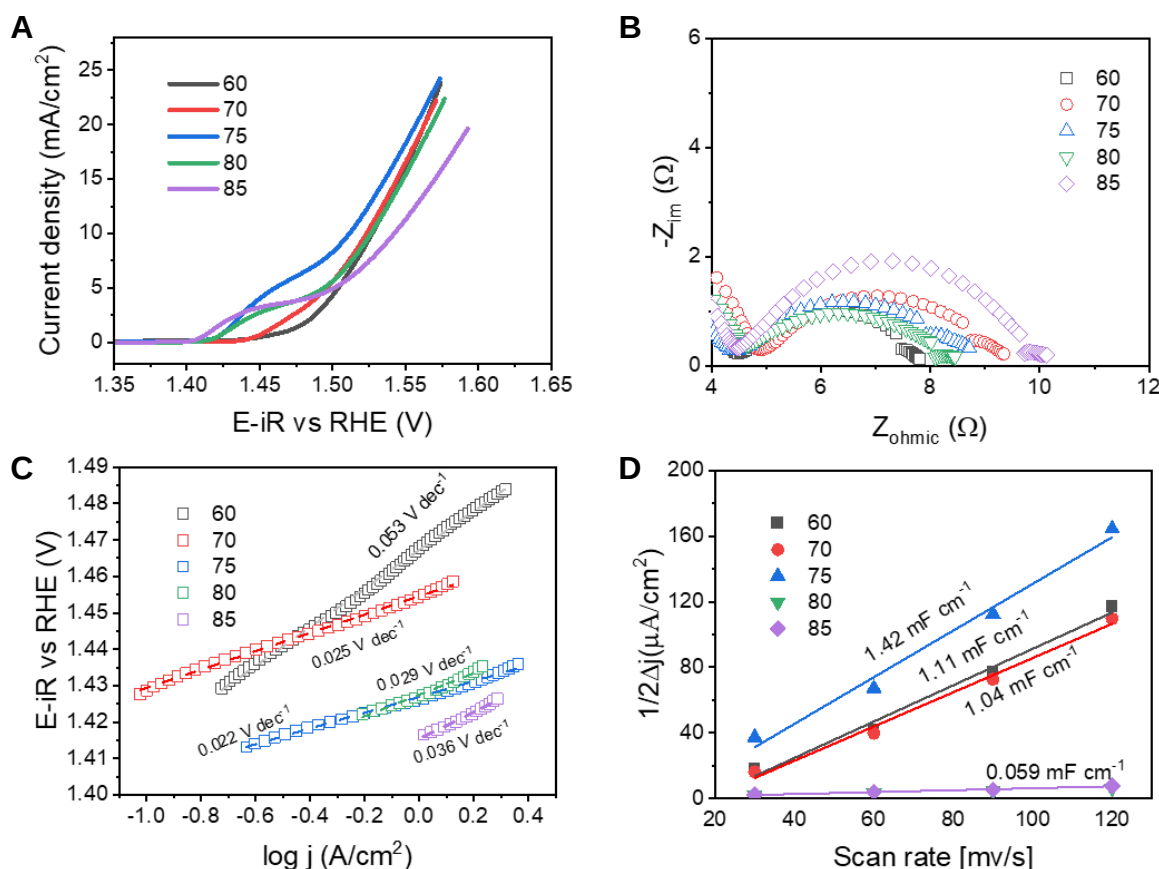


Figure 60. Electrochemical performance of NiFe LDH of 60, 70, 75, 80, and 85mM at the half-cell level, which was evaluated in 1.0 M KOH solution at room temperature (A) Ohmic resistance-corrected polarization curves (B) Electrochemical impedance spectra at 1.7 V. (C) Tafel plots. (D) Linear fitting curves of the non-Faradaic current as a function of CV scan rates for determining the double-layer capacitance and ECSA.

Given the intricate interplay of factors, the current study aims to expand on the existing knowledge by exploring various Ni/Fe ratios within the established performance range. This investigation is poised to relate composition, structure, and electrocatalytic performance. Ultimately, by understanding the optimal Ni/Fe ratio and its impact on the formation of oxygen-bridge metal structures, researchers hope to advance the development of high-performance OER catalysts for applications in energy conversion and storage systems.

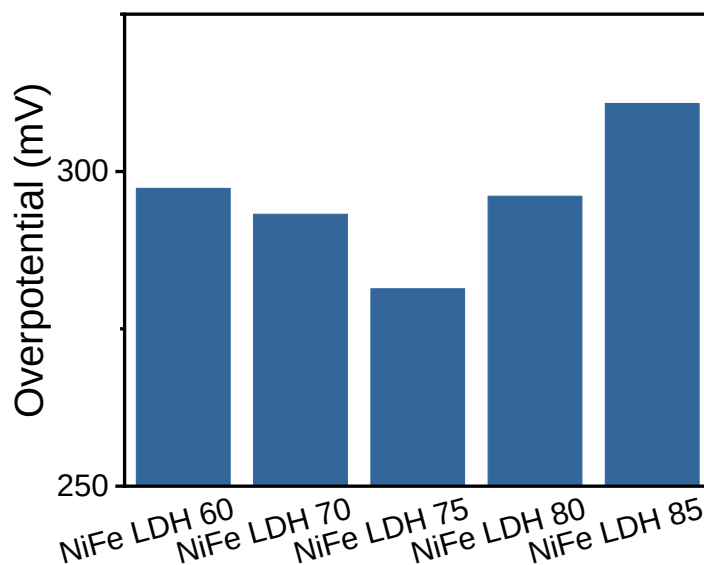


Figure 61. Comparison of overpotential at a current density of $10\text{mA}/\text{cm}^2$ using NiFe LDH 60, 70, 75, 80, 85 as the OER electrode in half cell.

The OER electrocatalytic performance normalized by the electrode area was summarized in Figure 60. The iR -corrected linear scan voltammetry (LSV) curves, which were corrected to a reversible hydrogen electrode (RHE), shown in Figure 60, presented the different OER performance of NiFe LDH with NiFe LDH 60, NiFe LDH 70, NiFe LDH 75, NiFe LDH 80, and NiFe LDH 85. The OER performance first tended to be improved by increasing the Ni/Fe ratio, while it decreased with further increasing the Fe/Ni ratio. As shown in Figure 61, NiFe LDH 75 expressed an extremely low overpotential of 281 mV at a current density of $10\text{mA}/\text{cm}^2$ [48]. At a low Ni/Fe ratio, NiFe LDH 60, 70, and 75, with increasing the Ni/Fe ratio, the performance increases, which is due to the fact that $\text{Ni}(\text{OH})_2$

became NiFe LDH [192]. With further increasing the Ni/Fe ratio, the performance tends to be worse because of the formation of oxide [48]. Therefore, an extremely high Ni concentration was unfavorable for OER.

Electrochemical impedance spectroscopy (EIS) could express charge transfer resistance (R_{ct}). As shown in Figure 60B, the NiFe LDH 75 exhibits a lower OER activation loss, which is consistent with the previous electrochemical analysis result LSV.

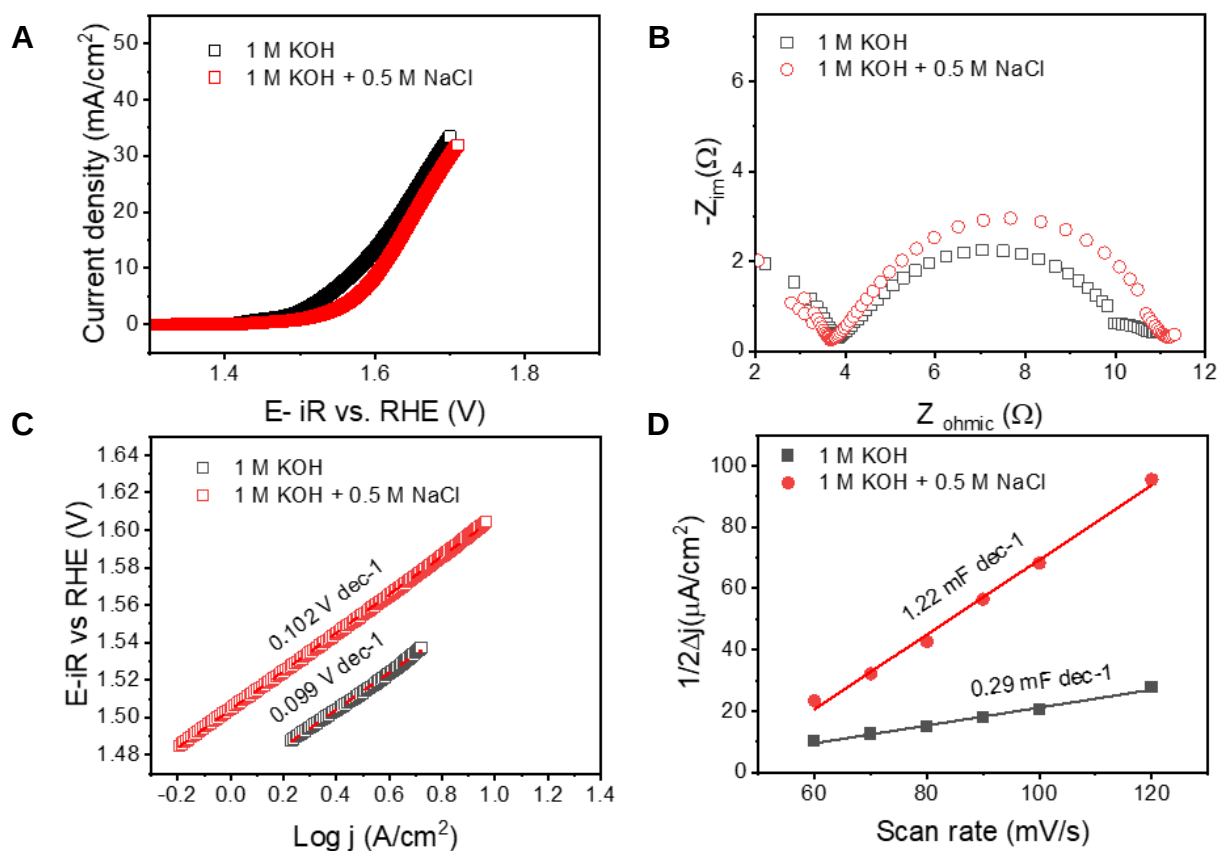


Figure 62. Electrochemical performance of NiFe LDH with 75mM at the half-cell level, which was evaluated in 1.0 M KOH and 1.0 M KOH+0.5 M NaCl solution at room temperature. (A) Ohmic resistance-corrected polarization curves (B) Electrochemical impedance spectra at 1.6 V. (C) Tafel plots. (D) Linear fitting curves of the non-Faradaic current as a function of CV scan rates for determining the double-layer capacitance and ECSA.

To further investigate the OER kinetic, Figure 60C presents the Tafel plots, which show that the Tafel slope of NiFe LDH 75 (0.022 V dec^{-1}) is the lowest. They also affirmed that increasing the Fe/Ni ratio can slightly enhance the OER electrocatalytic activity.

Additionally, as shown in Figure 60D, the double-layer capacitances were determined by linearly fitting the non-Faradaic current as a function of cyclic voltammetry (CV) scan rate, which were subsequently used to estimate the double-layer capacitance and electrochemically active surface area (ECSA). The ECSA is highly correlated with the number of active sites. As shown in Figure 60D, the measured values of C_{dl} showed the same trend as obtained by LSV.

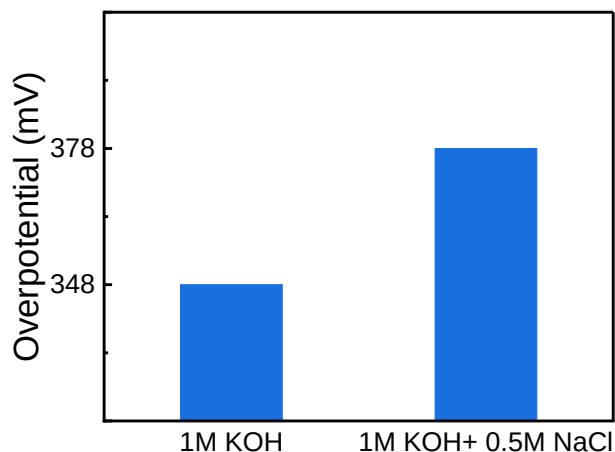


Figure 63. Comparison of overpotential at 10 mA/cm^2 of NiFe LDH 75 in the electrolyte of 1M KOH and 1M KOH+ 0.5M NaCl in half cell.

Among the various NiFe LDH samples studied, NiFe LDH 75 stands out with the highest Electrochemically Active Surface Area (ECSA) value of 1.42 mF/cm^2 . In contrast, NiFe LDH 60, NiFe LDH 70, NiFe LDH 80, and NiFe LDH 85 exhibit ECSA values of 1.11 mF/cm^2 , 1.04 mF/cm^2 , 0.059 mF/cm^2 , and 0.059 mF/cm^2 , respectively. Therefore, the ECSA values provide a clear indication of NiFe LDH 75's exceptional capability to create electrochemically active sites. This characteristic, coupled with the synergistic effects resulting from its specific composition, establishes NiFe LDH 75 as a standout candidate

for efficient and high-performance OER applications in the realm of energy-related technologies.

Based on previous literature results, seawater electrolysis leads to low performance compared to freshwater electrolysis. There are several reasons causing the low performance, such as high salinity, in which Cl^- could increase resistance, pH, and impurities due to organics [58,60,193]. In seawater, there is salt, including ions such as Na^+ , Mg^{2+} , and Ca^{2+} . They could react with OH^- , and the product could block the catalyst's active site and decrease the reaction rate [59]. Therefore, the challenge of seawater electrolysis was to reduce corrosion and resistance by catalyst selection and system fabrication, including operating conditions and configurations. Pretreatment could remove organic and other chemicals from the seawater to reduce corrosion and avoid competing reactions. Therefore, in this paper, simulated seawater was used to avoid these problems. For catalyst, high activity and long stability in seawater electrolysis are required [58].

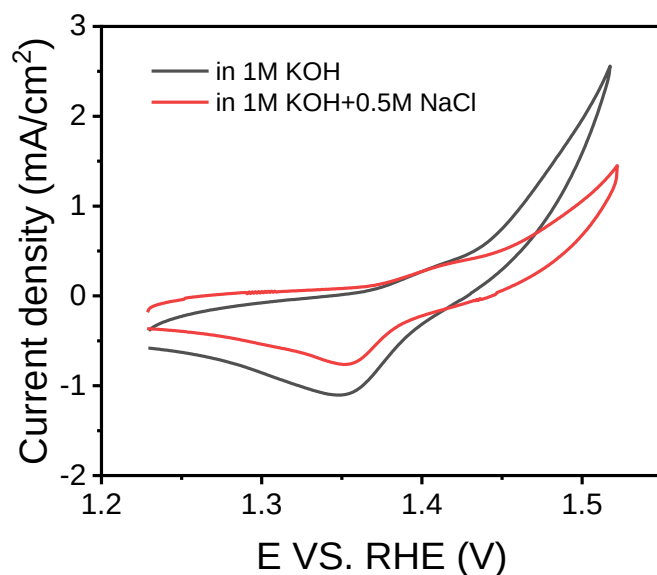


Figure 64. Comparison of redox of NiFe LDH 75 in the electrolyte of 1M KOH and 1M KOH+ 0.5M NaCl.

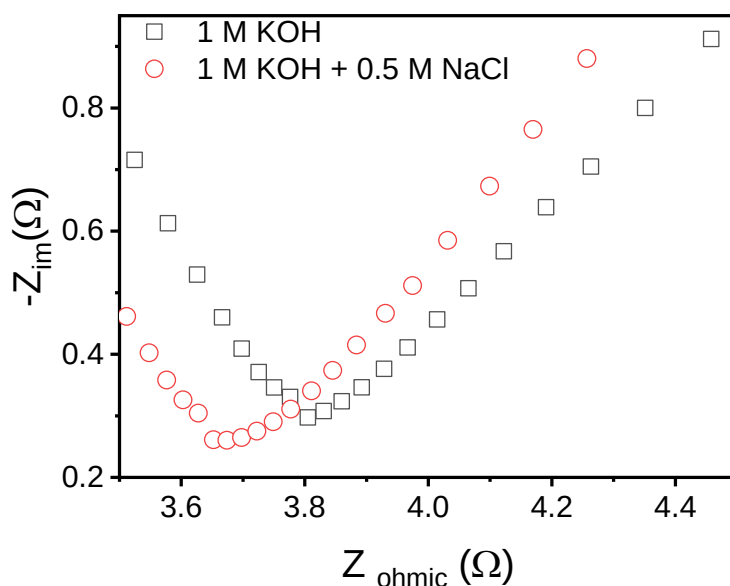


Figure 65. R_o in 1M KOH and 1M KOH+ 0.5M NaCl.

Figure 62 shows the NiFe LDH 75 using different electrolytes, including alkaline water (1M KOH) and simulated alkaline seawater (1M KOH+0.5M NaCl). The performance in alkaline water electrolytes is better than that in simulated seawater electrolytes, which is shown in Figure 62A. The tendency didn't change in 100% iR-correct and without iR-correct. There is no significant difference in water and seawater as the electrolyte in LSV, EIS, and Tafel slope. As shown in Figure 63, the overpotential in seawater is 378 mV, which is much higher than that in 1M KOH, 348 mV at 10 mA/cm². As shown in Figure 65, the ohmic resistance in seawater was lower due to high ionic conduction with Cl⁻ presence. However, there is a significant difference in double-layer capacitance. The composition of the electrolyte could impact the kinetics of electrochemical reactions, particularly in terms of charge storage mechanisms.

4.3.3 Electrochemical performance of the AEM Water Electrolyzers Level with NiFe LDH as the OER Catalysts

Significant advancements have been made in the development of extensive LDH-based OER electrocatalysts to enhance the efficiency of water electrolysis under alkaline

conditions [61]. However, because fabrication of high-quality membrane electrode assembly (MEA) has been studied less, less effort has been made to apply NiFe LDH as the OER catalysts for AEMWEs. Therefore, lab-scale AEM water electrolyzers single-cells were built and tested to assess the high performance of the NiFe LDH in seawater.

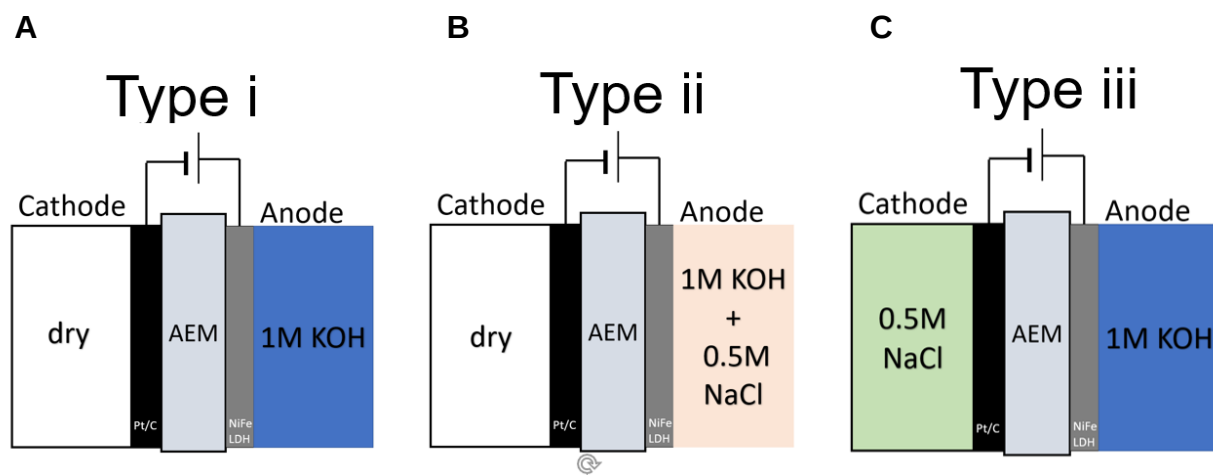


Figure 66. Schemes of AEM electrolyzers using independent electrolyte feeds with different electrolyte compositions (A) type i: 1M KOH is fed to the anode (B) type ii: 1M KOH+0.5 M NaCl is fed to the anode; (C) type iii: 0.5 M NaCl solution is fed to the cathode, and 1M KOH is fed to cathode.

The configuration of the solution fed to the anode and cathode is important for the seawater electrolysis performance [20,194]. Cho et al. [194] studied the effect of the electrolyte feed method in AEMWE. After KOH pretreatment in both the anode and cathode, the performance tends to be better because ohmic resistance decreases and ionic conductivity increases. Comparing the DI water fed to the cathode with no liquid fed to the cathode, the performance is better with no solution fed to the cathode. However, in the long-term performance test, the performance drop was huge with dry feed due to pH change. Soren Dresch et al. [60] found the KOH solution with a high concentration can lead to improved performance in alkaline seawater electrolysis. Their following seawater electrolysis study discovered that asymmetric electrolyte feed on the cathode and anode sides yields superior outcomes despite solely one-sided feeding [61].

Table 8. Comparison of different configuration

	Advantages	Disadvantages
Type i	High-purity hydrogen	
Type ii	High-purity hydrogen; Dry H ₂ production is feasible, and no separation process is required. Better stability compared with feeding 1M KOH to the cathode	Cl ⁻ oxidation on the OER side.
Type iii	Better performance compared with asymmetric feed Better stability compared with asymmetric feed	OER electrolyte becomes dilute as water flows from the cathode to the anode.

Therefore, in this work, three different asymmetric feeds were studied using 1M KOH solution. NiFe LDH 75 was used as an OER electrode for all single cells. Figure 66 displays the architecture of the AEM water electrolyzers. Type i: 1M KOH was fed to the anode. Type ii: 1M KOH+0.5M NaCl solution was fed to the anode. Type iii: 1M KOH solution was fed to the anode, and 0.5M NaCl solution was fed to the cathode.

Type i is the reference AEMWE for seawater electrolysis. Dry cathode operation is beneficial to produce pure H₂. Seawater fed at the cathode could rescue seawater and achieve better stability, as shown in Table 8.

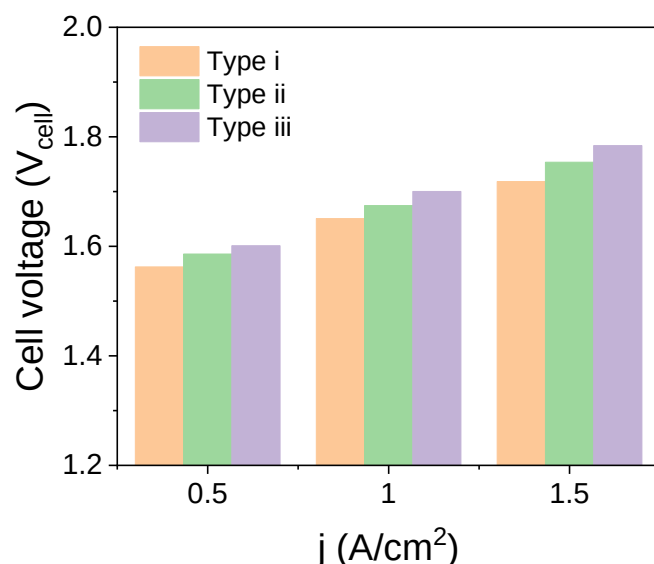


Figure 67. Comparison of cell voltage of NiFe LDH 75 with electrolyte feeding with type i, ii, and iii at a current density of 0.5A/cm², 1A/cm², and 1.5A/cm².

The operating cell voltage was limited to 1.8 V_{cell} , which was slightly higher than the potential of the occurrence of ClER above 1.72 V_{RHE} , even though 1.72 V_{cell} is not equivalent to 1.72 V_{RHE} . The performance of the AEM electrolyzer in simulated seawater, no matter the configuration, showed worse than that in 1M KOH, which led to the same trend in half cells due to Cl^- ion in electrolytes of 1.0 M KOH + 0.5 M NaCl [60,64]. To explore the effect of Cl^- , titration analysis with iodide is used to detect chlorine in the electrolyte on the OER side. GC will be used to determine the Faradaic efficiency of both OER and HER. The Faradaic efficiency is close to 100% in all configurations, and the energy efficiency was also high. Energy efficiency serves as a crucial metric to assess the extent of effective conversion of electrical energy into chemical reactions during the electrolysis process.

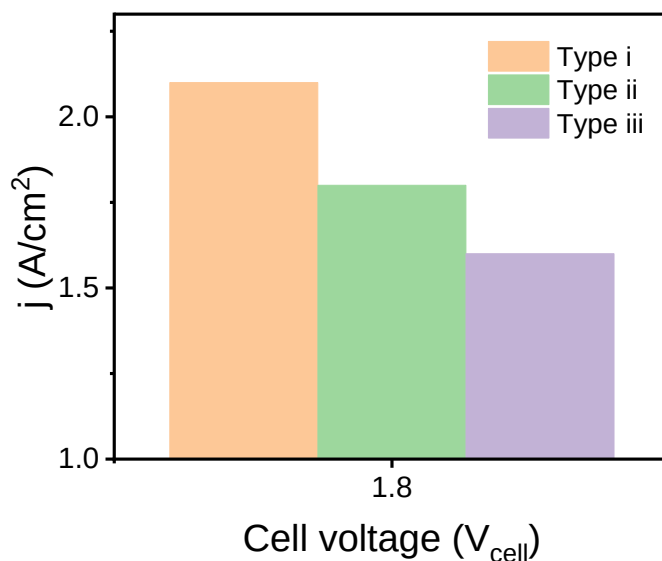


Figure 68. Comparison of the current density of NiFe LDH 75 with electrolyte feeding with type i, ii, and iii at the cell voltage of 1.8V.

