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# Nitrogen sites prevail over textural properties in N-doped carbons for the oxygen reduction reaction

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## Abstract

Nitrogen-doped carbon-based electrodes are among the most promising alternatives to platinum-based electrodes in the cathode of fuel cells and metal-air batteries, where the oxygen reduction reaction (ORR) takes place. Among the approaches for improving ORR activity, nitrogen functionalities and well-developed textural properties have proved very effective. Nonetheless, the question of which between nitrogen active sites or textural properties are more crucial in N-doped carbon materials remains unanswered. This work proposes a comparative and critical approach through the selective functionalization of four commercial activated carbons with different textural properties. This study highlights the greater importance of N-doping in relation to the textural properties of carbon materials, and provides fundamental insights for conclusively addressing the ongoing debate within the carbon community about the significance of these two factors in the context of ORR.

## 1. Introduction

The oxygen reduction reaction (ORR) in fuel cells and metal-air batteries has sluggish kinetics and high overpotential, which makes it necessary the use of high loadings of expensive electrocatalysts [1–4]. Platinum is by far the most active material towards this reaction, but its scarcity and high cost hinder the large-scale commercialization of platinum-based electrochemical devices [5–8]. One of the main alternatives is the use of metal-free carbon materials, as carbon is more abundant in nature and significantly reduces the cost of the cathode electrode [9–13]. The major limitation is the poor catalytic activity of undoped carbon materials, as they have a homogeneous charge distribution in the carbon layers, making them poorly reactive for chemisorbing and reducing oxygen molecules [14–17].

The introduction of heteroatoms or defects in general disturbs the charge density and localizes the electron density in their vicinity, which act as active sites where dioxygen molecules are attracted, chemisorbed and then reduced [18–20]. In terms of surface chemistry, introducing N functionalities into carbon materials has shown promise for enhancing ORR electrocatalysis [21–23]. It is worth mentioning here the controversy within the scientific community about active sites in N-doped carbon materials [22,23], in which graphitic and pyridinic species are proposed as the most active sites for the ORR. Besides, N-C-O-type species have been shown to be active for such a reaction [24,25]. The selective enrichment of carbon materials with graphitic-type nitrogen species has provided experimental evidence of the high efficiency of these nitrogen species in alkaline media [26].

Another interesting avenue for improving the catalytic activity of carbon materials is to tune the textural properties, as they have been shown to be crucial for the ORR performance of undoped carbon materials [27–29]. The properties of micropores, and in particular ultramicropores, go beyond transportation roles and encompass catalytic functions. Micropores serve as excellent nanoreactors in which the overlapping potential energy of the

pore walls facilitates the reduction of oxygen molecules at the interphase, leading to excellent catalytic activities. The impact of textural properties on ORR catalytic activity of undoped carbon materials has been extensively studied to conclude that the narrowest pores play a significant role in the catalytic activity of these materials [29–31].

Although these two factors have a substantial influence on the ORR electrocatalytic properties of carbon-based materials, it is worth mentioning that these parameters due to the different nature of these active sites, and cannot be easily compared. Therefore, these factors have always been examined individually, with no comprehensive study of the effect of N-doping on porous carbon materials for the ORR. Opening up new horizons in the field of carbon electrocatalysis requires a fair comparison between N functionalities and textural properties of carbon materials. Herein, the effect of textural properties on ORR catalytic activity of undoped and N-doped carbon materials is addressed through extensive physicochemical and electrochemical characterization. Four commercial activated carbons were doped using urea as the nitrogen-doping agent. The functionalization procedure led to highly selective N-doping without significantly altering the pristine textural properties, allowing a fair comparison of the role of N functionalities in N-doped carbon materials for the ORR.

## **2. Materials and methods**

### *2.1 Functionalization of activated carbons*

Commercial activated carbons (CAC: MSC30 and MSC20 from Kansai Coke and Chemicals Co., Ltd Japan, and CW30 and TH90I from Silcarbon) were functionalized by a two-step doping method using urea as the N-doping agent [26]. The CACs were physically mixed with urea in a 1:2 carbon-to-urea weight ratio and subjected to heat treatment at 350 °C under air flow (50 mL·min<sup>-1</sup>) for 3 h, the heating rate up to this temperature being 5 °C·min<sup>-1</sup>. The

materials were then thoroughly washed with water until neutral pH, and subjected to a second heat treatment under nitrogen flow ( $100 \text{ mL}\cdot\text{min}^{-1}$ ) at  $900 \text{ }^{\circ}\text{C}$  for 1h using a heating rate of  $5 \text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$  up to this temperature. The materials were labelled N-CAC, CAC being the name of the commercial carbon. The preparation of N-doped carbon materials is illustrated in Figure 1.

## *2.2 Physicochemical characterization*

The structure and morphology of the samples were observed using a JEM – ARM 200F Cold FEG high-resolution transmission electron microscope (HRTEM) at 200 kV. The carbon samples were suspended in ethanol and deposited in droplets on a holey carbon grid prior to analysis. Elemental mapping was performed using energy-dispersive X-ray spectroscopy (EDX) with a JEOL spectrometer (SDD) in scanning transmission microscopy (STEM) mode. All STEM images were acquired in high-angle annular dark field (HAADF) mode. Carbon, hydrogen, oxygen and nitrogen contents were obtained using a Vario EL cube analyzer (Elementar). In this device, 2 mg of each material are burnt at about  $1700 \text{ }^{\circ}\text{C}$  in a mixed atmosphere of helium and oxygen. The gases produced are selectively separated in a chromatographic column and quantified using a thermal conductivity detector (sensitivity  $\approx 40 \text{ ppm}$ ), allowing the calculation of C, H and N contents initially present in the materials. In a second experiment, the oxygen content was obtained by reducing the oxygen-containing combustion gases to CO, and quantifying the latter.

