

Article

Tuning High-Entropy Oxides for Oxygen Evolution Reaction Through Electrocatalytic Water Splitting: Effects of $(\text{MnFeNiCoX})_3\text{O}_4$ ($\text{X} = \text{Cr}, \text{Cu}, \text{Zn}, \text{and Cd}$) on Electrocatalytic Performance

Milad Zehtab Salmasi , Amir Narimani, Ali Omidkar and Hua Song ^{*} 

Department of Chemical and Petroleum Engineering, University of Calgary, 2500 University Dr. NW, Calgary, AB T2N 1N4, Canada; milad.zehtabsalma1@ucalgary.ca (M.Z.S.); amir.narimani@ucalgary.ca (A.N.); ali.omidkar1@ucalgary.ca (A.O.)

^{*} Correspondence: sonh@ucalgary.ca

Abstract

This research presents the development of spinel-type high-entropy oxide (HEO) catalysts with the general composition $(\text{MnFeNiCoX})_3\text{O}_4$, where X represents Cr, Cu, Zn, and Cd, synthesized through a solution combustion method. The impact of the fifth metal element on the oxygen evolution reaction (OER) was systematically explored using structural, morphological, and electrochemical characterization techniques. Among the various compositions, the Cr-containing catalyst, $(\text{MnFeNiCoCr})_3\text{O}_4$, displayed outstanding electrocatalytic behavior, delivering a notably low overpotential of 323 mV at a current density of 10 mA/cm² in 1.0 M KOH—surpassing the performance of benchmark RuO₂. Additionally, this material exhibited the smallest Tafel slope (56 mV/dec), the greatest double-layer capacitance (3.35 mF/cm²), and the most extensive electrochemically active surface area, all indicating enhanced charge transfer capability and high catalytic proficiency. The findings highlight the potential of element tailoring in HEOs as a promising strategy for optimizing water oxidation catalysis.

Keywords: water splitting; oxygen evolution reaction; high entropy oxides; solution combustion



Academic Editor: Muhammad Saeed Akhtar

Received: 4 July 2025

Revised: 21 August 2025

Accepted: 22 August 2025

Published: 1 September 2025

Citation: Zehtab Salmasi, M.; Narimani, A.; Omidkar, A.; Song, H. Tuning High-Entropy Oxides for Oxygen Evolution Reaction Through Electrocatalytic Water Splitting: Effects of $(\text{MnFeNiCoX})_3\text{O}_4$ ($\text{X} = \text{Cr}, \text{Cu}, \text{Zn}, \text{and Cd}$) on Electrocatalytic Performance. *Catalysts* **2025**, *15*, 827. <https://doi.org/10.3390/catal15090827>

Copyright: © 2025 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

In recent decades, the accelerating depletion of natural resources and mounting environmental challenges have catalyzed major advancements in the field of clean and sustainable energy technologies. Despite the rapid development of renewable energy sources, such as solar, wind, and tidal power, their inherent variability and dependence on environmental conditions present serious limitations in ensuring a stable and continuous energy supply. This intermittency highlights the urgent need for effective energy storage and conversion systems capable of bridging the gap between supply and demand. In this regard, hydrogen production through water electrolysis driven by renewable energy inputs has gained considerable attention as a viable and sustainable approach. Owing to its high gravimetric energy density and zero carbon emissions during utilization, hydrogen is widely regarded as one of the most promising clean energy carriers of the future [1,2]. However, one of the primary challenges limiting the widespread implementation of water electrolysis is the oxygen evolution reaction (OER), which occurs at the anode during electrochemical splitting of water. The OER is a multi-step, four-electron and four-proton

transfer process that suffers from sluggish kinetics and necessitates a high overpotential to proceed efficiently. This kinetic barrier significantly reduces the overall energy efficiency of the water-splitting process. As such, the development of highly active, durable, and cost-effective electrocatalysts is crucial to enhance the reaction rate and reduce energy losses. Currently, noble metal oxides such as iridium oxide (IrO_2) and ruthenium oxide (RuO_2) represent the benchmark catalysts for OER due to their exceptional catalytic activity and favorable electronic structures. Nonetheless, their practical application is severely constrained by issues including high cost, limited natural abundance, and insufficient long-term operational stability under harsh alkaline or acidic conditions [3,4]. These drawbacks have intensified global research efforts aimed at discovering alternative OER catalysts that are both economically viable and composed of earth-abundant elements. As a result, the design and development of noble-metal-free electrocatalysts with superior activity and stability have emerged as a pivotal direction in the pursuit of efficient and scalable hydrogen production technologies.

In recent years, a wide array of strategies has been explored to design highly efficient electrocatalysts for the OER, particularly focusing on non-precious transition metal oxides. These materials have attracted considerable interest due to their cost-effectiveness and earth-abundant nature. Researchers have made notable progress in enhancing OER activity by employing several design approaches. These include the careful selection of suitable transition metal oxides with favorable electronic configurations [5], the introduction of dopants to modulate electronic structure and surface properties [6], and the deliberate creation of structural defects, such as oxygen vacancies, to increase the number of active sites and facilitate charge transfer [7]. While these advancements have yielded catalysts with remarkable activity, a persistent and critical issue remains: the limited durability and chemical stability of these materials under harsh electrochemical conditions. This concern is especially prominent under real-world operational scenarios, which often involve prolonged electrolysis at elevated current densities and in highly alkaline or acidic electrolytes. Under such conditions, many single- or binary-component metal oxide catalysts are prone to dissolution, structural degradation, or phase transformations, ultimately leading to performance loss over time [8]. To address these limitations, a new category of materials, high-entropy materials (HEMs), has recently emerged as a promising alternative within the field of catalysis and materials science [9]. HEMs are composed of four or more principal elements in near-equimolar ratios, homogeneously distributed within a single-phase structure. This unique compositional complexity imparts a range of advantageous properties that are rarely observed in conventional materials. These benefits arise from four interrelated effects: lattice distortion (which alters the local atomic environment), sluggish atomic diffusion (which enhances thermal and structural stability), the cocktail effect (which leads to synergistic improvements in physical and chemical behavior), and high configurational entropy (which stabilizes the single-phase structure). Owing to these synergistic phenomena, high-entropy materials offer exceptional potential for electrocatalytic applications, including robust and stable OER catalysts capable of withstanding demanding operational environments.

High-entropy oxides (HEOs) represent a fascinating and rapidly growing class of materials that are structurally defined by the presence of four or more metal cations incorporated in equimolar or nearly equimolar ratios within a single-phase solid solution. Since their conceptual introduction, HEOs have gained widespread attention in the scientific community due to their exceptional thermodynamic resilience, notable structural integrity, and the presence of significant lattice distortion—all of which are primarily governed by entropy-driven stabilization mechanisms [10]. In contrast to conventional transition metal oxides, where only one or two types of metal ions occupy the lattice, HEOs exhibit a unique structural

motif characterized by the random and uniform distribution of multiple metal elements over shared crystallographic sites. This compositional complexity gives rise to several advantageous features. One of the most important is the generation of abundant surface defects, oxygen vacancies, and under-coordinated atomic sites—defect structures that are known to act as active centers for various catalytic reactions [11]. Moreover, the variation in ionic radii among the constituent metal ions leads to pronounced lattice distortions, which can significantly influence the electronic environment and alter the physicochemical behavior of the material. These distortions can fine-tune the electronic structure in a way that enhances catalytic activity and charge transport properties. Furthermore, the interactive or synergistic effects among the different metal elements contribute to the enhancement of overall performance, while also enabling a high degree of flexibility in compositional design. This tunability allows researchers to tailor the material's stoichiometry and optimize its catalytic function for specific applications. Due to their multifunctional capabilities and adjustable properties, HEOs have been explored across a wide spectrum of energy-related and catalytic applications. These include serving as electrocatalysts for the oxygen reduction reaction (ORR) [12], oxygen evolution reactions [13], as well as active components in energy storage devices such as batteries [14], and photoactive materials in photocatalysis [15]. The ability to integrate multiple functionalities into a stable single-phase structure has made HEOs an appealing platform for designing next-generation catalytic materials. As a result, their application has significantly expanded the design space and performance versatility of catalytic systems, marking them as a key innovation in the development of advanced energy and environmental technologies [16,17]. Recent advances have demonstrated that high-entropy oxides can achieve promising OER activity. For example, Wang et al. [18] reported a $(\text{CoCuFeMnNi})_3\text{O}_4$ catalyst with an overpotential of 400 mV at 10 mA/cm² in 1.0 M KOH, while Liu et al. [19] synthesized a defective $(\text{MgCoNiCuZn})\text{O}$ oxide reaching 360 mV under similar conditions. More recently, Zhang et al. [20] achieved 326 mV using a $(\text{Co}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Fe}_{0.2}\text{Zn}_{0.2})\text{Fe}_2\text{O}_4$ catalyst supported on CFP. Despite these advances, the overpotentials of most reported HEO systems remain higher than those of noble-metal benchmarks such as RuO_2 and IrO_2 .

