Microwave-Assisted Auto-Combustion Synthesis of Binary/Ternary Co$_{x}$Ni$_{1−x}$Ferrite for Electrochemical Hydrogen and Oxygen Evolution
Sanaz Chamani, Maasoumeh Khatamian,* Naeimeh Sadat Peighambardoust, and Umut Aydemir*

1. INTRODUCTION

The huge consumption of unsustainable carbon-emitting fossil fuels is the primary culprit for the current energy crunch and environmental concerns.$^{1,2}$ Hydrogen, a carbon-free energy source is a favorable response to confront the energy crisis and environmental issues such as global warming.$^{3,4}$ Discovering a completely new, environmentally benign, cheap, and efficient strategy to generate hydrogen is a persistent challenge. Electrochemical water splitting stands out among other systems regarding its benefits including hydrogen production with high purity and leaving no carbon footprints.$^{5−7}$ This process consists of two half-reactions, namely, hydrogen evolution reaction (HER) on the cathode and oxygen evolution reaction (OER) on the anode.$^{8,9}$ So far, precious-metal-based electrocatalysts such as Pt/C and RuO$_2$ have been identified as state-of-the-art materials to drive the reaction and lower the overpotential higher than the theoretical one, 1.23 V.$^{9,10}$

Over the past decades, plenty of attempts have been made to design and develop catalysts that alloys,$^{11−13}$ carbides,$^{14,15}$ nitrides,$^{16,17}$ oxides,$^{18−20}$ phosphides,$^{21−23}$ borides,$^{24,25}$ and chalcogenides$^{26,27}$ are some of the materials that have been widely explored. Amidst a wide spectrum of electrocatalytic chemicals, the well-known metal compounds of Fe, Co, and Ni—located in the same group with Ru, Ir, and Pt, individually and hence expected to show relatively identical catalytic traits—and different compositions of their mixed oxides are believed to have outstanding catalytic activity for electrolysis of water.$^{28,29}$ It is generally presumed that multinary mixed oxides should outperform their unary counterparts by the virtue of their intrinsic merits such as desirable electrical and catalytic abilities.$^{30−54}$ Keeping this in mind, to accurately evaluate the performance of these oxides, their compositions and particularly content of metal ions should be taken into consideration.$^{34}$

To narrow down the list of mixed metal oxides, some can hold a high potential for energy conversion and storage.$^{31−33,35}$ For instance, NiCo$_2$O$_4$,$^{36,37}$ Ni–Fe mixed oxide,$^{38}$ and (Fe, Co, Ni, and Mn) oxides$^{39,40}$ are favorable electrocatalysts for HER and/or OER. To this end, magnetic ferrites with a general

ABSTRACT: Enormous efforts have been dedicated to engineer low-cost and efficient electrocatalysts for both hydrogen evolution and oxygen evolution reactions (HER and OER, respectively). For this, the current contribution reports the successful synthesis of binary/ternary metal ferrites (Co$_x$Ni$_{1−x}$Ferrite; $x = 0.0, 0.1, 0.3, 0.5, 0.7$, and $1.0$) by a simple one-step microwave technique and subsequently discusses its chemical and electrochemical properties. The X-ray diffraction analysis substantiated the phase purity of the as-obtained catalysts with various compositions. Additionally, the morphology of the nanoparticles was identified via transmission electron microscopy. Further, the vibrating sample magnetometer justified the ferromagnetic character of the as-prepared products. The electrochemical measurements revealed that the as-prepared materials required the overpotentials of 422−600 and 419−467 mV for HER and OER, respectively, to afford current densities of 10 mA cm$^{-2}$. In the general sense, Ni cation substitution with Co influenced favorably toward both HER and OER. Among all synthesized electrocatalysts, Co$_{0.9}$Ni$_{0.1}$Ferrite displayed the highest performance in terms of OER in 1 M KOH solution, which is related to the synergistic effect of multiple parameters including the optimal substitution amount of Co, the highest Brunauer–Emmett–Teller surface area, the smallest particle size among all samples (26.71 nm), and the lowest charge transfer resistance. The successful synthesis of ternary ferrites carried out for the first time via a microwave-assisted auto-combustion route opens up a new path for their applications in renewable energy technologies.
formula of $\text{MFe}_2\text{O}_4$ (M = Ni, Co, Cu, Mn, and so on) are a critical family of mixed metal oxides with innate benefits such as tunable redox properties, high abundance, and inexpensiveness\(^{35}\) have attracted a great deal of research interest. The so-called nano-structured spinel ferrite represents a cubic, close packing configuration of oxygen atoms, in which $\text{M}^{2+}$ (M = Co, Ni) and $\text{Fe}^{3+}$ ions can fill tetrahedral or octahedral interstitial sites.\(^{41,42}\) Spinel ferrites have diverse applications in multidisciplinary areas but are not limited to high-density magnetic recording, magnetic fluids, sensors, and catalysis to name but a few.\(^{43,44}\)