The surface chemistry was also studied by X-ray photoelectron spectroscopy (XPS) in a VG-Microtech Multilab 3000 spectrometer, with a non-monochromatic Al  $K\alpha$  X-ray source under vacuum. The deconvolution of the N1s spectra was performed by least-squares fitting using Gaussian-Lorentzian (20:80) curves.

Nanoscale structural order was studied for all carbon samples by Raman spectroscopy using a Horiba XploRa Raman apparatus equipped with a 50 X long-range objective. The spectra were acquired between  $800$  and  $2000 \text{ cm}^{-1}$  with a circularly polarized laser of wavelength  $638$

nm, filtered at 10% maximum energy to prevent sample heating, and using a holographic grating of 1200 lines per nm.

The textural properties of the carbon materials were studied using N<sub>2</sub> and H<sub>2</sub> adsorption, the isotherms of which were obtained at -196 °C with a 3Flex manometric sorption analyzer (Micromeritics, Atlanta, GA). Prior to adsorption measurements, the samples were outgassed under secondary vacuum at 110 °C for 24h. The BET area ( $A_{BET}$ ) was calculated by applying the Brunauer-Emmet-Teller theory, using the adequate relative pressure range of the N<sub>2</sub> adsorption isotherm [32,33]. The NLDFT surface area ( $S_{NLDFT}$ ) was calculated from the combination of both N<sub>2</sub> and H<sub>2</sub> adsorption isotherms using a 2D non-local density functional model (2D-NLDFT) available in SAIEUS software (Micromeritics, Atlanta, GA). Pore size distributions (PSDs) and cumulative pore volumes were also calculated from the combination of the two isotherms. The other textural features were obtained by integrating the PSDs, such as total pore volumes,  $V_T$ ; ultramicropore volumes (corresponding to pore diameters less than 0.7 nm),  $V_{ult-micro}$ ; supermicropore volumes (corresponding to pore diameters between 0.7 and 2 nm),  $V_{sup-micro}$ ; micropore volumes (pore diameters less than 2.0 nm),  $V_{micro}$ ; and mesopore volumes (pore diameters between 2.0 and 50 nm),  $V_{MES}$ .

### *2.3 Electrochemical characterization*

ORR tests were performed using a rotating ring-disk electrode (RRDE) in a conventional three-electrode cell with an Autolab PGSTAT302 potentiostat (Metrohm, Netherlands). The working electrode was equipped with a glassy carbon disk of 5 mm diameter and a second platinum ring electrode. A reversible hydrogen electrode (RHE) immersed in the same working electrolyte and a graphite rod were used as reference and counter electrodes, respectively.

Prior to the electrochemical experiments, the glassy carbon working electrode was modified as follows [34]: 0.5 mg of the carbon material was dispersed in 0.125 mL of an aqueous solution containing 0.2 wt.% of Nafion ® and 20 wt.% of isopropanol. 4 drops of 8.42 µL were drop-cast onto the glassy carbon disk to reach a carbon loading of 0.68 mg·cm<sup>-2</sup>.

The electrocatalytic activity towards the ORR was evaluated by linear sweep voltammetry (LSV) in an oxygen-saturated 0.1 M KOH solution at a scan rate of 5 mV s<sup>-1</sup> in the potential range of 1.0 - 0.0 V vs RHE. To calculate the number of electrons transferred ( $n$ ), the platinum ring electrode was fixed at a constant potential of 1.5 V vs RHE. The equation is as follows:

$$n = \frac{4I_D}{I_D + I_R/N}$$

where the current obtained at the ring and disk (absolute value) is denoted  $I_R$  and  $I_D$ , respectively, and  $N$  is the collection efficiency of the RRDE, which was obtained experimentally by the reversible redox couple  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  and was determined to be 0.265.

### 3. Results and discussion

Figure 1 shows HRTEM images of all N-CAC samples, in which a typical disordered structure is observed in all materials, characteristic of activated carbons. In the N-CW30 sample, the presence of mesopores with a size of about 10 nm can be observed, while there are apparently only micropores in the other N-CACs. Moreover, EDX mapping analysis was also performed and Figure 1e-1h shows a homogenous distribution of nitrogen and oxygen moieties throughout the N-MS30 carbon material, confirming the successful introduction of dispersed heteroatoms by the two-step doping method.

