

Article

Evaluation of Bi-Functional Electrochemical Catalytic Activity of Co_3O_4 - CoFe_2O_4 Composite Spinel Oxide

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Abstract: Oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are important for developing energy systems such as fuel cells and metal–air batteries. Precious metal catalysts, such as Pt and IrO_2 , have been considered electrochemical catalysts because of their excellent activity for the ORR and OER. However, their disadvantages, such as low durability for long-term operation and high price, necessitate the development of alternative electrochemical catalysts. Transition metal oxides with excellent electrical conductivity, high efficiency, and stability have been considered alternative electrochemical catalysts owing to their ORR and OER activities, which are similar to those of precious metal catalysts. Therefore, in this study, composite catalyst materials comprising Co_3O_4 and CoFe_2O_4 spinel oxides were synthesized via hydrothermal synthesis. The synthesized composite oxides exhibit bi-functional electrochemical catalytic activity for ORR and OER owing to the large active surface area and increased number of oxygen vacancies via the nanostrain in Co_3O_4 nanoparticles.

Keywords: cobalt ferrite oxide; hydrothermal synthesis; oxygen reduction reaction (ORR); oxygen evolution reaction (OER); spinel oxide

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1. Introduction

As concerns about the excessive consumption of fossil fuels and energy depletion increase, intensive research is being conducted on developing sustainable and renewable energy technologies [1–5]. Therefore, efficient energy storage and conversion systems, such as metal–air batteries [6–8] and fuel cells [9–11], are attracting attention because of their high energy density, environmental friendliness, and cost-effectiveness. However, the slow kinetics of the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) in electrochemical energy systems limits the efficiency of fuel cells and metal–air batteries [12–15]. Therefore, developing efficient electrochemical catalysts for ORR and OER is important. Pt-based catalysts for the ORR and RuO_2 - and IrO_2 -based catalysts for the OER exhibit high electrochemical catalytic activity with high current density and low onset potential [16,17]. Although precious metal catalysts have high catalytic activity, commercializing them is difficult due to their high cost, scarcity, and low durability against long-term operation. As a result, various studies have been conducted on efficient catalysts based on non-precious metals to replace precious metal catalysts to overcome these shortcomings [17–21].

Non-precious metal-based transition metal oxides (TMOs), such as NiCo_2O_4 [22], LaMnO_3 [23], CuO [24], MnO_2 [25], MnCo_2O_4 [26], and Co_3O_4 [27], have been proposed as bifunctional electrochemical catalysts for ORR and OER because of their excellent stability and abundance [28,29]. Among the various TMOs, spinel oxide has the basic structural formula of AB_2O_4 , with divalent and trivalent metal ions located at the A-site and B-site, respectively [30]. Considering that spinel oxide has various valence states, it has excellent

redox stability compared to precious metal catalysts and has characteristics such as high abundance, low cost, and environmental friendliness [31,32]. Spinel-structured cobalt ferrite (CoFe_2O_4) has abundant metal ions in various valence states (Fe^{2+} , Fe^{3+} , Co^{2+} , and Co^{3+}) and has been reported to provide redox-active sites on the surface required for O_2 adsorption and activation [33,34]. Despite these properties, spinel ferrite exhibits limited electrochemical performance owing to the limited diffusion length at the electrode–electrolyte interface and low ion diffusion rate due to particle aggregation [35,36].

Chen et al. reported that the electrochemical performance of spinel oxides could be improved by synthesizing nanomaterials with uniform and large specific surface areas [37]. Various methods have been adopted to fabricate spinel-structured nanomaterials [38–41]. Hydrothermal synthesis, a promising method for synthesizing nanomaterials, is a method of synthesizing nanomaterials by applying heat to an aqueous solution and using pressure inside a container. This method has a high level of composition control at a low temperature, high reaction rate, is free of impurities, and is cost-effective compared to other synthesis methods. In addition, hydrothermal synthesis can control the morphology of nanoparticles by controlling parameters such as temperature, molar concentration, and time, thereby improving their electrochemical properties [42–44].

Therefore, in this study, the composite spinel oxide Co_3O_4 - CoFe_2O_4 was synthesized through one-pot hydrothermal synthesis by changing the ratio of Co_3O_4 to CoFe_2O_4 . The synthesized Co_3O_4 - CoFe_2O_4 has a uniform nanoparticle shape and a high specific surface area, and the coexistence of Co_3O_4 and CoFe_2O_4 according to the ratio shows bifunctional electrochemical catalytic activity for the ORR and OER.

2. Materials and Methods

2.1. Materials

Cobalt(II) acetate tetrahydrate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, 97%, Samchun Pure Chemical Co., Ltd., Pyeongtaek, Republic of Korea.) and iron (II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 99%, Samchun Pure Chemical Co., Ltd., Pyeongtaek, Republic of Korea.) were used as precursors. An ammonia solution (NH_4OH , 25–30%, Samchun Pure Chemical Co., Ltd., Pyeongtaek, Republic of Korea.) was used as the precipitant.

