Bifunctional N-doped graphene Ti and Co nanocomposites for the oxygen reduction and evolution reactions

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Abstract: Developing efficient, durable, and low cost catalysts based on earth-abundant elements for the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) is essential for renewable energy conversion and energy storage devices. We report herein a simple one-pot procedure for the synthesis of non-precious metals N-doped graphene composites employing urea as nitrogen source, and their application as bifunctional catalysts for both the ORR and OER in alkaline environment. In this study, the effects of the addition of Ti and Co on the structure and performance of the N-doped graphene composites are investigated. The incorporation of Ti leads to a composite with both anatase and rutile TiO₂ crystalline phases as well as Ti³⁺ species stabilized upon hybridization with N-doped reduced graphene oxide. The ORR onset potential for the Ti-based composite is 0.85V (vs. RHE) and the number of electrons transferred is 3.5, showing superior stability than Pt/C after accelerated potential cycling in alkaline solution. However, this composite shows low activity and stability for the OER. On the other hand, the composite consisting of metallic Co and Co₃O₄ nanocrystals grown on N-doped reduced graphene oxide exhibits the best performance as bifunctional catalyst, with ORR and OER onset potentials of 0.95 V and 1.51 V (vs. RHE), respectively, and a number of electrons transferred of 3.6 (ORR). The results reveal the presence of important structural features such as metallic Co as the predominant crystalline component, amorphous Co₃O₄ phase and the coordination of Co-N-doped graphene. All of them seem to be fundamental for the high activity and stability towards ORR and OER.

Keywords: electrocatalyst; oxygen reduction; oxygen evolution; N-doped graphene; titanium; cobalt

1. Introduction

Oxygen reduction (ORR) and evolution (OER) reactions are undoubtedly the most important electrochemical reactions associated with energy conversion and storage technologies, such as fuel cells or water electrolyzers, and the combination of both systems: unitized regenerative fuel cells (URFCs) [1, 2]. However, the sluggish kinetics of these reactions in acid environment at low temperature requires a large quantity of precious metals (e.g. Pt, Ir or Ru) to enhance reaction activity and durability [3-8]. The utilization of anion exchange membranes presents several potential advantages compared to its acidic Nafion-based counterpart, including improved kinetics of electrochemical reactions, materials stability, and easy water management [9-12]. Therefore, anion exchange membrane fuel cells and electrolyzers may hold great potential in the near future, providing an opportunity to use a host of non-platinum group metal catalysts [13]. Furthermore, anion exchange membranes unitized regenerative fuel cells (AEM-URFCs) have attracted attention in recent years because they involve interconversions between H_2 , O_2 , and H_2O in a single system [14, 15]. AEM-URFCs possess high specific energy, enjoy economies-of-scale advantages, are modular in nature, and require only environmentally benign and inexpensive reactants. This electrochemical system constitutes a promising technology for large-scale energy storage, which is extremely necessary when renewable and intermittent energy sources are used.

The rational design of superb catalysts with earth-abundant elements, superior reactivity, and sufficient stability under operating conditions, which are also bifunctional catalysts for both ORR and OER, is of urgent importance for the development of oxygen electrochemistry-involved devices [16]. Typically, good catalysts for ORR tend to exhibit poor OER performance and vice versa. Among all the nonprecious metal catalysts formulations studied, carbon-based catalysts hold the greatest promise to replace precious metals in the future due to their low-cost [1, 17-19]. In particular, N-doped carbon nanocomposites and earth-abundant transition metals have demonstrated remarkably improved catalytic activity and stability in alkaline electrolyte [1, 16]. The electrocatalytic active sites are formed by the coordination of metal-nitrogen-carbon (Me-N-C) species (Me = Co, Fe, Ni, Mn, etc.), where the morphology of carbon matrix has a determining role on activity (e.g. nanotubes, graphene) [17, 20-22]. Depending on the nanocarbon structure and transition metal, a synergetic effect towards enhanced performances can be observed. Synthesis conditions like the number of heat treatments in nitrogen-rich atmosphere or their temperature, undoubtedly influence the physico-chemical features of the electrocatalysts and, in turn, the electroactivity [23-25]. The interaction between d-electrons of metal moieties and π -electrons in the carbon basal plane modify the local electronic structure of the active sites, leading to a favorable adsorption of intermediates and a higher activity [16, 26-29].

Among these materials, cobalt-based N-doped carbon catalysts have attracted particular attention due to their low cost, high abundance and appropriate features to act as bifunctional catalysts for both the ORR and the OER [17, 23, 30-34]. However, a good understanding of the structure-activity relationship of these composites for ORR and OER under harsh operating conditions is still to be achieved. In contrast, only a few

research works have been reported with the application of titanium species as bifunctional electrocatalysts [7, 8, 35]. In these works, platinum is the active site, which is supported on TiN, TiCN or TiC materials. Furthermore, the low intrinsic conductivity and poor reactivity of TiO₂ are believed to hamper the efficient application of this material in electrocatalytic applications that require fast electron transport [36].

Herein, a simple one-pot method was investigated to synthesize nanocomposites of Co and Ti with N-doped graphene using urea as nitrogen source. Both composites have been characterized and tested as bifunctional catalysts for both the ORR and the OER under alkaline conditions. Additionally, accelerated durability tests have been performed in order to investigate the behavior of the systems under harsh conditions of applied potential.

2. Experimental

2.1. Chemicals and reagents

Graphite powder (>99.8% purity, particle size <20 μm), KMnO₄ (>99.8% purity), cobalt (II) chloride hexahydrate (CoCl₂·(H₂O)₆, > 97% purity), urea (CH₄N₂O, >98% purity) and sodium hydroxide (NaOH, 99.99%) were obtained from Sigma-Aldrich. Concentrated H₂SO₄ (96%) and H₂O₂ (30% v/v) were provided by Merck and Foret, respectively. Titanium (IV) n-butoxide (Ti[O(CH₂)₃CH₃]₄, >99% purity) and iridium (IV) oxide (IrO₂, 99% purity) were purchased from Alfa Aesar. Ethanol Absolute (CH₃CH₂OH, 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 MΩ cm) through Millipore system (Milli-Q®) was used in all the experiments.

2.2. Composites synthesis

Graphene oxide (GO) was synthesized from the graphite powder by a modified Hummer's method [37, 38]. For the synthesis of the composites, 0.4 g of GO was dispersed in ethanol (3 mL) by ultrasonication for 3 h. Then, an appropriate amount of metal precursor was added slowly to the solution, which was stirred for 30 min and sonicated for additional 30 min. After that, 2 g of urea was added to the mixture solution. Metal to urea molar ratio was kept at 1:20. This solution was stirred until urea was completely solubilized, which was left overnight to complete the gel formation. Finally, the gel was transferred to a quartz tubular reactor, heated at rate of 3°C·min⁻¹ and annealed at 800°C for 2 hours under N₂ atmosphere. The obtained material was thoroughly washed with water and acetone in order to remove impurities. The as-obtained composites were labeled as Ti/NrGO and Co/NrGO.