One of the key challenges in the development of HEMs lies in the vast array of possible elemental combinations and stoichiometric variations available for material design. This immense compositional flexibility creates a highly complex configuration space, making it exceedingly difficult to explore every potential formulation or to accurately decode the intricate correlations between atomic structure and catalytic behavior. Consequently, the rational and strategic selection of elemental constituents becomes essential to achieving desired performance outcomes. To simplify and streamline this exploration, a more targeted and efficient methodology has been proposed—namely, maintaining a consistent set of four widely utilized transition metals while systematically altering a fifth element [16]. Among the numerous transition metals available, manganese (Mn), iron (Fe), nickel (Ni), and cobalt (Co) are frequently selected due to their natural abundance, economic viability, and well-documented electrocatalytic activity, especially under alkaline electrochemical conditions [21]. These metals possess favorable electronic structures that facilitate strong interactions with catalytic intermediates, thereby enhancing reaction kinetics and contributing to superior catalytic performance [3]. Their ability to promote charge transfer and stabilize intermediate species makes them ideal candidates for constructing the base framework of HEMs. Building upon this foundational quaternary system, the current study explores how the substitution of the fifth metal influences the structural and functional characteristics of the resulting materials. Specifically, transition metals such as chromium (Cr), copper (Cu), zinc (Zn), and cadmium (Cd)—each exhibiting distinct 3d electron configurations and oxidation states—were individually introduced into the (MnFeNiCo)

matrix. The choice of Cr, Cu, Zn, and Cd as the fifth element was guided by considerations of structural compatibility and catalytic relevance. Their ionic radii are reasonably close to those of Mn, Fe, Ni, and Co in octahedral or tetrahedral coordination, which helps preserve the single-phase spinel framework and minimizes lattice strain. The multiple oxidation states accessible for Cr ($\text{Cr}^{3+}/\text{Cr}^{6+}$) and Cu ($\text{Cu}^+/\text{Cu}^{2+}$) can facilitate redox flexibility, while Zn^{2+} and Cd^{2+} introduce lattice distortion that may modulate active site environments. While previous studies, such as Guo et al. [22], examined the impact of different dopants (Mg, Mn, Zn, Cu) in a $(\text{FeCoNiCr})_3\text{O}_4$ framework on Ni foam electrode using hydrothermal synthesis, our work differs in both composition and methodology. We employ a $(\text{MnFeNiCoX})_3\text{O}_4$ system with $X = \text{Cr, Cu, Zn, and Cd}$ synthesized via a solution combustion method, which is more scalable and efficient. The inclusion of Cd and identification of Cr as the optimal fifth element offer new insights into the tunability and performance of high-entropy spinel oxides for OER applications. In addition, carbon fiber paper was utilized in this work as electrode. This systematic substitution aimed to generate a series of high-entropy oxide compositions, thereby enabling a controlled investigation of how variations in elemental makeup affect structural features, surface properties, and overall electrocatalytic activity. A comprehensive analysis was then carried out to elucidate the underlying structure–performance relationships and to identify optimal compositional strategies for enhancing OER efficiency.

2. Results and Discussion

2.1. Characterization of Electrocatalysts

Figure 1A displays the X-ray diffraction (XRD) patterns of the synthesized HEO electrocatalysts. All samples revealed characteristic diffraction peaks indicative of a face-centered cubic (FCC) spinel phase, which aligns well with the crystallographic data reported for the $\text{Fd}3m$ space group (PDF card No. 84-0482). The primary reflections were identified at 2θ angles of 18.4° , 30.4° , 35.8° , 37.5° , 43.4° , 54.0° , 57.6° , and 63.3° . These diffraction peaks correspond to the (111), (220), (311), (222), (400), (422), (511), and (440) crystallographic planes, respectively. The presence of these well-defined peaks confirms the successful formation of a single-phase spinel structure in all HEO samples, with no evidence of secondary phases or impurities. This consistent phase purity across the samples further supports the structural stability imparted by the high-entropy design [23–26]. As represented, all the synthesized powders are phase-pure and exhibit a spinel structure.

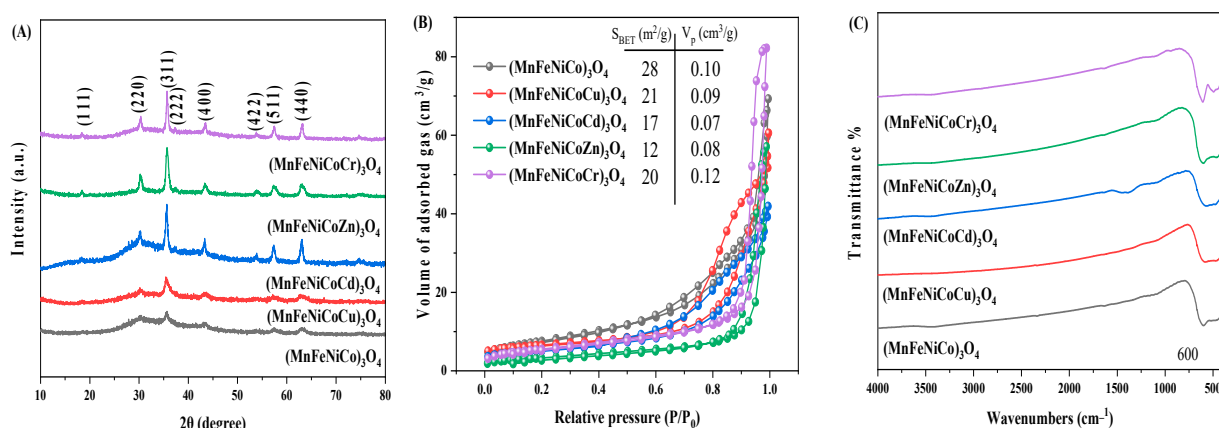


Figure 1. (A) XRD spectra, (B) N_2 adsorption–desorption isotherms, (C) FTIR spectra of the prepared samples.

To evaluate the surface and pore structure characteristics of the synthesized electrocatalysts, nitrogen adsorption–desorption measurements were conducted using the standard

Brunauer–Emmett–Teller (BET) method. As shown in Figure 1B, the adsorption isotherms for all four samples display typical Type IV behavior, which is indicative of the co-existence of both microporous and mesoporous structures within the catalysts, as classified by the IUPAC [27]. The presence of micropores contributes significantly to increasing the specific surface area (S_{BET}), thereby providing more surface sites for reactions. On the other hand, mesopores are essential for improving the accessibility of reactants to catalytic active sites and facilitating the escape of products [28]. All samples also exhibit H4-type hysteresis loops in their isotherms, further confirming the presence of slit-like pores commonly associated with aggregated plate-like particles or narrow pore openings [29]. As anticipated, the combined benefits of micro-, meso-, and macropores in facilitating oxygen transfer and detachment result in the superior textural properties of the fabricated electrocatalyst samples for OER. The S_{BET} of $(\text{MnFeNiCo})_3\text{O}_4$, $(\text{MnFeNiCoCu})_3\text{O}_4$, $(\text{MnFeNiCoZn})_3\text{O}_4$, $(\text{MnFeNiCoCd})_3\text{O}_4$, and $(\text{MnFeNiCoCr})_3\text{O}_4$ electrocatalysts obtained from the isotherms were 28, 21, 12, 17 and 20 m^2/g , respectively. Furthermore, the total pore volume (V_{P}) of $(\text{MnFeNiCo})_3\text{O}_4$, $(\text{MnFeNiCoCu})_3\text{O}_4$, $(\text{MnFeNiCoZn})_3\text{O}_4$, $(\text{MnFeNiCoCd})_3\text{O}_4$, and $(\text{MnFeNiCoCr})_3\text{O}_4$ samples were measured as 0.10, 0.09, 0.08, 0.07, and 0.12 cm^3/g , respectively. The $(\text{MnFeNiCoCr})_3\text{O}_4$ sample exhibits the highest V_{P} (a property that facilitates mass transport) among the tested catalysts, including $(\text{MnFeNiCo})_3\text{O}_4$, $(\text{MnFeNiCoCu})_3\text{O}_4$, $(\text{MnFeNiCoZn})_3\text{O}_4$, and $(\text{MnFeNiCoCd})_3\text{O}_4$. This increased porosity allows for more efficient diffusion of both reactants and oxygen products throughout the electrode structure, thus facilitating greater interaction with active sites. As a result, the overall electrocatalytic activity is improved, with faster reaction kinetics and enhanced OER performance attributed to superior mass transfer properties [30].

The FTIR spectra of the synthesized HEO samples are presented in Figure 1C. All compositions display comparable spectral features. The intense absorption peaks observed near 555 and 600 cm^{-1} can be assigned to O–M–O/M–O–M bending vibrations within MO_6 octahedra and to symmetric stretching modes of metal–oxygen bonds, respectively. The broadened and asymmetric nature of these bands across all spectra indicates distortion within the MO_6 units. Such distortion is likely a consequence of incorporating multiple transition metals with varying oxidation states, which introduces Jahn–Teller effects and polarizes the M–O bonds due to local lattice distortions and reduced structural symmetry [31–34].

The surface features of the synthesized high-entropy oxide (HEO) catalysts were examined using SEM, as shown in Figure 2. All five samples display porous nanostructures, although their exact morphologies vary depending on the fifth metal incorporated. The baseline $(\text{MnFeNiCo})_3\text{O}_4$ sample (Figure 2A–C) consists of interconnected, sponge-like nanoparticles that create a relatively open and porous network. When Cr is introduced, the resulting $(\text{MnFeNiCoCr})_3\text{O}_4$ sample (Figure 2D–F) appears more compact and densely interconnected, which could contribute to improved structural stability and better electron transport during oxygen evolution reactions. The surface of the $(\text{MnFeNiCoCu})_3\text{O}_4$ catalyst (Figure 2G–I) is noticeably rougher and made up of distinct nanograins, possibly increasing the surface area. In contrast, $(\text{MnFeNiCoZn})_3\text{O}_4$ (Figure 2J–L) shows a smoother and denser structure with fewer pores, which aligns with its lower BET surface area. The $(\text{MnFeNiCoCd})_3\text{O}_4$ sample (Figure 2M–O) has a looser, granular appearance, suggesting a more moderately porous texture. These differences clearly show that the fifth metal plays a significant role in shaping the surface structure, which can influence how efficiently each catalyst interacts with the electrolyte during operation.

