CoTiO₃/NrGO NANOCOMPOSITES FOR OXYGEN EVOLUTION AND OXYGEN REDUCTION REACTIONS: SYNTHESIS AND ELECTROCATALYTIC PERFORMANCE

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Abstract

Oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) catalysts play an important role in energy conversion and storage devices, but highly active and robust nonprecious metal catalysts are required to address the cost and durability issues. In this work, a modified gel methodology has been used to obtain nanocomposites of perovskite CoTiO₃ and N-doped reduced graphene oxide (NrGO). Moreover, the influence of the annealing extent in the synthesis has been studied. The composites show higher activity in oxygen evolution and reduction reactions in alkaline environment compared to sole ilmenite, which is related to a strong interaction between cobalt titanate and NrGO carbon matrix. The annealing duration appears as a key variable to modulate the physicochemical properties and the electrochemical behavior. The composite prepared at the largest duration (3 hours) exhibit enhanced bifunctional properties for ORR and OER, with onset potentials of 0.93 V and 1.53 V vs. RHE respectively, which is mainly attributed to higher concentration of nitrogen, larger extent of defects and/or the presence of more oxidized Co species in the nanocomposite.

Keywords: Oxygen evolution reaction, oxygen reduction reaction, N-doped graphene, CoTiO₃, composites, bifunctional.

1. Introduction

Nowadays, the rising demand of energy has contributed to increase the interest in the design and development of cost-effective and efficient catalysts for the oxygen evolution reaction (OER) and the oxygen reduction reaction (ORR), which can play an important role in energy conversion and storage devices, especially in fuel cells, metal-air batteries, electrolyzers and unitized regenerative fuel cells (URFC) [1-5]. Pt and its alloys are still the most active catalysts for ORR in acidic media, but they only show moderate activity for OER. In acidic media this has been solved by the use of Pt/IrO₂ and RuO₂ mixtures [6-12], but the high cost of platinum group metals and their poor stability have hindered their application in commercial devices. In recent years, the use of alkaline membranes in water electrolyzers and fuel cells has promoted the study of new non-noble metals as catalysts due to their enhanced kinetics at higher pH. Transition metals such as Ni, Co, Mn, Ta or Fe and their oxides have demonstrated appropriate properties as catalysts for OER [13-17] and ORR reactions [18-24].

Among all the nonprecious materials studied in the literature, carbon based catalysts with supported nanoparticles hold the greatest promise to replace precious metals due to their low cost and encouraging results regarding catalytic behavior. In particular, N-doped carbon structures like carbon nanotubes or reduced graphene oxide have shown good properties for ORR and/or OER in alkaline environment [20, 25-30]. The combination of N-doped carbons with Earth abundant transition metals to form bifunctional nanocomposite catalysts has demonstrated an improved catalytic activity and stability due to synergy effects between carbon structures and metal particles compared to parent sole materials. This remarkable activity has been associated to the Me-N-C active sites formation (Me = Ni, Co, Fe, etc.), where the different carbon structures like carbon nanotubes or graphene sheets play an important role on the catalyst activity [19, 29, 31, 32]. Specifically, cobalt based N-doped carbons have appeared as a good alternative to substitute noble-metal based catalysts in alkaline media due to their great properties as bifunctional catalysts [20, 33-36].

Ti formulations are potentially good candidates for electrocatalytic applications [37-41], but low activity values have been reported using TiO₂ as a sole ORR and/or

OER electrocatalyst [42, 43]. The low intrinsic conductivity and poor reactivity of TiO_2 are considered to hamper the efficiency of this material in electrocatalysis that require fast electron transport. However, the doping of TiO_2 with other metals or supporting titanium based nanoparticles on nanostructured carbon have improved activity in both reactions [20, 44-46]. Another possibility is the use of perovskite CoTiO_3 with a stable layer structure [47, 48], which could ensure the stability of ORR and OER performance. CoTiO_3 has the ilmenite structure with the Co^{2+} and Ti^{4+} ions occupying alternating layers perpendicular to the trigonal c axis of the unit cell [49]. Its structure has the hexagonal close packing of the oxide anions with two-thirds of the octahedral sites occupied by both Co^{2+} and Ti^{4+} cations. Jaramillo et al. explored the effect of temperature treatments on the OER activity, structure, and electronic state of CoTiO_x [50]. They found that the most active catalysts were XRD amorphous, which were achieved with low calcination temperatures. Electrochemical testing and X-ray absorption spectroscopy showed that the more active, amorphous catalysts undergo greater changes in oxidation state during OER than the less active, crystalline catalysts. An et al. reported a novel N-CoTi@ CoTiO_3 /C electrocatalyst, which exhibited superior ORR activity, durability and methanol tolerance in alkaline solution [51]. Theoretical calculations demonstrated that the surface oxide layer polarization effect caused by the intermetallic CoTi core played a key role in the activity. Moreover, recent studies of CoTiO_3 , combined with graphene to improve the electrical conductivity, have shown an increase of the electrochemical properties in the field of Li-ion batteries applications [52].