2.3. Physicochemical characterization

Non-metal composition was determined by elemental analysis in a Thermo Flash 1112 analyzer. Metal amount 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 with a Cu K α source. Chemical surface composition was determined by X-ray photoelectron spectroscopy (XPS) with a OMICRON ESCA+ spectrometer with dual x-ray source (MgK α =1253.6 eV, AlK α =1486.6 eV). CasaXPS software was used for obtaining atomic percentage compositions, using Gauss-Lorentz equations with the Shirley-type background. A 70%/30% Gaussian/Lorentzian line shape was used to evaluate peaks position and areas of the high-resolution spectra. Accurate binding energies (± 0.2 eV) were determined by referencing to the C 1s peak at 284.6 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. A HRTEM 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. The particle size distribution of each catalyst was calculated using frequency count method of Origin program measuring the diameter of at least 200 metallic nanoparticles. Scanning electron microscope (SEM) images were recorded using a Hitachi instrument, model TM-1000.

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 cm²) was used. The working electrode was prepared by depositing 30 μ L of catalytic ink onto the glassy carbon area. This catalyst ink was prepared by sonicating 4 mg of catalyst with 15 μ L of Nafion[®] (5wt%, Sigma-Aldrich), for a Nafion-to-catalyst mass ratio of 0.175:1, and 400 μ L of a mixture of isopropanol (IPA) and ultrapure water (IPA:H₂O, 3:2). The supporting electrolyte was a 0.1M NaOH aqueous solution. N₂ (99.99% Air Liquide) was employed to deoxygenate all solutions. O₂ (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 1.2 V vs RHE at a scan rate of 0.1 V s⁻¹ in deaerated supporting electrolyte. After that, a blank voltammetry between the same potential limits in N₂ at 0.02 Vs⁻¹ was recorded.

To determine the electrocatalytic activity of the catalysts two main reactions were studied: the ORR and the OER. The ORR activity was tested with a polarization curve 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 . Prior to ORR polarization curves, all the composites were maintained at 1.0 V for 60 s. This study was performed at different electrode rotation speeds (rpm) to calculate the number of electrons using Koutecký-Levich plots. The measurement was performed keeping the ring at 1.2 V vs. RHE in order to detect H_2O_2 formation. 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. In this case, the ring was kept at 0.4 V vs. RHE (for quantification of the evolved O_2 by ORR) [7].

In order to investigate the stability of the catalysts, two essays were performed considering both ORR and OER reactions. For the ORR, 6500 cycles were performed by triangular potential cycling between 0.4 and 0.9 V vs. RHE at a scan rate of 0.2 Vs^{-1} . After that, the ORR polarization curve was performed to compare this signal with initial results. For the OER, the stability was assessed by a chronopotentiometric procedure consisting of on/off rectangular cycles, maintaining 5 mA cm^{-2} of current density for 180 s followed by a period of 90 s at zero current, with a cut-off potential of 1.9 V vs. RHE [39-41].

3. Results and discussion

3.1. Physicochemical characterization of Ti/NrGO and Co/NrGO composites

Elemental analysis and ICP-OES values of Co/NrGO and Ti/NrGO are given in Table 1. Chemical analysis shows similar amount of metal loading and metal to carbon atomic ratio. However, elemental analysis reveals higher nitrogen content in the bulk material for the cobalt-based composite, from 2 wt% in Ti/NrGO to 9 wt% in Co/NrGO. Considering that the same procedure was used for both composites, it appears that cobalt aids in fixating nitrogen to the composite in a larger extent than titanium.

Table 1 Metal loading (from ICP-OES) and elemental analysis (Me= Ti or Co)

Sample	Metal loading (wt%)	C (wt%)	N (wt%)	Me/C atomic ratio
Ti/NrGO	22	54	2	0.1
Co/NrGO	25	59	9	0.09

The morphology of the composites was investigated by SEM. Figure 1 displays SEM images of Ti/NrGO (A) and Co/NrGO (B). Both composites show metal nanoparticles anchored on the N-doped reduced graphene oxide sheets. In general, the dispersion of the metal nanoparticles seems uniform in both catalysts with some agglomerates of small particles observed at low magnification SEM captures. However, both composites present great differences when observed by TEM. As shown in Figure 1C and E, TEM images of Co/NrGO show metal nanoparticles with an average diameter of 60 nm (histogram inserted in Figure 1E),

while the average particle size of the Ti/NrGO corresponds to 7 nm (Figure 1D and F, histogram inserted in Figure 1F).

The structures of the composites and graphene oxide (GO) were investigated by means of XRD (Figure 2A). GO exhibits an intense peak at $2\theta=10.8^\circ$ corresponding to the increased interlayer spacing of graphite due to the intercalation of oxygen-containing functional groups and water between the graphitic layers [42]. However, during the synthesis process of the Ti/NrGO and Co/NrGO composites, the diffraction peak of graphene oxide at 10.8° is considerably shifted to a higher 2θ angle of 26.6° , which can be attributed to disordered layers of graphitic carbon from graphene (JCPDS 13-0148) [43]. That means that the GO is converted to reduced graphene oxide (rGO), and at the same time, urea is carbonized to obtain nitrogen doped carbon (NrGO). Co/NrGO composite shows diffraction peaks at 2θ angles of 44.3° , 51.6° and 75.9° corresponding to cobalt with face-centered cubic structure (JCPDS 15-0806). These peaks correspond to the (111), (200) and (220) crystalline lattice facets, respectively, of metallic cobalt indicating that metallic Co is the dominant form of the crystalline component [31]. The X-ray diffraction pattern of the Ti/NrGO composite (Figure 2A) exhibits the diffraction peaks attributable to TiO_2 -Anatase (JCPDS 89-4921) and TiO_2 -Rutile phases (JCPDS 89-4202).