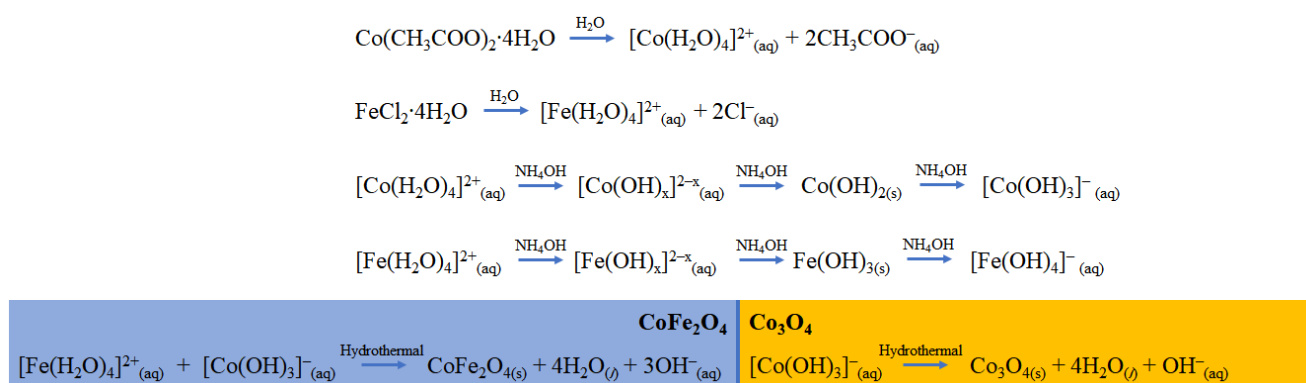
2.2. Synthesis of Composite Co_3O_4 - CoFe_2O_4 -X via Hydrothermal Method

Co_3O_4 - CoFe_2O_4 composite spinel oxide was synthesized by one-pot hydrothermal synthesis. $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (6.35 mmol) are added to 7.75 mL of distilled water in a ratio of Co_3O_4 : $\text{CoFe}_2\text{O}_4 = x$ at.% ($x = 0, 12.5, 25, 37.5$):100 at.%. After stirring the solution for 30 min, 6.25 mL of ammonia solution was slowly added using a syringe under stirring to adjust to pH 10 and stirred for 30 min. The solution was transferred to a Teflon-lined autoclave and heated at 453 K for 3 h and then cooled to room temperature. After repeated washing with distilled water and ethanol, the sample was dried overnight in an oven at 333 K to obtain a sample without additional calcination. Using the same method described above, Co_3O_4 was synthesized with 6.35 mmol of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$. The samples were named CFO, CO-CFO-12.5, CO-CFO-25, CO-CFO-37.5, and CO, respectively. CFO is CoFe_2O_4 , CO is Co_3O_4 , and in CO-CFO-X, X is the atomic percentage of CO in the composite oxides. The proposed reaction mechanism for formation of nanoparticle consisted of Co_3O_4 and CoFe_2O_4 . The reaction formula that can occur during hydrothermal synthesis is shown in Scheme 1.

2.3. Characterization

The crystal structure of the sample prepared by the one-pot hydrothermal synthesis was analyzed using X-ray diffraction (XRD, MiniFlex 600) with Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) in the 2θ range of 20 – 80° . Field-emission scanning electron microscopy (FE-SEM, S-4800, Hitachi, Tokyo, Japan.) was used to examine the sample morphology. The morphology and lattice structure of the electrode materials were analyzed by transmission electron microscopy (HR-TEM, JEM-2100F). The specific surface area, pore volume,

pore size distribution, and pore morphology of the samples were analyzed by N₂ adsorption/desorption isotherms at 77 K using the Brunauer–Emmett–Teller equation (BET, BELSORP-mini II). The binding of oxygen in the samples was analyzed by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250) using Al K α radiation. Electrochemical activity was evaluated using a rotating ring-disk electrode (RRDE, RRDE-3A Ver. 2.0) in 0.1 M KOH electrolyte solution with ORR of -0.8 V~ 0.2 V and OER of 0.3 V~ 1.0 V. ORR and OER scan rates were performed at 10 mV/s and 50 mV/s, respectively, with a Hg/HgO (1 M NaOH) electrode used as reference electrode and a platinum wire used as a counter electrode. Five microliters of catalyst ink were placed on a glassy carbon disk electrode and used as a working electrode to conduct an electrochemical catalyst performance test in an O₂ atmosphere.



Scheme 1. Proposed reaction mechanism of spinel oxide CFO, CO-CFO-X, and CO.

3. Results and Discussion

3.1. Characterization

The crystal phase and diffraction peaks of the spinel oxide CFO, CO-CFO-X, and CO obtained by X-ray diffraction analysis are shown in Figure 1. The XRD pattern of CFO was consistent with the diffraction peak of the cobalt ferrite spinel oxide phase (JCPDS No. 01-1121), and the diffraction peak of CO was consistent with that of the cobalt oxide phase (JCPDS No. 09-0418). The XRD pattern of the CO-CFO-X composite oxide exhibits CFO main peak at 35.4° and CO main peak at 36.7° . In addition, in the XRD results, the intensity of the main peak of CO increases as the mixing ratio of CO increases, indicating that the CO-CFO complex coexisting with CFO and CO was prepared through hydrothermal synthesis without high-temperature calcination. Compared with the intensity of the CO peaks, the intensity of CO in CO-CFO-X and the intensity of the CFO peaks are relatively low, related to the small crystal size [45]. The CO main peaks of the CO-CFO-12.5 and CO-CFO-25 samples are slightly shifted to high 2-theta angles, indicating that the lattice was expanded. However, in CO-CFO-37.5, which has a high CO content in the composite, the shift of the CO-related peaks was not confirmed [46].

