Synthesis and Characterisation of Cobalt Ferrite Coatings for Oxygen Evolution Reaction

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Abstract: In this paper, two novel procedures based on powder sedimentation, thermal treatment, and galvanostatic deposition were proposed for the preparation of porous cobalt ferrite (CoFe₂O₄) coatings with a metallic and organic binder for use as catalysts in the oxygen evolution reaction (OER). The electrochemical properties of the obtained electrode materials were determined as well, using both dc and ac methods. It was found that cobalt ferrite coatings show excellent electrocatalytic properties towards the oxygen evolution reaction (OER) with overpotential measured at a current density of 10 mAc⁻¹ from 287 to 295 mV and a Tafel slope of 35–45 mVdec⁻¹. It was shown that the increase in the apparent activity of the CoFe₂O₄ coatings with an organic binder results mainly from a large electrochemically active area. Incorporation of the nickel binder between the CoFe₂O₄ particles causes an increase in both the conductivity and the electrochemically active area. The Tafel slopes indicate that the same rate-determining step controls the OER for all obtained coatings. Furthermore, it was shown that the CoFe₂O₄ electrodes exhibit no significant activity decrease after 28 h of oxygen evolution. The proposed coating preparation procedures open a new path to develop high-performance OER electrocatalysts.

Keywords: cobalt ferrite; porous coatings; oxygen evolution reaction; water electrolysis catalysts; electrochemical impedance spectroscopy

1. Introduction

The oxygen evolution reaction (OER) plays an essential role in state-of-art energy storage and conversion devices. Nowadays, the major challenge is to obtain low-cost and high-performance catalysts for those reactions. Electrodes made of Pt, IrO₂, and RuO₂ are known OER catalysts, however they are not appropriate for large-scale applications because of their cost. Transition metals, such as Fe, Ni, Co, and Mn, show high electrocatalytic activity and stability in alkaline solutions. Thus, they are promising candidates for replacing precious metals catalysts. Sulphides, selenides, nitrides, carbides, hydroxides, oxy-hydroxides, and oxides of transition metals are extensively used as efficient electrocatalysts [1–6]. Because of their high catalytic activity, relatively low cost, and environmental friendliness, numerous studies of transition metal oxides have been performed. For example, it has been found that NiO [7], Co₃O₄ [8], MnO₂ [9], and Fe₂O₃ [10] exhibit high catalytic activity toward OER compared to RuO₂ and IrO₂. It was also found that nickel- and cobalt-based composites usually produce overpotentials in the OER reaction around 350–450 mV at a current density of 10 mAc⁻¹ [4–6].

Generally, spinel mixed metal oxides with formula AB₂O₄ (A, B = metal) exhibit higher electrochemical activity than the single-metal oxides. This is because of the electron jump among different valence states of ions in octahedral sites and additional metallic redox-active centres [11–16]. Between various spinel oxides, Fe-based spinels, e.g., CuFe₂O₄, NiFe₂O₄, and CoFe₂O₄, have been reported as promising electrocatalysts for OER [17]. However, the CoFe₂O₄ ferrite is one of the most interesting, especially for its excellent chemical stability, efficient electrocatalytic properties, high specific capacitance, low cost,
and environmental friendliness. Therefore, CoFe₂O₄ ferrite is a promising candidate as an electrode in water splitting, lithium-ion batteries, and supercapacitors [18–20]. Most of the mixed transition metal oxides catalysts are powders obtained by different methods, e.g., solvothermal, hydrothermal, electrodeposition, or spin coating [21,22]. Usually, to obtain an electrode, those powders are applied to a conductive substrate using a particle binder. However, polymeric binders are characterized by relatively poor electrical conductivity, which may influence the entire electrode’s electrocatalytic activity. Additionally, the low durability of polymeric binders may also cause the detachment of coating that is especially noticeable at higher current densities and vigorous O₂ evolution [23]. Another frequently used method for electrode preparation is to anchor metal oxides on a carbon substrate. In this case, to assure sufficient functional groups, the carbon substrate is treated with harsh oxidative agents, which can deteriorate the electrical conductivity of the substrate and cause environmental pollution [24]. To improve the performance of these materials, various methods of their modifications have been reported, e.g., by creating nanoporous structures, synergistic metal–metal interactions, or embedding nanoparticles of catalysts in carbon nanomaterials [24–26]. However, there is still a need to design new MFe₂O₄ electrocatalysts with a very porous surface, high electrical conductivity, and durability.