Figure 1. SEM images of Co/NrGO (A) and Ti/NrGO (B). TEM images of Co/NrGO (C and E) and Ti/NrGO (D and F). The insets are metal particle size distribution histograms of Co/NrGO (E) and Ti/NrGO (F)

The structural and morphological features of the composites were further investigated using Raman spectroscopy. The corresponding spectra of Co/NrGO, Ti/rGO and graphene oxide are displayed in Figure 2B. Both composites show two well-defined bands corresponding to the D and G bands of graphene which appear at around 1580 cm^{-1} and 1350 cm^{-1} , respectively. As is known, the G band related to the E_{2g} vibration mode of sp² carbon domains can be used to explain the degree of graphitization, while the D band is associated with structural defects and partially disordered structures of the sp² domains [44]. The extent of defects in the composites is quantified by estimating the relative intensities of these two bands (I_D/I_G ratio). For Co/NrGO and Ti/NrGO composites, the I_D/I_G values are 0.98 and 1.00, respectively, being slightly larger than graphene oxide ($I_D/I_G = 0.89$). This indicates that the density of defects of the resultant NrGO phase is similar between both composites and slightly larger for the graphene oxide used as precursor. It appears that the synthesis of composites introduced more surface defects, which could positively contribute to the electroactivity [45]. Furthermore, Raman bands at 476 cm^{-1} and 681 cm^{-1} in Co/NrGO composite can be assigned to F_{12g} and A_{1g} modes, respectively, of Co₃O₄ nanoparticles [46-48]. The presence of anatase and rutile phases of titania are also confirmed in the Raman spectrum of Ti/NrGO composite (Figure 2B). Weak Raman bands at 143, 199, 395 and 632 cm^{-1} are attributed to anatase phase of titania, while the presence of intense Raman bands at 243, 442 and 611 cm^{-1} can be related to the rutile phase of TiO₂ [49, 50].

Figure 2. (A) XRD patterns of GO, Ti/NrGO and Co/NrGO; (B) Raman spectra of Co/NrGO, Ti/NrGO and graphene oxide

The nature of the surface species of the composites was investigated by XPS analysis (Figure 3). The high-resolution XPS spectrum of the N 1s peak of Ti/NrGO (Figure 3A) and Co/NrGO (Figure 3B) composites reveals four components with the binding energies centered at about 398.1, 399.3, 400.7 and 402 eV, corresponding to pyridinic N, pyrrolic N, quaternary N and oxidized N, respectively. Moreover, Ti/NrGO shows an additional component centered at 396.5 eV assigned to N-Ti interaction.

Figure 3C displays the Ti 2p XPS spectrum of Ti/NrGO composite. This spectrum shows a structure of two overlapping doublets. The Ti 2p_{3/2} peak centered at 459.1 eV is attributed to Ti⁴⁺ state [51]. Upon comparison with a pristine TiO₂ sample [52, 53], it is observed that the signal is slightly shifted from the corresponding 458.5 eV peak to higher energy region. The shift of binding energy towards the higher energy region can be attributed to the transfer of electron density from Ti to NrGO in the prepared Ti/NrGO composite. Additionally, a shoulder peak at 456.9 eV is assigned to Ti³⁺ defects [51, 54]. Ti³⁺ species on the surface or in bulk TiO₂ are known to be unstable and easily oxidized upon calcination. However, these species are believed to be stabilized upon hybridization with N-doped reduced graphene oxide in our composite.

Figure 3D shows the Co 2p XPS spectrum of the Co/NrGO composite, which shows a complex structure of four overlapping doublets that can be ascribed to different contributions. The deconvolution of Co 2p profiles includes two pairs of spin-orbit doublet 2p_{3/2} and 2p_{1/2} implying the coexistence of Co²⁺ and Co³⁺ [17]. The first doublet of Co 2p_{3/2} and Co 2p_{1/2} at 781.1 eV and 796.1 eV respectively (separated by 15.03 eV) is related to Co₃O₄ [55]. The second doublet at 784.6 eV of Co 2p_{3/2} is associated to Co²⁺. The doublet centered at 787.5 eV could indicate the existence of Co-N bond [56, 57], and the Co 2p_{3/2} peak at 791.2 eV is assigned to shake-up (satellite) type peak, which indicates the presence of spinel Co₃O₄ with Co²⁺ in a tetrahedral coordination and an octahedral coordinated Co³⁺ [58].

Table 2. Summary of XPS data of the electrocatalysts (relative percentages in parenthesis).

Catalyst	BE (eV) N1s	BE (eV) Co2p _{3/2}	BE (eV) Ti2p _{3/2}	Surface metal loading (%wt)	Surface atomic ratio	
					Me/N	Me/C
Ti/NrGO	396.5 (8) 398.1 (30) 399.3 (24) 400.7 (22) 401.9 (16)	-	456.9 (12) 459.1 (88)	17	0.91	0.07
Co/NrGO	398.2 (35) 399.3 (26) 400.8 (27) 402.1 (12)	781.1 (43) 784.5 (29) 787.5 (28)	-	24	0.96	0.09

For better insight, the weight percentages of the elements are quantified using XPS and the corresponding values of atomic ratio Me/N and Me/C are presented in Table 2. The content of surface metal estimated from the XPS analysis is found to be 17 wt% for Ti/NrGO and 24 wt% for Co/NrGO. Both composites present similar atomic ratio Me/N and Me/C close to 0.9 and 0.08, respectively. The percentage of each type of nitrogen, titanium, cobalt and carbon species has been estimated by evaluating the total area of the individual peaks in the deconvoluted N 1s, Ti 2p, Co 2p and C1s respectively (Table 2). Comparing the Me/C

ratio from XPS (Table 2) and EA-ICP (Table 1), it appears that surface concentration is approximately the same as bulk concentration of metal species.

Figure 3. XPS high resolution spectra of: N1s of Ti/NrGO (A) and Co/NrGO (B) composites, Ti2p of Ti/NrGO composite (C) and Co2p of Co/NrGO composite (D).

3.2. Electrochemical characterization of composites towards oxygen reduction reaction (ORR)

The electrocatalytic activity of Ti/NrGO and Co/NrGO composites for the ORR was investigated by cyclic voltammetry in 0.1M NaOH aqueous solution (deaerated or saturated with O₂) and idle mode (no rotation). As shown in Figure 4, the CVs of the composites obtained in deaerated solution show a featureless voltammetric current, while their corresponding CVs obtained in O₂-saturated solution exhibit cathodic peaks corresponding to the reduction of O₂. This clearly indicates that both composites are electrochemically active for the ORR.

The cathodic sweep branch of Ti/NrGO and Co/NrGO composites recorded in O₂-saturated alkaline medium at a rotation rate of 1600 rpm is shown in Figure 4C. A commercial Pt/C (20 wt% Pt, Johnson & Matthey) catalyst was added for comparison. The voltammogram recorded in the deaerated electrolyte was used to subtract the capacitive current contribution from the curve measured in presence of O₂. As evidenced in Figure 4C, Pt/C shows the most positive onset potential, while the onset potential of the Co/NrGO is approximately 100 mV more positive than the one obtained with the Ti/NrGO composite (Table 3). Therefore, the ORR activity of the Co/NrGO is enhanced in comparison with the Ti/NrGO. 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 [29, 31, 59]. The enhanced electroactivity of the Co-based composite compared to the Ti-based one could be thus attributed to an improved kinetics for the catalytic sites derived from cobalt species [60]. Both in-house prepared NrGO-based catalysts present a lower net limiting diffusion current density (about -4.5 mA cm^{-2}) compared to Pt/C (-5.7 mA cm^{-2}), which is directly ascribed to a lower number of transferred electrons, according to the Levich equation, and as will be demonstrated by using Koutecký-Levich plots.