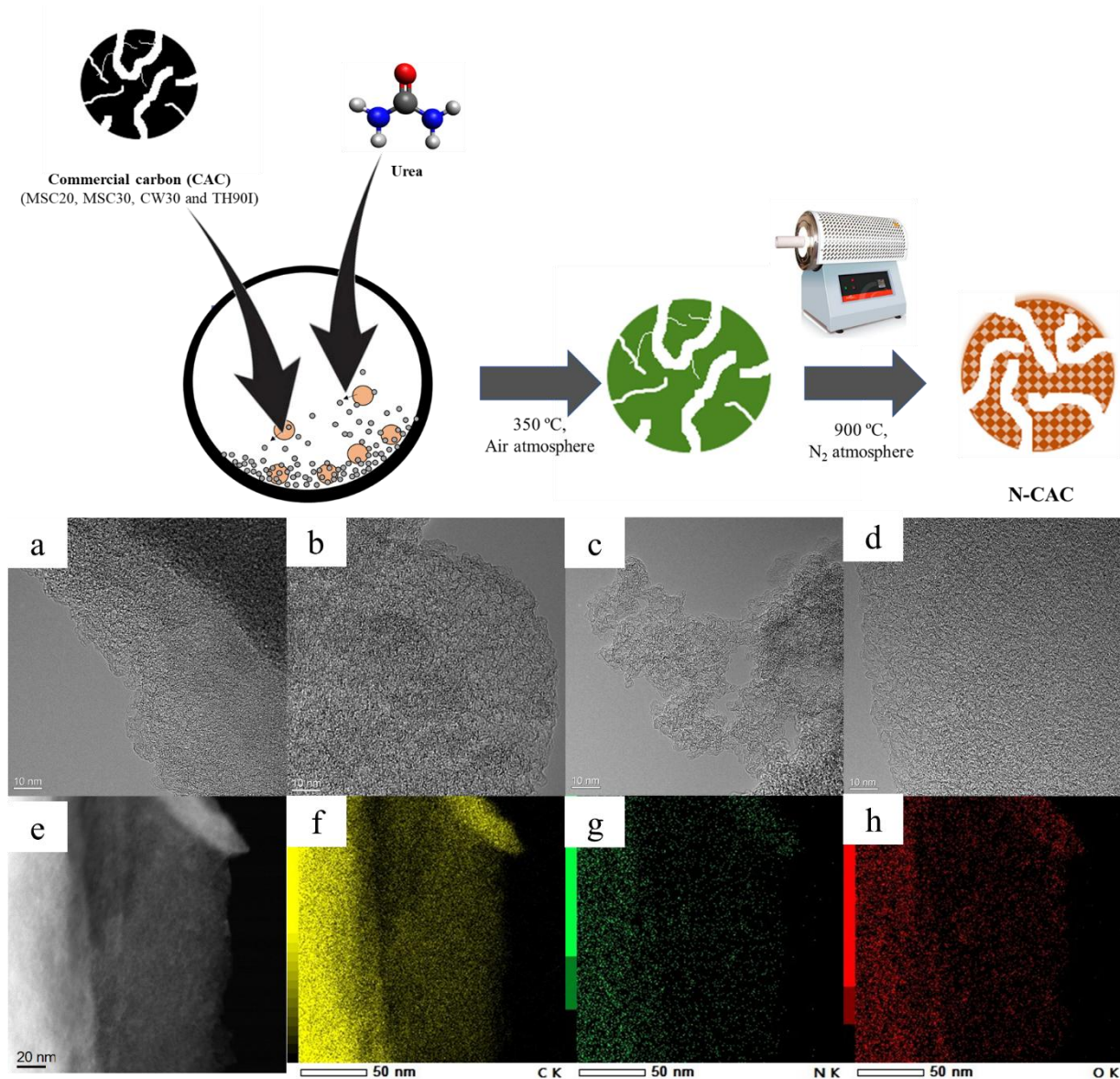


Figure 1 : (Top) Schematic illustration of urea functionalization and carbonization procedure. (Bottom) HRTEM images of (a) N-MSC20, (b) N-MSC30, (c) N-CW30, (d) N-TH90I pristine activated carbons. (e) HAADF image of N-MSC30 material and EDX mapping of the elements: (f) carbon, (g) nitrogen and (h) oxygen of the same image.

Heat treatment yields, and carbon, oxygen, hydrogen and nitrogen contents determined by elemental analysis, are gathered in Table S1 for all materials. After functionalization with urea, the heat treatment yields of N-CAC samples were highly dependent on the pristine CAC, likely due to variations in oxygen functionalities and structural order of the materials. As previously demonstrated, oxygen functionalities play a crucial role in urea functionalization by acting as reactive sites [35]. The oxygen content in CW30 decreased from 19.5 wt.% to 5 wt.% after the heat treatment at 900 °C. Moreover, it is worth mentioning that the higher the



oxygen content of the pristine CAC, the higher the N content after the 2-step doping method. This makes sense, since oxygen moieties are known to be excellent reactive points for urea [36].