Therefore, FE-SEM and HR-TEM analyses were performed to confirm the crystal sizes and lattices of the samples prepared using the hydrothermal synthesis method. Figure 2 shows the structures of CFO, CO-CFO-X, and CO synthesized by hydrothermal synthesis at 453 K using FE-SEM. The CFO sample (Figure 2a) and CO-CFO-X samples (Figure 2b–d) consist of small particles, as predicted by the low peak intensity in the XRD analysis. However, the CO sample (Figure 2e) shows that the nanoparticles are agglomerated compared to other samples, attributed to the high peak intensity in the XRD pattern [45]. The samples, except for CO, formed a porous structure and a material with uniformly distributed nanoparticles. These nanostructures can exhibit high catalytic performance because of their promising structural features [47]. Figure 3 shows the HR-TEM images of CFO, CO-CFO-12.5, and CO. In the HR-TEM images of the 10 nm scale bar of CFO, CO-CFO-12.5, and CO (Figure 3a–c), it is difficult to confirm the lattice parameter

values and the difference between the samples. However, in the TEM image of the 5 nm scale bar, CO-CFO-12.5 (Figure 3d) shows a lattice parameter value of 0.475 nm and CO (Figure 3e) 0.451 nm. Compared to CO, the CO-CFO-X nanocomposite had an expanded lattice, indicating that the lattice expands as the particle size decreases because of the small particle size of CFO-CO-X compared to the CO sample, as confirmed in the SEM image (Figure 2) [48,49].

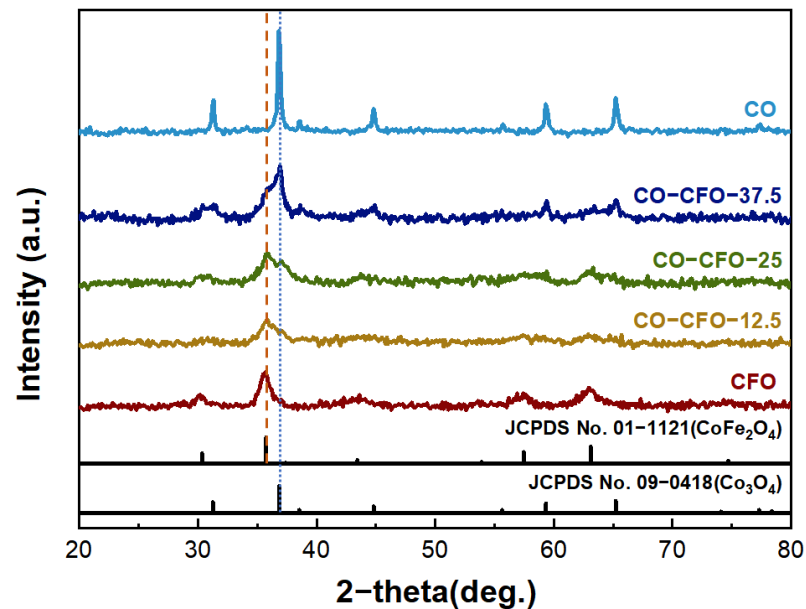


Figure 1. XRD patterns of spinel oxide CFO, CO-CFO-X, and CO.