Figure 4. Cyclic voltammetries in N_2 and O_2 comparison of Ti/NrGO (A) and Co/NrGO (B) in 0.1M NaOH at a scan rate of $0.02 \text{ V}\cdot\text{s}^{-1}$. ORR linear voltammety of Co/NrGO, Ti/NrGO and commercial Pt/C catalyst (C) in 0.1M NaOH, at a scan rate of $0.005 \text{ V}\cdot\text{s}^{-1}$ and at rotation rate of 1600 rpm.

To gain insight into the electron-transfer kinetics involved in the ORR, polarization curves of the catalysts in O_2 -saturated 0.1M NaOH solution were measured at various rotation rates. Figure 5A and B display the voltammetric profiles of the polarization curves of Co/NrGO and Ti/NrGO composites, respectively. Both catalysts show an increased current intensity with increasing rotation rate due to the enhancement of the oxygen diffusion. For the study of the number of transferred electrons (n), Koutecký-Levich (K-L) plots derived from the ORR polarization curves have been plotted in Figure 5C and D [61], following the K-L equation (Equation 1):

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} = \frac{1}{j_k} + \frac{1}{0.62 n F C_{\text{O}_2} D_{\text{O}_2}^{2/3} \nu^{-1/6} \omega^{1/2}} \quad (\text{Eq. 1})$$

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_{O_2} is the diffusion coefficient of O_2 in 0.1M NaOH ($1.9 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), C_{O_2} is the solubility of O_2 in 0.1M NaOH ($1.2 \cdot 10^{-6} \text{ mol cm}^{-3}$) and ν is the kinematic viscosity of 0.1M NaOH ($1.1 \cdot 10^{-2} \text{ cm}^2 \text{ s}^{-1}$) [62-64].

Figure 5 Linear sweep voltammetries in O₂-saturated 0.1M NaOH aqueous solution for Co/NrGO (A) and Ti/NrGO (B) composites, the legend indicates RDE rotation rate, scan rate = 0.005 V·s⁻¹. Koutecký-Levich plots for Co/NrGO (C) and Ti/NrGO (D) composites at various electrode potentials.

The number of transferred electrons is similar for both composites, with values of 3.5 and 3.6 for the Ti-based and the Co-based composites, respectively. Moreover, n value barely changes with the applied potential, as observed in the inset graphs of Figures 5C and 5D. It indicates a reduction mechanism close to complete reduction of oxygen to water ($n = 4$) but with a small contribution of sites (about 25%) with partial reduction to hydrogen peroxide. As a consequence, the largest difference between the two composites was found in the potential at which oxygen reduction occurs rather than in the mechanism. Indeed, by comparing the half-wave potential reported in Table 3 ($E_{1/2}$), i.e. the potential in the mixed kinetic-diffusion controlled region, ORR takes place at an overpotential about 60 mV lower in the case of the cobalt-based composite. Nevertheless, the gap is still about 40 mV when compared to a Pt/C catalyst as a reference for the ORR.

Table 3 Electrokinetic parameters from ORR and OER electrochemical characterization

Sample	$E_{\text{onset ORR}}$ (V)	$E_{1/2}$ (V)	n (electron transfer)	$\Delta E_{1/2}$ after 6500 cycles (mV)	$E_{\text{onset OER}}$ (V)
Ti/NrGO	0.85	0.75	3.5	8	1.65
Co/NrGO	0.95	0.81	3.6	13	1.51
Pt/C	1.00	0.85	4.0	120	na
IrO ₂	na	na	na	na	1.53

na = not applicable

3.3. Electrochemical characterization of composites towards oxygen evolution reaction (OER)

The activity of composites and IrO₂ commercial sample (Alfa Aesar, 99% purity) toward OER by water oxidation in alkaline medium was studied by the ring-disk technique. The bottom panel of Figure 6 shows the anodic current delivered by the disk electrode during the anodic sweep potential, whereas the top panel depicts the current delivered by the ring electrode that is fixed at 0.4 V vs. RHE. Thus, molecular oxygen produced at the disk is further reduced at the ring and, consequently, the oxygen evolution reaction can be discerned from side reactions.

An anodic faradaic current is observed at potentials higher than 1.5 V vs. RHE for all catalysts. The onset potential for this anodic current increases in the following way: Co/NrGO < IrO₂ < Ti/NrGO. The rise of the ring signal indicates that anodic currents developed at the disk electrode at higher potentials than 1.5 V are related to the water oxidation reaction, i.e. oxygen evolution reaction. Moreover, the determination of the onset potential is more accurate from the ring signal since side reactions, such as formation of metal oxides, do not account to the ring current. The onset potential values for Co/NrGO and IrO₂ are 1.51 V and 1.53 V, respectively. It is noticeable the low activity of Ti/NrGO toward the OER in this potential range. Therefore, Co/NrGO composite develops the highest catalytic activity toward the OER.

Figure 6 OER activities of Ti/NrGO, Co/rGO and IrO₂ catalysts in 0.1 M NaOH at 1600 rpm. Low panel: Disk signal recorded at 5 mV·s⁻¹. Top panel: ring's current recorded at 0.4 V vs. RHE.

3.4. Composites electrochemical stability

To study the electrochemical stability of the catalysts, two different accelerated durability tests were performed. The first accelerated durability test was executed for the ORR by potential cycling between 0.4 and 0.9 V vs. RHE in O₂-saturated 0.1M NaOH electrolyte for 6500 cycles at a scan rate of 0.2 V s⁻¹. The ORR linear sweep voltammeteries before and after the potential cycling procedure are presented in the bottom panels of Figure 7(A-C). The half wave potential decay ($\Delta E_{1/2}$) for Ti/NrGO and Co/NrGO composites are found to be 8 mV and 13 mV, respectively (Table 3). Thus, the degradation in the composites is much less prominent than in the Pt/C catalyst (120 mV). On the other hand, the limiting current density decreased after cycling for our catalysts. According to Levich equation, this decay could be ascribed to either a variation of the number of transferred electrons (n) or to diffusion related phenomena, since the other parameters remained unchanged. The H₂O₂ formation yield, determined from the ring current directly associated to the formation of hydrogen peroxide, was observed to barely change after potential cycling, about 20% associated to $n = 3.6$. The electrochemical response in the deaerated electrolyte was also determined by cyclic voltammetry before and after the 6500 potential cycles, as shown in Figure 7(D-E). A significant increase of double layer capacitance was noticed, indicating the formation of oxygen functionalities on the graphene surface. Hence, a larger extent of surface oxidation may cause a slight decrease of apparent diffusion coefficient through the porosity of carbon composite, thus affecting negatively the limiting current density after the stability test. In any case, these accelerated durability results clearly indicate that both composites have remarkable stability under the induced electrochemical environments at relatively high

positive potentials which occur during fuel cell start/stop operation compared to a Pt-based benchmark catalyst.

