Electrospun carbon nanofibers loaded with spinel-type cobalt oxide as bifunctional catalysts for enhanced oxygen electrocatalysis

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Abstract

The electrocatalysis of oxygen in alkaline media is a challenging issue, influencing the performance of many electrochemical devices: fuel cells, unitized regenerative fuel cells, electrolyzers and metal-air batteries. This new manuscript proposes the synthesis of graphitic carbon nanofibers obtained by electrospinning with a cobalt-based spinel oxide, Co₃O₄/CNF. By means of a simple, reproducible and scalable method, a bifunctional catalyst with a promising performance is obtained, being able of carrying out the electrocatalysis of oxygen (oxidation of water, evolution and reduction of oxygen) in a basic solution. The combination of the active species on cobalt oxide (Co²⁺, Co³⁺ and Co-N_x), along with active species in the carbon nanofiber (graphitic and pyridinic N), gives rise to a catalyst with a remarkable reversibility (difference between E_{half-wave-potential} (reduction) and E_{10 mA/cm²} (evolution)): $\Delta E = 790 \text{ mV}$, a low over-potential for the evolution of oxygen ($\eta = 416 \text{ mV}$) and 959 mV of oxygen reduction onset potential, equal to that of a benchmark catalyst, Pt/C.

Keywords: bifunctional air electrodes, oxygen reduction; oxygen evolution; spinel; electrospinning.

1. Introduction

Research on bi-functional catalysts for air electrodes, i.e, positive electrodes in metal-air batteries is continuously increasing [1–10]. Metal-air batteries (MABs), operating in alkaline media and using Zn, Fe, Mg, etc. at the negative electrode, present promising features in comparison to conventional lithium-ion batteries, such as high energy densities, low cost (since abundant materials are used) as well as environmental safety [11–18]. Air electrodes take oxygen from the air, making these batteries extraordinary light, another advantage in comparison to conventional ones. However, the development of these devices has been hindered by the lack of a stable and efficient bifunctional catalyst for the air electrode. In fact, the electrocatalysis of oxygen is very challenging, given that the air electrode must be both active and long-lasting for both the oxidation of water, also called oxygen evolution (shorten as OER), which proceeds when a battery is charged, and the reduction of oxygen (shorten as ORR), occurring on discharging. The ability of the bifunctional catalyst to carry out these two reactions determines the electrochemical performance of the battery [1,15,17,19,20].

Oxides based on transition metals have been widely investigated for their role as bifunctional materials [2,3,25,26,4,5,7,9,21–24], being cobalt-based oxides the most active catalysts for the electrocatalysis of oxygen [8,27,36,37,28–35]. Co-based oxides are interesting as bifunctional materials for oxygen reactions thanks to their low cost, ample stability and suitable performance for the OER and ORR [4,27,38–40]. On the contrary, these oxides present a relatively small surface area and a poor electrical conductivity. For these reasons, usually combining them with carbon nanostructures is desirable for achieving a catalytic activity close to the benchmark catalysts, i.e. precious metals. One way of promoting catalytic activity and stability is by designing tailored composite carbon-based bifunctional catalysts with particular geometries [1,9,41]. Yet,

under corrosive (high potentials) conditions occurring during charging of MABs, durability of carbon-based materials is a challenge that must be still further improved [42]. The use of nanostructured carbonaceous structures like carbon nanowires, carbon nanotubes/nanofibers could alleviate this issue, since they present an enhanced resistance towards corrosion compared to other carbons [43–48]. For the preparation of these materials, the electrospinning technique is recognized as a fast and efficient way. This method is also useful for producing active metals supported on carbon nanofibers (CNFs) [49,50]. Recently, in our laboratories, CNFs modified with cobalt (Co^0 and Co^{2+}), CoO-Co/CNF , were prepared by electrospinning and tested as air electrodes. The stability and reversibility (meaning bifunctionality) of the $\text{Co}^0\text{-Co}^{2+}$ system were remarkable [51]. In the present work, the latter catalyst, after the electrospinning preparation, has been oxidized with the aim of synthesizing the pure spinel structure (Co_3O_4) supported on CNFs. The electrochemical behavior of the Co-based spinel has been compared with the previously developed CoOCo/CNF to elucidate the catalytic activity of the two systems for ORR and OER in relation with their physico-chemical properties.