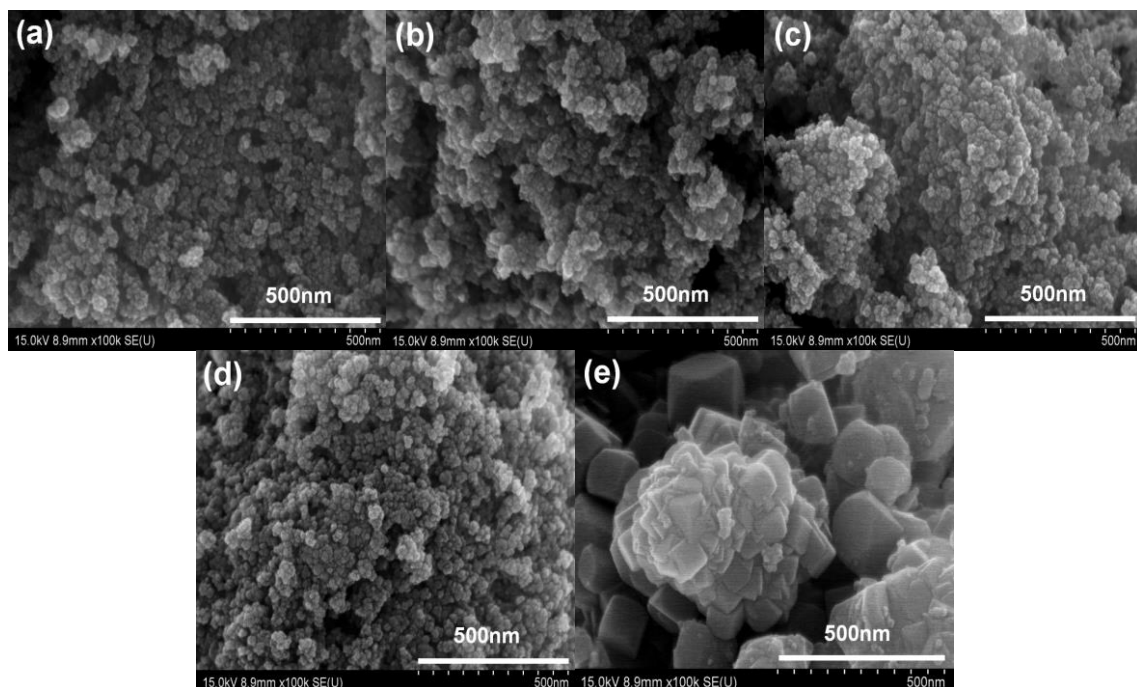


Figure 2. FE-SEM images of (a) CFO (b) CO-CFO-12.5 (c) CO-CFO-25 (d) CO-CFO-37.5 and (e) CO.

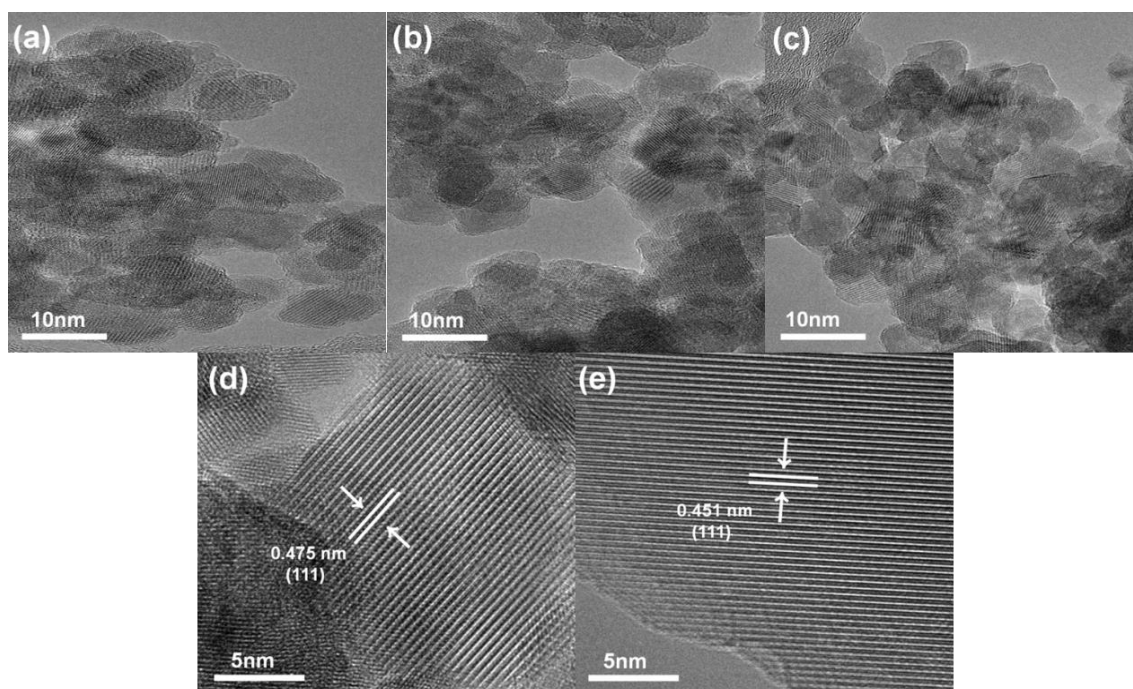


Figure 3. HR-TEM images of (a) CFO (b,d) CO-CFO-12.5 and (c,e) CO.

N₂ adsorption–desorption was performed to confirm the specific surface area, pore volume, and pore size distribution of the CFO, CO-CFO-X, and CO samples. As shown in Figure 4a, the N₂ adsorption and desorption isotherms of CFO and CO-CFO-X show a type IV curve containing a hysteresis loop, indicating a mesopore structure. In contrast, the N₂ adsorption and desorption isotherms of the CO sample correspond to type II nonporous structures. In the pore size distribution through the Barrett–Joyner–Halenda model (BJH), CO has relatively developed macropores, while the CFO and CO-CFO-X samples have well-developed mesopores (Figure 4b). Table 1 summarizes the specific surface area and average pore size of the samples obtained by calculating the results of the nitrogen adsorption/desorption experiment using the BET and BJH calculations. As shown in Table 1, CFO had the highest specific surface area (104.71 m²/g) and the smallest average pore diameter (24.41 nm). In hydrothermal synthesis, according to the CO ratio, the higher the CO ratio in CO-CFO-X, the smaller the specific surface area value and the larger the average pore diameter. CO had the lowest specific surface area (24.92 m²/g) and the largest average pore diameter (163.19 nm). In the hydrothermal synthesis process, CFO, which has slow crystal growth, inhibited the crystal growth of CO; therefore, a composite oxide with a large specific surface area and well-developed mesopores was prepared. The presence of mesopores in CO-CFO-X can serve as a channel for rapid ion diffusion and improve its performance as an electrochemical catalyst; in addition, a high specific surface area affects the ORR current density [50,51].