This work has been carried out to study the electrocatalytic activity of the CoFe₂O₄ coatings during oxygen evolution reaction. Two different methods of electrode preparation have been used. In the first method, a coating consisting of a combination of CoFe₂O₄ powder and PEG 4000 (as a binder) was deposited by sedimentation on a metallic substrate. Subsequently, such prepared coating was subjected to heat treatment at 800 °C in an inert atmosphere. The second method used was the electrolytic co-deposition of nickel and CoFe₂O₄ powder. Electrodeposition seems to be an interesting alternative in coatings production that contain mixed metal oxides powders and metallic binders. Additionally, a nickel substrate subjected to the analogous treatment like CoFe₂O₄ coatings was also investigated.

2. Results and Discussion

2.1. CoFe₂O₄ Powder and Coating Characterization

The phase composition of the as-obtained and annealed (800 °C, 1 h, air) CoFe₂O₄ powder is shown in Figure 1. In both cases, X-ray diffraction patterns show the presence of the reflexes coming from the single-phase spinel cobalt ferrite with cubic crystal structure (space group: Fd3m, lattice constant: a = 8.4101 Å, reference code: 04-009-8438 ICDD PDF4+ 2015). Note that XRD lines obtained for as-obtained CoFe₂O₄ particles are broadened due to some lattice strain [27]. The values of crystallite size calculated using the Williamson–Hall method [28] for as-obtained and annealed CoFe₂O₄ powders were 10(1) nm and 15(1) nm, respectively. Thus, one can state that CoFe₂O₄ powders are nanocrystalline phases and a 50% increase in the crystallite size is observed after annealing.

Figure 2 shows the SEM images of the examined samples, i.e., CFOPEG, CFONi, and CFO₆Ni, and Ni substrate. One can see that the images obtained for CFOPEG and CFONi electrodes represent a relatively homogenous distribution of cobalt ferrite particles, while the image obtained for CFO₆Ni shows some agglomerates of CoFe₂O₄ particles separated from each other. Thus, heat treatment of CoFe₂O₄ powder (800 °C, 1 h, air) influences the shape of the electrode surface. Note that CoFe₂O₄ particles, independent of fabrication procedure applied, distinctly enlarge the surface roughness of the electrode in comparison with nickel substrate. The increased surface area should increase the electrocatalytic activity of the CoFe₂O₄ coatings towards oxygen evolution.
Figure 1. X-ray diffraction patterns of (a) as-received and (b) annealed at 800 °C for 1 h in the air CoFe$_2$O$_4$ powder.

Figure 2. Surface morphology of (a) Ni substrate and (b) CFO$_{PEG}$, (c) CFO$_{Ni}$, (d) CFO$_{Ni}^{a-r}$ coatings.

2.2. Electrochemical Characterisation of CoFe$_2$O$_4$ Coatings

Investigations of the electrolytic oxygen evolution on the Ni and CoFe$_2$O$_4$ electrodes were carried out using dc and ac methods. In Figure 3a, quasi-stationary polarisation curves $j$ vs. $E$ are shown. It can be observed that the CoFe$_2$O$_4$ electrodes are more efficient than the Ni electrode. Among the CoFe$_2$O$_4$ electrodes, the lowest and the highest performance is observed for CFO$_{Ni}^{a-r}$ and CFO$_{Ni}$ electrodes, respectively. For the linear part of polarisation curves, the Tafel equation $\eta = a + b \log|j|$ can be used to determine characteristic parameters of the electrode-electrolyte system. The parameters provide information about the mechanism (Tafel slope $b$) and the rate (apparent exchange current density $j_0$) of OER. It
can be seen from Figure 3b that all investigated electrodes show a well-defined Tafel region with a slope changing from 35 to 56 mV dec⁻¹ (see also Table 1).

![Image of a graph showing polarisation curves and Tafel plots for CoFe2O4 coatings in 1 M KOH.](image_url)

**Figure 3.** (a) polarisation curves, (b) Tafel plots and (c) chronopotentiometric curves obtained for CoFe2O4 electrodes in 1 M KOH.

**Table 1.** The Tafel slope \( b \), the apparent exchange current density \( j_0 \), the overpotential at a current density of 10 mA cm⁻² \( \eta_{10} \) and the average roughness factor \( R_{f(\text{av})} \) obtained for CoFe2O4 electrodes in 1 M KOH solution during OER.

| Catalyst | \( b \) (mV dec⁻¹) | \( j_0 \) (A cm⁻²) | \( \eta_{10} \) (mV) | \( R_{f(\text{av})} \) | \( j_0/R_{f(\text{av})} \) (A cm⁻²) |
|----------|---------------------|--------------------|---------------------|---------------------|-------------------------|
| Ni       | 56                  | \( 3.2 \times 10^{-10} \) | 438                 | 12                  | \( 2.7 \times 10^{-11} \) |
| CFOPEG   | 35                  | \( 4.2 \times 10^{-11} \) | 295                 | 1850                | \( 2.3 \times 10^{-14} \) |
| CFONi    | 45                  | \( 4.6 \times 10^{-9} \)  | 287                 | 2487                | \( 1.8 \times 10^{-12} \) |
| CFOPEG Ni| 51                  | \( 1.0 \times 10^{-9} \)  | 359                 | 93                  | \( 1.1 \times 10^{-11} \) |