2. Experimental

2.1. Preparation of electrospun CNF with cobalt-oxide

$\text{Co}_3\text{O}_4/\text{CNF}$ was prepared as in a previous paper [51]. A further step was added, consisting on a treatment in air at 350 °C (30 min) inside a tube furnace in order to obtain the spinel phase (Co_3O_4) for the cobalt species. The product was denoted as $\text{Co}_3\text{O}_4/\text{CNF}$.

2.2. Solid-state characterization

$\text{Co}_3\text{O}_4/\text{CNF}$ was characterized by several solid-state characterization techniques: Thermogravimetry in air, X-Ray Photoelectron spectroscopy, X-Ray diffraction,

transmission electron microscopy and nitrogen physisorption. Details on techniques can be found in reference [52].

2.3. Electro-catalytic activity evaluation

The electro-catalytic activity of the spinel-type cobalt oxide on electrospun nanofibers was determined by electrochemical measurements performed in two different systems: rotating disk and gas-diffusion electrodes. Details on these techniques can be found in previous papers of our group [51–54]. Co_3O_4 was compared with a CoO-Co/CNF , from a previous work [51], and with Pt- and Ir-based materials, as benchmark catalysts. Pt/Vulcan and IrO_2 were obtained as described in detail in [42] and in [55], respectively. The catalyst loading was the same for all the catalysts: $50 \mu\text{g cm}^{-2}$ for RDE measurements, $0.5 \pm 0.02 \text{ mg cm}^{-2}$ for GDE measurements. In all cases, Nafion content was 30 wt. % of the ink.

3. Results and discussion

3.1 Physico-chemical features

In order to identify the suitable oxidation temperature to obtain a well-defined Co_3O_4 spinel structure, the TGA and DSC analyses were carried out on the intermediate CoO-Co/CNF sample in air atmosphere. TGA and DSC profiles of CoO-Co/CNF sample (Fig. 1a) show a first sharp peak at around 350°C that can be assigned to cobalt oxidation. A second peak in a temperature range $380\text{--}450^\circ\text{C}$ is due to the carbon nanofibers decomposition. Therefore, the 30-minute procedure in air at 350°C is considered the right compromise to obtain the oxidation of Co species avoiding the total burning of carbon nanofibers. Figure 1b shows the thermogravimetric profile of the $\text{Co}_3\text{O}_4/\text{CNF}$ in air. The percentage of oxide present is about 36 wt.%. The higher content of Co_3O_4 compared to

the CoO-Co/CNF sample (containing 20%wt. of CoO-Co) is due to a partial decomposition of carbon nanofibers that occurs during the oxidation process at 350 °C.

Figure 1. TGA and DSC profiles in air for: (a) CoO-Co/CNF [51]; (b) Co₃O₄/CNF

The XRD spectrum, shown in Figure 2, presents the relative peaks of the cubic spinel structure. The peak appearing at 26 degrees is assigned to carbon of graphitic character, whose formation is favoured by the presence of cobalt (known as a graphitization catalyst [56]). Crystallite size, calculated by the Scherrer's formula, was around 10 nm.

Figure 2. X-ray diffraction profiles for the spinel-type catalyst $\text{Co}_3\text{O}_4/\text{CNF}$.

TEM image (Fig. 3a) shows the carbon nanofibers formation in which a good distribution of Co_3O_4 nanoparticles throughout these occurred. A CNFs size of about 200-300 nm is observed while an average Co_3O_4 particles size of about 11 nm is calculated, as also corroborated by XRD. The image at high magnification (Fig. 3b) shows the Co nanoparticles surrounded by the graphitic planes of carbon nanofibers characterized by a d-spacing value of about 0.34 nm.

Figure 3. Images showing morphology of CNF, along with the crystallographic planes and dispersion over the surface of Co_3O_4 at a) low and b) high magnification.

Figure 4 shows the adsorption-desorption isotherm (on the left) with the pore size distribution (on the right). The mixed spinel oxide and carbon nanofibers show type II isotherms, typical of macroporous solids and present a hysteresis loop attributable to the presence of mesopores (representing the 26 % of the porosity). Co₃O₄/CNF presents a S_{BET} equal to 187 m² g⁻¹.