Figure 7. ORR activity by linear sweep voltammetry at 1600 rpm (bottom) and H₂O₂ yield (top) by RRDE experiments in O₂-saturated 0.1M NaOH electrolyte at the beginning and after 6500 potential cycles (0.4-0.9 V vs. RHE) for Pt/C (A), Co/NrGO (B) and Ti/NrGO (C) catalysts. Cyclic voltammograms in the deaerated electrolyte before and after 6500 potential cycles for (D) Co/NrGO and (E) Ti/NrGO.

The second accelerated durability test consisted of chronopotentiometric measurement with rectangular cycles at 5 mA·cm⁻² for 180 s followed by open circuit (zero current) during 30 s, with a cut-off potential of 1.9 V vs. RHE. Figure 8 shows the stability cycles of Co/NrGO (Figure 8A) and Ti/NrGO (Figure 8B) in 0.1M NaOH. This kind of fast and highly demanding test accelerates the degradation of the material at highly positive potentials [37]. As can be ascertained from Figure 8A, the Co/NrGO sustains 18 cycles prior to reaching the cut-off potential (1.9 V vs. RHE) in the evolution region. Therefore, the stability of the composite is significantly improved by using cobalt in the composite. However, Ti/NrGO reaches the cut-off in the first charge-discharge cycle, which means that Ti composite is not stable enough under comparable oxygen production rate.

Figure 8 Chronopotentiometric rectangular cycles at 5 mA cm⁻² for the Co/NrGO (A) and Ti/NrGO (B) in 0.1M NaOH.

3.5. Interpretation of results

It is known that the nanostructures of highly graphitized carbon are greatly dependent on the employed transition metals and nitrogen–carbon precursors, which are directly correlated to their catalytic activity [1, 21]. Furthermore, the catalytic performance of the composites is related with the chemical nature of the surface catalytic sites, which essentially depends on the synthesis method. In this work, a simple one-pot method via gel formation has been used to synthesize composites of Co and Ti with N-doped graphene using urea as nitrogen source. The carbon derived from the carbonization process of urea-graphene serves as a matrix for hosting active nitrogen and metal moieties.

For N-doped graphene, although the origin of the kinetic activity of N-doped carbon materials is still being explored, extensive experimental and theoretical investigations point to those of pyridinic and quaternary nitrogen which play a crucial role in ORR activity [65, 66]. The differences in the electronegativity of quaternary N promote the exchange of electrons between N atoms and adjacent C p_z orbitals, and then O₂ dissociation on the adjacent C atoms is improved along with the formation of a strong chemical bond between O and C [67]. While pyridinic N can be beneficial for the onset potential, other N species such as pyrrolic or oxidized N contribute in a lesser extent to the ORR activity of carbon materials. Recent research has shown that pyridinic N in N-doped carbons creates the active sites for the ORR, accompanied by the formation of Lewis basic sites, on which the oxygen molecule is adsorbed on carbon atoms adjacent to the pyridinic N as the initial step of ORR [68]. But for metal-N_x/C, the situation might differ, the nature of the active sites remains under investigation [66]. In our composites, the percentage of pyridinic N and quaternary N depend on the transition metal used. According to Table 2 the total amount of pyridinic N and quaternary N is 52% in Ti/NrGO and 62 % in Co/NrGO, which seems to be important for improving the ORR activity of the Co/NrGO composite. But also, a possible Co-N interaction should not be discarded. Liang et al. reported a hybrid material containing Co₃O₄ nanocrystals grown on reduced graphene oxide, which exhibited excellent performance towards the ORR. They proposed that N groups could induce nucleation and anchor sites for Co₃O₄ nanocrystals [69].

Although the activity of the Ti/NrGO is not as good as that of Co/NrGO composite, it is important to note that we have obtained an active titanium-based composite in the ORR in alkaline environment, free of noble metal. The ORR onset potential for the Ti-based composite is 0.85V (vs. RHE) and the number of electrons transferred is 3.5, showing superior stability than Pt/C after accelerated potential cycling in alkaline solution. Recently, Boppella et al. reported the synthesis of active and stable hybrid material TiO₂/rGO hollow nanospheres for oxygen reduction reaction applications [51]. The results were attributed to a cooperative effect of the hybridization of TiO₂ with rGO, Ti³⁺ self-doping and the formation of a carbon-coating layer over the TiO₂ particles. Though the structure of our titanium-based composite differs from the previous one, TiO₂/rGO hollow nanospheres, we also observed the presence of Ti³⁺ species by XPS. The greatest novelty of our Ti/NrGO composite lies in the doping of graphene with nitrogen, which can facilitate interaction with Ti³⁺, as observed by XPS, and play an important role in providing an enhanced number of active sites for oxygen reduction reaction.

Due to the pyrolysis of precursor metals, a wide variety of structures are formed, and understanding which component of the composite is responsible for ORR and OER activities is tangled. According to XRD, chemical analysis and XPS results, the incorporation of Ti leads to a composite with both TiO₂ anatase and rutile crystalline phases and Ti³⁺ species stabilized upon hybridization with N-doped reduced graphene oxide. The ORR onset potential for the Ti-based composite is 0.85V (vs. RHE) and the number of electrons transferred is 3.5, showing superior stability than Pt/C after accelerated potential cycling in alkaline solution. However, this composite shows low activity and stability for the OER. On the other hand, the composite consisting of metallic Co and Co₃O₄ nanocrystals grown on N-doped reduced graphene oxide exhibits the best performance as bifunctional catalyst, with ORR and OER onset potentials of 0.95 V and 1.51 V (vs. RHE), respectively, and a number of electrons transferred of 3.6. The results reveal the presence of important structural features such as metallic Co as the predominant crystalline component, amorphous Co₃O₄ phase and a possible coordination of Co-N-doped graphene. All of them seem to be fundamental for the high activity and stability to ORR and OER.

In summary, in good agreement with electrochemical measurements, the addition of Co metals to N-doped graphene composite have demonstrated to be active for ORR and OER in alkaline environment. The synergy effects of nitrogen doped graphene and Co/Co₂O₃ benefit the active site formation and facilitate the high performance for oxygen reduction and evolution reactions. Therefore, Co/NrGO composite offers an excellent combination of high activity and long-term performance durability.

4. Conclusions

Cobalt and Titanium N-doped graphene composites have been synthesized by a one-step procedure through the reaction of graphene oxide, urea and metal precursor. The introduction of metal to the carbon-nitrogen matrix with graphene as carbon backbone induces changes in the surface chemistry with the creation of metal-nitrogen bonds, as deduced by XPS analysis. The synergy effects of nitrogen-doped graphene and Co/Co₂O₃ benefit the active site formation and facilitate the high performance for oxygen

reduction and evolution reactions. The addition of Ti and Co metals to N-doped graphene composites creates active sites for the ORR in alkaline environment. Furthermore, Co/NrGO exhibits higher activity as bifunctional catalyst for both ORR and OER than Ti/NrGO, but the latter exhibited slightly larger stability after potential cycling in ORR.