The performance of seawater electrolysis was highest in type ii feeding, as shown in Figure 71 A. The result from type iii was similar but lower. The AEM electrolyzer electrolyte fed by the configuration of type i, ii, and iii, yielded current densities of 2.1, 1.8, and 1.6 mA /cm², respectively, at 1.80 V_{cell} , which is shown in Figure 67. They also lead to high energy efficiencies of 78.2%, 73.71%, and 77.4% at 500mA/cm² in types i, ii, and ii, respectively, as shown in Figure 75.

The AEM seawater electrolysis performance was worse than AEMWE because of Cl^- in seawater. Figure 71 B indicates that the 1M KOH electrolyte feed was consistently performed in EIS. Alkaline seawater feed on either side shows lower performance, as shown in Figure 71A and Figure 71B. To better understand it, EIS spectra were performed in Figure 71 B. The ohmic loss is ascribed to the sum of the electrical and ionic resistance. Figure 65 shows the ohmic resistance increases in seawater electrolysis. The ohmic resistance of seawater, type ii and type iii were larger than that in freshwater, type i, because the Cl^- competed with OH^- in seawater and reduced the ionic OH^- membrane conductivity. Yoo See Park and Soren Dresp found similar results [60,62].

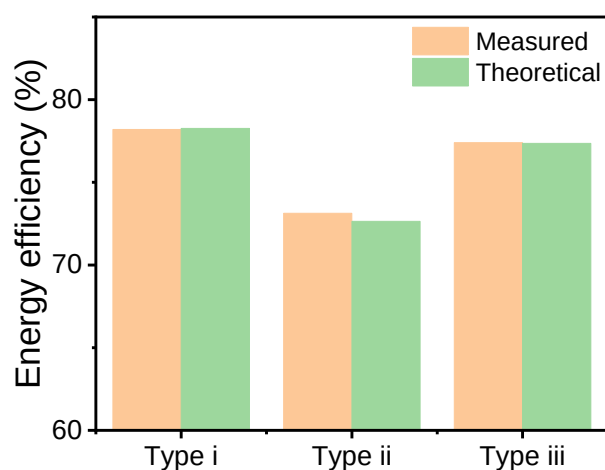


Figure 69. Comparison of energy efficiency of H₂ of NiFe LDH 75 with electrolyte feeding with type i, ii, and iii at the current density of 0.5A/cm².

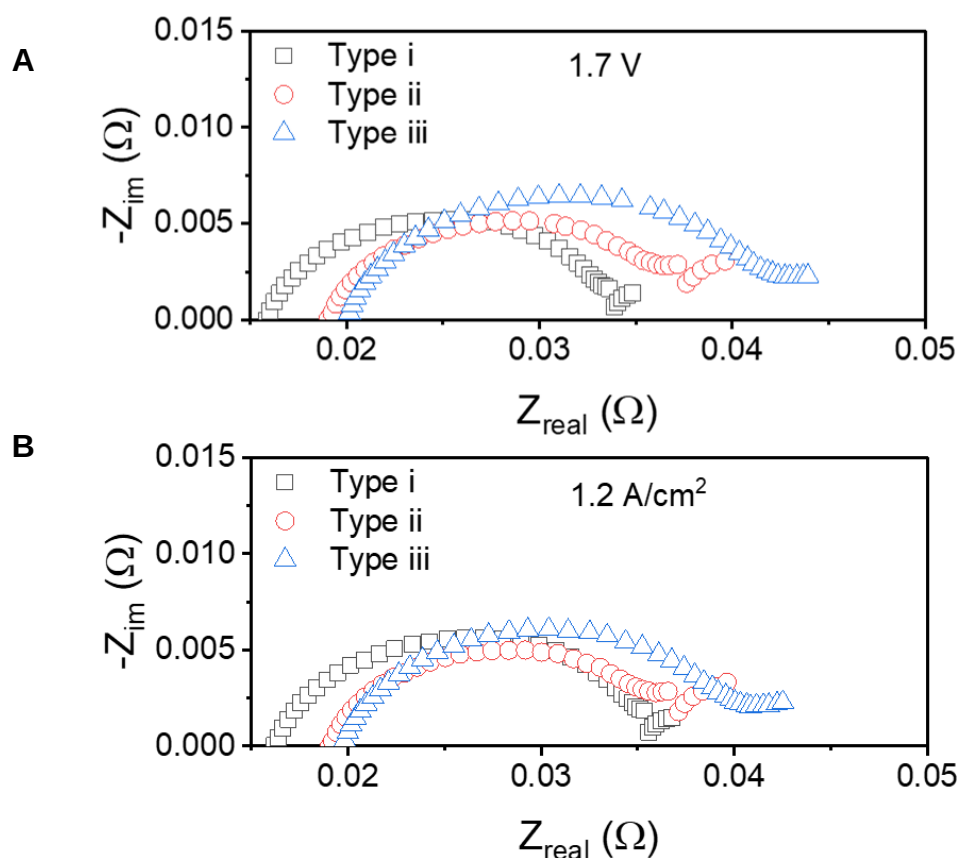


Figure 70. Electrochemical impedance spectra of NiFe LDH 75 with electrolyte feeding with type i, ii, and iii at (A) 1.7V (B) 1.2A/cm².

Figure 78 shows the ohmic loss in seawater electrolysis, types ii and iii, were close, indicating the electrical conductivities of types ii and iii are similar. But both of them are larger in type i, freshwater. In addition, Figure 79 shows the activation loss in types i and ii were close, smaller than type iii. Therefore, the performance decreased between types i and ii due to Cl^- in the anode side. For type iii, it was due to both ohmic and activation loss. The concentration loss was too small and could be ignored.

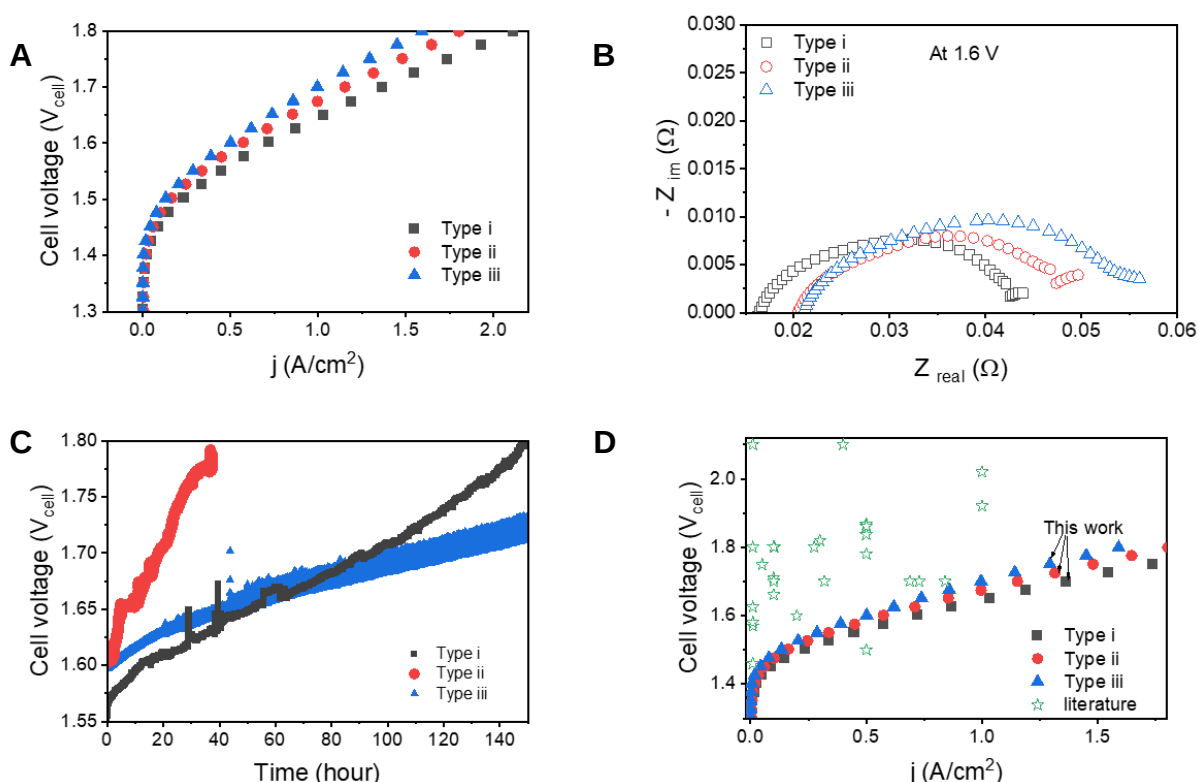


Figure 71. The performance of AEM electrolyzer with NiFe LDH 75 as anode catalyst with asymmetric electrolyte feeds of type A, B, C, and D. (A) polarization curves of AEM water electrolyzers (B) electrochemical impedance spectra (C) a preliminary stability testing of AEMWE at 50C and a current density of $0.5 \text{ A}/\text{cm}^2$ [60,64–83].

To maintain the long-term stability of seawater electrolyzers, it is crucial to avoid oxidation of Cl^- in seawater to hypochlorite (OCl^-) in alkaline conditions. In any seawater configuration, there is no OCl^- detected by the iodometric titration method. To study the

stability of the NiFe-LDH gas diffusion electrode placed in seawater electrolyzers with asymmetric electrolyte feed, Figure 71 C shows a galvanostatic test at a current density of $500\text{mA}/\text{cm}^2$. There was a huge voltage drop in type ii, because NaCl could barrier the OH^- transportation through the membrane, causing the current drop in seawater. The stability of type iii is great, up to 140 hours. It was PH change during the test. Water flowed from cathode to anode, causing PH change. The voltage drop became small at low PH [60].

In Figure 71 D, a comprehensive assessment of my catalyst's performance is presented in comparison with data from the literature. The referenced literature data is sourced from Table 4. The noteworthy finding is that my catalyst outperforms a majority of catalysts in the context of water splitting. This result underscores the significant advancement achieved by my catalyst in the field.

By showcasing superior performance compared to a considerable number of counterparts, my catalyst demonstrates a competitive edge within the realm of Oxygen Evolution Reaction (OER) catalysts. This observation underscores the potential and significance of my catalyst's contributions to advancing the field of OER research. The implications extend beyond the confines of this study, potentially shaping future advancements in the development of catalysts for water splitting applications.

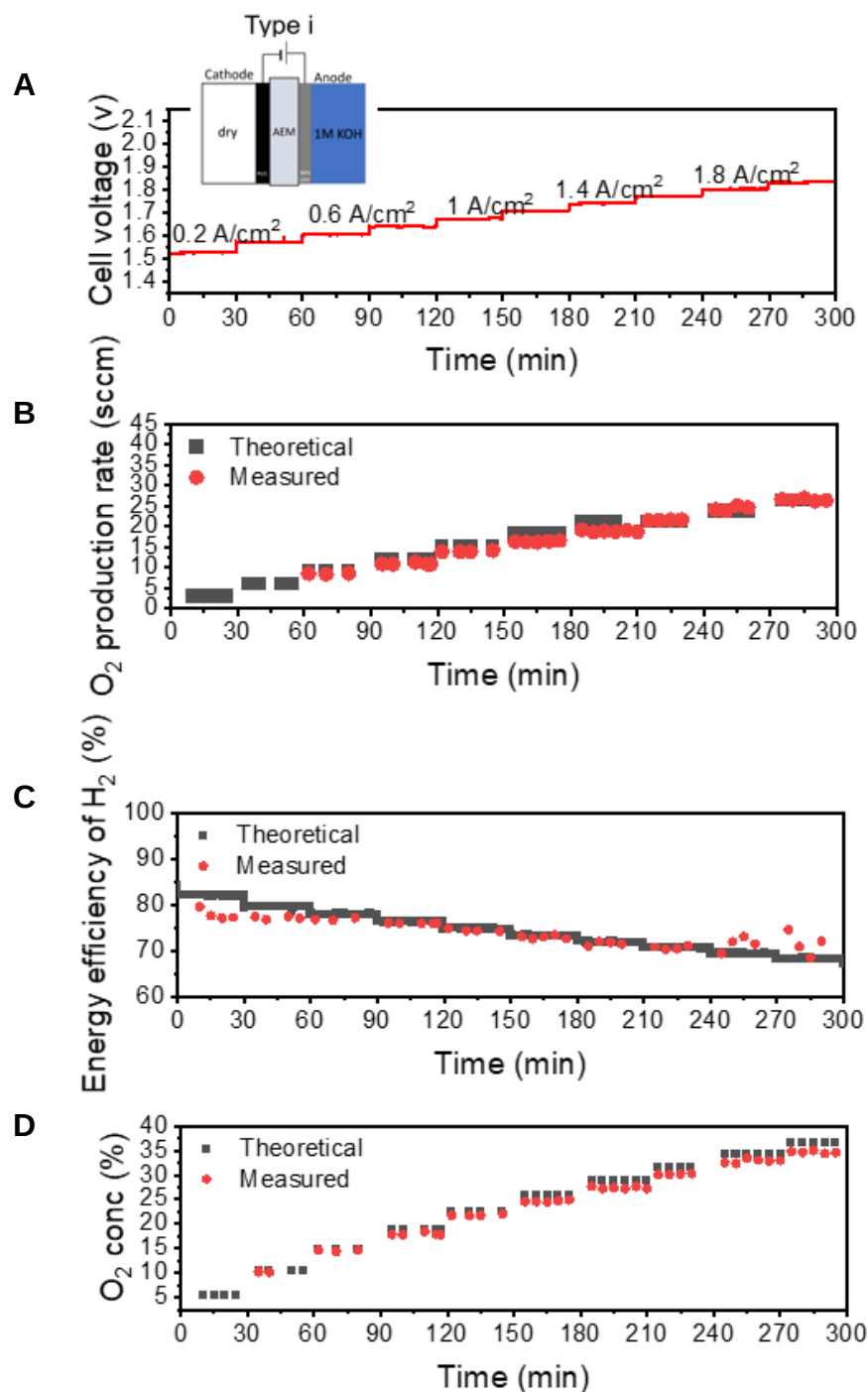


Figure 72. Stepped constant current tests with current holds of 30 min of NiFe LDH 75 as anode catalyst with type i electrolyte feed: asymmetric 1M KOH at the anode and dry at the cathode with (A) cell voltage (B) O₂ production rate (C) energy efficiency of H₂. (D) O₂ gas concentration.

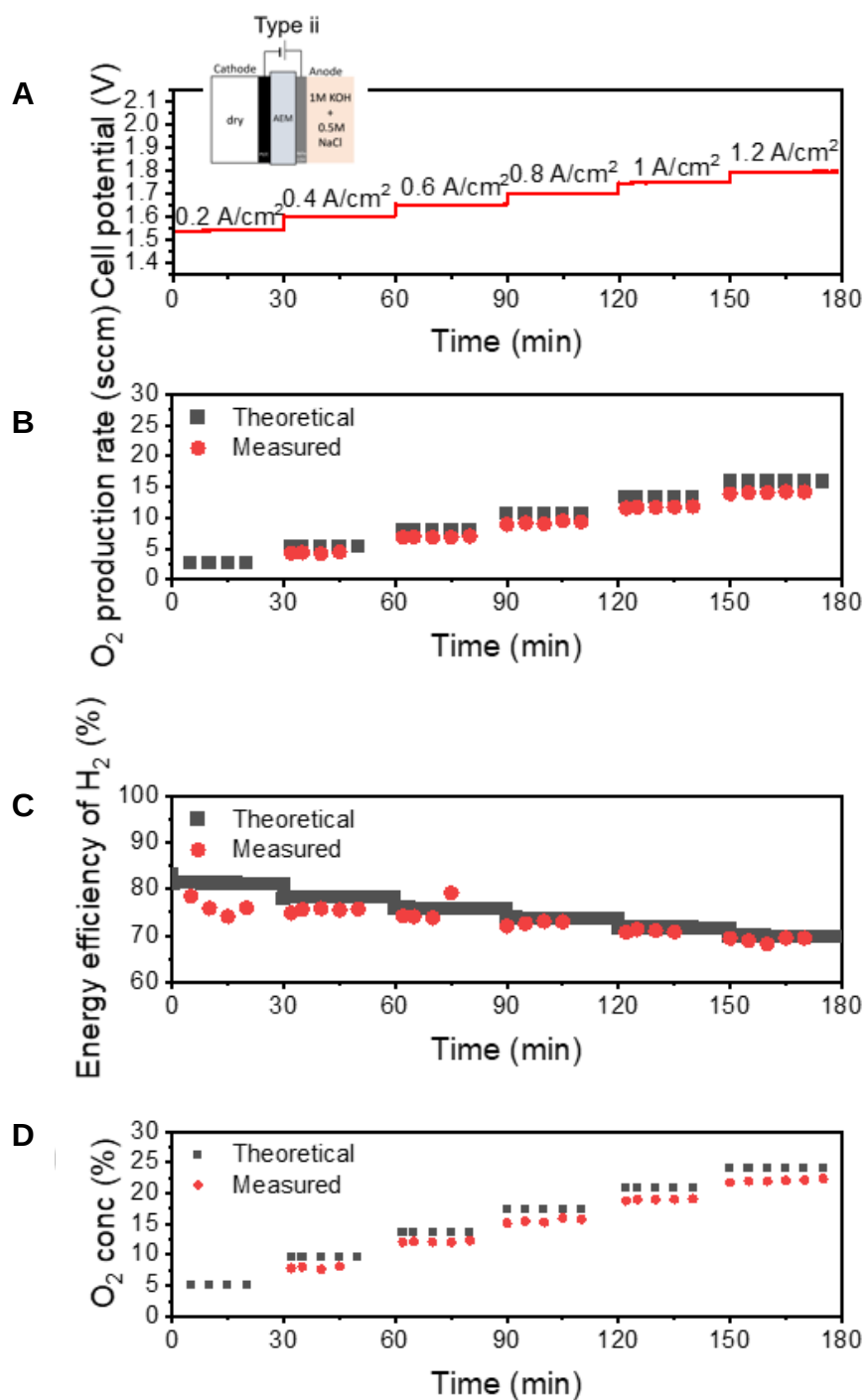


Figure 73. Stepped constant current tests with current holds of 30 min as anode catalyst with type ii electrolyte deed: asymmetric 1M KOH+0.5M NaCl at the anode and dry at the cathode with (A) cell voltage (B) O₂ production rate (C) energy efficiency of H₂ (D) O₂ gas concentration.

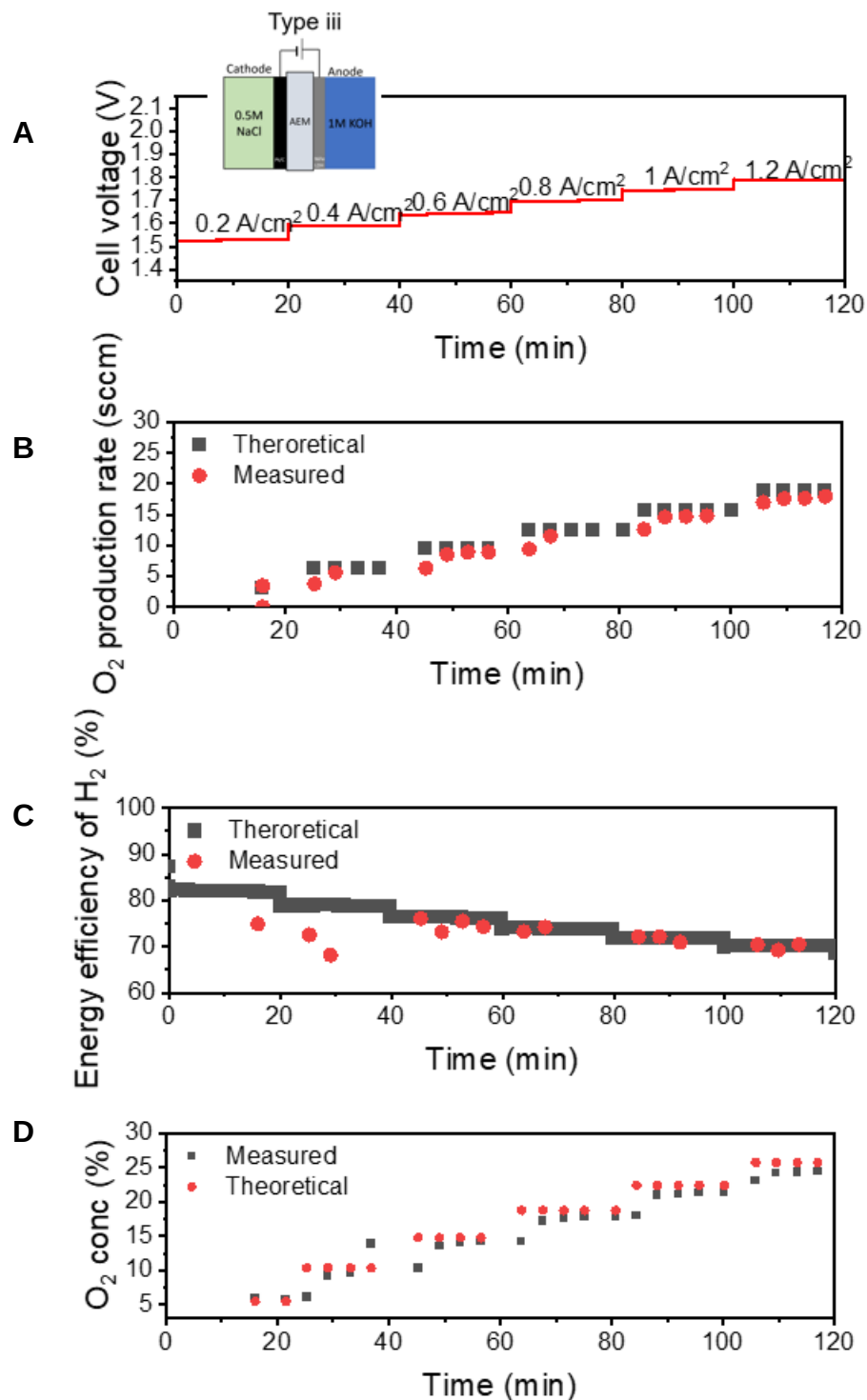


Figure 74. Stepped constant current tests with current holds of 20 min as anode catalyst with type iii electrolyte deed: asymmetric 1M KOH at the anode and 0.5M NaCl at the cathode with (A) cell voltage (B) O₂ production rate (C) energy efficiency of H₂ (D) O₂ gas concentration.

High Faradaic efficiencies were also crucial for water electrolysis. In this study, the determination of Faradaic efficiencies for O_2 played a pivotal role, which was accomplished through the application of gas chromatography (GC) during a galvanostatic test.

Figure 72, Figure 73, and Figure 74 expressed the chronopotentiometry (CP). In essence, these figures illustrate a series of tests involving varying levels of current, ranging from 0.2 A/cm^2 to 1.8 A/cm^2 of type i (water electrolysis), and 0.2 A/cm^2 to 1.2 A/cm^2 of type ii and iii (seawater electrolysis). The intriguing aspect of these experiments is that although the measured cell voltage varied for the various electrolyte feeds, the oxygen production rate levels of type i, ii, iii, are similar for all electrolytes in Figure 72B, Figure 73B, and Figure 74B. This uniformity in oxygen production rates is a strong indicator of consistent catalytic behavior across different electrolyte conditions.

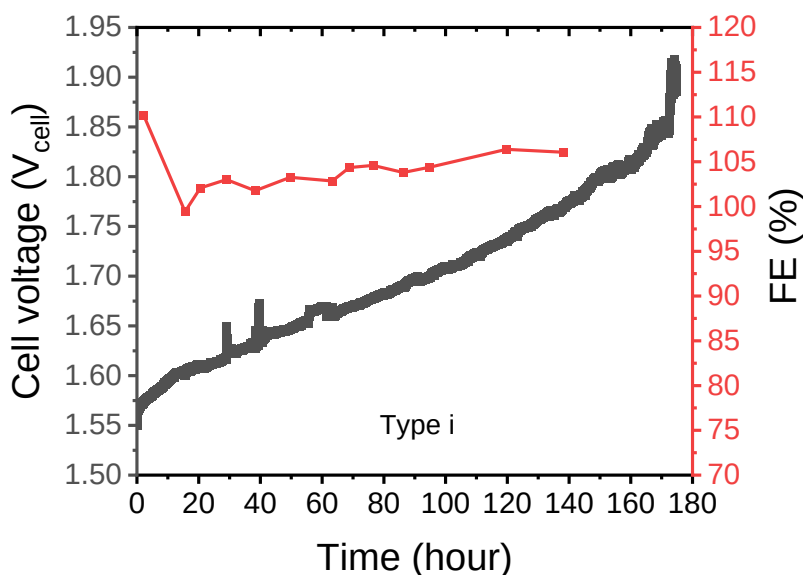


Figure 75. Stability test with Faradaic efficiency (FE) of type i at 500 mA/cm^2 .