Figure 4. (Left) Profiles for the adsorption-desorption isotherms obtained from N₂ physisorption and (right) representation of pore size distribution versus differential pore volume for the electrospun Co₃O₄/CNF. (Areas in grey show mesopores and macropores percentage).

XPS analysis allowed determining the concentration (atomic %) of the investigated elements (**Table 1**) as well as the oxidation state of the cobalt species. Deconvolution profiles are showed in **Figures 5a to 5d**. The Co2p spectrum (**Fig. 5a**) consists of two main peaks at binding energy values of 779.8 eV (Co2p_{3/2}) and 795.2 eV (Co2p_{1/2}) with a spin-orbit splitting energy of 15.4 eV in agreement with the value reported in literature for Co₃O₄ spinel structure [57]. Moreover, two shake-up satellite peaks at around 787.4 eV and 803.6 eV are observed. The shake-up satellites are located at a binding energy value of about 9 eV higher than the main peaks indicating that the cobalt is present only

in the spinel structure Co_3O_4 [58]. The deconvolution of $\text{Co}2\text{p}$ spectra also confirms the presence of the peaks due to the Co species in the Co^{2+} (779.63 eV and 780.8 eV) and Co^{3+} (794.7 eV and 796.2 eV) oxidation states. Another peak at 782 eV is attributable to the presence of cobalt associated with nitrogen Co-N_x .

Table 1. Atomic concentration of the elements obtained from XPS spectra.

Elements	C1s	N1s	O1s	Co2p
(at %)	83.8	2.8	9.5	3.8

Figure 5. Deconvoluted XPS profiles for a) $\text{Co}2\text{p}$; b) $\text{N}1\text{s}$; c) $\text{C}1\text{s}$ and d) $\text{O}1\text{s}$.

The amount (at %) of all the cobalt species are reported in Table 2. A higher percentage of Co^{2+} with respect to Co^{3+} is calculated.

Table 2. Co and N species (XPS atomic concentration).

Type	Species				
Co-Species	Co³⁺	Co²⁺	Co-N_x		
%	27.8	43.6	28.6		
N-Groups	N_P	Co-N_x	N_{Pr}	N_G	N_{ox}
%	23.0	21.0	5.3	41.0	9.7

As reported in literature, the presence of an excess of cobalt (II) could cause a disorder lattice structure leading to the creation of a larger number of oxygen vacancies [59]. The oxygen vacancies on the surface of Co₃O₄ improve the electrical conductivity and increase the availability of active sites enhancing the electrocatalytic activity for OER [60,61]. The deconvolution of N1s spectra (Fig. 5b) shows the presence of different peaks associated with nitrogen species whose amounts are reported in Table 2. Pyridinic N (denoted as N_P) was assigned to peaks at 398 eV. Graphitic N (denoted as N_G) was ascribed to peaks appearing at 401 eV. Both species derived from the PAN precursors [51,62]. Co-N_x species appeared at 399 eV. A small contribution from pyrrolic N (denoted as N_{Pr}) appearing at 400 eV and oxidized N (denoted as N_{ox}) at 403 eV were also found, respectively (Table 2). The C1s spectrum (Fig. 5c) was divided in four contributions corresponding to graphitic carbon (284.8 eV) and amorphous carbon (285.5 eV), as the main contributors, and in a lower intensity, C-O/C-N (286.5 eV) and C=O/C=N (287.6 eV), indicative of the presence of hydroxyl and carbonyl species as well as nitrile species, respectively. Moreover, a further peak is identified at 289 eV attributable to carboxylic species (O=C-O) [63]. The peaks deconvolution analysis of O1s spectrum (Fig.5d) reveals the presence of metal oxygen bonds (Co-O) with a peak centered at 529.8 eV. The peak at 530.7 eV can be ascribed to the oxygen in OH-group form. The peak at 531.5 eV is due to the O₂⁻ ions at low coordination number in the

oxide sample [64]. C-OH phenolic groups were also found on the surface of carbon nanofibers surface as confirmed by the peak at 533.4 eV [65].