Table 1. The comparison of SSAs, pore volume, and average pore diameter of CFO, CO-CFO-X, CO.

Sample	Specific Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Average Pore Diameter (nm)
CFO	104.71	0.3483	24.41
CO-CFO-12.5	93.54	0.2976	28.07
CO-CFO-25	95.02	0.3168	28.07
CO-CFO-37.5	79.70	0.2841	28.07
CO	24.92	0.0237	163.19

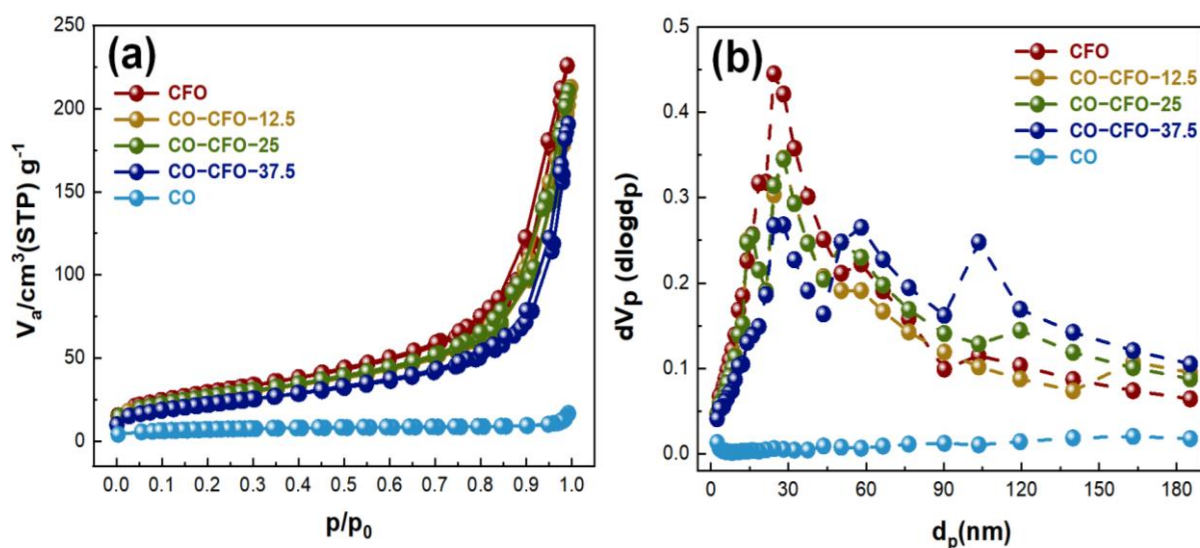


Figure 4. (a) Nitrogen adsorption-desorption isotherms of CFO, CO-CFO-X, and CO (b) Barrett-Joyner-Halenda (BJH) pore size distribution.

X-ray photoelectron spectroscopy (XPS) was performed to confirm the change in oxygen vacancies with an increase in the CO ratio. Figure 5 shows the O 1s XPS spectra. The O 1s peaks consisted of a lattice oxygen peak at approximately 529 eV and an adsorbed oxygen peak at approximately 531 eV. The area ratios of O_{ad}/O_L in the O 1s spectra of CFO, CO-CFO-12.5, CO-CFO-25, CO-CFO-37.5, and CO were 1.36, 1.40, 1.43, 1.42, and 1.56, respectively. CO (Figure 5e) showed the highest ratio of oxygen vacancies and CFO (Figure 5a) showed the lowest ratio of oxygen vacancies. As the ratio of CO in CO-CFO-X increases, the oxygen vacancy ratio tends to increase, attributed to an increase in the ratio of CO with relatively large oxygen vacancies. However, the CO-CFO-25 sample, containing relatively little CO, had more oxygen vacancies than the CO-CFO-37.5 sample. Therefore, the oxygen vacancies in the CO-CFO-X sample are affected by the occurrence of oxygen vacancies according to the expansion of the lattice structure, as confirmed by XRD peak shift and TEM lattice images [52,53]. Many studies have shown that an increase in oxygen vacancies increases the reactivity and number of active sites, reduces the hindrance to the adsorption of H_2O , and lowers the weak metal-oxygen bond to facilitate electron exchange, thereby affecting the electrocatalytic performance [54–56].