Raman spectroscopy was performed to evaluate changes in structural order after N-doping. All carbon materials show the typical profile of disordered ACs with contributions related to the D<sub>1</sub> and G bands. The G band appears at around 1595 cm<sup>-1</sup> and is related to the vibration of crystalline graphitic carbon, whereas the D<sub>1</sub> band appears at around 1350 cm<sup>-1</sup> and is related to the presence of defects [37,38]. The I<sub>D</sub>/I<sub>G</sub> ratio serves as an indicator of structural order in amorphous carbon materials [39]. Our data indicate that an increase in N-doping is associated with a reduction in the I<sub>D</sub>/I<sub>G</sub> ratio, see Figure S1 which shows the correlation between I<sub>D</sub>/I<sub>G</sub> ratio of the pristine CAC and the final N-doping. This observation can be attributed to the enhanced efficacy of N-doping with carbon defects. If carbon materials are compared before (Figure 2a) and after the functionalization procedure (Figure 2b), slight variations can be observed in the I<sub>D</sub>/I<sub>G</sub> ratio, which is always higher in the materials after the functionalization strategy. This is strongly related to the post treatment at 900 °C after urea functionalization, since high temperatures in carbonization processes often increase the structural order of amorphous carbon materials through condensation and dehydration reactions. This increase is particularly noticeable for N-TH90I and N-CW30, as the pristine CACs possessed a highly disordered structure. Interestingly, after N-doping and heat treatment at 900 °C, all N-CAC samples showed similar I<sub>D</sub>/I<sub>G</sub> ratio of around 1.15, highlighting the similar structural order of the resulting N-CACs. Nevertheless, the slight broadening of the D band is associated with a more disordered distribution of the amorphous carbon clusters [40], suggesting the presence of a large number of defects in N-CW30 and N-MS30. Carbon rings with a number of carbon atoms other than six also tend to broaden the D band of the Raman spectra [40], which can be related to the presence of nitrogen functionalities. It is worth noting here that the

intermediate material, i.e. that obtained prior to the heat treatment at 900 °C and after urea functionalization in air, already exhibits a reduction in D-band width in the Raman spectra of the CACs. As shown in Figure S2 for the case of MSC30, the narrowing of the D band after urea functionalization in air at 350 °C indicates that the air treatment may also contribute to the removal of carbon atoms from the most disordered areas in the CACs.

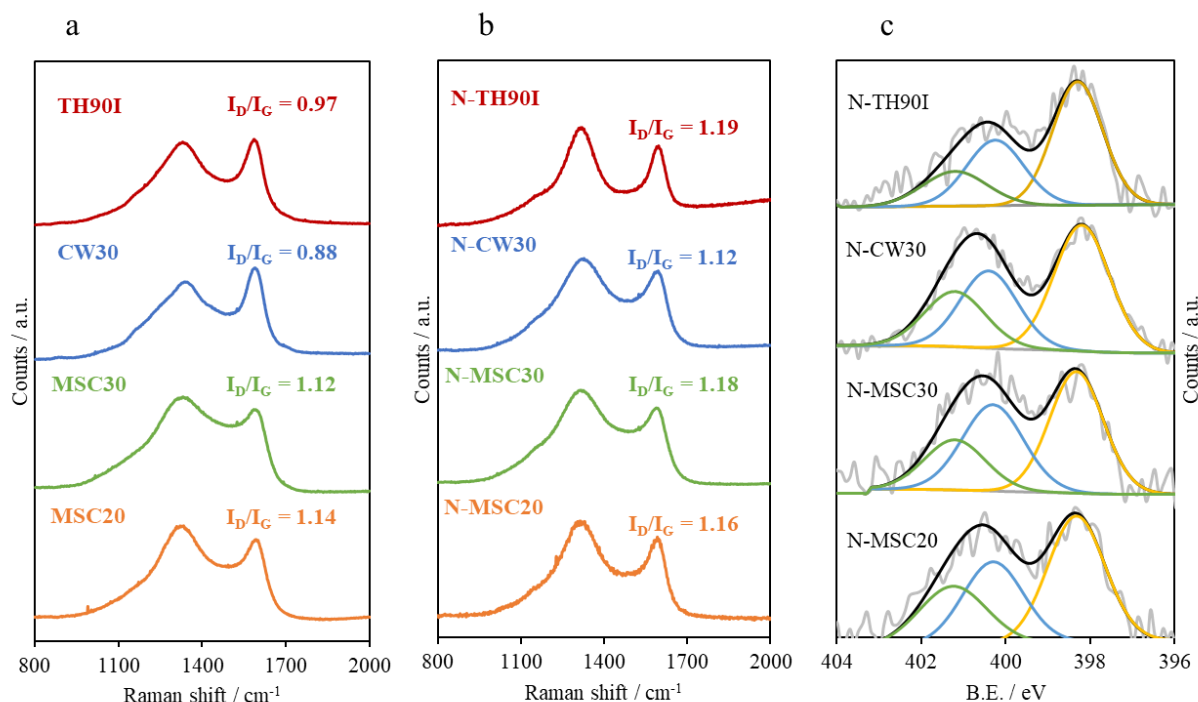


Figure 2: 1<sup>st</sup>-order Raman spectra of all (a) CAC and (b) N-CAC materials obtained at a wavelength of 638 nm. (c) N1s spectra of all carbon materials obtained after the functionalization procedure with urea and heat treatment at 900 °C. The yellow peak represents pyridinic-N species, the blue peak represents pyridonic and/or pyrrolic-N species, and the green peak represents graphitic-N species. FWHM = 1.4 - 1.8 eV.

XPS analyses were performed for all N-CACs to identify the nitrogen species and quantify the nitrogen and oxygen species on the surface of the carbon materials. Table S2 shows the atomic contents of C, O and N at the surface. As expected, the N content at the surface of the carbon materials is always higher than in the bulk (see again Table S1), since the post-functionalization of CACs with urea takes place mainly on the most accessible surface. Furthermore, there are significant differences in N contents: while N-MSC20 had an N content of about 2 at.%, N-CW30 had almost double that, at around 3.8 at.%. It is worth

mentioning here that the N content at the surface followed a similar trend to that observed in the bulk. This is related to the total O content of the pristine CAC since, as mentioned above, the O moieties act as reactive sites with urea molecules, leading to a higher N content when large amounts of O groups are found in the pristine ACs [36].