Thus far, multiple approaches have been adopted for the synthesis of nano-structured ferrites including but not limited to sol–gel, hydrothermal, solvothermal, high-energy ball milling, chemical co-precipitation, and citric acid combustion.\(^{45–48}\) Nonetheless, costly and complicated processes along with low production rates are the typical flaws from which these methods suffer.\(^{45}\) Amidst the documented techniques, microwave combustion synthesis has gained extensive research interest. High rates of reaction, shorter reaction time, less energy usage, high yield, and quality of resulting products are some of the merits of the microwave combustion method as opposed to other synthetic routes.\(^{45–48}\)

We present herein the synthesis of binary/ternary metal ferrites $[\text{Co}_x\text{Ni}_{1-x}\text{Ferrite} \ (x = 0.0, 0.1, 0.3, 0.5, 0.7, \text{and } 1.0)]$ by the aid of auto-combustion approach using microwave for the first time. The as-prepared materials were explored for their magnetic, chemical, and electrochemical properties. The results disclosed that increasing Co concentration, in general, has a positive impact on both HER and OER performance.

## 2. RESULTS AND DISCUSSION

### 2.1. Characterization

The X-ray diffractometer (XRD) was employed to verify the structural phase purity and determine the crystallite size of the prepared spinel nanoparticles. Figure 1a depicts the reflected characteristic peaks of the $\text{Co}_x\text{Ni}_{1-x}\text{Ferrite}$ nanoparticles. The appeared XRD peaks at $2\theta$ about 18.41, 30.29, 35.68, 37.33, 43.37, 53.82, 57.37, 63.1, and 74.57 can be indexed to the (111), (220), (311), (222), (400), (422), (511), (440), and (533) planes, separately, which confirmed the presence of a single-phase cubic spinel structure without secondary phases matched very well with the JCPDS card no. 74-2081 for NiFe$_2$O$_4$ and JCPDS card no. 77-0426 for CoFe$_2$O$_4$, respectively. To calculate the average particle size the Scherrer’s equation was exploited according to the following relation

$$D = \frac{k\lambda}{\beta \cos \theta}$$

where $D$ denotes the average particle size, $k = 0.89$ is the shape factor of a particle, $\lambda = 1.5406$ Å is the X-ray wavelength used, $\beta$ is the full width at half-maximum of the XRD (311) peak, and $\theta$ is Bragg’s angle in degrees unit. The average particle size of the magnetic nanoparticles was estimated in the range of 26–43 nm (refer to Table S1). It should be pointed out that dashed line around $2\theta$ of 63.1 from top to the bottom by increasing Co quantity, peak shifts to smaller $2\theta$ which is an indication of Co substitution in the structure of NiFerrite, and therefore larger lattice parameters (see Figure 1b).

The construction of $\text{Co}_x\text{Ni}_{1-x}\text{Ferrite}$ nanoparticles was substantiated by Fourier transform infrared characterization (FT-IR). In accordance with Figure 2, no secondary absorption bands regarding organic groups were detected above 1000 cm$^{-1}$. The two metal–oxygen (M–O) absorption bands observed in the range of 400–600 cm$^{-1}$ can be attributed to the vibration of ions in the crystal lattices. The presence of maximum bands within the 500–600 cm$^{-1}$ corresponds to cardinal stretching vibrations of the metal at the tetrahedral site, whereas the bands usually witnessed under 450 cm$^{-1}$, are indexed to the octahedral metal stretching site.

