Towards more efficient and stable bi-functional electrocatalysts for oxygen electrodes using FeCo₂O₄/CNF prepared by electrospinning

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ABSTRACT

In the present work, an iron-cobaltite spinel supported on N-containing carbon nanofibers shows a remarkable activity for the oxygen evolution reaction (OER) in alkaline solution, with an overpotential ($\eta_{10\text{mAcm}^{-2}}$) of 130 mV, one of the lowest values in literature so far. This material is also an excellent catalyst for the oxygen reduction reaction (ORR), what leads to an extraordinary reversible behavior ($\Delta E = E_{\text{OER}} - E_{\text{ORR}} = 480$ mV), being an economic and easy-scalable candidate for the air electrode of metal-air batteries, or for electrochemical devices where the oxygen evolution or the oxygen reduction are involved. In the present research, Fe partially replaces Co atoms in the

Co₃O₄ spinel structure, in order to obtain a more economically feasible material, leading to a FeCo₂O₄/CNF, by using an electrospinning preparation procedure previously adopted for the Co₃O₄/CNF synthesis. The substitution of iron in the Co₃O₄/CNF spinel entails an outstanding onset potential towards the OER of 1.36 V vs. RHE, which is 120 mV lower compared to the pure spinel (Co₃O₄/CNF). An optimal distribution of the FeCo₂O₄ particles on the carbon nanofiber surface, with 3-nm-size particles, allows exposing abundant active sites, mainly Co³⁺ and Fe³⁺, responsible for the enhanced activity towards the OER, and Fe-N_x moieties and N-sites (N-graphitic/pyridinic), more active for the ORR. Besides FeCo₂O₄/CNF shows a well-developed porous structure, favoring the mass transfer, a parameter particularly important for the ORR. In order to assess the stability of the catalysts for rechargeable alkaline metal-air batteries, cycling operation and chronopotentiometric experiments are carried out, showing a stable potential for 24 h.

1. Introduction

Rechargeable alkaline metal–air batteries are envisaged as commercially viable energy storage devices due to their high theoretical energy densities respect to lithium-ion batteries [1–3]. Despite their advantages, they do not still offer adequate practical energy density and life cycle; in fact, critical problems arise from the positive electrode, such as slow kinetics of the oxygen reduction (ORR) and oxygen evolution (OER) reactions [4,5]. To date, the state-of-the-art catalysts are Pt/C for the ORR and IrO₂ for the OER [6–10]. However, the scarcity and high cost of these noble metals hinder the widespread commercialization of metal-air batteries. Research efforts have been focused on replacing these expensive noble metals with cheap materials [11–18]. Mixed valence oxides of transition metals with a spinel structure (in particular cobaltite spinel oxides) have attracted much attention due to their high abundance, low cost and considerable catalytic activity for the ORR and OER [4,19–22]. However, the electrical conductivity of these materials is still not enough for the application in metal-air batteries. One pursued approach to increase the conductivity is to combine these oxides with carbon, in particular graphitic structures, in order to keep suitable stability under cycling operation [23,24]. Furthermore, carbonaceous materials, doped with N, have been recently designated to facilitate the ORR [25–28]. In fact, bare carbon materials show poor ORR activity, forming hydrogen peroxide as the main product, through a 2 e⁻ transfer process; whereas, N-doping can help to increase the number of active sites and to weaken the O-O bonds, leading to a more efficient 4 e⁻ transfer process for the ORR [29,30]. Generally, carbon nanotubes (CNTs), carbon nanofibers (CNFs), hollow structured carbons, etc. are good options as supports due to their large specific surface area and superb conductivity [24,31,32]. Furthermore, the N-doping of carbon materials also provides more defects and, thus, anchoring sites for the deposition of metals or

