

Article

N/S Co-Doped Mesoporous Carbon Hollow Spheres: Toward Efficient and Durable Oxygen Reduction

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Abstract

This study reports the design of N- and S-doped ordered mesoporous carbon hollow spheres (OMCHS) as metal-free electrocatalysts for the oxygen reduction reaction (ORR) in alkaline media. Three electrocatalysts were synthesized using molecular precursors: (i) 2-thiophenemethanol (S-OMCHS), (ii) 2-pyridinecarboxaldehyde/2-thiophenemethanol (N1-S-OMCHS), and (iii) pyrrole/2-thiophenemethanol (N2-S-OMCHS). Among them, S-OMCHS exhibited the best activity ($E_{\text{onset}} = 0.88$ V, $E_{1/2} = 0.81$ V, $n \approx 3.95$), surpassing both co-doped analogs. After conducting an accelerated degradation test (ADT), S-OMCHS and N1-S-OMCHS showed improved catalytic behavior and outstanding long-term stability. Surface analysis confirmed that performance evolution correlates with heteroatom reorganization: S-OMCHS retained and regenerated thiophene-S and C=O/quinone species, while N1-S-OMCHS converted N-quaternary into N-pyridinic/pyrrolic, both enhancing O₂ adsorption and *OOH reduction through synergistic spin-charge coupling. Conversely, oxidation of N and loss of thiophene-S in N2-S-OMCHS led to partial deactivation. These results establish a direct link between surface chemistry evolution and electrocatalytic durability, demonstrating that controlled heteroatom doping stabilizes active sites and sustains the four-electron ORR pathway. The approach provides a rational design framework for next-generation, metal-free carbon electrocatalysts in alkaline fuel cells and energy conversion technologies.

Keywords: metal-free electrocatalysts; ORR; high-stability; mesoporous carbon; dual-doped



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1. Introduction

The development of more efficient and sustainable systems for electricity production is essential to contribute significantly to the decarbonization of this human activity [1]. In this regard, anion-exchange membrane fuel cells (AEMFCs) offer the advantage of avoiding the use of KOH while retaining the benefits of alkaline fuel cells. However, the development of non-noble metal electrocatalysts with high catalytic activity for the ORR remains a challenge. In recent years, metal-free electrocatalysts have been developed as a feasible alternative to replace Pt/C. The catalytic activity toward the ORR in these alternative materials can be mainly enhanced through heteroatom doping, since it alters the local charge and spin density of the carbon matrix, which in turn enables O₂ chemisorption, decreases the reaction energy barrier, and facilitates O–O bond cleavage, thereby promoting the ORR [2–4].

Nitrogen is the most widely used heteroatom for this purpose. It has been reported that some N-doped carbon electrocatalysts exhibit catalytic activity for the ORR comparable to that of Pt/C, mainly due to the unique electronic properties derived from the conjugation between the nitrogen lone-pair electrons and the π -conjugated carbon structure [5,6]. In this context, sulfur is a less-studied doping heteroatom than nitrogen. It is used as a dopant in metal-free electrocatalysts because it exhibits high electrocatalytic activity toward the ORR. Sulfur incorporation into the sp^2 carbon lattice may induce strain and stress, modify the charge distribution, and facilitate oxygen chemisorption—a necessary step to promote the ORR [7,8]. In this regard, Yang et al. synthesized S-doped graphene with an onset potential (E_{onset}) similar to that of the Pt/C electrocatalyst, with an electron transfer number of ($n = 3.82$) and a current density (j) of 5.34 mA cm^{-2} at 0.7 V vs. RHE [9]. Likewise, the work of Xiang et al. reported that S-doped oxidized acetylene black displayed good catalytic activity for the ORR ($E_{\text{onset}} = 0.93 \text{ V}$ vs. RHE and $n = 3.9$), and a half-wave potential ($E_{1/2}$) of 0.71 V vs. RHE, [10].

On the other hand, heteroatoms co-doping metal-free electrocatalysts have attracted much attention since they can increase catalytic activity. Dual doping of heteroatoms in the carbon lattice was believed to produce a high number of active sites for the ORR. For example, N/S co-doped graphene has shown enhanced catalytic activity for the ORR than graphene separately doped with S or N heteroatoms [11]. In addition, Yang et al. have shown that an N/S co-doped biocarbon generates a j value between -3 and -4.5 mA cm^{-2} , with n between 3.2 and 3.9 , and $E_{\text{onset}} = 0.88 \text{ V/RHE}$ in alkaline media [12]. Additionally, You et al. show that N/S co-doped carbon nanospheres exhibit high catalytic activity for the ORR ($E_{\text{onset}} = 0.88 \text{ V/RHE}$, $n = 3.82$) along with outstanding long-term stability (5% loss after 5.5 h of the test of the limit current density) in an alkaline media [13].

Recently, the ordered mesoporous carbon hollow spheres (OMCHS) have played a decisive role in ORR studies. It offers an excellent morphology, high hierarchical surface area ($\sim 2000 \text{ m}^2 \text{ g}^{-1}$), a high number of mesopores, and good electrical conductivity (30.2 S m^{-1}). Han et al. report that OMCHS promote the ORR in alkaline media with a catalytic activity like that of commercial Pt/C ($E_{\text{onset}} = 0.9 \text{ V/RHE}$, $n = 3.8$) [14]. Moreover, the investigation by Zhou et al. demonstrates that N-doped OMCHS exhibits comparable performance for the ORR to Pt/C ($E_{\text{onset}} = 0.98 \text{ V/RHE}$, $n = 3.9$) [15]. Additionally, Pang et al. show that mesoporous carbon hollow spheres promote the ORR in neutral and alkaline electrolyte ($E_{\text{onset}} = 0.83 \text{ V/RHE}$, $n = 4$) [16]. Moreover, the analysis of N-doped hollow mesoporous carbon nanospheres by Duraisamy et al. indicates that electrocatalysts have an outstanding activity toward ORR ($E_{\text{onset}} = 0.84 \text{ V/RHE}$, $E_{1/2} = 0.83 \text{ V/RHE}$, $n = 4$) [17]. Qiu et al. report that N-doped nano-hollow capsule carbon nanocages obtain and behaved high performance for the ORR and electrochemical stability in alkaline media ($E_{\text{onset}} = 0.87 \text{ V/RHE}$, $E_{1/2} = 0.73 \text{ V/RHE}$, $n = 3.81$) [18].

Also, the investigation by Yan et al. shows that N-doped hollow carbon polyhedron promotes the ORR in alkaline media with a catalytic activity like that of Pt/C ($E_{\text{onset}} = 0.98 \text{ V/RHE}$, $E_{1/2} = 0.86 \text{ V/RHE}$, $n = 4$) [19]. Moreover, Fan et al. reported that N-doped carbon covered hollow carbon nanoparticles exhibit high performance for the ORR and high long-term stability ($E_{\text{onset}} = 0.87 \text{ V/RHE}$, $E_{1/2} = 0.76 \text{ V/RHE}$, $n = 3.7$) [20]. N/S co-doped hollow mesoporous carbon spheres investigated by Yong et al. exhibits a high $E_{1/2}$, high methanol tolerance, and high long-term durability ($E_{\text{onset}} = 0.9 \text{ V/RHE}$, $E_{1/2} = 0.85 \text{ V/RHE}$, $n = 3.98$) [21]. Xiong et al. report that N/S co-doped hollow mesoporous carbon spheres show a good performance for the ORR and electrochemical stability ($E_{\text{onset}} = 0.85 \text{ V/RHE}$, $E_{1/2} = 0.77 \text{ V/RHE}$, $n = 4$) [22]. In this context, the design and fabrication strategies play an important role for OMCHS to enhance their ORR performance [23].

Additionally, Table S1 summarizes the electrochemical parameters concerning the catalytic activity for the ORR of N- S- or N/S-codoped metal-free electrocatalysts recently published.

In this work, OMHCS were synthesized using a silica core hard-template approach, which enables precise control of particle size, shell thickness, and pore structure while ensuring excellent structural integrity during carbonization. This method was selected because it provides greater uniformity and reproducibility than soft-template or template-free routes, as extensively reported in previous studies [24–26]. We designed the synthesis of hard-template OMCHS using two different nitrogen sources: (i) 2-pyridinecarboxaldehyde or (ii) pyrrole, to promote the formation of N-pyridinic or N-pyrrolic nitrogen species, respectively, and 2-thiophenemethanol to promote the formation of thiophene species on the surface of the metal-free electrocatalysts. It is worth mentioning that this study is complementary to another work previously reported, where only nitrogen was used as a dopant [27].

2. Materials and Methods

2.1. Synthesis of S-Doped and N/S Co-Doped OMCHS

The ordered mesoporous carbon hollow spheres (OMCHS) were synthesized via a hard-template method using monodisperse silica spheres—prepared by the Stöber process—as sacrificial cores. This route was chosen for its precise control of particle size and monodispersity; under the selected conditions, uniform silica particles of ~120 nm were obtained. After coating them with a resorcinol–formaldehyde (37%, Sigma Aldrich, St. Louis, MO, USA) shell containing heteroatom precursors, the composite was carbonized to form a conductive carbon layer. Finally, the silica templates were removed by hydrofluoric acid (40%, Merck, Germany) etching, yielding hollow mesoporous carbon spheres with uniform morphology and high structural integrity. The detailed synthesis procedure is described in the following section.

The N/S co-doped OMCHS were synthesized by slightly modifying the methodology that we previously reported [27]. The silica cores were prepared by the Stöber method mixing 120 mL of ethanol anhydrous (Et-OH, 0.003 H₂O, Merck, St. Louis, MO, USA), 22.8 mL of deionized water (DW), 2.6 mL of ammonium hydroxide (28–30%, Sigma Aldrich, USA), and 4.8 mL of tetraethyl orthosilicate (TEOS, 98%, Sigma Aldrich, St. Louis, MO, USA) was stirred for 7 h. Then, 366 mL of DW and 37.2 mL of Et-OH were added to the mixture and stirred for 10 min. Then, 12.4 mL of cetyltrimethylammonium chloride (CTAC, 25%, Sigma Aldrich, St. Louis, MO, USA) were gradually added to the solution and stirring for 15 min.

