N-doped graphene catalysts with high nitrogen concentration for the oxygen reduction reaction

Giovanni Lemes¹, David Sebastián¹, Elena Pastor², María J. Lázaro^{1*}

¹ *Instituto de Carboquímica (ICB-CSIC). C/ Miguel Luesma Castán 4, 50018, Zaragoza, Spain.*

² *Instituto Universitario de Materiales y Nanotecnología, Universidad de La Laguna. App 456, 38206, La Laguna, Spain.*

*Corresponding author: mlazaro@icb.csic.es

Abstract

Nitrogen doped reduced graphene oxide (NrGO) catalysts and composites of these with carbon nitride (CN) with nitrogen content as high as 19.8 wt% and 35.8 wt%, respectively, have been synthesized by thermal annealing of multilayer graphene oxide and urea at different temperatures. Nitrogen has been effectively introduced as a mix of pyridinic, pyrrolic, pyridonic and quaternary bonding configurations into the carbon lattice of graphene upon removal of CN phase over 650°C. The electrocatalytic activity towards oxygen reduction reaction (ORR) in 0.1 M NaOH has been investigated. NrGO catalysts with less nitrogen content show better performance than composites. NrGO produced at 800°C presents the best activity with half-wave potential of 0.76 V vs. RHE and a mean number of electrons of 3.7, which are close to a commercial Pt/C catalyst. This study concludes that a high concentration of nitrogen atoms in multilayer reduced graphene oxide does not necessarily produce a highly active electrocatalyst, suggesting that carbon in the neighbourhood of nitrogen atoms are the active sites for ORR in alkaline medium.

Keywords

Oxygen Reduction Reaction; Graphene; Carbon Nitride; Nitrogen doping; Electrocatalyst

1. Introduction

Green energy systems have been intensively studied as necessary alternative due to the global energy demand-growth and the exhaustion of fossil fuels [1]. In this field, fuel cells (FCs) are clean and efficient electrochemical devices that continuously and directly convert the chemical energy of externally supplied fuel and oxidant to electrical energy [2]. Platinum is the most used electrocatalyst at the cathode of commercial FCs, but its high cost and scarcity are limiting the large-scale commercialization of this technology [3]. Therefore, developing low-cost and high performance oxygen reduction reaction (ORR) electrocatalysts is an important point in FCs research and development [4–9]. Carbon-based materials have been studied as alternative to Pt because they present a promising activity for the ORR in alkaline environment, larger availability and low cost [10,11].

Graphene (G) is a two-dimensional (2D) carbon material consisting of sp^2 carbon atoms with high mechanical strength, high thermal and chemical stability, high electrical conductivity and large surface area [11]. Furthermore, the modification of the surface via nitrogen-doping tunes the chemical nature of the active sites improving the electrocatalytic activity towards ORR [12–14]. Several methods have been investigated for the doping of graphene sheets with nitrogen and other heteroatoms including B, S and P [15–18]. Yu et al. investigated the influence of morphology concluding that a 2D arrangement of graphene sheets favors the electrocatalytic activity due to a higher accessibility to active sites [19]. Zhang et al. attributed the enhanced activity of doped graphene to the density of nitrogen-carbon active sites [20]. There is not a unanimous opinion about which nitrogen species improves the ORR activity. On the one hand, some authors observed that increasing quaternary nitrogen content on carbon resulted in an improvement of ORR activity [21–24]; on the other hand, some other works led to conclude that pyridinic moiety has a key role for ORR activity [25–27]. Finally, some authors recognize the positive influence of both pyridinic and quaternary nitrogen species [8,11,28]. In any case, current doping procedures based on thermal annealing of graphene oxide (GO) with nitrogen-

rich precursors, allow the introduction of a limited amount of nitrogen, not higher than 18 wt% [29].

Graphitic carbon nitride (CN) is analogous in structure to graphite, possesses high nitrogen content (61 wt% in C_3N_4) and has been proposed as potential electrocatalyst for the ORR [30,31]. Unfortunately, CN usually presents a nonporous structure characterized by a very low surface area [32]. A composite material of CN and G should hypothetically combine a graphene based structure with a very high density of nitrogen active sites [33,34].

Graphene oxide (GO) synthesized by Hummers' method has been widely used as precursor to obtain reduced graphene oxide (rGO) based electrocatalysts [35–37]. On the other hand, urea has been used as nitrogen source on GO doping procedures and to synthesize CN because it is a low-cost industrial material and acts as good reducing agent [23,38–40]. During the annealing process under inert atmosphere, urea decomposes to form organic intermediates (melamine, melem, melon, etc.) which finally produce CN [41,42]. Meanwhile, gaseous NH_3 and carbon nitride, produced during urea decomposition, are used as both reducing and expanding agents, as well as nitrogen sources for the incorporation of nitrogen atoms into the graphene matrix [11,43]. An important aspect regarding the annealing procedure is that the treatment temperature is limited, since CN decomposes at 700°C [44].

In this work, a one-step doping procedure was used to obtain nitrogen-doped reduced graphene oxide (NrGO) and composites of the latter with carbon nitride (CN), as a function of the treatment temperature. CN-NrGO composites with nitrogen content as high as 35.8 wt% and NrGO with 19.8 wt% of nitrogen were successfully synthesized and studied as electrocatalysts for ORR for the first time.

2. Experimental

2.1. Reagents and materials

Graphite powder (>99.8%), KMnO_4 (>99.8%), urea (98%) and NaOH (99.99%) were purchased from Sigma-Aldrich, concentrated H_2SO_4 and H_2O_2 (30% v/v) were provided by Merck and Foret, respectively. High purity N_2 and O_2 (Carburos Metálicos, Spain) were used for the deaeration of electrolyte solutions and the preparation of O_2 -saturated solutions, respectively. All aqueous solutions were prepared with ultrapure water (Milli-Q water, 18.2 M Ω cm).

2.2. Synthesis of GO

GO was synthesized according to modified Hummers' method by exfoliation of graphite [35,36]. Briefly, 1 g of the graphite powder was added to 30 mL of concentrated H_2SO_4 cooled in an ice bath. Then 3.5 g of KMnO_4 was gradually added to the previous dispersion while stirring and cooling continuously. The mixture was then diluted with 52 mL of ultrapure water and stirred for 1 hour at 35 °C. Subsequently, the solution was heated to 98 °C and left for another 30 minutes. Next, 200 mL of ultrapure water was slowly introduced followed by 1.25 mL of 30% v/v H_2O_2 , maintaining the stirring for 30 minutes. Finally, the obtained GO was thoroughly washed with water and centrifuged several times until the supernatant becomes neutral pH and then dried at 60 °C overnight.

2.3. Synthesis of rGO and NrGO

In a typical synthesis of NrGO, 500 mg of GO was dispersed in 25 mL of ultrapure water and 5 g of urea was added. The mixture was sonicated for 30 minutes and then dried at 60 °C. The solid was transferred to a furnace for thermal annealing at different temperatures (500 °C, 600 °C, 700 °C, 800 °C) for 2 hours under N_2 flow. These samples are denoted as CN-NrGO500, CN-NrGO600, NrGO700 and NrGO800, respectively. For the rGO, the process was identical without urea and the annealing process took place at 600 °C.