oxides, enhancing the interactions among the components [33]. This could significantly affect the electronic structure of metal centers and consequently change the binding energy of the oxygen molecules on the catalyst surface [34]. Accordingly, a combination of the spinel oxide with the carbonaceous support could promote the catalytic activity and the bi-functionality for the ORR and OER through a synergistic effect [35]. Recently, electrospun CNFs loaded with spinel-type cobalt oxide ($\text{Co}_3\text{O}_4/\text{CNF}$) was investigated as bifunctional oxygen electrodes showing good reversibility [36]. Since the European Commission included cobalt in the list of critical raw materials (CRMs) [37] in terms of high supply risk and economic importance, it is necessary the partial substitution of cobalt in Co_3O_4 with cheaper and more available alternative elements by preserving its high electrochemical effectiveness. Furthermore, as widely reported in literature, the partial replacement of Co in spinel Co_3O_4 with Ni, Fe and Mn can enhance the electron conductivity and electrocatalytic activity thanks to the formation of a ternary spinel oxide structure in which two distinct cations coexist [34,35,38]. Many scientific papers report a deep investigation of the spinel NiCo_2O_4 [39,40] as bifunctional oxygen electrocatalyst but fewer reports are present in the literature on the FeCo_2O_4 [41–43]. In the present work, Fe partially replaced Co atoms in the Co_3O_4 spinel structure, leading to a $\text{FeCo}_2\text{O}_4/\text{CNF}$, by using the same preparation procedure previously adopted for the $\text{Co}_3\text{O}_4/\text{CNF}$ synthesis. Herein, the $\text{FeCo}_2\text{O}_4/\text{CNF}$ catalyst has been physico-chemically studied in terms of structure, morphology and surface properties; these features have been correlated to the electrochemical behavior for the ORR and OER in comparison with previously developed catalysts and state-of-the-art materials reported in the literature.

2. Experimental

2.1. Materials and methods

The FeCo_2O_4 spinel oxide supported on carbon nanofibers ($\text{FeCo}_2\text{O}_4/\text{CNF}$) was synthesized by using the electrospinning technique. For this purpose, a solution was prepared by dissolving in N,N-Dimethylformamide (Sigma Aldrich, 99.8%) appropriate amounts of Iron (II) acetate ($\text{Fe}(\text{OAc})_2$, Sigma Aldrich, 99.9%), Cobalt (II) acetate tetrahydrate ($\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, Sigma Aldrich, 99%) and Polyacrylonitrile (PAN, Sigma Aldrich, Mw= 150,000) used as metal oxide and carbon nanofibers precursors, respectively. The synthesis procedure by electrospinning and the operating conditions are the same as reported in our previous works [36,44]. The obtained electrospun fibers were subjected to a stabilization thermal treatment at 270 °C in static air for 30 min and to a subsequent carbonization process at 900 °C for 1 h under a helium flow equal to 80 cc min⁻¹. The Fe-Co-CNF composite material was treated in static air at 350 °C for 30 min in order to obtain the spinel FeCo_2O_4 supported on carbon nanofibers ($\text{FeCo}_2\text{O}_4/\text{CNF}$) as reported in literature [36]. All thermal treatments were performed using a furnace (LENTON, LTF 12/38/500) equipped with a quartz-tube.

2.2. Physico-chemical characterization

Physico-chemical investigations were carried out on the synthesized sample to obtain information about its structure and morphology. Differential scanning calorimetric (DSC) and thermogravimetric (TG) analyses were performed (409C NETZSCH-Gerätebau GmbH analyzer) on the $\text{FeCo}_2\text{O}_4/\text{CNF}$ to determine the amount of FeCo_2O_4 in the final composite material. The crystal structure was analyzed by X-ray diffraction technique using a Philips X-pert 3710 with Cu K α radiation operating at 40 kV and 20 mA. The surface analysis of the synthesized sample was performed by the X-ray

photoelectron spectroscopy (XPS) using a Physical Electronics (PHI) 5800-01 spectrometer equipped with a monochromatic Al K α X-ray source at 300 W. The fitting and interpretation of XPS spectra The PHI Multipak 6.1 software was used for the interpretation of XPS data. The morphology and the microstructure of the FeCo₂O₄/CNF were investigated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) by a Philips XL30 S FEG microscope and a FEI CM12 instrument, respectively. The surface area and pore size were calculated by nitrogen adsorption/desorption at 77.3 K employing an ASAP 2020 M Micrometrics instrument. The Brunauer-Emmet-Teller equation (BET) and the Barrett-Joyner-Halenda (BJH) method were used to determine the surface area and the total pore volume, respectively.