Of significant note, all the Faradaic efficiencies for oxygen production (FE_{O_2}) remained consistently high, frequently reaching values close to 100%, which is shown in Figure 75. This intriguing result suggests that the electrolysis process primarily favored the desired oxygen production reaction over the unintended oxidation of chloride ions (Cl^-) during the electrolysis process. The fact that the Faradaic efficiencies remained high

and stable and that Cl^- oxidation was minimal was further confirmed through a separate technique known as Iodometric titration.

The stability and Faradaic efficiency (FE) of NiFe LDH as an oxygen evolution reaction (OER) electrocatalyst were extensively investigated in various electrolyte configurations with types i, ii, and iii, and shown in Figure 75, Figure 76, and Figure 77. Based on these results, it becomes evident that type iii exhibits exceptional stability along with maintaining a high FE. Type iii represents a specific electrolyte configuration in this study.

As shown in Figure 76, a notable trend emerges when observing the behavior of NiFe LDH over time. After a continuous operation of 35 hours, it is observed that at the constant current density of 500 mA/cm^2 , the potential (voltage) required for the OER process to occur begins to increase rapidly. This potential increase could be indicative of specific changes occurring at the electrode-electrolyte interface, which might influence the catalytic behavior of the material. Furthermore, the FE also becomes less in type ii. This phenomenon highlights the importance of stability and consistent performance over extended operational periods, especially when aiming for practical applications.

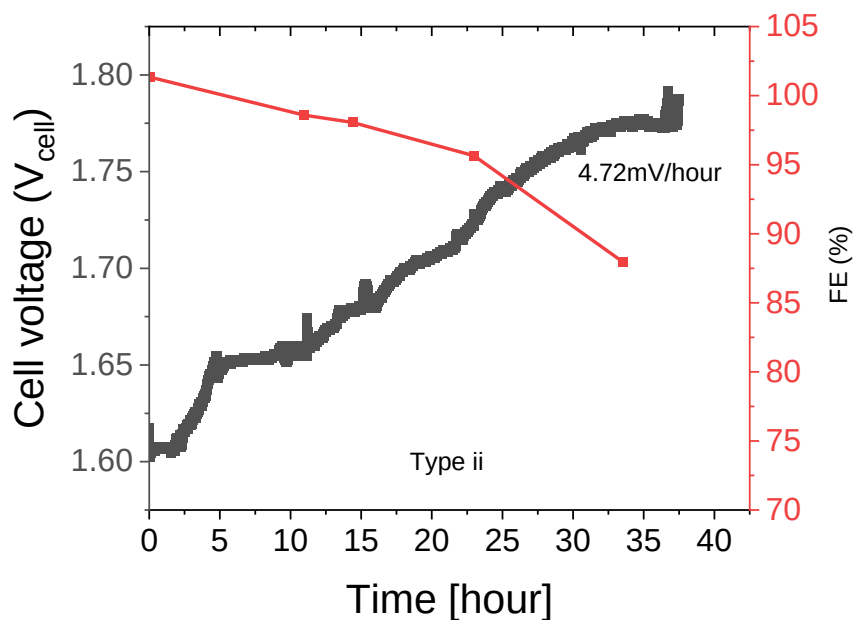


Figure 76. Stability test with Faradaic efficiency (FE) of type ii at 500 mA/cm^2 .

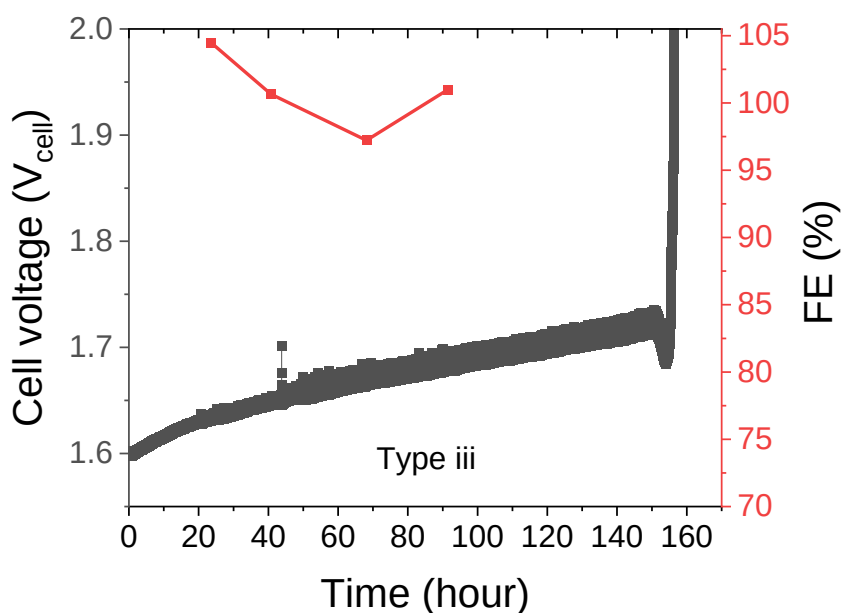


Figure 77. Stability test with Faradaic efficiency (FE) of type iii at 500 mA/cm².

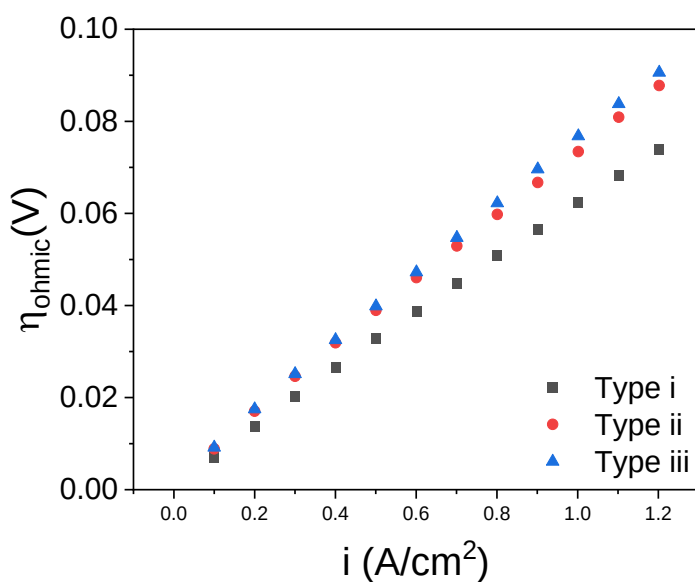


Figure 78. The ohmic loss as a function of current density.

Figure 78 provides insights into the ohmic loss in a single cell test. A distinct trend becomes evident upon analysis that in type i, the ohmic resistance is notably lower compared to type ii and iii. Additionally, the ohmic loss of types ii and iii is similar.

The determination of the ohmic overpotential (η_{ohmic}) involves measuring the ohmic resistance of AEMWEs using the x-intercept value obtained from the Nyquist plot of the EIS experiment. This measurement is conducted across a wide range of current density, with precise timing of the corresponding current values. This procedure unveils the occurrence of the iR drop or ohmic overpotential within the system. As a result, it becomes possible to generate an iR-corrected potential that holds significance for plotting the behavior of AEMWEs[195].

In type i, its lower ohmic loss suggests that the resistance encountered within the system is comparatively reduced. This can be attributed to the specific conditions of type i electrolyte configuration. The lower resistance contributes to the more efficient transfer of current within the cell, leading to improved performance and efficiency.

On the other hand, the similarity in the ohmic losses between type ii and iii electrolyte configurations indicates that the resistance encountered in these two configurations is similar. This equivalence in resistance implies that the transfer of electrical current encounters similar challenges in both type ii and iii environments, seawater.

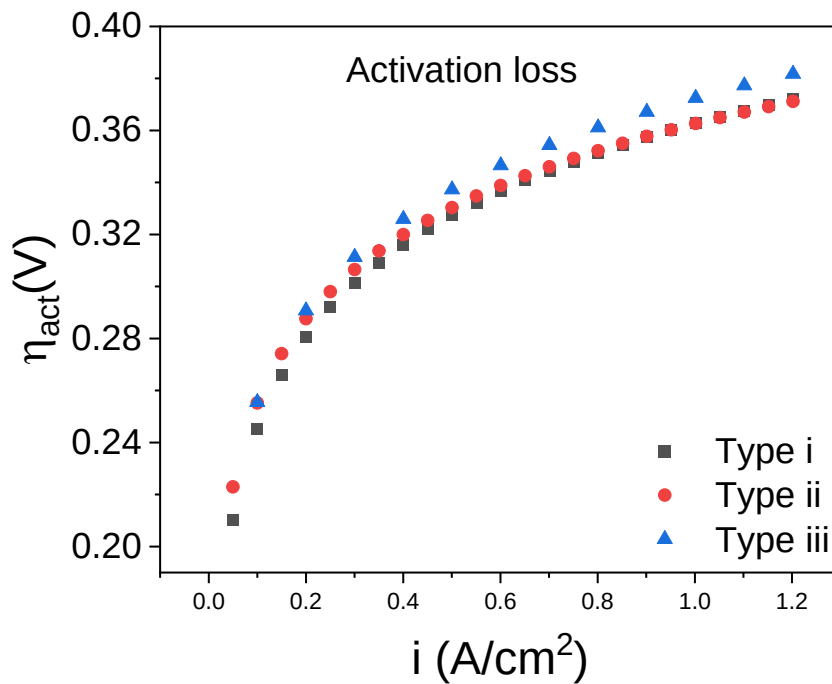


Figure 79. The activation loss as a function of current density.

The ohmic losses observed in both type ii and iii electrolyte configurations are notably higher compared to type i. This finding suggests that the electrolyte compositions of type ii and iii, which involve seawater, inherently introduce higher resistance to electrical current flow when compared to the electrolyte of type i, which likely involves freshwater.

Figure 79 presents valuable information regarding the activation loss in a single cell test. It is also named kinetic overpotentials of anion exchange membrane seawater electrolyzers. It is used to understand the additional energy required to initiate an electrochemical reaction at the electrodes [195].

The activation loss also referred to as kinetic overpotentials (η_{act}), is graphed using a linear approximation within the Tafel region. This procedure involves subtracting the obtained value from the thermodynamic equilibrium potential (E_{Nernst}) [195].

A distinct pattern emerges upon analysis that unlike ohmic loss observed in three different types of electrolyte configurations, the activation losses in type i and ii are close and notably lower than in type iii. High activation losses indicate that a significant amount of energy is required to initiate the desired electrochemical reaction, leading to a less efficient conversion of electrical energy into the desired chemical transformation. Lower activation losses, on the other hand, suggest that the reaction can proceed more readily and efficiently. The close and lower activation losses observed in type i and ii configurations, in contrast to type iii, suggest differing reaction kinetics and efficiency levels across these configurations.

Figure 80 shows concentration loss. While it's often overlooked due to its relatively small magnitude, its importance in understanding overall system efficiency cannot be underestimated. Concentration loss is a factor that contributes to the overpotential required for electrochemical reactions to proceed.

Concentration loss pertains to the drop in potential caused by the depletion or accumulation of reactants or products at the electrode-electrolyte interface. This phenomenon becomes pronounced when the rate of reaction is high, leading to a concentration gradient near the electrode surface. Figure 80 likely illustrates how

concentration loss affects the overall electrochemical performance, shedding light on its impact.

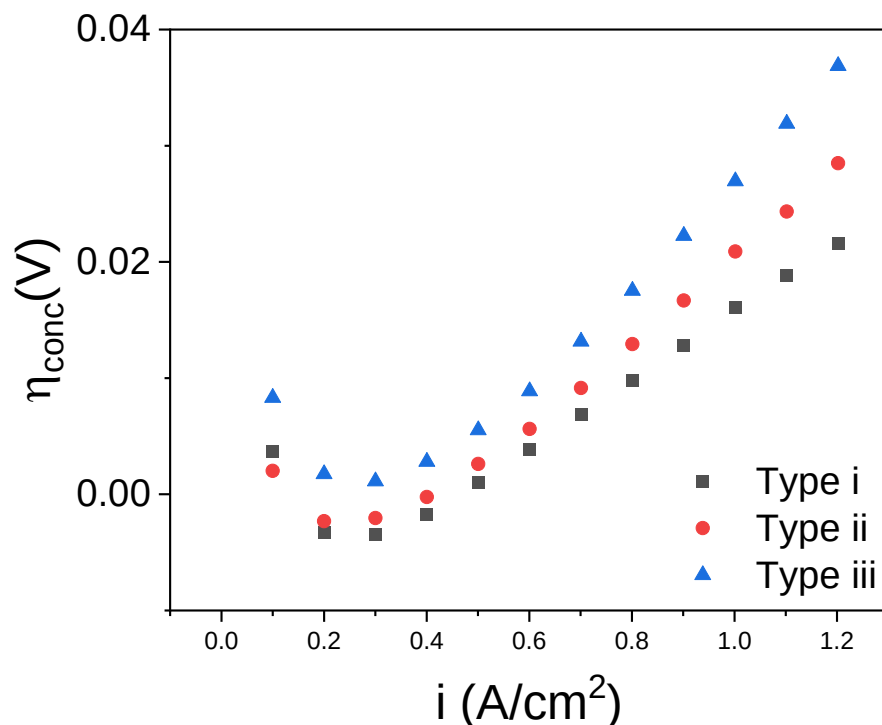


Figure 80. The concentration loss as a function of current density.

Concentration loss is an intriguing variable in the electrochemical analysis. It can be quantified by comparing the total overpotential needed for the reaction with the combined sum of the ohmic overpotential (resistance-related voltage drop) and the activation overpotential (energy barrier-related voltage drop). By subtracting the sum of these two components from the total overpotential, the concentration loss can be calculated.

While it's true that concentration loss is often considered negligible, understanding its contribution can be important in specific scenarios. When dealing with fast reaction rates or specific conditions that accentuate concentration gradients, the impact of concentration loss could be more significant than anticipated. This prompts us to critically assess whether concentration loss truly deserves to be disregarded or if there are

instances where accounting for it might offer more accurate insights into the system's behavior.

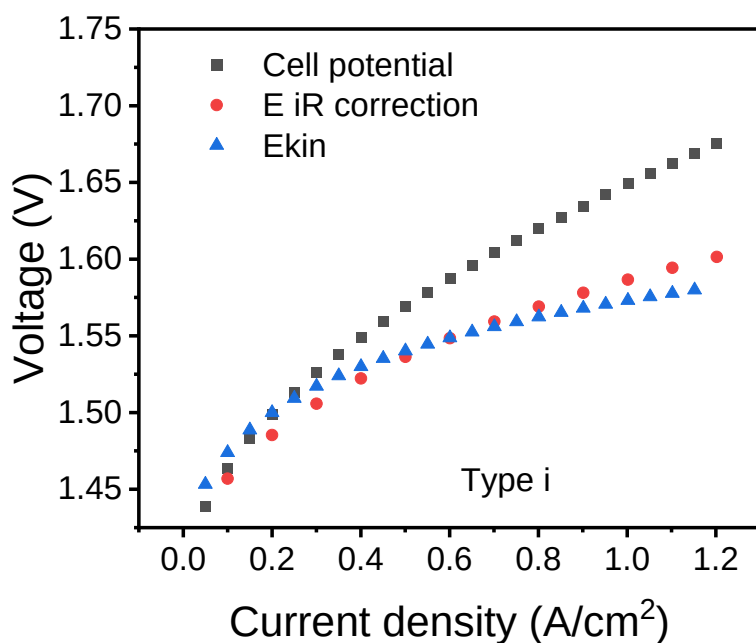


Figure 81. The cell voltage, iR correct voltage and kinetic voltage as a function of current density of type i.

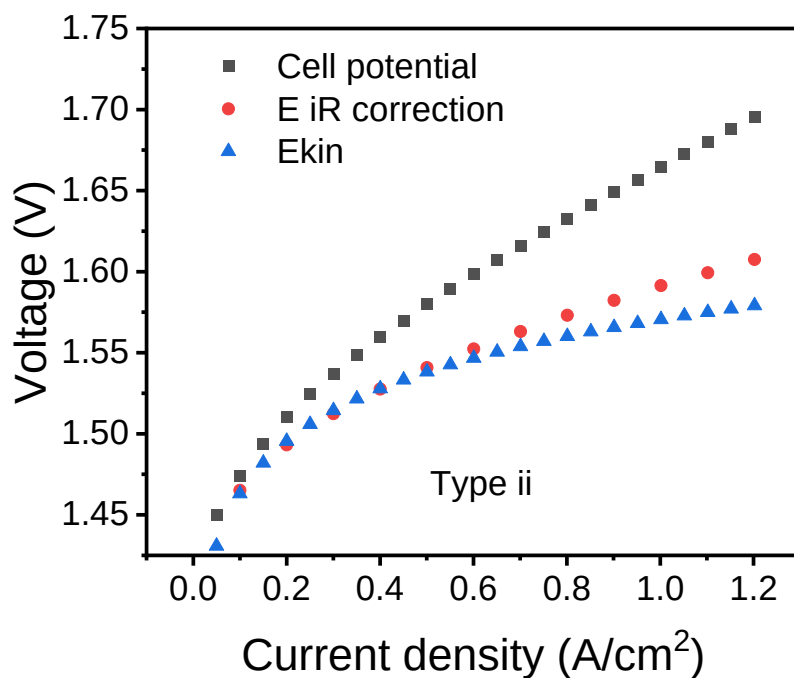


Figure 82. The cell voltage, iR correct voltage and kinetic voltage as a function of current density of type ii.

Figure 81, Figure 82, and Figure 83 provide a comparative view of each corrected polarization curve, systematically eliminating irreversible losses one by one. In particular, the term " $E_{iR\text{-corrected}}$ " corresponds to the iR -corrected potential, which accounts for the influence of ohmic losses. On the other hand, " E_{kin} " represents the kinetic potential, determined by linear approximation within the Tafel region [195].

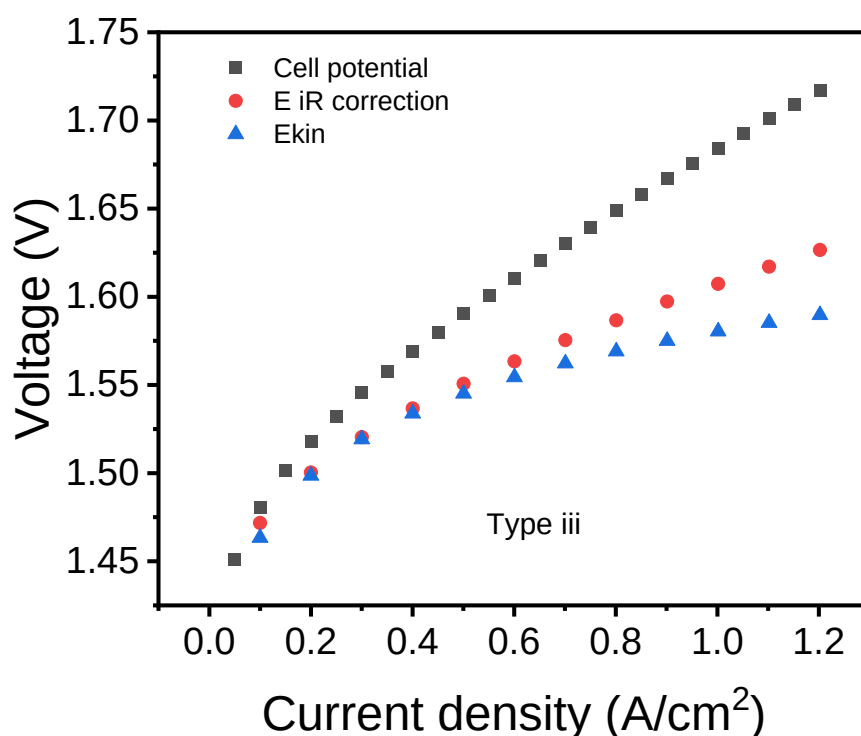


Figure 83. The cell voltage, iR correct voltage and kinetic voltage as a function of the current density of type iii.

Therefore, based on the above results, the implementation of an anion exchange membrane (AEM) in seawater electrolysis has proven to be a practical and effective method for producing hydrogen (H_2) with notably high energy efficiency. This suggests

that the process is successful in converting seawater into hydrogen fuel while optimizing the utilization of energy resources.

An intriguing discovery is made regarding the behavior of NiFe LDH (Nickel-Iron Layered Double Hydroxide), as evidenced in Figure 84. This discovery involves an interesting phenomenon termed "activity recovery." Essentially, it implies that the catalytic activity of NiFe LDH experiences a rejuvenation or resurgence under certain conditions. This phenomenon has significant implications, particularly in scenarios where energy sources such as wind and solar are irregular and intermittent. It suggests that this activity recovery could enable the efficient utilization of these intermittent energy sources, as the catalytic material's performance could potentially be sustained over periods of varying energy input. Soren's findings also align with this phenomenon, lending further credibility and significance to the observed behavior [60]. This cross-validation from another source adds weight to the importance of understanding and harnessing this activity recovery in practical applications.

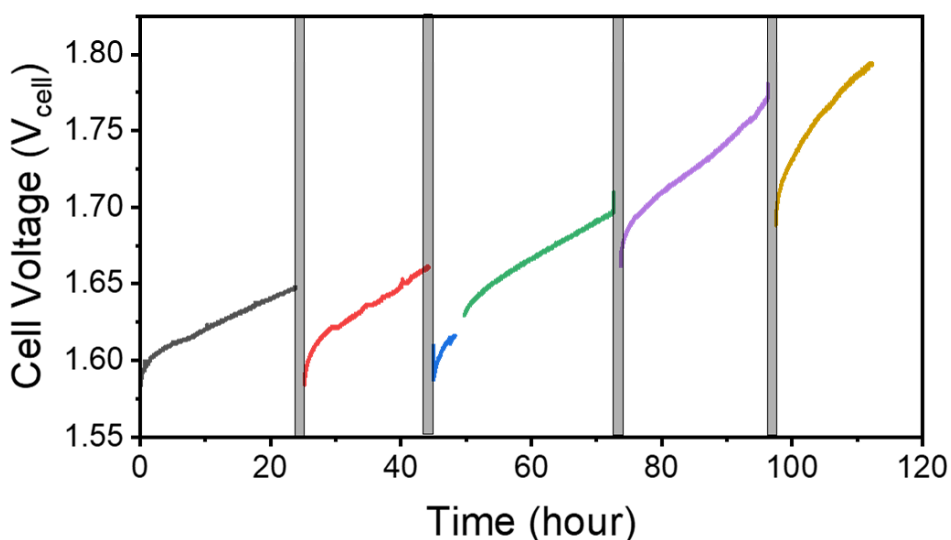


Figure 84. Intermittent stability test of NiFe LDH 75 with electrolyte feeding with type i.

Additionally, there is an interesting phenomenon. When the electrode becomes thicker, compared with previous work in this study, the current density achieves higher

levels at the same cell potential. However, the Faradaic efficiency becomes lower, falling below 100%. Faradaic efficiency refers to the effectiveness of a Faradaic process in electrochemical systems. In simple terms, it measures how well an electrochemical reaction produces the desired product, H_2 , or consumes reactants while accounting for any side reactions or losses. As illustrated in Figure 85, the system yielded specific current density values: 2.63 A/cm² in type i and 2.29 A/cm² in type ii, both attained at a cell voltage of 1.8 V with a Faradaic efficiency of around 77%. Even though the Faradaic efficiency is lower than the previous result, these findings still provide empirical evidence of the system's ability to generate hydrogen efficiently under different conditions and shed light on its performance characteristics.

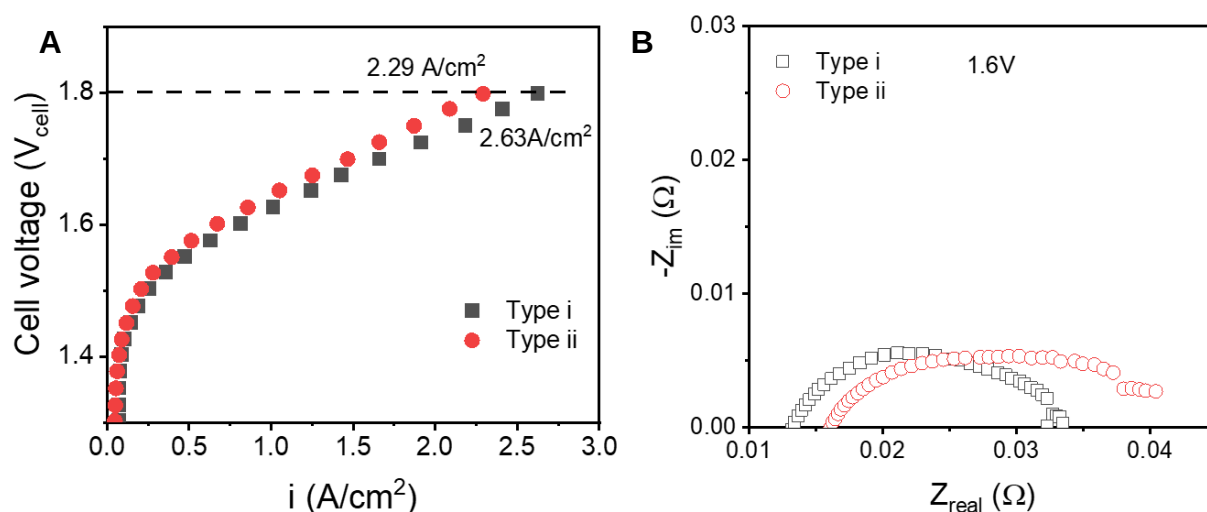


Figure 85. NiFe LDH 75 with electrolyte feeding with type i (A) polarization curves of AEM water electrolyzers at faradic efficiency about 77% (B) electrochemical impedance spectra at 1.6V.