3.2. Electrocatalytic activity evaluation

The activity of the spinel electro-catalyst towards the oxygen evolution and the oxygen reduction reactions was evaluated in an alkaline solution by means of rotating disk electrode (RDE) measurements. Fig. 6 shows the profiles for the assessment of the activity towards the reduction reaction for the Co₃O₄/CNF. LSVs were recorded at 1600 rpm rotation speed in a 1 M KOH basic solution saturated with oxygen, in comparison to a previously reported catalyst, CoO-Co/CNF, and to SoA benchmark catalysts: for the ORR, Pt/C and, for the OER, IrO₂ [51].

3.2.1. Oxygen reduction reaction

Both cobalt-based materials present almost the same onset potential, 0.92 V *vs.* RHE, as Pt/C (only 3 mV more positive). This is a remarkable result for a non-precious metal catalyst. Besides, the spinel Co₃O₄/CNF reaches a limiting current density comparable to that of Pt/C, and significantly superior to its counterpart CoO-Co/CNF. This may be due to the differences in the oxidation state of cobalt in Co₃O₄/CNF and CoO-Co/CNF. Co₃O₄/CNF presents a mixture of Co²⁺ and Co³⁺ (28 at. % of Co³⁺ and 44 at. % of Co²⁺).

Fig. 6. Linear Sweep Voltammetries recorded (a) during oxygen reduction reaction for the spinel-type electro-catalyst (rotation speed = 1600 rpm). Benchmark catalysts (Pt/C and CoO-Co/CNF) are also tested for the sake of comparison as state-of-the-art catalyst.

It has been proved that Co^{2+} species favour the ORR due to the favoured adsorption of O_2 . This entails the creation of OH^- (due to the subsequent electron transfer) that carry on the reaction [4]. With this in consideration, CoO-Co/CNF should present a higher ORR activity, due to the higher amount of Co^{2+} (75 at. % vs 44 % for $\text{Co}_3\text{O}_4/\text{CNF}$). However, N-sites also play a major role in oxygen electrocatalysis. Recently, it has been reported that the quaternary N atoms in N-doped carbon materials enhance O_2 adsorption and accelerated the ORR by providing electrons to the p-conjugated system [33,66]. The percentage of N-species, as determined by XPS, in both Co-based samples differs considerably. The most notable difference is the amount of graphitic N, being almost double for the $\text{Co}_3\text{O}_4/\text{CNF}$ material (41 at. % vs. 28 at. % for CoO-Co/CNF), what would explain the higher ORR activity for the spinel-type material. Besides, both cobalt-based

samples present cobalt atoms bonded to N in the form of Co-N_x, showing Co₃O₄/CNF a higher percentage of this ORR-active species (29 at % vs. 21 at % for CoO-Co/CNF). Co-N_x sites are also recognized as contributors to the initial adsorption of oxygen, which is subsequently converted to the intermediate reaction products. The higher amount of Co-N_x species in the spinel-type material also contributes to its higher catalytic activity (in comparison to CoO-Co/CNF) [51]. In summary, a combination of different O-active species (graphitic N, i.e. *quaternary N bonds*, Co-N_x and Co²⁺) are responsible for the enhanced catalytic activity of the spinel-type electrocatalyst assessed in this work. Figure 7a shows the LSV curves at different rotation speed for Co₃O₄/CNF along with the Koutecky-Levich plots (Figure 7b) that provide the number of electrons exchanged during the oxygen reduction reaction. K-L plots determined a 4 e⁻ mechanism (4.07 e⁻). This indicates that our catalyst performs the ORR through the preferred and more efficient 4e⁻-mechanism, reducing O₂ to H₂O. The CoOCo/CNF catalyst presented also a 4 e⁻ mechanism (with a value of 3.8 e⁻ determined from the Koutecky-Levich plots, as described in detail in ref. [51]).

Figure 7. (a) Profiles for LSV curves obtained at 100, 200, 400, 1000, 1600 and 2500 rpm in a solution of KOH (1M) saturated with O₂ (scan rate = 5 mV s⁻¹). (b) Representation of the Koutecky-Levich plots at different voltages to determine kinetic parameters.