The OER mechanism consists of the following steps [29]:

\[
\text{M} + \text{OH}^- \leftrightarrow \text{MOH} + e^-, \tag{1}
\]

\[
\text{MOH} + \text{OH}^- \leftrightarrow \text{MO}^- + \text{H}_2\text{O}, \tag{2}
\]

\[
\text{MO}^- \leftrightarrow \text{MO} + e^-, \tag{3}
\]

\[
2\text{MO} \leftrightarrow 2\text{M} + \text{O}_2. \tag{4}
\]
Either (1) or (3) electrochemical reaction may be the rate-determining step (rds). When the surface coverage by OH is much smaller than one and the reaction (1) is rds, then the Tafel slope \( b = 2.3RT/\beta F \). However, if the reaction (3) is rds, then \( b = 2.3RT/(1 + \beta)F \) [29]. Assuming transfer coefficient \( \beta = 0.5 \) and temperature 25 °C, the theoretical Tafel slope for the reaction (1) is equal to 120 mVdec⁻¹ and for the reaction (3) 40 mVdec⁻¹. The Tafel slopes \( b \) obtained for all investigated CoFe₂O₄ coatings indicate that the OER proceeds via the same mechanism, with the third reaction step as the rate-determining step. The experimental \( b \) values higher than 40 mVdec⁻¹ indicate that the transfer coefficient is lower than 0.5. According to literature reports, it can be caused by anion adsorption and the nonuniform distribution of the surface electric field on the rough electrodes [29].

The parameter \( j_0 \) obtained for CFO₉₅ and CFO₉₅ Ni is ca. one order of magnitude higher in comparison with nickel electrode and ca. two orders of magnitude higher than for CFOPEG. Such behaviour could be explained by the higher electrical conductivity of nickel (\( \sigma \sim 10^6 \, \Omega^{-1}\)cm⁻¹) in comparison with cobalt ferrite particles (\( \sigma \sim 10^{-7} \, \Omega^{-1}\)cm⁻¹) [30]. Therefore, for CFONi and CFO₉₅ Ni electrodes, the electrolytically deposited nickel used as a particle binder causes an increase in the apparent exchange current density of the whole electrode.

The apparent activity of different electrodes could be compared using overpotential \( \eta \) determined at selected current density (in this work, \( j = 10 \, \text{mAcm}^{-2} \)). For CoFe₂O₄ electrodes, the parameter \( \eta_{10} \) is from 80 mV to 150 mV lower in comparison with the nickel substrate (see Table 1). Thus, one can state that CoFe₂O₄ electrodes characterise higher apparent activity towards OER with respect to Ni electrode. It was also found that the apparent activity of CFO₉₅ Ni electrode modified by nickel binder is the highest among all investigated electrodes. For comparison, different kinds of CoFe₂O₄ electrodes reported in the literature for OER in alkaline media (1 M KOH or 1 M NaOH) are gathered in Table 2. All these data confirm that the CFOPEG, CFO₉₅ Ni, and CFO₉₅ Ni electrodes reveal high activity towards OER.

### Table 2. Comparison of cobalt ferrite catalysts reported in the literature.

| Catalyst                  | \( b \) (mVdec⁻¹) | \( \eta_{10} \) (mV) | Reference          |
|---------------------------|-------------------|----------------------|--------------------|
| CoFe₂O₄ (powders)         | 35                | 295                  | this work          |
| CoFe₂O₄ (powders)         | 45                | 287                  | this work          |
| CoFe₂O₄ (powders)         | 69                | 360                  | [12]               |
| CoFe₂O₄ (powders)         | 126               | 435                  | [12]               |
| CoFe₂O₄ (hollow nanofibers)| 95                | 414                  | [11]               |
| CoFe₂O₄ (thick films)     | 54                | 490                  | [13]               |
| CoFe₂O₄ (nanoparticles)   | 73                | 378                  | [14]               |
| CoFe₂O₄ (nanoplates)      | 61                | 360                  | [15]               |
| CoFe₂O₄ (nanofibers)      | 107               | 340                  | [16]               |