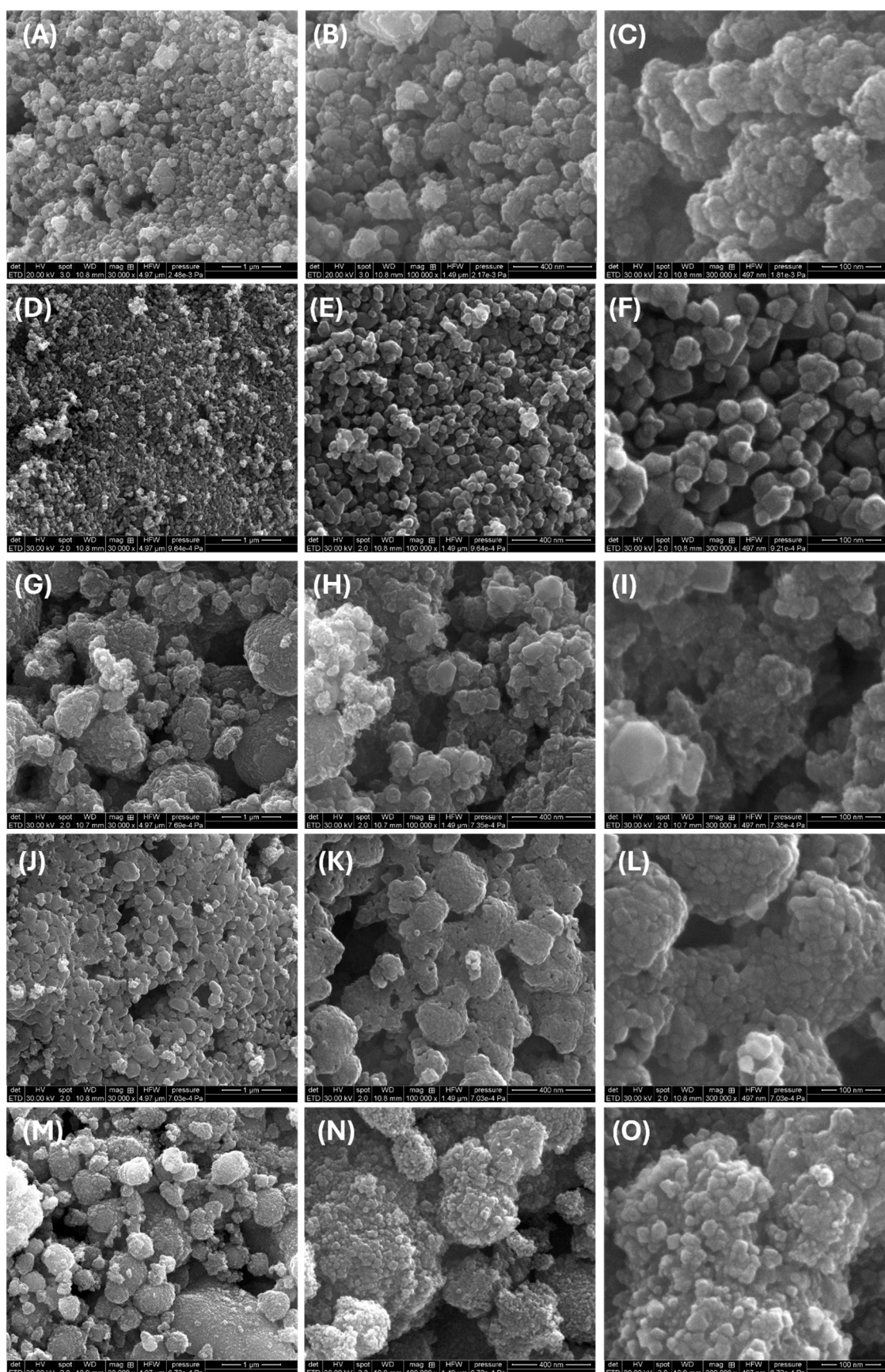


Figure 2. SEM images of (A–C) $(\text{MnFeNiCo})_3\text{O}_4$, (D–F) $(\text{MnFeNiCoCr})_3\text{O}_4$, (G–I) $(\text{MnFeNiCoCu})_3\text{O}_4$, (J–L) $(\text{MnFeNiCoZn})_3\text{O}_4$, and (M–O) $(\text{MnFeNiCoCd})_3\text{O}_4$ samples.

To look deeper into the internal structure and elemental distribution, HR-TEM, HAADF-STEM, and EDX mapping analyses were utilized. Figure 3 presents the results for $(\text{MnFeNiCo})_3\text{O}_4$. The HR-TEM and HAADF images (Figure 3A–C) show that the particles are well-crystallized, with visible lattice fringes. The EDX maps (Figure 3D–I) confirm that all four metals—Mn, Fe, Ni, and Co—are uniformly distributed throughout the material, indicating successful and homogeneous synthesis. Figure 4 presents the HR-TEM and EDX characterization of the $(\text{MnFeNiCoCr})_3\text{O}_4$ catalyst, which demonstrated the highest electrocatalytic activity in OER tests. As shown in Figure 4, the TEM image (Figure 4A) reveals clear crystal fringes, and the HAADF image (Figure 4B) supports the high crystallinity of the sample. The corresponding EDX dot-mapping images (Figure 4C–I) show that all five metal elements, including Cr, are evenly spread throughout the particles. This consistent dispersion likely contributes to the superior electrocatalytic performance of this composition, as it ensures all elements can play a role in the reaction. To corroborate the homogeneity and morphological trends across all compositions, additional SEM and EDX mapping results are provided in the Supplementary Materials (Figures S1–S5). These images confirm that each sample exhibits a uniform distribution of its constituent metals. While there are some differences in particle size and porosity—likely caused by the nature of the fifth metal—all samples show successful integration of elements and well-formed nanostructures. Overall, the SEM, TEM, and EDX results demonstrate that all HEO catalysts were synthesized successfully with uniform elemental distribution and nanostructured morphology. The subtle differences in surface structure, porosity, and particle connectivity—tuned by the fifth metal—can significantly impact how each material performs during OER, highlighting the importance of compositional design in developing high-performance electrocatalysts.

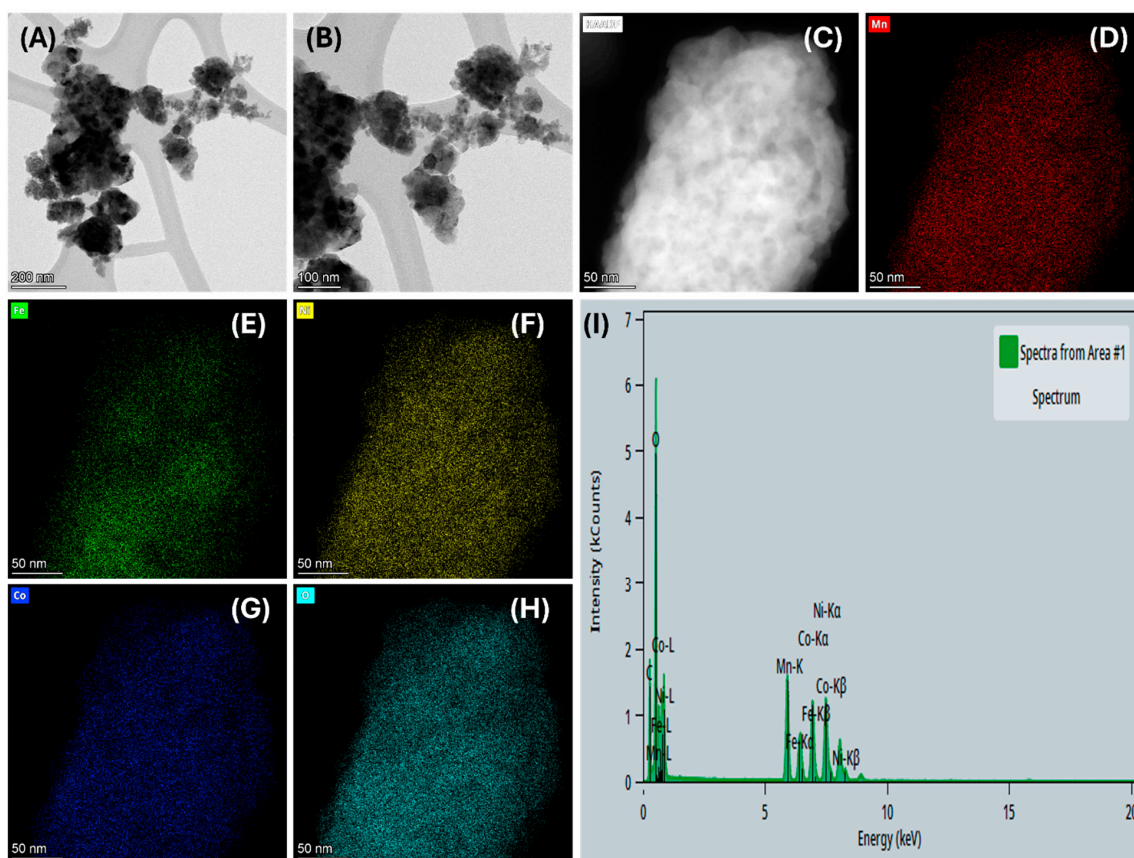


Figure 3. (A,B) HR-TEM image, (C) HAADF, and (D–I) EDX dot-mapping images of $(\text{MnFeNiCo})_3\text{O}_4$ sample.