In this work, a new synthesis method has been investigated to obtain composites of CoTiO_3 and N-doped reduced graphene oxide (NrGO) using urea as a nitrogen source. The influence of the annealing duration in the nanocomposites synthesis has been studied. All composites have been characterized and tested as bifunctional catalysts for both, OER and ORR, under alkaline conditions. In addition, the stability of the composites was tested by accelerated durability tests under harsh conditions.

2. Experimental

2.1. Chemicals and reagents

Graphite powder (>99.8% purity, particle size <20 μm), KMnO_4 (>99.8% purity), cobalt (II) chloride hexahydrate ($\text{CoCl}_2(\text{H}_2\text{O})_6$, >97% purity), urea ($\text{CH}_4\text{N}_2\text{O}$, >98% purity), sodium hydroxide (NaOH , 99.99%) and Nafion[®] (5 wt. %) were purchased from Sigma-Aldrich. Concentrated H_2SO_4 (96%) and H_2O_2 (30% v/v) were provided by Merck and Foret, respectively. Titanium (IV) n-butoxide ($\text{Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4$, >99% purity), iridium (IV) oxide (IrO_2 , 99% purity) and CoTiO_3 were purchased from Alfa Aesar. Ethanol ($\text{CH}_3\text{CH}_2\text{OH}$, 96% purity) was acquired from Panreac. The commercial Pt/C catalyst with 20 wt% Pt was purchased from the Johnson Matthey Corp. All the chemicals were used as received without further purification. Ultrapure water (18.2 $\text{M}\Omega\text{ cm}$) through Millipore system (Milli-Q[®]) was used in all the experiments.

2.2. Catalyst synthesis

A modified gel methodology has been used to synthesize cobalt (II) titanate catalysts supported on nitrogen-doped reduced graphene oxide ($\text{CoTiO}_3/\text{NrGO}$) [20]. Graphene oxide (GO) was synthesized from graphite powder by a modified Hummer's method [53]. An appropriate amount of a mixture of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and n-titanium butoxide in ethanol were employed to obtain a nominal metal loading of 40 wt. % on the carbon derived from the urea/GO matrix, with a Co:Ti atomic ratio of 1:1. For the preparation of the composites, graphene oxide was added to the mixture of metals and sonicated for 30 min to obtain a well dispersed solution, followed by the addition of urea. This solution was stirred until urea was completely solubilized and left overnight to complete the gel formation. Finally, the gel was transferred to a quartz tubular reactor, heated at rate of $3^\circ\text{C} \cdot \text{min}^{-1}$ and annealed at 700°C for 1, 2 or 3 hours under N_2 atmosphere. The obtained material was thoroughly washed with water and acetone in order to remove impurities. The as-obtained composites were labeled as $\text{CoTiO}_3/\text{NrGO}$ (1h), $\text{CoTiO}_3/\text{NrGO}$ (2h) and $\text{CoTiO}_3/\text{NrGO}$ (3h). Commercial CoTiO_3 (Alfa Aesar) was used as reference.

2.3. Physicochemical characterization

The composition of the catalysts was determined by elemental analysis in a Thermo Flash 1112 analyzer (C, H, N, S), while the metal concentration was determined by inductively coupled plasma – optical emission spectroscopy (ICP-OES) using a SPECTROBLUE AMETEK spectrometer. The crystalline structure of the materials was determined by X-ray diffraction (XRD), using a Bruker D8 Advance polycrystalline powder X-ray diffractometer. Chemical surface composition was determined by X-ray photoelectron spectroscopy (XPS) with an OMICRON ESCA+ spectrometer with dual X-ray source ($MgK\alpha=1253.6$ eV, $AlK\alpha=1486.6$ eV). Raman spectra were recorded at room temperature with a Renishaw in Via Raman Microscope spectrometer equipped with a laser beam emitting at 532 nm and 5 mW output power. TEM JEOL 2100F operating at an accelerating voltage of 200 kV was used to obtain transmission electronic microscope (TEM) images, which allows evaluating the morphology and the metallic nanoparticles size in the catalysts. An energy dispersive X-ray (EDX) detector (INCA x-sight by Oxford Instruments) is coupled to the TEM, which allows the possibility of semi-quantitative chemical analysis. By using the scanning transmission electron microscopy (STEM) unit, Z-contrast images as well as the chemical characterization of areas of few nanometers were done. Specimens were prepared dispersing the materials ultrasonically in ethanol and depositing a few drops onto copper grids covered with Lacey carbon film. Scanning electron microscope (SEM) images were recorded using a Hitachi instrument, model TM-1000, with samples supported on a carbon based adhesive film.

