Electrochemical Synthesis of Co$_3$O$_4-x$ Films for Their Application as Oxygen Evolution Reaction Electrocatalysts: Role of Oxygen Vacancies

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Herein we report the synthesis of efficient Co$_3$O$_4$ electrocatalysts toward the oxygen evolution reaction (OER) in alkaline media. Co$_3$O$_4$ films were obtained by thermal treatment of Co electrodeposited from electrolytic solutions containing glycine at different pH values. Co$_3$O$_4$ films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The grain size of the electrocatalysts decreases to 100 nm and the oxygen vacancies content increases, as the pH of the solution was increased during the synthesis. Linear Sweep voltammetry (LSV) and Chronopotentiometry techniques were employed to evaluate the electrocatalytic activity of the films. Co$_3$O$_4$ electrocatalysts obtained at pH values higher than 7 exhibit a better electrocatalytic performance than the obtained at pH values less than 4, such as a potential to reach 1.5 mAcm$^{-2}$ of 0.6 V and 0.68 mV, respectively. Co$_3$O$_4$ synthesized under alkaline conditions exhibit the best charge transfer resistance with 4.3 G during OER electrolysis. The improvement is associated to the presence of oxygen vacancies that promote the activity and stability of the electrocatalysts toward the OER.

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The electrochemical oxygen evolution reaction in alkaline media (OER: $4\text{OH}^− \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^−$) plays a key role in the efficient hydrogen production and solar refinery process. The OER is very important in several electrochemical technologies such as: water electrolyzers, solar water-splitting devices and rechargeable Li-Air Batteries. The OER involves a four electron transfer process and it is more challenging due to the slow kinetics, the high over-potentials and the low catalytic stability of the electrocatalysts.

It is well known that the efficient OER electrocatalysts such as Pt, Ir or Ru introduce high cost barriers to larger-scale applications because contain precious metals, however, electrocatalysts composed of earth-abundant and inexpensive materials are a promising alternative.

Recently, the investigation and development of electrocatalysts for OER is based on the use of transition metals or their compounds, such as cobalt, nickel, iron, copper, zinc and manganese. Among all electrocatalysts reported the cobalt-containing oxides have been investigated due to their high performance for the OER.

One of the recent approaches to increase the catalytic activity of single metal oxide catalysts is defect engineering by inducing impurities such as oxygen vacancies in metal oxides. In literature it can be found that oxygen vacancies improve electrical conductivity, optical and reductive properties and enhance the catalytic activity of metal oxides. Several methods have been developed to create oxygen vacancies in metal oxides: thermal treatment under a reducing, oxygen depleted atmosphere or vacuum, bombardment using high energy particles, and doping with metal or non-metal ions. However, these methods require very controlled conditions.

Electrodeposition technique allows the obtaining of thin and homogeneous films, the development of specific morphologies, usage of cheap raw materials, low energy consumption and control of parameters such as applied potential, the pH value of the electrolytic solution, deposition time and the selection of the substrate. What's more, the use of different complexing agents allows the obtaining of nanostructured electrodes and grant the electrocatalyst specific properties. Nakaoka et al. prepared Co$_3$O$_4$ films by incorporating glycine as the complexing agent in alkaline media, which showed a compact morphology similar to the obtained from sol-gel technique. NiO electrocatalysts obtained from Ni-Glycine complexes showed a better photoelectrochemical performance than those obtained from non-glycinated complexes.

The aim of the present work is the development of a facile synthesis to obtain Co$_3$O$_4$ films from electrolytic baths containing glycine, on FTO substrates, with oxygen vacancies in order to improve the electrocatalytic activity and stability of the Co$_3$O$_4$ electrocatalyst toward the OER in alkaline media.

Experimental

**Chemicals.**—CoCl$_2$ $\cdot$ 6H$_2$O (99.999%) and Glycine (H$_2$NCH$_2$COOH, Ultrapure Bioreagent) were obtained from J. T. Baker. NaOH Pellets (98%) and HCl (95–98%) were purchased from J. T. Baker, which were used to adjust the pH of each solution. Fluorine-doped tin oxide (FTO, Sigma-Aldrich $\sim$72/cm$^2$) coated glass was used as the substrate. Deionized (DI) Milli-Q water was used as the solvent in all electrochemical experiments.