Figure S3 shows full XPS spectra of N-CACs. The N1s spectra were deconvoluted in accordance with the literature [24,41]: pyridinic N species at 398.3 eV, pyrrolic and pyridonic species at 400.3 eV and graphitic (or quaternary) nitrogen at 401.2 eV. The quantification of each peak can be found in Table S2. Figure 2c shows the N1s spectra of all samples, highlighting important features of the functionalization strategy. A significant contribution from pyridinic species is observed for all materials, with also a smaller contribution of pyridonic and graphitic nitrogen. As observed, N oxidation states do not seem to have any relationship with textural properties, showing a similar N1s profile whatever the pristine CAC (Figure 2c), offering a unique opportunity to analyze the role of the textural properties of N-doped carbon materials with the same type of N species in ORR.

The textural properties of all carbon materials were characterized by N<sub>2</sub> (Figure 3) and H<sub>2</sub> adsorption isotherms (Figure S4) at -196 °C. Prior to analysis, the materials were degassed under secondary vacuum for 24 h at 110 °C. The results obtained are gathered in Table S3. Figure 3 shows the results of N<sub>2</sub> adsorption-desorption isotherms for CACs before and after functionalization and heat treatment. MSC30 and MSC20 are CACs with a large  $A_{BET}$  of around 2500-3000 m<sup>2</sup>·g<sup>-1</sup>, while CW30 and TH90I exhibit lower values of around 1000-1500 m<sup>2</sup>·g<sup>-1</sup>. It is worth noting the large mesopore volume in MSC30 and CW30, whereas MSC20 and TH90I are mainly microporous carbon materials. In detail, sample MSC20 shows a type Ia isotherm, characteristic of microporous carbon materials [33]. This is confirmed by Figure 3b, in which the pore size distribution (PSD) shows mainly the presence of micropores, around 90 % of the total pore volume. Similarly, the TH90I sample shows mainly the

presence of micropores, but has a lower surface area. On the other hand, the MSC30 sample shows a type I(b) isotherm [33], characteristic of carbon materials with a broad PSD and typical of super-activated carbons, with the presence of both micropores and narrow mesopores. This is confirmed by the PSD in Figure 3b. Sample CW30 shows a combination of type I and IV isotherms, and thus the PSD shows the existence of pores up to 3.0 nm, with a moderate  $A_{BET}$  of about  $1700 \text{ m}^2 \cdot \text{g}^{-1}$ . This confirms that the selected CACs exhibit significant textural differences with similar N functionalities, allowing a fair comparison of their catalytic activity taking into account only to surface area and PSD.