2.4. Electrochemical characterization

All electrochemical measurements were performed at room temperature in a three-electrode system controlled by a potentiostat/galvanostat AUTOLAB PGSTAT302N. A reversible hydrogen electrode (RHE) in the supporting electrolyte was used as reference electrode, while a high surface glassy-carbon rod was employed as counter electrode. For the working electrode, a rotating ring disk electrode (RRDE)

with a Pt ring and a glassy carbon disk of 5 mm of diameter (0.196 cm^2) was used. The working electrode was prepared by depositing $30 \text{ }\mu\text{L}$ of catalytic ink onto the glassy carbon area. This catalyst ink was prepared by sonication of 4 mg of catalyst with $15 \text{ }\mu\text{L}$ of Nafion® and 400 mL of ethanol. The supporting electrolyte was a 0.1M NaOH aqueous solution. N_2 (99.99% Air Liquide) was employed to deaerate all solutions. O_2 (99.995% Air Liquide) was employed to obtain a saturated solution for the oxygen reduction reaction studies. Before electrocatalytic studies, all composites were submitted to activation process based on 50 cyclic voltammograms (CVs) between 0.05 and 1 V vs. RHE, at a scan rate of $0.1 \text{ V}\cdot\text{s}^{-1}$ in the deaerated supporting electrolyte. After that, a blank voltammetry was recorded in the same conditions with a scan rate of $0.02 \text{ V}\cdot\text{s}^{-1}$.

To determine the electrocatalytic activity of the catalysts two main reactions were studied: the ORR and the OER. The ORR activity was tested with polarization curves between 1.0 and 0.05 V vs. RHE (negative going scan) obtained at a scan rate of $0.005 \text{ V}\cdot\text{s}^{-1}$ while continuously flowing O_2 and at different electrode rotation speeds (rpm). For the OER measurement, a polarization curve between 0.7 and 1.8 V vs. RHE (positive going scan) was recorded at $0.005 \text{ V}\cdot\text{s}^{-1}$ and 1600 rpm. The stability of the catalysts towards the ORR has been studied by a chronoamperometric method, measuring the evolution of the current density at a constant potential of 0.6 V vs. RHE. Stability tests for the OER consisted of chronopotentiometric square cycles applying $0.005 \text{ A}\cdot\text{cm}^{-2}$ for 180 s followed by $-0.0005 \text{ A}\cdot\text{cm}^{-2}$ for 90 s with a rotation rate of 900 rpm and following the variation of potential with time with a cut-off condition of 1.8 V vs. RHE.

3. Results and discussion

3.1. Physicochemical characterization of $\text{CoTiO}_3/\text{NrGO}$ composites

Chemical composition was determined by elemental analysis and ICP-OES (Table 1). The concentration of cobalt and titanium is very similar in all composites and negligible effect of the annealing duration has been noted. On the other hand, the

elemental analysis reveals a slight increase of nitrogen content with the annealing time from 3.5 to 4.6 wt. %.

Table 1. Elemental analysis and metal loading (wt. %) and molar fraction of TiO₂ phases (%)

Sample	Co	Ti	C	N	W _R	W _A
CoTiO ₃ /NrGO (1h)	19	21	34	3.5	56	44
CoTiO ₃ /NrGO (2h)	18	19	36	4.1	52	48
CoTiO ₃ /NrGO (3h)	19	20	36	4.6	48	52

W_R = molar fraction of TiO₂ rutile; W_A = molar fraction of TiO₂ anatase

The crystallographic phases of the composites at different annealing time and commercial CoTiO₃ were investigated by XRD [49, 54]. The diffraction peak at $2\theta = 26.6^\circ$ confirms the complete reduction of the graphene oxide, which can be attributed to the presence of disordered layers of graphitic carbon from graphene (JCPDS 13-0148) [55]. That means that the GO is successfully converted to reduced graphene oxide (rGO).