The shell's synthesis of the hollow spheres was carried out adding to the solution with the silica cores 6.4 mM of resorcinol (99%, Sigma Aldrich, St. Louis, MO, USA) and 8.6 mM of formaldehyde solution (37%, Sigma Aldrich, St. Louis, MO, USA) as carbon precursors, along with and 2-thiophenemethanol (98%, Sigma Aldrich, St. Louis, MO, USA) as sulfur doping agent (labeled S-OMCHS). The synthesis of co-doped OMCHS was carried out by separately mixing a solution containing the silica cores with 2-pyridinecarboxaldehyde (99%, Sigma Aldrich, St. Louis, MO, USA) or pyrrole (98%, Sigma Aldrich, St. Louis, MO, USA) with 2-thiophenemethanol, to obtain N-pyridinic/thiophene (labeled N1-S-OMCHS) and N-pyrrole/thiophene (labeled N2-S-OMCHS) species. Subsequently, 2.5 mL of TEOS (99 %, Sigma Aldrich, St. Louis, MO, USA) was added to the solutions and stirred for 12 h. Then, the solution was poured into sealed steel autoclaves covered with Teflon and heated at 100 °C for 24 h. Afterwards, the powders were washed with Et-OH/DW solution and dried at 60 °C. The powders were carbonized at 1000 °C under nitrogen atmosphere (99.999%, Infra, Mexico City, Mexico) for 4 h using a heating rate of 5 °C min^{−1}. Finally, silica cores were leached with a 10% *v/v* hydrofluoric acid (48–52%) for 48 h, then the powder was washed with DW and dried at 60 °C.

2.2. Physicochemical Features

The metal-free electrocatalysts were analyzed by Raman spectroscopy (Thermo Scientific DXR2, Waltham, MA, USA), X-ray diffraction (XRD, Bruker D2 Phaser 2nd Gen, Bremen, Germany) techniques in order to determine their structural properties. The morphology was observed by Field-Emission Scanning Electron Microscopy (FESEM), in a Jeol JSM-7800F Prime microscope, and by Transmission Electron Microscopy (HR-TEM), in a Hitachi HT7700 (Tokyo, Japan). The N₂ adsorption/desorption (Quantachrome Nova, Boynton Beach, FL, USA) was used to study the textural properties. Non-local-density functional theory (DFT) method was employed for the specific surface area calculations (SSA). Additionally, pore size distribution curves were calculated from the desorption isotherms using the Barrett–Joyner–Halenda (BJH) model.

2.3. Electrochemical Characterization

For electrochemical measurements a potentiostat (VSP-300, Bio-Logic, Claix, France) was used, which was coupled to a Rotating Ring Disk Electrode (RRDE) set-up. A three-electrode cell configuration with the following components: (i) Ag/AgCl (Sat. KCl solution) into a Luggin capillary was used as reference electrode, (ii) Pt mesh as counter electrode, and (iii) 0.5 M KOH solution as electrolyte. All potentials were converted to the Reversible Hydrogen Electrode (RHE). Working electrodes were prepared from catalyst inks containing 10 mg of metal-free electrocatalyst, 1 mL of propanol, and 60 µL of Nafion[®] solution (5%, Sigma Aldrich, St. Louis, MO, USA). An aliquot of 10 µL of the ink was deposited onto a glassy carbon electrode (5.61 mm diameter) by pipette drop-casting. The catalyst loading was 0.48 mg cm^{−2}, consistent with typical values reported for metal-free catalysts in alkaline media.

Cyclic voltammetry (CV) curves were acquired in N₂-saturated electrolyte in a potential range of 1.2 to 0.05 V/RHE at a scan rate of 20 mV s^{−1}. Meanwhile, the catalytic activity for the ORR was evaluated in the same potential range in O₂-saturated electrolyte and a scan rate of 5 mV s^{−1} at several rotation rates (ω = 400, 800, 1200, 1600, and 2000 rpm). The background current was determined before the ORR catalytic activity measurements (N₂-saturated electrolyte, 5 mV s^{−1}, 2000 rpm), and then the correction was subtracted to eliminate the contribution of non-faradaic currents. The current density (*j*) was normalized concerning the geometric area of the glassy carbon.

Simultaneously, the catalytic activity for the ORR was evaluated by the RRDE technique with an Au ring. The percentage of hydroperoxide anion produced (%HO₂[−]) and the electron transfer number (*n*) were calculated with the Equations S1 and S2, respectively, which can be consulted in the Supplementary Information Section, as well as the parameters under which the accelerated degradation test (ADT) was carried out. Additionally, in the Supplementary Section, the formulas for the calculation of the mass activity for the metal-free electrocatalysts are also included.

2.4. Use of Generative AI (GenAI) Tools

During the preparation of this manuscript, the authors used the AI-based assistant ChatGPT (GPT-5 model, OpenAI) exclusively for linguistic enhancement and for the organization of the initial draft of the “Introduction” and “Discussion” Sections. No part of the data analysis, experimental design, scientific conclusions, or interpretation of results was generated by the tool. All scientific content presented herein was critically reviewed, validated, and authored by the listed researchers.

3. Results and Discussion

3.1. Physicochemical Characterization of N-S-Doped OMCHS

Figure 1 displays the Raman spectra of S-OMCHS, N1-S-OMCHS, and N2-S-OMCHS, having the typical signals of carbon-based materials: (i) D band at ca. 1329 cm^{-1} related to lattice disorder, attributed to the C-C vibrations of the sp^3 defect sites; and (ii) the G signal at ca. 1588 cm^{-1} corresponding to sp^2 hybridization from C=C bonds (graphitized lattice) due to π interactions. The Raman spectral analysis grants the evaluation of the disorder and defects in carbon materials through the measurement of the D and G intensity ratio. The I_D/I_G ratios of S-OMCHS, N1-S-OMCHS, and N2-S-OMCHS are 1.57, 1.67, and 1.84, respectively. It can be noticed that the I_D/I_G ratio increases when the carbon structures are co-doped with nitrogen and sulfur species. These are higher than those of non-doped OMCHS ($I_D/I_G = 1.51$), and nitrogen-doped OMCHS (ex., N1-OMCHS, and N2-OMCHS, I_D/I_G value of 1.44, and 1.32, respectively) published in a previous work [24]. This feature suggests that using two different heteroatoms as dopants promotes the formation of less ordered structures. The substitutional co-doping influences the OMCHS, expanding their lattice due to the presence of aromatic groups and sp^3 bonds, which increases the intensity of the D interband (defective sites).

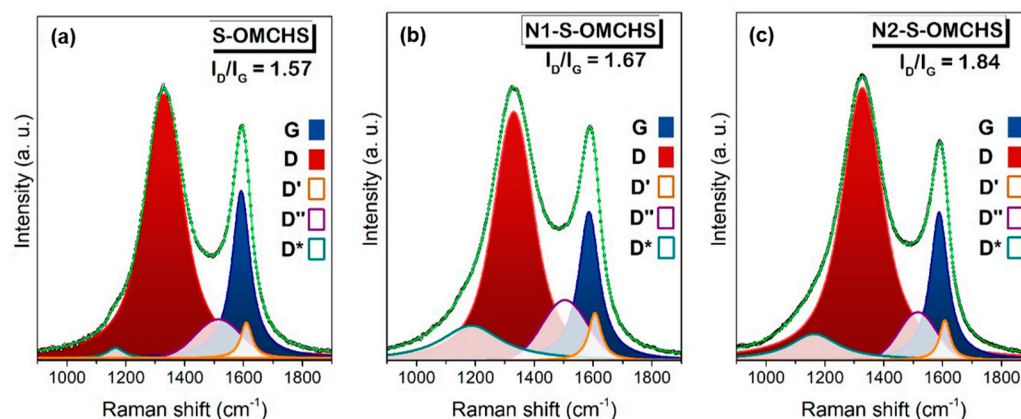


Figure 1. Raman spectra of (a) S-OMCHS, (b) N1-S-OMCHS, and (c) N2-S-OMCHS. The G, D, D', and D* interbands were fitted with a Lorentzian function, whereas the D'' band was fitted with a Gaussian function.

The Raman deconvolution spectra have been investigated to find alternatives to the I_D/I_G ratio, showing the formation of five interbands: D' (ca. 1607 cm^{-1}), D'' (ca. 1510 cm^{-1}), and D* (ca. 1173 cm^{-1}) interbands. The D' interband corresponds to the stretching vibrations of the aromatic rings in the graphite crystallites shielded by oxygen functional groups or attached to edge carbon atoms. Meanwhile, the D'' interband is explained by asymmetric vibrational stretching modes of sp^2 carbons near defects, causing out-of-plane deformations. Nevertheless, the origin of the D'' interband is still discussed [28,29]. The $I_{D''}/I_G$ ratios are increasing in the order S-OMCHS < N2-S-OMCHS < N1-S-OMCHS ($0.23 < 0.32 < 0.41$, respectively). This increase in $I_{D''}/I_G$ ratios is in accord with the investigation by Claramunt et al., where the intensity of the G interband decreases when the intensity of the D'' interband increases [29]. Meanwhile, the D* interband can be attributed to amorphous impurities in the graphitic lattice, adsorbed ions, or stretching vibrations of the sp^2 - sp^3 bonds of polyene-like structures [30]. The I_{D^*}/I_G ratio intensity is 0.06, 0.24, and 0.18 for S-OMCHS, N1-S-OMCHS, and N2-S-OMCHS, respectively. N1-S-OMCHS shows the highest $I_{D''}/I_G$ and I_{D^*}/I_G ratios indicating a high defects number, favoring oxygen chemisorption by interrupting π conjugation on the electrocatalyst surface [2].

The XRD patterns of S-OMCHS, N1-S-OMCHS, and N2-S-OMCHS are shown in Figure 2a. The three patterns show two well-defined peaks, the first at 2θ around $23\text{--}25^\circ$, which are assigned to the (002) plane of the graphite interlayer. The second peak at $\sim 44^\circ$ (2θ) corresponds to the (101) graphite plane [31]. A slight shift towards a higher angle is observed for the (002) plane by more than 1° (2θ) in the N/S co-doped OMCHS when compared to S-OMCHS electrocatalyst. This displacement of the (002) plane indicates a decrease in the interlayer distance of the N/S-doped OMCHS electrocatalysts, which confirm the important lattice contraction when co-doping OMCHS. It has been observed that carbon-based materials obtained at a low temperature of synthesis, low heat rate during the pyrolysis, and short time of annealing are characterized by greater interplanar distances [32]. Meanwhile, in oxide systems, such as those reported by Guan et al. [33], such shifts are often linked to strain and phase segregation under operando conditions, in carbon-based frameworks this effect is associated with heteroatom incorporation and the resulting perturbation of the local carbon lattice.