In practical terms, an important criterion is the long-term stability of the catalysts. The stability of the cobalt ferrite electrodes in 1 M KOH solution was tested using the chronopotentiometry method at the constant current density of 50 mAcm⁻² (see Figure 3c). Percentage change of the measured potential determined for time period from 1 to 28 h is 5% for Ni, 3% for CFOPEG, 1% for CFO₉₅ Ni and 7% for CFO₉₅ Ni. Thus, it can be stated that all investigated electrodes are relatively stable in an alkaline environment. Figure 4 shows the SEM images and corresponding maps of Ni, Fe, Co elements distribution for the CFOPEG and CFO₉₅ Ni electrodes after 28 h of oxygen evolution. Comparison with images obtained before OER (Figure 2) indicates that the surface of CFOPEG and CFO₉₅ Ni electrodes remained almost unchanged. Thus, SEM images confirm the conclusion obtained from electrochemical measurements. The distribution maps of elements indicate that the electrode surface consists of the porous coating made of CoFe₂O₄ particles (or their agglomerates) and nickel substrate in the case of CFOPEG or nickel binder in the case of CFO₉₅ Ni.
Complex impedance plots obtained for (a) Ni, (b) CFO_{PEG}, (c) CFO_{Ni}, and (d) CFO_{Ni}^{-}\text{PEG} electrodes after 28 h of oxygen evolution at the current density \( j = 50 \text{ mAcm}^{-2} \).

Impedance spectra measured for selected potentials are shown in Figure 5. For all investigated electrodes, two semicircles on Nyquist plots are observed. There is a small potential-independent semicircle in the high-frequency region, and a potential-dependent semicircle in the low-frequency region. Such a shape of spectra is typical for porous electrodes. The potential-independent semicircle can be related to the geometry of the electrode surface, whereas the potential-dependent semicircle corresponds to the Faradaic reaction [31–33]. Thus, a model with two-time constants can adequately describe the response of porous CoFeO\(_4\) electrodes during OER.

**Figure 4.** Surface morphology of (a) CFO_{PEG} and (b) CFO_{Ni} electrodes after 28 h of oxygen evolution at the current density \( j = 50 \text{ mAcm}^{-2} \).

**Figure 5.** Complex impedance plots obtained for (a) Ni, (b) CFO_{PEG}, (c) CFO_{Ni} and (d) CFO_{Ni}^{-}\text{PEG} electrodes during the oxygen evolution process in 1 M KOH; symbols are experimental data, and lines were modelled using the electrical equivalent circuit shown in Figure 6.

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**Figure 4.** Surface morphology of (a) CFO_{PEG} and (b) CFO_{Ni} electrodes after 28 h of oxygen evolution at the current density \( j = 50 \text{ mAcm}^{-2} \).
An electrical equivalent circuit used to describe the investigated process is shown in Figure 6. It contains solution resistance \( R_s \), coating capacitance \( \text{CPE}_l \), coating resistance \( R_l \), charge transfer resistance \( R_{ct} \), and double layer capacitance \( \text{CPE}_dl \). Note that the deviation of solid electrodes from purely capacitive behaviour (caused by physical nonuniformity or uneven distribution of active sites) has been taken into account using CPE elements instead of capacitors. The following equation describes the impedance of the CPE element: \( Z_{\text{CPE}} = \frac{1}{T(j\omega)^\phi} \), where \( T \) is the capacity parameter and \( \phi \) is the dispersion parameter related to the depression angle [31–33].

For all obtained electrodes, the value of charge transfer resistance decreases with increasing overpotential, which corresponds to the decreasing diameter of the low-frequency semicircle (see Figure 5). Furthermore, comparing \( R_{ct} \) with the \( R_l \), it was found that \( R_{ct} \gg R_l \). Thus, \( R_{ct} \) governs the electrode kinetic. The relation \( \eta \) vs. \( \log(R_{ct}^{-1}) \) for all investigated electrodes is shown in Figure 7. It was found that \( R_{ct} \) values obtained for CoFe\(_2\)O\(_4\) electrodes at lower overpotentials can be over 100 times lower than that obtained for Ni electrode and in both cases gradually decreases with increasing overpotential. Additionally, \( \eta \) vs. \( \log(R_{ct}^{-1}) \) curves show well-defined linear regions with slopes from 40 to 48 mVdec\(^{-1}\). Note that the obtained slopes correlate with Tafel coefficients obtained from \( \eta \) vs. \( \log(j) \) curves.

The double layer capacitance \( C_{dl} \) can be determined using the equation: \( C_{dl} = |T/((R_s + R_l)^{-1} + R_{ct}^{-1})|^{1/\phi} \) [32]. The relation between \( C_{dl} \) and \( \eta \) for all obtained coatings is shown in Figure 8. It was found that the smallest value of \( C_{dl} \) was obtained for the nickel electrode, as should be expected. CFO\(_\text{Ni} \) and CFO\(_\text{PEG} \) coatings exhibit, respectively, ca. 200 times and ca. 150 times higher \( C_{dl} \) (average value) in comparison with nickel electrode.
The phase composition of CoFe$_2$O$_4$ coatings was determined by X-ray diffraction technique (XRD) using a Philips X’Pert PW 3040/60 diffractometer (PANalytical, Almelo, Netherlands) equipped with CuK$_\alpha$ radiation. The ICDD cards were used for phase identification.