2.4. Physical characterization

The physical properties of the prepared catalysts were obtained via X-ray diffraction (XRD), elemental analysis (EA), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), physisorption, Raman spectroscopy and transmission electron microscopy (TEM).

XRD measurements were conducted using powder diffraction procedures analyzed by Cu K α radiation (power 1600 W) generated in a Bruker D8 Advance diffractometer. Raman spectroscopy measurements were performed using a Horiba Jobin Yvon HR800 UV with a 532 nm laser. EA was performed using a Thermo Flash 1112 analyser. Textural properties were measured with a Micromeritics ASAP 2020 instrument, and the specific surface area was calculated applying the Brunauer-Emmer-Teller (BET) equation. XPS was performed with ESCA+ OMICRON system using Mg K α radiation ($h\nu = 1253.6$ eV). The deconvolution of the N1s peaks was carried out with CasaXPS software considering the sensitivity factors provided by the manufacturer, Shirley background and a 70% Gaussian/30% Lorentzian line shape. TGA was recorded on a Libra F1 Netzsch thermobalance under inert atmosphere. TEM images were observed using a JEOL-2000 FXII microscopy operated at 200 kV, dispersing the samples ultrasonically in ethanol and depositing a few drops onto copper grids covered with Lacey carbon film.

2.5. Electrochemical measurements

Oxygen reduction reaction (ORR) activity was measured at room temperature with a μ AUTOLABIII potentiostat/galvanostat in a three-electrode electrochemical cell and using a 3 mm diameter glassy carbon (GC) rotating disk electrode (RDE) as working electrode, a reversible hydrogen electrode (RHE) as reference electrode, and a high surface carbon rod as counter electrode. The electrolyte used was 0.1 M NaOH. To prepare the graphene-based catalyst ink, 2 mg of powder was dispersed in a mixture of 0.306 mL of water, 0.061 mL of isopropyl alcohol and 15 μ L of Nafion solution (5 wt%). The mixture was sonicated to form a

well dispersed and homogenous ink. 20 μL of catalyst ink was dropped on the polished RDE. Catalyst loading on the RDE was $1100 \mu\text{g}\cdot\text{cm}^{-2}$. A Pt/C (E-TEK, 20 wt% Pt) commercial catalyst was evaluated for comparison purposes, with a similar ink preparation procedure for a Pt/C loading of $250 \mu\text{g cm}^{-2}$.

3. Results and discussion

3.1. Materials characterization

The crystalline structure of the prepared materials has been studied by XRD analysis. Figure 1a displays the diffractogram patterns of all samples while the dashed vertical line indicates the position of the reflection associated to the (002) plane of graphite (JCPDS #08-0415). Structural parameters determined by XRD are summarized in Table 1. The mean inter-layer spacing (d_{002}) was estimated applying Bragg's law, and mean crystallite size along the c-axis (L_c) was calculated applying the Scherrer formula to (002) reflection, with $K = 0.89$ [45]. The average number of layers was calculated using $n = (L_c/d_{002})+1$. The XRD pattern of GO is the typical of multilayer graphene materials and exhibits a unique diffraction peak at $2\theta = 10.8^\circ$, corresponding to an inter-planar distance of 0.820 nm. This value is much higher than the inter-planar distance of graphite (0.336 nm) because of the proliferation of functional groups within the graphenic layers during the oxidation and exfoliation of graphite to GO. Whereas, the XRD of rGO shows a broad peak at $2\theta = 26.4^\circ$, equivalent to layer-to-layer distance of about 0.338 nm and a small peak at $2\theta = 12.0^\circ$, related to traces of non-reduced GO. All the N-doped graphene and composite samples exhibit a single reflection centred at 2θ between 26.3° and 26.6° , and no peaks at 11° - 12° . This indicates the absence of GO and the effective reduction of materials upon thermal annealing with urea.

Sample	(002) peak position ($^\circ$)	d_{002} (nm)	L_c (nm)	Number of layers
Graphite	26.56	0.336	51.7	~150
CN	27.23	0.327	3.55	12
GO	10.77	0.820	6.49	9

rGO	26.35	0.338	3.92	12
CN-NrGO500	26.59	0.335	2.92	10
CN-NrGO600	26.59	0.335	2.93	10
NrGO700	26.40	0.337	2.62	9
NrGO800	26.31	0.338	3.65	12

Table 1. Comparison of crystallographic parameters obtained by XRD

Figure 1b shows the diffractogram in detail of the (002) reflection for nitrogen-doped and composite materials and the relative position of rGO and CN. CN-NrGO500 and CN-NrGO600 samples present a broad diffraction peak at $2\theta = 26.6^\circ$, while in NrGO700 and NrGO800 it appears at 26.4° and 26.3° , respectively. The calculated inter-planar distances are 0.335 nm (CN-NrGO500 and CN-NrGO600), 0.337 nm (NrGO700) and 0.338 nm (NrGO800). Tighter packaging of CN-NrGO500 and CN-NrGO600 is attributed to the presence of graphitic carbon nitride (CN) which is characterized by an inter-layer distance of 0.326 nm ($2\theta = 27.3^\circ$) [44,46]. On the other hand, rGO, NrGO700 and NrGO800 present similar distance between graphene sheets. This result (> 0.336 nm) can be attributed to the absence of CN in the samples treated at high temperature together with the presence of trace amounts of residual oxygenated groups within rGO sheets [44,47].

Figure 1. XRD patterns of (a) N-doped reduced graphene oxide catalysts, rGO, GO and graphite; (b) detailed XRD pattern of N-doped materials on carbon (002) diffraction peak.

Raman spectroscopy analysis (Figure S1) gives information about the structure and ordering degree of carbon materials. In particular, the ratio between D and G peaks (I_D/I_G), displayed in Figure 2, can be used to evaluate the disordering degree in graphene [48–51]. The I_D/I_G ratio decreases from 1.28 in GO to 1.04 in rGO, because the thermal reduction process causes a

diminution of the oxygenated groups within the graphene lattice, and thus the ordering degree rises. Interestingly, the samples treated with urea present higher I_D/I_G ratios than GO and rGO. This effect could be attributed to the incorporation of nitrogen into the carbon matrix, increasing the number of defects into the structure, even if they are characterized by a lower oxygen concentration and higher reduction degree than rGO, as evident from EA and XRD. In addition, I_D/I_G ratio slightly decreases with the annealing temperature, most probably because the presence of the CN phase in the composites contributes with a higher I_D/I_G ratio than doped graphene alone [52]. The in-plane crystallite size (L_a) was calculated from I_D/I_G ratio using the Tuinstra and Koenig equation [53]. Figure 2 shows L_a is lower for all the samples treated with urea because it produces an expansion during its decomposition, causing mechanically the partial break of the graphenic structure [11]. Whereas, rGO presents higher crystallite size because the thermal reduction without urea recovers part of the graphitic structure.