4.4 Conclusions

In this study, first, highly active electrocatalyst NiFe LDH with different Ni/Fe ratios was investigated in half cell test. NiFe LDH 75 leads to an overpotential of 282 mV at a current density of 10mA/cm². Then, the performance of NiFe LDH with a Ni/Fe ratio of

75/25 (NiFe LDH 75) was measured in simulated seawater, achieving an overpotential of 378 mV at a current density of 10 mA/cm², which is slightly higher than that in 1M KOH. However, it is better than the previous report catalyst, IrO₂. Additionally, to identify the optimal configuration, the different asymmetric electrolyte feeds were demonstrated in seawater electrolysis. All seawater electrolysis achieved an exceptional current density of >1 A/cm² at 1.8V, and high Faradaic efficiency, close to 100%. NiFe LDH as OER electrodes still express outstanding performance, with a current density of 1.8 A/cm² achieved at 1.8V in asymmetric electrolyte feed (1M KOH and 0.5M NaCl at anode feed). However, the degradation is significant. Additionally, for electrolyte feed (1M KOH at anode and 0.5M NaCl at cathode feed), a total stability time of 140 h is attained at a current density of 500 mA/cm². The FE_{O₂} is close to 100%, with an energy conversion efficiency of 77% demonstrated, even though the measured electrode potential slightly increases with a degradation rate of 1.32 mV/h. Moreover, all configurations do not lead to Cl⁻ oxidation during electrolysis. With this technique, seawater was used in water electrolysis directly. Our NiFe LDH 75 AEM catalyst operated in simulated seawater demonstrated superior performance compared to the previously reported AEM electrolyzers conducted in 1.0 M KOH.

Chapter 5- Optimizing NiCoFeOOH on Iron Foam for Anion Exchange Membrane Water Electrolyzers

5.1 Introduction

Developing clean, renewable energy sources to replace fossil fuels has become urgent due to the global energy crisis and global warming. As a practical and clean hydrogen production method, electrochemical water splitting is different from photocatalytic water splitting, which is intermittent and depends on daytime [52,196].

As one type of electrochemical water splitting, anion exchange membrane water electrolyzers (AEMWEs) combine the advantages of both alkaline water electrolyzers (AWEs) and proton exchange membrane water electrolyzers (PEMWEs). Conventional AWEs use non-noble metal catalysts, but their performance is poor. PEMWEs have high performance and durability, but their catalysts are expensive. AEMWEs use non-noble catalysts, and their performance is better than AWEs [52].

However, due to the sluggish kinetics of the anodic oxygen evolution reaction (OER) in the alkaline media, AEMWEs suffer from low efficiency and poor stability. Therefore, it is crucial to discover a cost-effective and efficient catalyst.

Non-precious and earth-abundant transition-metal catalysts, such as Ni, Cu, Co-based catalysts, NiFe LDH, NiOOH, NiFe alloys, and so on, exhibit great activity, which can be employed as OER catalysts [52]. The effective oxyhydroxide catalyst can be synthesized via a simple fabrication process. However, FeOOH is unstable and has low electrical conductivity. Therefore, doping is used to improve performance. Trotochaud et al. [54] found that the Fe doping of NiOOH on Ni foam enhances the activity, which is due to the disorder of γ -NiOOH crystal. Yang et al. [55] improved its conductivity and stability by Co doping on FeOOH. Kim et al. [56] studied S-(Co, Fe)OOH as the catalyst to enhance the activity of (Co,Fe)OOH.

Additionally, to achieve high efficiency, recently, electrodes that combined the catalyst layer and gas diffusion layer (GDL) as AEMWE electrodes have been studied. These two separated assemblies can lower electron transfer kinetics, which could increase contact resistance. Furthermore, in conventional electrodes, an ionomer was used as a binder in the catalyst layer, which could also increase ohmic resistance.

Moreover, during the preparation process, the catalyst layer is dense and thick. This catalyst dispersion could block the active area. They could reduce mass transfer between reactants and products. Park et al. [52] demonstrated AEMWEs with excellent performance, achieving a current density of 3.6 A/cm^2 at 1.9 V and 70°C using NiFeOOH on the stainless steel paper (SUS) substrate by combining GDL and catalyst layer. Kahnamouei et al. [57] prepared S-(Fe/Ni)OOH on carbon cloth and stainless-steel substrate to improve the activity.

Here, we optimized cobalt–iron (oxy)hydroxide (CoFeOOH/FF), which was directly grown on Fe foam via the galvanic corrosion method, with different Co concentrations to achieve great activity of OER catalysts. Then, Ni-incorporated CoFeOOH on Fe foam (NiCoFeOOH/FF) with different Ni concentrations was prepared. CoNiFeOOH with a Co/Ni ratio of 20:10 (NiCoFeOOH/FF 10) exhibits outstanding OER activity, which achieves superior catalytic performance, attaining a current density of 10 mA/cm^2 at a low overpotential of 234 mV in 1.0 M KOH at room temperature in half cell test. Additionally, NiCoFeOOH/FF 10 is implemented as the anode of AEMWE, which delivers an exceptional current density of 1.6 A/cm^2 at 1.8V and 50°C .

5.2 Experimental Section

5.2.1 Materials Synthesis: CoFeOOH and CoNiFeOOH on Iron Foam

CoFeOOH and NiCoFeOOH were synthesized directly on Fe foam via the galvanic corrosion reaction [56]. First, to synthesize CoFeOOH, Fe foam (FF) is cleaned in 1M HCl for 20 minutes to remove oxides on the surface. Then, it is immediately washed with deionized water (DI water). Subsequently, FF is soaked in Co solution, which is a stoichiometric amount of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ dissolved into deionized water (DI water) at room temperature. Table 9 shows more experiment details about $\text{Co}(\text{NO}_3)_2$ solution information. After 24 hours, the obtained product is dried in a vacuum, followed by DI water washing and compressed air drying.

For CoNiFeOOH, the same process was followed, and a stoichiometric amount of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and nickel(II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were dissolved into DI

water in the reaction step. Table 10 shows the concentration information of $\text{Co}(\text{NO}_3)_2$ and $\text{Ni}(\text{NO}_3)_2$ solution.

Table 9. CoFeOOH fabrication on Fe foam with different Co concentrations

DI water [mL]	$\text{Co}(\text{NO}_3)_2$ [milli mol]	$\text{Co}(\text{NO}_3)_2$ Concentration [mM]	Time [hours]
100	1	10	24
100	2	20	48
100	2	20	24
100	3	40	24
100	8	80	24

Table 10. NiCoFeOOH fabrication on Fe foam with different Ni concentrations

DI water [mL]	$\text{Co}(\text{NO}_3)_2$ [milli mol]	$\text{Co}(\text{NO}_3)_2$ Concentration [mM]	$\text{Ni}(\text{NO}_3)_2$ Concentration [mM]	Time [hours]
100	2	20	10	24
100	2	20	30	24
100	2	20	50	24
100	2	20	70	24
100	2	20	90	24

To identify the impact of preparation time on the catalytic performance, different preparation times, including 24 hours and 48 hours, were used with a $\text{Co}(\text{NO}_3)_2$ concentration of 20 mM.

In addition, to identify the different salt effects on the catalyst structure, CoCl_2 and $\text{Co}(\text{NO}_3)_2$ were used to prepare CoFeOOH/FF 20 via the same process method as $\text{Co}(\text{NO}_3)_2$.

5.2.2 Structural Characterization

The X-ray diffraction (XRD) patterns were collected using a Rigaku MiniFlex diffractometer with a Cu K α radiation source operated at 30 kV and 15 mA (2θ : 5.1-90°, scanning speed: 1°/min). Scanning electron microscopy (SEM) was performed with a Hitachi S-3400N.

5.2.2 Electrochemical Characterization at the Half-cell Level

All electrochemical measurements at the half-cell level were carried out using a Gamry Reference 1000. The electrode on the Fe foam was tested in a three-electrode cell with 1 M KOH solution as the electrolyte. A graphite rod and Hg/HgO were used as the counter and reference electrodes, respectively. All potentials versus the reference electrode were converted into potentials versus the reversible hydrogen electrode (RHE) using the Nernst equation. The polarization curves for OER were recorded at a scan rate of 5 mV/s, and iR was corrected. The double-layer capacitance (C_{dl}) was calculated by cyclic voltammetry (CV) with different scan rates in the non-Faradaic region in 1 M KOH. The electrochemical impedance spectroscopy (EIS) was conducted at 1.63 V (vs. RHE) from 200 kHz to 10 Hz with an AC voltage of 10.0 mV. All electrochemical characterizations at the half-cell level were conducted at room temperature.

5.2.3 Evaluation of the OER Electrocatalysts at the AEM Water Electrolyzer Level

The hardware for testing AEMWE single cell was purchased from Fuel Cell Technologies, Inc. A titanium plate with the flow pattern was used as the anode flow channel, and the graphite plate with the flow pattern was used as the cathode flow channel. The gold-plated connectors were used as the current collector. The anion exchange membrane (AEM, X37-50) was purchased from Dioxide materials. The anode was NiCoFeOOH and CoFeOOH on Fe foam. The cathode ink solution was prepared by mixing Pt/C (40 wt.%, HISPEC 4000, Johnson Matthey) with a Nafion binder on carbon cloth with a microporous layer. The loading amount of HER catalysts was approximately $1.0 \pm 0.05 \text{ mg}_{\text{Pt}}/\text{cm}^2$. 1 M KOH solution was used as the electrolyte media, which was

supplied to the AEM electrolyzer at a flow rate of 5 mL/min. A hot plate and a heater embedded in the single-cell hardware were used to control the operating temperature. All electrochemical characterizations at the single-cell level were performed at 50 °C. The active electrode area of all AEM electrolyzers is 2.8 cm². The electrochemical performance of the AEM electrolyzers was evaluated using a Gamry Interface 5000 and a DC power supply (Keysight Technologies E36313A). The single-cell polarization curves were measured by recording the voltage at a constant current mode. The durability of AEM electrolyzers was tested at a constant current of 0.5 A/cm².

The AEMWE energy efficiency on a lower heating value of H₂ basis (LHV) is calculated using the following equation.

$$\text{AEMWE energy efficiency (\%)} = \frac{\Delta H_{H_2, LHV} \times n_{H_2, measured}}{I \times V} \times 100 \% \dots \text{Equation 9}$$

where $\Delta H_{H_2, LHV}$ is the lower heating value of hydrogen (241.8 kJ/mol). $n_{H_2, measured}$ is the measured hydrogen production rate (mol/s). I is the applied current (A). V is the applied voltage (V).

The ohmic overpotential (η_{ohmic}) is determined by measuring the ohmic resistance AEMWEs under various currents and timing the corresponding current, which leads to the iR drop or ohmic overpotential [195]. The iR -corrected potential of AEM single cells could be plotted. The activation loss (kinetic overpotentials) (η_{act}) is then plotted using a linear approximation in the Tafel region and subtracting from it the thermodynamic equilibrium potential (E_{Nernst}) at 50 °C. Additionally, the overpotential ascribed to mass transport can be calculated by determining the difference between total overpotential and the sum of ohmic overpotential and activation overpotential. In this work, the current density of AEM single cells is relatively low, leading to negligible mass transport overpotential. Therefore, the mass transport overpotential of AEM single cell is not considered in this work.

5.3 Results and Discussion

5.3.1 Structural Properties of NiCoFeOOH on Fe Foam

The binder-free electrodes, CoFeOOH and CoNiFeOOH on Fe foam (CoFeOOH/FF and NiCoFeOOH/FF) electrodes, were prepared via surface corrosion [62]. The Fe alloy from Fe foam could be oxidized to Fe^{2+} . Then, it could be continued oxidizing to Fe^{3+} due to O_2 from the air. After the coprecipitation in $\text{Co}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$, CoFeOOH could be prepared on the Fe form surface. More fundamental details are shown in section 2.1.3. The electrochemical reactions to prepare CoFeOOH could be shown as the following equations [94].

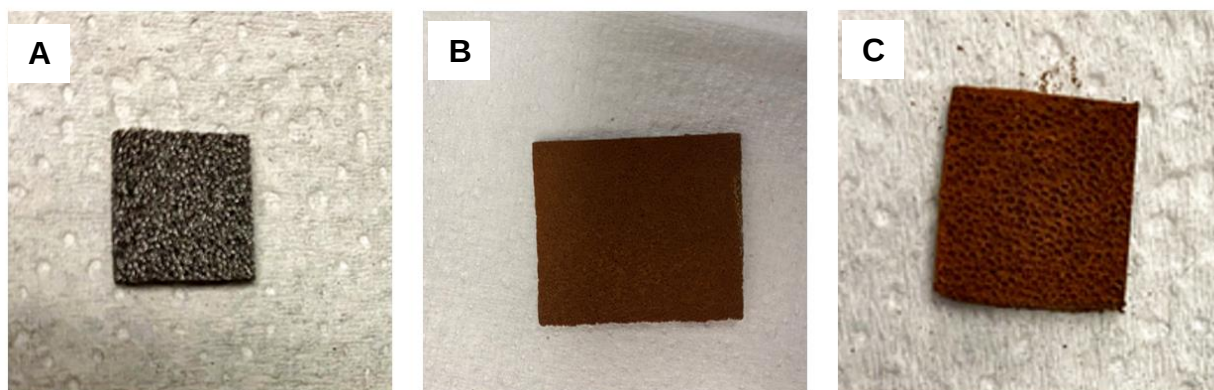
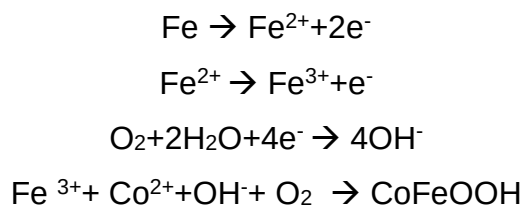


Figure 86. Electrode morphology. (A) Fe foam; (B) CoFeOOH with 20mM Co on Fe foam (C) CoNiFeOOH with 20mM Co and 10mM Ni on Fe foam

To optimize the amount of Ni and Co, CoFeOOH on Fe foam (CoFeOOH/FF) with Co of 10, 20, 40, 80 mM (abbreviation with CoFeOOH/FF 10, CoFeOOH/FF 20, CoFeOOH/FF 40, and CoFeOOH/FF 80, respectively) and CoNiFeOOH on Fe foam (NiCoFeOOH/FF) with Co 20 mM, and Ni of 10, 30, 50, 70, 90 mM (abbreviation with NiCoFeOOH/FF 10, NiCoFeOOH/FF 30, NiCoFeOOH/FF 50, NiCoFeOOH/FF 70 and NiCoFeOOH/FF 90, respectively) were synthesized, followed by electrochemical test as OER electrode. Figure 87 to Figure 95 and Figure 86 display their structural properties. These electrodes are porous. After Co and Ni doping, electrodes change color from bright silver of Fe foam to reddish catalyst, shown in Figure 86.

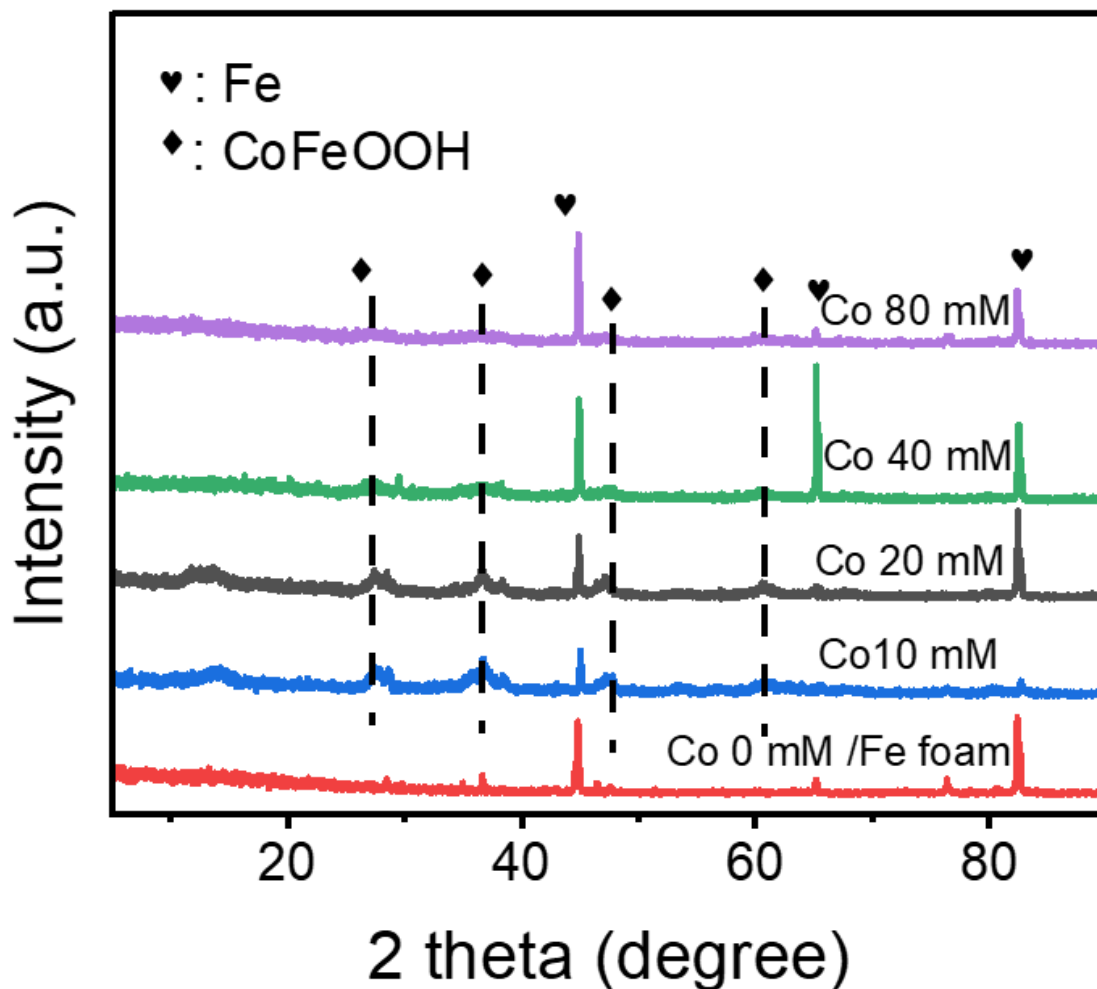


Figure 87. XRD of CoFeOOH with different Co concentrations.

First, the impact of Co concentration is discussed in this section. The crystallinity of CoFeOOH on Fe foam surface with different Co concentrations was examined using X-ray diffractometry (XRD) shown in Figure 87, which performs the crystal structure of CoFeOOH grown directly on Fe foam (FF). All samples show iron peaks at 44.5 (110), 65.3 (200), and 82.5 (211) with high intensity in the XRD patterns [56]. The peaks belonging to CoFeOOH are weak due to strong Fe peaks from the substrate. All of the CoFeOOH/FF samples show similar prominent peaks.

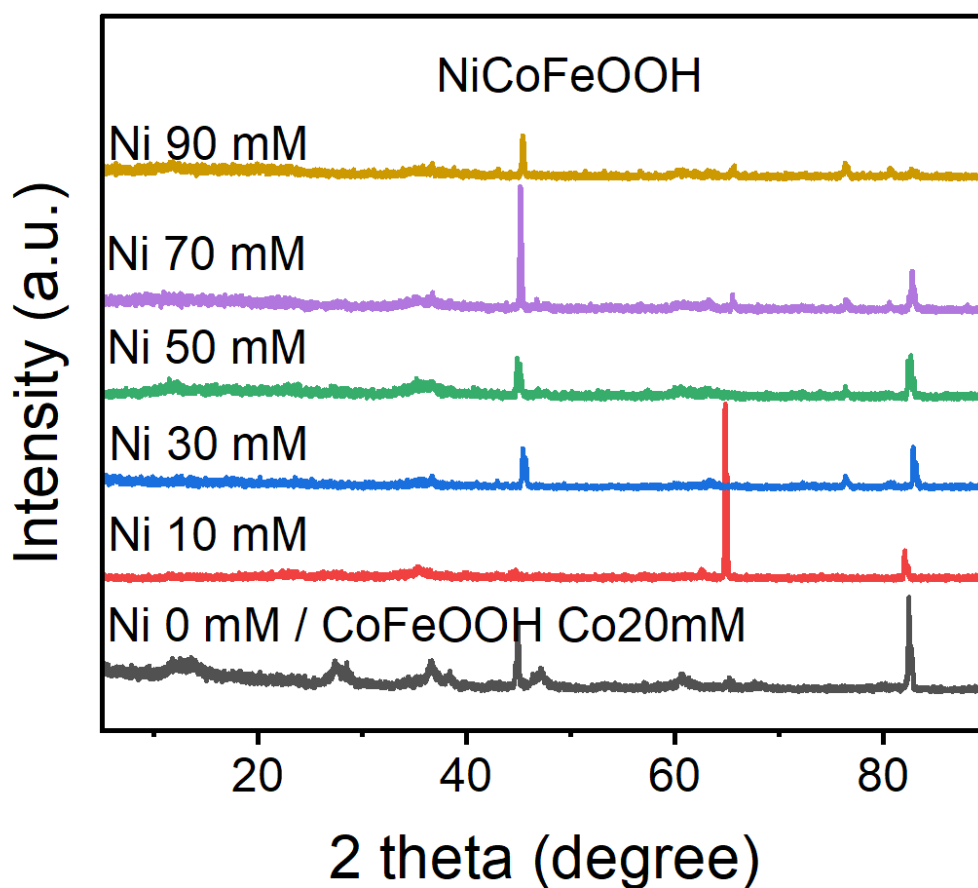


Figure 88. XRD of NiCoFeOOH with different Ni concentrations.

Then, the impact of Ni concentration is discussed. The crystallinity of NiCoFeOOH on Fe foam surface with different Ni concentration were examined using XRD, shown in Figure 88, which determines the crystal structure of NiCoFeOOH/FF grown directly on FF. All NiCoFeOOH/FF samples show similar major peaks of the OOH catalyst. Therefore, after Ni doping, no phase transformations were observed [197].

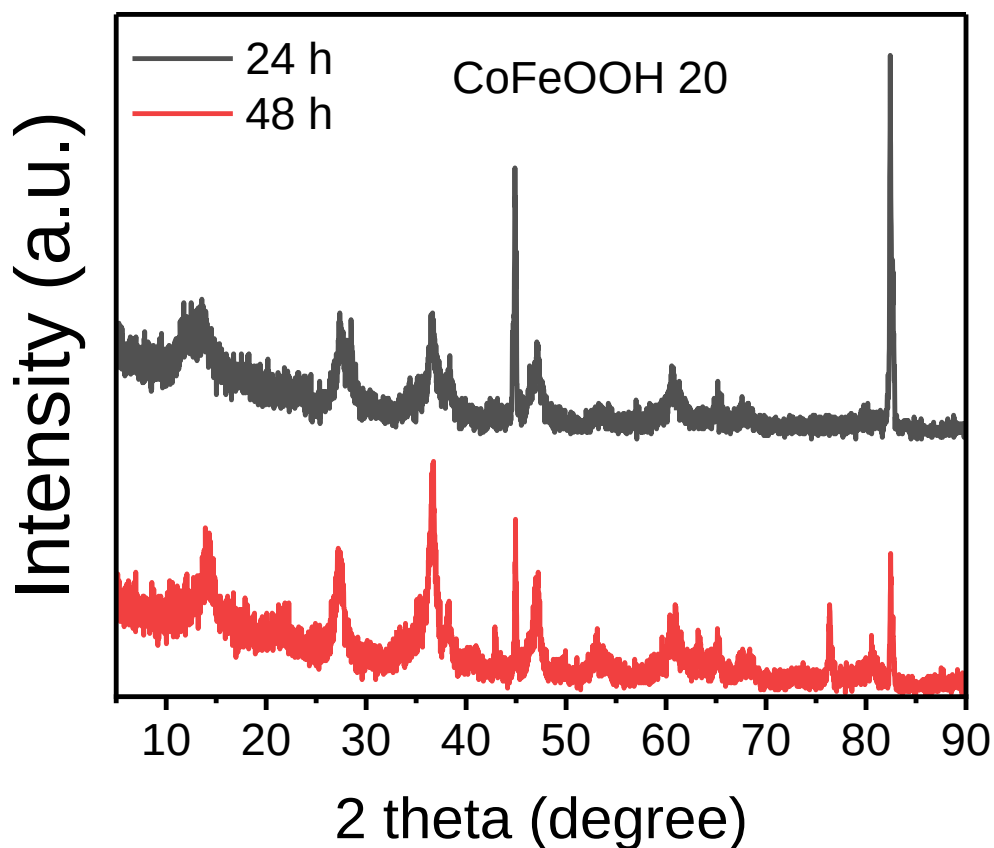


Figure 89. XRD of CoFeOOH 20 with a preparation time of 24 and 48 hours.