**Co$_3$O$_4$ films synthesis.**—The electrodeposition of cobalt, on fluorine-doped tin oxide (FTO) coated glass substrates, was carried from an electrolytic solution with chemical composition of 0.1 mol dm$^{-3}$ CoCl$_2$ $\cdot$ 6H$_2$O and 1.3 mol dm$^{-3}$ glycine at different pH: 2.0 (solution S$_2$), 4.0 (solution S$_4$), 7.0 (solution S$_7$), 10.0 (solution S$_{10}$) and 13.0 (solution S$_{13}$). The measurement of the solutions’ pH was performed at a pH-meter Starter 2100 OHAUS. Absorbance spectra of the solutions were recorded on an UV-Vis spectrophotometer (UV-Vis Lambda XLS+) using a quartz cell for liquid samples at room temperature.
The electrodereposition experiments were carried out in a conventional three-electrode electrochemical cell for the metallic-cobalt electrodereposition from the prepared solutions. FTO-coated glass plates (cut into 2.5 × 0.8 cm pieces) were used as working electrode, the exposed geometric area in the electrolytic solution was 1.0 cm². Graphite bar and a saturated calomel electrode were used as counter and reference electrodes, respectively. Substrates were cleaned and sonicated for 10 minutes in acetone, ethanol and deionized water. Before electrochemical experiments, the electrolytic solutions were deoxygenated by direct N2 gas bubbling for 20 minutes. The electrochemical tests were run using a potentiostat/galvanostat AUTOLAB PGSTAT30 equipment coupled to a computer with the NOVA 1.11 software for control of the experiments and data acquisition. In order to obtain the CoO₂ electrode catalyst, the Co films were annealed in an electrical furnace under air atmosphere at 450 °C for 2 h.

Characterizations.—X-ray diffraction (XRD) patterns of the CoO₂ films were recorded using a Bruker D8 Advance with Cu-Kα radiation (λα = 1.5406 Å). XRD data were acquired from 20 = 15° to 70° (step 0.045°, scan rate 0.6° min⁻¹). SEM images were collected using a JEOL JSM-6510LV microscope. X-ray photoelectron spectra of the CoO₂ films were recorded using a K-Alpha X-ray Photoelectron Spectrometer, Thermo Scientific with Al Kα (1486.7 eV). The chemical composition of the films obtained was determined by Glow Discharge Emission Spectrometry (GDOES) using a GD-Profilometer 2, Horiba.

Electrochemical measurements.—Linear sweep voltammetry (LSV) technique was employed to evaluate the electrocatalytic activity of films in the range of potential from 0 to 1 V at 2 mV s⁻¹, in a three electrodes electrochemical cell containing a 1.0 mol dm⁻³ NaOH solution. The nanostructured films (1 × 1 cm²), graphite bar and calomel saturated electrode (SCE) were used as working, counter and reference electrode, respectively. The chemical and catalytic stability of all films were tested in 1.0 mol dm⁻³ NaOH solution at 25 °C. After every test the electrolyte solutions were purged with N2 gas for 20 minutes. Electrochemical Impedance Spectroscopy measurements were run in a 1.0 mol dm⁻³ NaOH solution in the range of frequencies from 1 to 100000 Hz at different potentials with the finality to obtain the electrochemical active surface area and the Mott-Schottky plots (1/C² against E).

Results and Discussion

Thermodynamic study.—To become acquainted of the different chemical species present in the electrolytic solutions a thermodynamic study of the cobalt–glycine species that are stable in aqueous solution at the studied conditions was carried out.

It is well known that Cobalt (II) ions have an octahedral coordination in aqueous solution. However, Glycine (H₂NCH₂COOH) is the simplest amino acid, which exists under three different forms in aqueous solutions depending on the pH value: H₂G (cation), H₃NCH₂COO⁻ (zwitterion) and H₂NCH₂COO⁻ (anion) labelled as: H₆G⁺, HG and G⁻, respectively. The pK’s values of glycine are: pKa₁ = 2.07 and pKa₂ = 9.97 at 25 °C. 37–39 The curve e, obtained from solution S₁₀, shows a bigger intensity and formation of a shoulder (at ca. 540 nm), which is attributed to the formation of non-aqueous complexes as a consequence of the total replacement of water molecules by glycine molecules.