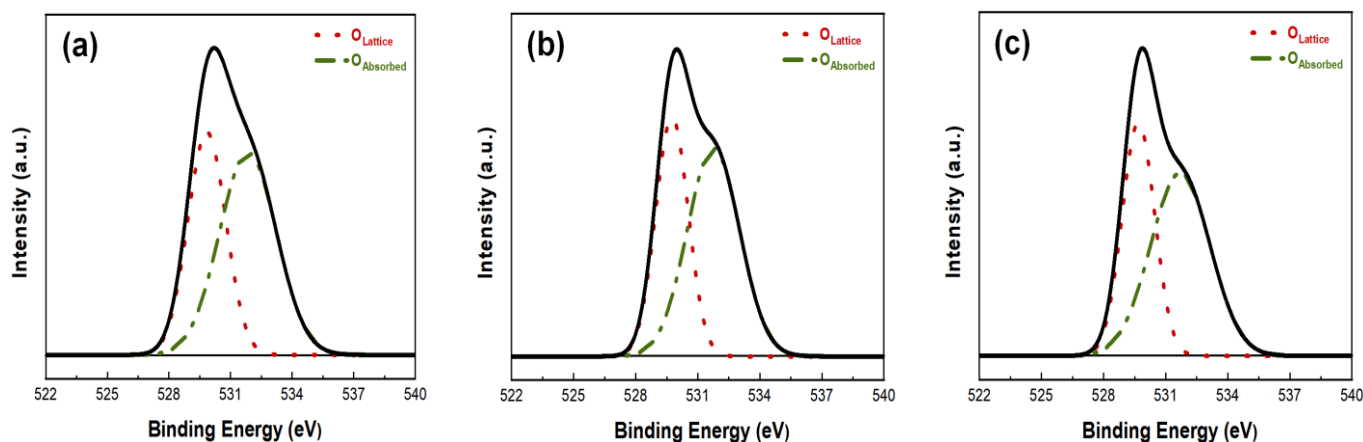


Figure 5. Cont.

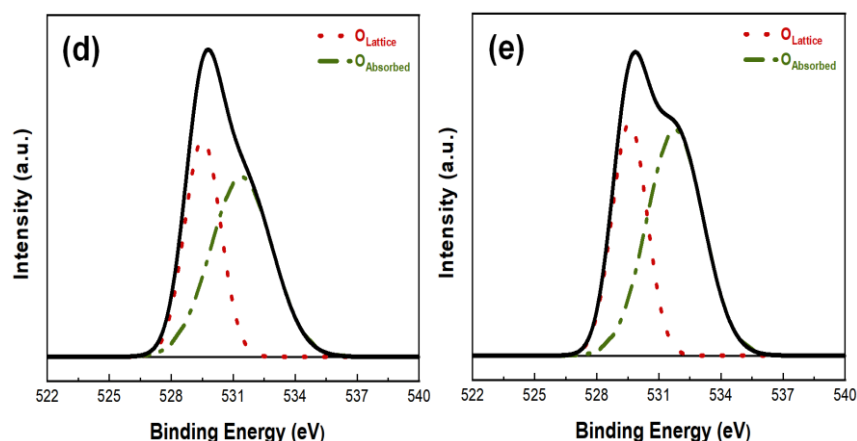


Figure 5. X-ray photoelectron spectrum of O 1s (a) CFO (b) CO-CFO-12.5 (c) CO-CFO-25 (d) CO-CFO-37.5, and (e) CO.

3.2. Electrochemical Measurement

Figure 6 shows the ORR results for CFO, CO-CFO-X, and CO metal oxides. Pt/C, known to have a low onset potential and high ORR activity, was measured under the same conditions as CO-CFO-X. In Figure 6a, Pt/C shows high ORR activity with a limiting current density value of -3.8 mA/cm^2 at -0.2 V . In the ORR curve (Figure 6a), the CO sample with a low specific surface area ($24.92 \text{ m}^2/\text{g}$) has a current density value of -1.6 mA/cm^2 , and the CFO sample with a high specific surface area ($104.71 \text{ m}^2/\text{g}$) has a current density value of -3.4 mA/cm^2 . The current density in the diffusion-controlled region was determined by the diffusion rate of oxygen, i.e., the higher the current density value of the diffusion-controlled region, the higher the electrocatalytic activity for ORR. The diffusion current is affected by the geometric surface of the electrode, and the current density increases with specific surface area [57,58]. The onset potentials of CFO, CO-CFO-12.5, CO-CFO-25, CO-CFO-37.5, and CO were -0.278 V , -0.270 V , -0.270 V , -0.279 V , and -0.297 V , respectively. The electrochemical and catalytic properties are similar because the nanocomposites are based on Co materials. However, compared to CFO, the onset potential and current density of the CO sample were lower, indicating low ORR performance. Despite the increase in the ratio of CO, the CO-CFO-X nanocomposite showed a slightly improved ORR performance compared to CFO owing to the formation of nanoparticles and the increase in oxygen vacancies. Many studies have reported that the improvement in ORR properties is related to the formation of oxygen vacancies on the catalyst surface [59–61]. In the calculated electron transfer number (Figure 6b), all the catalysts show a similar four-electron reaction. In the four-electron reaction, H_2O is generated directly without passing through the intermediate substance H_2O_2 to reduce the reaction pathways and achieve desirable reduction reactivity [62].

IrO_2 , known to have good OER activity, was measured under the same conditions to compare the performance of CFO, CO-CFO-X, and CO on the OER. Figure 7a shows the potential values at the same current density of 5 mA/cm^2 because it is difficult to compare the onset potential values. At 5 mA/cm^2 , the potentials of IrO_2 , CFO, CO-CFO-12.5, CO-CFO-25, CO-CFO-37.5, and CO were 0.937 , 0.806 , 0.779 , 0.759 , 0.755 , and 0.792 V , respectively. The CFO, CO-CFO-X, and CO samples had higher current densities and lower potential values than those of IrO_2 . A lower potential at the same current density increases the OER efficiency and improves the reaction kinetics of the electrocatalytic process [63].