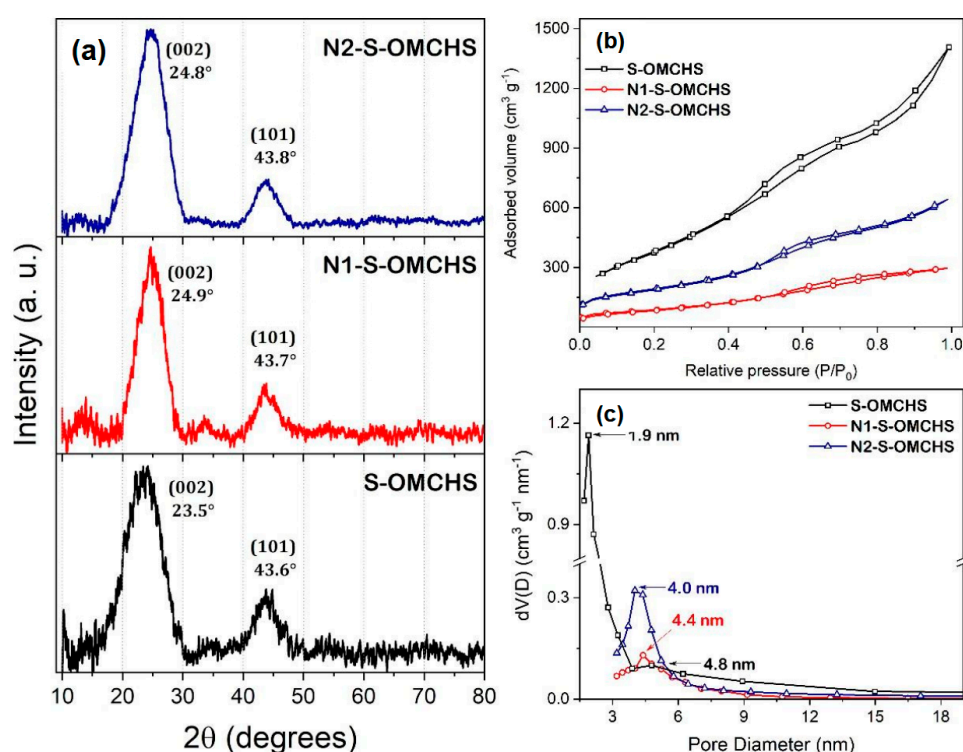


Figure 2. (a) XRD patterns, (b) N_2 adsorption–desorption isotherms, and (c) BJH desorption pore size distribution of S-OMCHS, N1-S-OMCHS, and N2-S-OMCHS.

Figure 2b shows the N_2 adsorption/desorption isotherms of the metal-free electrocatalysts, which show a hysteresis loop characteristic of type IV(a) isotherms. The N1-S-OMCHS and N2-S-OMCHS show H1-type hysteresis, indicating the presence of a mesopore framework with a uniform size, which is characteristic of mesoporous materials [34]. On the other hand, the S-OMCHS isotherm shows a combination of H2(a) and H3-type hysteresis. This behavior within P/P_0 intervals of 0.40 to 0.79 and 0.80 to 0.90 is attributed to the initial filling of the mesopores of the shell, followed by the adsorption of N_2 in the hollow core [35]. The textural properties of the metal-free electrocatalysts are summarized in Table 1. The specific surface area (SSA) is 1007, 283, and $622 m^2 g^{-1}$ for S-OMCHS, N1-S-OMCHS, and N2-S-OMCHS, respectively. The average pore size distribution curves (Figure 2c) show the existence of rough micropores (1.9 nm) in S-OMCHS, with mesopores centered at 4.8 nm in the shell of the carbon spheres. Meanwhile, N1-S-OMCHS and N2-S-OMCHS have an

average pore size distribution centered at 4.4 and 4.0 nm, respectively, indicating their mesoporous nature in the shell. The pore volume is 1.88, 0.43, and 0.91 $\text{cm}^3 \text{g}^{-1}$ for S-OMCHS, N1-S-OMCHS, and N2-S-OMCHS, respectively. S-OMCHS shows a higher pore volume, even higher than that of OMCHS ($1.37 \text{ cm}^3 \text{g}^{-1}$). These results suggest that the mixture of 2-pyridinecarboxaldehyde/2-thiophenemethanol and pyrrole/2-thiophenemethanol as nitrogen/sulfur sources are responsible for the variations in the SSA and pore features. The combination of these nitrogen/sulfur sources can form non-graphitic carbon structures after pyrolysis, and these have a higher tendency to collapse, resulting in higher pore size and lower SSA [36].

Table 1. Textural and morphological features of S-OMCHS, N1-S-OMCHS, and N2-S-OMCHS.

Sample	SSA ($\text{m}^2 \text{g}^{-1}$)	Average Pore Size (nm)	Pore Volume ($\text{cm}^3 \text{g}^{-1}$)	Average Diameter (Avg., nm)	Wall Thickness (Avg., nm)
S-OMCHS	1007	1.9	1.88	262 ± 15	45
N1-S-OMCHS	283	4.4	0.43	260 ± 19	46
N2-S-OMCHS	622	4.0	0.91	276 ± 17	34

FE-SEM images of S-OMCHS, N1-S-OMCHS, and N2-S-OMCHS are shown in Figure 3a–c. These three metal-free electrocatalysts have a well-defined morphology of rough nanospheres. Nevertheless, the spheres forming N1-S-OMCHS are rougher and more irregular in shape than those of S-OMCHS and N2-S-OMCHS. The micrograph of N1-S-OMCHS shows several spheres broken due to the leaching of the hard core. This is in good agreement with the lowest SSA on this electrocatalyst. Even though the average diameter and the wall thickness of S-OMCHS and N1-S-OMCHS are rather similar (Table 1). Regarding the N2-S-OMCHS, it has the thinnest wall thickness and a diameter slightly larger than the other two electrocatalysts. Figure 3d–f show TEM images of S-OMCHS, N1-S-OMCHS, and N2-S-OMCHS, respectively, at which the effect of co-doping with sulfur–nitrogen compared to mono-heteroatom doping on their morphology is more clearly observed. The rough sphere of S-OMCHS shows a relatively thin hollow-shell interface and a rather homogeneous wall thickness. On the contrary, N1-S-OMCHS and N2-S-OMCHS have an irregular wall with some pits in the outer layer, along with a less defined and thicker hollow-shell interface. These features are responsible for the lower SSA values of N1-S-OMCHS and N2-S-OMCHS than S-OMCHS.

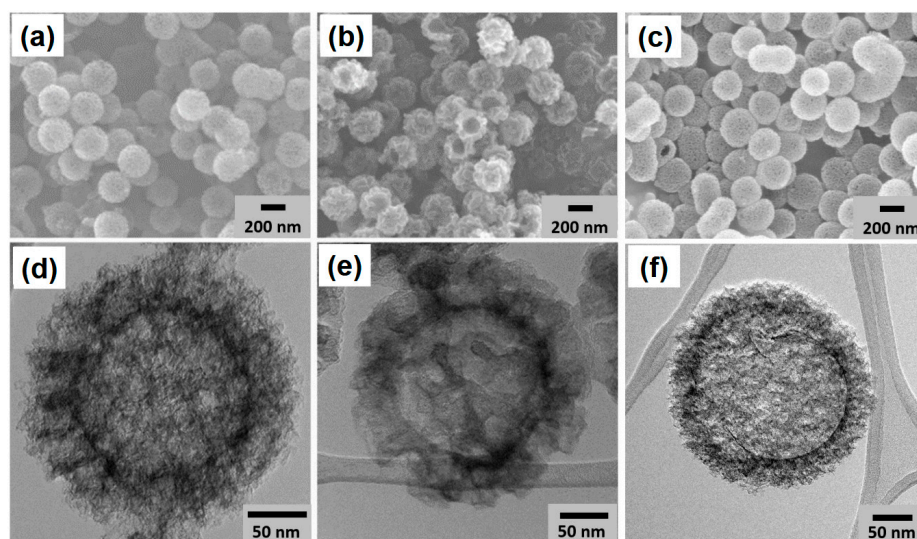


Figure 3. FE-SEM and TEM images of (a,d) S-OMCHS, (b,e) N1-S-OMCHS, and (c,f) N2-S-OMCHS.

On the other hand, the EDX elemental mapping (Supplementary Figure S1) verifies the uniform spatial distribution of C, N, and S within the mesoporous carbon hollow structures, confirming an effective heteroatom incorporation into the carbon matrix rather than a surface-confined modification. A minor Si signal was also detected, which is attributed to residual silica from the hard-template synthesis; however, this trace amount is structurally embedded and does not contribute to or interfere with the electrochemical response of the electrocatalysts.

3.2. Catalytic Activity of the N/S Co-Doped OMCHS for the ORR

Figure 4a shows the CVs of S-OMCHS, N1-S-OMCHS, and N2-S-OMCHS, with a semi-rectangular shape that indicates an effect of electronic double-layer capacitance by non-faradaic processes. The value of S-OMCHS is higher compared with the two other electrocatalysts, in good accordance with its higher SSA. Interestingly, N1-S-OMCHS has the smallest surface area; however, it delivers a higher j than N2-S-OMCHS, which suggests that other surface phenomena besides SSA influence the electrochemical behavior of the co-doped electrocatalysts (e.g., enhanced electrocatalyst–electrolyte interactions). N2-S-OMCHS generates the lowest j , indicating that the use of these sources of heteroatoms may hinder such electrocatalyst–electrolyte interaction, reducing its electrochemical performance.