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Table I. Equilibrium constants for the overall formation of complexes in the Co(II)-glycine-water system obtained from the literature. 37–39 βᵢ = [MLᵢ][M][L]ᵢ⁻¹.

|       | Glycine | OH⁻ | Cl⁻ |
|-------|---------|-----|-----|
|       | log β₁ | log β₂ | log β₃ | log β₁ | log β₂ | log β₃ | log β₁ | log β₂ | log β₃ |
| Co    | 4.69   | 8.46 | 10.81 | 4.30   | 8.40 | 9.70  | 10.20  | 2.40   | 1.60  |

are clearly distinguishable in this diagram that may affect to electrodereposition process of cobalt. The speciation plot indicates that in pH range from 0 to 6.0, the CoCl⁺ ions are not complexed by the glycine and CoCl⁺ is the predominant species. In the second region for pH values between 6.0 and 7.5, it is possible to observe that a mixture of the species CoG⁺, Co₂G²⁻ and CoG₃⁻ coexist in the solution. The third zone, above pH 7.5, is characterized by the presence of CoG₄⁻ as the predominant species. These results indicate that different complexes are predominant in function of the pH of the solution. In addition, a spectrophotometric study was carried out to identify the formation of the different species of cobalt: CoCl⁺, Co₂G²⁻ and CoG₃⁻. Figure 2 shows a comparison of UV-vis spectra obtained from different solutions of Co(II). Curve a, corresponds to solution without glycine, which contain a cobalt concentration of 0.1 mol dm⁻³. Curves b-f were obtained using the solutions S₂, S₃, S₄, S₁₀ and S₁₅, respectively.

The curves b and c shows the absorption spectrum obtained from solutions S₂ and S₃ where it is not possible to observe significant changes with respect to curve a. The comparison of curves a, b and c indicates that under these conditions the predominant cobalt ions are the Co(II)-chloride complexes. The curve d, obtained from solution S₅, shows the effect of increasing pH in solution, which provokes a displacement of the principal band toward relatively smaller wavelength values and the appearance of a new band at ca. 370 nm; this behavior is associated to the partial replacement of water molecules by glycine molecules.

Figure 1. Species repartition diagram for the Co(II)-glycine-water system.
pH = 13 (curve f) the absorption intensities increase considerably, which makes hard to obtain a full absorption spectrum. Nevertheless, the broad band between 400–600 nm is still present. The behavior is associated to the distortion of the octahedral coordination of Co(II) due to the incorporation of glycine in the formation of the Co-glycine complexes, where glycine acts as bidentate ligand through the –NH2 groups, giving place to binuclear structures with octahedral arrangement.

Based on these results, it is possible to propose the use of glycine as a complexing agent effective to maintain the solubility of cobalt ions in alkaline media forming the CoG2 and CoG3 complexes.

**Cyclic voltammetric studies.**—Figure 3 shows the typical cyclic voltammograms obtained from solutions containing Co(II) ions, chloride ions and glycine molecules at different pH values. FTO coated glass and a bar of graphite were used as working and counter electrodes, respectively, during the experiments. The potential scan was initiated in the negative direction from the open circuit potential (EOCP) at scan rate of 20 mVs⁻¹ in all cases. In the negative direction scan, the cathodic current increases sharply corresponding to the reduction of predominant complex in each electrolyte. The comparison of all curves in Figure 3 indicates that the onset potential (E onset) of reduction of cobalt-complexes was shifted to a more negative potential as well as the equilibrium potential (E eq) when the pH of the solution was increased. The potential shift of the E eq is associated to the different species that are involved in the electrochemical reduction in each solution. Curves a and b show an E eq close to −0.63 V; these curves share the same E eq although they were obtained at different pH values, 2 and 4, respectively, this indicates that the same species is reduced in both solutions. Additionally, the calculated ratio of anodic and cathodic charges from curves a (Qa/Qc = 0.43) and b (Qa/Qc = 0.76) indicates that hydrogen production is taking place during Co electrodeposition at pH=2. Curve c shows an E eq of −0.83 V meanwhile curves d and e, exhibit an E eq close to −1.0 V. Based on these results, it is possible to propose that CoCl⁺ is the reduced species in solutions S2 and S4, as well as CoG2 complex is reduced in solutions S10 and S13 and that CoG3 is the main precursor in solution S7 as it was predicted in Figure 1. Based on these results and from the species repartition diagram constructed for the Co(II)-glycine-water system in function of pH of the solution, it is possible to suggest that CoCl⁺ is the reduced species in solutions S2 and S4, as proposed in the following equation:

\[
\text{CoCl}^+ + 2e^- \leftrightarrow \text{Co} (0) + \text{Cl}^- \]

The conditional equilibrium potential (E' Co(0)/CoCl⁺) of this reaction depends on the concentration of Cl⁻ and Co(II) ions.

\[
E'_{\text{Co(0)/CoCl}^+} = E^0_{\text{Co(0)/CoCl}^+} + 0.03 \text{log} \left( \frac{[\text{CoCl}^+]}{[\text{Cl}^-]} \right) \]

Similarly, CoG2 is the main precursor in solution S7, as it was predicted in Figure 1 and it can be reduced to Co(0) as follows:

\[
\text{CoG}_2 + 2\text{H}^+ + 2e^- \leftrightarrow \text{Co} (0) + 2\text{HG} \]

In this case, the corresponding conditional equilibrium potential (E' Co(0)/CoG2) depends on the concentrations of H⁺, Co(II) and the complexing agent, G.

\[
E'_{\text{Co(0)/CoG}_2} = E^0_{\text{Co(0)/CoG}_2} + 0.03 \text{log} \left( \frac{[\text{CoG}_2][\text{H}^+]^2}{[\text{HG}]^2} \right) \]

Finally, the CoG3 complex can be reduced to Co(0), from solutions S10 and S13, as indicated in Equation 5.

\[
\text{CoG}_3 + 2e^- \leftrightarrow \text{Co} (0) + 3\text{G}^- \]

The conditional equilibrium potential (E' Co(0)/CoG3) depends on the concentrations of Co(II) and glycine, G.

\[
E'_{\text{Co(0)/CoG}_3} = E^0_{\text{Co(0)/CoG}_3} + 0.03 \text{log} \left( \frac{[\text{CoG}_3]}{[\text{G}^-]^3} \right) \]

It is important to mention that during the reduction of CoG3 to Co(0), from solution S13, it might be a possible adsorption of Co(OH)2 over the surface of the electrode, which can be formed at values of pH≥13 under the studied conditions (see Figure 1).

Moreover, the displacement of the E onset can be associated with the adsorption-desorption of glycine molecules on FTO electrode surface, which almost completely inhibits the discharge of the cobalt ions and blocks most of the active sites at which the reduction process occurs, provoking an increase in the overpotential for desorption of the glycine from the electrode surface. Curve e, obtained at pH = 13, shows a cathodic peak prior to the current related to the Co₂⁺ reduction process, this may be associated to the reduction of adsorbed Co(OH)₂ over the surface of the FTO electrode. Results from Figure 1 indicate that Co(OH)₂ formation is possible at pH values close and higher than 13. Figure 3 shows that at more positive potentials than E eq, an anodic peak is observed in each voltammogram, which is related to the dissolution of the electrodeposited cobalt. Based on the potentials at

Figure 2. UV-Vis spectra obtained from solutions: a) S0, b) S2, c) S4, d) S7, e) S10 and f) S13.

Figure 3. Cyclic voltammogram recorded on FTO substrate from the different prepared solutions with a scan rate of 20 mVs⁻¹ at 25°C. a) S2, b) S4, c) S7, d) S10 and e) S13.
Figure 4. Comparison of X-ray diffraction patterns of the different Co₃O₄ electrocatalysts.

which the electrodeposition of cobalt is occurring, several films were obtained on FTO substrates at different potential values, which are: −1.15 V (S₂), −1.20 (S₄), −1.25 V (S₆), −1.3 V (S₁₀) and −1.4 V (S₁₃). All films were deposited cathodically until a charge of 0.7 C was reached.