2.3. Electrochemical characterization

The assessment of the catalytic activity of the FeCo₂O₄/CNF catalyst was performed in a conventional 3-electrode cell equipped with a gas diffusion working electrode (GDWE). The detailed description of the experimental set-up can be found elsewhere [44,45]. Briefly, an ink of the catalyst was prepared and sprayed onto a hydrophobic backing layer. The ink consisted of a 70 wt.% of FeCo₂O₄/CNF, a 30 wt % of Nafion® (5 wt.% solution) and isopropanol. The final loading on the electrode (14 mm diameter) was $0.5 \pm 0.02 \text{ mg cm}^{-2}$ of FeCo₂O₄. The electrolyte was a 6 M KOH solution, freshly prepared under inert atmosphere and from high-purity reagents (Sigma-Aldrich), in which the GDWE was immersed along with the reference electrode (Hg|HgO, AMEL, 112 mV vs. SHE) and the counter-electrode (glassy carbon bar). All potentials in the text are referred to the reversible hydrogen electrode (RHE).

Both ORR and OER were evaluated by means of linear sweep voltammetries. ORR was evaluated in the range of potential from 1.1 to 0.2 V vs. RHE feeding oxygen to the back of the GDWE, whereas OER was performed from 1.2 to 1.8 V vs. RHE feeding He. In both cases a scan rate of 5 mV s^{-1} was employed. Stability tests consisted of a chronopotentiometry at -80 mA cm^{-2} for 24 h and 50 fast charge-discharge cycles (120 s each) at $\pm 20 \text{ mA cm}^{-2}$.

3. Results and discussion

3.1 Physico-chemical features

The DSC profile in **Figure 1** of the $\text{FeCo}_2\text{O}_4/\text{CNF}$ composite material shows a main exothermic peak at 360°C corresponding to a weight loss in the TG profile of about 60% due to the combustion of carbon nanofibers. Successively, the mass change is negligible with a further increase in temperature up to 1000°C and a broad exothermic peak is evident in the DSC curve indicative of the crystallization completion process. Therefore, the TG-DSC analysis allowed determining an amount of FeCo_2O_4 equal to 40 wt.% in the composite sample.

Fig. 1 TG/DSC analysis profiles in air for FeCo₂O₄/CNF.

The XRD pattern of the synthesized sample (**Figure 2**) exhibits the peaks at 19.0°, 31.3°, 36.6°, 44.8°, 55.7°, 59.0°, 65.4° corresponding to the planes (111), (220), (311), (400), (422), (511), (440) of the FeCo₂O₄ spinel structure (JCPDS 04-0850), respectively [46]. The broad peak at 26.2° can be assigned to the (002) peak of graphitic carbon in carbon nanofibers. The mean crystallite size of the FeCo₂O₄, calculated from the XRD peaks broadening and the Scherrer equation, is about 3 nm.

Fig. 2 XRD patterns of FeCo₂O₄/CNF

The lower magnification TEM image of FeCo₂O₄-CNF (**Figure 3a**) shows the presence of numerous nanoparticles, which are closely connected with each other and stacked along the nanofibers, but also properly distributed along the whole surface of the carbon material. This is a remarkable finding, given the high loading of the catalyst (40 wt. %). The crystalline lattice structures of FeCo₂O₄ are evident in the higher magnification TEM images (**Figure 3b**). The latter illustrates that the lattice fringes of FeCo₂O₄ exhibit inter-planar spacing of about 0.28 nm which can be indexed to the crystal faces (220) of spinel phase. Moreover, the graphitic planes of the carbon nanofibers,

characterized by an inter-planar distance equal to about 0.35 nm, are also evident in **Figure 3b**. The size distribution curve exhibits an average particle size of about 3 nm (**Figure 3c**) according to the XRD data.