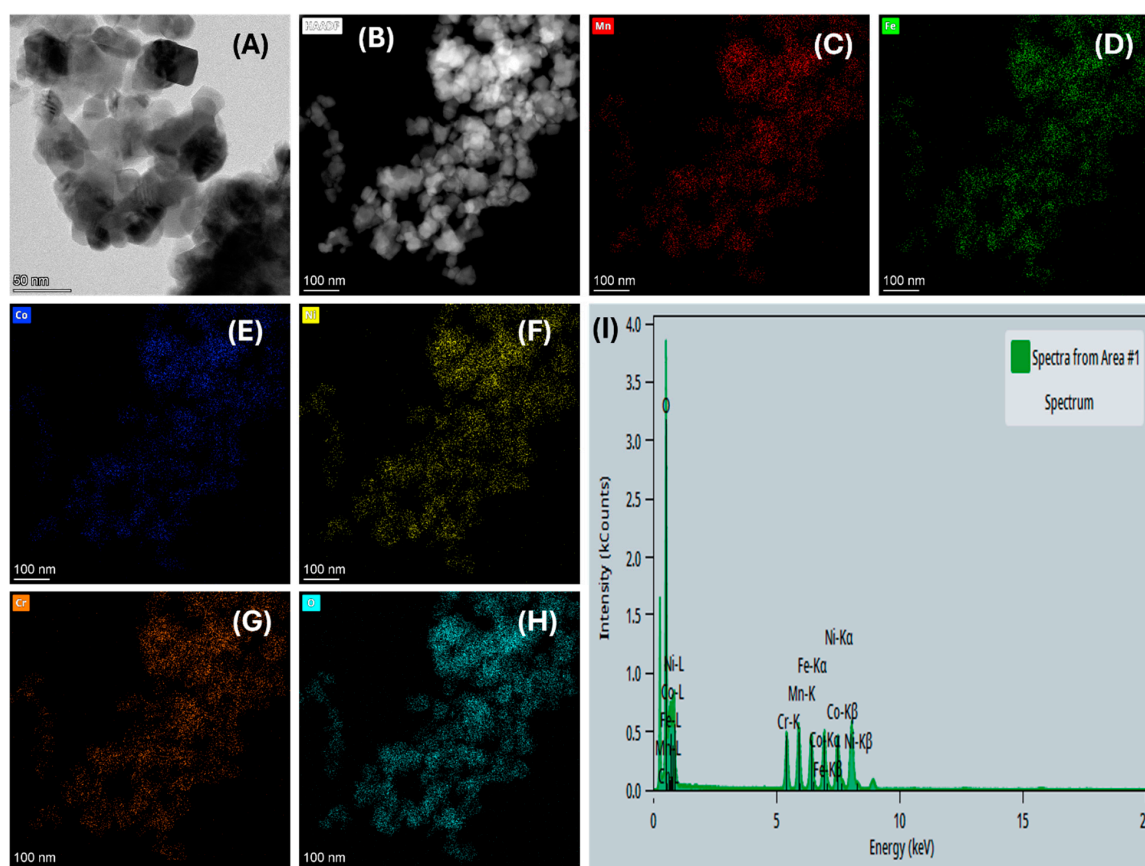


Figure 4. (A) HR-TEM image, (B) HAADF, and (C–I) EDX dot-mapping images of $(\text{MnFeNiCoCr})_3\text{O}_4$ sample.

The XPS analysis of the $(\text{MnFeNiCoCr})_3\text{O}_4$ catalyst is presented in Figure 5, while the survey spectrum confirming the presence of all constituent elements is shown in Figure S6. The Mn 2p spectrum (Figure 5A) exhibits two distinct features at 641.4 eV and 643.6 eV, corresponding to Mn^{2+} 2p_{3/2} and Mn^{3+} 2p_{3/2}, respectively [35]. In the Fe 2p region (Figure 5B), four primary peaks are resolved at 710.7 and 714.7 eV (Fe 2p_{3/2}) and at 723.4 and 727.7 eV (Fe 2p_{1/2}), accompanied by satellite peaks at 718.4 and 732.4 eV, confirming the coexistence of Fe^{2+} and Fe^{3+} oxidation states [36]. The Ni 2p spectrum (Figure 5C) reveals peaks at 854.0 eV (Ni 2p_{3/2}) and 871.6 eV (Ni 2p_{1/2}), along with shake-up satellites at 860.3 and 878.5 eV, indicating the predominance of Ni^{2+} species [37]. The Co 2p spectrum (Figure 5D) shows two deconvoluted peaks at 778.8 eV (Co^{3+}) and 780.9 eV (Co^{2+}) for the 2p_{3/2} component with a satellite at 784.9 eV, and corresponding 2p_{1/2} features at 794.3 eV (Co^{3+}) and 796.3 eV (Co^{2+}) with a satellite peak at 801.3 eV [38]. The Cr 2p spectrum (Figure 5E) displays contributions from both Cr^{3+} (576.5 and 586.1 eV) and Cr^{6+} (578.7 and 588.1 eV), associated with the Cr 2p_{3/2} and Cr 2p_{1/2} levels [39]. Finally, the O 1s spectrum (Figure 5F) can be deconvoluted into three components at 529.7, 530.8, and 531.7 eV, which are assigned to lattice oxygen (O_1 , M–O bonds), oxygen defects (O_2 , related to oxygen vacancies), and surface chemisorbed oxygen species (O_3), respectively [40].

Furthermore, the elemental composition of the $(\text{MnFeNiCo})_3\text{O}_4$ ($\text{MnFeNiCoCr})_3\text{O}_4$ catalysts confirmed an equimolar distribution of metals across all samples, consistent with the intended synthesis design. To validate this result, X-ray fluorescence (XRF) elemental analysis was carried out, and the data indicated nearly equimolar concentrations of the constituent metals, as summarized in Table S1.

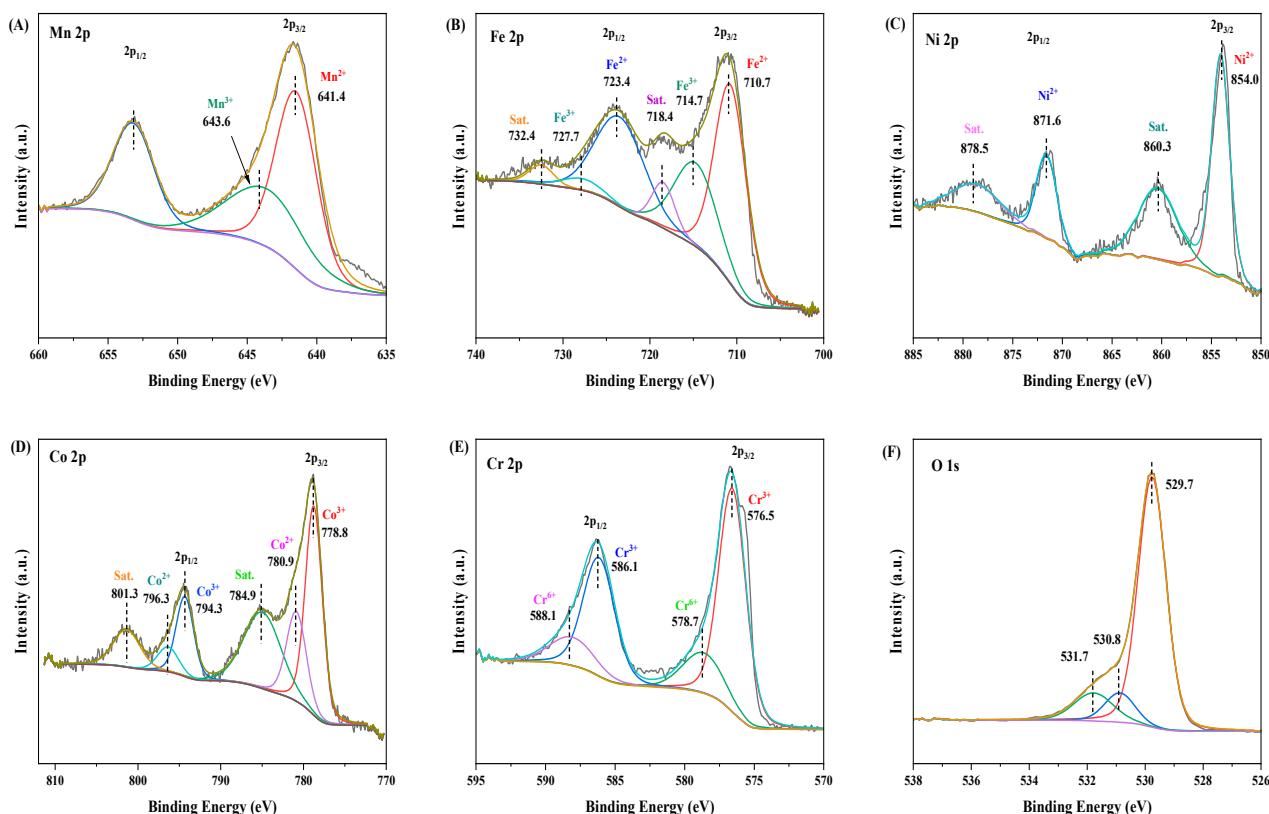


Figure 5. (A) Mn 2p, (B) Fe 2p, (C) Ni 2p, (D) Co 2p, (E) Cr 2p, and (F) O 1s high resolution XPS spectra of the $(\text{MnFeNiCoCr})_3\text{O}_4$ sample.

2.2. OER Performance

LSV at the scan rate of 5 mV/s was employed to assess the OER performance of the prepared HEO electrocatalysts. As depicted in Figure 6A, the $(\text{MnFeNiCoCr})_3\text{O}_4$ catalyst demonstrated the lowest overpotential, registering 323 mV at a current density of 10 mA/cm². This value was notably lower than its counterparts: 45 mV less than $(\text{MnFeNiCo})_3\text{O}_4$, 75 mV less than $(\text{MnFeNiCoCu})_3\text{O}_4$, 79 mV less than $(\text{MnFeNiCoZn})_3\text{O}_4$, and 94 mV less than $(\text{MnFeNiCoCd})_3\text{O}_4$. According to the recorded values provided in Table 1, a similar pattern was observed when considering the onset potential, which $(\text{MnFeNiCoCr})_3\text{O}_4$ demonstrated the lowest onset value of 260 mV at a current density of 1 mA/cm². The Tafel slope serves as a crucial parameter for characterizing the catalytic kinetics and mechanism of OER electrocatalysis. The Tafel slope for each sample was derived from the LSV curves, specifically within the current density range of approximately 1 to 10 mA/cm². A smaller Tafel slope indicates faster kinetics for the OER [41]. As depicted in Figure 6B, the Tafel slopes for the catalysts were determined as follows: $(\text{MnFeNiCoCr})_3\text{O}_4$ was 56 mV/dec, $(\text{MnFeNiCoCu})_3\text{O}_4$ was 69 mV/dec, $(\text{MnFeNiCoZn})_3\text{O}_4$ was 76 mV/dec, $(\text{MnFeNiCoCd})_3\text{O}_4$ was 89 mV/dec, and $(\text{MnFeNiCo})_3\text{O}_4$ was 58 mV/dec. In comparison, the commercially available ruthenium (IV) oxide (RuO_2), used as a standard benchmark sample, exhibited an overpotential of 338 mV at current density of 10 mV/cm² and a Tafel slope of 62 mV/dec. The electrocatalytic activity of quinary-metal $(\text{MnFeNiCoCr})_3\text{O}_4$ was notably competitive and even superior to that of RuO_2 , showcasing the advanced performance of synthesized $(\text{MnFeNiCoCr})_3\text{O}_4$ nanoparticles in electrochemical OER. Therefore, both the LSV test and Tafel slope analyses indicate the superior OER performance of $(\text{MnFeNiCoCr})_3\text{O}_4$. Furthermore, $(\text{MnFeNiCoCr})_3\text{O}_4$ demonstrates strong catalytic activity for the OER, surpassing many other HEO catalysts documented in the recent literature, as detailed in Table 2.