3. Materials and Methods

3.1. Cobalt Ferrite Powder Synthesis

The CoFe$_2$O$_4$ powder was synthesised using the coprecipitation method [27] and reagents of analytical purity (POCh, Gliwice, Poland). Hence, 0.6 moldm$^{-3}$ of FeCl$_3$·6H$_2$O and 0.3 moldm$^{-3}$ of CoCl$_2$·6H$_2$O solutions were mixed in ultrapure water with a resistivity of 18.2 MΩcm. Precipitating agent, i.e., NaOH (2 moldm$^{-3}$), was slowly added to the stirred chlorides solution. Coprecipitation was conducted in a Teflon vessel at a temperature of 50 °C for two hours. Subsequently, the synthesised powder was rinsed in distilled water, centrifuged for five minutes at 300 rpm, and dried at 50 °C for 48 h. The powder was also ground in an agate mortar to break agglomerates into smaller particles. In further study, the as-received and post-thermal treatment (800 °C, 1 h, air) CoFe$_2$O$_4$ powder was used. The phase composition of CoFe$_2$O$_4$ powder was determined by X-ray diffraction technique (XRD) using a Philips X’Pert PW 3040/60 diffractometer (PANalytical, Almelo, Netherlands) equipped with CuK$_\alpha$ radiation. The ICDD cards were used for phase identification.

3.2. Preparation of Cobalt Ferrite Coatings

Cobalt ferrite coatings were deposited on a nickel plate (Nickel 201, Ni ≥ 99.0%). Before the deposition process, the nickel plate with a working area of 0.5 cm$^2$ was mechanically polished using abrasive papers (P320, P600, P1000), and subsequently rinsed in acetone in an ultrasonic bath for 10 min. The studied coatings were produced by applying two different procedures. In the first case, a mixture of the thermally treated CoFe$_2$O$_4$ powder (20 mg per 10 mL of solution) and polyethylene glycol 4000 (PEG 4000) (20 mg per 10 mL of solution) in acetone was prepared. Additionally, 5 mg of sodium dodecyl

![Figure 8. Double layer capacitance $C_{dl}$ versus overpotential $\eta$ obtained for CoFe$_2$O$_4$ electrodes in 1 M KOH during the oxygen evolution process.](image-url)
sulfate (SDS) was added as a surfactant to the mixture. To obtain a homogeneous colloid, the prepared mixture was placed in an ultrasonic bath for 30 min. Subsequently, the nickel substrate was immersed in the mixture. The coating was deposited by sedimentation on a metallic substrate until all the solvent had evaporated. The obtained coating was subjected to heat treatment at 800 °C for 1 h in an argon atmosphere. In this paper, coating obtained in that way will be referred to as CFO<sub>PEG</sub>. In the second case, to obtain CoFe<sub>2</sub>O<sub>4</sub> coating with a metallic binder, electrochemical deposition was used. Nickel was deposited from the bath with the following composition (concentrations in g dm<sup>−3</sup>): NiSO<sub>4</sub>·7H<sub>2</sub>O—84, NiCl<sub>2</sub>·6H<sub>2</sub>O—10, H<sub>3</sub>BO<sub>3</sub>—8, to which 20 mg of cobalt ferrite powder and 5 mg of SDS was added. Note that nickel electrodeposition started when CoFe<sub>2</sub>O<sub>4</sub> powder settled by sedimentation on the surface of the metallic substrate. Nickel binder was deposited under galvanostatic conditions at current density <i>j</i> = 10 mA cm<sup>−2</sup> and time 20 min. The deposition process was carried out at the temperature 20 °C. The Faradaic yield of nickel deposition was ca. 70%. In this paper, coatings obtained in that way will be referred to as CFO<sub>Ni</sub> (in the case of thermally treated CoFe<sub>2</sub>O<sub>4</sub> powder) and CFO<sub>PEG</sub><sub>Ni</sub> (in the case of as-received CoFe<sub>2</sub>O<sub>4</sub> powder). Using a JEOL JSM—6480 (JEOL Ltd., Tokyo, Japan) scanning electron microscope (SEM) with energy dispersive spectroscopy (EDS) attachment, the surface morphology and chemical composition of the obtained CoFe<sub>2</sub>O<sub>4</sub> coatings were determined.