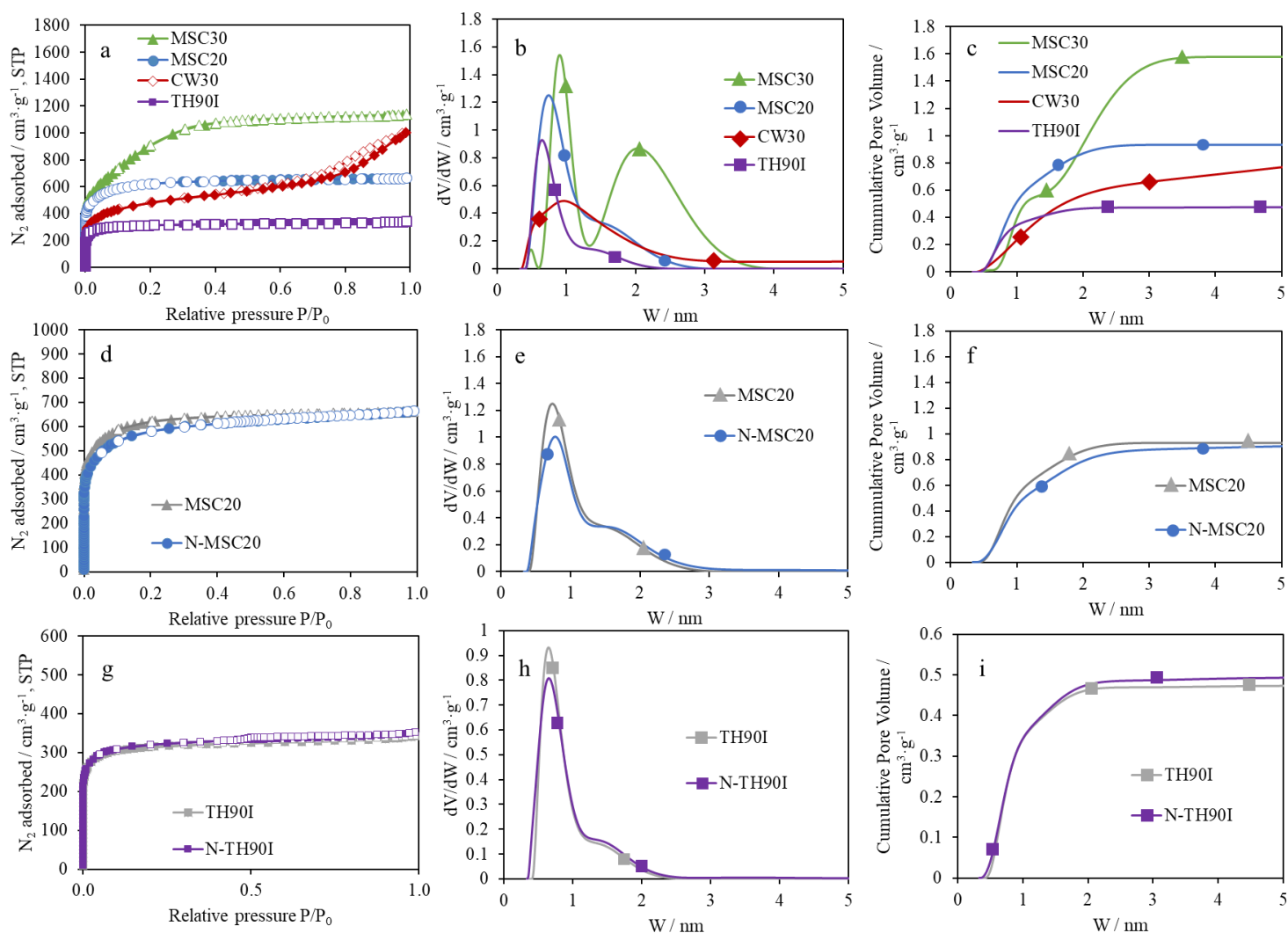


Figure 3: (a) N<sub>2</sub> adsorption-desorption isotherms at -196 °C (full and empty symbols stand for adsorption and desorption points, respectively), (b) pore size distributions, and (c) cumulative pore volumes of all CACs. (d) N<sub>2</sub> adsorption-desorption isotherms, (e) pore size distributions and (f) cumulative pore volumes of MSC20 and N-MSC20. (g) N<sub>2</sub> adsorption-desorption isotherms, (h) pore size distributions and (i) cumulative pore volumes of TH90I and N-TH90I.

Concerning N-CACs, N-doping did not lead to significant changes in the textural properties of the pristine CACs, especially in microporous carbon samples, i.e., MSC20 (Figure 3d-f), and TH90I (Figure 3g-i). On the other hand, MSC30 and CW30 underwent slight modifications in their textural properties, as shown in Figures S5 and S6, respectively. Here, it is worth noting that the PSD and cumulative pore volume of MSC20 (Figures 3d-f) and TH90I (Figure 3g-i) remained unchanged, while MSC30 and CW30 underwent more significant changes (Figures S5 and S6). In particular, the PSD profile of CW30 was significantly modified, leading to a defined contribution at 0.7 nm.

The N-functionalization presented here allowed similar nitrogen species to be selectively introduced into the carbon matrix, as demonstrated by XPS, while retaining most of the textural properties of the pristine CACs. Hence, these materials enable evaluation of whether surface chemical functions or textural properties are more important for ORR using N-doped carbon materials. Therefore, hereafter, the catalytic activities of N-doped and undoped CACs were evaluated as electrocatalysts for the oxygen reduction reaction.

Figure 4a shows the LSV curves for the CACs, showing moderate catalytic activity for all of them towards the ORR. However, significant differences are observed depending on their textural properties. MSC30 is the undoped CAC with the best catalytic performance in terms of  $E_{\text{ONSET}}$  (0.83 V) and limiting current density, closely followed by MSC20 and TH90I samples with an  $E_{\text{ONSET}}$  of 0.82 V. This value is typical of undoped carbon materials for ORR electrocatalysis, as observed in the literature [42,43]. Finally, CW30 sample shows poor activity ( $E_{\text{ONSET}} = 0.74$  V), which is comparable to the catalytic activity of the glassy carbon disk [44].