The influence of preparation time on the catalyst structure was made by comparing the result from 24 hours and 48 hours. These time durations were examined specifically in the context of a $\text{Co}(\text{NO}_3)_2$ concentration of 20 mM. As depicted in Figure 89, it tends to be clear that there is no discernible variance in crystal phases observed for the CoFeOOH/FF 20 catalyst.

This analysis is instrumental in elucidating the impact of corrosion time on the structural characteristics of the catalyst. By contrasting the catalysts prepared over 24 hours with those prepared over 48 hours, we aim to uncover any potential changes or developments in the material's crystal phases. In this particular instance, the focus is directed toward the CoFeOOH/FF 20 catalyst variant.

However, while no crystal phase differences were detected, there could still be other subtle structural modifications or variations in the catalyst's properties that are not

captured by crystallographic analysis alone. Therefore, further characterization techniques and studies in the next section are necessary to comprehensively understand the impact of preparation time on the overall catalyst structure and performance.

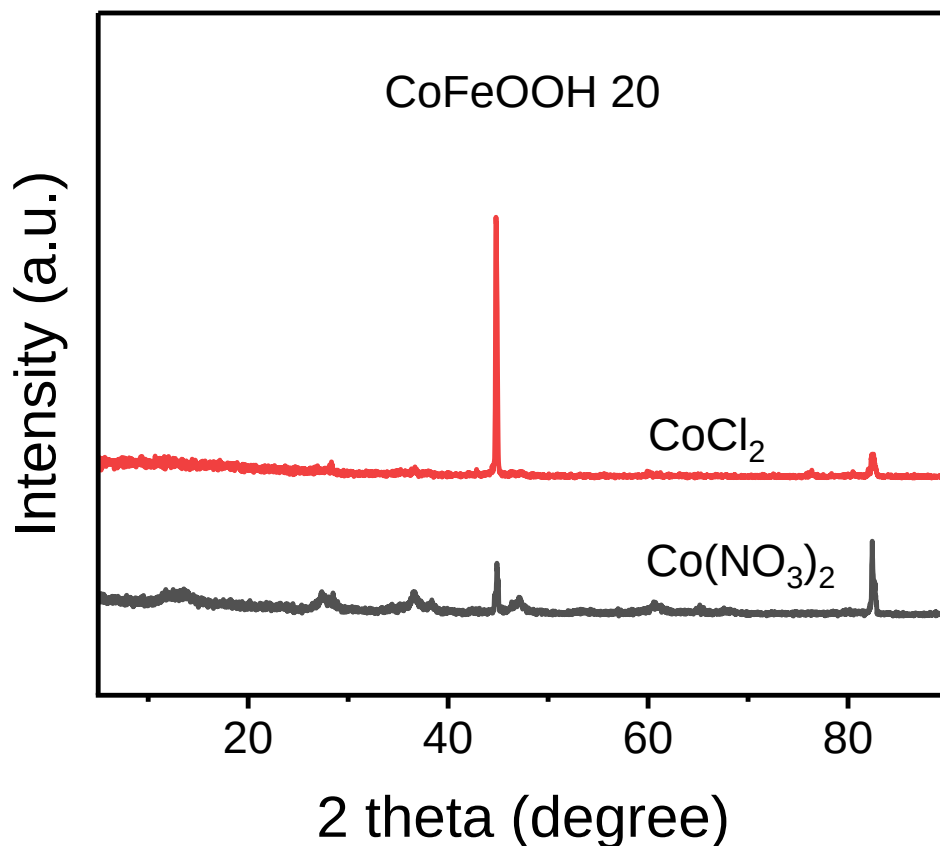


Figure 90. XRD of CoFeOOH 20 prepared with Co(NO₃)₂ and CoCl₂.

To identify the different salt effects on the catalyst structure, CoCl₂ and Co(NO₃)₂ are used to prepare CoFeOOH/FF 20. Figure 90 shows there is no crystal phase difference for CoFeOOH/FF 20. However, the peaks belonging to CoFeOOH/FF 20 are weaker in the preparation method with CoCl₂.

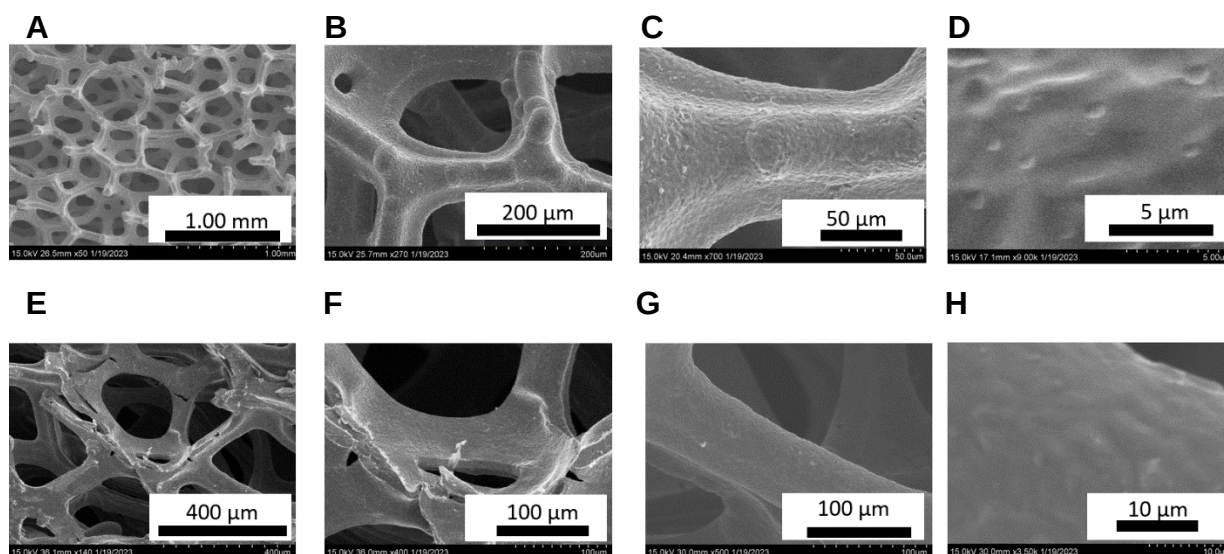


Figure 91. SEM images of pure Fe foam of (A)~(D): top view; (E)~(H): cross-section.

To deeply understand the morphological and microstructural attributes of both CoNiFeOOH/FF and CoFeOOH/FF catalysts, scanning electron microscopy (SEM) is conducted, as shown in Figure 91 to Figure 95. Notably, the Fe Foam (FF) substrate displayed a pristine and smooth surface. However, the iron foam substrate exhibits an array of perforations, manifesting as numerous cavities within the structure, with an average size of approximately 150 μm .

Upon closer examination, the bone-like section of the substrate (depicted in Figure 91D) revealed the presence of protuberances and raised features on its surface, contributing to a textured appearance. Remarkably, no discernible disparity was observed between the surface's top view and its cross-sectional perspective when scrutinized under SEM, indicating consistency in the microstructural features throughout.

Furthermore, as detailed in Figure 91 to Figure 95, the CoNiFeOOH and CoFeOOH catalysts' morphologies were thoroughly studied. These images provide a comprehensive visual representation of the catalysts' external characteristics, offering insights into their texture, structure, and features. Collectively, the SEM observations contribute valuable data for a deeper understanding of the catalysts' morphology and

microstructure, laying a foundation for subsequent discussions and analyses about their functional properties and potential applications.

After Co doping, a needle-like catalyst formed on the Fe foam surface, as shown in Figure 92, which provides abundant active sites and allows facile mass diffusion. Gao et al. [198] found similar results in that the catalyst showed karst landform features on the surface of Ni foam. Yang et al. [55] found nanorod arrays of CoFeOOH grown on iron foam. In addition, Figure 92G shows the catalyst only on the Fe foam surface by checking the cross area, and the catalyst grew uniformly on the Fe foam surface.

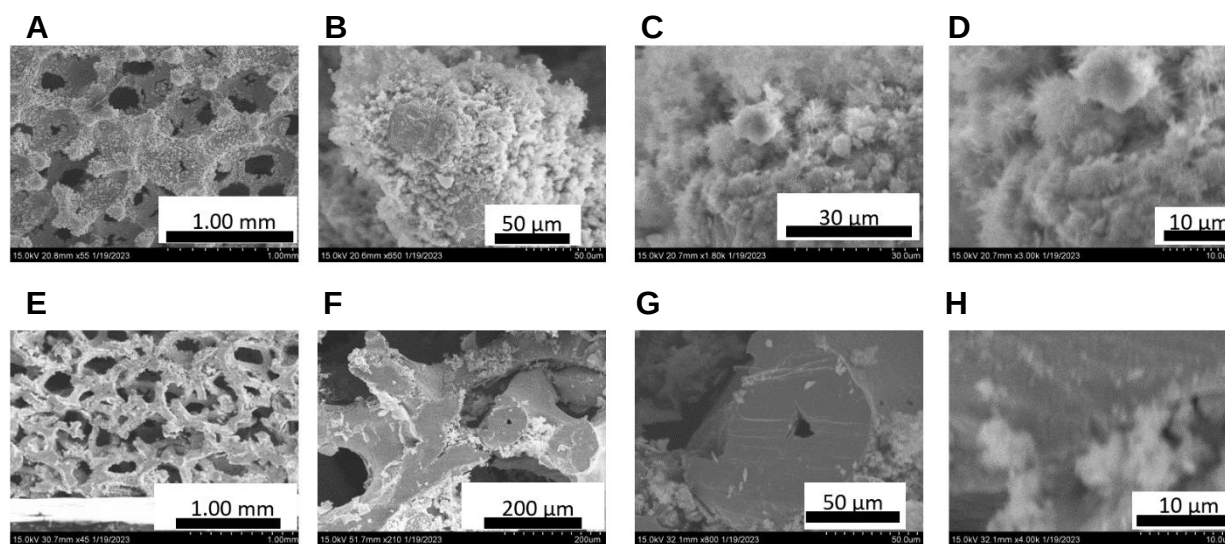


Figure 92. SEM images of CoFeOOH/FF Co 20mM on Fe foam of (A)~(D): top view; (E)~(H): cross-section.

Following the introduction of Co doping, a phenomenon analogous to that observed in CoFeOOH/FF occurs, leading to the emergence of needle-like catalyst structures on the surface of the iron foam substrate. This phenomenon is depicted in both Figure 93 and Figure 94, where the resultant needle-like structures are visually evident. Interestingly, this needle-like catalyst formation on the iron foam surface is consistent with both the NiCoFeOOH catalyst and the previously discussed CoFeOOH catalyst.

Intriguingly, the NiCoFeOOH catalyst, when grown on the iron foam substrate, also demonstrates a propensity for uniform growth solely on the surface of the iron foam. This

uniform growth is depicted in the images captured in Figure 93 and Figure 94, reinforcing the notion that the catalyst's arrangement and distribution remain relatively consistent despite the introduction of nickel doping.

Moreover, the morphological characteristics of CoFeOOH and NiCoFeOOH catalysts is striking similar. Both catalyst variants exhibit comparable morphologies, emphasizing a consistent structural resemblance between the two, despite the incorporation of nickel. This visual alignment underscores the potential for similar catalytic properties and behavior between these closely related catalyst compositions, thereby laying the foundation for further investigation into their comparative performance in catalytic applications.

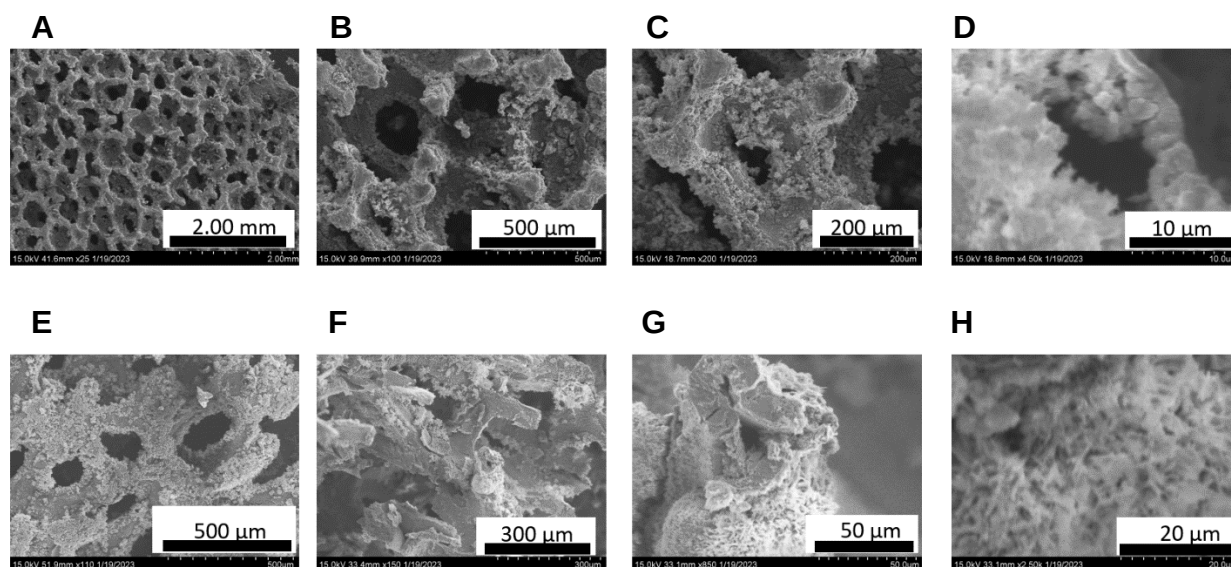


Figure 93. SEM images of NiCoFeOOH/FF Ni10 mM and Co 20 mM on Fe foam of (A)~(D): top view; (E)~(H): cross-section

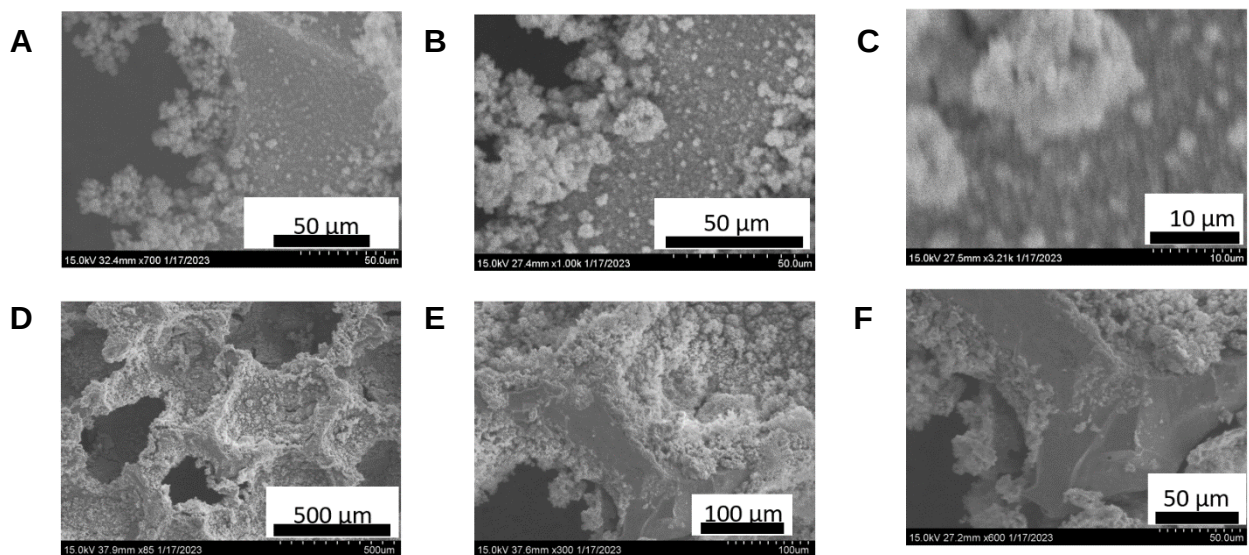


Figure 94. SEM images of NiCoFeOOH/FF Ni 50 mM of (A)~(C): top view; (D)~(F): cross-section view.

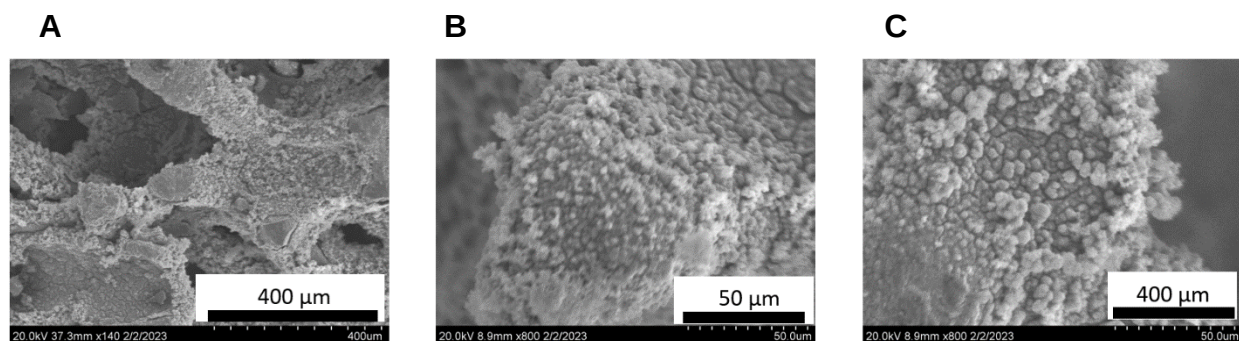


Figure 95. (A)~(C): SEM images of NiCoFeOOH/FF Ni 30 mM after the electric test.

Figure 95 shows the morphological evolution of NiCoFeOOH/FF 30 after the electrochemical test. Evidently, post-testing, observable changes are discernible in the needle-like components of the catalyst. These alterations manifest as potential dissolution within the electrolytic environment or a transformation into spherical structures, as evidenced by the modified morphology. This visual depiction underscores the dynamic nature of the catalyst's constituents under the influence of the electrochemical conditions, substantiating the dynamic interplay between the catalyst's composition and the surrounding electrolyte during the testing process.

5.3.2 Electrochemical Properties of NiCoFeOOH on Fe Foam at the Half-cell Level

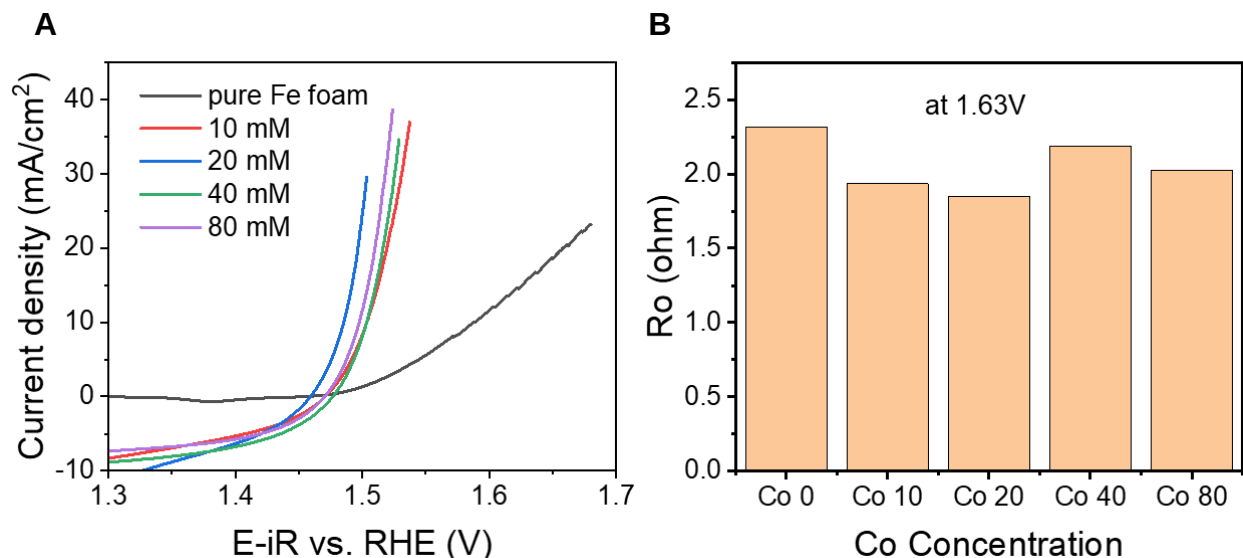


Figure 96. Electrochemical performance in different Co concentrations of CoFeOOH at half-cell, which is evaluated in 1.0M KOH solution at room temperature. (A) Ohmic resistance-corrected polarization curves and (B) Electrochemical impedance spectra

First, the impact of Co concentration is discussed in this section. The OER electrocatalytic activity of the unified electrode, CoFeOOH/FF with different Co concentration, are examined with linear sweep voltammetry (LSV) in 1.0 M KOH, using a graphite rod and Hg/HgO electrode as the counter and reference electrodes, respectively, shown in Figure 96. Electrochemical tests were performed to confirm the effect of Co. Due to the influence on the OER catalytic activity of the concentration of Co, optimizations of CoFeOOH/FF were reported in Figure 96. Figure 96A shows LSV curves of CoFeOOH/FF with different Co concentrations. Figure 96B shows the ohmic resistance of CoFeOOH/FF with different Co concentrations. CoFeOOH/FF 20 achieves better performance, with an overpotential of 248 mV demonstrated at a current density of 10 mA/cm² and 320 mV at 150 mA/cm², which is much lower than that of other concentrations shown in Figure 97. Therefore, after the Co dopant, the OER electrocatalytic activity is enhanced.

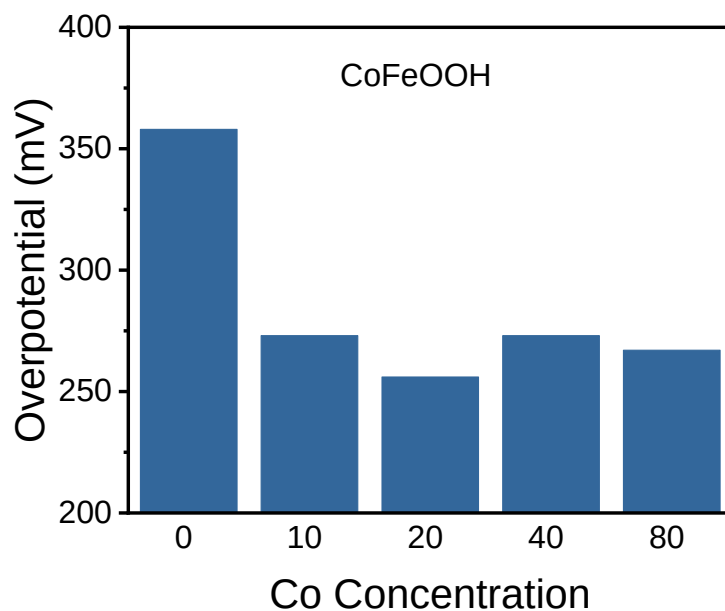


Figure 97. Overpotential of half-cell test at a current density of 10mA/cm² using CoFeOOH prepared with different Co concentrations.

Furthermore, it is noteworthy that among the variations tested, the CoFeOOH catalyst containing 20 mM exhibits the most exceptional performance in the half-cell tests. To delve into the influence of the preparation time factor, two distinct durations, stirring 24 and 48 hours, were selected for examination. This investigation of preparation time's impact is presented in Figure 98, where the effect on the Linear Sweep Voltammetry (LSV) curves is displayed.

Interestingly, the results displayed in Figure 98 indicate that the performance of the catalyst remains relatively unchanged despite the extension of the reaction time by two-fold. This finding implies that the observed catalytic behavior is not substantially affected by longer preparation times within this examined range. This consistency in performance underscores the robustness of the CoFeOOH catalyst and suggests that its catalytic activity is well-established and not strongly influenced by minor variations in the preparation duration.

Supporting this conclusion, the X-ray Diffraction (XRD) analysis, as depicted in Figure 89, also reinforces the notion of preparation time's limited impact. This figure illustrates that the phase composition remains consistent across different preparation

times, indicating that the crystalline structure of the catalyst isn't primarily affected by variations in reaction duration. Collectively, these findings highlight the stability and reliability of the CoFeOOH catalyst's performance, suggesting that its effectiveness is more strongly linked to its inherent properties rather than the specific preparation times investigated in this study.