3.3. Electrochemical Measurements

Electrochemical tests were performed in 1 M KOH solution using a three-electrode cell with saturated calomel electrode (SCE) as a reference electrode and platinum mesh as a counter electrode. Working electrodes were CoFe<sub>2</sub>O<sub>4</sub> coatings with a geometric surface area of 0.5 cm<sup>2</sup>. The ohmic drop between the reference and working electrode was reduced using a Luggin capillary. All electrochemical experiments were carried out at a temperature of 20 °C. For the data registration, a PARSTAT 2273 system and the PowerSuite 2.58 software (Princeton Applied Research, Oak Ridge, TN, USA) were used. Values of measured potentials were converted from SCE to reversible hydrogen electrode (RHE) according to the following formula: \( E_{\text{RHE}} = E_{\text{SCE}} + 0.059pH + 0.241 \). The overpotential (η) for the oxygen evolution reaction was calculated using the equation: \( \eta = E_{\text{RHE}} - 1.23 \).

Quasi-stationary polarisation curves \( j \) vs. \( E \) were recorded using the linear sweep voltammetry (LSV) technique within the potential range from 1.22 V to 1.85 V vs. RHE and sweep rate \( v = 10 \text{ mV min}^{-1} \). Before measurements, CoFe<sub>2</sub>O<sub>4</sub> electrodes were conditioned at an anodic potential of 1.85 V for 5 h. The ohmic drop compensation was conducted during measurements using the current interrupt technique [4].

The spectra were registered using the electrochemical impedance spectroscopy (EIS) method. The impedance spectra were recorded potentiostatically at selected \( dc \) potentials from the interval where the OER takes place. Before the recording of each spectrum, electrodes were held at the appropriate potential for 5 min. Spectra were registered in the frequency range from 20 kHz to 10 mHz with a density of 10 points per decade. The amplitude of the \( ac \) signal was 10 mV<sub>rms</sub>. For the quantitative analysis of obtained data, the ZSimpWin 3.21 software was used.

To evaluate long-term stability of the CoFe<sub>2</sub>O<sub>4</sub> electrodes, the chronopotentiometry technique was used. The test was carried out at the current density \( j = 50 \text{ mA cm}^{-2} \) for 28 h.

4. Concluding Remarks

This paper reports on two new procedures for the preparation of porous cobalt ferrite coatings with a metallic and organic binder for use as catalysts in the oxygen evolution reaction (OER). The parameter \( \eta_{10} \) indicates that all investigated CoFe<sub>2</sub>O<sub>4</sub> coatings exhibit significantly higher apparent activity towards OER than nickel substrate in 1 M KOH. In particular, CoFe<sub>2</sub>O<sub>4</sub> coating with PEG applied as a binder shows overpotential \( \eta_{10} = 295 \text{ mV} \) at a current density of 10 mA cm<sup>−2</sup> and Tafel slope \( b = 35 \text{ mV dec}^{-1} \). CoFe<sub>2</sub>O<sub>4</sub> coating with Ni binder (\( \eta_{10} = 287 \text{ mV} \) and \( b = 45 \text{ mV dec}^{-1} \)) shows comparable catalytic activity towards OER. It was stated that the main reason for the superior catalytic activity of CFO<sub>PEG</sub> coating
is the large electrochemically active surface area. In contrast, the excellent catalytic activity of CoFe$_2$O$_4$ coating containing nickel binder between the ferrite particles is caused by increasing both the conductivity and the electrochemically active surface area. It was also shown that the obtained CoFe$_2$O$_4$ electrodes maintain their catalytic activity for at least 28 h at a current density of 50 mA cm$^{-2}$. It can be stated that this work offers a new path for the design of high-performance OER electrocatalysts using both sintering and electrodeposition techniques.