XRD patterns of all synthesized composites display well-defined diffraction peaks of CoTiO₃ ilmenite (JCPDS 77-1373) [49, 54]. Additionally, the diffraction peaks corresponding to phases of TiO₂ anatase (JCPDS 21-1272) and rutile (JCPDS 89-4202) are present in all CoTiO₃/NrGO composites [56-58]. The diffraction peaks at $2\theta = 44.2^\circ$, 51.5° and 75.9° of the composites annealed during 2 and 3 hours are associated to metallic Co (111), (200) and (220) lattice facets, respectively, which correspond to a face-centered cubic structure (JCPDS 15-0806) [20]. Moreover, no peaks were observed for cobalt oxide phases.

The molar ratio of anatase and rutile in the composites was determined from the XRD peak intensity ratio according to the method of Spurr and Myers [59]:

$$W_R = 1/[1 + 0.8(I_A/I_R)] \quad (1)$$

$$W_A = 1 - W_R \quad (2)$$

where W_A and W_R are the molar fractions of anatase and rutile, I_A and I_R are the peak intensities of anatase (101) and rutile (110). Table 1 displays the values of W_R and W_A for the composites. It can be observed that the molar fraction of anatase increases from 44 % to 52 % with the annealing time, while the molar fraction of rutile decreases from 56 % to 48 %.

The size of the crystalline domains was obtained from the Scherrer equation assessed with the data obtained from the X-ray diffraction patterns (Table 2) [60]. It can be observed that the crystallite size of the different phases increases with the annealing time. CoTiO_3 particle size was calculated using the (104) reflection. The results show an increment of approximately 10 nm in the CoTiO_3 crystallite size from 1 hour to 3 hours of annealing time. TiO_2 crystallite sizes were calculated using (200) and (101) planes for anatase and rutile, respectively. As shown in Table 2, the crystallite size of anatase and rutile increases up to three times upon treatment for three hours compared to the counterpart annealed for one hour. Metallic Co crystallite sizes were calculated using (111) plane. A similar evolution of the size of this phase was observed, increasing the average particle size of cobalt with the annealing duration.

Table 2. Crystallite sizes from XRD patterns (nm).

Catalyst	CoTiO_3	Cobalt	TiO_2 (anatase)	TiO_2 (rutile)	Graphene
$\text{CoTiO}_3/\text{NrGO}(1\text{h})$	42.4	-	15.8	24.3	3.9
$\text{CoTiO}_3/\text{NrGO}(2\text{h})$	45.3	24.1	31.6	37.4	3.3
$\text{CoTiO}_3/\text{NrGO}(3\text{h})$	51.2	31.1	43.4	43.8	3.0

The morphology and the detailed structures of the as-synthesized composites were investigated by SEM and TEM. The low-magnification SEM images presented in Figure 2 show entangled graphene sheets with porous texture developed from the interstitial spaces within them. Other than graphene, TEM (Figure S1) and SEM (Figure 2) images show that all catalysts are composed of distributed metallic nanoparticles, with some agglomerates occurring especially for longer annealing. As shown in Supplementary Figure S2, the particle size distributions of all composites, revealing that catalysts annealed for 1 and 2 hours present a similar distribution. In these

composites, 80% of particles approximately show sizes between 10-30 nm and only a small population of particles has sizes over 50 nm. Whereas, the particle size distribution of the catalyst annealed for 3h shows that the main portion of particles are between 10-30 nm (50% approx.), but with a larger population of particles with sizes between 30 and 90 nm. Therefore, the average particle size values calculated from TEM images are in line with crystallite sizes from XRD results (Table 2).

We further investigated the elemental distribution using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), as shown in Figure 3. The presence of Ti and Co elements were verified by the elemental mapping of CoTiO₃/NrGO nanocomposites. Along them, Ti (blue) and Co (red) distribute on the whole graphene surface heterogeneously. As annealing duration increases, higher amount of larger particles are observed. All composites show some parts with similar Ti and Co distribution, which can be assigned to the presence of CoTiO₃ phases. However, larger particles show greater density of Ti compared with Co, which can be ascribed to a higher concentration of TiO₂.