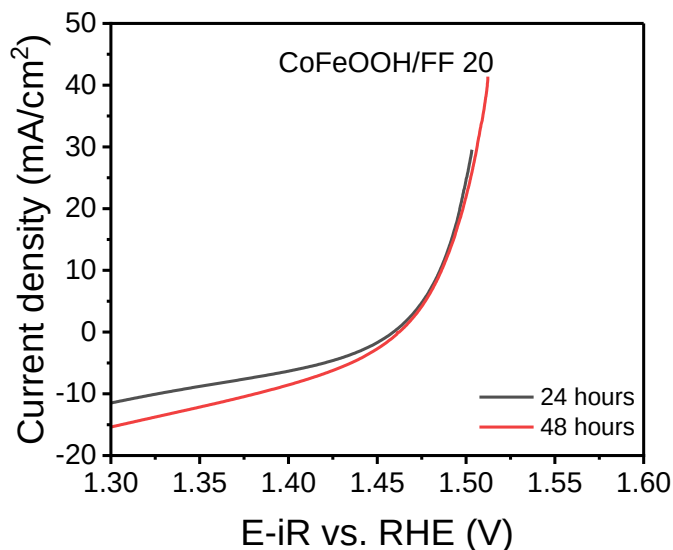


Figure 98. Ohmic resistance-corrected polarization cures of CoFeOOH on Fe foam with different preparation periods.

To investigate the Co salt effects on the catalyst structure, CoCl_2 and $\text{Co}(\text{NO}_3)_2$ are used to prepare CoFeOOH/FF 20. Figure 99 shows the LSV cures. It is clear that the performance of the method with $\text{Co}(\text{NO}_3)_2$ is much better than the method with CoCl_2 , as shown in Figure 100. As mentioned in XRD, Figure 90, CoCl_2 shows weak CoFeOOH/FF peaks. There may be less catalyst on Fe foam with CoCl_2 . Therefore, in preparation, if CoCl_2 is used to replace $\text{Co}(\text{NiO}_3)$, the CoFeOOH peaks in XRD are not significant, and the performance is also worse.

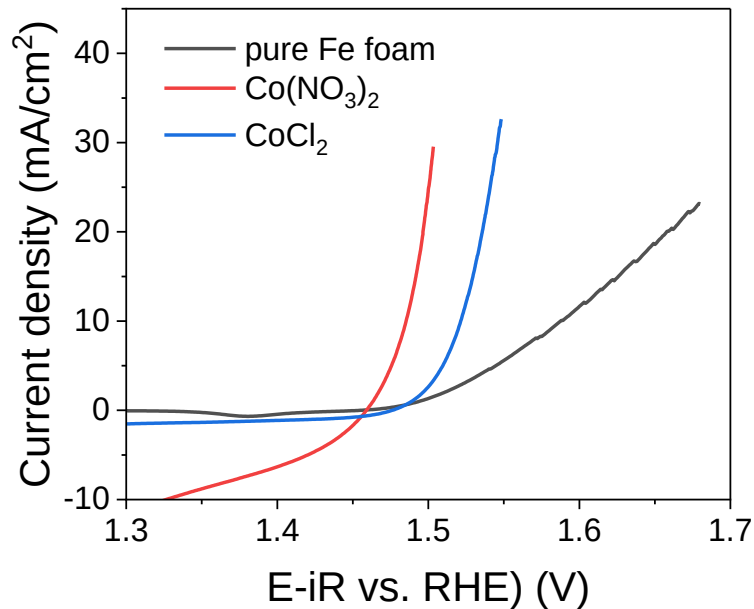


Figure 99. Ohmic resistance-corrected polarization curves of CoFeOOH FF with different salts fabrication.

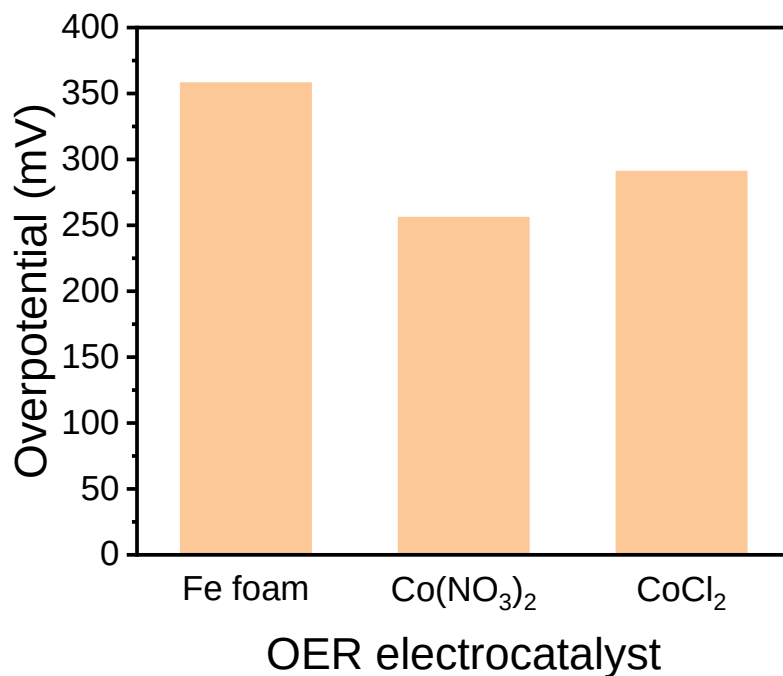


Figure 100. Overpotential of half-cell test with different Co salts at a current density of 10mA/cm².

Figure 101 illustrates the stability plot of CoFeOOH/FF 20 as an OER electrochemical catalyst. Impressively, the catalyst maintains its activity consistently for a remarkable duration of up to 80 hours. This highlights the robust and enduring catalytic performance of CoFeOOH/FF 20 in driving the Oxygen Evolution Reaction. The observed stability over this prolonged time span emphasizes the potential of this catalyst for sustained and efficient performance in OER applications. Such endurance in the catalytic of CoFeOOH/FF 20 underscores the catalytic promise, making it a compelling candidate for prolonged stability in OER catalyst.

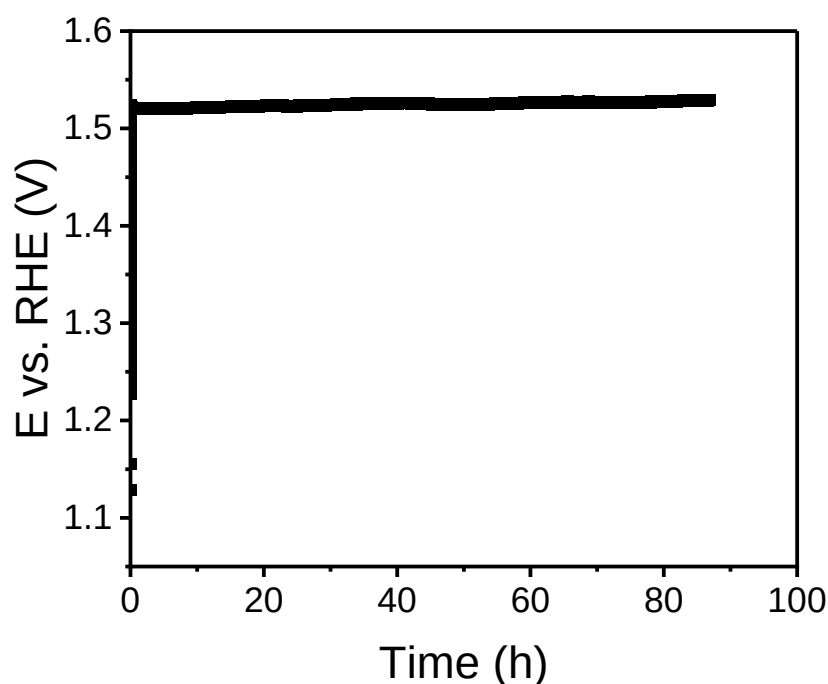


Figure 101. Stability testing of sample CoNiOOH 20 mM at room temperature and a current density of 10mA/cm².

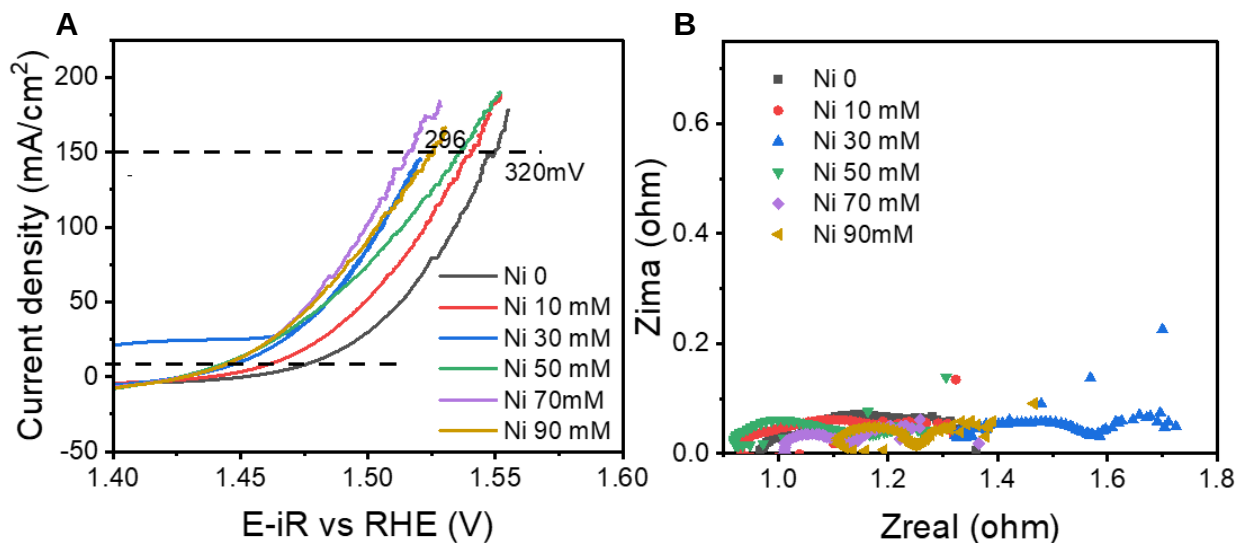


Figure 102. Electrochemical performance of NiCoFeOOH with different Ni concentrations at half-cell, which are evaluated in 1.0M KOH solution at room temperature. (A) Ohmic resistance-corrected polarization curves and (B) Electrochemical impedance spectra.

Then, the impact of Ni concentration is discussed in this section. The OER electrocatalytic activity of the unified electrode, NiCoFeOOH/FF with different Ni concentrations, was also examined with linear sweep voltammetry (LSV) in 1.0 M KOH at room temperature, using a graphite rod and Hg/HgO electrode as the counter and reference electrodes, respectively, as shown in Figure 102. Electrochemical tests were performed to confirm the effect of Ni. Due to the influence on the OER catalytic activity of the Ni concentration, optimizations of NiCoFeOOH/FF were reported in Figure 102. Figure 102A shows LSV curves of NiCoFeOOH/FF with different Ni concentrations. As shown in Figure 104, NiCoFeOOH/FF 10 leads to better performance, and the measured overpotential, 234 mV at 10 mA/cm² and 310 mV at 150 mA/cm², which is much lower than others. Therefore, after Ni dopant, the OER electrocatalytic activity is enhanced. As shown in Figure 103, the ohmic resistance of NiCoFeOOH/FF 30 is high.

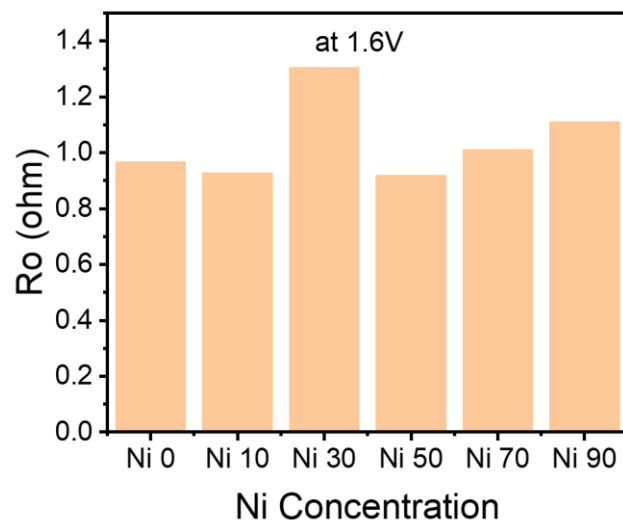


Figure 103. Ohmic resistance, R_o , of NiCoFeOOH at different Ni concentrations.

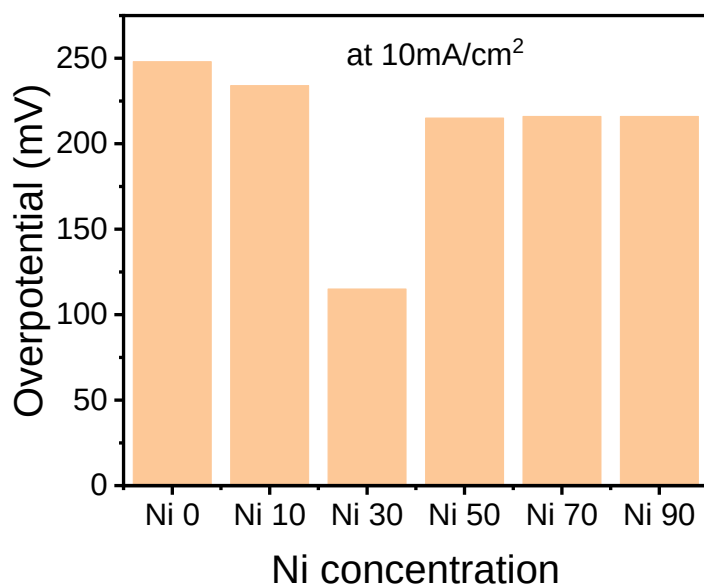


Figure 104. Potential at 10mA/cm² of half-cell test with NiCoFeOOH with different Ni contractions.

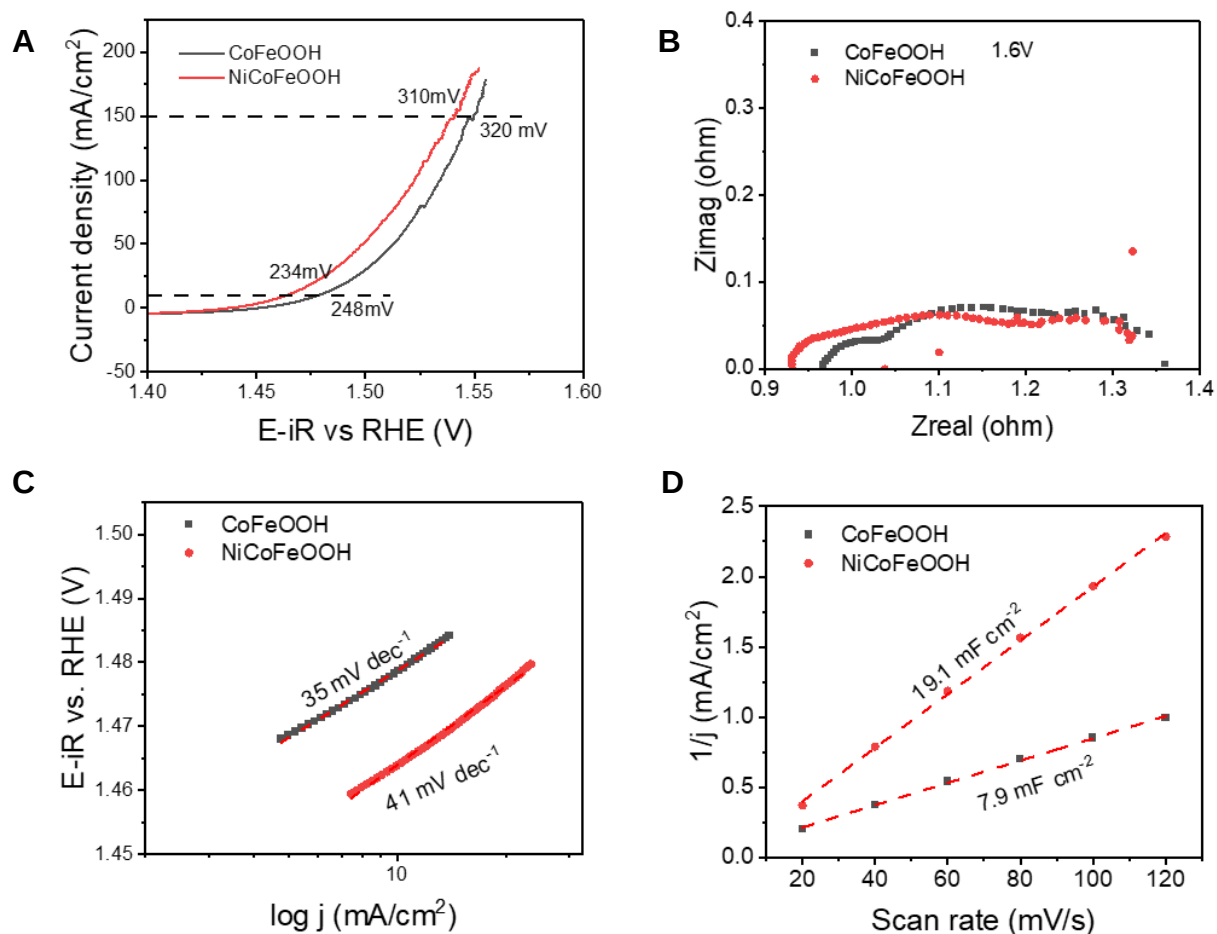


Figure 105. Electrochemical performance at the half-cell level, which is evaluated in 1.0 M KOH solution at room temperature. (A) Ohmic resistance-corrected polarization curves of CoFeOOH with Co 20mM on Fe foam, CoNiFeOOH with Co 20mM, and Ni 10mM on Fe foam. (B) Electrochemical impedance spectra CoFeOOH with Co 20mM on Fe foam, CoNiFeOOH with Co 20mM, and Ni 10mM on Fe foam at 1.6 V. (C) Tafel plots of CoFeOOH with Co 20mM on Fe foam, and CoNiFeOOH with Co 20mM, and Ni 10mM on Fe foam.

The OER electrocatalytic activity of the unified electrode, CoFeOOH/FF 20, and NiCoFeOOH/FF10 were examined with linear sweep voltammetry (LSV) in 1.0 M KOH, using a graphite rod and Hg/HgO electrode as the counter and reference electrodes, respectively, shown in Figure 105. Electrochemical tests were performed to confirm the effect of Ni. Due to the influence on the OER catalytic activity of the concentration of Ni

and Co, optimizations of CoFeOOH/FF, and NiCoFeOOH/FF are reported in Figure 96 and Figure 102. Figure 105A shows LSV curves of CoFeOOH/FF 20, and NiCoFeOOH/FF 10. NiCoFeOOH/FF 10 achieves better performance, and the measured overpotential, 234 mV at 10 mA/cm² and 310mV at 150 mA/cm², is much lower than that of CoFeOOH/FF 20, 248 mV at 10 mA/cm² and 320 mV at 150 mA/cm², shown in Figure 106. Therefore, after Ni dopant, the OER electrocatalytic activity is enhanced.

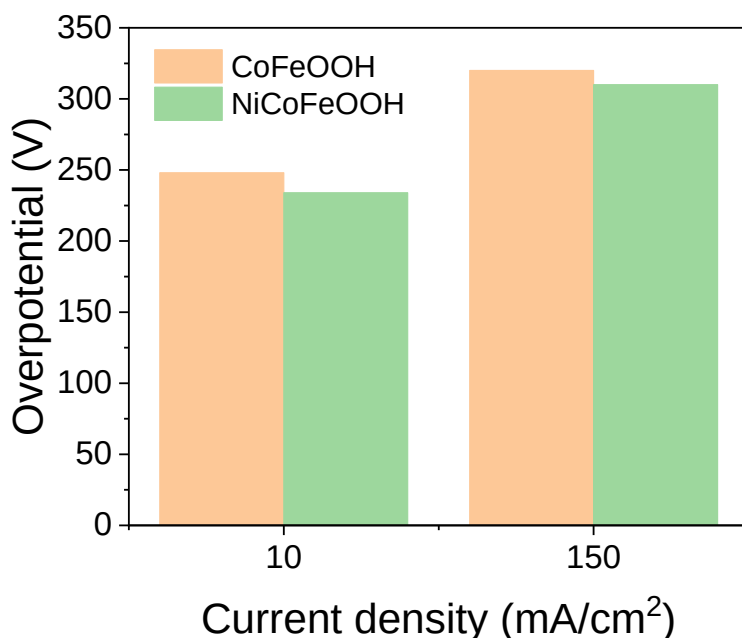


Figure 106. Overpotential at the current density of 10 mA/cm² and 150 mA/cm².

Figure 105C shows the Tafel plot of the catalysts, which is essential to report the kinetics of the OER catalysts. Tafel slopes observed for CoFeOOH/FF 20 and NiCoFeOOH/FF 10 are 35 and 41 mV dec⁻¹, and the rate-determining step (RDS) is the second electron transfer [56]. Electrochemical impedance spectroscopy (EIS) expresses the electron charge transfer properties. They are measured at 1.6 V to evaluate the ohmic resistance (Rs) and the charge transfer resistance (Rct) shown in Figure 105B.

The electrochemically active surface area (ECSA) is another critical parameter to evaluate the electrocatalytic activity using the double-layer capacitance (Cdl) determined by cyclic voltammetry in the non-Faradaic region, as shown in Figure 105D.

NiCoFeOOH/FF 10 shows a large ECSA, 19.1 mF/cm², indicating an efficient electrocatalyst caused abundant active sites [56].

5.2.3 Electrochemical performance of the AEM Water Electrolyzers Level with NiCoFeOOH on Fe Foam as the OER Catalysts

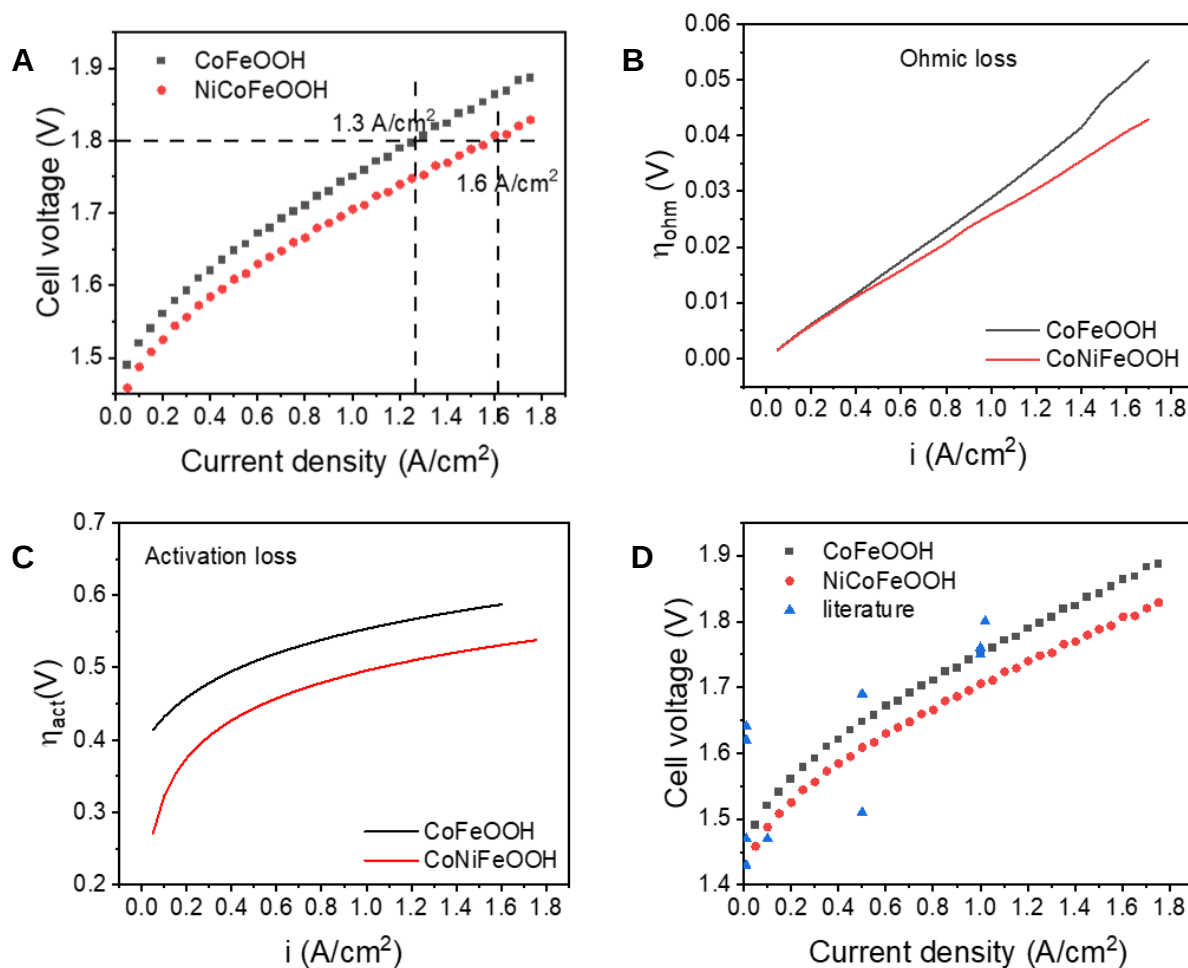


Figure 107. OER performance at the AEMWE single-cell level and 50 °C. (A) Polarization curves of AEM water electrolyzers with CoFeOOH with Co 20mM on Fe foam, CoNiFeOOH with Co 20mM, and Ni 10mM on Fe foam as the OER electrocatalysts. (B) The ohmic loss is a function of current density. (C) The activation loss is a function of current density. (D) performance comparison of

AEMWE demonstrated in this work with the oxyhydroxide catalyst literature [52,56,102,199–208].