Figure 2. Histogram of I_D/I_G ratio and L_a obtained by Raman.

The chemical composition of all samples was determined by EA. As can be seen in Figure 3a, the oxygen content decreases from 45.9 wt% on GO to 11.6 wt% in rGO because of the

thermal reduction process with consequent removal of oxygen groups. The oxygen content of the N-doped samples is less than 6 wt%. This lower oxygen content compared to rGO is a consequence of the reducing power of urea. Figure 3b shows the atomic carbon/oxygen ratio increase with the thermal treatment. It is ascribed to the decomposition of CN and the oxygenated functional groups of GO.

Nitrogen content also decreases with the increment of the treatment temperature. Catalysts treated at 500 °C and 600 °C have a 35.8 wt% and 30.6 wt% of nitrogen, respectively, because of the presence of CN in the composite. NrGO700 and NrGO800 also have a high concentration of nitrogen (19.8 wt% and 13.5 wt%, respectively) but evidences in TGA results indicate that this heteroatom is linked to the graphene lattice (see TGA discussion) and does not come from CN. The diminution of nitrogen content with temperature is due to the decomposition of labile nitrogen groups (see XPS discussion).

Figure 3. Histograms of (a) chemical composition in weight percentage and (b) C/O atomic ratio of N-doped reduced graphene oxide catalysts, rGO and GO by elemental analysis.

TGA under nitrogen gas flow results are displayed in Figure 4. The composites (CN-NrGO500 and CN-NrGO600) exhibit an important weight loss with maximum rate occurring at approximately 650 °C (Figure 4b). NrGO700 and NrGO800 present a continuing trend with no breaking point. The weight loss at about 650 °C is a consequence of the CN decomposition,

becoming unstable above 600 °C [44]. Thus, these results demonstrate that CN-NrGO500 and CN-NrGO600 are composites of carbon nitride with reduced graphene oxide, containing 42 wt% and 31 wt% of CN, respectively, while CN is not present in NrGO700 and NrGO800 samples. This confirms also the XRD and EA evidences as discussed before.

Figure 4. (a) Thermogravimetric and (b) differential thermogravimetric analyses under nitrogen atmosphere of N-doped reduced graphene oxide catalysts.

The chemical speciation of nitrogen was characterized by the analysis of N1s peak in XPS, as shown in Figure 5. Five N functionalities can be associated to the NrGO phase: pyridinic N (398.2 eV), pyrrolic N and pyridonic N (399.7 eV), quaternary N (401.0 eV) and N-O (403 eV) as shown in Figure 5 [54,55]. Whereas, three N functionalities can be identified in CN: N1 (398.7 eV), N2 (399.7 eV) and N3 (401.0 eV) as shown in Figure S2 of the supporting information [40]. It must be considered here that the signals related to pyrrolic N, pyridonic N and N2 overlap at 399.7 eV, while quaternary N and N3 have also similar binding energies at about 401 eV, making these two groups of species undistinguishable by XPS. Other nitrogen moieties can be more easily differentiated: pyridinic N and N1 appear at slightly different binding energies, pointing out the presence of NrGO and CN, respectively.

The samples treated at 500 °C and 600 °C show N1 as the principal contribution, while the content of pyridinic N is almost negligible. In bare CN, 64% of nitrogen is in the form of N1, as shown in Table 2. Moreover, in CN-NrGO500 and CN-NrGO600 the N1 moiety represents about 40%. This lower percentage of N1 moiety on the composite materials obtained at 500-600°C suggests that part of nitrogen is introduced in the graphitic lattice of rGO as either pyrrolic N, pyridonic N or quaternary N. These results thus confirm the presence of the CN phase and the starting of the doping process at 500-600°C [56–58]. On the other hand, pyridinic nitrogen is the most abundant moiety in NrGO700 and NrGO800, while N1 signal has disappeared. This aspect proves the absence of CN upon annealing at temperatures higher than the decomposition of CN (approximately at 650 °C). C1s spectra (Figure S3) also show a peak at 288.2 eV related to CN structure which does not appear in NrGO700 and NrGO800 [44]. This is an additional indication of the removal of carbon nitride upon annealing at 700 and 800°C.

Sample	at % N	Pyridinic 398.2 eV	N1 398.7 eV	Pyrrolic- Pyridonic N2 400.0 eV	Quaternary N3 401.0 eV	N-Oxides 403.0 eV
CN	47.7	0	64.3	21.6	14.1	0
CN-NrGO500	38.4	0	38.1	30.1	27.8	3.9

CN-NrGO600	22.9	3.6	41.8	34.8	19.6	0.2
NrGO700	15.0	49.5	0	28.7	20.4	1.4
NrGO800	12.9	41.3	0	31.5	24.2	3.0

Table 2. N1s distribution for doped samples determined by XPS

Figure 5e depicts the net atomic content of each nitrogen moiety (at%) as a function of the treating temperature. On CN-NrGO composites, the loss of nitrogen is substantial by treating the sample at 600°C if compared to that obtained at 500°C, and N1, N2 and N3 moieties diminish. Concerning NrGO samples, the concentration of pyridinic N decreases from 7.4% to 5.4% by upon annealing at a temperature 100 °C higher, while pyrrolic/pyridonic N and quaternary N barely decrease, presenting thus a larger thermal stability [42].

Figure 5. Nitrogen 1s XPS analyses of (a) CN-NrGO500; (b) CN-NrGO600; (c) NrGO700; (d) NrGO800; (e) Atomic speciation of nitrogen with respect to total atomic content (from XPS N1s and survey analyses).

Representative TEM images in Figure 6 reveal a homogeneous morphology in all samples. The typical laminar structure of graphene with partially corrugated 2-dimensional sheets is clearly recognized in GO and rGO samples. Interestingly, CN-NrGO500 displays a completely different aspect (Figure 6c), related the presence of a different phase covering the graphene sheets,

which suggests that CN grew on graphene layers forming a composite [52]. This newly observed phase is more evident in the borders of graphene sheets, as identified by a darker homogeneous bordering layer with thickness of approximately 10 nm. Moreover, during the acquisition of the images, the CN-NrGO composites framework exhibited continuous movement as they were more affected by the electron beam of TEM, which is typically observed in thin films with lower conductivity, as it is our case with the CN phase [52]. Whereas, the TEM images of CN-NrGO600 (Figure 6d) do not present obvious presence of this darker phase attributable to CN but only some traces, which suggests a lower content of CN, according also to TGA results. N-doped graphene oxide presents a similar morphology than reduced graphene oxide in the case of CN-NrGO600, NrGO700 and NrGO800, where wrinkled graphene sheets are recognizable (Figures 6d-7f). It confirmed thus that CN was completely removed at temperatures higher than 600 °C.