Structural features of the composite catalysts have been also studied using Raman spectroscopy. Figure 4 shows Raman spectra of the synthesized materials and commercial CoTiO₃. Pure CoTiO₃ exhibits intense Raman bands at 159, 203, 228, 260, 330, 377, 448 and 688 cm⁻¹ (Figure 4A). The presence of CoTiO₃ is confirmed in all composites. The Raman bands of CoTiO₃/NrGO (1h) correspond to the incipient formation of CoTiO₃ particles on the doped graphene sheet. An increase of the annealing duration leads to well-formed CoTiO₃ in CoTiO₃/NrGO (2h) and CoTiO₃/NrGO (3h) composites, in line with the higher crystallite sizes observed by XRD. Raman bands assigned to anatase at 155, 199, 395, 509 and 609 cm⁻¹ and rutile at 398 and 608 cm⁻¹ (A and R in Figure 4A), can be observed in the synthesized composites [61]. No bands related with cobalt oxides have been found by Raman spectroscopy.

According to Figure 4B, two well defined bands at 1350 and 1590 cm⁻¹ confirm the presence of the graphene's D and G bands, respectively. It is known that D band is related with structural defects and partially disordered structures of the sp² domains in graphene sheets, while G band is related with the E_{2g} vibrational mode of sp² carbon domains that can be used to explain the graphitization degree of graphene structure

[20]. The extent of defects in the composites was quantified by evaluating the relative intensities of these bands (I_D/I_G). For CoTiO₃/NrGO composites annealed during 1, 2 and 3 hours, the value of I_D/I_G were 0.99, 1.03 and 1.07, respectively. This indicates that the graphitization degree decreases with the annealing time, and is lower than graphene oxide ($I_D/I_G = 0.89$). The increasing value of I_D/I_G factor indicates that at higher annealing times, a higher number of defects are introduced in the resultant NrGO matrix. This fact could improve the catalytic activity in the electrocatalytic reactions of interest in this work (ORR/OER).

X-ray photoelectron spectroscopy (XPS) was used in order to obtain further information about the catalysts surface. Figure 5 displays the spectra of N 1s, Ti 2p and Co 2p core-level of composites and commercial CoTiO₃ (red dashed line). Charge correction was applied to all spectra considering the position of C1s at 284.6 eV. N1s core-level of composites was resolved in four peaks at ca. 398.3, 399.3, 401.1 and 404.0 eV, corresponding to pyridinic N, pyrrolic N, quaternary N and N-oxides species, respectively [20]. The presence of pyridinic, pyrrolic and quaternary nitrogen confirms that urea has been carbonized to obtain nitrogen doped graphene (NrGO).

Ti 2p orbital region for CoTiO₃ shows the binding energies of Ti 2p_{3/2} and Ti 2p_{1/2} peaks at 458 and 463.8 eV, respectively. The splitting energy of 5.8 eV between Ti 2p_{3/2} and Ti 2p_{1/2} is a typical value for Ti⁴⁺[62]. The composites show a shift of the binding energy for Ti 2p towards higher energy region (~ 1 eV) with respect to that of bulk CoTiO₃. This shift is related to the transfer of electron density from titanium to NrGO sheets in the CoTiO₃/NrGO composites, which strongly suggest an interaction between N-doped reduced graphene oxide and titanium compound [44, 46, 51].

The spectra for Co 2p core level are showed in Figure 5 (right column). CoTiO₃ presents binding energies of Co 2p_{3/2} and Co2p_{1/2} at 781.05 and 797.3 eV, respectively, and the respective 'satellite' peaks, which can be attributed to Co²⁺-like species [51]. The Co XPS spectra of CoTiO₃/NrGO (1h) was similar to CoTiO₃, indicating that the oxidation state of Co for this composite resembles that of the commercial cobalt titanate. The widening of Co-related peaks with the annealing time suggests the formation of more oxidized cobalt species. There is not shift of the binding energy of Co 2p core level in the composites compared with CoTiO₃.

3.2. Electrochemical characterization

Cyclic voltammetry studies have been carried out for the as-synthesized composites and CoTiO_3 in the potential range between 0.05 and 1.15 V vs. RHE at a scan rate of $0.02 \text{ V}\cdot\text{s}^{-1}$. Figure 6 shows the voltammograms obtained for all the catalysts studied in the present work at room temperature in deaerated 0.1 M NaOH. The presence of reduced graphene oxide contributes to a larger double layer capacitance if compared to the cobalt titanate alone, especially in $\text{CoTiO}_3/\text{NrGO}$ (3h). The increase of capacitance with the annealing duration of composites may be ascribed to the presence of more oxidized cobalt species, as was observed by XPS, which redox reactions apparently increase the pseudo-capacitance of these materials, or related to the lower graphitization degree of carbon matrix as detected in Raman spectra.