To accomplish efficient application in AEMWE, extensive OOH-based OER electrocatalysts have been developed [61]. However, less unified electrodes with iron foam as a substrate have been done to apply NiCoFeOOH/FF as the OER catalysts for AEMWEs. As a result, previous work on NiCoFeOOH/FF OER electrocatalysts hasn't been thoroughly examined on a single-cell scale. In this paper, lab-scale AEM water electrolyzer single-cells were built and tested to assess the high performance of the NiCoFeOOH/FF. Figure 107 displays the performance of the AEMWE with the binder-free unified electrode.

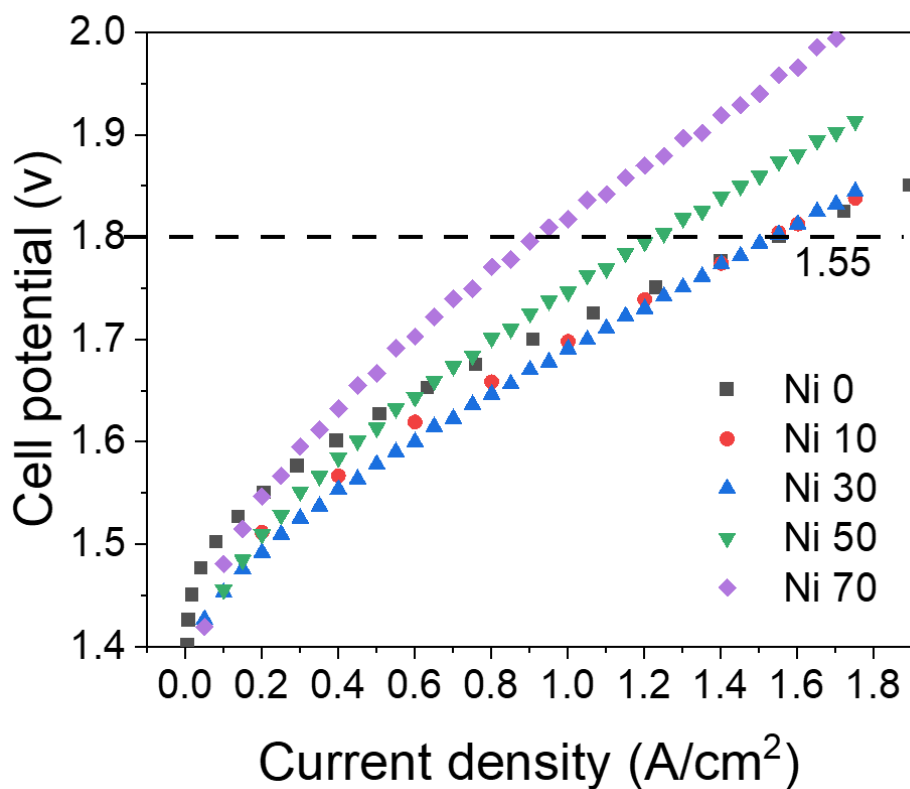


Figure 108. NiCoFeOOH with different Ni concentrations on Fe foam at 60°C.

NiCoFeOOH/FF 10 is significantly better than CoFeOOH/FF 20 as an OER catalyst in AEMWE. The optimization of NiCoFeOOH/FF is investigated. First, Unified electrodes with different Ni:Co ratios were prepared using precursor solutions with Ni:Co

atomic ratios of 1:2, 3:2, 5:2, and 7:2, and polarization curves are shown in Figure 108. Among the AEMWEs, NiCoFeOOH 10, which is prepared from the precursor solution with a Ni:Co ratio of 1:2, showed the highest AEMWE performance. Figure 102 indicates that the catalytic activity followed the order $70 > 30 > 90 > 50 > 10 > 0$ in the half cell. As all the components of the unified electrodes were the same except for the catalyst, the changes in ohmic resistance were related to the electrical conductivity of the catalyst layer.

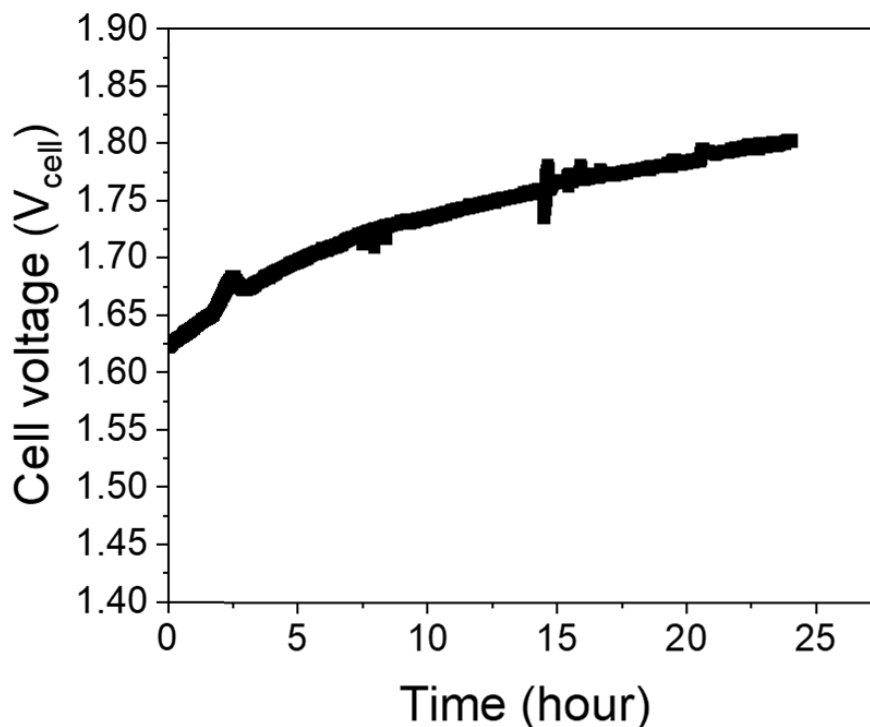


Figure 109. Stability of CoFeOOH with 20 mM at 0.5mA/cm² at 60°C.

Finally, the optimized unified electrode of CoFeOOH/FF 20 and NiCoFeOOH/FF 10 in AEMWE are examined to investigate the effect of Ni-doped on CoFeOOH/FF. Figure 107 A shows the polarization curves. After Ni doped, the unified AEMWE of NiCoFeOOH/FF 10 exhibited higher performance enhancement compared to the AEMWE of CoFeOOH/FF 20, as presented in Figure 107 A. In addition, the ohmic resistance and activation loss of the unified AEMWE of NiCoFeOOH/FF 10 is lower than that of the CoFeOOH/FF 20 shown in Figure 107 B and Figure 107 C. These results imply that the application of Ni-doped in the unified electrode in AEMWE improved electron

transport and catalyst utilization. Figure 107 D shows our work is outstanding in the literature.

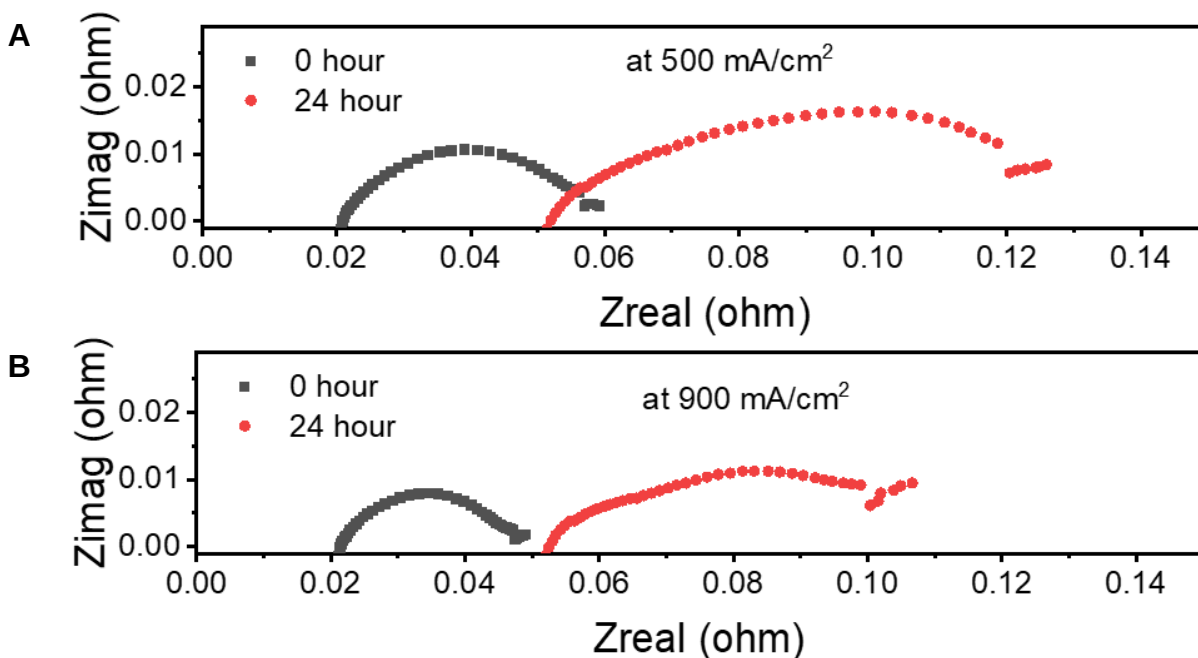


Figure 110. Stability of CoFeOOH with 20 mM at 60°C at the current density of (A) 500 mA/cm²; (B) 900 mA/cm².

In addition, Figure 109 provides a comprehensive insight into the stability aspect of CoFeOOH with 20 mM Co in 25 hours. This graphical representation offers a visual depiction of how the material's properties evolve, shedding light on its durability and performance under these specific conditions.

Additionally, Figure 110 presents an Electrochemical Impedance Spectroscopy (EIS) analysis, showcasing a comparative study of the initial state and the state after the 24-hour stability test. The EIS data offers a profound understanding of the electrical behavior of the system. Notably, both the ohmic resistance and polarization resistance exhibit noticeable changes following the stability test. The ohmic resistance, which represents the material's inherent resistance to the flow of current, as well as the polarization resistance, indicating the hindrance encountered during electrochemical reactions, display an evident increase.

This observed change in resistance values underscores a significant shift in the material's electrochemical behavior, potentially attributed to various factors such as structural changes, ion concentration alterations, or surface modifications.

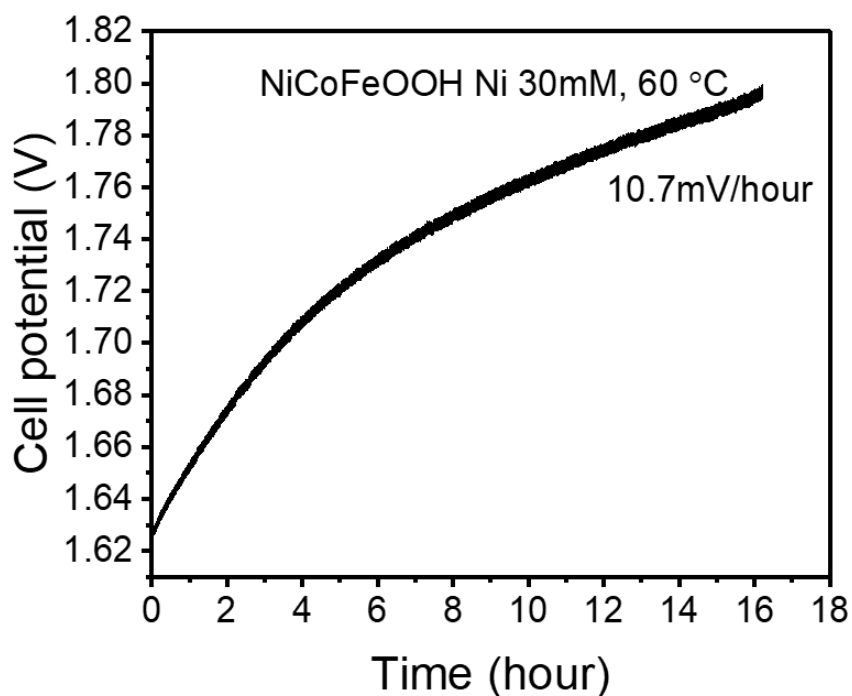


Figure 111. Stability of NiCoFeOOH/FF Ni 30 mM at 60°C and a current density of 0.5 A/cm².

Presented in Figure 111 is a detailed account of the stability evaluation conducted on NiCoFeOOH 30mM at 60°C. This experimental setup offers a comparative perspective to the earlier findings observed in CoFeOOH 20. In a manner akin to the CoFeOOH 20mM case, the cell potential of NiCoFeOOH 30 undergoes a swift and discernible increase, noticeable after 16 hours. This intriguing parallelism in the behavior of the two materials implies the presence of common underlying factors influencing their stability under these conditions.

It is worth highlighting the significance of pursuing enhanced stability in future studies. The substantial and rapid increase in cell potential observed after a relatively short period underscores the need for further investigations and development strategies to enhance the stability of these materials. Such improvements are pivotal not only for

optimizing the performance of these materials but also for unlocking their full potential in practical applications. By delving deeper into the root causes of this observed instability and devising strategies to mitigate it, researchers can pave the way for more reliable and durable materials, ultimately contributing to advancements in various fields where these materials find utility.

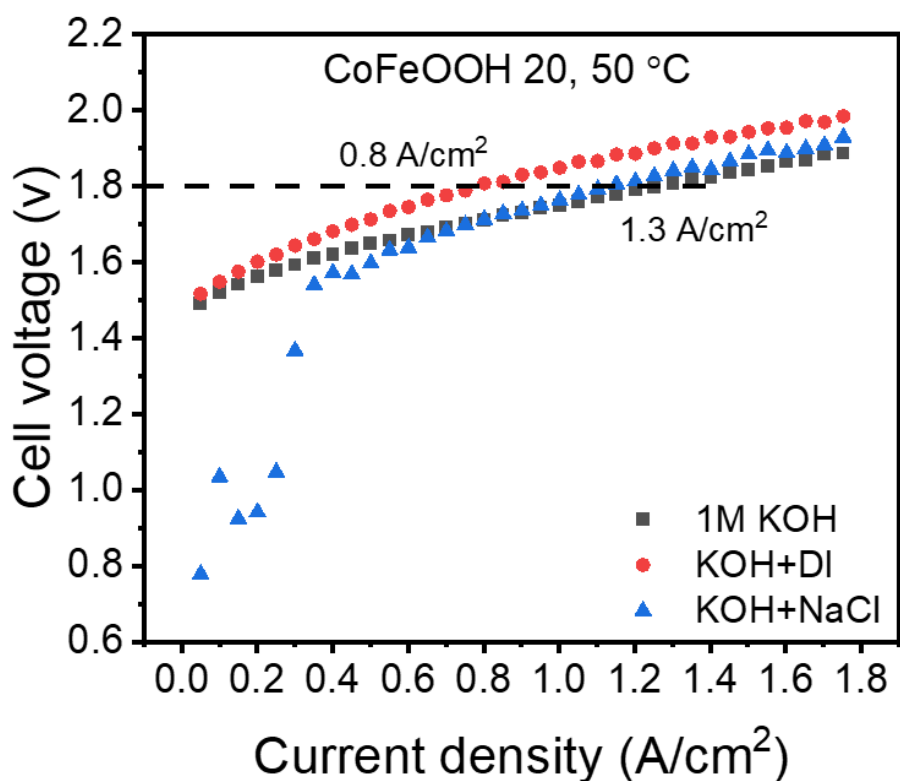


Figure 112. Polarization curves of CoFeOOH/FF Co 20 mM at 50°C in different electrolytes.

Figure 112 provides a comprehensive overview of the performance characteristics of the material under investigation across various electrolyte environments. Specifically, three distinct electrolyte conditions are examined: 1M KOH, 1M KOH+DI, and 1 M KOH +0.5 M NaCl. Each electrolyte environment presents a unique set of conditions that can impact the material's behavior. In 1M KOH+DI and 1 M KOH+0.5 M NaCl, the performance becomes worse.

5.4 Conclusions

In this work, a three-dimensional unified, binder-free electrode consisting of a CoFeOOH and NiCoFeOOH layer electrodeposited on Fe foam was prepared as an AEMWE anode to express the superior catalytic performance of the AEMWE in 1M KOH at 50 °C. NiCoFeOOH shows a high electrochemical surface area. The unified electrode showed higher catalytic. When applied in a practical AEMWE, the unified NiCoFeOOH electrode in AEMWE exhibited an outstanding current density performance of 1.6 A/cm² at 1.8 V, which is among the highest performances to be reported for an AEMWE with an electrocatalyst for the oxygen evolution reaction to date. This enhancement is due to its structural characteristics, which improve catalyst utilization, electrical conductivity, and durability. Therefore, the unified electrodes can be considered as an alternative to conventional electrodes to enhance the performance and durability of AEMWEs and thereby reduce their cost.

Chapter 6 – Perovskites of $\text{La}_x\text{Ce}_{1-x}\text{Ni}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ as Oxygen Evolution Electrocatalysts for High-Performance Anion Exchange Membrane Water Electrolyzers

6.1 Introduction

Developing clean sustainable energy sources has become essential in response to the prevailing global energy crisis and the escalating concerns surrounding climate change. As one type of renewable energy, hydrogen is used to replace fossil energy and stands as a compelling solution. Currently, electrochemical water splitting, a widely recognized technique, is a frequently employed method of generating hydrogen.

As one type of electrochemical water splitting, anion exchange membrane water electrolyzers (AEMWEs) combines the advantages of both alkaline water electrolyzers (AWEs) and proton exchange membrane water electrolyzers (PEMWEs). From alkaline water electrolyzers, AEMWEs inherit the capacity to operate under mild operating conditions, negating the need for expensive catalysts and materials commonly associated with harsher conditions. Additionally, the concept of an anion exchange membrane allows for the utilization of non-precious metal catalysts, further enhancing cost-effectiveness. On the other hand, compared with proton exchange membrane water electrolyzers, AEMWEs can function with a remarkable degree of precision facilitated by the selective permeability of anion exchange membranes. This complex control over ion transport translates to heightened efficiency and improved safety.

However, despite the notable advantages associated with anion exchange membrane water electrolyzers (AEMWEs), their performance is hindered by significant limitations. AEMWEs suffer from low efficiency and poor hydrogen production rate, hampered by the sluggish kinetics of the anodic oxygen evolution reaction (OER) in the alkaline media. Therefore, it is crucial to discover an efficient catalyst to increase the reaction rate.

As we mentioned in section 1.5.2, perovskite is one type of low-cost, efficient OER electrocatalyst. Extensive perovskites have been demonstrated to increase OER performance. For example, Wang et al. demonstrated $\text{LaNi}_{0.8}\text{Fe}_{0.2}\text{O}_3$ that displayed an overpotential of 302 mV at a current density of 10 mA/cm² [41]. Zhao et al. employed

$\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (LSCF) as the OER electrocatalyst, achieving an overpotential of 248mV at a current density of 10 mA/cm² [42]. Zhu et al. recognized that the hybridization between the RP phase, and the perovskite phase increased the metal-oxygen covalency, which accelerated the oxygen-ion diffusion and improved the OER activity [43].

In this chapter, we demonstrated a comprehensive exploration of a set of unique perovskite oxides known as $\text{La}_x\text{Ce}_{1-x}\text{Ni}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ ($\text{L}_x\text{C}_{1-x}\text{N}_y\text{F}_{1-y}$). Notably, the composition of $\text{L}_{0.9}\text{C}_{0.1}\text{N}_{0.7}\text{F}_{0.3}$ exhibits outstanding OER activity, which achieves a current density of 10mA/cm² at an impressively low overpotential of 338mV in 1.0 M KOH electrolyte at room temperature. Both $\text{L}_{0.9}\text{C}_{0.1}\text{N}_{0.7}\text{F}_{0.3}$ and $\text{L}_{0.9}\text{C}_{0.1}\text{N}_1$ show interest behavior during the stability test, which the performance exhibits an encouraging upward trend during the initial phases of the stability test.

6.2 Experimental Section

6.2.1 Materials Synthesis: Perovskites

$\text{La}_x\text{Ce}_{1-x}\text{Ni}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ ($\text{L}_x\text{C}_{1-x}\text{N}_y\text{F}_{1-y}$) were synthesized via the Pechini process [141,142]. A stoichiometry amount of La_2O_3 was first dissolved into a nitric acid solution to make $\text{La}(\text{NO}_3)_3$ solution, which was then mixed with cerium (III) nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), nickel(II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), and iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$). This mixture was then dissolved in deionized water (DI water). The chelating agents (i.e., citric acid and ethylenediaminetetraacetic acid (EDTA)) with chelating agents-to-total metal cations ratios (C/I ratios) of 1.5 were added to the above solution, which was followed by the addition of ammonium hydroxide solution to adjust its pH to ~10. This solution was subsequently stirred at 250 °C until a gel was formed. The gel was immediately transferred to a drying oven at 175 °C for 24 h, followed by calcination under air at 900 °C for three hours to obtain the as-fired perovskites.

6.2.2 Structural Characterization

The X-ray diffraction (XRD) patterns of all samples were collected using a Rigaku MiniFlex diffractometer with a Cu K α radiation source operated at 30 kV and 15 mA (2 θ : 5.1-90°, scanning speed: 1°/min).

6.2.3 Electrochemical Characterization at the Half-cell Level

All electrochemical measurements at the half-cell level were carried out using a Gamry Reference 1100. A rotating disk electrode (RDE, 0.198 cm² of glassy carbon electrode, Pine instrument) was tested in a three-electrode cell with 1 M KOH solution as the electrolyte. A graphite rod and Hg/HgO were used as the counter and reference electrodes, respectively. All potentials versus the reference electrode were converted into potentials versus the reversible hydrogen electrode (RHE) using the Nernst equation. The OER ink solution was prepared by mixing the perovskites (20 mg) with 5 wt.% Nafion solution (100 μ L) and ethanol (900 μ L). The polarization curves for OER were recorded at a scan rate of 5 mV/s, and iR was corrected. The double-layer capacitance (C_{dl}) was calculated by cyclic voltammetry (CV) with different scan rates in the non-Faradaic region in 1 M KOH. The electrochemical impedance spectroscopy (EIS) was conducted at 1.6 V (vs. RHE) from 200 kHz to 10 Hz with an AC voltage of 20.0 mV. All electrochemical characterizations at the half-cell level were conducted at room temperature.

6.3 Results and Discussion

6.3.1 Structural Properties of Perovskites

The perovskites, $L_xC_{1-x}N_yF_{1-y}$, were synthesized through the strategic one-pot wet-chemistry approach. In this study, a comprehensive exploration was conducted, delving into both A-site and B-site factors, which played instrumental roles in shaping the resulting perovskite performance. To confirm the perovskite crystal phase, the X-ray diffraction (XRD) analysis was employed, with the outcomes shown in Figure 113. Similar with Wang's result, the prominent peaks show at angular position of 23°, 33°, 40°, 47°, 53°, 58°, 69°, 73°, 78°, 83° and 87°, align with the distinct peaks associate with the (012), (110)/(104), (202), (024), (122), (300), (220), (306), (128), (226), and (404) crystallographic orientations, respectively [209]. These major peaks closely correspond

to the well-known characteristics of the hexagonal perovskite crystal structure. Therefore, their crystalline structure shows a pure perovskite phase.

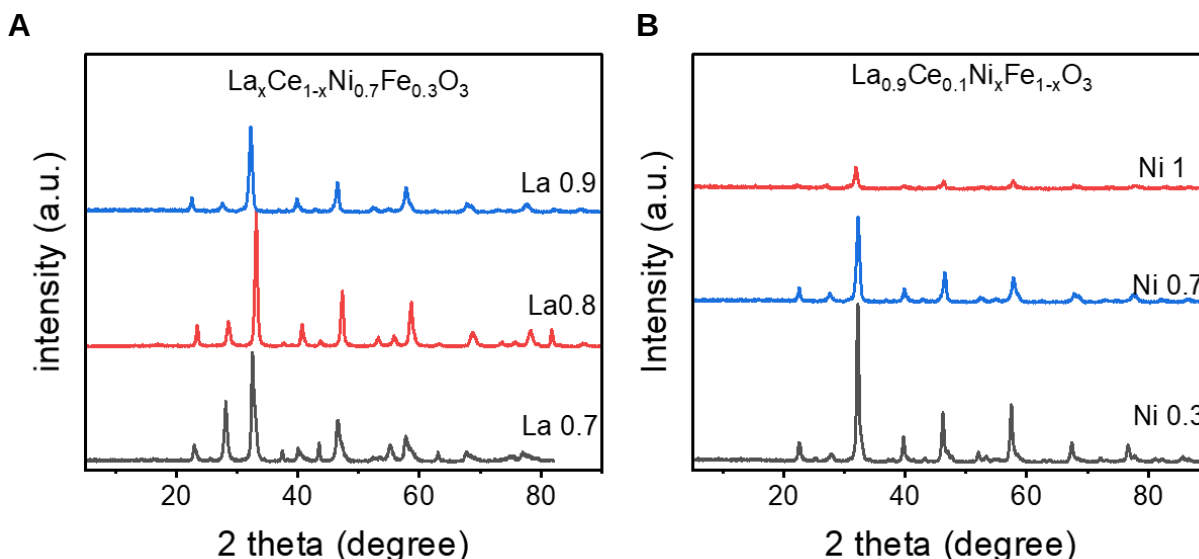


Figure 113. XRD patterns of (A) $\text{La}_{0.7}\text{Co}_{0.3}\text{Ni}_{0.7}\text{Fe}_{0.3}$, $\text{La}_{0.8}\text{Co}_{0.2}\text{Ni}_{0.7}\text{Fe}_{0.3}$, and $\text{La}_{0.9}\text{Co}_{0.1}\text{Ni}_{0.7}\text{Fe}_{0.3}$ (B) $\text{La}_{0.9}\text{Co}_{0.1}\text{Ni}_{0.3}\text{Fe}_{0.7}$, $\text{La}_{0.9}\text{Co}_{0.1}\text{Ni}_{0.7}\text{Fe}_{0.3}$, and $\text{La}_{0.9}\text{Co}_{0.1}\text{Ni}_1$.