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References

- [1] G. Wu, A. Santandreu, W. Kellogg, S. Gupta, O. Ogoke, H. Zhang, H.-L. Wang, L. Dai, Carbon nanocomposite catalysts for oxygen reduction and evolution reactions: From nitrogen doping to transition-metal addition, *Nano Energy* 29 (2016) 83-110.
- [2] B. Paul, J. Andrews, PEM unitised reversible/regenerative hydrogen fuel cell systems: State of the art and technical challenges, *Renewable and Sustainable Energy Reviews* 79(Supplement C) (2017) 585-599.
- [3] Y. Wang, D.Y.C. Leung, J. Xuan, H. Wang, A review on unitized regenerative fuel cell technologies, part-A: Unitized regenerative proton exchange membrane fuel cells, *Renewable and Sustainable Energy Reviews* 65 (2016) 961-977.
- [4] N.-T. Suen, S.-F. Hung, Q. Quan, N. Zhang, Y.-J. Xu, H.M. Chen, Electrocatalysis for the oxygen evolution reaction: recent development and future perspectives, *Chemical Society Reviews* 46(2) (2017) 337-365.
- [5] N. Danilovic, R. Subbaraman, K.C. Chang, S.H. Chang, Y. Kang, J. Snyder, A.P. Paulikas, D. Strmcnik, Y.T. Kim, D. Myers, V.R. Stamenkovic, N.M. Markovic, Using Surface Segregation To Design Stable Ru-Ir Oxides for the Oxygen Evolution Reaction in Acidic Environments, *Angewandte Chemie International Edition* 53(51) (2014) 14016-14021.
- [6] M. Shao, Q. Chang, J.-P. Dodelet, R. Chenitz, Recent Advances in Electrocatalysts for Oxygen Reduction Reaction, *Chemical Reviews* 116(6) (2016) 3594-3657.
- [7] M. Roca-Ayats, G. García, J.L. Galante, M.A. Peña, M.V. Martínez-Huerta, Electrocatalytic stability of Ti based-supported Pt₃Ir nanoparticles for unitized regenerative fuel cells, *International Journal of Hydrogen Energy* 39(10) (2014) 5477-5484.
- [8] M. Roca-Ayats, E. Herreros, G. García, M.A. Peña, M.V. Martínez-Huerta, Promotion of oxygen reduction and water oxidation at Pt-based electrocatalysts by titanium carbonitride, *Applied Catalysis B: Environmental* 183 (2016) 53-60.
- [9] L. An, T.S. Zhao, Y.S. Li, Carbon-neutral sustainable energy technology: Direct ethanol fuel cells, *Renewable & Sustainable Energy Reviews* 50 (2015) 1462-1468.
- [10] A. Indra, P.W. Menezes, C. Das, Schmei, M. Driess, Alkaline electrochemical water oxidation with multi-shelled cobalt manganese oxide hollow spheres, *Chemical Communications* 53(62) (2017) 8641-8644.
- [11] Z. Shan, P.S. Archana, G. Shen, A. Gupta, M.G. Bakker, S. Pan, NanoCOT: Low-Cost Nanostructured Electrode Containing Carbon, Oxygen, and Titanium for Efficient Oxygen Evolution Reaction, *Journal of the American Chemical Society* 137(37) (2015) 11996-12005.

- [12] H.W. Zhang, D.Z. Chen, Y. Xianze, S.B. Yin, Anion-Exchange Membranes for Fuel Cells: Synthesis Strategies, Properties and Perspectives, *Fuel Cells* 15(6) (2015) 761-780.
- [13] M.V. Martínez-Huerta, M.J. Lázaro, Electrocatalysts for low temperature fuel cells, *Catalysis Today* 285 (2017) 3-12.
- [14] J.W. Desmond Ng, Y. Gorlin, T. Hatsukade, T.F. Jaramillo, A Precious-Metal-Free Regenerative Fuel Cell for Storing Renewable Electricity, *Advanced Energy Materials* 3(12) (2013) 1545-1550.
- [15] J.W.D. Ng, M. Tang, T.F. Jaramillo, A carbon-free, precious-metal-free, high-performance O₂ electrode for regenerative fuel cells and metal-air batteries, *Energy & Environmental Science* 7(6) (2014) 2017-2024.
- [16] C. Tang, Q. Zhang, Can metal-nitrogen-carbon catalysts satisfy oxygen electrochemistry?, *Journal of Materials Chemistry A* 4(14) (2016) 4998-5001.
- [17] Q. Wang, W. Hu, Y. Huang, Nitrogen doped graphene anchored cobalt oxides efficiently bi-functionally catalyze both oxygen reduction reaction and oxygen evolution reaction, *International Journal of Hydrogen Energy* 42(9) (2017) 5899-5907.
- [18] X. Zhong, Y. Jiang, X. Chen, L. Wang, G. Zhuang, X. Li, J.-g. Wang, Integrating cobalt phosphide and cobalt nitride-embedded nitrogen-rich nanocarbons: high-performance bifunctional electrocatalysts for oxygen reduction and evolution, *Journal of Materials Chemistry A* 4(27) (2016) 10575-10584.
- [19] J.-C. Li, P.-X. Hou, S.-Y. Zhao, C. Liu, D.-M. Tang, M. Cheng, F. Zhang, H.-M. Cheng, A 3D bi-functional porous N-doped carbon microtube sponge electrocatalyst for oxygen reduction and oxygen evolution reactions, *Energy & Environmental Science* 9(10) (2016) 3079-3084.
- [20] G. Wu, P. Zelenay, Nanostructured Nonprecious Metal Catalysts for Oxygen Reduction Reaction, *Accounts of Chemical Research* 46(8) (2013) 1878-1889.
- [21] Q. Li, R. Cao, J. Cho, G. Wu, Nanocarbon Electrocatalysts for Oxygen Reduction in Alkaline Media for Advanced Energy Conversion and Storage, *Advanced energy materials* 4(6) (2014).
- [22] L. Osmieri, R. Escudero-Cid, A.H.A. Monteverde Videla, P. Ocón, S. Specchia, Application of a non-noble Fe-N-C catalyst for oxygen reduction reaction in an alkaline direct ethanol fuel cell, *Renewable Energy* (2017).
- [23] L. Osmieri, A.H.A. Monteverde Videla, S. Specchia, Activity of Co-N multi walled carbon nanotubes electrocatalysts for oxygen reduction reaction in acid conditions, *Journal of Power Sources* 278 (2015) 296-307.
- [24] M. Ferrandon, A.J. Kropf, D.J. Myers, K. Artyushkova, U. Kramm, P. Bogdanoff, G. Wu, C.M. Johnston, P. Zelenay, Multitechnique Characterization of a Polyaniline-Iron-Carbon Oxygen Reduction Catalyst, *The Journal of Physical Chemistry C* 116(30) (2012) 16001-16013.
- [25] L. Osmieri, A.H.A. Monteverde Videla, S. Specchia, Optimization of a Fe-N-C electrocatalyst supported on mesoporous carbon functionalized with polypyrrole for oxygen reduction reaction under both alkaline and acidic conditions, *International Journal of Hydrogen Energy* 41(43) (2016) 19610-19628.
- [26] B.Y. Xia, Y. Yan, N. Li, H.B. Wu, X.W. Lou, X. Wang, A metal-organic framework-derived bifunctional oxygen electrocatalyst, 1 (2016) 15006.
- [27] J. Du, F. Cheng, S. Wang, T. Zhang, J. Chen, M(Salen)-derived Nitrogen-doped M/C (M = Fe, Co, Ni) Porous Nanocomposites for Electrocatalytic Oxygen Reduction, *Sci. Rep.* 4 (2014).
- [28] M.H. Seo, D. Higgins, G. Jiang, S.M. Choi, B. Han, Z. Chen, Theoretical insight into highly durable iron phthalocyanine derived non-precious catalysts for oxygen reduction reactions, *Journal of Materials Chemistry A* 2(46) (2014) 19707-19716.
- [29] B. Aghabarari, N. Nezafati, M. Roca-Ayats, M.C. Capel-Sánchez, M.J. Lázaro, M.V. Martínez-Huerta, Effect of molybdophosphoric acid in iron and cobalt graphene/chitosan composites for oxygen reduction reaction, *International Journal of Hydrogen Energy* (2017).