To further investigate the textural properties of the catalysts, nitrogen physisorption experiments were carried out. Figure S4a displays the nitrogen adsorption/desorption isotherms. Interestingly, adsorbed nitrogen increases with the annealing temperature of the N-doped samples. This behavior agrees with the previous discussion, because CN phase has a poor porous development [32], thus confirming the removal of CN and the increase of porosity. BET surface area also increases with the annealing temperature (Figure S4b). GO displays the highest BET surface area because the interlayer spacing is higher than in reduced samples. Moreover, GO, NrGO700 and NrGO800 present larger hysteresis than the composites, suggesting that the doped samples present mesoporous structure.

Figure 6. Representative TEM images of (a) GO; (b) rGO; (c) CN-NrGO500; (d) CN-NrGO600; (e) NrGO700; (f) NrGO800.

3.2. Electrocatalytic reduction of oxygen

The catalytic activity of NrGOs towards ORR was evaluated in an RDE with hydrodynamic voltammetry in 0.1 M NaOH solution at room temperature. Figure 7a displays the comparison of the linear sweep voltammetry (LSV) curves obtained in O₂-saturated electrolyte with a rotation rate of 1600 rpm, including a commercial Pt/C catalyst for comparison purposes. The graphene-based samples show the typical sigmoidal wave, approaching a negative constant current density (cathodic) when scanning the potential from 1 V vs. RHE towards more negative values (i.e. larger overpotentials). Such current plateau is known as the diffusion limiting current density (i_d) and is given by the Levich equation to rely on the number of electrons and the characteristics of the electrolyte. The maximum current density among noble metal-free catalysts was obtained for the sample treated at the highest temperature: NrGO800. rGO and CN-NrGO500 present similar diffusion limiting current densities (1.6 mA·cm⁻²), but the introduction of nitrogen in the latter (composite) results in a negative shift for the reaction at low current density of about 80 mV compared to the undoped graphene material. For the rest of N-doped graphene samples, the higher the annealing temperature the higher the current density at a fixed potential.

Table 3 presents some ORR electro-kinetic parameters, including the onset and half-wave potentials, the number of transferred electrons (n) at 0.2 V vs. RHE, the kinetic current density (i_k) at 0.6 V vs. RHE, as well as the Tafel slope (b) and the exchange current density (i_0). The onset potential gives an indication of the energy required to initiate the reduction reaction. CN-NrGO500, CN-NrGO600 and rGO require much larger overpotential to start the ORR, while NrGO700 and NrGO800 onset potentials are much closer to the commercial Pt/C catalyst. The half-wave potential serves also as a good indicator of the catalytic activity in the kinetic-diffusion mixed region. The better ORR performance of nitrogen doped graphene catalysts compared with rGO can be attributed to the presence of N atoms on the graphene lattice creating more active sites [23]. However, it seems that the activity is not directly related with

the nitrogen content but, on the contrary, it follows an indirect correlation. Indeed, CN-NrGO composites (annealing process at 500 °C and 600 °C) characterized by the highest nitrogen content present lower activity than their NrGO counterparts treated at 700 °C and 800 °C. This phenomenon could be ascribed to the low electrical conductivity of the carbon nitride phase, hindering electron transport and charge transfer [59,60]. In addition to this, the nitrogen species which controls the ORR is still an open discussion [24,25,59,61].

The Koutecky-Levich (K-L) plots were constructed based on LSV curves at different rotation rates and K-L equation (Equation 1), where i is the measured current density, i_k is the kinetic current density, n is the electron transfer number, F is Faraday's constant (96485 C·mol⁻¹), C_{O_2} is the saturation concentration of dissolved oxygen in the electrolyte (1.16·10⁻⁶ mol·cm⁻³), D_{O_2} is the diffusion coefficient of oxygen in the solution (1.9·10⁻⁵ cm²·s⁻¹), ν is the solution kinetic viscosity (0.011 cm²·s⁻¹) and ω is the rotation rate (rad·s⁻¹) [62].

$$1/i = 1/i_k + 1/(0.62 \cdot n \cdot F \cdot C_{O_2} \cdot D_{O_2}^{2/3} \cdot \nu^{-1/6} \cdot \omega^{1/2}) \quad (1)$$

Two different reaction mechanisms are commonly accepted for the ORR in alkaline media: a sequential 2x2-electron pathway (Equations 2 and 3) and a direct 4-electron pathway (Equation 4) [63].

Figures 7b and 7d display the polarization curves of NrGO700 and NrGO800 respectively, at different rotation rates. These catalysts are the most active ones in the present investigation. The diffusion-limited current density increases with the rotation rate, which indicates that the

ORR is under reactant's diffusion control according to K-L equation. Figures 7c and 7e represent K-L plots of NrGO700 and NrGO800, respectively, at three different potentials. A linear behaviour of the inverse current with the inverse of the square root of rotation speed is observed. The slopes related to 2 and 4 electrons transfer mechanisms are included into the graphs as a reference (dotted lines). NrGO700 catalyst exhibits a slight increase in the K-L slope with overpotential, *i.e.* indicating a 4 electrons transfer mechanism at 0.6 V vs. RHE but a mixed $2e^-/4e^-$ mechanism at larger overpotentials (0.2 and 0.4 V vs. RHE). On the other hand, NrGO800 appears to proceed through $4e^-$ regardless the applied potential. Table 3 displays n values calculated at 0.2 V vs RHE, this is, in the diffusion controlled zone, aimed to compare the whole set of catalysts. rGO, CN-NrGO500, CN-NrGO600 and NrGO700 present n values of 2.4, 2.9, 3.0 and 3.2 respectively, while NrGO800 and commercial Pt/C exhibit a number of electrons much closer to 4, with $n = 3.7$ and 3.9, respectively. The results indicate a mixed $2 \times 2e^-$ mechanism with increased importance of a more efficient reduction of oxygen as the annealing temperature increases.

Figure 7. Electrocatalytic performance towards ORR in O_2 -saturated 0.1 M NaOH electrolyte. Scan rate $2 \text{ mV}\cdot\text{s}^{-1}$: (a) LSVs at 1600 rpm; (b) LSVs of NrGO700 at different rotation speeds; (c) Koutecky-Levich plot of NrGO700 at different potentials; (d) LSVs of NrGO800 at different rotation speeds ; (e) Koutecky-Levich plot of NrGO800 at different potentials; (f) Tafel plots of N-doped reduced graphene oxides, rGO and Pt/C catalysts.

The kinetic current density (i_k) was also calculated from the intercept of the K-L plots with the Y-axis at 0.6 V vs RHE, this is, in the mixed kinetic-diffusion control region. The trend of kinetic current follows the previous discussion, with absolute value increasing from $8.5 \text{ mA}\cdot\text{cm}^{-2}$ to $104 \text{ mA}\cdot\text{cm}^{-2}$ with the annealing temperature (Table 3), being the maximum the one obtained for NrGO800, which indicates a better turnover frequency.