**Co₃O₄ films synthesis and characterization.**—Co₃O₄ films were obtained from thermal treatment of metallic cobalt electrodeposited from the different electrolytic solutions. In the literature it has been shown that the formation of Co₃O₄ occurs at 400 °C under air atmosphere. From these results we choose 450 °C as the formation temperature of Co₃O₄ using films of electrodeposited cobalt. The time of the thermal treatment was 2 h.

Figure 4 shows the XRD patterns of Co₃O₄ films obtained after thermal treatment using the cobalt-metal films electrodeposited from electrolytic solutions S₂, S₄, S₆, S₁₀ and S₁₃; the Co₃O₄ films will be labeled as FS₂, FS₄, FS₁₀ and FS₁₃, respectively. In Figure 4, it is possible to observe that peaks at 2θ = 19°, 31.27°, 36.85°, 38.55°, 44.81°, 55.6°, 59.35° and 65.23° match the planes (111), (220), (311), (222), (400), (422), (511) and (440) of the spinel Co₃O₄ structure (JCPDS 00-043-1003). Metallic cobalt was not detected by XRD analysis after thermal treatment, which means that the electrodeposited cobalt completely reacts with oxygen to produce Co₃O₄ at 450 °C. In all cases, the additional peaks (marked with asterisk) correspond to FTO substrate.

Figure 5 shows SEM images of the Co₃O₄ nanostructures corresponding to films obtained by electrodeposition and thermal treatment from the different Co (II) complexes: CoCl⁺, CoG₂ and CoG⁻. As can be seen, the morphology of the obtained Co₃O₄ films from CoCl⁺ complexes (Figures 5a and 5b) depends on the pH of the solution. The Figure 5a shows Co₃O₄ films formed by particles with flake shape and aligned vertically, and Figure 5b shows a flatter surface without a characteristic morphology. This changes in morphology might be a consequence of the interference of hydrogen evolution during electrodeposition at pH = 2. On the contrary, films prepared from Co-Glycine complexes change radically the morphology. Figures 5c–5d show Co₃O₄ films with a morphology formed by spherical particles, whose average size decreases with pH value in solution is increased. Figure 5e show the smallest particles with a diameter of approximately 100 nm. Following the above observations, it is clear that the particle size and shape of Co₃O₄ particles are markedly controlled by the pH of solution and complex used as precursor for electrodeposition. In this way, it is important to notice that the use of Co-glycine complexes allows the obtaining of semi-spherical morphologies of Co₃O₄ electrodes.

Figure 6a shows a typical GDS elemental composition profile of the film FS₁₀. It was found that the average film thickness of Co₃O₄ electrodeposited on FTO substrate is approximately 200 nm. Figure 6b shows the profilometry analysis of the surface of film FS₁₀ and it is possible to observe that a height value of approximately 230 nm was registered, which is similar with the obtained in analysis by GDS. Similar average thickness was observed for all Co₃O₄ films.

**Electrochemical impedance spectroscopy (EIS) measurements.**—The electrochemically active surface area (ECSA), of all Co₃O₄ films, was calculated from EIS technique. Figure 7 displays the Nyquist plots at 0.1 V for the Co₃O₄ films in 1.0 M NaOH in the frequency range of 1 Hz-10 kHz with an amplitude of 10 mV.

The insert in Figure 7 shows the simplified Randles circuit model, that combines the high frequency resistance of the electrolyte, ionic charge transfer resistance and double layer capacitance at the front contact, and restricted diffusion of the inserted species. The evaluation of double-layer capacitance and the ECSA were carried out by Equations 7 and 8 following the methodology proposed by Charles C. L. McCrory.

\[
C_d = \left[ Q_0 \left( \frac{1}{R_s} + \frac{1}{R_{ct}} \right) \right]^{1/\alpha} \tag{7}
\]
The value of \( C_s \), the specific capacitance of the sample or the capacitance of an atomically smooth planar surface of the material per unit area under identical electrolyte conditions was 27 \( \mu \)F cm\(^{-2}\).\(^4\)\(^7\)

Table II shows the results of ECSA obtained for obtained Co\(_3\)O\(_4\) films. It is possible to observe a similar value of approximately 4.0 cm\(^2\) for almost all cases. For the case of the film FS\(_4\) was obtained an ECSA value of 2.0 cm\(^2\), which is half of value obtained in the other cases. This result can be associated to the morphology of this Co\(_3\)O\(_4\) film observed in Figure 5b, where it was possible to observe a compact grains, which provokes a decrease in the ECSA value.