- [30] Y. Su, Y. Zhu, H. Jiang, J. Shen, X. Yang, W. Zou, J. Chen, C. Li, Cobalt nanoparticles embedded in N-doped carbon as an efficient bifunctional electrocatalyst for oxygen reduction and evolution reactions, *Nanoscale* 6(24) (2014) 15080-15089.
- [31] B. He, X. Chen, J. Lu, S. Yao, J. Wei, Q. Zhao, D. Jing, X. Huang, T. Wang, One-pot Synthesized Co/Co₃O₄-N-Graphene Composite as Electrocatalyst for Oxygen Reduction Reaction and Oxygen Evolution Reaction, *Electroanalysis* 28(10) (2016) 2435-2443.
- [32] S. Mao, Z. Wen, T. Huang, Y. Hou, J. Chen, High-performance bi-functional electrocatalysts of 3D crumpled graphene-cobalt oxide nanohybrids for oxygen reduction and evolution reactions, *Energy & Environmental Science* 7(2) (2014) 609-616.
- [33] M. Fayette, A. Nelson, R.D. Robinson, Electrophoretic deposition improves catalytic performance of Co₃O₄ nanoparticles for oxygen reduction/oxygen evolution reactions, *Journal of Materials Chemistry A* 3(8) (2015) 4274-4283.
- [34] T. Zhang, C. He, F. Sun, Y. Ding, M. Wang, L. Peng, J. Wang, Y. Lin, Co₃O₄ nanoparticles anchored on nitrogen-doped reduced graphene oxide as a multifunctional catalyst for H₂O₂ reduction, oxygen reduction and evolution reaction, *Scientific Reports* 7 (2017) 43638.
- [35] S. Sui, L. Ma, Y. Zhai, TiC supported Pt-Ir electrocatalyst prepared by a plasma process for the oxygen electrode in unitized regenerative fuel cells, *Journal of Power Sources* 196(13) (2011) 5416-5422.
- [36] R. Hahn, F. Schmidt-Stein, J. Salonen, S. Thiemann, Y. Song, J. Kunze, V.-P. Lehto, P. Schmuki, Semimetallic TiO₂ Nanotubes, *Angewandte Chemie International Edition* 48(39) (2009) 7236-7239.
- [37] W.S. Hummers, R.E. Offeman, Preparation of Graphitic Oxide, *Journal of the American Chemical Society* 80(6) (1958) 1339-1339.
- [38] J. Flórez-Montaño, A. Calderón-Cárdenas, W. Lizcano-Valbuena, J.L. Rodríguez, E. Pastor, Ni@Pt nanodisks with low Pt content supported on reduced graphene oxide for methanol electrooxidation in alkaline media, *International Journal of Hydrogen Energy* 41(43) (2016) 19799-19809.
- [39] C. Alegre, C. Busacca, O. Di Blasi, V. Antonucci, A.S. Aricò, A. Di Blasi, V. Baglio, A combination of CoO and Co nanoparticles supported on electrospun carbon nanofibers as highly stable air electrodes, *Journal of Power Sources* 364(Supplement C) (2017) 101-109.
- [40] C. Alegre, E. Modica, A.S. Aricò, V. Baglio, Bifunctional oxygen electrode based on a perovskite/carbon composite for electrochemical devices, *Journal of Electroanalytical Chemistry* (2017).
- [41] R.D. McKerracher, C. Alegre, V. Baglio, A.S. Aricò, C. Ponce de León, F. Mornaghini, M. Rodlert, F.C. Walsh, A nanostructured bifunctional Pd/C gas-diffusion electrode for metal-air batteries, *Electrochimica Acta* 174(Supplement C) (2015) 508-515.
- [42] A. Kaniyoor, T.T. Baby, T. Arockiadoss, N. Rajalakshmi, S. Ramaprabhu, Wrinkled Graphenes: A Study on the Effects of Synthesis Parameters on Exfoliation-Reduction of Graphite Oxide, *The Journal of Physical Chemistry C* 115(36) (2011) 17660-17669.
- [43] Y. Wu, S. Liu, H. Wang, X. Wang, X. Zhang, G. Jin, A novel solvothermal synthesis of Mn₃O₄/graphene composites for supercapacitors, *Electrochimica Acta* 90(Supplement C) (2013) 210-218.
- [44] K.N. Kudin, B. Ozbas, H.C. Schniepp, R.K. Prud'homme, I.A. Aksay, R. Car, Raman Spectra of Graphite Oxide and Functionalized Graphene Sheets, *Nano Letters* 8(1) (2008) 36-41.
- [45] Z.-H. Sheng, L. Shao, J.-J. Chen, W.-J. Bao, F.-B. Wang, X.-H. Xia, Catalyst-Free Synthesis of Nitrogen-Doped Graphene via Thermal Annealing Graphite Oxide with Melamine and Its Excellent Electrocatalysis, *ACS Nano* 5(6) (2011) 4350-4358.