The differences in the catalytic behaviour were further analysed by Tafel plots (Equation 5) applied to the LSV recorded at 1600 rpm. iR -free potential ($E_{iR\text{-free}}$) was obtained by removing the ohmic overpotential to experimental data. To do this, the ohmic resistance was obtained by AC electrochemical impedance spectroscopy experiments at high frequency ($> 10 \text{ kHz}$) at

open circuit potential, which was close to 70 $\Omega \cdot \text{cm}^2$ in all experiments. The exchange current density (i_o) was calculated as the intercept of the linear fitting with the X-axis at the reversible potential for ORR (1.23 V vs. RHE), b is the Tafel slope and i_k is the kinetic current density.

$$E_{iR-rrse} = a + b \log(i_k) \quad (5)$$

Tafel plots are useful to study the reaction mechanism and to identify the rate determining step (rds) of the process through the calculated Tafel slope. In this context, it is accepted that O_2 can be reduced in alkaline media following two different reaction mechanisms [37]:

Associative mechanism:

Dissociative mechanism:

In N-doped carbon materials, the associative mechanism is more energetically favored [64]. In this case, a Tafel slope of $60 \text{ mV}\cdot\text{dec}^{-1}$ (close to $2.3RT/F$ at room temperature) is associated to Equation 8 as the *rds* [65], while larger values may indicate a change in the ORR mechanism to a less effective reaction pathway. Figure 7f represents the Tafel plots at low overpotential of graphene-based catalysts, together with commercial Pt/C, and Table 3 summarizes the calculated Tafel slope values. For Pt/C, NrGO800 and rGO, Tafel slopes are $59.1 \text{ mV}\cdot\text{dec}^{-1}$, $65.4 \text{ mV}\cdot\text{dec}^{-1}$ and $63.2 \text{ mV}\cdot\text{dec}^{-1}$, respectively. The other catalysts of the series present higher Tafel slopes of $70.8 \text{ mV}\cdot\text{dec}^{-1}$, $83.5 \text{ mV}\cdot\text{dec}^{-1}$ and $98.3 \text{ mV}\cdot\text{dec}^{-1}$ for CN-NrGO600, NrGO700 and CN-NrGO500, respectively. In general, the increase of annealing temperature for both composite CN-NrGO and NrGO materials results in a decrease of the Tafel slope from approximately $100 \text{ mV}\cdot\text{dec}^{-1}$ towards $60 \text{ mV}\cdot\text{dec}^{-1}$. A Tafel slope of $120 \text{ mV}\cdot\text{dec}^{-1}$ is indicative of a mechanism in which the first electron transfer (Equation 7) represents the *rds*. Being the associative mechanism the dominating for ORR in N-doped graphene [64], it appears that the *rds* changes from Equation 7 ($120 \text{ mV}\cdot\text{dec}^{-1}$) towards Equation 8 ($60 \text{ mV}\cdot\text{dec}^{-1}$) as the annealing temperature increases. This could be related to the slower transfer of electrons at the surface of the CN phase in the composites, and its removal leads to a more efficient mechanism of ORR in the N-doped graphenes.

The exchange current density (i_0 , Table 3) is a parameter that represents the electrochemical reaction rate at equilibrium ($E^0 = 1.23 \text{ V vs. RHE}$), and determines how rapidly the electrochemical reaction can occur [2]. Interestingly, NrGO700 presents higher i_0 than commercial Pt/C catalyst and one order of magnitude higher than the NrGO800 catalyst. On the other hand, the calculated i_0 for CN-NrGO composites are in the same order of magnitude than NrGO800, while rGO exhibits an i_0 two orders of magnitude lower than N-doped reduced graphene oxide catalysts.

	n	$i_k \text{ (mA}\cdot\text{cm}^{-2})$ @ 0.6 V vs.	Onset potential	Half-wave potential	Tafel slope ($\text{mV}\cdot\text{dec}^{-1}$)	i_0 ($\text{mA}\cdot\text{cm}^{-2}$)

	@ 0.2 V vs. RHE	RHE	(V vs. RHE) @ -0.1 mA·cm ⁻²	E _{1/2} (V vs. RHE)	@1600rpm	@ 1.23 V vs. RHE
rGO	2.36	24.2	0.77	0.65	63.2	6.44·10 ⁻⁹
CN-NrGO500	2.86	8.54	0.70	0.56	98.3	4.46·10 ⁻⁷
CN-NrGO600	3.01	41.9	0.81	0.65	70.8	1.17·10 ⁻⁷
NrGO700	3.19	80.5	0.87	0.72	83.5	6.39·10 ⁻⁶
NrGO800	3.66	104.0	0.88	0.76	65.4	4.53·10 ⁻⁷
Pt/C	3.92	124.3	0.95	0.84	59.1	1.65·10 ⁻⁶

Table 3. Comparison of ORR parameters for reduced graphene oxide, N-doped rGO, composites and a commercial Pt catalyst.

As a summary, the effect of nitrogen content on the catalytic activity towards ORR is presented in Figure 8. The electrocatalytic performance is represented by means of the kinetic current density, the half-wave potential and the average number of electrons. All these parameters point towards an optimum nitrogen content in the order of approximately 10-15 wt%. In our catalysts, the nitrogen speciation does not vary with annealing temperature to establish a direct correlation of activity with the concentration of a certain nitrogen species. Instead the total amount of nitrogen significantly changes. Consequently, these results suggest that nitrogen atoms are not the properly active sites for ORR since an increase of their content does not result necessarily in a better ORR activity, but carbon atoms influenced by nitrogen in the neighbourhood in graphene sheets are the real active species [25,66].

Figure 8. ORR catalytic activity as function of nitrogen content (wt%): kinetic current density, half-wave potential and number of electrons transferred.

4. Conclusions

N-doped reduced graphene oxide and composites of NrGO with carbon nitride with different nitrogen content were successfully synthesized by a simple thermal method using urea as nitrogen source and reducing agent. The physicochemical characterization indicated the effective incorporation of nitrogen into the graphene lattice, the homogeneity of the samples and confirmed composites present very high amount of nitrogen (19-35 wt%) compared to the state of the art due to the presence of CN phase together with NrGO. Electrochemical studies demonstrated that nitrogen doping improves the ORR catalytic behaviour of graphene.

However, the increase in carbon nitride affects negatively the ORR performance of the electrocatalysts, with the sample annealed at 800 °C, that lacks CN, presenting the best catalytic activity. Finally, it is reported that a high concentration of nitrogen atoms into the material does not produce a highly active electrocatalyst, and carbon atoms of the graphene lattice bonded to nitrogen are identified as the real active species for ORR.

Acknowledgements

Authors acknowledge the financial support given by the Spanish Ministry of Science, Innovation and Universities (MICINN) through projects ENE2014-52158-C2-1-R and 2-R and ENE2017-83976-C2-1-R and 2-R (co-founded by FEDER) and Aragón Government to support “Grupo de Conversion de Combustibles” (T06_17R). G. Lemes and D. Sebastián thank the Aragon Government and MICINN for their Ph.D. grant and Ramón y Cajal research contract (RyC-2016-20944), respectively.