To inspect the surface morphology and chemical composition of the ferrite powders. Scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy absorption bands}\(^{49,50}\)

![Figure 1. (a,b) XRD patterns of the prepared $\text{Co}_x\text{Ni}_{1-x}\text{Ferrite}$ samples.](image-url)

![Figure 2. FT-IR spectrum of synthesized $\text{Co}_x\text{Ni}_{1-x}\text{Ferrite}$ samples.](image-url)
(EDS) elemental analyses were conducted. Figure 3a−c exhibits the dense agglomeration of nanoparticles for both doped and undoped samples which can be attributed to the magnetic properties of the synthesized materials (SEM images of remaining materials are included in Figure S1). Even though the accurate shape of particles cannot be evidenced, the transmission electron microscopy (TEM) image shown in Figure 3d manifests the cubic shape of the particles. It should be noted that further data regarding the elemental studies of the samples can be observed in Supporting Information, Figure S2, and Table S2. The high-resolution TEM (HRTEM) images of Co$_{0.9}$Ni$_{0.1}$Ferrite (Figure 4) shows the lattice fringes with a lattice spacing of 0.496 nm, corresponding to the (111) of CoFerrite.

The magnetic properties of Co$_x$Ni$_{1-x}$Ferrite nanoparticles were achieved through a vibrating sample magnetometer at room temperature. A very clear hysteresis loop was exhibited (Figure 5) from the $M$−$H$ measurements, which proves the ferromagnetic nature of magnetic ferrite nanoparticles. Multiple magnetic features can be achieved via the hysteresis loops including saturation magnetization ($M_s$), coercivity ($H_c$), and remanence magnetization ($M_r$), and the observed values are summarized in Table 1. It was observed that the highest $M_s$ value and coercivities ($H_c$) for CoFerrite is 66.4 emu/g and 1174.5 Oe. The result manifests that $M_s$ and $H_c$ of the samples are in direct correlation with Co content. The magnetic moments of Ni$^{2+}$ and Co$^{2+}$ are 2.82 $\mu_B$ and 3.87 $\mu_B$ (Bohr magneton), respectively. Therefore, proliferation in the number of Ni$^{2+}$ sites replaced by Co$^{2+}$ brings about larger $M_s$ and $M_r$ (remanence) values. On the contrary, $H_c$ values grow bigger as a result of the larger ion radius of Co$^{2+}$ (0.78 Å) as opposed to Ni$^{2+}$ (0.7 Å), giving rise to the lattice expansion (refer to Figure 1b). Thus, the widening of both interplanar spatial spacings of the particles impedes the response of particles to the external magnetic field.

### Table 1. Variation of $M_s$, $H_c$, and $M_r$ of Spinel Co$_{Ni_{1-x}}$Ferrite Nanoparticles

<table>
<thead>
<tr>
<th>sample</th>
<th>$M_s$</th>
<th>$H_c$</th>
<th>$M_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiFerrite</td>
<td>41.5</td>
<td>−129.6</td>
<td>13</td>
</tr>
<tr>
<td>Co$<em>{0.1}$Ni$</em>{0.9}$Ferrite</td>
<td>47.2</td>
<td>−294.2</td>
<td>18.2</td>
</tr>
<tr>
<td>Co$<em>{0.3}$Ni$</em>{0.7}$Ferrite</td>
<td>51.3</td>
<td>−639.7</td>
<td>23.8</td>
</tr>
<tr>
<td>Co$<em>{0.5}$Ni$</em>{0.5}$Ferrite</td>
<td>55</td>
<td>−863.7</td>
<td>27</td>
</tr>
<tr>
<td>Co$<em>{0.7}$Ni$</em>{0.3}$Ferrite</td>
<td>55.7</td>
<td>−1004.8</td>
<td>27</td>
</tr>
<tr>
<td>Co$<em>{0.9}$Ni$</em>{0.1}$Ferrite</td>
<td>62.8</td>
<td>−1019.9</td>
<td>30.5</td>
</tr>
<tr>
<td>CoFerrite</td>
<td>66.4</td>
<td>−1174.5</td>
<td>32.5</td>
</tr>
</tbody>
</table>