3.2.1. Oxygen reduction reaction

The polarization curves of $\text{CoTiO}_3/\text{NrGO}$ composites recorded in O_2 -saturated alkaline medium at a rotation rate of 1600 rpm are shown in Figure 7A. A commercial CoTiO_3 (Alfa Aesar) sample was also studied for comparison. The current was corrected by the capacitive contribution from the curve measured in absence of O_2 . As evidenced in Figure 7A, CoTiO_3 presents the lowest onset potential at approximately 0.72 V vs. RHE (at $-0.1 \text{ mA}\cdot\text{cm}^{-2}$). Besides, the onset potentials of the composites show similar values above 0.9 V vs. RHE. The $\text{CoTiO}_3/\text{NrGO}$ (3h) catalyst yielded the best performance with the onset potential at 0.93 V vs. RHE and higher current density within the whole interval of potentials studied. The composites with shorter annealing duration show lower current densities, with the onset potential around 0.90 V vs. RHE.

Comparing the ORR activity of the three composites (Figure 7A) with the catalytic activity of commercial sole CoTiO_3 and sole nitrogen doped reduced graphene oxide (NrGO) [63], It is demonstrated that the interaction of cobalt and titanium oxides with the nitrogen doped graphene enhances the activity towards the ORR. For the nitrogen doped based composites, the catalyst annealed for 3 hours shows the highest current

density at 0.6 V vs. RHE. It is well-known that nitrogen-doped carbon with transition metals such as Fe or Co presents a good catalytic activity for the ORR in alkaline electrolyte [26, 28]. This fact could explain the better results of CoTiO₃/NrGO (3h), which have the highest amount of nitrogen in the structure. In order to compare these activity differences, Tafel slopes for the ORR are reported in Figure 7B. Three different results have been observed for each studied catalysts: 63mV·dec⁻¹, 99mV·dec⁻¹ and 46mV·dec⁻¹ for CoTiO₃/NrGO (1h), (2h) and (3h), respectively. Some research papers report that Tafel values near to 60mV·dec⁻¹ are characteristic for the behavior of platinum based materials which perform the desired 4e⁻ pathway [64, 65]. Shinagawa et al. have deepened the study of the mechanism of the ORR in alkaline media electrodes [66], considering an associative mechanism reported by Adzic et al. [67]. According to this mechanism, there are three main reactions which can determine the global reaction rate at low overpotential (equations 3 to 5):

According to Shinagawa results, the composite annealed for 1h with a Tafel slope of 66 mV·dec⁻¹ behaves through a reaction mechanism where the rate determining step is the adsorption of a hydrogen atom from water onto the metal oxide surface (equation 4). In the composite annealed for 2h, the Tafel slope is 99 mV·dec⁻¹, suggesting that both reactions in equations 3 and 4, i.e. reduction of MO₂ complex and the subsequent hydrogen adsorption, are controlling the overall process. On the other hand, the Tafel slope calculated for the composite annealed for 3 hours is near to 40 mV·dec⁻¹, demonstrating that, in this case, the mechanism is controlled by the reduction of the MO₂H complex. The catalytic pathway of the catalysts was investigated by Koutecky-Levich (K-L) plots from the analysis of linear sweep voltammetries (LSVs) at various rotating speeds (ω). Figure 8 shows the results related to CoTiO₃/NrGO (3h) as an example. Figure 8A shows the increase in the cathodic current with the rotating speed associated to the increase of the Levich current density with the square root of ω .

K-L plots for CoTiO₃/NrGO (3h) catalyst (the most active one) are depicted in Figure 8B, whereas K-L plots for the other two nanocomposites are reported in Figure S3, together with dotted lines indicating the slope with the theoretical *n* value of 2 and 4 transferred electrons, calculated using K-L equation (equation 6) [20]:

$$\frac{j}{j_d} = \frac{j_k}{j_k + j_d} \quad (6)$$

where *j* is the experimental current density, *j_k* is the kinetic current density, *j_d* is the diffusion limited current density, *ω* is the electrode rotation rate (rad·s⁻¹), *F* is the Faraday constant (96485 C·mol⁻¹), *D_{O2}* is the diffusion coefficient of O₂ in 0.1M NaOH (1.9·10⁻⁵ cm² s⁻¹), *C_{O2}* is the solubility of O₂ in 0.1M NaOH (1.2·10⁻⁶ mol cm⁻³) and *ν* is the kinematic viscosity of 0.1M NaOH (1.1·10⁻² cm² s⁻¹).