3.2.2. Oxygen evolution reaction

The oxygen evolution reaction performance, shown in Figure 8, shows that the $\text{Co}_3\text{O}_4/\text{CNF}$ catalyst presents the best performance, 120 mA cm^{-2} at 1.8 V vs RHE, outperforming both the IrO_2 -benchmark catalyst and the $\text{CoO-Co}/\text{CNF}$ catalyst. The mechanism for catalytic active sites is still unknown, but it has been proved that catalysts with higher amounts of Co^{3+} species present higher OER activities. This could be due to a preferred absorption of OH^- anions on Co^{3+} species, acting as active species for the OER [4]. On the other hand, also N-sites have been reported as active for the OER. Recently, Yang *et al.* determined that N in the form of pyridinic species accepts electrons from adjacent C atoms. This facilitates the adsorption of OH^- and OOH^- (water oxidation intermediates), being the rds (rate-determining step) for OER in basic media. The difference in pyridinic-N between $\text{CoO-Co}/\text{CNF}$ and $\text{Co}_3\text{O}_4/\text{CNF}$ is small, but there is a significant difference in the amount of Co^{3+} between the two examined samples. $\text{CoO-Co}/\text{CNF}$ does not present cobalt in the oxidation state III, Co^{3+} , so the main explanation for the large activity of Co_3O_4 for the OER versus $\text{CoO-Co}/\text{CNF}$ might reside on that.

Fig. 8. Linear Sweep Voltametries recorded during the oxygen evolution reaction (rotation speed = 1600 rpm, He atmosphere) for the spinel-type electro-catalyst, in comparison with CoO-Co/CNF and IrO₂ as benchmark catalysts.

At these high potentials, carbon materials may be oxidized to CO₂. Other authors have studied the behaviour in different media of several nanostructured carbonaceous materials, like carbon blacks and CNFs [48,67,68] showing that the stability of carbon at high potentials is a critical aspect. In a previous work, we carried out a comparison between the carbon material (electrospun CNF) and the Co-based CNF (CoO-Co/CNF), so as to determine the effect of the CNF on the electro-activity for the evolution of oxygen. In that case, the activity for the OER of the CoO-Co/CNF electro-catalyst was so high that, the contribution to the current density due to the oxidation of carbon, was considered negligible [51].

The choice of using cobalt oxides as bifunctional catalysts has attracted a great deal of research [8,27–33]. The bifunctional behaviour of the air electrodes is vital for the correct performance of the battery. A way to evaluate the reversibility (i.e. the bifunctionality) of the system is the use of the parameter ΔE , i.e, the value corresponding to the difference between potentials at a certain current density on both reactions. For the OER, the value of the potential at 10 mA cm^{-2} is considered, whereas for the ORR, the half-wave potential is used. ΔE along with other parameters such as onset potential, overpotential for the OER (η) are shown in Table 3, in comparison to the most recent works in the literature. The voltage at 10 mA cm^{-2} (denoted as $E_j = 10$) is generally used to evaluate OER activity [27,69]. The spinel type material, $\text{Co}_3\text{O}_4/\text{CNF}$ possesses an ΔE value equal to 795 mV, within the best two-three values reported in literature (up to our knowledge). On the other hand, our over-potential for the OER is slightly higher (416 mV) in comparison to lower values (such as 280, 340 mV) [27,31,40,69,70]. However, the catalysts employed are obtained with more complex carbon structures such as graphene, particular exposed faces of the Co_3O_4 structure, etc., not so easily scalable as our Co_3O_4 spinel on electrospun carbon nanofibers.

Table 3. Electrochemical parameters obtained from the RDE measurements (E_{onset} , E_{hwp} , and I_d stand for onset potential, half-wave potential, and diffusion-limited current density on the reduction of oxygen, respectively. For the oxygen evolution, η_{OER} denotes the over-potential at $I = 10 \text{ mA cm}^{-2}$, I_s stands for the current density at 1.70 V vs. RHE and $\Delta E / \text{mV}$ ($E_{\text{ORR}} - E_{\text{OER}}$) is the voltage difference between the E_{hwp} and E_{OER} (at 10 mA cm^{-2}).