Fig. 3. TEM images of FeCo₂O₄/CNF at low (a) and high (b) magnification. (c) particle size distribution

The N₂ sorption isotherm (**Figure 4a**) exhibits a type IV isotherm with a hysteresis loop in the P/P₀ range of 0.4-1.0 indicative of a high mesoporosity (**Figure 4b**) in the investigated sample. The BET surface area is about 350 m²·g⁻¹ and the total pore volume is 0.47 cm³·g⁻¹.

Fig. 4 (a) N₂ sorption isotherm and (b) pore size distribution of FeCo₂O₄-CNF.

The XPS survey spectrum in **Figure 5a** shows the presence of Fe, Co, C, O and N elements on the surface of FeCo₂O₄-CNF. The concentration (atomic %) of all the elements is reported in **Table 1**.

Table 1: Atomic concentration of the elements determined by XPS analysis.

Elements (at %)	C1s	N1s	O1s	Co2p	Fe2p
	51.5	1.8	22.3	15.6	8.8

The surface composition was analysed by the multi-peak fitting of every spectrum and the fitted XPS spectra are reported in **Figures 5b to 5f**. The Fe/Co elemental ratio is 0.56 according to the formula of spinel FeCo₂O₄. The Co2p spectrum in **Figure 5b** shows two main peaks attributable to Co2p_{3/2} and Co2p_{1/2} which can be further fitted to four peaks. The two peaks at 779.5 eV and 794.8 eV are attributed to Co³⁺ ions, another two peaks at 780.8 eV and 796.5 eV are attributed to Co²⁺ ions. The Co²⁺/Co³⁺ atomic ratio is about 0.75 indicating a larger amount of Co³⁺ ions on the material surface. Two further peaks centred at 787 eV and 803 eV can be attributed to the presence of satellite

peaks. These latter are fitted in four peaks due to the contribution of the Co^{2+} and Co^{3+} ions [47].

In the Fe2p spectrum (**Figure 5c**) two peaks are observed at 710.7 eV and 724.1 eV according to the spin-orbit peaks of the Fe $2p_{3/2}$ and Fe $2p_{1/2}$ respectively, indicative of the existence of Fe^{3+} ions. Moreover, a “shoulder” satellite peak centred at 714.6 eV is due to the presence of Fe^{2+} . The peak at about 718 eV can be assigned to the satellite peaks of Fe $2p_{3/2}$ [48]. The deconvolution of the N1s spectrum (**Figure 5d**) produced four peaks centred at 398 eV, 399.4 eV, 400.9 eV and 401.6 eV corresponding to the pyridinic-N (N_P) species, the metal bonded nitrogen (N-M) species, the pyrrolic-N (N_Pr) species and the graphitic-N (N_G), respectively. The pyridinic-N and graphitic-N species derived from the PAN precursor [49]. The C1s spectrum (**Figure 5e**) shows an asymmetric peak with a tail at higher binding energy, typical of nitrogen-doped carbon materials [50]. The C1s is fitted into four peaks, the peaks at 284.8 eV, 285.5 eV, 286.3 eV and 288.2 eV that can be attributed to the graphitic carbon (C=C), amorphous carbon (C-C), carbon bonded oxygen and nitrogen species (C=O/C=N) and carboxylic species (O=C-OH), respectively [47]. The deconvolution analysis of O 1s spectrum (**Figure 5f**) shows the presence of metal oxygen bonds (M-O) with a peak centred at 529.5 eV. The peak at 530.6 eV can be ascribed to the oxygen in OH groups. The peak at 531.5 eV may be attributed to the carbonyl groups (C=O) and the O^{2-} ions in low coordination number within the matrix of FeCo_2O_4 (oxygen defects or vacancies, O_V) in oxide surface. A further peak at 532.5 eV can be attributed to the presence of adsorbed water on the surface [47]. The concentration (atomic %) of the species on the $\text{FeCo}_2\text{O}_4/\text{CNF}$ surface are reported in **Table 2**.

Table 2. Atomic concentration (%) of the species on the FeCo₂O₄/CNF surface determined by XPS analysis.