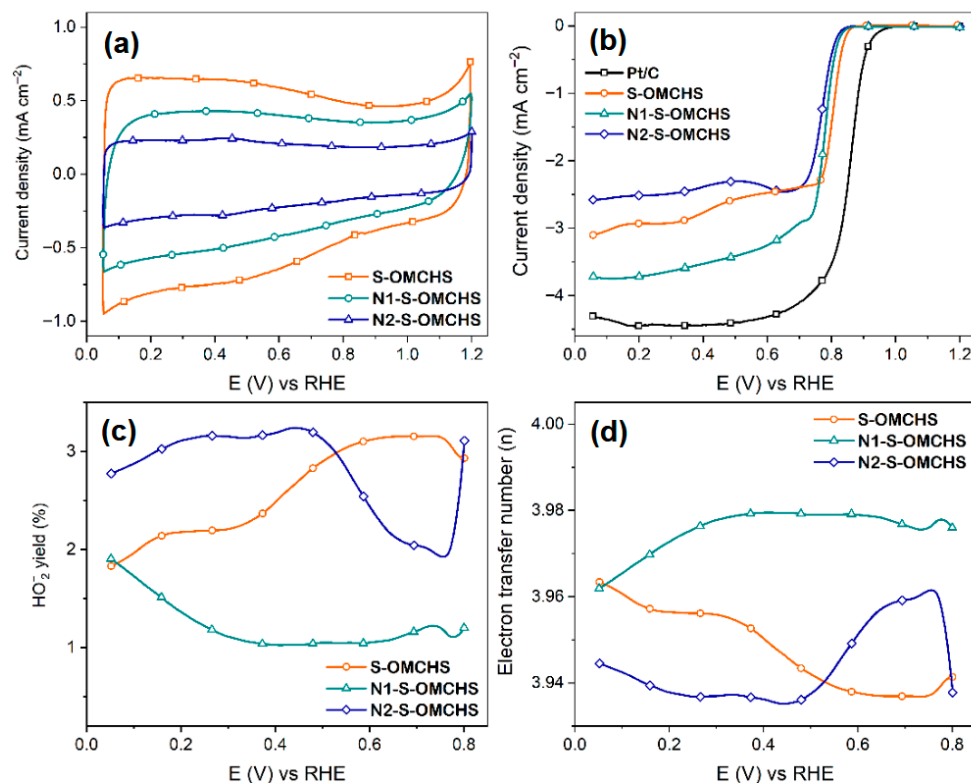


Figure 4. (a) CVs of S-OMCHS, N1-S-OMCHS, and N2-S-OMCHS were collected at 20 mV s⁻¹. Electrolyte: N₂-saturated 0.5 mol L⁻¹ KOH. (b) Negative scan only of the CVs of the ORR at 2000 rpm of S-OMCHS, N1-S-OMCHS, N2-S-OMCHS, and Pt/C. Electrolyte: O₂-saturated 0.5 mol L⁻¹ KOH. (c) %HO₂⁻, and (d) n plots at the electrocatalysts.

Polarization curves of the ORR at 2000 rpm of the metal-free and Pt/C electrocatalysts are shown in Figure 4b. S-OMCHS exhibits an E_{onset} at the first cycle of 0.88 V/RHE (Table 2), which is more positive than those of N1-S-OMCHS (0.86 V/RHE) and N2-S-OMCHS (0.85 V/RHE). This improvement clearly reflects the beneficial influence of sulfur heteroatoms on the ORR kinetics in alkaline medium. The incorporation of sulfur atoms into the carbon lattice promotes the redistribution of spin density and the formation of electron-

rich defect sites, facilitating O₂ adsorption and activation through *OOH intermediates. Unlike nitrogen, whose higher electronegativity primarily induces local charge polarization, sulfur modulates the spin configuration of the adjacent carbon atoms, generating active centers that enhance the four-electron pathway efficiency. Similar observations have been reported for S-doped carbon frameworks, where the presence of C–S–C and thiophene-S motifs reduced the energy barrier for O–O bond cleavage and improved the overall catalytic onset potential [37].

Table 2. Electrochemical parameters of the ORR at N/S co-doped OMCHS at the 1st and after 3000th cycles.

Samples	E _{onset} (V/RHE)		E _{1/2} (V/RHE)		j at 0.8 V/RHE (mA cm ^{−2})		HO ₂ [−] at 0.4 V/RHE (%)		n at 0.4 V/RHE	
	1st	3000th	1st	3000th	1st	3000th	1st	3000th	1st	3000th
S-OMCHS	0.88	0.88	0.81	0.82	−1.49	−1.69	2.4	1.1	3.95	3.97
N1-S-OMCHS	0.86	0.88	0.78	0.78	−0.60	−0.72	1.0	1.9	3.97	3.96
N2-S-OMCHS	0.85	0.84	0.77	0.76	−0.42	−0.30	3.2	4.1	3.93	3.91

The E_{onset} value obtained for S-OMCHS (0.88 V/RHE) also compares favorably with recent reports on sulfur-doped carbon systems such as S-doped porous graphene frameworks (0.77 V/RHE [38]), S-doped reduced graphene oxide (0.74 V/RHE [39]), S-doped carbon nanohorns (0.60 V/RHE [40]), and S-doped ordered mesoporous carbon (0.85 V/RHE [41]). This superior performance suggests that the ordered mesoporous hollow architecture of OMCHS further contributes to the exposure of accessible S-related active sites and facilitates efficient mass transport of O₂ and electrolyte species during operation.

In contrast, the N/S co-doped materials (N1-S-OMCHS and N2-S-OMCHS) display slightly lower E_{onset} values (0.86 V and 0.85 V vs. RHE, respectively), which remain comparable to those reported for other N/S co-doped carbons, such as N/S co-doped porous nanospheres (1.01 V/RHE [42]), N/S self-doped biocarbons (0.88 V/RHE [12]), N/S granular carbons (0.85 V/RHE [43]), N/S-doped CNTs (0.95 V/RHE [44]) and N/S-doped porous carbons (0.91 V/RHE [45]). The slightly diminished onset potential observed in our materials may arise from competing effects between the nitrogen and sulfur dopants: while pyridinic- and graphitic-N sites enhance charge delocalization and favor *OOH adsorption, the incorporation of sulfur—through thiophenic or sulfonic configurations—can modify the local spin and charge distribution, occasionally reducing the density of highly active N-induced sites when the dopant balance is not optimized.

The half-wave potential (E_{1/2}) values listed in Table 2 further confirm this trend: S-OMCHS exhibits a more positive E_{1/2} (0.81 V/RHE) than N1-S-OMCHS (0.78 V/RHE) and N2-S-OMCHS (0.77 V/RHE), indicating enhanced kinetics for the ORR process. The current densities at 0.8 V vs. RHE (−1.49, −0.60, and −0.42 mA cm^{−2} for S-OMCHS, N1-S-OMCHS, and N2-S-OMCHS, respectively) corroborate the higher activity of S-OMCHS. Notably, N1-S-OMCHS shows higher j values at potentials below 0.75 V/RHE, suggesting that at higher overpotentials the synergistic coupling between N and S sites becomes more significant—consistent with literature reports that associate N with charge modulation and S with spin modulation, jointly favoring the stabilization of *OOH and *OH intermediates [46].

Overall, these results confirm that while S doping alone confers excellent onset potential and kinetics via enhanced spin density and defect-driven activation of O₂, the N/S co-doped systems benefit from a complementary mechanism that enhances activity at larger overpotentials, as both dopants contribute to a cooperative modulation of adsorption

energy and electronic density—key descriptors for optimizing ORR catalysis in metal-free carbon materials [47].

Figure S2a–c show 1st cycle polarization curves of the ORR at several rotation rates. The three electrocatalysts show kinetic, mixed, and diffusion-controlled characteristic regions of the ORR. Moreover, Figure S2d,e show plots of ring current at the same rotation rate of the ORR. From the data of the ORR polarization curves and ring current plots obtained at 2000 rpm, the %HO₂[−] and *n* values are obtained. The %HO₂[−] and *n* values of N2-S-OMCHS are the highest in Table 2, even though it is not a poor performance. These results imply that the ORR at S-OMCHS, N1-S-OMCHS, and N2-S-OMCHS follows a 4e[−] transfer mechanism, with a very low %HO₂[−] yield. It should be mentioned that the electrocatalysts shown in this work outperform other carbon-based electrocatalysts in terms of %HO₂[−] and *n* values, as shown in Table S2. Contrary to expectations, the N/S co-doped OMCHS show a lower catalytic activity for the ORR than S-doped OMCHS. This suggests that although the N/S co-doped OMCHS have a higher number of defects (*I*_D^{*}/*I*_G and *I*_D^{''}/*I*_G ratios), it does not guarantee a better catalytic activity as mentioned before. However, their catalytic performance is good.

3.3. Surface Chemical Composition of S-Doped and N/S-Doped OMCHS Before ADT

The surface chemical composition of powders of S-OMCHS, N1-S-OMCHS, and N2-S-OMCHS, determined by XPS, is shown in Table S3. The electrocatalysts are formed by carbon (C 1s), oxygen (O 1s), sulfur (S 2p), and nitrogen (N 1s) in the case of the co-doped, confirming the incorporation of the heteroatoms during the in-situ doping. The carbon concentration in S-OMCHS is around 95 at. %, while for N1-S-OMCHS and N2-S-OMCHS is about 90 at. %. The oxygen concentration increases in the order S-OMCHS < N2-S-OMCHS < N1-S-OMCHS. Meanwhile, the sulfur content is rather low, with a similar concentration in S-OMCHS and N1-S-OMCHS (0.2 at. %), which is less at N2-S-OMCHS (0.1 at. %). Moreover, the nitrogen content of N1-S-OMCHS is higher than that of N2-S-OMCHS (1.2 and 0.9 at. %, respectively). Thus, successful co-doping with heteroatoms has been achieved, even though with a low concentration, particularly that of S-species. No silicon has been detected, an indication of an effective leaching of the hard core, in good agreement with the micrographs of Figure 3.

High-resolution spectra (Figure 5) reveal the chemical environments of C, S, and N in the as-prepared catalysts. In the C 1s region (Figure 5a–c), eight components were identified at binding energies corresponding to sp²-C=C (284.7 eV), sp³-C–C (285.7 eV), C–O (286.6 eV), C=O (287.6 eV), CF₂–SO₃H (288.96 eV), CF (290.3 eV), CF₂ (291.9 eV), and CF₃ (293.4 eV). The fluorine-containing species originates from the Nafion[®] binder [48]. The dominance of the C=C signal (53.8, 50.5, and 48.0 at.% for S-OMCHS, N1-S-OMCHS, and N2-S-OMCHS, respectively); Table S3 confirms a partially graphitic carbon framework, consistent with Raman analysis. The relative content of C–O groups is similar among the samples (4.3–4.7 at. %), whereas the concentration of C=O species is slightly higher in S-OMCHS. This suggests a moderate level of surface oxidation, partly attributed to methanol functionalization.