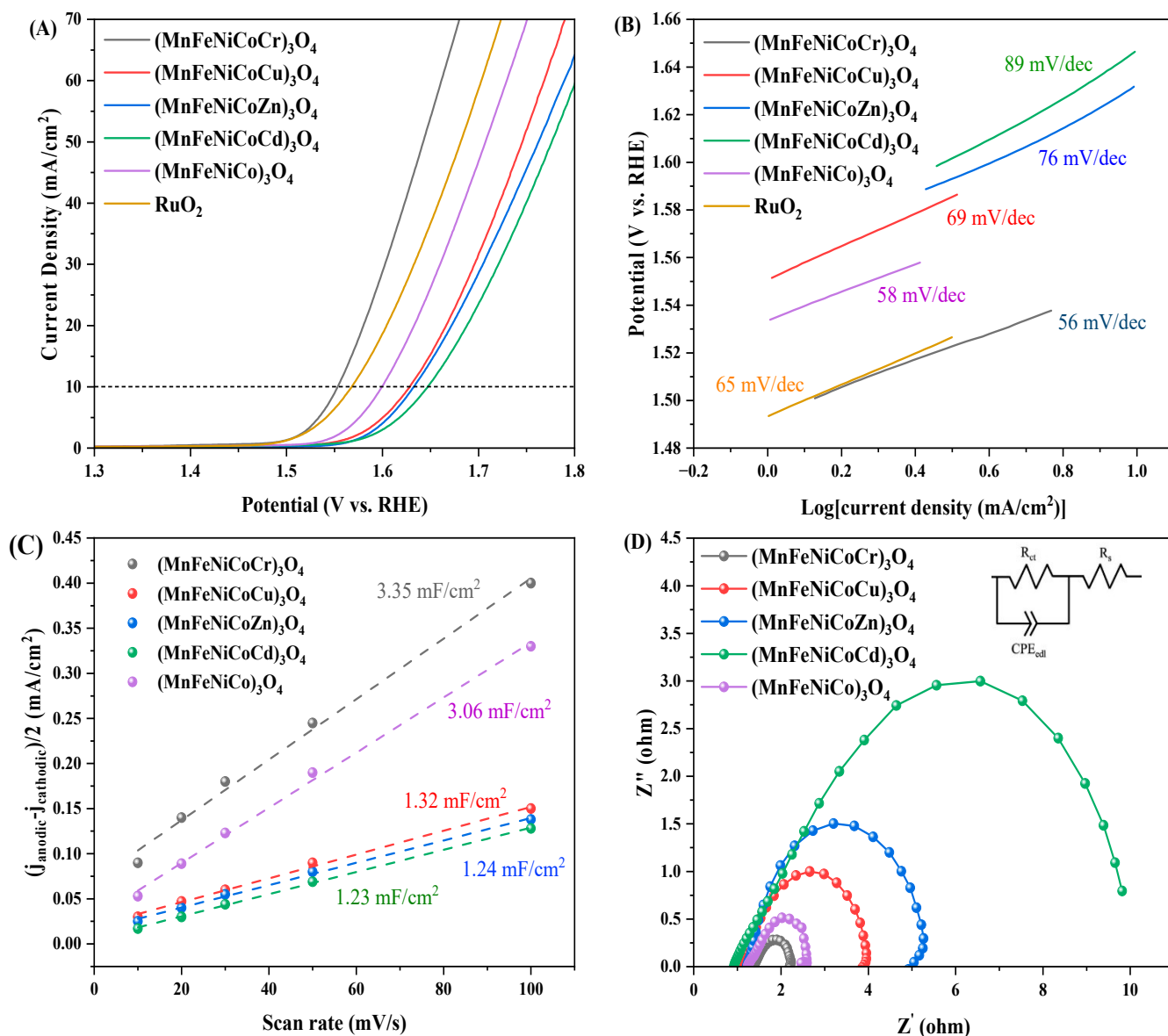


Figure 6. (A) LSV curves at the scan rate of 5 mV/s, (B) Tafel slope; (C) Electrical-double layer capacitance (C_{edl}) of all samples; and (D) Nyquist plot of the prepared samples.

Table 1. Electrochemical characteristics of the synthesized HEO electrocatalysts.

Electrocatalyst	Overpotential at Current Density of (mV)			Tafel Slope (mV/dec)	C_{edl} (mF/cm^2)
	1 (mA/cm^2)	10 (mA/cm^2)	100 (mA/cm^2)		
$(\text{MnFeNiCo})_3\text{O}_4$	303	368	582	58	3.06
$(\text{MnFeNiCoCd})_3\text{O}_4$	332	417	665	89	1.23
$(\text{MnFeNiCoZn})_3\text{O}_4$	335	402	664	76	1.24
$(\text{MnFeNiCoCu})_3\text{O}_4$	321	398	622	69	1.32
$(\text{MnFeNiCoCr})_3\text{O}_4$	260	323	504	56	3.35

To gain deeper insights into the electrochemical properties of the catalysts, the ECSA value of the samples was determined by calculating the C_{edl} , as described in Section 3.4. To determine the C_{edl} of the samples, CV measurements were conducted at various scan rates of 10, 20, 30, 50, and 100 mV/s within the non-faradaic region of 1.0 to 1.2 V (vs. RHE), as shown in Figure 7. At the midpoint of the potential window (1.1 V), both the cathodic current (j_{cathodic}) and anodic current (j_{anodic}) were recorded. By plotting

$\Delta j = (j_{\text{anodic}} - j_{\text{cathodic}})/2$ as a function of scan rate, a linear relationship was obtained, as depicted in Figure 6C. The slope of this plot represents the C_{edl} . The C_{edl} of $(\text{MnFeNiCoCr})_3\text{O}_4$, $(\text{MnFeNiCoCu})_3\text{O}_4$, $(\text{MnFeNiCoZn})_3\text{O}_4$, $(\text{MnFeNiCoCd})_3\text{O}_4$, and $(\text{MnFeNiCo})_3\text{O}_4$ were calculated as 55, 22, 20, 20, and 51 cm^2 , respectively.

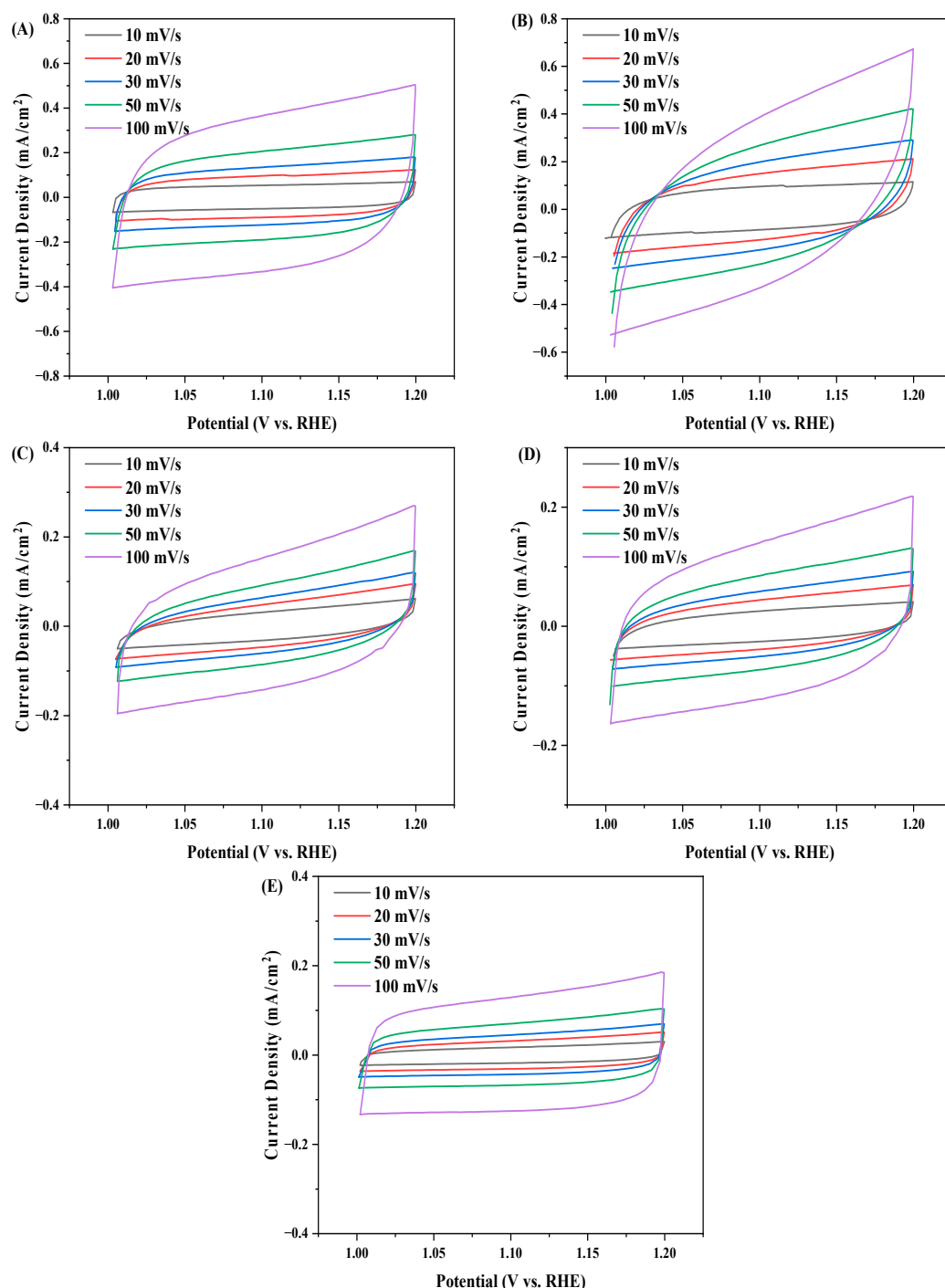


Figure 7. Cyclic voltammetry scans of (A) $(\text{MnFeNiCo})_3\text{O}_4$, (B) $(\text{MnFeNiCoCr})_3\text{O}_4$, (C) $(\text{MnFeNiCoCu})_3\text{O}_4$, (D) $(\text{MnFeNiCoZn})_3\text{O}_4$, and (E) $(\text{MnFeNiCoCd})_3\text{O}_4$ samples.