Type	Species			
Co-species	Co ²⁺	Co ³⁺		
	43	57		
Fe-species	Fe ²⁺	Fe ³⁺		
	30	70		
C-Groups	C-C sp ²	C-C sp ³	C=O, C=N	O=C-OH
	47	27	19	7
O-Groups	M-O	O-H	C=O, O _v	Ads. water
	28	25	24	23
N-Groups	N _p	N-M	N _{pr}	N _G
	22	16	19	43

Fig. 5: XPS spectra of FeCo₂O₄/CNF composite: (a) survey spectrum; (b) core level spectrum of Co2p; (c) core level spectrum of Fe2p; (d) core level spectrum of N1s; (e) core level spectrum of C1s; (f) core level spectrum of O1s.

3.2 *Electro-chemical performance*

The obtained catalyst was compared with a pure spinel $\text{Co}_3\text{O}_4/\text{CNF}$ from a previous work [36]. The partial substitution of cobalt atoms with iron atoms leads to a spinel catalyst with a remarkable activity towards both the oxygen reduction and the oxidation of water (oxygen evolution) and superior to the one of the pure spinel $\text{Co}_3\text{O}_4/\text{CNF}$, as shown in Figure 6. Besides, a benchmark catalyst for the ORR, Pt/C (in house made, as in reference [51], and commercial IrO_2 (Alfa-Aesar) as benchmark catalyst for the OER, were also investigated (catalyst loading and Nafion content were equal to those of the assessed catalysts; 0.5 mg cm^{-2} of active phase and 30 wt.% Nafion content). As expected, Pt/C presents the highest onset potential ($1.03 \text{ V vs. RHE @ } 1 \text{ mA cm}^{-2}$) for the oxygen reduction reaction, although at high current densities (around 550 mA cm^{-2} and @ 0.7 V vs. RHE) the $\text{FeCo}_2\text{O}_4/\text{CNF}$ outperforms the commercial catalyst. $\text{FeCo}_2\text{O}_4/\text{CNF}$ presents an onset potential of 0.88 V vs. RHE , slightly higher than that observed for $\text{Co}_3\text{O}_4/\text{CNF}$ (0.86 V vs. RHE). The inset shows the overpotential for both the ORR (calculated at 1 mA cm^{-2}) and the OER (calculated at 10 mA cm^{-2}).

Figure 6. Linear sweep voltammetry for the assessed catalysts towards the oxygen reduction and evolution reactions, **(b)** inset shows the overpotential for both the ORR (calculated at 1 mA cm⁻²) and the OER (calculated at 10 mA cm⁻²). Scan rate = 5 mV s⁻¹; 6M KOH solution. The current density for the ORR is reported positive in this plot.

The onset potential towards the oxygen evolution reaction is outstanding (1.36 V vs. RHE at 10 mA cm⁻²) with a difference of more than 100 mV compared to the pure spinel (Co₃O₄/CNF) and a commercial IrO₂. This means an overpotential for the OER of 130 mV, which is one of the lowest values in literature for this reaction [41,52,53]. The remarkable activity towards the OER is mainly due to the presence of the active sites on the spinel. Bare CNF was studied in a previous paper for the OER, and its activity towards this reaction was almost negligible [44].

The enhanced activity of the FeCo₂O₄/CNF spinel towards both reactions leads to a remarkable reversibility ($\Delta E = E_{\text{OER}} - E_{\text{ORR}}$) value of only 480 mV, which is 120 mV lower than the value for the pure spinel. The reversibility value is the difference

between the onset potentials of OER and ORR; it gives an estimation of the bifunctional behavior of the catalyst. The lower this value, the higher the efficiency in the battery. Our $\text{FeCo}_2\text{O}_4/\text{CNF}$ spinel shows an outstanding reversibility, with a ΔE value of 480 mV, much lower than many others found in literature. For example, Bai et al designed an atomic iron- and nitrogen-codoped graphene catalyst with a combined ORR and OER potential gap of 0.605 V [54]. Xiao et al. prepared FeCo_x alloy nanoparticles encapsulated in N-doped porous carbon/multiwalled carbon nanotubes composites obtained by means of a controlled one-step alginate biomass carbonization strategy [55]. They obtained a hybrid material with a remarkable bifunctional activity and long-term stability for both ORR/OER and with a corresponding bifunctional activity parameter (ΔE) of 0.80 V. Kang-Wen et al. proved the importance of the oxygen vacancies in iron cobaltite spinels, by creating laser induced oxygen vacancies in FeCo_2O_4 [41]. Although they do not report ΔE value, it can be estimated around 550 mV in RDE. In our case, the presence of the N-doped CNFs enhances the catalytic activity of the iron cobaltite spinel, favoring a lower value of ΔE , with respect to Kang-Wen *et al.* studies. [41] Wu et al. designed a CoFe-doped graphene material, also showing remarkable activity as bifunctional catalyst, with an overpotential of 293 mV for the OER and a gap (ΔE) of 636 mV [56]. This results are summarized in Table 3.