**2.2. Electrochemical Studies.** The electrochemical properties of prepared catalysts for HER and OER were evaluated on GC = with 0.125 mg cm$^{-2}$ catalyst loading as a working electrode in 1 M KOH solution. Figure 6a demonstrates the linear sweep voltammetry (LSV) polarization curves of electrocatalysts toward HER inclusive of GC and 10% Pt/C. As it can be seen, GC shows insignificant electrochemical activity, verifying its inertness. On the contrary, 10% Pt/C reveals a low onset potential of 198 mV to achieve 10 mA cm$^{-2}$. The overpotential values of the as-synthesized samples are tabulated in Table 2. A glance at this table discloses the fact that NiFerrite suffers from low performance (600 mV at 10 mA cm$^{-2}$), whereas CoFerrite enjoys the highest performance (422 mV at 10 mA cm$^{-2}$) relative to other samples. Not to mention that HER performance and Co concentration are roughly in direct relation, suggesting that increasing Co content leads to a positive effect on HER activity. In fact, the Co element is believed to be a favorable factor in improving HER due to its moderate H-bonding energy. Incorporation of trace amount of Co into the lattice of catalysts can substantially alter the electronic structure.$^{49−51}$ The earlier studies manifested that the catalytic performance is strongly dependent on the Co doping levels, and thus only a proper concentration of Co can boost the inherent conductivity and decline the adsorption energy of H atoms ($\Delta G_{H^+}$). For an instance, for Co-doped...
FeS$_2$ nanosheets, it was found that a Co/Fe ratio of 1:9 resulted in the highest HER activity. The density functional theory calculations revealed that the Co doping greatly decreased the energy barrier of H adsorption on the FeS$_2$ surface. Considering the points mentioned above, the same scenario can be developed for the present work—in that the adsorption energy of H atoms on the surface has gradually decreased with increasing Co concentration, giving rise to the best HER performance for the case of CoFerrite.50,52

Catalysts based on earth-abundant Co have received tremendous research interest owing to their intrinsic electrocatalytic capacity toward HER and/or OER.53−56 Previous studies have validated that spinels of cobalt can contribute to higher electronic conductivity as well as the number of active sites, which in turn reflect in greater electrochemical features.57

Previously, it has been proven that the electronic structure of a catalyst can be modulated and thereby promoted by the incorporation of more cations. Comparing bimetallic spinels of Co and Ni in this work, we can notice the positive impact of cation introduction in both cases of HER and OER. Compared to HER, NiFerrite still holds inferior performance for OER. However, Co$_{0.9}$Ni$_{0.1}$Ferrite is the best performing catalyst (419 mV at 10 mA cm$^{-2}$), exceeding the performance of CoFerrite (434 mV at 10 mA cm$^{-2}$), thanks to optimized charge transfer between bimetals of Co and Ni (Figure 6c). In many cases, the incorporation of more metal atoms can modify the adsorption energy of reaction intermediates and improve catalytic activity.58,59 In addition, according to the calculated particle size in Table S1, the smallest size corresponds to Co$_{0.9}$Ni$_{0.1}$Ferrite (26.71 nm), a beneficial contribution to OER electrocatalytic activity.34

It should be pointed out that benchmark RuO$_2$ was also evaluated toward OER, implying that as-synthesized catalysts are less efficient, yet fairly promising regarding their economic precursors, green fabrication method, and easily scalable procedure.

In principle, Co-containing ferrites are preferably viewed as favorable electrocatalysts toward OER,34,60,61 in which their activities can be altered by size, morphology,62 and hybrid forming.63,64 The surface of Co-bearing catalysts under alkaline conditions transforms to thermodynamically stable species such as Co-(oxy) hydroxide (CoOOH) which can function as active sites for the oxygen-evolving reaction.2 It is believed that the OER mechanism is subject to the occurrence of four successive steps.

**Step 1:** Co$^{II} + 3OH^- \leftrightarrow Co^{III} OOH + H_2O(l) + e^-$

**Step 2:** Co$^{III} OOH + OH^- \leftrightarrow Co^{IV} O(OH)_2 + e^-$

Table 2. Overpotential Values of As-prepared Catalysts for HER and OER in 1 M KOH Medium and Corresponding Brunauer–Emmett–Teller (BET) Surface Area