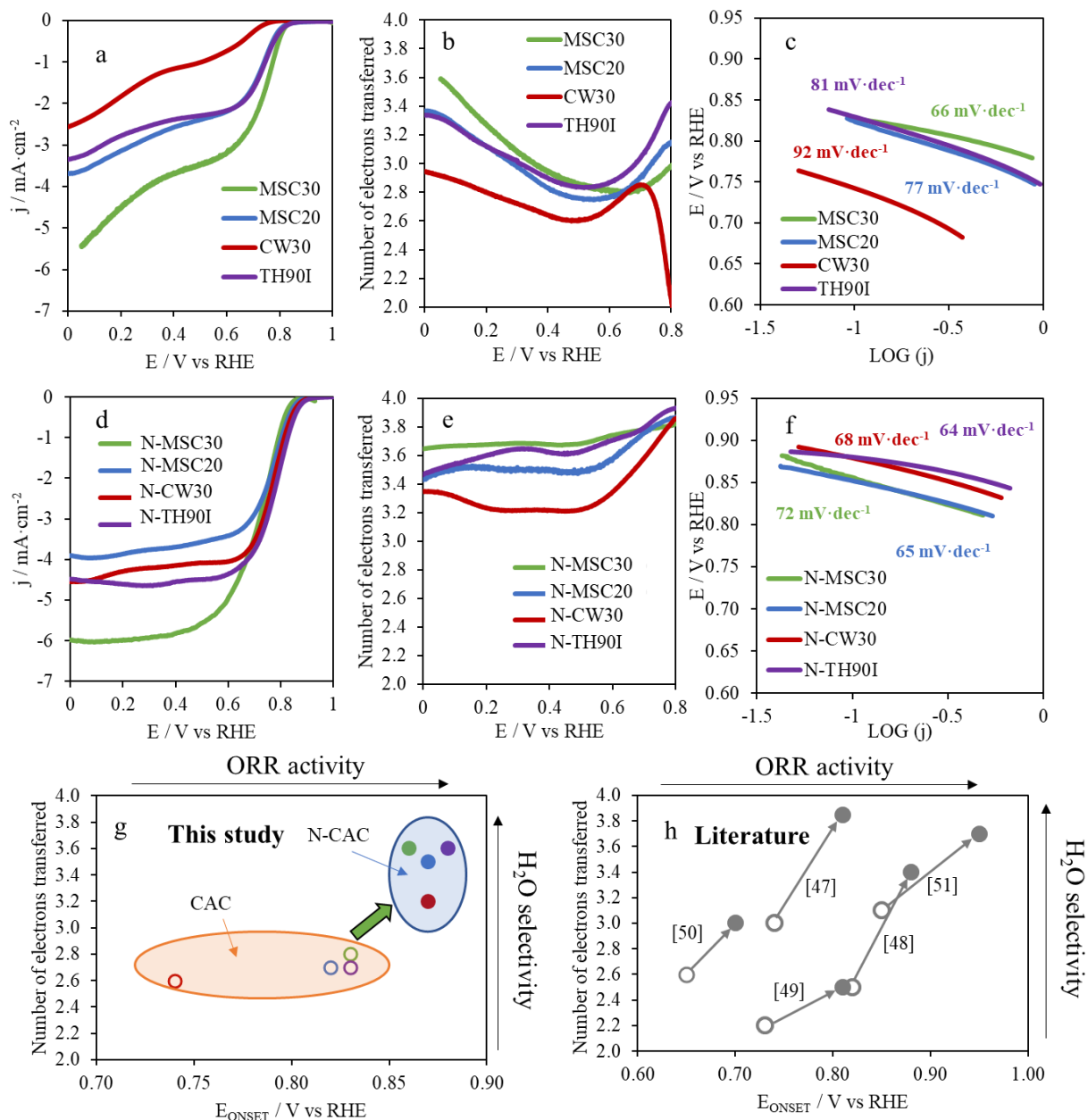


Figure 4: (a) LSV curves and (b) number of electrons transferred for pristine activated carbons. (c) Tafel slopes calculated from LSV curves for all CAC materials. (d) LSV curves, (e) number of electrons transferred and (f) Tafel slopes for N-CAC materials. Scan rate =  $5 \text{ mV} \cdot \text{s}^{-1}$ . Rotation speed = 1600 rpm. Electrolyte =  $\text{O}_2$ -saturated 0.1 M KOH solution. (g) Schematic illustration of  $E_{\text{ONSET}}$  and number of electrons transferred in CAC and N-CAC materials. (h) Schematic representation of  $E_{\text{ONSET}}$  and number of electrons transferred of different N-doped carbon materials before (light grey dots) and after (dark grey dots) post-functionalization treatments in the literature.

Concerning undoped CACs, textural properties seem to be of paramount importance, with materials featuring large volumes of micropores being those exhibiting better catalytic activity for the ORR, while materials featuring large volumes of mesopores show lower catalytic activity. Furthermore, the total surface area does not seem to play a crucial role in the catalysis towards the ORR in undoped CACs. This confirms previous studies in which solely

micropores were clearly identified as responsible for the ORR in pure carbons [29,45]. Furthermore, the number of electrons transferred (Figure 4b) shows that undoped CACs exhibit a high hydrogen peroxide production (i.e., high selectivity towards the 2-electron pathway), which is not recommendable for fuel cells and metal-air batteries, as hydrogen peroxide is a strong oxidizing agent that can damage most components of these electrochemical devices. Tafel slopes were calculated from LSV curves, with only slight difference between CAC samples (see Figure 4c).

For N-CACs, N-doping led to a significant improvement of the ORR catalytic activity independently of the CAC, confirming that this N-doping method using urea and heat treatment is a promising route to induce a significant enhancement of catalytic activity. The improvement in catalytic activity is observed for all N-CACs (see Figures 4c and S7-10), and it is especially remarkable when CW30 material is used as precursor. This is not only related to the nitrogen functional groups that have been introduced into the carbon material, but also to the changes in textural properties after the doping procedure. CW30 underwent a significant structural change after N-doping and heat treatment, so it cannot be used to evaluate the relative importance of textural properties and surface chemistry since both parameters were altered during the functionalization and carbonization procedure. N-MS30 also showed significant textural differences when compared to MS30, making this material of little use for a fair comparison. In contrast, MS20 and TH90I showed almost identical textural properties to N-MS20 and N-TH90I, respectively, with the main difference being their surface chemistry, allowing an appropriate assessment of the role of N-doping in the catalytic activity for the ORR.