Table S2. Electrochemical performance is obtained from the GDE by measuring the E_{onset} stands for onset potential for the ORR, this value is measured at 1 mA cm^{-2} , whereas for the OER at 10 mA cm^{-2} . η_{OER} denotes the over-potential for the OER at $I = 10 \text{ mA cm}^{-2}$ and $\Delta E / \text{mV}$ ($E_{\text{OER}} - E_{\text{ORR}}$) is the voltage difference between the E_{onset} for the OER and the ORR. Potentials are referred against RHE.

Catalyst	ORR		OER		Reversibility	[KOH]/ System	Ref
	E_{onset} @ $1 \text{ mA cm}^{-2} / \text{V}$	η_{ORR} @ $1 \text{ mA cm}^{-2} / \text{mV}$	$E_{\text{OER}} / \text{V}$ @ 10 mA cm^{-2}	η_{OER} @ $10 \text{ mA cm}^{-2} / \text{mV}$	$\Delta E^* / \text{mV}$ ($E_{\text{ORR}} - E_{\text{OER}}$)	mol/L	
FeCo ₂ O ₄ /CNF	0.88	350	1.36	130	480		
Co ₃ O ₄ /CNF	0.86	370	1.46	230	600	6M, GDWE	This work
Pt/Vulcan	1.03	200	-	-	-		
IrO ₂	-	-	1.47	240	-		
Fe-N-GO	1.03	200	1.50	275	605	0.1 M, RDE	[54]
Fe-N-GO	-	-	1.42	194	-	1 M, RDE	[54]
FeCox-NC/CNTs	0.90	330	1.59	360	808	0.1 M, RDE	[55]
Laser-induced FeCo ₂ O ₄	0.95	280	1.50	276	550	0.1M, RDE	[41]
FeCo-etched-graphene	-	-	1.52	293	636	1M, RDE	[56]
N-Fe/C	0.82	410	1.69	460	740	0.1M, RDE	[57]

**some values might differ given that ΔE is calculated considering slightly different current densities (E_{ORR} can be measured at -1 mA cm^{-2} , -3 mA cm^{-2} or be the half-wave potential in RDE).*

The remarkable activity of the iron-cobaltite spinel, FeCo₂O₄/CNF, with respect to the pure Co₃O₄/CNF spinel is due to several factors. The major differences between both spinels reside in the porosity and the crystallite size. The iron-based spinel presents a remarkable porosity, with $350 \text{ m}^2 \cdot \text{g}^{-1}$ of surface area (compared to $187 \text{ m}^2 \cdot \text{g}^{-1}$ for Co₃O₄/CNF) and a really open structure mainly formed by mesopores (80% of the porosity) and macropores. It is known that the pore structure plays an important role in the ORR, since an interconnected porous structure is vital to promote the mass transfer, what results in an enhanced ORR activity [45,58]. Probably due to this extended

porosity, the $\text{FeCo}_2\text{O}_4/\text{CNF}$ presents a low crystallite size (3 nm), i.e, particles are properly distributed on the surface of the carbon material and this has limited the growth of the crystallites. This means that there is a larger amount of exposed sites, with respect to the pure Co-based spinel (with a crystallite size of 10 nm) [51]. These two factors are greatly responsible for the enhanced activity of the iron cobaltite spinel towards both reactions. There are other issues also contributing to this remarkable activity for $\text{FeCo}_2\text{O}_4/\text{CNF}$. Some authors have reported that oxygen vacancies in iron-based spinels are responsible for their activity towards ORR and OER [41]. The introduction of iron in the structure of cobalt spinel creates oxygen vacancies, which should increase the conductivity of the material, what finally entails a higher catalytic activity.