Catalyst	ORR			OER			Reversibility	[KOH]	Ref
	E_{onset}	$E_{\text{hwp}} / \text{mV}$	I_d	$E_{\text{OER}} / \text{mV @ } 10 \text{ mA cm}^{-2}$	$\eta_{\text{OER @ } 10 \text{ mA cm}^{-2}} / \text{mV}$	$I_s \text{ @ } 1.7 \text{ V (vs RHE)} / \text{mA cm}^{-2}$	$\Delta E / \text{mV} (E_{\text{ORR}} - E_{\text{OER}})$	mol/L	
Co₃O₄/CNF	919	851	-3.8	1646	416	34	795	1M	This work
CoO-Co/CNF	922	858	-2.9	1667	437	19	809		[51]
Pd/Vulcan	912	846	-3.6	1698	479	9	852		
Pt/Vulcan	944	855	-3.8	1741	510	6	886		
IrO₂	827	589	-2.0	1671	442	14	1082		
Co₃O₄-NP/N-rGO	890	760	-5.5	1610	380	85	850	0.1 M	[33]
Co₃O₄-NF (C)	≈ 650	610	≈ -4.8	≈ 1650	≈ 420	≈ 80	≈ 1040	1 M	[27]
Co₃O₄/N-GAs*	970	870	-5.2	1660	430	≈ 15	790	1 M	[69]
Co-N@HCS	962	864	-5.5	1720	490	≈ 8	856	0.1 M	[40]
Co@Co₃O₄/N-CNT	-	800	≈ -4.5	1650	420	≈ 25	850	0.1 M	[31]
Co-oxide/3D-G	900	810	-1.9	1570	340	≈ 25	760	1 M	[70]

The activity of the spinel material was also evaluated in a gas diffusion electrode to test our catalyst in more realistic conditions. Polarizations were performed in the same potential window employed during the RDE studies. Besides, durability of the catalyst was evaluated with a long test (21-hour chronopotentiometry) at a current density of -80 mA/cm². The activity of the Co₃O₄/CNF was also evaluated before and at the end of the test, as shown in Figure 9a. During the chronopotentiometry test (Figure 9b), the potential shows a stable behaviour (being kept between 0.72 and 0.68 V vs RHE). Before the end of the test (after ca. 18 h of experiment), there was an interruption of the current; successively, the potential rose around 40 mV. The activity of the Co₃O₄/CNF (Figure 9a) in terms of potential slightly improves after the chronotest, showing the remarkable stability of our catalyst.

Fig.9. (a) Profile for the polarization curves during oxygen reduction and oxygen evolution reactions, recorded in a gas diffusion-type working electrode in a 6 M KOH electrolyte for the spinel-type material, Co₃O₄/CNF, at the beginning (BoT) and at the end (EoT) of the chronopotentiometric test. The employed scan rate was equal to 5 mV s⁻¹. (b) Potential profile during the chronopotentiometric test (21 h) at reduction currents (negative) of 80 mA/cm² flowing O₂ in the electrolyte.

4. Conclusions

A spinel type Co₃O₄ oxide was synthesized by electrospinning of a conductive polymer. Electrospun carbon nanofibers with well distributed Co₃O₄ spinel-type particles were obtained by a simple, scalable and reproducible method. Co₃O₄/CNF presented a remarkable electro-catalytic activity as bifunctional catalyst, being able to catalyze the oxygen reduction and the oxygen evolution reactions. This work proved the suitability of the spinel cobalt oxide to be used in the positive electrode (acting as air electrode) in a metal-air battery, or other devices needing bifunctionality.

The combination of both conductivity and porous structure of the carbon material, along with the presence of oxygen-active species were responsible for the remarkable catalytic performance of this material for the electro-catalysis of oxygen. In particular, the presence

of both Co^{2+} , graphitic-N and Co-N_x enhanced the oxygen reduction reaction, whereas abundance of Co^{3+} and pyridinic N were responsible for the excellent performance towards the oxygen evolution reaction. The spinel type material showed electrochemical features of interest such as low evolution overpotential, superior or comparable onset and half-wave potentials to the ones for the SoA catalyst, Pt/C as well as a remarkable reversibility. The activity of the spinel material was also evaluated in a gas diffusion electrode to test our catalyst in more realistic conditions. During the chronopotentiometry test, the potential shows a stable behavior. Besides, the activity of the $\text{Co}_3\text{O}_4/\text{CNF}$ in terms of potential slightly improved after the chronotest, showing the remarkable stability of our catalyst. For these reasons, spinel- Co_3O_4 on electrospun nanofibers are expected to be a convenient and promising material acting as air electrodes on metal-air batteries.

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