It is known that the ORR can proceed through 2e⁻ or 4e⁻ pathways. The number of transferred electrons have been calculated from Eq. 6 in order to determine the main pathway for each composite, obtaining three different values of 3.1, 2.9 and 3.5 transferred electrons for the CoTiO₃/NrGO (1h), (2h) and (3h), respectively. This suggests a similar behavior for the composites annealed for 1 and 2h, where the reaction follows a mixed mechanism close to 3 e⁻. However, in the catalyst annealed for 3h the number of transferred electrons is larger, making evident an enhanced performance of the catalyst sites for this composite.

In order to determine the stability of the catalysts for the ORR, a chronoamperometric method was performed keeping a constant potential of 0.6 V vs. RHE and recording the evolution of the current along 25000 s. The current change was normalized considering the initial current (Figure 9). CoTiO₃/NrGO composites annealed for 1 and 2 hours exhibited almost the same current loss after stability test (~10%), whereas the composite annealed for 3h was the most stable catalyst with a current loss of only 2.5%.

3.2.2. Oxygen evolution reaction

OER activity of the synthesized composites has also been studied by LSV. Figure 10 shows the IR compensated LSV between 1.1 and 1.85 V vs. RHE in deaerated 0.1 M NaOH. Figure 10A shows the catalytic activity of the CoTiO₃-based composites in comparison with a commercial CoTiO₃ as a reference. The onset potential was above 1.6 V vs. RHE for the CoTiO₃ commercial sample, whereas the composite catalysts exhibit a much lower onset potential. It is also worth mentioning that the activity of sole nitrogen doped reduced graphene oxide was much lower than commercial CoTiO₃ for the OER (not shown), in line with previous works [68, 69]. Among them, those annealed for 1 and 2 hours showed the same onset potential at 1.55 V vs. RHE, while the lowest value was obtained with the composite annealed for 3h, showing an onset potential of 1.53 V vs. RHE.

However, at larger overpotential, the composites annealed for 1 and 3 hours showed lower current values compared to the one annealed for 2 hours. To better individuate the reaction determining step, Tafel plots have been calculated from the polarization curves. Figure 10B shows Tafel slope values for the composites, being 140 mV·dec⁻¹, 136 mV·dec⁻¹ and 146 mV·dec⁻¹ for the composites annealed for 1, 2 and 3 hours, respectively. In addition, Tafel slope of commercial CoTiO₃ has been calculated being 69 mV·dec⁻¹. According to Shinagawa et al., the values of composites are near to the theoretical value of 120 mV·dec⁻¹, which suggests that the rate determining step of the overall process is the oxidation of the hydroxide anions in the metals surface, supposing a single-site mechanism (equation 7) [66]:

where M denotes an active site in the catalyst surface. In line with these results, the three composites showed the same kinetic behaviour for the OER. Tafel slopes show that commercial CoTiO₃ has better kinetic behavior for the OER than synthesized catalysts, however it has worse E_{onset} and lower j values. This can be related with the electron transfer between cobalt titanate and NrGO demonstrated by XPS, which makes metals positively charged in the composites, resulting in the improvement of adsorption capacity and electrochemical activity compared to sole ilmenite [46].

The current differences between composites should be associated with the exchange current density (j_0) for each composite.

Table 3. Tafel slopes and exchange current density values calculate for each sample.

Sample	Tafel slope $\text{mV}\cdot\text{dec}^{-1}$	j_0 $\text{mA}\cdot\text{cm}^{-2}$
CoTiO₃ /NrGO (1h)	140	$3,2\cdot 10^{-6}$
CoTiO₃ /NrGO (2h)	136	$2,5\cdot 10^{-6}$
CoTiO₃ /NrGO (3h)	146	$10\cdot 10^{-6}$

According to the results summarized in Table 3, the catalyst with the highest exchange current density is the one annealed 3h, confirming the good behaviour for the OER and confirming that this is the best catalyst for this reaction, despite performing lower current density than CoTiO₃/NrGO (2h) at larger overpotential.