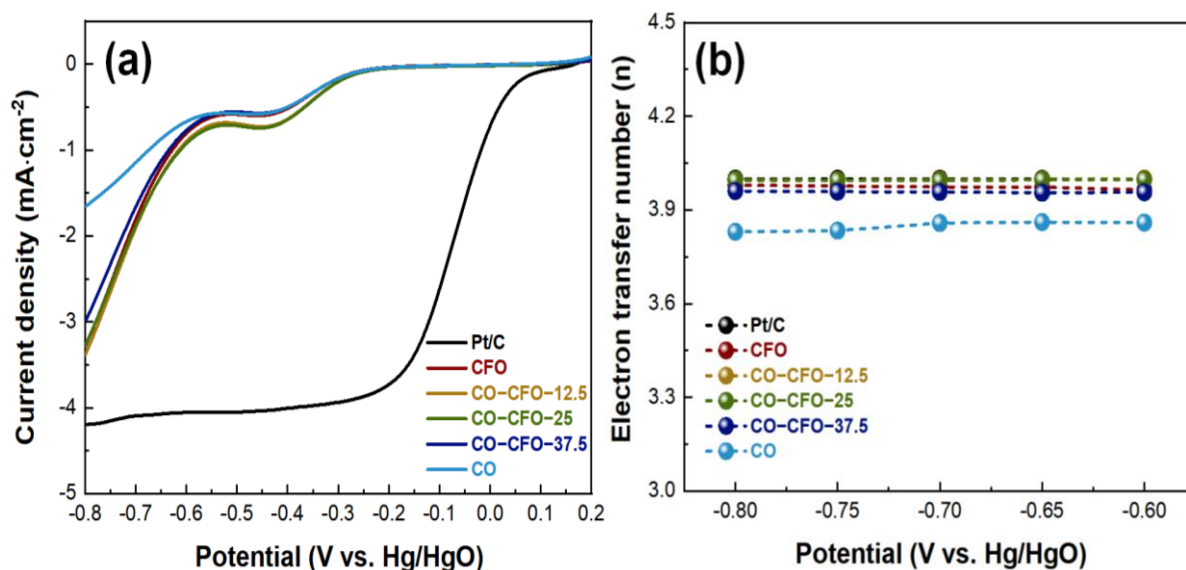


Figure 6. (a) Linear sweep voltammograms (LSV) for ORR curves and (b) Electron transfer number.

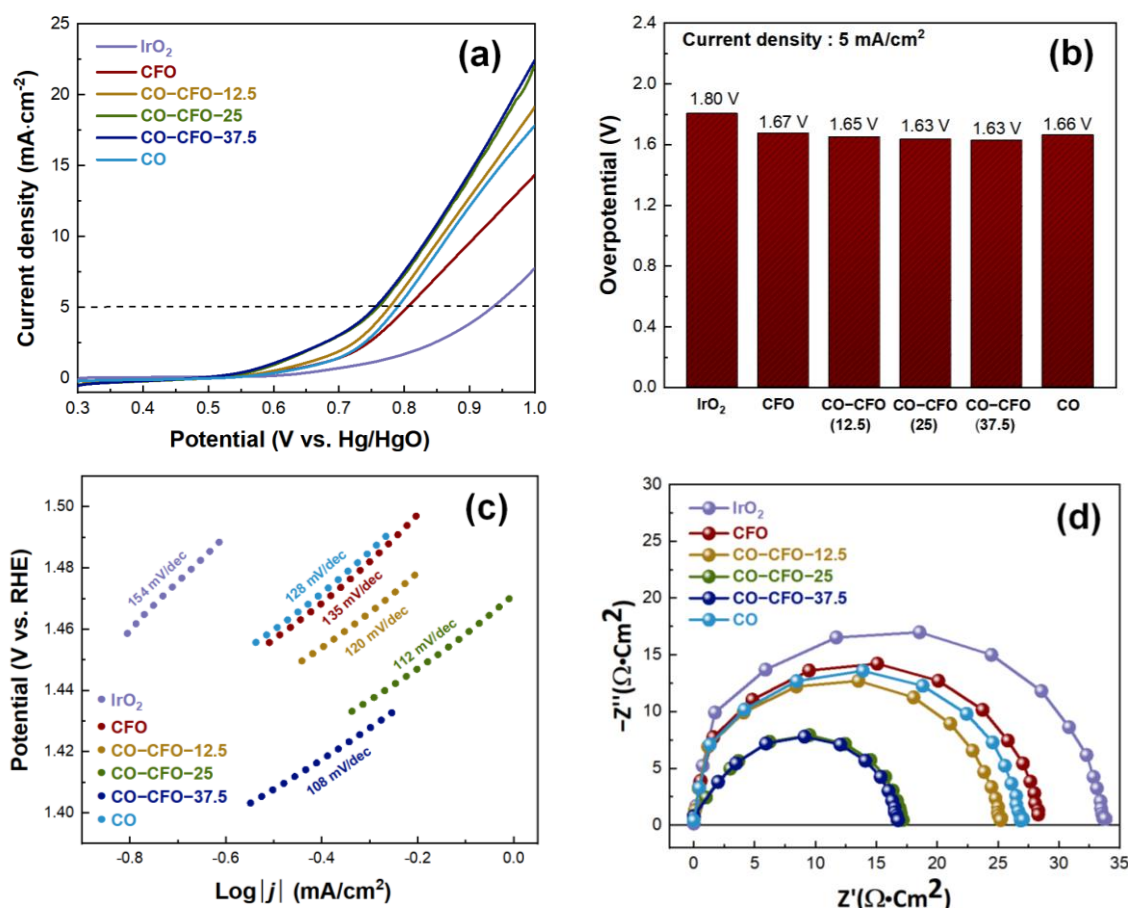


Figure 7. (a) Linear sweep voltammograms (LSV) for OER curves, (b) OER overpotential values of the electrodes measured at the same current density of 5 mA/cm^2 , (c) Tafel slope in OER of electrodes, (d) electrochemical impedance spectroscopy (EIS) of electrodes measured in the range of 7 MHz to 10 mHz.