References

- [1] M.S. Dresselhaus, I.L. Thomas, Alternative energy technologies, *Nature*. 414 (2001) 332–337. doi:10.1038/35104599.
- [2] J. Zhang, PEM fuel cell electrocatalysts and catalyst layers: fundamentals and applications, Springer Science & Business Media, 2008. doi:10.1007/978-1-84800-936-3.
- [3] D. Sebastián, A. Serov, I. Matanovic, K. Artyushkova, P. Atanassov, A.S. Aricò, V. Baglio, Insights on the extraordinary tolerance to alcohols of Fe-N-C cathode catalysts in highly performing direct alcohol fuel cells, *Nano Energy*. 34 (2017) 195–204. doi:10.1016/j.nanoen.2017.02.039.
- [4] C. Lo Vecchio, A.S. Aricò, V. Baglio, Application of low-cost Me-N-C (Me = Fe or Co) electrocatalysts derived from edta in direct methanol fuel cells (DMFCs), *Materials (Basel)*. 11 (2018) 1193. doi:10.3390/ma11071193.
- [5] C. Lo Vecchio, A.S. Aricò, G. Monforte, V. Baglio, EDTA-derived Co–N–C and Fe–N–C electro-catalysts for the oxygen reduction reaction in acid environment, *Renew. Energy*. 120 (2018) 342–349. doi:10.1016/j.renene.2017.12.084.
- [6] D. Sebastián, V. Baglio, A.S. Aricò, A. Serov, P. Atanassov, Performance analysis of a non-platinum group metal catalyst based on iron-aminoantipyrine for direct methanol fuel cells, *Appl. Catal. B Environ*. 182 (2016) 297–305. doi:10.1016/j.apcatb.2015.09.043.

- [7] L. Zhang, J. Zhang, D.P. Wilkinson, H. Wang, Progress in preparation of non-noble electrocatalysts for PEM fuel cell reactions, *J. Power Sources*. 156 (2006) 171–182. doi:10.1016/j.jpowsour.2005.05.069.
- [8] M.M. Hossen, K. Artyushkova, P. Atanassov, A. Serov, Synthesis and characterization of high performing Fe-N-C catalyst for oxygen reduction reaction (ORR) in Alkaline Exchange Membrane Fuel Cells, *J. Power Sources*. 375 (2018) 214–221. doi:10.1016/j.jpowsour.2017.08.036.
- [9] A. Serov, M.J. Workman, K. Artyushkova, P. Atanassov, G. McCool, S. McKinney, H. Romero, B. Halevi, T. Stephenson, Highly stable precious metal-free cathode catalyst for fuel cell application, *J. Power Sources*. 327 (2016) 557–564. doi:10.1016/j.jpowsour.2016.07.087.
- [10] E. Negro, A.H.A. Monteverde, V. Baglio, A.S. Aricò, S. Specchia, G.J.M. Koper, Fe – N supported on graphitic carbon nano-networks grown from cobalt as oxygen reduction catalysts for low-temperature fuel cells, *Appl. Catal. B, Environ.* 166–167 (2015) 75–83. doi:10.1016/j.apcatb.2014.10.074.
- [11] M. Vikkisk, I. Kruusenberg, U. Joost, E. Shulga, I. Kink, K. Tammeveski, Electrocatalytic oxygen reduction on nitrogen-doped graphene in alkaline media, *Appl. Catal. B Environ.* 147 (2014) 369–376. doi:10.1016/j.apcatb.2013.09.011.
- [12] B. Tang, S. Wang, R. Li, X. Gou, J. Long, Urea treated metal organic frameworks-graphene oxide composites derived N-doped Co-based materials as efficient catalyst for enhanced oxygen reduction, *J. Power Sources*. 425 (2019) 76–86. doi:10.1016/j.jpowsour.2019.04.007.
- [13] L. Wan, G. Zang, X. Wang, L. Zhou, T. Li, Q. Zhou, Tiny crystalline grain nanocrystal NiCo 2O_4 /N-doped graphene composite for efficient oxygen reduction reaction, *J. Power Sources*. 345 (2017) 41–49. doi:10.1016/j.jpowsour.2017.01.122.
- [14] E. Bayram, G. Yilmaz, S. Mukerjee, A solution-based procedure for synthesis of nitrogen doped graphene as an efficient electrocatalyst for oxygen reduction reactions in acidic and alkaline electrolytes, *Appl. Catal. B Environ.* 192 (2016) 26–34. doi:10.1016/j.apcatb.2016.03.043.
- [15] G. Jo, J. Sanetuntikul, S. Shanmugam, Boron and phosphorous-doped graphene as a metal-free electrocatalyst for the oxygen reduction reaction in alkaline medium, *RSC Adv.* 5 (2015) 53637–53643. doi:10.1039/C5RA06952A.
- [16] Z. Sheng, H. Gao, W. Bao, F. Wang, X. Xia, Synthesis of boron doped graphene for oxygen reduction reaction in fuel cells, *J. Mater. Chem.* 22 (2012) 390–395. doi:10.1039/c1jm14694g.
- [17] Z. Yang, Z. Yao, G. Li, G. Fang, H. Nie, Z. Liu, X. Zhou, X. Chen, S. Huang, Sulfur-Doped Graphene as an Efficient Metal-free Cathode Catalyst for Oxygen Reduction, *ACS Nano*. 6 (2012) 205–211. doi:10.1021/nn203393d.
- [18] R. Li, Z. Wei, X. Gou, W. Xu, Phosphorus-doped graphene nanosheets as efficient metal-free oxygen reduction electrocatalysts, *RSC Adv.* 3 (2013) 9978–9984. doi:10.1039/c3ra41079j.
- [19] Z. Yu, J. Piao, Z. Liang, Synthesis of 2D nitrogen-doped mesoporous carbon catalyst for oxygen reduction reaction, *Materials (Basel)*. 10 (2017) 1–10.

doi:10.3390/ma10020197.