<table>
<thead>
<tr>
<th>sample</th>
<th>HER overpotential (mV)</th>
<th>OER overpotential (mV)</th>
<th>BET surface area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C</td>
<td>198</td>
<td>290</td>
<td>85.52</td>
</tr>
<tr>
<td>RuO$_2$</td>
<td>566</td>
<td>7.08</td>
<td>4.66</td>
</tr>
<tr>
<td>NiFerrite</td>
<td>541</td>
<td>467</td>
<td>5.88</td>
</tr>
<tr>
<td>Co$<em>{0.1}$Ni$</em>{0.9}$Ferrite</td>
<td>495</td>
<td>451</td>
<td>7.12</td>
</tr>
<tr>
<td>Co$<em>{0.3}$Ni$</em>{0.7}$Ferrite</td>
<td>446</td>
<td>467</td>
<td>9.45</td>
</tr>
<tr>
<td>Co$<em>{0.5}$Ni$</em>{0.5}$Ferrite</td>
<td>451</td>
<td>419</td>
<td>12.10</td>
</tr>
<tr>
<td>Co$<em>{0.7}$Ni$</em>{0.3}$Ferrite</td>
<td>451</td>
<td>419</td>
<td>12.10</td>
</tr>
<tr>
<td>Co$<em>{0.9}$Ni$</em>{0.1}$Ferrite</td>
<td>451</td>
<td>419</td>
<td>12.10</td>
</tr>
<tr>
<td>CoFerrite</td>
<td>422</td>
<td>343</td>
<td>11.35</td>
</tr>
</tbody>
</table>
Step 3: $\text{Co}^{II} \text{O(OH)}_2 + 2\text{OH}^- \leftrightarrow \text{Co}^{IV} \text{O}_2 + 2\text{H}_2\text{O}(l) + 2\text{e}^-$

Step 4: $\text{Co}^{IV} \text{O}_2 + \text{OH}^- \leftrightarrow \text{Co}^{III} \text{O} + \text{O}_2(\text{g}) + \text{e}^-$

From a thermodynamic point of view, the last step is irreversible ($\Delta G > 0$). Thus, one of three remaining reversible steps is the rate-controlling step. During OER, $\text{Co}^{II}/\text{Co}^{III}/\text{Co}^{IV}$ mixed states are the dominating cobalt species. Here, $\text{Co}^{III} \text{OOH}$, $\text{Co}^{IV} \text{O(OH)}_2$, and $\text{Co}^{IV} \text{OO}_2$ represent the adsorbed intermediates on the surface-active sites, and $(l)$ and $(g)$ denote liquid and gas phases, individually. Concerning the investigated samples and particularly the best-performing one, $\text{Co}_{0.9}\text{Ni}_{0.1}\text{Ferrite}$, the catalyst goes under partial oxidation, converting to $\text{Co}^{III} \text{OOH}$ followed by an electron release (step 1). Nest, $\text{Co}^{IV} \text{OOH}$ reacts with another $\text{OH}^-$, producing $\text{Co}^{IV} \text{O(OH)}_2$ and an electron (step 2). Afterward, $\text{Co}^{IV} \text{O(OH)}_2$ reacts with two other $\text{OH}^-$, generating $\text{Co}^{IV} \text{OO}_2$, two water molecules, and two electrons (step 3). Finally, $\text{Co}^{IV} \text{OO}_2$ combines with another $\text{OH}^-$ to form $\text{O}_2$ gas, a $\text{Co}^{IV} \text{OOH}$, and an electron (step 4). As a whole, mixed cobalt states on the catalyst surface create more active sites and hence encourage the charge transfer.

From Figure 6b, calculated Tafel slopes can be seen. The Tafel slope is a key indicator to ascertain the HER kinetics, establishing the rate-controlling step during the reaction. From the two general routes reported in the literature for hydrogen evolution under basic conditions are as follows:

a) $\text{H}_2\text{O}(1) + \text{e}^- + \text{o}$
   $\rightarrow \text{H}^0 + \text{OH}^- + \text{aq}$, Volmer reaction

b) $\text{H}^0 + \text{H}_2\text{O}(1) + \text{e}^-$
   $\rightarrow \text{H}_2(\text{g}) + \text{OH}^- + \text{aq}$, Heyrovsky reaction

c) $\text{H}_2\text{O}(1) + \text{e}^- + \text{o}$
   $\rightarrow \text{H}^0 + \text{OH}^- + \text{aq}$, Volmer reaction

d) $\text{H}^0 + \text{H}^0 \rightarrow \text{H}_2(\text{g}) + 2\text{e}^-$, Tafel reaction