EIS is employed to evaluate the interfacial characteristics of electrodes and the reaction kinetics at the electrode surface. The half-circle in the Nyquist plot serves as an indicator for the charge transfer resistance (R_{ct}) of the electrode. The Nyquist plots for all the samples are presented in Figure 6D. An equivalent circuit, comprising electrolyte resistance (R_s), charge transfer resistance (R_{ct}), and a constant phase element (CPE), is shown in the inset

of the figure. Notably, the $(\text{MnFeNiCoCr})_3\text{O}_4$ catalyst displays the smallest diameter, which is lower than those of $(\text{MnFeNiCo})_3\text{O}_4$, $(\text{MnFeNiCoCu})_3\text{O}_4$, $(\text{MnFeNiCoZn})_3\text{O}_4$, and $(\text{MnFeNiCoCd})_3\text{O}_4$. This indicates the superior charge transfer kinetics and excellent electronic conductivity at the interface between the $(\text{MnFeNiCoCr})_3\text{O}_4$ catalyst and the electrolyte [42].

Table 2. OER performance comparison between some recently reported HEMs and $(\text{MnFeNiCoCr})_3\text{O}_4$ catalyst synthesized in this work.

Electrocatalyst	Substrate	Overpotential at 10 mA/cm ² (mV)	Tafel Slope (mV/dec)	Electrolyte	Reference
$(\text{CoCuFeMnNi})_3\text{O}_4$	GCE	400	76.7	1.0 M KOH	[18]
$(\text{MgCoNiCuZn})\text{O}$	CFP	360	61.4	1.0 M KOH	[19]
$(\text{FeCrCoNiAl}_{0.1})\text{O}_x$ -films	Titanium foil	381	60.9	1.0 M KOH	[43]
$(\text{Co}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{Fe}_{0.2}\text{Zn}_{0.2})\text{Fe}_2\text{O}_4$	CFP	326	53.6	1.0 M KOH	[20]
$(\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cr}_{0.2}\text{Cu}_{0.2})_3\text{O}_4$	Ni foam	338	71.4	1.0 M KOH	[22]
$(\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cr}_{0.2}\text{Mn}_{0.2})_3\text{O}_4$	Ni foam	298	59	1.0 M KOH	[22]
NiCuCo-sulfides	GCE	340	96	1.0 M KOH	[44]
$(\text{MnFeNiCoCr})_3\text{O}_4$	CFP	323	56	1.0 M KOH	This work

Incorporation of Cr into the $(\text{MnFeNiCo})_3\text{O}_4$ lattice plays a crucial role in modulating the electronic structure and surface chemistry, thereby enhancing OER activity. Chromium commonly exists in multiple oxidation states ($\text{Cr}^{3+}/\text{Cr}^{6+}$), as confirmed by the XPS spectra (Figure 5E), which provides additional redox flexibility to participate in electron transfer during OER. The presence of Cr^{3+} ions increases metal–oxygen covalency and promotes the formation of oxygen vacancies, both of which accelerate charge transport and create more active sites for adsorbing oxygenated intermediates such as $^*\text{OH}$, $^*\text{O}$, and $^*\text{OOH}$ [34]. Furthermore, the high electronegativity difference between Cr and the other transition metals can induce lattice distortion, locally modify the d-band center and thus lower the adsorption energy of intermediates, which contributes to faster reaction kinetics [31]. These synergistic effects explain the superior performance of $(\text{MnFeNiCoCr})_3\text{O}_4$ compared to other compositions in this study. Lattice distortion arising from ionic size differences (e.g., incorporation of Cr) enhances defect density and oxygen vacancy formation, which in turn improves charge transfer and increases the number of accessible active sites. Moreover, the configurational stability of the high-entropy framework helps maintain structural integrity under prolonged OER operation [22].

In addition to activity, long-term durability is a crucial parameter for assessing catalyst performance. The stability of RuO_2 and $(\text{MnFeNiCoCr})_3\text{O}_4$ was evaluated through 20 h chronopotentiometry testing (Figure 8). Over this period, RuO_2 exhibited a 4.2% decline in performance, whereas $(\text{MnFeNiCoCr})_3\text{O}_4$ showed even a slight improvement of 3.7% in performance. The decrease in potential and improvement in performance for the high-entropy oxide may be associated with surface reconstruction during the OER process, which can generate additional active sites and contribute to sustained catalytic activity [45].

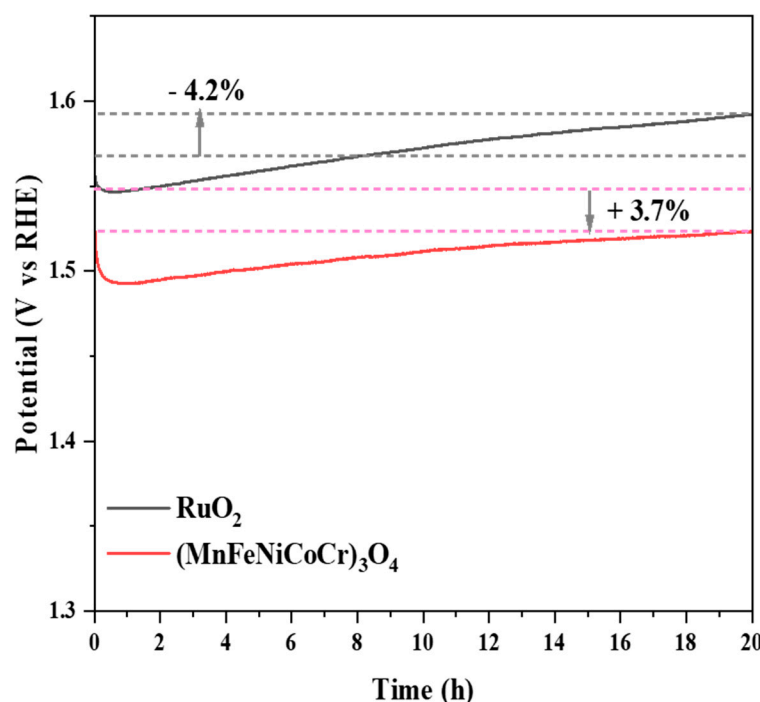


Figure 8. Chronopotentiometry test of RuO_2 and $(\text{MnFeNiCoCr})_3\text{O}_4$ catalysts at fixed current density of 10 mA/cm^2 .

3. Experimental Section

3.1. Materials

The detailed information regarding the chemicals used in the manuscript is provided in the Supplementary Materials.

3.2. Catalyst Synthesis

The solution combustion synthesis method was utilized to prepare high-entropy oxide catalysts. To create an isoatomic precursor solution, 10 mmol quantities of various metal nitrates—specifically, manganese (II) nitrate tetrahydrate, iron (III) nitrate nonahydrate, nickel (II) nitrate hexahydrate, and cobalt (II) nitrate hexahydrate—were accurately measured. These compounds were then dissolved in 10 mL of distilled water and thoroughly blended. Subsequently, a pre-made urea solution was introduced as the fuel required for the solution combustion process, and the mixture was continuously stirred at 80°C at a speed of 300 rpm until a gel-like solution was obtained. This gel-like solution was then subjected to a furnace at 350°C for 1 h. Following this, it was taken out and allowed to cool naturally. The resulting $(\text{MnFeNiCo})_3\text{O}_4$ material was pulverized and subsequently calcined at 600°C for four hours in a furnace, with a heating rate of 10°C/min and then air-cooled. This identical methodology was employed to synthesize $(\text{MnFeNiCoCr})_3\text{O}_4$, $(\text{MnFeNiCoCu})_3\text{O}_4$, $(\text{MnFeNiCoZn})_3\text{O}_4$, and $(\text{MnFeNiCoCd})_3\text{O}_4$ powders.

3.3. Characterization Techniques

The detailed information regarding the catalysts' characterization is provided in the Supplementary Materials.

3.4. Electrochemical Tests

Electrochemical testing of the synthesized catalysts was carried out using a Bio-Logic Science potentiostat, employing a standard three-electrode configuration within a single-compartment electrochemical cell. The reference electrode used was Ag/AgCl , while

a platinum mesh served as the counter electrode. All experiments were conducted in a 1.0 M KOH aqueous solution, which functioned as the electrolyte medium. For the working electrode, a carbon fiber paper (CFP, 1 cm × 1 cm, supplied by Alfa) was used as the substrate, onto which the catalyst was deposited. Prior to performing the OER measurements, the electrolyte was saturated with oxygen by bubbling O₂ gas through the solution for 30 min. This pre-conditioning step ensured that the dissolved oxygen level was sufficient to reflect accurate OER activity. The working electrode was prepared by fabricating a catalyst ink. Specifically, 5 mg of catalyst powder was dispersed in a solvent mixture composed of 800 µL deionized water and 170 µL isopropanol, followed by the addition of 30 µL Nafion solution as a binder. The resulting suspension was subjected to ultrasonic treatment for 30 min to achieve uniform dispersion with catalyst concentration of 5 mg/mL. After sonication, 150 µL of the homogeneous ink was drop-cast onto the surface of the carbon fiber paper with catalyst amount of 0.75 mg/cm² and subsequently allowed to dry under vacuum conditions at moderate temperature for 2 h. This preparation method ensured good adhesion and uniform catalyst coverage on the electrode surface, which is critical for consistent and reliable electrochemical measurements.