- [20] L. Zhang, Z. Xia, Mechanisms of oxygen reduction reaction on nitrogen-doped graphene for fuel cells, *J. Phys. Chem. C*. 115 (2011) 11170–11176. doi:10.1021/jp201991j.
- [21] B. Zheng, J. Wang, F. Wang, X. Xia, Synthesis of nitrogen doped graphene with high electrocatalytic activity toward oxygen reduction reaction, *Electrochem. Commun.* 28 (2013) 24–26. doi:10.1016/j.elecom.2012.11.037.
- [22] Z. Lin, M. Song, Y. Ding, Y. Liu, M. Liu, C. Wong, Facile preparation of nitrogen-doped graphene as a metal-free catalyst for oxygen reduction reaction, *Phys. Chem. Chem. Phys.* 14 (2012) 3381–3387. doi:10.1039/c2cp00032f.
- [23] L.T. Soo, K.S. Loh, A.B. Mohamad, W.R.W. Daud, W.Y. Wong, Effect of nitrogen precursors on the electrochemical performance of nitrogen-doped reduced graphene oxide towards oxygen reduction reaction, *J. Alloys Compd.* 677 (2016) 112–120. doi:10.1016/j.jallcom.2016.03.214.
- [24] H.B. Yang, J. Miao, S.-F. Hung, J. Chen, H.B. Tao, X. Wang, L. Zhang, R. Chen, J. Gao, H.M. Chen, L. Dai, B. Liu, Identification of catalytic sites for oxygen reduction and oxygen evolution in N-doped graphene materials: Development of highly efficient metal-free bifunctional electrocatalyst, *Sci. Adv.* 2 (2016) e1501122–e1501122. doi:10.1126/sciadv.1501122.
- [25] T. Xing, Y. Zheng, L.H. Li, B.C.C. Cowie, D. Gunzelmann, S.Z. Qiao, S. Huang, Y. Chen, Observation of Active Sites for Oxygen Reduction Reaction on Nitrogen-Doped Multilayer Graphene, *ACS Nano*. 8 (2014) 1–5. doi:10.1021/nn501506p.
- [26] 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* (80-.). 351 (2016) 361–365. doi:10.1126/science.aad0832.
- [27] K. Mamtani, D. Jain, D. Dogu, V. Gustin, S. Gunduz, A.C. Co, U.S. Ozkan, Insights into Oxygen Reduction Reaction (ORR) and Oxygen Evolution Reaction (OER) Active Sites for Nitrogen-doped Carbon Nanostructures (CN x) in Acidic Media, *Appl. Catal. B Environ.* 220 (2017) 88–97. doi:10.1016/j.apcatb.2017.07.086.
- [28] L. Lai, J.R. Potts, D. Zhan, L. Wang, C.K. Poh, C. Tang, H. Gong, Z. Shen, J. Lin, R.S. Ruoff, Exploration of the active center structure of nitrogen-doped graphene-based catalysts for oxygen reduction reaction, *Energy Environ. Sci.* 5 (2012) 7936–7942. doi:10.1039/c2ee21802j.
- [29] K. Gopalakrishnan, A. Govindaraj, C.N.R. Rao, Extraordinary supercapacitor performance of heavily nitrogenated graphene oxide obtained by microwave synthesis, *J. Mater. Chem. A*. 1 (2013) 7563–7565. doi:10.1039/c3ta11385j.
- [30] Y. Feng, X. Yao, M. Wang, Z. Hu, X. Luo, H.T. Wang, L. Zhang, The atomic structures of carbon nitride sheets for cathode oxygen reduction catalysis, *J. Chem. Phys.* 138 (2013) 164706. doi:10.1063/1.4802188.
- [31] Y. Zheng, J. Liu, J. Liang, M. Jaroniec, S.Z. Qiao, Graphitic carbon nitride materials: controllable synthesis and applications in fuel cells and photocatalysis, *Energy Environ. Sci.* 5 (2012) 6717–6731. doi:10.1039/c2ee03479d.
- [32] S.M. Lyth, Y. Nabee, S. Moriya, S. Kuroki, M.A. Kakimoto, J.I. Ozaki, S. Miyata, Carbon

- nitride as a nonprecious catalyst for electrochemical oxygen reduction, *J. Phys. Chem. C*. 113 (2009) 20148–20151. doi:10.1021/jp907928j.
- [33] H. Jiang, Y. Zhu, Y. Su, Y. Yao, Y. Liu, X. Yang, C. Li, Highly dual-doped multilayer nanoporous graphene: efficient metal-free electrocatalysts for the hydrogen evolution reaction, *J. Mater. Chem. A*. 3 (2015) 12642–12645. doi:10.1039/C5TA02792F.
  - [34] Y. Fu, J. Zhu, C. Hu, X. Wu, X. Wang, Covalently coupled hybrid of graphitic carbon nitride with reduced graphene oxide as a superior performance lithium-ion battery anode., *Nanoscale*. 6 (2014) 12555–12564. doi:10.1039/c4nr03145h.
  - [35] W.S. Hummers, R.E. Offeman, Preparation of Graphitic Oxide, *J. Am. Chem. Soc.* 80 (1958) 1339–1339. doi:10.1021/ja01539a017.
  - [36] J. Florez-Montano, A. Calderon-Cardenas, W. Lizcano-Valbuena, J.L. Rodriguez, E. Pastor, Ni@Pt nanodisks with low Pt content supported on reduced graphene oxide for methanol electrooxidation in alkaline media, *Int. J. Hydrogen Energy*. 41 (2016) 19799–19809. doi:10.1016/j.ijhydene.2016.06.166.
  - [37] L.M. Rivera, S. Fajardo, C. Arevalo, G. Garcia, E. Pastor, S- and N-Doped Graphene Nanomaterials for the Oxygen Reduction Reaction, *Catalysts*. 7 (2017) 278. doi:10.3390/catal7090278.
  - [38] Z.J. Lu, M.W. Xu, S.J. Bao, K. Tan, H. Chai, C.J. Cai, C.C. Ji, Q. Zhang, Facile preparation of nitrogen-doped reduced graphene oxide as a metal-free catalyst for oxygen reduction reaction, *J. Mater. Sci.* 48 (2013) 8101–8107. doi:10.1007/s10853-013-7622-0.
  - [39] Z. Yang, H. Nie, X. Chen, X. Chen, S. Huang, Recent progress in doped carbon nanomaterials as effective cathode catalysts for fuel cell oxygen reduction reaction, *J. Power Sources*. 236 (2013) 238–249. doi:10.1016/j.jpowsour.2013.02.057.
  - [40] J. Liu, T. Zhang, Z. Wang, G. Dawson, W. Chen, Simple pyrolysis of urea into graphitic carbon nitride with recyclable adsorption and photocatalytic activity, *J. Mater. Chem.* 21 (2011) 14398. doi:10.1039/c1jm12620b.
  - [41] P.M. Schaber, J. Colson, S. Higgins, D. Thielen, B. Anspach, J. Brauer, Thermal decomposition (pyrolysis) of urea in an open reaction vessel, *Thermochim. Acta*. 424 (2004) 131–142. doi:10.1016/j.tca.2004.05.018.
  - [42] L.K. Putri, B.-J. Ng, W.-J. Ong, H.W. Lee, W.S. Chang, S.-P. Chai, Heteroatom nitrogen- and boron-doping as a facile strategy to improve photocatalytic activity of standalone reduced graphene oxide in hydrogen evolution, *ACS Appl. Mater. Interfaces*. 9 (2017) 4558–4569. doi:10.1021/acsami.6b12060.
  - [43] F. Pan, J. Jin, X. Fu, Q. Liu, J. Zhang, Advanced oxygen reduction electrocatalyst based on nitrogen-doped graphene derived from edible sugar and urea, *ACS Appl. Mater. Interfaces*. 5 (2013) 11108–11114. doi:10.1021/am403340f.
  - [44] A. Thomas, A. Fischer, F. Goettmann, M. Antonietti, J.-O. Müller, R. Schlögl, J.M. Carlsson, Graphitic carbon nitride materials: variation of structure and morphology and their use as metal-free catalysts, *J. Mater. Chem.* 18 (2008) 4893. doi:10.1039/b800274f.
  - [45] C. Botas, P. Álvarez, C. Blanco, R. Santamaría, M. Granda, M.D. Gutiérrez, F. Rodríguez-Reinoso, R. Menéndez, Critical temperatures in the synthesis of graphene-like materials