Therefore, the adsorption–desorption process either takes place via the Volmer–Heyrovsky mechanism (a,b) or the Volmer–Tafel mechanism (c,d). Here, $\text{o}$ and $\text{H}^0$ stand for available active sites and hydrogen atoms adsorbed on the active sites, respectively. The estimated Tafel slopes for the Volmer reaction, Heyrovsky reaction, and Tafel reaction are respective values of $\sim 120$ mV dec$^{-1}$, $\sim 40$ mV dec$^{-1}$, and $\sim 30$ mV dec$^{-1}$. The results exhibit that commercial 10% Pt/C as a reference material has a slope of $86.5$ mV dec$^{-1}$ which is in the region of $40–120$ mV dec$^{-1}$, suggesting the Volmer–Heyrovsky mechanism. Among the prepared samples, $\text{CoFerrite}$ and $\text{Co}_{0.9}\text{Ni}_{0.1}\text{Ferrite}$ display the smallest Tafel slopes ($72.7$ mV dec$^{-1}$ and $81.1$ mV dec$^{-1}$) compared to other catalysts and reference material, suggesting the Volmer–Heyrovsky path. The corresponding Tafel plots for OER are shown in Figure 6d. According to this figure, $\text{RuO}_2$ owns the smallest Tafel slope (68.4 mV dec$^{-1}$) and hence enjoys the fastest kinetics. Amidst the as-synthesized electrocatalysts, $\text{Co}_{0.9}\text{Ni}_{0.1}\text{Ferrite}$ holds the lowest slope value (89.1 mV dec$^{-1}$), which is in line with its OER performance. The preceding statements accord with the BET results, meaning that the sample endowing with the highest BET surface area enjoys the best OER activity (Table 2). It should be noted that the comparison of present results with those of previously reported spinel catalysts in OER and HER has been tabulated in Table S3.

Because catalytic sustainability has a central role in water splitting applications, the longevity of the best-performing catalysts in OER ($\text{Co}_{0.9}\text{Ni}_{0.1}\text{Ferrite}$) and HER (CoFerrite) were also measured and recorded at a current density of 10 mA cm$^{-2}$ (Figure 7). Moreover, the microstructure of these materials after electrochemical operations was studied (see Figure S3). According to the SEM images, no pronounced alteration was detected after OER and HER experiments on the working and reference electrodes. CPE and $\text{Rct}$ stand for the impedances of the interfacial reactions on the surface, including capacitive component and Faraday resistance, respectively. Capacitive component ($\text{CPE}$) and $\text{Rct}$ are key elements in the matrices of as-obtained electrocatalysts.

The electrochemical impedance spectroscopy (EIS) experiments were performed to inspect the charge transfer resistance. Figure 8 presents the Nyquist plots along with equivalent circuits once the samples were placed in contact with electrolyte. Re indicates the resistance of the solution between the working and reference electrodes. CPE and $\text{Rct}$ stand for the impedances of the interfacial reactions on the surface, namely, capacitive component and Faraday resistance, individually. Finally, Warburg impedance ($W$) was added to the equivalent circuit, indicating that diffusion is the controlling step on the surface.

Figure 7. Chronopotentiometric curves recorded at a current density of 10 mA cm$^{-2}$ of the best-performing catalysts.
two types of behavior based on the cobalt content. Those with low Co loadings ($x = 0, 0.1, 0.3,$ and 0.5) display a completely diffusion controlling manner on account of their high Warburg resistance. In this context, the ionic diffusion is suppressed, resulting in a severe decline in the ionic path. On the contrary, those with high Co concentrations ($x = 0.7, 0.9,$ and 1.0) enjoy a low Warburg resistance, manifesting a more capacitive manner than the other samples. Consequently, the ion diffusion path is alleviated more efficiently, and capacitive current can be improved. It is worth noting that the Co$_{0.9}$Ni$_{0.1}$Ferrite showed the lowest $R_{ct}$ and Warburg resistance among the second group of samples, providing more efficacious capacitive current and therefore enhanced electrocatalytic activity.