Stability tests were carried out to investigate the behaviour of the composites upon applying constant current densities by monitoring the variation of potential with time. Figure 11 shows the variation of potential with time. A cut-off value of 1.8 V vs. RHE was established. An increase of OER potential was observed for all the composites with a larger resistance to degradation caused by larger annealing durations. The composites annealed during 3h (CoTiO₃/NrGO 3h) resisted 7 cycles (a total of 1260 s) before achieving the cut-off condition, while the number of cycles was lower for the other two composites. These results indicate an improvement of stability with annealing time, suggesting that this is a proper strategy to increase durability. After the stability test, the catalytic ink used was kept and TEM images were obtained (Figure S4). In the images, an increment on particle size and agglomeration degree is observed on the used catalysts, and especially on CoTiO₃/NrGO composites annealed during 1 and 2 hours.

These results highlight the bifunctional behaviour of cobalt titanates supported on N-doped reduced graphene oxide. In particular, CoTiO₃/NrGO (3h) exhibited enhanced bifunctional properties for ORR and OER in alkaline environment, i.e. improved

catalytic activity and stability. This catalyst also showed a significant stability, keeping a constant potential when subjected to chronopotentiometric tests.

4. Conclusions.

Composites formed by cobalt titanate and nitrogen doped reduced graphene oxide were synthesized by a sol-gel simple procedure. The annealing duration appears as a key variable to modulate the physico-chemical properties, and as a consequence, the electrochemical behavior. The composite prepared at the largest duration (CoTiO₃/NrGO (3h)) exhibited the best electroactivity for both the oxygen reduction and evolution reactions. In particular, for the ORR, the overall reaction rate is determined by different steps as a function of the composite characteristics, pointing to an important correlation in the modulation of the electro-activity. From the observed trends, the enhanced ORR/OER behavior related to larger extent of annealing could be attributed to higher concentration of nitrogen, larger extent of defects and/or the presence of more oxidized Co species in the titanate, all of them improving the charge transfer through more efficient reaction mechanisms.

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Figure captions

Figure 1. XRD patterns of composites and commercial CoTiO_3 . Most relevant peaks of anatase, rutile, cobalt titanate and cobalt phases have been labeled as A, R, CT and Co respectively.

Figure 2. SEM images of (A) $\text{CoTiO}_3/\text{NrGO}$ (1h), (B) $\text{CoTiO}_3/\text{NrGO}$ (2h) and (C) $\text{CoTiO}_3/\text{NrGO}$ (3h) composites.

Figure 3. STEM-EDX mappings of $\text{CoTiO}_3/\text{NrGO}$ catalysts

Figure 4. Raman spectra of the synthesized composites and commercial CoTiO_3 (A) between 100 and 1000 cm^{-1} ; and composites (B) between 1100 and 1750 cm^{-1} Raman shift.

Figure 5. XPS spectra of $\text{CoTiO}_3/\text{NrGO}$ (3h), $\text{CoTiO}_3/\text{NrGO}$ (2h) and $\text{CoTiO}_3/\text{NrGO}$ (1h) where A) is the N1s core level, B) Ti 2p core level and C) Co 2p core level.

Figure 6. Cyclic voltammograms of composites in deaerated 0.1M NaOH aqueous solution at scan rate of $0.02 \text{ V}\cdot\text{s}^{-1}$

Figure 7. (A) Linear sweep voltammetry of synthesized catalyst in a O_2 saturated 0.1M NaOH solution with $0.005 \text{ V}\cdot\text{s}^{-1}$ scan rate, 1600 rpm. (B) Tafel plots of the $\text{CoTiO}_3/\text{NrGO}$ catalysts

Figure 8. Electrochemical study of $\text{CoTiO}_3/\text{NrGO}$ (3h) composite. (A) Linear sweep voltammetry in a O_2 saturated 0.1M NaOH solution with $0.005 \text{ V}\cdot\text{s}^{-1}$ scan rate at different RDE speed rotation rates indicated in the legend (rpm). (B) Koutecky-Levich plot at different potentials (vs. RHE).

Figure 9. Relative current variation with time recorded by chronoamperometry at 0.6 V vs. RHE.

Figure 10. (A) OER activity of the synthesized composites in comparison with commercial CoTiO_3 in deaerated 0.1 M NaOH aqueous solution at 1600 rpm at $0.005 \text{ V}\cdot\text{s}^{-1}$ scan rate. (B) Tafel plots of synthesized catalysts.

Figure 11. Stability tests performed applying constant current values of $0.005 \text{ A}\cdot\text{cm}^{-2}$ during 180 seconds for the OER and $-0.0005 \text{ A}\cdot\text{cm}^{-2}$ during 90 seconds for the ORR.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

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Figure 8

Figure 9

Figure 10

Figure 11