- [46] X.-C. Dong, H. Xu, X.-W. Wang, Y.-X. Huang, M.B. Chan-Park, H. Zhang, L.-H. Wang, W. Huang, P. Chen, 3D Graphene-Cobalt Oxide Electrode for High-Performance Supercapacitor and Enzymeless Glucose Detection, *ACS Nano* 6(4) (2012) 3206-3213.
- [47] X. Wang, L. Song, H. Yang, W. Xing, H. Lu, Y. Hu, Cobalt oxide/graphene composite for highly efficient CO oxidation and its application in reducing the fire hazards of aliphatic polyesters, *Journal of Materials Chemistry* 22(8) (2012) 3426-3431.
- [48] A.H.A. Monteverde Videla, P. Stelmachowski, G. Ercolino, S. Specchia, Benchmark comparison of Co₃O₄ spinel-structured oxides with different morphologies for oxygen evolution reaction under alkaline conditions, *Journal of Applied Electrochemistry* 47(3) (2017) 295-304.
- [49] Z.S. Khalifa, Grain size reduction on nanostructured TiO₂ thin films due to annealing, *RSC Advances* 7(48) (2017) 30295-30302.
- [50] M.V. Martínez-Huerta, J.L.G. Fierro, M.A. Bañares, Monitoring the states of vanadium oxide during the transformation of TiO₂ anatase-to-rutile under reactive environments: H₂ reduction and oxidative dehydrogenation of ethane, *Catalysis Communications* 11(1) (2009) 15-19.
- [51] R. Boppella, J.-E. Lee, F.M. Mota, J.Y. Kim, Z. Feng, D.H. Kim, Composite hollow nanostructures composed of carbon-coated Ti³⁺ self-doped TiO₂-reduced graphene oxide as an efficient electrocatalyst for oxygen reduction, *Journal of Materials Chemistry A* 5(15) (2017) 7072-7080.
- [52] M.P.S. D.Briggs, in: M.P.S.E. D.Briggs, *Practical Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy*, Wiley, New York (1990).
- [53] M. Roca-Ayats, G. García, M. Soler-Vicedo, E. Pastor, M.J. Lázaro, M.V. Martínez-Huerta, The role of Sn, Ru and Ir on the ethanol electrooxidation on Pt₃M/TiCN electrocatalysts, *International Journal of Hydrogen Energy* 40(42) (2015) 14519-14528.
- [54] G. Fu, P. Zhou, M. Zhao, W. Zhu, S. Yan, T. Yu, Z. Zou, Carbon coating stabilized Ti³⁺-doped TiO₂ for photocatalytic hydrogen generation under visible light irradiation, *Dalton Transactions* 44(28) (2015) 12812-12817.
- [55] P. Chen, F. Yang, A. Kostka, W. Xia, Interaction of Cobalt Nanoparticles with Oxygen- and Nitrogen-Functionalized Carbon Nanotubes and Impact on Nitrobenzene Hydrogenation Catalysis, *ACS Catalysis* 4(5) (2014) 1478-1486.
- [56] Y. Chen, S. Jie, C. Yang, Z. Liu, Active and efficient Co-N/C catalysts derived from cobalt porphyrin for selective oxidation of alkylaromatics, *Applied Surface Science* 419(Supplement C) (2017) 98-106.
- [57] G. Wu, Z. Chen, K. Artyushkova, F.H. Garzon, P. Zelenay, Polyaniline-derived Non-Precious Catalyst for the Polymer Electrolyte Fuel Cell Cathode, *ECS Transactions* 16(2) (2008) 159-170.
- [58] S. Bala, I. Mondal, A. Goswami, U. Pal, R. Mondal, Co-MOF as a sacrificial template: manifesting a new Co₃O₄/TiO₂ system with a p-n heterojunction for photocatalytic hydrogen evolution, *Journal of Materials Chemistry A* 3(40) (2015) 20288-20296.
- [59] G. Wu, K.L. More, C.M. Johnston, P. Zelenay, High-Performance Electrocatalysts for Oxygen Reduction Derived from Polyaniline, Iron, and Cobalt, *Science* 332(6028) (2011) 443-447.
- [60] L. Osmieri, A.H.A. Monteverde Videla, P. Ocón, S. Specchia, Kinetics of Oxygen Electroreduction on Me-N-C (Me = Fe, Co, Cu) Catalysts in Acidic Medium: Insights on the Effect of the Transition Metal, *The Journal of Physical Chemistry C* 121(33) (2017) 17796-17817.
- [61] A.J. Bard, L.R. Faulkner, *ELECTROCHEMICAL METHODS: Fundamentals and Applications*, JOHN WILEY & SONS, INC. (2001).

- [62] R. Chen, H. Li, D. Chu, G. Wang, Unraveling Oxygen Reduction Reaction Mechanisms on Carbon-Supported Fe-Phthalocyanine and Co-Phthalocyanine Catalysts in Alkaline Solutions, *The Journal of Physical Chemistry C* 113(48) (2009) 20689-20697.
- [63] P. Singh, D.A. Buttry, Comparison of Oxygen Reduction Reaction at Silver Nanoparticles and Polycrystalline Silver Electrodes in Alkaline Solution, *The Journal of Physical Chemistry C* 116(19) (2012) 10656-10663.
- [64] S. Hebié, M. Bayo-Bangoura, K. Bayo, K. Servat, C. Morais, T.W. Napporn, K. Boniface Kokoh, Electrocatalytic activity of carbon-supported metallophthalocyanine catalysts toward oxygen reduction reaction in alkaline solution, *Journal of Solid State Electrochemistry* 20(4) (2016) 931-942.
- [65] J. Zhang, H. Li, P. Guo, H. Ma, X.S. Zhao, Rational design of graphitic carbon based nanostructures for advanced electrocatalysis, *Journal of Materials Chemistry A* 4(22) (2016) 8497-8511.
- [66] X.B. Liu, I.S. Amiinu, S.J. Liu, K. Cheng, S.C. Mu, Transition metal/nitrogen dual-doped mesoporous graphene-like carbon nanosheets for the oxygen reduction and evolution reactions, *Nanoscale* 8(27) (2016) 13311-13320.
- [67] D. Deng, X. Pan, L. Yu, Y. Cui, Y. Jiang, J. Qi, W.-X. Li, Q. Fu, X. Ma, Q. Xue, G. Sun, X. Bao, Toward N-Doped Graphene via Solvothermal Synthesis, *Chemistry of Materials* 23(5) (2011) 1188-1193.
- [68] D. Guo, R. Shibuya, C. Akiba, S. Saji, T. Kondo, J. Nakamura, Active sites of nitrogen-doped carbon materials for oxygen reduction reaction clarified using model catalysts, *Science* 351(6271) (2016) 361-365.
- [69] Y. Liang, Y. Li, H. Wang, J. Zhou, J. Wang, T. Regier, H. Dai, Co₃O₄ nanocrystals on graphene as a synergistic catalyst for oxygen reduction reaction, *Nat Mater* 10(10) (2011) 780-786.