The overpotential (V) value in Figure 7b was calculated as the E_{RHE} value using the formula $E_{\text{RHE}} = E_{\text{Hg}/\text{HgO}} + 0.059 \text{ pH} + E^{\circ}_{\text{Hg}/\text{HgO}}$. IrO₂ has the highest overpotential value

at 1.80 V. On the other hand, the CO-CFO electrode shows a relatively low overpotential values. These high overpotential values require more energy than thermodynamically calculated to cause the redox reaction. On the other hand, a low overpotential value works efficiently for electrochemical kinetics. Therefore, it can be confirmed that the CO-CFO electrode is effective as an OER electrochemical catalyst. The Tafel slope is one of the parameters that determine OER kinetics. In Figure 7c, the corresponding Tafel plots calculated by polarization curves show that the CFO, CO-CFO-12.5, CO-CFO-25, CO-CFO-37.5, and CO exhibit Tafel slopes of 135, 120, 112, 108, and 128 mV/dec, respectively. These Tafel slopes are smaller than IrO₂ (154 mV/dec), suggesting accelerated OER kinetics of the CO-CFO catalysts and efficient electron and mass transfer. Electrochemical impedance spectroscopy (EIS) was used to investigate the kinetics of the OER process (Figure 5d). The measurement was conducted under the conditions of 0.9 V and 10 mV in the range of 7 MHz to 10 mHz. The measured polarization resistances of IrO₂, CFO, CO-CFO-12.5, CO-CFO-25, CO-CFO-37.5, and CO were 33.79, 28.31, 25.21, 17.18, 16.80, and 27.06 $\Omega\cdot\text{cm}^2$, respectively. The small polarization resistance indicates fast electrochemical reaction at the interface between electrode materials and electrolyte. These changes in electrochemical performance may related with the oxygen vacancy and morphology of nanocomposites. CO with the most oxygen vacancies showed higher OER activity than CFO with small oxygen vacancies. CO-CFO-25 and CO-CFO-37.5, which have more oxygen vacancies than CO-CFO-12.5, have lower potential values at the same current density. The increase of oxygen vacancies is attributed to OER performance. CO-CFO-X nanocomposites with less oxygen vacancies than CO shows better OER performance. Although CO has a relatively large number of oxygen vacancies, the small specific surface area and the formation of macropores originate from the growth of large particles. The small surface area induces low OER performance owing to the fewer interfaces where electrochemical reactions occur. However, well-developed mesopores and macropores provide transport channels to improve contact with oxygen and enable fast long-distance transport of electrolyte ions, resulting in a relatively high OER performance [64]. Therefore, the CO-CFO-X nanocomposite has a high specific surface area related to the surface reaction and has many oxygen vacancies, indicating good activity in OER [65].

4. Conclusions

In this study, CFO, CO-CFO-X, and CO spinel oxides with a higher specific surface area than other synthesis methods were synthesized through hydrothermal synthesis. CFO, CO-CFO-X, and CO were synthesized without impurities at the low reaction temperature of 453 K. In the synthesis process, CFO, which has slow crystal growth, inhibited the crystal growth of CO, thereby forming CO-CFO-X nanocomposites (79.70~95.02 m²/g) having a larger specific surface area than CO (24.92 m²/g) and well-developed mesopores. The lattice expansion of CO-CFO-12.5 and CO-CFO-25 was indicated using XRD and TEM analysis, and the lattice expansion is affected by the occurrence of oxygen vacancies. CO-CFO-12.5 and CO-CFO-25 (onset potentials: −0.270 V) showed improved ORR performance compared to CFO (onset potentials: −0.278 V) owing to lattice strain and increased oxygen vacancies. CO-CFO-X nanocomposite showed higher stability and OER activity than IrO₂ owing to the presence of well-developed mesopores and macropores. The increase of oxygen vacancies is attributed to the OER performance, but the small specific surface area of CO reduces the interface where the electrochemical reaction occurs, resulting in lower OER performance than the CO-CFO-X nanocomposite. Therefore, CO-CFO-X suggests that it is a bifunctional electrochemical catalyst with high activity in the ORR/OER due to high specific surface area, lattice strain, and oxygen vacancies. Using the improved electrochemical catalytic performance of the CO-CFO-X nanocomposite developed in this study, we plan to conduct application research on fuel cells, metal–air batteries, or water electrolysis systems.

Author Contributions: Writing—original draft, J.-W.P.; Writing—review & editing, Y.-W.J. All authors have read and agreed to the published version of the manuscript.

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

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