Figure 8 shows the Mott-Schottky plots of the synthesized films, where the capacitance \( C \) was obtained from the impedance measurement. From the Mott-Schottky equation:\(^4\)\(^8\)

\[
\frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_0 A^2 e N_D} \left( E - V_{fb} - \frac{k_B T}{e} \right)
\]

Where \( C \) and \( A \) are the interfacial capacitance and area, respectively, \( \varepsilon \) the dielectric constant, \( N_D \) the number of donors, \( E \) the applied potential, \( k_B \) is Boltzmann’s constant, \( T \) the absolute temperature and \( e \) is the electronic charge. Furthermore, the value of \( N_D \) can also be conveniently found from the slope knowing \( \varepsilon \) and \( A \).

The slope of the linear part of the curve in the Mott-Schottky plot is negative, which indicates that Co\(_3\)O\(_4\) is a \( p \)-type semiconductor. Additionally, from Figure 8 it is possible to estimate the value of flatband potential, \( V_{fb} = 0.20 \) V, which corresponds to the valence band value. In Figure 8 it is clear to observe that the slope values of films FS\(_2\), FS\(_7\), FS\(_{10}\) and FS\(_{13}\) are very similar; only FS\(_4\) has a higher slope value.

It can be found in literature, Ov increases the catalytic activities of metal oxides acting in some cases as active sites for catalysis, but also affect the energy states of a semiconductor.\(^3\)\(^3\),\(^4\)\(^8\),\(^4\)\(^9\) Since the ECSA approaches the electrochemically active sites in the surface area, in this case the Ov (as it will be seen in following sections) which also affect the free charge carriers, \( N_D \); therefore, an increase in the ECSA would lead to a higher \( N_D \) value. This agrees with the obtained results. Table II summarizes the \( N_D \) values of all Co\(_3\)O\(_4\) films. Finally, the increase in the charge carrier density of Co\(_3\)O\(_4\) films FS\(_2\), FS\(_7\), FS\(_{10}\) and FS\(_{13}\) is due to the decrease in the recombination rate within the space charge layer region.\(^5\)\(^0\)
Table II. Capacitance, electro chemical surface area and ND obtained.

| Sample | Parameters                  | Capacitance/μF | ECSA/cm² | ND          |
|--------|-----------------------------|----------------|----------|-------------|
| FS2    | Rs = 30.85 Ω Q₀ = 229 μF  | 115            | 4.20 ± 0.64 | 1.22 × 10¹⁹ |
|        | Rct = 33 kΩ α = 0.89       |                |          |             |
| FS4    | Rs = 59.18 Ω Q₀ = 138 μF  | 57.1           | 2.11 ± 0.31 | 4.91 × 10¹⁸ |
|        | Rct = 22 kΩ α = 0.88       |                |          |             |
| FS7    | Rs = 27.81 Ω Q₀ = 224 μF  | 111            | 4.12 ± 0.61 | 1.13 × 10¹⁹ |
|        | Rct = 22 kΩ α = 0.89       |                |          |             |
| FS10   | Rs = 29.82 Ω Q₀ = 236 μF  | 108            | 4.01 ± 0.60 | 1.21 × 10¹⁹ |
|        | Rct = 19 kΩ α = 0.88       |                |          |             |
| FS13   | Rs = 29.12 Ω Q₀ = 251 μF  | 112            | 4.15 ± 0.62 | 1.33 × 10¹⁹ |
|        | Rct = 22 kΩ α = 0.90       |                |          |             |