The S 2p spectra (Figure 5d–f) of catalyst inks exhibit two intense peaks at 168.22 and 169.41 eV, assigned to S 2p_{3/2} and S 2p_{1/2} states of SO₃H moieties originating from Nafion[®] [49,50]. In the case of S-OMCHS, an additional low-binding-energy peak at 163.9 eV is observed, corresponding to thiophene-S (C–S–C) species, which are characteristic of S-doped carbon nanostructures [51]. This signal is weak but distinct and absent in the N1-S-OMCHS and N2-S-OMCHS inks, likely overshadowed by the strong Nafion[®] contribution and possible spectral overlap with N-induced states.

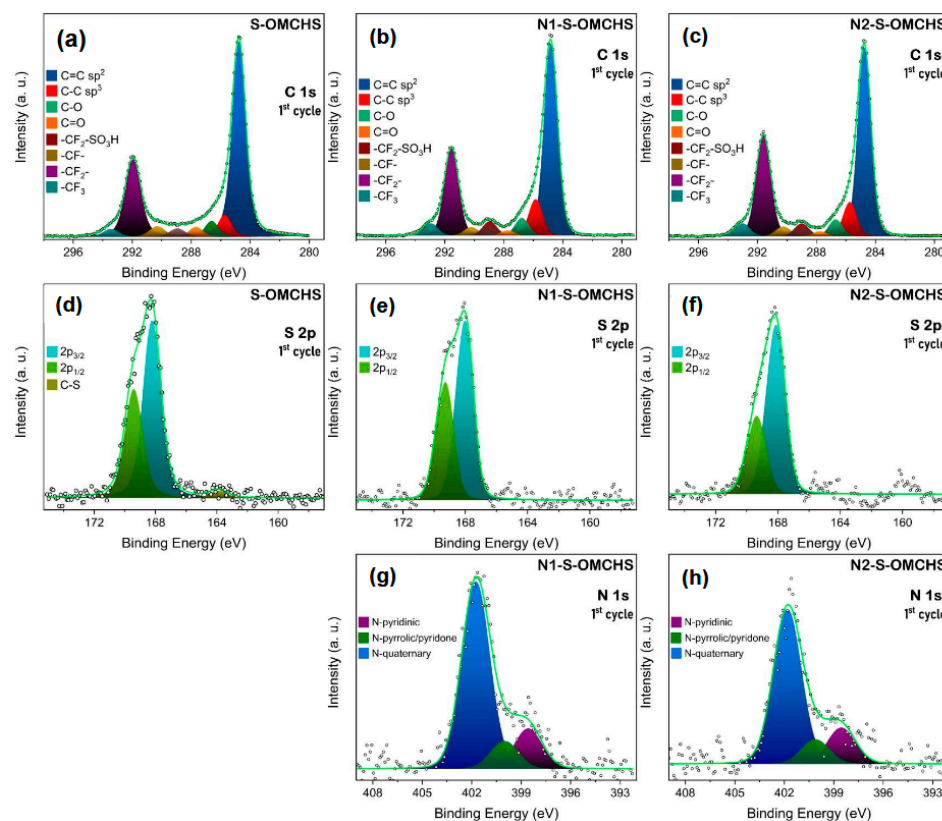


Figure 5. Deconvoluted high-resolution XPS spectra of S-OMCHS, N1-S-OMCHS, and N2-S-OMCHS. (a–c) C 1s region, (d–f) S 2p region, and (g,h) N 1s region. The analysis has been performed on catalyst inks, i.e., containing Nafion[®] solution. Plots from the 1st cycle.

To eliminate interference from Nafion[®], XPS analysis was also performed on powder samples (Figure S3). The S 2p spectra of S-OMCHS show two components at 162.8 and 164.1 eV, confirming the presence of thiophene-S species. N1-S-OMCHS exhibits three peaks (168.1, 169.5, and 164.2 eV), corresponding to oxidized-S (C–SO_x–C) and thiophene-S. Meanwhile, N2-S-OMCHS displays only oxidized-S species (168.2 and 169.5 eV) [40,52]. Therefore, the presence of thiophene-S and oxidized-S functionalities verifies the successful incorporation of sulfur during doping with 2-thiophenemethanol. Both species have been associated with enhanced ORR activity in S-doped carbon electrocatalysts [53,54]; however, the thiophene-S configuration is particularly beneficial because its conjugated C–S–C bonds facilitate π -electron delocalization, spin-density redistribution, and the adsorption/activation of O₂ molecules.

The N 1s spectra of N1-S-OMCHS and N2-S-OMCHS (Figure 5g–h) display three components corresponding to pyridinic-N, pyrrolic/pyridone-N, and quaternary-N species [55]. Interestingly, the relative abundance of quaternary-N is remarkably high (73.2% and 71.8% for N1-S-OMCHS and N2-S-OMCHS, respectively; Table S3, which differs from the single-N-doped counterparts, where pyridone and pyrrolic-N predominate [27]. This shift suggests strong chemical interaction between N and S precursors during co-doping, promoting the formation of graphitic-like nitrogen species and stabilizing the carbon framework.

Overall, the XPS results confirm the formation of heteroatom-doped carbon frameworks containing thiophene-S, oxidized-S, and quaternary-N functionalities. According to recent theoretical and experimental studies [49,51,53,56,57], these sites directly influence ORR kinetics by modulating spin density, charge distribution, and adsorption energy of oxygen intermediates. The presence of thiophene-S enhances O₂ activation via spin polarization, while quaternary-N improves electron conductivity and the binding of *OOH

species, yielding the cooperative electronic environment required for the four-electron pathway. The compositional contrast among S-OMCHS, N1-S-OMCHS, and N2-S-OMCHS thus provides a rational explanation for the electrochemical trends discussed above: S-OMCHS achieves higher onset and half-wave potentials due to the prevalence of thiophene-S species, whereas the slightly lower performance of N2-S-OMCHS correlates with its predominance of oxidized-S functionalities.

3.4. Catalytic Activity for the ORR and Surface Chemical Composition of S Doped and N/S Co-Doped OMCHS After ADT

Figure 6a–c depicts the polarization curves of the ORR at the S-OMCHS, N1-S-OMCHS, and N2-S-OMCHS electrocatalysts in the 1st and 3000th cycles. After ADT, E_{onset} of S-OMCHS remains constant, while $E_{1/2}$ shifts by 10 mV to a more positive value. Meanwhile, E_{onset} of N1-S-OMCHS shifts to 20 mV to more positive potentials, with $E_{1/2}$ maintaining the same value compared to the 1st cycle. In contrast, E_{onset} and $E_{1/2}$ are displaced by 10 mV towards more negative potentials after ADT at N2-S-OMCHS. In addition, j at 0.8 V/RHE increases 13.4 and 20.0% after ADT at S-OMCHS and N1-S-OMCHS, respectively, decreasing in the case of N2-S-OMCHS after ADT. Therefore, the S-OMCHS and N1-S-OMCHS show higher electrochemical stability after ADT than N2-S-OMCHS.

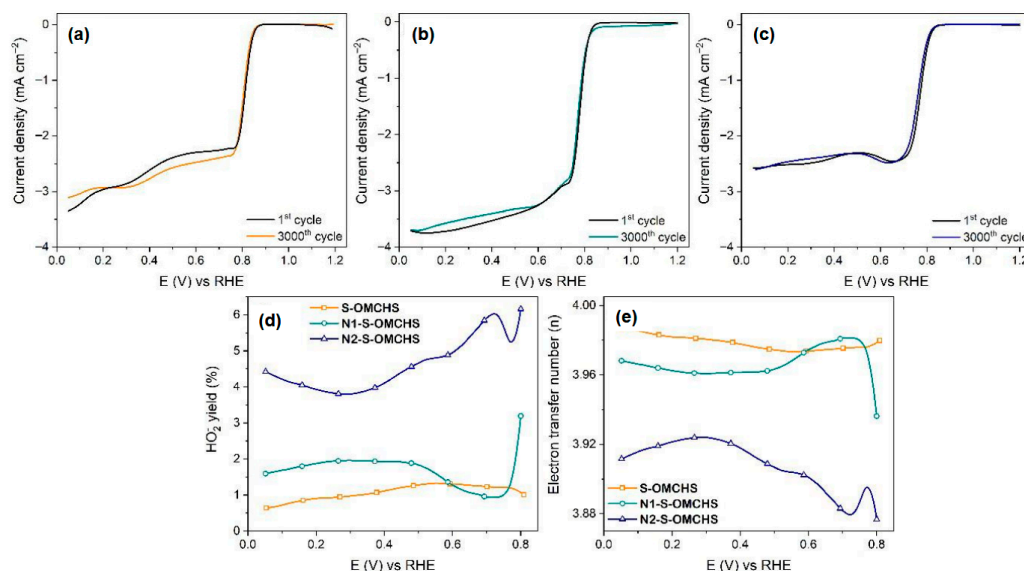


Figure 6. Negative scan only of the CVs of the ORR at 2000 rpm (1st and 3000th cycles) at (a) S-OMCHS, (b) N1-S-OMCHS, and (c) N2-S-OMCHS. Electrolyte: O₂-saturated 0.5 mol L⁻¹ KOH, scan rate = 5 mV s⁻¹ at 2000 rpm. (d) %HO₂⁻ and (e) n plots at the 3000 cycles.

In the case of the HO₂⁻ yield (Figure 6d), the values are less than 2.5% at S-OMCHS and N1-S-OMCHS. Contrary, N2-S-OMCHS have values higher than 4%. Moreover, the three electrocatalysts have been close to 4e⁻ (Figure 6e). However, S-OMCHS has the highest value of n at 0.4 V/RHE (3.97, Table 2), followed by N1-S-OMCHS and N2-S-OMCHS (3.96 and 3.91, respectively, Table 2). Thus, N1-S-OMCHS shows the highest stability after ADT in terms of E_{onset} , $E_{1/2}$, %HO₂⁻, and n . When comparing the electrochemical performance of N/S co-doped OMCHS after ADT, it is observed that they are more stable than N-doped OMCHS, which denotes a significant effect on performance with the addition of 2-thiophenemethanol as a sulfur source.