Figure S10 shows that the introduction of N functional groups is of paramount importance in achieving highly efficient catalytic activity with an  $E_{\text{ONSET}}$  of almost 0.90 V in N-TH90I, which is much higher compared to pristine TH90I ( $E_{\text{ONSET}} = 0.82$  V). The relevance of N



functional groups in TH90I samples is also observed in the limiting current density (from  $-4.5 \text{ mA}\cdot\text{cm}^{-2}$  to  $-2.3 \text{ mA}\cdot\text{cm}^{-2}$  at  $0.5 \text{ V}$  vs. RHE for N-TH90I and pristine TH90I, respectively). The number of electrons transferred also clearly depends on the presence of N functional groups, showing a much higher value of  $n$  in samples doped with nitrogen species (Figure S11). In the case of TH90I, the value of  $n$  for the pristine activated carbon was around 2.7 at  $0.5 \text{ V}$  vs RHE, rising to 3.6 at the same potential after N-doping. This significant change in the value of  $n$  indicates different active sites for ORR present in TH90I and N-TH90I.

A similar trend was observed when using MSC20 (Figure 4d-f and Figure S9), with the introduction of nitrogen species improving the catalytic activity in terms of  $E_{\text{ONSET}}$  and limiting current density. The number of electrons transferred is also clearly higher when the doped materials are used, from 2.7 for pristine MSC20 to 3.5 for N-MSC20. Therefore, the comparison of the ORR electrocatalytic activity of N-doped and undoped carbon materials with almost identical textural properties shows that the role of N functional groups is very important, always leading to a higher  $E_{\text{ONSET}}$ , limiting current density and, more significantly, a larger number of electrons transferred. The superior catalytic performance of N-doped carbons compared to undoped carbons has been widely associated with the presence of pyridinic and graphitic N species [46,47], although pyridonic N can also provide high catalytic performance for the ORR [25,48,49]. In N-CACs, there is a large contribution from all these nitrogen species, leading to a low overpotential for such a reaction.

As all N-CACs show the same N1s profile after the functionalization procedure and, therefore, similar surface chemistry, the role of textural properties in N-doped carbon materials can be studied by evaluating and comparing N-MSC20, N-MSC30, N-CW30 and N-TH90I samples. Figure 4d shows the LSV curves of all N-CACs, the main difference being their texture. Figure S12 shows that the  $E_{\text{ONSET}}$  values of all N-CACs are rather similar, suggesting that textural properties are not decisive in the kinetic region, but that the N active sites govern

their catalytic properties. To confirm further the crucial role of nitrogen active sites in the ORR, Tafel slopes were calculated from LSV curves. As observed in Figure 4f, Tafel slopes around  $70 \text{ mV} \cdot \text{dec}^{-1}$  were found for all N-CACs, indicating the same rate-determining step and ORR mechanism. This reveals that ORR in N-CAC materials proceeds through the same N active sites, regardless of their textural properties. Nevertheless, the role of defects cannot be discarded in enhancing ORR activity. A similar trend is observed in the number of electrons transferred. This value is close to 4 for N-CACs, while 2-electron pathways are obtained with CACs. It should be noted that these conclusions have been drawn for porous carbon materials and cannot be extrapolated to non-porous carbon materials. Indeed, it is widely known that a certain amount of development of textural properties is required to facilitate oxygen transport from the electrolyte to the active sites. Finally, it is worth mentioning that the textural properties seem to play a role in the diffusion region through the combination of the reduction of oxygen to  $\text{H}_2\text{O}_2$  and the subsequent reduction of hydrogen peroxide to hydroxide anion at lower potentials [29].

These results indicate that textural properties are of paramount importance for ORR when using undoped carbon materials, as shown in Figure 4a, as micropores can act as nanoreactors. In the narrowest pores, the physical adsorption forces and charge transfer between a carbon surface and adsorbed oxygen indeed result in weakening of the O-O bond, leading to dissociation of the dioxygen molecule [27]. However, if N-doped carbons are used, the nitrogen groups are more catalytically active than the micropores, resulting in a loss of dependence between catalytic activity and textural properties. The high catalytic activity and selectivity to water of nitrogen species predominates in ORR electrocatalysis, and the relevance of textural properties is reduced. The aforementioned trend can be seen in Figure 4g for the CAC and N-CAC materials, where the introduction of nitrogen results in improved catalytic activity and selectivity. This observation is further supported by the existing

literature on the post-functionalization of carbon materials [50–54], where analogous trends have been reported for all materials (see Figure 4h and Table S4).

#### 4. Conclusions

This work provides unique insights into the effect of textural properties and nitrogen active sites in carbon materials for the oxygen reduction reaction (ORR). Selective N functionalization of four different commercial activated carbons (CACs) was performed using urea, which allowed the same type of N functional groups to be introduced into each of them. The ORR performance of CACs was dependent on their microporosity, whereas in the case of N-CACs, the dependence on textural properties was overshadowed by the higher catalytic activity of the nitrogen active sites. Based on the results presented here, we could show that the nitrogen active sites definitely prevail over the microporosity in terms of ORR catalytic activity. Furthermore, our results reveal that developing the textural properties of N-doped carbon materials does not lead to enhanced ORR activity. Instead, the N functionalities govern the ORR, relegating texture to a secondary role. These findings could potentially contribute to shedding light on the longstanding debate within the carbon community regarding countless questions about the impact of texture- enhancement techniques in N-doped carbon-based ORR electrocatalysts.

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