**XPS analysis.** Additionally, a XPS study was carried out to determine the surface chemical composition of the Co₃O₄ films. Figure 9a and 9b shows XPS spectra of Co₃O₄ films FS2 and FS10, respectively. In Figures 9a–9b it is possible to note that Co 2p spectrum is formed by two main 2p₃/2 and 2p₁/2 spin-orbit lines at 779 and 795 eV, respectively. Figures 9c and 9d shows XPS spectra of O 1s of films FS2 and FS10, respectively. Figure 9 shows three different signals at approximately 530 eV, 531 eV, and 532 eV. These binding energies are related to oxygen bonded to cobalt in the lattice (Co-O), oxygen vacancies or defects (Ov) and chemisorbed or dissociated (Oc) oxygen species, respectively. Due to physically absorbed hydroxyl groups can be easily removed under the ultrahigh vacuum condition of the XPS system, the hydroxyl signal (~531 eV) corresponds to strongly bonded hydroxyl groups to surface defects, which are the Ov.⁵²,⁵³ Numerical integration of the signals of Co⁳⁺ and Co⁴⁺ in Figures 9a–9b was performed to determine the Co³⁺/Co²⁺ ratio; same mathematical technique was used to determine the amount of oxygen vacancies (Ov) in Co₃O₄ and the results are shown in Figure 10. Results show that as the pH of the solutions, used for the electrodeposition of cobalt, increases the Co³⁺/Co²⁺ ratio is diminished. On the contrary, the oxygen vacancies are increased as the pH solution is increased. The increase of the Co²⁺ ions can be related to the amount of Ov, due to the presence of Ov in Co₃O₄ create new defect states located in the bandgap energy of this material and thus free electrons are generated on these defect states. These free electrons lead to the reduction of Co³⁺ ions to Co²⁺ ions.⁵³ It can also be proposed that the formation of Ov is consequence of the combustion of occluded glycine during the electrodeposition process. Figure 11a shows a typical GDS elemental composition profile of the metallic cobalt film obtained from solution S10 before the thermal process.
treatment. In this figure it is possible to observe a cobalt film thickness of approximately 250 nm. Figure 11b corresponds to the zoom of Figure 11a. The Figure 11b shows the presence of nitrogen, carbon and hydrogen near the deposit surface, which are associated to the presence of glycine. These results support that glycine molecules are occluded in the coating of metallic cobalt during the electrodeposition process, which are oxidized during the thermal treatment provoking the direct formation of oxygen vacancies and indirect increase in Co²⁺ ions on the Co₃O₄ electrocatalysts. In the literature, ⁵⁴ it has been reported that the glycine combustion occurs at 400 °C with the formation of carbon dioxide, water and ammonia.

Electrocatalytic performance.—The electrocatalytic activity of the synthesized Co₃O₄ films toward the OER in 1.0 mol dm⁻³ NaOH was measured and compared. To study the electrocatalytic performance of the Co₃O₄ films, the electrochemical technique of linear scan voltammetry was performed using these films as electrodes. All measurements were conducted at a scan rate of 2 mV s⁻¹.

As shown in Figure 12a, to reach a current density of 1.5 mA cm⁻², the films FS₂, FS₄, FS₇, FS₁₀, FS₁₃ and commercial Co₃O₄ films required a potential of 0.68 V, 0.65 V, 0.63 V, 0.61 V, 0.60 V and 0.80 V, respectively. These results indicate that in all cases, the Co₃O₄ films synthesized in this work have a better performance toward the OER, compared to commercial Co₃O₄. The comparison of electrocatalytic activity among Co₃O₄ films synthesized indicates that a smaller applied potential is necessary to achieve a current density of 1.5 mA cm⁻² when the Co₃O₄ films were synthesized under alkaline conditions from Co-Glycine complexes. As shown in Figure 12a, FS₁₀ is the best electrocatalyst among the six electrodes, giving much higher current density at the same potential. These results reveal that the formation of oxygen vacancies in Co₃O₄ films enhances the electrocatalytic activity of this material which makes it suitable for its application as a good electrocatalyst for OER.