6.3.2 Electrochemical Properties of Perovskites at the Half-cell Level

To assess the electrocatalytic performance of oxygen evolution reaction (OER), drop-coating and three-electrode system techniques were employed. In this process, the OER catalyst was carefully coated onto a rotating glassy carbon disk electrode as a working electrode. This approach investigates the performance with which the catalyst facilitates the OER process. The performance evaluation of OER involves the analysis of Polarization curves, Nyquist plots, and Tafel slope, which provide valuable insights into the catalyst's behavior, as shown in Figure 114.

Figure 114A–C exhibits the OER activity of $\text{La}_x\text{Ce}_{1-x}\text{Ni}_y\text{Fe}_{1-y}$ with a constant Ni/Fe ratio of 7/3. Polarization curves, as illustrated in Figure 114A, offer a graphical representation of the relationship between the current density and the applied potential during the OER process. These curves describe the current density changes as the potential is varied. A particularly noteworthy trend becomes apparent when examining the influence of elevated La content, as illustrated in Figure 114A. With the elevation of La content, a

simultaneous and rapid surge in current density becomes notably pronounced at the same potential level. This development suggests that higher La content significantly bolsters the catalyst's effectiveness in promoting the oxygen evolution reaction (OER). The noticeable upsurge in current density directly marks an advantage in converting reactants into products, thereby indicating a substantial improvement in the catalytic activity of the material.

Electrochemical impedance spectroscopy (EIS) is also tested under the catalytic operation condition and used for further exploration of the electrode surface kinetic. The corresponding Nyquist plots are shown in Figure 114 B. The ohmic resistance (R_o) as intrinsic resistance for the different LCNF samples remains nearly constant under the catalytic operation condition (1.6 V). On the other hand, polarization resistance (R_p) is the primary resistance in the OER process [34]. The decrease of the charge-transfer resistance can improve the OER catalytic activity. Thus, $L_{0.9}C_{0.1}N_{0.7}F_{0.3}$ exhibits the lower value of R_p , further indicating that $L_{0.9}C_{0.1}N_{0.7}F_{0.3}$ possesses higher OER performance, which is consistent with LSV result [209].

The Tafel plot shown in Figure 114 C is used to evaluate the chemical kinetics. The Tafel slope is calculated by matching the linear part of the Tafel plot obtained from polarization curves. $L_{0.9}C_{0.1}N_{0.7}F_{0.3}$ exhibits the Tafel slope of 52.4 mV dec^{-1} . This result demonstrates that $L_{0.9}C_{0.1}N_{0.7}F_{0.3}$ and $L_{0.9}C_{0.1}N_1$ have higher reaction rates and OER kinetic. Although the Tafel slope is not the smallest in Figure 114C, $L_{0.9}C_{0.1}N_{0.7}F_{0.3}$ is still active for OER.

Figure 114D – F exhibits the OER activity of $L_xC_{1-x}N_yF_{1-y}$ with a constant La/Ce ratio of 9. Notably, an exciting trend unfolds with the elevation of nickel content shown in Figure 114D. As Ni content increases, a corresponding rapid escalation in current density becomes evident at the same potential level. This phenomenon indicates that higher nickel content enhances the catalyst's ability to facilitate the OER. The observed increase in current density reveals a more efficient conversion of reactants into products, reflecting improved catalytic activity.

Comparing the performances of two catalyst compositions, $L_{0.9}C_{0.1}N_{0.7}F_{0.3}$ and $L_{0.9}C_{0.1}N_1$, reveals intriguing findings. Despite having slightly different compositions, these catalysts exhibit closely aligned catalytic activities. Specifically, they both demonstrate an

overpotential of 338 mV at 10 mA/cm². This observation underscores the notable impact of nickel concentration on the catalytic behavior of the materials.

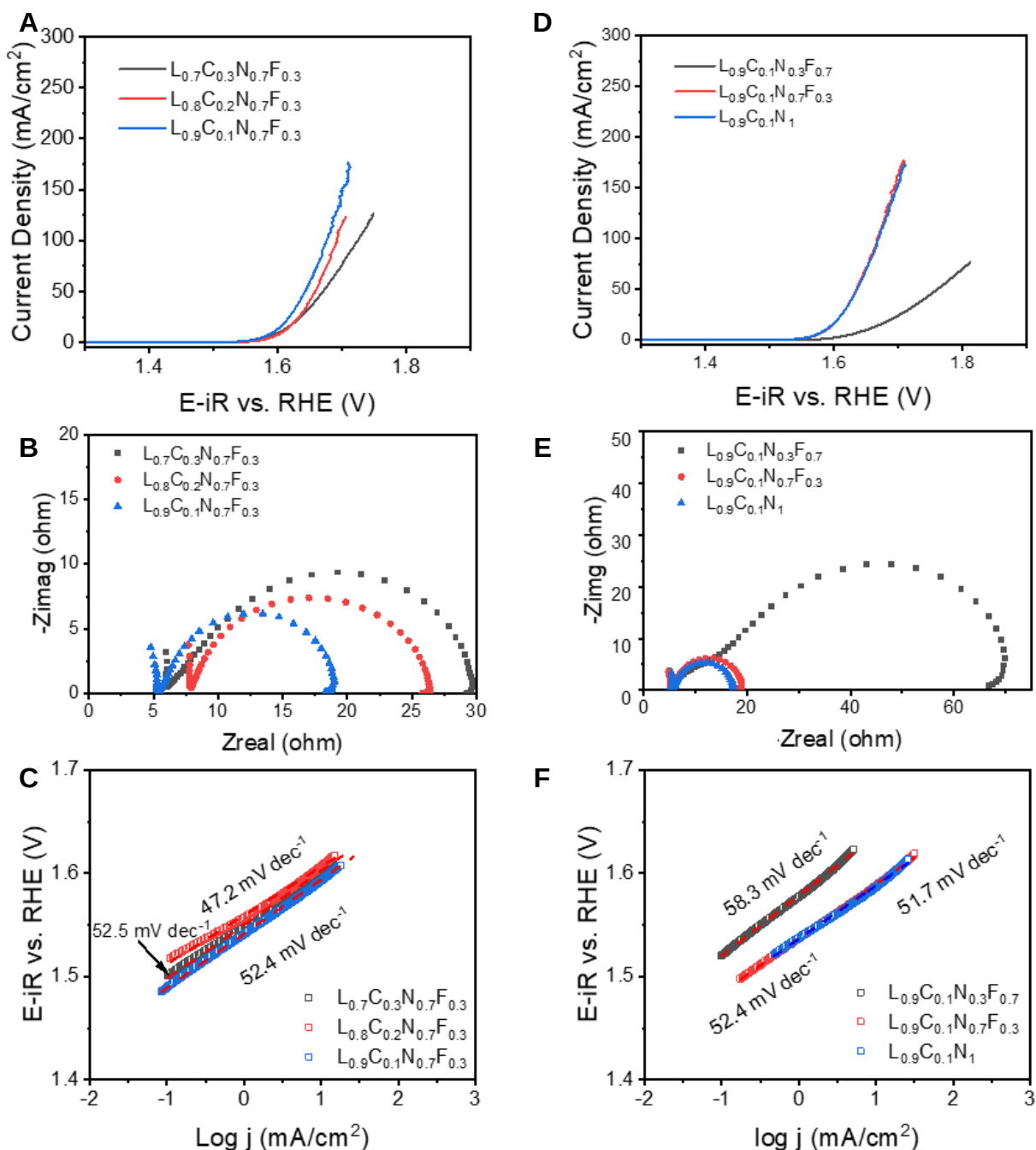


Figure 114. Electrochemical performance of perovskites at the half-cell level, which is evaluated in 1.0 M KOH solution at room temperature. Ni_1 (A) Ohmic resistance-corrected polarization curves of perovskites $L_{0.7}C_{0.3}N_{0.7}F_{0.3}$, $L_{0.8}C_{0.2}N_{0.7}F_{0.3}$, and $L_{0.9}C_{0.1}N_{0.7}F_{0.3}$ (B) Electrochemical impedance spectra of

perovskites $\text{L}_{0.7}\text{Co}_{0.3}\text{Ni}_{0.7}\text{Fe}_{0.3}$, $\text{L}_{0.8}\text{Co}_{0.2}\text{Ni}_{0.7}\text{Fe}_{0.3}$, and $\text{L}_{0.9}\text{Co}_{0.1}\text{Ni}_{0.7}\text{Fe}_{0.3}$ (C) Tafel plots of perovskites $\text{L}_{0.7}\text{Co}_{0.3}\text{Ni}_{0.7}\text{Fe}_{0.3}$, $\text{L}_{0.8}\text{Co}_{0.2}\text{Ni}_{0.7}\text{Fe}_{0.3}$, and $\text{L}_{0.9}\text{Co}_{0.1}\text{Ni}_{0.7}\text{Fe}_{0.3}$ (D)) Ohmic resistance-corrected polarization curves of $\text{L}_{0.9}\text{Co}_{0.1}\text{Ni}_{0.3}\text{Fe}_{0.7}$, $\text{L}_{0.9}\text{Co}_{0.1}\text{Ni}_{0.7}\text{Fe}_{0.3}$, and $\text{L}_{0.9}\text{Co}_{0.1}\text{Ni}_1$ (E) Electrochemical impedance spectra of $\text{L}_{0.9}\text{Co}_{0.1}\text{Ni}_{0.3}\text{Fe}_{0.7}$, $\text{L}_{0.9}\text{Co}_{0.1}\text{Ni}_{0.7}\text{Fe}_{0.3}$, and $\text{L}_{0.9}\text{Co}_{0.1}\text{Ni}_1$ (F) Tafel plots of $\text{L}_{0.9}\text{Co}_{0.1}\text{Ni}_{0.3}\text{Fe}_{0.7}$, $\text{L}_{0.9}\text{Co}_{0.1}\text{Ni}_{0.7}\text{Fe}_{0.3}$, and $\text{L}_{0.9}\text{Co}_{0.1}\text{Ni}_1$.

It is consistently confirmed in the electrochemical impedance spectroscopy (EIS) shown in Figure 114 E, and Tafel slope results, illustrated in Figure 114 F. The Tafel plot shown in Figure 114 F is used to evaluate the reaction kinetic. The Tafel slope is calculated by matching the linear part of the Tafel plot obtained from polarization curves. $\text{L}_{0.9}\text{Co}_{0.1}\text{Ni}_{0.7}\text{Fe}_{0.3}$ and $\text{L}_{0.9}\text{Co}_{0.1}\text{Ni}_1$ exhibit the lower Tafel slope of 52.4 and 51.7 mV dec⁻¹, respectively. This result demonstrates that $\text{L}_{0.9}\text{Co}_{0.1}\text{Ni}_{0.7}\text{Fe}_{0.3}$ and $\text{L}_{0.9}\text{Co}_{0.1}\text{Ni}_1$ have higher reaction rates and OER kinetic.

6.3.3 Special Electrochemical Properties - Stability of Perovskites at the Half-cell Level

LCNF has a unique character. As shown in Figure 115, in the stability tests with 22 hours, $\text{L}_{0.9}\text{Co}_{0.1}\text{Ni}_{0.7}\text{Fe}_{0.3}$ is more stable compared with $\text{L}_{0.9}\text{Co}_{0.1}\text{Ni}_1$. The reason could be that the synergy of Ni and Fe is more beneficial in improving the OER catalytic activity than the single interaction of pure Ni.

The distinctive characteristics of LCNF are notably evident. Figure 115 illustrates the outcomes of stability tests conducted for 22 hours. Among the tested compositions, it becomes apparent that $\text{L}_{0.9}\text{Co}_{0.1}\text{Ni}_{0.7}\text{Fe}_{0.3}$ exhibits more excellent stability than $\text{L}_{0.9}\text{Co}_{0.1}\text{Ni}_1$. This observed stability trend can be attributed to the advantageous synergy arising from the combined presence of nickel and iron within LCNF, as opposed to the individual effects of pure Fe or pure Ni interactions [209]. This synergistic effect stemming from the collaboration of Ni and Fe elements has a considerable impact on improving the catalytic activity for the Oxygen Evolution Reaction (OER). The intricate interplay between these two metals enhances the overall electrocatalytic properties of LCNF, making it more

proficient in facilitating the OER process. This synergy could involve increased active sites, optimized charge transfer pathways, and improved stability of reaction intermediates.

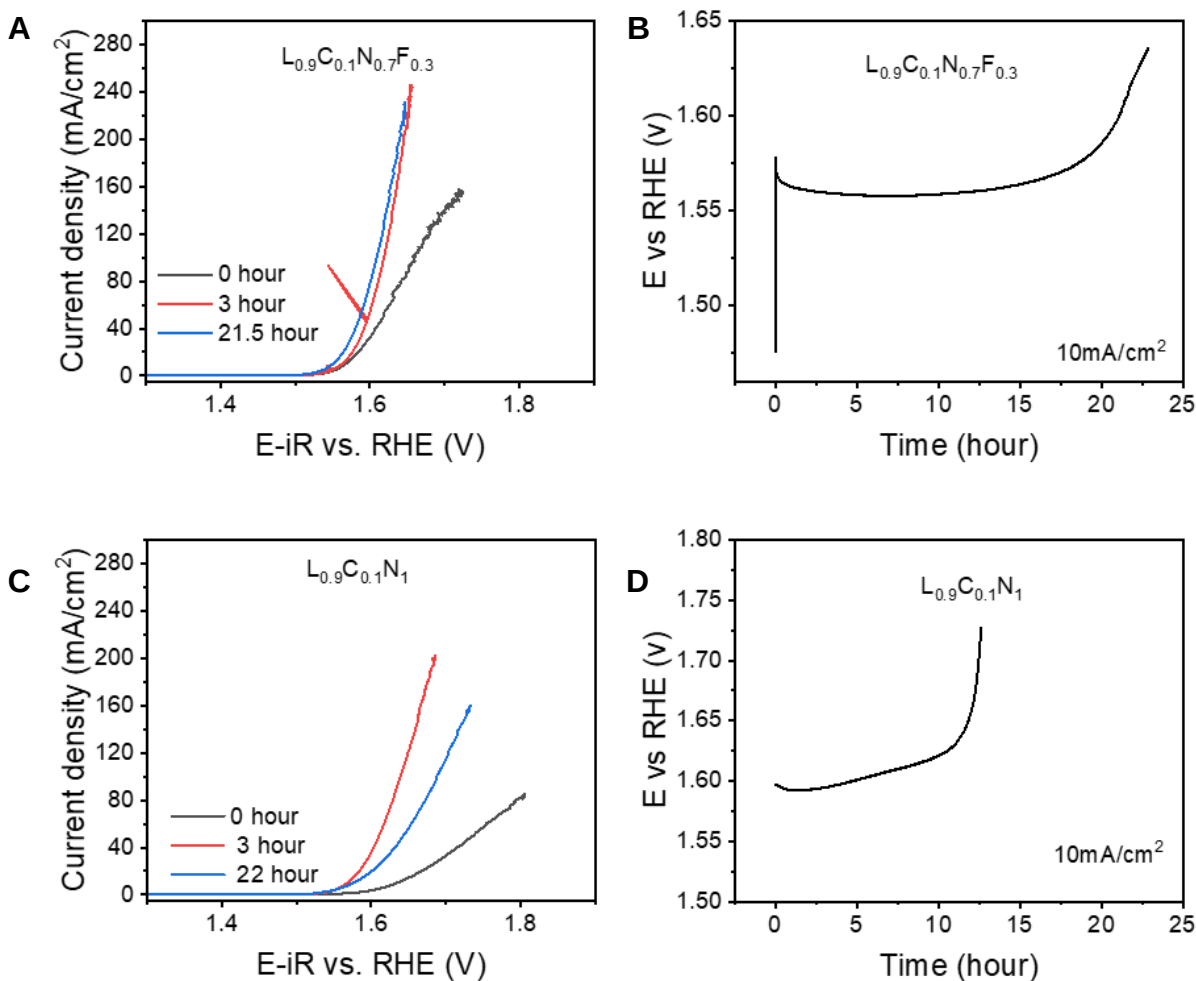


Figure 115. (A) Ohmic resistance-corrected polarization curves of $L_{0.9}C_{0.1}N_{0.7}F_{0.3}$ at different times. (B) stability testing of $L_{0.9}C_{0.1}N_{0.7}F_{0.3}$. (C) Ohmic resistance-corrected polarization curves of $L_{0.9}C_{0.1}N_1$ at different times. (D) stability testing of $L_{0.9}C_{0.1}N_1$ at room temperature and a current density of 10 mA/cm².

The stable behavior of $L_{0.9}C_{0.1}N_{0.7}F_{0.3}$ during the extended stability tests showcases its potential for practical applications where consistent and long-lasting catalytic performance is paramount. This finding also highlights the importance of

considering compositional synergy when designing advanced electrocatalytic materials, underlining the benefits of combining multiple elements to achieve enhanced catalytic properties.

To gain deeper insights into the crystal structure following the electrochemical stability testing, a comprehensive XRD (X-ray Diffraction) analysis was conducted. Figure 116 provides a visual representation of the XRD patterns obtained before and after subjecting the $\text{L}_{0.9}\text{Co}_{0.1}\text{N}_{0.7}\text{F}_{0.3}$ coating on the carbon cloth to stability testing at the half-cell level.

Upon closely examining these patterns, it becomes evident that no significant change in the crystal phases is present. This outcome indicates that, despite the rigorous stability testing, the fundamental crystalline structure of the $\text{L}_{0.9}\text{Co}_{0.1}\text{N}_{0.7}\text{F}_{0.3}$ coating remains consistent and unchanged. This observation holds valuable significance as it suggests that the coating's structural integrity remains intact even under the conditions of the stability tests.

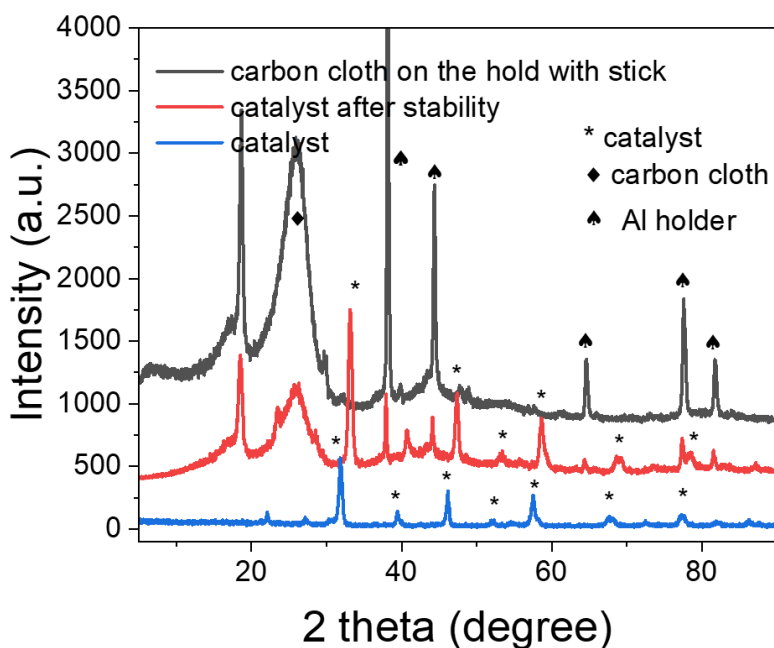


Figure 116. XRD patterns of $\text{L}_{0.9}\text{Co}_{0.1}\text{N}_{0.7}\text{F}_{0.3}$, $\text{L}_{0.9}\text{Co}_{0.1}\text{N}_{0.7}\text{F}_{0.3}$ on carbon cloth after stability testing, and carbon cloth.

This stable behavior in terms of crystal phases signifies the material's robustness and resilience against the potential structural transformations that could arise from

prolonged exposure to electrochemical processes. The absence of phase change serves as an indicator of the coating's ability to maintain its original crystallographic configuration, highlighting its durability and suitability for sustained electrochemical applications.

Therefore, the XRD analysis provides a clear depiction of the crystal structure before and after electrochemical stability testing, with no observable phase changes. This confirms the coating's structural stability and underscores its suitability for enduring demanding electrochemical environments without compromising its fundamental crystallographic properties.

6.4 Conclusions

In this chapter, we demonstrate a novel unique perovskite oxide, known as $\text{La}_x\text{Ce}_{1-x}\text{Ni}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$ ($\text{L}_x\text{C}_{1-x}\text{N}_y\text{F}_{1-y}$). Notably, $\text{L}_{0.9}\text{C}_{0.1}\text{N}_{0.7}\text{F}_{0.3}$ exhibits outstanding performance in the oxygen evolution reaction (OER), achieving 10 mA/cm^2 at a low overpotential of 338 mV in 1.0 M KOH. Both $\text{L}_{0.9}\text{C}_{0.1}\text{N}_{0.7}\text{F}_{0.3}$ and $\text{L}_{0.9}\text{C}_{0.1}\text{N}_1$ exhibit a distinctive characteristic, where the performance exhibits enhancement during the initial stages of the stability test. This intriguing behavior underscores the unique characteristics of these materials and their potential for catalytic applications.

Chapter 7 - General Conclusion and Future Work

This dissertation delves into the exploration of three different types of oxygen evolution reaction (OER) electrochemical catalysts. They are perovskite, NiFe LDH, and NiCoFeOOH, all aimed at facilitating hydrogen generation.

In Chapter 3, the Ruddlesden-Popper perovskite, $\text{La}_x\text{Sr}_{4-x}\text{Ni}_y\text{Fe}_{3-y}\text{O}_{10-\delta}$, is evaluated in anion exchange membrane water electrolyzers as an OER electrochemical catalyst. This hybrid perovskite demonstrates superior performance attributable to its optimized interfacial area between various phases, single-layer perovskite phase, and two Ruddlesden-Popper phases.

In Chapter 4, another catalyst, NiFe LDH, is introduced for hydrogen generation within simulated seawater. Multiple electrolyte configurations are meticulously examined, drawing comparisons between water electrolysis and seawater splitting. An optimal configuration, offering enhanced stability, is discussed.

In Chapter 5, a different type of electrode, 3-D unified NiCoFeOOH on iron foam, is discussed. This electrode design seamlessly integrates a gas diffusion layer with a catalyst layer, eliminating the need for binders.

In chapter 6, another single layer perovskite, $\text{La}_x\text{Ce}_{1-x}\text{Ni}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$, is discussed. This unique catalyst presents distinctive characteristics, where the performance exhibits enhancement during the initial stages of the stability test. This peculiarity holds significant promise for advancing the field of hydrogen generation.

Overall, this dissertation has demonstrated different types of OER electrochemical catalysts in AEMWEs. They exhibit outstanding performance, marked by high activity and stability.

However, it's noteworthy that the stability of OER catalyst remains a persistent challenge, as previously highlighted. To address this concern, exploring platinum group metal (PGM)-free catalysts becomes imperative. Alternative materials like perovskite structures and oxides. A new catalyst should be designed to improve the performance could be investigated. The quest for improved stability necessitates the deliberate design of novel catalysts that not only enhance performance but also demonstrate enhanced endurance over prolonged use.

In addition, the scope of the investigation should extend beyond catalysts alone. The exploration of alternative electrode methods holds considerable promise. One promising avenue is the in-depth study of 3-D unified electrodes, potentially through modifications on the substrate, such as Ni or Fe foam. While this dissertation touches on one type of unified electrode, there exists a world of unexplored possibilities. Diversifying the electrode methodologies is essential. For example, experimenting with different substrates, such as carbon cloth and Ni foam, as new electrode materials could yield valuable insights and innovations.

Furthermore, it's crucial to recognize the potential for advancement in single-cell fabrication methods. Enhancing the precision and efficiency of the fabrication process can significantly impact the overall performance of the electrochemical systems. This aspect presents a prime opportunity for optimization and innovation within the field.

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