Perazzolo et al. report that after ADT, the surface concentration of N functional groups decreases because of their higher liability compared to thiophene groups, leading to an increase in the surface of carbon and a decrease in the limiting current of the ORR [57]. In addition, Liang et al. suggest that strong bonding between N, S, and C improves the

chemical and mechanical properties of the latter, enhancing its electrochemical stability [11]. In this context, the high stability shown for S-doped and N/S co-doped OMCHS is possible due to a strong interaction bonding between the N, S, and C atoms that prevents the loss of N functional groups. Moreover, polarization curves of the ORR before and after ADT in Figure 6a–c show that the limiting current (in the range of 0.8 to 0.05 V vs RHE) varies only slightly at S-OMCHS, N1-S-OMCHS, and N2-S-OMCHS, suggesting that the losses of S and N species at the electrocatalysts are low, thus sustaining a similar catalytic activity as that of the 1st cycle.

Aiming to explain the performance and electrochemical stability of S-OMCHS, N1-S-OMCHS, and N2-S-OMCHS after ADT, an analysis of their surface chemical composition has been performed by XPS. Figure 7a–c show the high-resolution spectra in the C 1s region of the electrocatalysts after the 3000th cycle. Eight signals are observed, which correlate with those before ADT (Figure 5a–c), even though with some variations in their relative concentration (Table S3). The C=C bonding increases at S-OMCHS and N1-S-OMCHS (65.3 and 51.5 at. %); meanwhile, N2-S-OMCHS decreases. The relative concentration of the Nafion-related species after ADT decreases a 22 and 5% for S-OMCHS and N1-S-OMCHS, respectively. N2-S-OMCHS maintains a relative concentration like that before ADT. These values indicate that in the co-doped OMCHS, there is better interaction between the binder and the electrocatalyst, decreasing the detachment of the electrocatalyst during ADT.

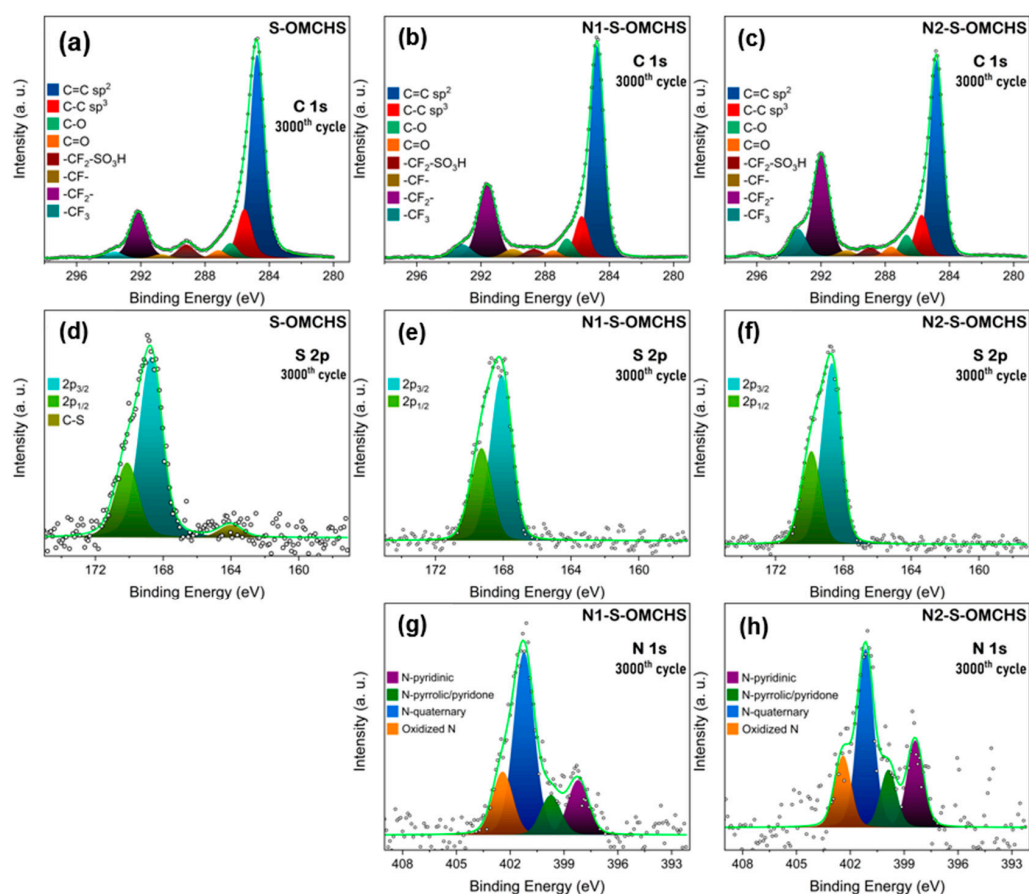


Figure 7. Deconvolution of the high-resolution XPS spectra of the N/S-doped OMCHS (catalyst inks). (a–c) C 1s, (d–f) S 2p, and (g,h) N 1s region. 3000th cycle.

The deconvoluted S 2p region of the electrocatalysts at the 3000th cycle is shown in Figure 7d–f. The S-OMCHS electrocatalyst shows a signal at 163.98 eV due to thiophene-S species. The peak is more intense after ADT compared to that of the 1st cycle (Figure 5d). Therefore, this species not only remains, but its relative concentration also increases from

2.6 before 4.8 at. %, after cycling (Table S3). Such thiophene-S species are not observed at N1-S-OMCHS and N2-S-OMCHS. Meanwhile, the signals corresponding to the $^{-}\text{SO}_3$ species of Nafion[®] at the $2p_{3/2}$ and $2p_{1/2}$ states are still observed at the electrocatalysts [58]. The high-resolution spectra of the N 1s region of N1-S-OMCHS and N2-S-OMCHS after 3000 cycles (Figure 7g,h) show four peaks at ca. 398.4, 399.9, 401.2, and 402.4 eV, which are related to N-pyridinic, N-pyrrolic/N-pyridone, N-quaternary, and oxidized-N [59]. It should be noticed that oxidized-N species have not been detected during analysis of the 1st cycle (Figure 5g,h and Table S3). Rather, this species is formed from the 3000 cycles at which N1-S-OMCHS and N2-S-OMCHS are submitted, with a similar relative concentration in both cases. To a greater or lesser extent, there is an increase in the relative concentration of N-pyridinic and N-pyrrolic/N-pyridone species at N1-S-OMCHS and N1-S-OMCHS after cycling. Moreover, the relative concentration of N-quaternary shows an important decrease at both electrocatalysts after ADT (Table S3).

After performing ADT, Perazzolo et al. have found that the most stable nitrogen species are the N-quaternary, N-pyridine, and N-pyrrole show higher stability [57]. The results shown in this work disagree with those of Ref. [57], in the sense that the relative concentration of N-quaternary decreases drastically after ADT, while that of N-pyridine and N-pyrrole increases (more clearly at N2-S-OMCHS). The emergence of the oxidized-N species, along with the increase in N-pyridine and N-pyrrole, suggests that N-quaternary has been oxidized after ADT. Therefore, these can be explained by the stability or modifications of the nitrogen species, as well as an interaction between the N, S, and C atoms that contribute to the electrochemical stability of S-OMCHS, N1-S-OMCHS, and N2-S-OMCHS after ADT.

Figure S4 compiles the high-resolution O 1s spectra of the electrocatalysts before and after ADT to elucidate the evolution of oxygen-containing functional groups (OFGs). Prior to ADT, S-OMCHS exhibits three signals at 531.9, 533.4, and 535.5 eV, assigned to $^{-}\text{SO}_3$, C–O (phenolic/ether), and $^{-}\text{OCF}_2$ environments, respectively; N1-S-OMCHS and N2-S-OMCHS additionally display a lower-binding-energy contribution at ~531.1 eV consistent with C=O/quinone-like moieties. The $^{-}\text{SO}_3$ and $^{-}\text{OCF}_2$ features originate from the Nafion[®] binder [60] and are therefore treated as a constant background associated with the ionomer; in contrast, the C–O and C=O signals are on the carbon surface. After ADT, S-OMCHS develops clear C=O species (Figure S4d), evidencing electrochemical oxidation of near-surface carbon sites during cycling.

From a mechanistic perspective, such enrichment in carbonyl/quinone groups is non-innocent: (i) C=O/quinone functionalities are known to stabilize the $^*\text{OOH}$ intermediate through specific adsorption and/or hydrogen-bonding interactions, thereby lowering the kinetic barrier for the first electron-transfer step and often biasing the reaction toward the $2e^-$ pathway to H_2O_2 relative to purely C–O sites [61]; (ii) density functional theory further shows that installing C–O and C=O motifs on sp^2 carbon produces local charge/spin redistribution, rendering the adjacent carbon atoms positively polarized and thus more competent for $^*\text{O}_2$ / $^*\text{OOH}$ adsorption—the true active centers in metal-free carbons [58,61]. In N,S-codoped frameworks such as N1-S-OMCHS and N2-S-OMCHS, these OFGs can additionally interact with dopant-induced electronic perturbations and edge defects, cooperatively tuning $^*\text{OOH}$ binding energy and the $2e^-/4e^-$ selectivity window. Altogether, the emergence/intensification of the C=O component after ADT supports a scenario in which operando surface oxidation modifies the population of OFGs and, consequently, the microkinetics of ORR on these mesoporous carbons; this evolution should be considered when correlating XPS-derived site inventories with activity/selectivity trends. For completeness, we note that assignments near 531–533 eV may exhibit partial overlap between sulfonate oxygen and lattice carbonyls; hence, comparisons across samples are best made

by normalizing to C 1s (and, where relevant, tracking F 1s from Nafion®) to decouple ionomer contributions from genuine changes in carbon-bound OFGs.

Figure 8a shows the mass catalytic activity plots before ADT of the electrocatalysts. S-OMCHS has a Tafel slope of 40 mV decade^{−1}, while those of N1-S-OMCHS and N2-S-OMCHS are 45 and 43 mV decade^{−1}, respectively. These values are also lower than those of Pt/C (63 mV decade^{−1}), demonstrating the good catalytic activity for the ORR of the metal-free electrocatalysts. After ADT (Figure 8b), there is a slight increase in the Tafel slope. Moreover, the mass current density is similar at the 3000th cycle compared to those at the 1st, confirming the high electrochemical stability of S-OMCHS, N1-S-OMCHS, and N2-S-OMCHS.