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**References**

1. Hu, X.; Tian, X.; Lin, Y.-W.; Wang, Z. Nickel foam and stainless steel mesh as electrocatalysts for hydrogen evolution reaction, oxygen evolution reaction and overall water splitting in alkaline media. *RSC Adv.* **2019**, *9*, 31563–31571. [CrossRef]
2. Aziz, A.; Asif, M.; Ashraf, G.; Iftikhar, T.; Hu, J.; Xiao, F.; Wang, S. Boosting electrocatalytic activity of carbon fiber@fusiform-like copper-nickel LDHs: Sensing of nitrate as biomarker for NOB detection. *J. Hazard. Mater.* **2022**, *422*, 126907. [CrossRef] [PubMed]
3. Assif, A.; Aziz, A.; Ashraf, G.; Iftikhar, T.; Sun, Y.; Xiao, F.; Liu, H. Unveiling microbiologically influenced corrosion engineering to transfigure damages into benefits: A textile sensor for H$_2$O$_2$ detection in clinical cancer tissues. *Chem. Eng. J.* **2022**, *427*, 131398. [CrossRef]
4. Colli, A.N.; Girault, H.H.; Battistel, A. Non-precious electrodes for practical alkaline water electrolysis. *Materials* **2019**, *12*, 1336. [CrossRef] [PubMed]
5. Chen, F.; Zhang, L.L.; Wu, H.; Guan, C.; Yang, Y.; Qiu, J.; Lyu, P.; Li, M. Bifunctional oxygen evolution and supercapacitor electrode with integrated architecture of NiFe-layered double hydroxides and hierarchical carbon framework. *Nanotechnology* **2019**, *30*, 325402. [CrossRef]
6. Wang, Y.; Qiao, M.; Li, Y.; Wang, S. Tuning surface electronic configuration of NiFe LDHs nanosheets by introducing cation vacancies (Fe or Ni) as highly efficient electrocatalysts for oxygen evolution reaction. *Small* **2018**, *14*, 1800136. [CrossRef] [PubMed]
7. Nardi, K.L.; Yang, N.Y.; Dickens, C.F.; Strickler, A.L.; Bent, S.F. Creating highly active atomic layer deposited NiO electrocatalysts for the oxygen evolution reaction. *Adv. Energy Mater.* **2015**, *5*, 1500412. [CrossRef]
8. Zhu, X.L.; Wang, P.; Wang, Z.Y.; Liu, Y.Y.; Zheng, Z.K.; Zhang, Q.Q.; Zhang, X.Y.; Dai, Y.; Whangbo, M.H.; Huang, B.B. Co$_3$O$_4$ nanobelt arrays assembled with ultrathin nanosheets as highly efficient and stable electrocatalysts for the chlorine evolution reaction. *J. Mater. Chem. A* **2018**, *6*, 12718–12723. [CrossRef]
9. Meng, Y.T.; Song, W.Q.; Huang, H.; Ren, Z.; Chen, S.Y.; Suib, S.L. Structure–property relationship of bifunctional MnO$_2$ nanostructures: Highly efficient, ultra-stable electrochemical water oxidation and oxygen reduction reaction catalysts identified in alkaline media. *J. Am. Chem. Soc.* **2014**, *136*, 11452–11464. [CrossRef] [PubMed]
10. Jung, J.W.; Jang, J.S.; Yun, T.G.; Yoon, K.R.; Kim, I.D. Three-dimensional nanofibrous air electrode assembled with carbon nanotubes-bridged hollow Fe$_2$O$_3$ nanoparticles for high-performance lithium-oxygen batteries. *ACS Appl. Mater. Interfaces* **2018**, *10*, 6531–6540. [CrossRef]
11. Silva, V.D.; Ferreira, L.S.; Simeos, T.A.; Medeiros, E.S.; Macedo, D.A. 1D hollow MFe$_2$O$_4$ (M = Cu, Co, Ni) fibers by solution blow spinning for oxygen evolution reaction. *J. Colloid Interface Sci.* **2019**, *540*, 59–65. [CrossRef]
12. Ferreira, L.S.; Silva, T.R.; Santos, J.R.D.; Silva, V.D.; Raimundo, R.A.; Morales, M.A.; Macedo, D.A. Structure, magnetic behavior and OER activity of CoFe$_2$O$_4$ powders obtained using agar-agar from red seaweed (Rhodophyta). *Mater. Chem. Phys.* **2019**, *237*, 121847. [CrossRef]
13. Sagu, J.S.; Mehta, D.; Wijayantya, K.G.U. Electrocatalytic activity of CoFe$_2$O$_4$ thin films prepared by AACVD towards the oxygen evolution reaction in alkaline media. *Electrochem. Commun.* **2018**, *87*, 1–4. [CrossRef]
14. Kargar, A.; Yavuz, S.; Kim, T.K.; Liu, C.-H.; Kuru, C.; Rustomji, C.S.; Jin, S.; Bandaru, P.R. Solution-processed CoFe2O4 nanoparticles on 3D carbon fiber papers for durable oxygen evolution reaction. ACS Appl. Mater. Interfaces 2015, 7, 17851–17856. [CrossRef]

15. Mahala, C.; Sharma, M.D.; Basu, M. 2D nanostructures of CoFe2O4 and NiFe2O4: Efficient oxygen evolution catalyst. Electrochim. Acta 2018, 273, 462–473. [CrossRef]

16. Zhang, Z.; Zhang, J.; Wang, T.; Li, Z.; Yang, G.; Bian, H.; Li, J.; Gao, D. Durable oxygen evolution reaction of one dimensional spinel CoFe2O4 nanofibers fabricated by electrospinning. RSC Adv. 2018, 8, 5338–5343. [CrossRef]

17. Li, M.; Xiong, Y.P.; Liu, X.T.; Bo, X.J.; Zhang, Y.F.; Han, C.; Guo, L.P. Facile synthesis of electrospun MFe2O4 (M = Co, Ni, Cu, Mn) spinel nanofibers with excellent electrocatalytic properties for oxygen evolution and hydrogen peroxide reduction. Nanoscale 2015, 7, 8920–8930. [CrossRef]