All recorded electrochemical potentials were converted to the reversible hydrogen electrode (RHE) scale using the standard equation: $E_{(RHE)} = E_{(Ag/AgCl)} + 0.059 \times pH + 0.197 \text{ V}$ [46]. This conversion ensured consistency in comparing electrocatalytic activity across different studies. To evaluate the OER performance of the catalysts, linear sweep voltammetry (LSV) was conducted at a scan rate of 5 mV/s, and the resulting data were used to construct Tafel plots for kinetic analysis. The electrochemical active surface area (ECSA) of the catalyst-coated electrodes was estimated through the determination of their electrochemical double-layer capacitance (C_{edl}). This was achieved by performing cyclic voltammetry (CV) within a non-faradaic potential range, specifically from 1.0 to 1.2 V vs. RHE, in a 1.0 M KOH electrolyte. CV scans were recorded at different scan rates ranging from 10 to 100 mV/s. The capacitive current was then determined at the midpoint potential (1.1 V vs. RHE) by calculating half the difference between the anodic and cathodic currents, i.e., $(j_{anodic} - j_{cathodic})/2$. A plot of this value versus the corresponding scan rate produced a straight line, whose slope represents the C_{edl} . The ECSA was then calculated using the relation: $ECSA = C_{edl} \times A_{CFP}/C_{edl-flat}$, where A_{CFP} is the geometrical surface area of the carbon fiber paper (used as the electrode substrate), and $C_{edl-flat}$ denotes the specific double-layer capacitance of a smooth, flat surface, typically taken as 60 µF/cm² [29,45]. This approach allows for a semi-quantitative comparison of the electrochemically active surface available on different catalyst samples. Additionally, to probe the charge transfer resistance and interfacial properties of the catalysts, electrochemical impedance spectroscopy (EIS) was performed at an applied potential of 1.58 V vs. RHE. A small AC voltage amplitude of 10 mV was superimposed, and the impedance spectra were collected over a frequency range spanning from 100 kHz to 0.1 Hz.

4. Conclusions

This work systematically investigated the structure–activity relationships of four high-entropy oxide (HEO) catalysts (MnFeNiCo)₃O₄—(MnFeNiCoCu)₃O₄, (MnFeNiCoZn)₃O₄, (MnFeNiCoCd)₃O₄, and (MnFeNiCoCr)₃O₄—toward the oxygen evolution reaction (OER) in alkaline conditions. All catalysts exhibited phase-pure spinel structures with uniform elemental distribution and porous nanostructures, as confirmed by XRD, SEM, HR-TEM, and elemental mapping. Electrochemical tests revealed significant differences in catalytic performance, attributed to the electronic and structural contributions of the fifth dopant metal. Notably, (MnFeNiCoCr)₃O₄ achieved the lowest overpotential (323 mV at 10 mA/cm²) and the highest ECSA and C_{edl} among all tested materials. These findings underscore the

importance of element selection in high-entropy catalyst design and demonstrate that Cr incorporation significantly boosts catalytic efficiency by enhancing charge transfer and surface accessibility. This study offers a rational pathway to engineer highly active, noble-metal-free electrocatalysts for sustainable water splitting. Beyond OER, the elemental substitution strategy employed in this work provides a general framework for optimizing high-entropy oxides in a wide range of catalytic applications. By systematically tailoring the fifth metal within a stable quaternary backbone, this approach can be extended to design efficient catalysts for hydrogen evolution, CO₂ reduction, nitrogen fixation, and other energy conversion and environmental remediation reactions. Such targeted compositional tuning offers a rational pathway to accelerate the discovery of next-generation multifunctional catalysts.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/catal15090827/s1>, S1: Materials; S2: Characterization techniques; Figure S1: (A–F) elemental mapping images of (MnFeNiCo)₃O₄ sample; Figure S2: (A) SEM image and (B–H) elemental mapping images of (MnFeNiCoCr)₃O₄ sample; Figure S3: (A) SEM image and (B–H) elemental mapping images of (MnFeNiCoCu)₃O₄ sample; Figure S4: (A) SEM image and (B–H) elemental mapping images of (MnFeNiCoZn)₃O₄ sample; Figure S5: (A) SEM image and (B–H) elemental mapping images of (MnFeNiCoCd)₃O₄ sample; Figure S6: (A) Full XPS spectrum and (B) XPS spectrum of C 1s of (MnFeNiCoCr)₃O₄ sample; Table S1: Quantities of metal species constituting the multiple transition metal systems through XRF analysis.

Author Contributions: M.Z.S.: conceptualization, investigation, writing—original draft; A.N.: resources, writing—review and editing; A.O.: resources, writing—review and editing; H.S.: conceptualization, supervision, project administration, writing—review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Data will be made available on request.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Liu, Y.; Zhou, D.; Deng, T.; He, G.; Chen, A.; Sun, X.; Yang, Y.; Miao, P. Research progress of oxygen evolution reaction catalysts for electrochemical water splitting. *ChemSusChem* **2021**, *14*, 5359–5383. [CrossRef]
2. Zehtab Salmasi, M.; Omidkar, A.; Nguyen, H.M.; Song, H. MXenes as electrocatalysts for hydrogen production through the electrocatalytic water splitting process: A mini review. *Energy Rev.* **2024**, *3*, 100070. [CrossRef]
3. Kim, J.S.; Kim, B.; Kim, H.; Kang, K. Recent progress on multimetal oxide catalysts for the oxygen evolution reaction. *Adv. Energy Mater.* **2018**, *8*, 1702774. [CrossRef]
4. Nguyen, T.X.; Huang, Z.-T.; Ting, J.-M. Iron-concentration adjusted Multi-Metal oxides for optimized oxygen evolution reaction performance. *Appl. Surf. Sci.* **2021**, *570*, 151160. [CrossRef]
5. García-Mota, M.; Vojvodic, A.; Metiu, H.; Man, I.C.; Su, H.; Rossmeisl, J.; Nørskov, J.K. Tailoring the activity for oxygen evolution Electrocatalysis on rutile TiO₂ (110) by transition-metal substitution. *ChemCatChem* **2011**, *3*, 1607–1611. [CrossRef]
6. Wu, Z.; Zou, Z.; Huang, J.; Gao, F. Fe-doped NiO mesoporous nanosheets array for highly efficient overall water splitting. *J. Catal.* **2018**, *358*, 243–252. [CrossRef]
7. Xiao, Z.; Huang, Y.-C.; Dong, C.-L.; Xie, C.; Liu, Z.; Du, S.; Chen, W.; Yan, D.; Tao, L.; Shu, Z. Operando identification of the dynamic behavior of oxygen vacancy-rich Co₃O₄ for oxygen evolution reaction. *J. Am. Chem. Soc.* **2020**, *142*, 12087–12095. [CrossRef]
8. Song, J.; Wei, C.; Huang, Z.-F.; Liu, C.; Zeng, L.; Wang, X.; Xu, Z.J. A review on fundamentals for designing oxygen evolution electrocatalysts. *Chem. Soc. Rev.* **2020**, *49*, 2196–2214. [CrossRef]
9. Ma, Y.; Ma, Y.; Wang, Q.; Schweidler, S.; Botros, M.; Fu, T.; Hahn, H.; Brezesinski, T.; Breitung, B. High-entropy energy materials: Challenges and new opportunities. *Energy Environ. Sci.* **2021**, *14*, 2883–2905. [CrossRef]
10. Sarkar, A.; Wang, Q.; Schiele, A.; Chellali, M.R.; Bhattacharya, S.S.; Wang, D.; Brezesinski, T.; Hahn, H.; Velasco, L.; Breitung, B. High-entropy oxides: Fundamental aspects and electrochemical properties. *Adv. Mater.* **2019**, *31*, 1806236. [CrossRef]