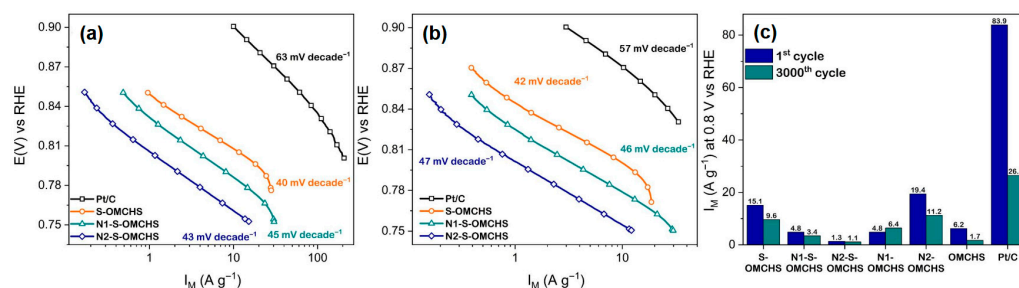


Figure 8. Mass catalytic activity of S-OMCHS, N1-S-OMCHS, and N2-S-OMCHS at 2000 rpm at (a) 1st cycle and (b) 3000th cycle compared with a commercial 20%Pt/C catalyst. (c) The mass current density of S-doped, N/S co-doped, N-doped, and non-doped OMCHS at 0.8 V/RHE.

For comparison purposes, those of the electrocatalysts characterized in previous work [27] are also shown in Figure 8c. It is observed that N2-OMCHS has a higher mass current density, followed by S-OMCHS, OMCHS, N1-OMCHS, N1-S-OMCHS, and N2-S-OMCHS (19.4, 15.1, 6.2, 4.8, 4.8, and 1.3 A g^{−1} at 0.8 V/RHE, respectively) before ADT. After ADT, the electrocatalysts show a decrease in the mass current density, which represents a loss of 73, 42, 36, 29, and 15% for OMCHS, N2-OMCHS, S-OMCHS, N1-S-OMCHS, and N2-S-OMCHS, respectively. On the contrary, N1-OMCHS shows an increase of 133% (6.4 A g^{−1}). Therefore, N1-OMCHS shows the highest electrochemical stability. However, N2-S-OMCHS and N1-S-OMCHS electrocatalysts show good electrochemical stability despite the low mass current density compared to the other electrocatalysts (e.g., S-OMCHS and N2-OMCHS).

3.5. Correlation Between Surface Chemical Evolution and ORR Performance Before and After ADT

Figure 9 illustrates the mechanistic evolution of the surface chemistry of the S-OMCHS, N1-S-OMCHS, and N2-S-OMCHS catalysts before and after ADT, highlighting the transformation of S- and N-containing species and their impact on the ORR. The schematic provides a qualitative overview of how thiophene-S, oxidized-S, and various nitrogen configurations (pyridinic, pyrrolic, quaternary, and N-oxidized) evolve under electrochemical conditions, while Table S4 quantitatively correlates these transformations with the changes in E_{onset} , $E_{1/2}$, and kinetic current density ($j_{0.8\text{V}}$). Together, these datasets reveal the interplay between structural stability, chemical reorganization, and catalytic performance: improvements or degradations in ORR activity can be directly traced to the gain, preservation, or loss of specific heteroatom sites identified by XPS and summarized in the post-ADT profiles.

For S-OMCHS, the XPS and schematic analyses confirm that the concentration of thiophene-S (C–S–C) species increased after the ADT, while minor oxidized-S species and newly formed C=O/quinone groups appeared on the surface. These changes indicate moderate surface oxidation accompanied by a reinforcement of spin-active sulfur sites.

The coexistence of thiophene-S and carbonyl functionalities promotes O_2 adsorption and $^*OOH$ intermediate stabilization through a favorable spin–charge coupling mechanism. As a result, the S-OMCHS catalyst exhibits a slight positive shift in both onset and half-wave potentials, together with improved current density, demonstrating that its active sulfur sites are structurally stable and even rejuvenated under electrochemical operation.

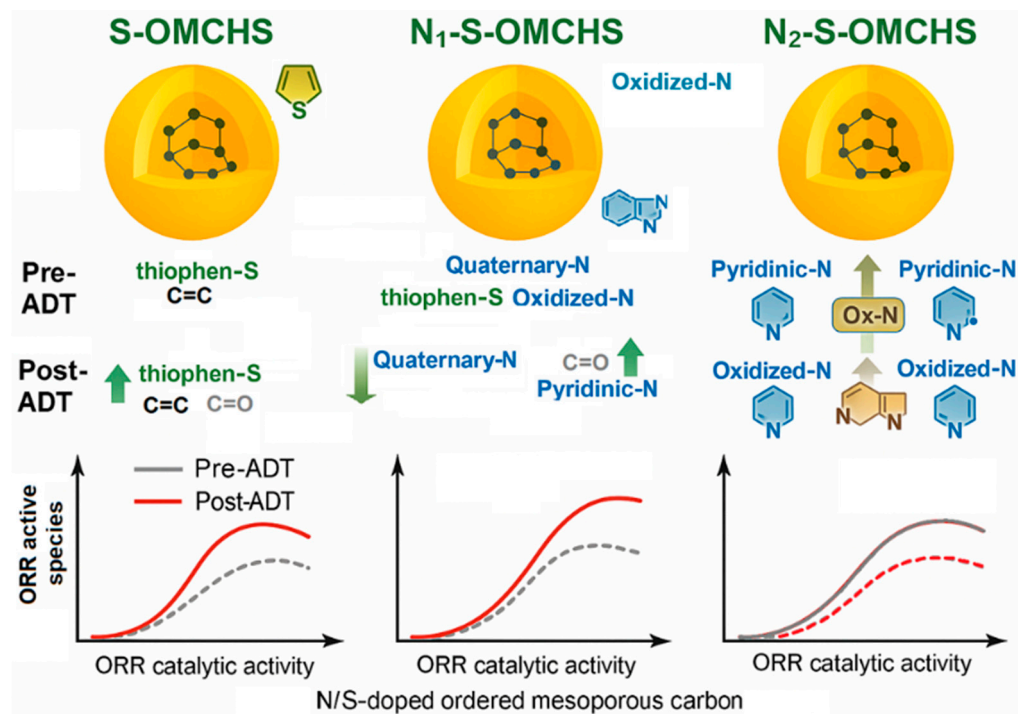


Figure 9. Evolution of surface species and ORR activity before and after ADT in S-OMCHS, N1-S-OMCHS, and N2-S-OMCHS. Arrows indicate whether the concentration of XPS-detected surface species increases or decreases for each electrocatalyst before and after ADT.

In the case of N₁-S-OMCHS, the surface chemistry underwent a more complex reorganization. The initially dominant quaternary-N fraction partially converted into pyridinic-N, pyrrolic-N, and oxidized-N species after the ADT. Simultaneously, thiophene-S sites remained stable, and a small increase in C=O groups was observed. This redistribution of nitrogen functionalities generates new electrochemically accessible centers and enhances the polarity and hydrophilicity of the surface, facilitating the adsorption of oxygen intermediates. The coexistence of stable thiophene-S and newly formed pyridinic/pyrrolic-N species results in a cooperative modulation of spin and charge density, leading to an improved onset potential (+20 mV) and excellent stability over 3000 cycles. This behavior confirms a strong N–S synergistic effect, in which nitrogen improves electron delocalization and sulfur sustains the spin-induced activation of O_2 .

In contrast, N₂-S-OMCHS exhibits a less favorable evolution during the ADT. The quaternary-N species, initially dominant, were progressively oxidized to N-oxide forms, while S remained exclusively as oxidized-S ($C-SO_x-C$) without regeneration of thiophene-S. This loss of conductive N-species and the absence of spin-active sulfur centers reduce the electronic density at the Fermi level, weakening the O_2 adsorption and $^*OOH$ dissociation steps. Consequently, both onset and half-wave potential slightly decrease (≈ -10 mV), and the current density drops, indicating partial deactivation of the catalytic surface.

Overall, the results confirm that the electrocatalytic durability and activity of these OMCHS materials are governed by the dynamic stability of heteroatom sites. The retention or regeneration of thiophene-S and the adaptive transformation of nitrogen species toward pyridinic/pyrrolic configurations contribute positively to long-term ORR performance,

while excessive oxidation or the absence of spin-active sulfur leads to degradation. This interplay between chemical composition and electrochemical behavior highlights the crucial role of heteroatom engineering in achieving both activity and durability in metal-free carbon-based electrocatalysts.

4. Conclusions

This work systematically explored the influence of heteroatom doping and electrochemical aging on the physicochemical and catalytic behavior of sulfur-doped (S-OMCHS) and nitrogen/sulfur co-doped ordered mesoporous carbon hollow spheres (N1-S-OMCHS and N2-S-OMCHS) as metal-free electrocatalysts for the oxygen reduction reaction (ORR) in alkaline media. The study demonstrates that the simultaneous incorporation of nitrogen and sulfur through molecular precursors—2-thiophenemethanol, 2-pyridinecarboxaldehyde, and pyrrole—enables precise control over the formation of thiophene-S, N-quaternary, N-pyridinic, and N-pyrrolic species within a robust carbon framework. The hard-template route based on silica cores produced uniform hollow spheres with ordered mesoporosity, high structural integrity, and accessible surface area, which together enhanced mass transport and exposure of active sites.

Comprehensive XPS analysis before and after ADT revealed that the catalytic stability and ORR activity are governed by the dynamic evolution of surface heteroatom species. For S-OMCHS, the regeneration and persistence of thiophene-S groups after ADT, together with mild surface oxidation (formation of C=O/quinone groups), led to improved onset and half-wave potentials, confirming the robustness of spin-active sulfur centers. In N1-S-OMCHS, the partial transformation of N-quaternary into N-pyridinic and pyrrolic species generated new electroactive sites, maintaining high durability and even enhancing the onset potential. In contrast, N2-S-OMCHS suffered oxidation of N-species and absence of thiophene-S regeneration, resulting in a moderate decline in activity. These findings establish a clear structure–function correlation between heteroatom configuration, surface chemistry evolution, and catalytic response. The results also highlight the complementary electronic roles of nitrogen and sulfur: nitrogen modulates charge distribution and conductivity, whereas sulfur adjusts spin density and facilitates O₂ activation. Their cooperative interaction yields a favorable spin–charge coupling environment that sustains the four-electron ORR pathway even after prolonged cycling.