3. CONCLUSIONS

In summary, Co$_{x}$Ni$_{1-x}$Ferrite ($x = 0.0, 0.1, 0.3, 0.5, 0.7$ and 1.0) nanoparticles with varying compositions were successfully prepared using a microwave auto-combustion method. The adopted combustion approach is a facile, highly affordable, and readily adaptable route to synthesize non-polluting materials. The resultant products were manipulated as HER and OER electrocatalysts in a 1 M KOH medium. The electrochemical experiments proved that CoFerrite (422 mV at $-10$ mA cm$^{-2}$) and Co$_{0.9}$Ni$_{0.1}$Ferrite (419 mV at 10 mA cm$^{-2}$) possess the best electrocatalytic activities for HER and OER, separately. From the Tafel slope point of view, Co$_{0.9}$Ni$_{0.1}$Ferrite holds the smallest value for OER, 89.1 mV dec$^{-1}$, suggesting alleviated kinetics compared to other samples. The same behavior was observed for HER kinetics except that, Co$_{0.9}$Ni$_{0.1}$Ferrite has slower kinetics than CoFerrite (81.1 mV dec$^{-1}$ vs 72.7 mV dec$^{-1}$). Our findings pave the path for developing green electrocatalysts by the virtue of highly economical precursors.

4. EXPERIMENTAL SECTION

4.1. Preparation of Catalysts. The reaction process was elaborated in our previous work. In brief, for a normal synthesis procedure, Fe(NO$_3$)$_3$·9H$_2$O, Ni(NO$_3$)$_2$·6H$_2$O, and Co(NO$_3$)$_2$·6H$_2$O were employed as metal sources, and NH$_4$CH$_2$COOH and NH$_4$NO$_3$ were utilized as the fuel and oxidizer, respectively. In order to prepare Co$_{x}$Ni$_{1-x}$Fe$_2$O$_4$ ($x = 0.0, 0.1, 0.3, 0.5, 0.7$ and 1.0) nanoparticles, first Fe(NO$_3$)$_3$·9H$_2$O (2 mmol), Co(NO$_3$)$_2$·6H$_2$O and Ni(NO$_3$)$_2$·6H$_2$O with certain molar ratios, NH$_4$CH$_2$COOH (3 mmol), and NH$_4$NO$_3$(6 mmol) were mixed. The mixture was then transferred into an alumina crucible covered by a jacket layer of CuO to draw the microwave energy and generate calcination heat. For thermal treatment, the alumina crucible was placed in a domestic microwave oven with a power of 450 W for 30 min. The resulting powder was collected, washed several times with distilled water and ethanol to remove the residual initial materials, and dried in a hot air oven at 80°C for 24 h. The final products were labeled as Co$_{0.9}$Ni$_{0.1}$Ferrite (refer to Figure 9).

4.2. Apparatus and Procedure. 4.2.1. Apparatus. To examine the structural aspects of the as-synthesized materials, a Rigaku Mini Flex 600; Cu Kα ($λ = 1.5418$ Å) XRD was used. XRD patterns were recorded in the $2θ$ ranging from 10 to 90°. A zero-background powder specimen holder was utilized for the XRD analysis of all samples. To identify the functional groups a JASCO 6800 FTIR FULL VACUUM & FTIR MICROSCOPE FT-IR apparatus was employed and the spectra were collected in the wavenumber region of 4000–400 cm$^{-1}$ with the aid of the KBr pellet approach. Field emission scanning electron microscopy (FESEM) images were achieved on a TESCAN MIRA3 microscope, operated at 15 kV. In addition, EDS was carried out by Zeiss Ultra Plus FESEM at an accelerating voltage of 5 kV. Further examination on morphology was accomplished through TEM images, taken by a Hitachi HT7700 TEM instrument, functioning at the

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**Figure 8.** Nyquist plots of Co$_{x}$Ni$_{1-x}$Ferrite nanoparticles.