18. Karthigayan, N.; Manimuthu, P.; Priya, M.; Sagadevan, S. Synthesis and characterisation of NiFe2O4, CoFe2O4 and CuFe2O4 thin films for anode material in Li-ion batteries. Nanomater. Nanotechnol. 2017, 7, 1847980417711084. [CrossRef]

19. Nikam, S.M.; Sharma, A.; Rahaman, M.; Teli, A.M.; Mujawar, S.H.; Zahn, D.R.T.; Patil, P.S.; Sahoo, S.C.; Salvan, G.; Patil, P.B. Pulsed laser deposited CoFe2O4 thin films as supercapacitor electrodes. RSC Adv. 2020, 10, 19353–19359. [CrossRef]

20. Zhang, L.H.; Wei, T.; Jiang, Z.M.; Liu, C.Q.; Jiang, H.; Chang, J.; Sheng, L.Z.; Zhou, Q.H.; Yuan, L.B.; Fan, Z.J. Electrostatic interaction in electrospun nanofibers: Double-layer carbon protection of CoFe2O4 nanosheets enabling ultralong-life and ultrahigh-rate lithium ion storage. Nano Energy 2018, 48, 238–247. [CrossRef]

21. Richter, P.; Plassmeyer, P.N.; Harzdorf, J.; Ruffer, T.; Lang, H.; Kalbacova, J.; Johrmann, N.; Schulze, M.; Hietschold, M.; Arekapudi, S.S.P.; et al. High quality magnetic oxide thin films prepared via aqueous solution processing. Chem. Mater. 2016, 28, 4917–4927. [CrossRef]

22. Kennaz, H.; Harat, A.; Guellati, O.; Momodu, D.Y.; Barzegar, F.; Dangbegnon, J.K.; Manyala, N.; Guerioune, M. Synthesis and electrochemical investigation of spinel cobalt ferrite magnetic nanoparticles for supercapacitor application. J. Solid State Electrochem. 2018, 22, 835–847. [CrossRef]

23. Lu, X.; Zhao, C. Electrophoretic deposition of hierarchically structured three-dimensional nickel–iron electrodes for efficient oxygen evolution at high current densities. Nat. Commun. 2015, 6, 6616. [CrossRef] [PubMed]

24. Liang, Y.; Li, Y.; Wang, H.; Dai, H. Strongly coupled inorganic/nanocarbon hybrid materials for advanced electrocatalysis. J. Am. Chem. Soc. 2013, 135, 2013–2036. [CrossRef] [PubMed]

25. Liang, Y.; Li, Y.; Wang, H.; Zhou, J.; Wang, J.; Regier, T.; Dai, H. Co3O4 nanocrystals on graphene as a synergistic catalyst for oxygen reduction reaction. Nat. Mater. 2011, 10, 780–786. [CrossRef]

26. Gong, M.; Li, Y.; Wang, H.; Liang, Y.; Wu, J.Z.; Zhou, J.; Wang, J.; Regier, T.; Wei, F.; Dai, H. An advanced Ni–Fe layered double hydroxide electrocatalyst for water oxidation. J. Am. Chem. Soc. 2013, 135, 8452–8455. [CrossRef]

27. Kubisztal, M.; Kubisztal, J.; Karolus, M.; Prusik, K.; Haneczok, G. Collective superspin glass state of interacting cobalt ferrite nanoparticles. IEEE Trans. Magn. 2019, 55, 2301306. [CrossRef]

28. Williamson, G.K.; Hall, W.H. X-ray line broadening from filed aluminium and wolfram. Acta. Metall. 1953, 1, 22–31. [CrossRef]

29. Yan, Z.; Liu, H.; Hao, Z.; Yu, M.; Chen, X.; Chen, J. Electrodeposition of (hydro)oxides for an oxygen evolution electrode. Chem. Sci. 2020, 11, 10614–10625. [CrossRef]

30. Ajroud; L.; Milki, N.; Bessais; L.; Madigou, V.; Villain, S.; Leroux, C. Magnetic, electric and thermal properties of cobalt ferrite nanofibers. Mater. Res. Bull. 2014, 59, 49–58. [CrossRef]

31. Lasia, A. Electrochemical Impedance Spectroscopy and Its Applications, 1st ed.; Springer: New York, NY, USA, 2014; pp. 203–250. [CrossRef]

32. Kubisztal, J.; Budniok, A.; Lasia, A. Study of the hydrogen evolution reaction on nickel-based composite coatings containing molybdenum powder. Int. J. Hydrogen Energy 2007, 32, 1211–1218. [CrossRef]

33. Louie, M.W.; Bell, A.T. An investigation of thin-film Ni–Fe oxide catalysts for the electrochemical evolution of oxygen. J. Am. Chem. Soc. 2013, 135, 12329–12337. [CrossRef] [PubMed]