- by thermal exfoliation-reduction of graphite oxide, *Carbon N. Y.* 52 (2013) 476–485. doi:10.1016/j.carbon.2012.09.059.
- [46] Y. Sun, C. Li, Y. Xu, H. Bai, Z. Yao, G. Shi, Chemically converted graphene as substrate for immobilizing and enhancing the activity of a polymeric catalyst., *Chem. Commun.* 46 (2010) 4740–4742. doi:10.1039/c001635g.
- [47] Y. Cao, Z. Zhang, J. Long, J. Liang, H. Lin, H. Lin, X. Wang, Vacuum heat-treatment of carbon nitride for enhancing photocatalytic hydrogen evolution, *J. Mater. Chem. A* 2 (2014) 17797–17807. doi:10.1039/C4TA03070B.
- [48] A. Kaniyoor, S. Ramaprabhu, A Raman spectroscopic investigation of graphite oxide derived graphene, *AIP Adv.* 2 (2012) 032183. doi:10.1063/1.4756995.
- [49] D. Torres, J.L. Pinilla, R. Moliner, I. Suelves, On the oxidation degree of few-layer graphene oxide sheets obtained from chemically oxidized multiwall carbon nanotubes, *Carbon N. Y.* 81 (2015) 405–417. doi:10.1016/j.carbon.2014.09.073.
- [50] A.C. Ferrari, Raman spectroscopy of graphene and graphite: Disorder, electron–phonon coupling, doping and nonadiabatic effects, *Solid State Commun.* 143 (2007) 47–57. doi:10.1016/j.ssc.2007.03.052.
- [51] A. Cuesta, P. Dhamelincourt, J. Laureyns, A. Martínez-Alonso, J.M.D. Tascón, Raman microprobe studies on carbon materials, *Carbon N. Y.* 32 (1994) 1523–1532. doi:10.1016/0008-6223(94)90148-1.
- [52] S.S. Shinde, A. Sami, J.H. Lee, Nitrogen- and Phosphorus-Doped Nanoporous Graphene/Graphitic Carbon Nitride Hybrids as Efficient Electrocatalysts for Hydrogen Evolution, *ChemCatChem.* 7 (2015) 3873–3880. doi:10.1002/cctc.201500701.
- [53] F. Tuinstra, J.L. Koenig, Raman Spectrum of Graphite, *J. Chem. Phys.* 53 (1970) 1126–1130. doi:10.1063/1.1674108.
- [54] W. Shen, Z. Li, Y. Liu, Surface Chemical Functional Groups Modification of Porous Carbon, *Recent Patents Chem. Eng.* 1 (2008) 27–40. doi:10.2174/2211334710801010027.
- [55] D. Salinas-Torres, S. Shiraishi, E. Morallón, D. Cazorla-Amorós, Improvement of carbon materials performance by nitrogen functional groups in electrochemical capacitors in organic electrolyte at severe conditions, *Carbon N. Y.* 82 (2015) 205–213. doi:10.1016/j.carbon.2014.10.064.
- [56] Z. Mou, X. Chen, Y. Du, X. Wang, P. Yang, S. Wang, Forming mechanism of nitrogen doped graphene prepared by thermal solid-state reaction of graphite oxide and urea, *Appl. Surf. Sci.* 258 (2011) 1704–1710. doi:10.1016/j.apsusc.2011.10.019.
- [57] R.P. Rocha, A.G. Gonçalves, L.M. Pastrana-Martínez, B.C. Bordoni, O.S.G.P. Soares, J.J.M. Órfão, J.L. Faria, J.L. Figueiredo, A.M.T. Silva, M.F.R. Pereira, Nitrogen-doped graphene-based materials for advanced oxidation processes, *Catal. Today.* 249 (2014) 192–198. doi:10.1016/j.cattod.2014.10.046.
- [58] X. Xu, T. Yuan, Y. Zhou, Y. Li, J. Lu, X. Tian, D. Wang, J. Wang, Facile synthesis of boron and nitrogen-doped graphene as efficient electrocatalyst for the oxygen reduction reaction in alkaline media, *Int. J. Hydrogen Energy.* 39 (2014) 16043–16052. doi:10.1016/j.ijhydene.2013.12.079.

- [59] Y. Zhang, J. Ge, L. Wang, D. Wang, F. Ding, X. Tao, W. Chen, Manageable N-doped graphene for high performance oxygen reduction reaction., *Sci. Rep.* 3 (2013) 2771. doi:10.1038/srep02771.
- [60] S. Yang, X. Feng, X. Wang, K. Müllen, Graphene-based carbon nitride nanosheets as efficient metal-free electrocatalysts for oxygen reduction reactions, *Angew. Chemie - Int. Ed.* 50 (2011) 5339–5343. doi:10.1002/anie.201100170.
- [61] D. Chanda, A.S. Dobrota, J. Hnát, Z. Sofer, I.A. Pašti, N. V. Skorodumova, M. Paidar, K. Bouzek, Investigation of electrocatalytic activity on a N-doped reduced graphene oxide surface for the oxygen reduction reaction in an alkaline medium, *Int. J. Hydrogen Energy.* 43 (2018) 12129–12139. doi:10.1016/j.ijhydene.2018.05.012.
- [62] 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, *J. Solid State Electrochem.* (2015) 931–942. doi:10.1007/s10008-015-2932-6.
- [63] G. Zhang, Q. Wei, X. Yang, A.C. Tavares, S. Sun, RRDE experiments on noble-metal and noble-metal-free catalysts: Impact of loading on the activity and selectivity of oxygen reduction reaction in alkaline solution, *Appl. Catal. B Environ.* 206 (2017) 115–126. doi:10.1016/j.apcatb.2017.01.001.
- [64] L. Yu, X. Pan, X. Cao, P. Hu, X. Bao, Oxygen reduction reaction mechanism on nitrogen-doped graphene: A density functional theory study, *J. Catal.* 282 (2011) 183–190. doi:10.1016/j.jcat.2011.06.015.
- [65] T. Shinagawa, A.T. Garcia-Esparza, K. Takanabe, Insight on Tafel slopes from a microkinetic analysis of aqueous electrocatalysis for energy conversion, *Sci. Rep.* 5 (2015) 1–21. doi:10.1038/srep13801.
- [66] J. Quílez-Bermejo, E. Morallón, D. Cazorla-Amorós, Oxygen-reduction catalysis of N-doped carbons prepared: Via heat treatment of polyaniline at over 1100 °C, *Chem. Commun.* 54 (2018) 4441–4444. doi:10.1039/c8cc02105h.