11. Zhai, Y.; Ren, X.; Wang, B.; Liu, S. High-entropy catalyst—A novel platform for electrochemical water splitting. *Adv. Funct. Mater.* **2022**, *32*, 2207536. [\[CrossRef\]](#)
12. Li, T.; Yao, Y.; Ko, B.H.; Huang, Z.; Dong, Q.; Gao, J.; Chen, W.; Li, J.; Li, S.; Wang, X. Carbon-supported high-entropy oxide nanoparticles as stable electrocatalysts for oxygen reduction reactions. *Adv. Funct. Mater.* **2021**, *31*, 21010561. [\[CrossRef\]](#)
13. He, L.; Kang, H.; Hou, G.; Qiao, X.; Jia, X.; Qin, W.; Wu, X. Low-temperature synthesis of nano-porous high entropy spinel oxides with high grain boundary density for oxygen evolution reaction. *Chem. Eng. J.* **2023**, *460*, 141675. [\[CrossRef\]](#)
14. Yen, J.-Z.; Yang, Y.-C.; Tuan, H.-Y. Interface engineering of high entropy Oxide@ Polyaniline heterojunction enables highly stable and excellent lithium ion storage performance. *Chem. Eng. J.* **2022**, *450*, 137924. [\[CrossRef\]](#)
15. Akrami, S.; Murakami, Y.; Watanabe, M.; Ishihara, T.; Arita, M.; Fuji, M.; Edalati, K. Defective high-entropy oxide photocatalyst with high activity for CO₂ conversion. *Appl. Catal. B* **2022**, *303*, 120896. [\[CrossRef\]](#)
16. Lee, S.A.; Bu, J.; Lee, J.; Jang, H.W. High-entropy nanomaterials for advanced electrocatalysis. *Small Sci.* **2023**, *3*, 2200109. [\[CrossRef\]](#)
17. Albedwawi, S.H.; Aljaberi, A.; Haidemenopoulos, G.N.; Polychronopoulou, K. High entropy oxides-exploring a paradigm of promising catalysts: A review. *Mater. Des.* **2021**, *202*, 109534. [\[CrossRef\]](#)
18. Wang, D.; Liu, Z.; Du, S.; Zhang, Y.; Li, H.; Xiao, Z.; Chen, W.; Chen, R.; Wang, Y.; Zou, Y.; et al. Low-temperature synthesis of small-sized high-entropy oxides for water oxidation. *J. Mater. Chem. A* **2019**, *7*, 24211–24216. [\[CrossRef\]](#)
19. Liu, F.; Yu, M.; Chen, X.; Li, J.; Liu, H.; Cheng, F. Defective high-entropy rocksalt oxide with enhanced metal-oxygen covalency for electrocatalytic oxygen evolution. *Chin. J. Catal.* **2022**, *43*, 122–129. [\[CrossRef\]](#)
20. Zhang, Y.; Lu, T.; Ye, Y.; Dai, W.; Zhu, Y.; Pan, Y. Stabilizing Oxygen Vacancy in Entropy-Engineered CoFe₂O₄-Type Catalysts for Co-prosperity of Efficiency and Stability in an Oxygen Evolution Reaction. *ACS Appl. Mater. Interfaces* **2020**, *12*, 32548–32555. [\[CrossRef\]](#) [\[PubMed\]](#)
21. Dai, W.; Lu, T.; Pan, Y. Novel and promising electrocatalyst for oxygen evolution reaction based on MnFeCoNi high entropy alloy. *J. Power Sources* **2019**, *430*, 104–111. [\[CrossRef\]](#)
22. Guo, Y.; Zhang, X.; Wei, H.; Yu, H.; Xie, Y. Construction of spinel (Fe_{0.2}Co_{0.2}Ni_{0.2}Cr_{0.2}M_{0.2})₃O₄ (M = Mg, Mn, Zn, and Cu) high-entropy oxides with tunable valance states for oxygen evolution reaction. *J. Alloys Compd.* **2024**, *989*, 174304. [\[CrossRef\]](#)
23. Du, J.; Bao, S.; Li, W.; Chen, Y.; Fan, B. Structural, thermal, magnetic and microwave-absorbing properties of spinel-structured high entropy oxide (MnFeCoNiX)₃O₄ (X = Zn, Cu, Cr). *Ceram. Int.* **2024**, *50*, 14697–14707. [\[CrossRef\]](#)
24. Du, Y.; Yang, F.; Li, J.; Jiang, M.; Yin, J.; Hu, Q.; Zhang, J. Electrocatalytic performances of high-entropy spinel oxide (Cr_{1/5}Mn_{1/5}Ni_{1/5}Fe_{1/5}Co_{1/5})₃O₄ for oxygen reduction/evolution reactions in alkaline electrolyte. *J. Alloys Compd.* **2024**, *1004*, 175923. [\[CrossRef\]](#)
25. Mao, A.; Quan, F.; Xiang, H.-Z.; Zhang, Z.-G.; Kuramoto, K.; Xia, A.-L. Facile synthesis and ferrimagnetic property of spinel (CoCrFeMnNi)₃O₄ high-entropy oxide nanocrystalline powder. *J. Mol. Struct.* **2019**, *1194*, 11–18. [\[CrossRef\]](#)
26. Arun, S.R.; Jacob, G. Exploring the charge storage ability of the spinel-type high entropy oxide (MnFeCoNiZn)₃O₄ nanoparticles for supercapacitor applications. *Chem. Eng. J. Adv.* **2025**, *21*, 100708. [\[CrossRef\]](#)
27. Zehtab Salmasi, M.; Omidkar, A.; Ying, H.; Song, H. Enhanced phenol degradation in wastewater using non-thermal plasma coupled with NiO/g-C₃N₄ nanocomposite catalyst. *J. Environ. Chem. Eng.* **2025**, *13*, 117180. [\[CrossRef\]](#)
28. Xu, H.; Liu, L.; Gao, J.; Du, P.; Fang, G.; Qiu, H.-J. Hierarchical nanoporous V₂O₃ Nanosheets anchored with alloy nanoparticles for efficient electrocatalysis. *ACS Appl. Mater. Interfaces* **2019**, *11*, 38746–38753. [\[CrossRef\]](#)
29. Moradi, M.; Hasanvandian, F.; Bahadoran, A.; Shokri, A.; Zerangnasrabad, S.; Kakavandi, B. New high-entropy transition-metal sulfide nanoparticles for electrochemical oxygen evolution reaction. *Electrochim. Acta* **2022**, *436*, 141444. [\[CrossRef\]](#)
30. Cychosz, K.A.; Guillet-Nicolas, R.; García-Martínez, J.; Thommes, M. Recent advances in the textural characterization of hierarchically structured nanoporous materials. *Chem. Soc. Rev.* **2017**, *46*, 389–414. [\[CrossRef\]](#)
31. Duan, Y.; Sun, S.; Xi, S.; Ren, X.; Zhou, Y.; Zhang, G.; Yang, H.; Du, Y.; Xu, Z.J. Tailoring the Co 3d-O 2p covalency in LaCoO₃ by Fe substitution to promote oxygen evolution reaction. *Chem. Mater.* **2017**, *29*, 10534–10541. [\[CrossRef\]](#)
32. Ansari, A.A.; Ahmad, N.; Alam, M.; Adil, S.F.; Ramay, S.M.; Albadri, A.; Ahmad, A.; Al-Enizi, A.M.; Alrayes, B.F.; Assal, M.E. Physico-chemical properties and catalytic activity of the sol-gel prepared Ce-ion doped LaMnO₃ perovskites. *Sci. Rep.* **2019**, *9*, 7747. [\[CrossRef\]](#)
33. Phadtare, D.; Kondawar, S.; Athawale, A.; Rode, C. Crystalline LaCoO₃ perovskite as a novel catalyst for glycerol transesterification. *Mol. Catal.* **2019**, *475*, 110496. [\[CrossRef\]](#)
34. Nguyen, T.X.; Liao, Y.-C.; Lin, C.-C.; Su, Y.-H.; Ting, J.-M. Advanced High Entropy Perovskite Oxide Electrocatalyst for Oxygen Evolution Reaction. *Adv. Funct. Mater.* **2021**, *31*, 2101632. [\[CrossRef\]](#)
35. Zhao, X.; Li, X.; Yan, Y.; Xing, Y.; Lu, S.; Zhao, L.; Zhou, S.; Peng, Z.; Zeng, J. Electrical and structural engineering of cobalt selenide nanosheets by Mn modulation for efficient oxygen evolution. *Appl. Catal. B* **2018**, *236*, 569–575. [\[CrossRef\]](#)

36. He, L.; Wang, N.; Sun, B.; Zhong, L.; Yao, M.; Hu, W.; Komarneni, S. High-entropy FeCoNiMn (oxy) hydroxide as high-performance electrocatalyst for OER and boosting clean carrier production under quasi-industrial condition. *J. Clean. Prod.* **2022**, *356*, 131680. [\[CrossRef\]](#)
37. Fu, H.Q.; Zhang, L.; Wang, C.W.; Zheng, L.R.; Liu, P.F.; Yang, H.G. 1D/1D hierarchical nickel sulfide/phosphide nanostructures for electrocatalytic water oxidation. *ACS Energy Lett.* **2018**, *3*, 2021–2029. [\[CrossRef\]](#)
38. Zhang, W.; Ma, X.; Zhong, C.; Ma, T.; Deng, Y.; Hu, W.; Han, X. Pyrite-type CoS₂ nanoparticles supported on nitrogen-doped graphene for enhanced water splitting. *Front. Chem.* **2018**, *6*, 569. [\[CrossRef\]](#) [\[PubMed\]](#)
39. Kim, D.-C.; Ihm, S.-K. Application of spinel-type cobalt chromite as a novel catalyst for combustion of chlorinated organic pollutants. *Environ. Sci. Technol.* **2001**, *35*, 222–226. [\[CrossRef\]](#)
40. Kim, J.H.; Jang, Y.J.; Kim, J.H.; Jang, J.-W.; Choi, S.H.; Lee, J.S. Defective ZnFe₂O₄ nanorods with oxygen vacancy for photoelectrochemical water splitting. *Nanoscale* **2015**, *7*, 19144–19151. [\[CrossRef\]](#) [\[PubMed\]](#)
41. Guo, Y.; Park, T.; Yi, J.W.; Henzie, J.; Kim, J.; Wang, Z.; Jiang, B.; Bando, Y.; Sugahara, Y.; Tang, J. Nanoarchitectonics for transition-metal-sulfide-based electrocatalysts for water splitting. *Adv. Mater.* **2019**, *31*, 1807134. [\[CrossRef\]](#) [\[PubMed\]](#)
42. Liang, Z.; Huang, Z.; Yuan, H.; Yang, Z.; Zhang, C.; Xu, Y.; Zhang, W.; Zheng, H.; Cao, R. Quasi-single-crystalline CoO hexagrams with abundant defects for highly efficient electrocatalytic water oxidation. *Chem. Sci.* **2018**, *9*, 6961–6968. [\[CrossRef\]](#) [\[PubMed\]](#)
43. Zhao, S.; Wu, H.; Yin, R.; Wang, X.; Zhong, H.; Fu, Q.; Wan, W.; Cheng, T.; Shi, Y.; Cai, G.; et al. Preparation and electrocatalytic properties of (FeCrCoNiAl_{0.1})Ox high-entropy oxide and NiCo-(FeCrCoNiAl_{0.1})Ox heterojunction films. *J. Alloys Compd.* **2021**, *868*, 159108. [\[CrossRef\]](#)
44. Wu, X.; Li, S.; Liu, J.; Yu, M. Mesoporous hollow nested nanospheres of Ni, Cu, Co-based mixed sulfides for electrocatalytic oxygen reduction and evolution. *ACS Appl. Nano. Mater.* **2019**, *2*, 4921–4932. [\[CrossRef\]](#)
45. Lao, Y.; Huang, X.; Liu, L.; Mo, X.; Huang, J.; Qin, Y.; Mo, Q.; Hui, X.; Yang, Z.; Jiang, W. Structure-activity relationship study of high entropy oxides catalysts for oxygen evolution reaction. *Chem. Eng. J.* **2024**, *481*, 148428. [\[CrossRef\]](#)
46. Moradi, M.; Hasanvandian, F.; Ghahraman Afshar, M.; Larimi, A.; Khorasheh, F.; Niknam, E.; Rahman Setayesh, S. Incorporation of Fe in mixed CoCu-alkoxide hollow sphere for enhancing the electrochemical water oxidation performance. *Mater. Today Chem.* **2021**, *22*, 100586. [\[CrossRef\]](#)

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.