Figure 12b shows the Tafel slopes obtained from data in Figure 12a. All Tafel slopes are close to 59 mV dec⁻¹, this slope is characteristic of an OER mechanism involving a reversible one-electron transfer prior to a chemical limiting step. ⁵⁵ Tafel slope of commercial Co₃O₄, 123 mV dec⁻¹, is characteristic of the Rate-determining step (RDS) proposed in Equation 10, which corresponds to the adsorption of OH⁻ over the active site. However, the synthesized electrocatalysts, enriched with Ov show a Tafel slope corresponding to the RDS of Equation 11. The decrease of the Tafel slope might be a consequence of the OH adsorbed in the Ov of the electrocatalysts. Since the hydroxyl radicals, OH, are already adsorbed in the surface of Co₃O₄ (due to OH is adsorbed in the superficial Ov, as explained in XPS analysis section), a Tafel slope decrease with a tendency to the RDS of Equation 11 with 59 mV dec⁻¹ would be expected.

| Rate-determining Step | Tafel Slope/mV dec⁻¹ |
|-----------------------|---------------------|
| M + OH⁻ → MOH + e⁻    | 120 [10]            |
| MOH + OH⁻ → MO⁻ + H₂O | 59 [11]             |
| MO⁻ → MO + e⁻         | 39 [12]             |
| 2MO → 2M + O₂         | 15 [13]             |

Figure 11. a) Typical GDS elemental composition profile of the metallic cobalt film obtained from solution S₁₀ before the thermal treatment and b) Zoom of the curve (a).

Figure 10. Co³⁺/Co²⁺ ratio and relative of oxygen vacancies (Ov) in Co₃O₄ obtained from numerical integration of data shown in Figure 9.
Midterm stability of the electrocatalysts was tested by the potential-time plot applying a current density of 5 mA cm\(^{-2}\), shown in Figure 13a. As it was to expect, all Co\(_3\)O\(_4\) electrocatalyst shows a great stability during the OER electrolysis with a steady state potential. However, differences appears at EIS measurement during OER electrolysis. Figure 13b shows the Nyquist plot obtained at 0.7 V. There is a decrease in the calculated charge transfer resistance (R\(_{ct}\)) of FS\(_7\), FS\(_9\) and FS\(_{11}\) electrocatalysts (5.3, 4.3 and 4.8 \(\Omega\), respectively) respect to FS\(_7\) and FS\(_{11}\) (6.7 and 7.5 \(\Omega\)), which means that electrocatalysts obtained from glycinate complexes exhibit a much more rapid electron transfer and therefore a better conductivity. These results are comparable to those obtained from Co\(_3\)O\(_4\) nanocubes and nanorods which obtained 8.6 \(\Omega\) and 4.5 \(\Omega\) during the OER process.\(^{19}\) Finally, as shown in Figure 12a, a plateau appears at potentials > 0.7 V which can be misread as a mass transport effect. However, results in Figure 13b shows only a semi-circle related to the OER faradaic process without any mass transfer contribution (e.g. Warburg diffusion).

The above results indicate that not only glycinate complexes grant a great ECSA and ND to Co\(_3\)O\(_4\) electrocatalysts, but also generate defects such as oxygen vacancies that improve the electrocatalytic activity of Co\(_3\)O\(_4\) toward the OER in alkaline media.

Conclusions

In summary, Co\(_3\)O\(_4\) films were obtained on FTO through thermal treatment of electrodeposited Co from different Co species. XPS analysis showed that the content of oxygen vacancies increases when Co-glycine complexes are used in the electrodeposition process and these defects decrease the Co\(^{3+}\)/Co\(^{2+}\) ratio on the Co\(_3\)O\(_4\) catalyst. The required potential to reach 1.5 mAc cm\(^{-2}\) was 0.68 V, 0.65 V, 0.63 V, 0.61 V and 0.60 V for FS\(_2\), FS\(_4\), FS\(_7\), FS\(_{10}\), FS\(_{13}\) electrocatalyst respectively, whereas commercial Co\(_3\)O\(_4\) 0.8 V to reach the same current density. Although all Co\(_3\)O\(_4\) electrocatalyst exhibit a great stability performance during OER electrolysis, glycinate complexes grant properties, such as a large ECSA, ND and defects as oxygen vacancies, to Co\(_3\)O\(_4\) which promote the electrocatalytic activity and improves the charge transfer resistance of the electrodes toward the OER in alkaline media.
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