**Figure 9.** Schematic illustration of synthesis procedure.

**Table 3.** Calculated Values of the Equivalent Circuit Elements for the Samples

<table>
<thead>
<tr>
<th>sample</th>
<th>Re (Ω)</th>
<th>CPE-T (mFsp$^{-1}$)</th>
<th>CPE-P (Ω)</th>
<th>Rct (Ω)</th>
<th>W−R (Ω)</th>
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</thead>
<tbody>
<tr>
<td>NiFerrite</td>
<td>12.5</td>
<td>8.6 × 10$^{-4}$</td>
<td>0.8</td>
<td>218</td>
<td>17365</td>
</tr>
<tr>
<td>Co$<em>{0.1}$Ni$</em>{0.9}$Ferrite</td>
<td>10.85</td>
<td>7.56 × 10$^{-6}$</td>
<td>0.86</td>
<td>191.3</td>
<td>9891</td>
</tr>
<tr>
<td>Co$<em>{0.3}$Ni$</em>{0.7}$Ferrite</td>
<td>12.14</td>
<td>1.23 × 10$^{-6}$</td>
<td>0.91</td>
<td>184.6</td>
<td>8617</td>
</tr>
<tr>
<td>Co$<em>{0.5}$Ni$</em>{0.5}$Ferrite</td>
<td>11.9</td>
<td>1.14 × 10$^{-7}$</td>
<td>0.78</td>
<td>172.9</td>
<td>35871</td>
</tr>
<tr>
<td>Co$<em>{0.7}$Ni$</em>{0.3}$Ferrite</td>
<td>13.17</td>
<td>7.74 × 10$^{-5}$</td>
<td>0.70</td>
<td>10391</td>
<td>410.2</td>
</tr>
<tr>
<td>Co$<em>{0.9}$Ni$</em>{0.1}$Ferrite</td>
<td>12.6</td>
<td>8.4 × 10$^{-3}$</td>
<td>0.83</td>
<td>7365</td>
<td>152.4</td>
</tr>
<tr>
<td>CoFerrite</td>
<td>12.1</td>
<td>3.8 × 10$^{-3}$</td>
<td>0.79</td>
<td>9538</td>
<td>161.7</td>
</tr>
</tbody>
</table>
accelerating voltage of 120 kV. The high-resolution transmission electron microscope images were obtained by the Thermo Scientific Talos F200S 200 kV TEM. The magnetic tests were implemented at ambient conditions employing a vibrating sample magnetometer, model VSM, LKBFB, with a maximum magnetic field of 10 kOe. Finally, to determine the BET specific surface area of the powder products, a Micromeritics ASAP 2010 instrument was exploited.

4.2.2. Electrode Fabrication. The catalysts inks were made by thoroughly mixing 1 mg of resulting powders in a 480 μL pure ethanol–deionized water mixture (380:100) under ultrasonication for 20 min, followed by the addition of 5% wt NaCl solution (5 μL) to the mentioned mixture, accompanied by another 20 min of ultrasonication. 10 μL of the homogeneous catalyst ink was pipetted out on the - fresh surface of cleaned glassy carbon (GC). Finally, the drying process of the catalyst-coated surface of the GC electrode was carried out in the presence of an air atmosphere at 80 °C for 120 min. To construct the working electrodes of reference commercial materials, 10% Pt/C and RuO2, identical steps were followed. The loading amount of catalysts for each run was about ~0.125 mg/cm2.

4.2.3. Electrochemical Measurements. To evaluate the electrochemical characteristics of the prepared electrocatalysts, we followed a similar strategy to our earlier report 19. Succinctly, the electrochemical tests were performed on a VersaSTAT Potentiostat Galvanostat by means of a three-electrode cell containing reversible hydrogen electrode (RHE; HydroFlex) and Pt wire as reference and counter electrodes, respectively, under 1 M KOH medium. A 3 mm-diameter GC was employed as a working electrode, polished with Al2O3 slurry (0.3 μm) and ultrasonically washed with distilled water and ethanol each for 10 min prior to each run. To this end, the LSV curves were recorded from 0 to −1.2 V and 0 to +1.8 V toward HER and OER, separately. The required overpotential for water reduction and oxidation were calculated at a current density of 10 mA cm−2. Furthermore, a frequency ranged from 100 kHz and 0.1 Hz with a 10 mV RMS sinusoidal modulation at 0 V was considered to obtain the EIS curves.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c05183.

Data of SEM images, EDS elemental mappings, crystallite size table, table of the HER and OER performances of previous works, and SEM images and EDS graphs after electrochemical experiments (PDF)

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Author Contributions
S.C. synthesized and characterized the electrocatalysts. N.S.P. prepared the electrodes and conducted the electrochemical experiments. M.K. and U.A. supervised the whole project from synthesis to interpretation of the results. All authors contributed to the writing of the manuscript and approved its final version.

Notes
The authors declare no competing financial interest.

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REFERENCES

porous chainlike architecture for efficient oxygen evolution reaction. 


(65) Feng, Y.; Li, Y.; Hou, F. Preparation and electrochemical properties of Cr doped LiV3O8 cathode for lithium ion batteries. Mater. Lett. 2009, 63, 1338–1340.