It is still controversial what are the active sites for transition metal oxides for both the oxygen reduction and the oxygen evolution reactions. With respect to the oxygen reduction reaction, it is known that Co^{2+} species enhance the ORR, by contributing to the adsorption of oxygen. On the other hand, the presence of Co^{3+} species enhances the catalytic activity towards the OER due to the preferred absorption of OH^- anions on Co^{3+} species, acting as active species for the OER [36]. It has recently been established that iron plays an important role in the activity of iron-cobalt (oxy)hydroxides. Burke et al. reported that the incorporation of Fe on cobalt-based (oxy)hydroxides provides the primary OER active sites in the mixed phases [59]. Another factor to be taken into account is that the electrospun carbon nanofibers acting as support for the FeCo_2O_4 particles present N-groups, that are widely recognized for their activity in alkaline media towards both ORR and OER [60]. Furthermore, Fe- N_x sites are recognized as active sites for ORR both in acidic and alkaline environment [61–63] and more active than Co- N_x [64]. This also explains the best behavior of the catalyst containing Fe in

substitution of Co atoms. The N coordination influences the electronic structure of Fe and thus modifies the physicochemical property of the Fe site. As reported by Bai et al., DFT calculations and experimental results reveal that FeN₄-moieties embedded into a graphene matrix should be active sites for both ORR and OER [54].

The durability of the FeCo₂O₄/CNF was assessed with two different tests. The first one consisted of fast cycles at $\pm 20 \text{ mA cm}^{-2}$. Two potential cut-offs were imposed during the experiment: 0.5 V vs. RHE for the ORR and 1.8 V vs. RHE for the OER. As can be seen in **Figure 7**, the mixed-spinel catalyst shows a very stable behavior for 50 cycles, with a difference of 620 mV between the potentials for the OER and the ORR.

Figure 7. Charge-discharge cycles performed at $\pm 20 \text{ mA cm}^{-2}$ in an oxygen saturated 6M KOH solution.

The second test performed to investigate the durability consisted in imposing a current of -80 mA cm^{-2} for 24 h in an oxygen saturated solution. This current density is suitable for metal-air battery applications in electric cars [65]. **Figure 8** shows the variation of potential with time for the $\text{FeCo}_2\text{O}_4/\text{CNF}$. At the beginning of the test, the potential decreased 40 mV, and then maintained a fairly constant behavior (spikes in the measurement are due to the bubbles formed in the electrode, disturbing the capillary Luggin). After a short-cut of electricity occurred at the 20th hour, the experiment was re-started showing a rise in potential of 70 mV, indicating that the performance of the electrode can be recovered. In general, a stable potential value was kept along the test, which can be considered as an indication of suitable stability of the material for application in energy storage or conversion electrochemical devices.

Figure 8. Long-term stability test consisting on chronopotentiometry at -80 mA cm^{-2} .

5. Conclusions

An iron-cobaltite spinel supported on carbon nanofibers was successfully synthesized by electrospinning. The partial substitution of cobalt atoms with iron atoms led to a spinel catalyst with superior activity towards both the oxygen reduction and evolution reactions compared to the pure spinel $\text{Co}_3\text{O}_4/\text{CNF}$. Furthermore, the iron-cobaltite spinel, supported on carbon nanofibers, showed a remarkable reversibility ($\Delta E=480$ mV), due to the outstanding OER activity and a good ORR performance. These electrochemical features were attributed to the introduction of iron in the structure of cobalt spinel, creating oxygen vacancies, which should increase the conductivity of the material, together with the presence of Fe-N_x moieties, which are more active than Co-N_x species. This allowed to obtain a good bifunctional catalyst. The stability of the material was assessed by chronopotentiometric and cycling measurements confirming the promising characteristics of the synthesized iron-cobaltite catalyst.

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Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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