In summary, this work provides fundamental insight into the stability mechanisms of heteroatom-doped carbon electrocatalysts, demonstrating that controlled doping with thiophene- and pyridinic-type functionalities can achieve both high activity and long-term durability without relying on noble metals. The approach presented here offers a rational design platform for the next generation of metal-free cathode catalysts in alkaline fuel cells and other electrochemical energy conversion systems.

Supplementary Materials: References [62–80] are cited in the supplementary materials. The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/chemistry7060187/s1>, Figure S1. Elemental mapping of the metal-free electrocatalysts. Figure S2. 1st cycle polarization and ring current potential curves of the ORR at (a–d) S-OMCHS, (b–e) N1-S-OMCHS, and (c–f) N2-S-OMCHS performed in O₂-saturated 0.5 mol L^{−1} KOH, at a scan rate of 5 mV s^{−1}; Figure S3. Deconvoluted high-resolution spectra of S-OMCHS, N1-S-OMCHS, and N2-S-OMCHS in the S 2p region; Figure S4. High-resolution O 1s spectra of S-OMCHS, N1-S-OMCHS, and N2-S-OMCHS at the 1st and 3000th cycles; Table S1. Electrochemical parameters of different metal-free electrocatalysts for the ORR.; Table S2. Comparison of catalytic performance for the ORR in terms of the E_{onset}, E_{1/2}, %HO-, and *n* of recently reported non-platinum electrocatalysts; Table S3. XPS atomic relative concentration (RC) of the C 1s, S 2p, and N1s regions of electrocatalysts before (1st cycle) and after (3000th cycle) ADT.

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References

1. Ahmed, S.; Islam, M.T.; Karim, M.A.; Karim, N.M. Exploitation of renewable energy for sustainable development and overcoming power crisis in Bangladesh. *Renew. Energy* **2014**, *72*, 223–235. [\[CrossRef\]](#)
2. Zhang, J.; Zhang, J.; He, F.; Chen, Y.; Zhu, J.; Wang, D.; Mu, S.; Yang, H. Defect and Doping Co-Engineered Non-Metal Nanocarbon ORR Electrocatalyst. *Nano-Micro Lett.* **2021**, *13*, 65. [\[CrossRef\]](#) [\[PubMed\]](#)
3. Ma, R.; Lin, G.; Zhou, Y.; Liu, Q.; Zhang, T.; Shan, G.; Yang, M.; Wang, J. A review of oxygen reduction mechanisms for metal-free carbon-based electrocatalysts. *NPJ Comput. Mater.* **2019**, *5*, 78. [\[CrossRef\]](#)
4. Zhu, Y.P.; Guo, C.; Zheng, Y.; Qiao, S.Z. Surface and Interface Engineering of Noble-Metal-Free Electrocatalysts for Efficient Energy Conversion Processes. *Acc. Chem. Res.* **2017**, *50*, 915–923. [\[CrossRef\]](#) [\[PubMed\]](#)
5. Chen, Z.; Higgins, D.; Tao, H.; Hsu, R.S.; Chen, Z. Highly Active Nitrogen-Doped Carbon Nanotubes for Oxygen Reduction Reaction in Fuel Cell Applications. *J. Phys. Chem. C* **2019**, *113*, 21008–21013. [\[CrossRef\]](#)
6. Bao, X.; von Deak, D.; Biddinger, E.J.; Ozkan, U.S.; Hadad, C.M. A computational exploration of the oxygen reduction reaction over a carbon catalyst containing a phosphinate functional group. *Chem. Commun.* **2010**, *46*, 8621–8623. [\[CrossRef\]](#)
7. Wang, D.; Su, D. Heterogeneous nanocarbon materials for oxygen reduction reaction. *Energy Environ. Sci.* **2014**, *7*, 576–591. [\[CrossRef\]](#)
8. Ge, X.; Sumboja, A.; Wu, D.; An, T.; Li, B.; Goh, F.W.T.; Hor, T.S.A.; Zong, Y.; Liu, Z. Oxygen Reduction in Alkaline Media: From Mechanisms to Recent Advances of Catalysts. *ACS Catal.* **2015**, *5*, 4643–4667. [\[CrossRef\]](#)
9. Yang, Z.; Yao, Z.; Li, G.; Fang, G.; Nie, H.; Liu, Z.; Zhou, X.; Chen, X.; Huang, S. Sulfur-doped graphene as an efficient metal-free cathode catalyst for oxygen reduction. *ACS Nano* **2012**, *6*, 205–211. [\[CrossRef\]](#)
10. Xiang, Q.; Zou, X.; Qiang, Y.; Hu, B.; Cen, Y.; Xu, C.; Liu, L.; Zhou, Y.; Chen, C. Self-assembly porous metal-free electrocatalysts templated from sulfur for efficient oxygen reduction reaction. *Appl. Surf. Sci.* **2018**, *462*, 65–72. [\[CrossRef\]](#)
11. Liang, J.; Jiao, Y.; Jaroniec, M.; Qiao, S.Z. Sulfur and nitrogen dual-doped mesoporous graphene electrocatalyst for oxygen reduction with synergistically enhanced performance. *Angew. Chem. Int. Ed.* **2012**, *51*, 11496–11500. [\[CrossRef\]](#)
12. Yang, S.; Mao, X.; Cao, Z.; Yin, Y.; Wang, Z.; Shi, M.; Dong, H. Onion-derived N, S self-doped carbon materials as highly efficient metal-free electrocatalysts for the oxygen reduction reaction. *Appl. Surf. Sci.* **2018**, *427*, 626–634. [\[CrossRef\]](#)
13. You, C.; Liao, S.; Li, H.; Hou, S.; Peng, H.; Zeng, X.; Liu, F.; Zheng, R.; Fu, Z.; Li, Y. Uniform nitrogen and sulfur co-doped carbon nanospheres as catalysts for the oxygen reduction reaction. *Carbon* **2014**, *69*, 294–301. [\[CrossRef\]](#)
14. Han, C.; Wang, S.; Wang, J.; Li, M.; Deng, J.; Li, H.; Wang, Y. Controlled synthesis of sustainable N-doped hollow core-mesoporous shell carbonaceous nanospheres from biomass. *Nano Res.* **2014**, *7*, 1809–1819. [\[CrossRef\]](#)
15. Zhou, T.; Zhou, Y.; Ma, R.; Zhou, Z.; Liu, G.; Liu, Q.; Zhu, Y.; Wang, J. Nitrogen-doped hollow mesoporous carbon spheres as a highly active and stable metal-free electrocatalyst for oxygen reduction. *Carbon* **2017**, *114*, 177–186. [\[CrossRef\]](#)
16. Pang, Y.; Wang, K.; Xie, H.; Sun, Y.; Titirici, M.M.; Chai, G.L. Mesoporous Carbon Hollow Spheres as Efficient Electrocatalysts for Oxygen Reduction to Hydrogen Peroxide in Neutral Electrolytes. *ACS Catal.* **2020**, *10*, 7434–7442. [\[CrossRef\]](#)
17. Duraisamy, V.; Krishnan, R.; Kumar, S.M.S. N-Doped Hollow Mesoporous Carbon Nanospheres for Oxygen Reduction Reaction in Alkaline Media. *ACS Appl. Nano Mater.* **2020**, *3*, 8875–8887. [\[CrossRef\]](#)

18. Qiu, Z.; Huang, N.; Ge, X.; Xuan, J.; Wang, P. Preparation of N-doped nano-hollow capsule carbon nanocage as ORR catalyst in alkaline solution by PVP modified F127. *Int. J. Hydrogen Energy* **2020**, *45*, 8667–8675. [\[CrossRef\]](#)
19. Yan, J.; Zheng, X.; Wei, C.; Sun, Z.; Zeng, K.; Shen, L.; Sun, J.; Rummeli, M.; Yang, R. Nitrogen-doped hollow carbon polyhedron derived from salt-encapsulated ZIF-8 for efficient oxygen reduction reaction. *Carbon* **2021**, *171*, 320–328. [\[CrossRef\]](#)
20. Fan, M.; Pan, X.; Lin, W.; Zhang, H. Carbon-Covered Hollow Nitrogen-Doped Carbon Nanoparticles and Nitrogen-Doped Carbon-Covered Hollow Carbon Nanoparticles for Oxygen Reduction. *ACS Appl. Nano Mater.* **2020**, *3*, 3487–3493. [\[CrossRef\]](#)
21. Zheng, Y.; Chen, S.; Zhang, K.; Guan, J.; Yu, X.; Peng, W.; Song, H.; Zhu, J.; Xu, J.; Fan, X.; et al. Template-free construction of hollow mesoporous carbon spheres from a covalent triazine framework for enhanced oxygen electroreduction. *J. Colloid. Interface Sci.* **2022**, *608*, 3168–3177. [\[CrossRef\]](#)
22. Xiong, W.; Li, H.; Cao, R. Nitrogen and sulfur dual-doped hollow mesoporous carbon spheres as efficient metal-free catalyst for oxygen reduction reaction. *Inorg. Chem. Commun.* **2020**, *114*, 107848. [\[CrossRef\]](#)
23. Zhang, C.; Li, J.; Li, C.; Chen, W.; Guo, C. Surface and interface engineering of hollow carbon sphere-based electrocatalysts for the oxygen reduction reaction. *J. Mater. Chem. A* **2021**, *9*, 25706–25730. [\[CrossRef\]](#)
24. Wei, Z.; Zhang, J.; Wang, H.; Li, X. Mesoporous Carbon Materials: Synthesis Methods, Properties, and Advanced Applications. *Front. Mater.* **2025**, *12*, 154392. [\[CrossRef\]](#)
25. Pavlenko, V.; Khosravi, H.S.; Żółtowska, S.; Haruna, A.B.; Zahid, M.; Mansurov, Z.; Supiyeva, Z.; Galal, A.; Ozoemena, K.I.; Abbas, Q.; et al. A Comprehensive Review of Template-Assisted Porous Carbons: Modern Preparation Methods and Advanced Applications. *Mater. Sci. Eng. R Rep.* **2022**, *149*, 100682. [\[CrossRef\]](#)
26. Deng, X.; Zhao, Z.; Fang, Y.; Yu, J. Protocol for the Nanocasting Method: Preparation of Ordered Mesoporous Carbon and Related Materials. *Chem. Mater.* **2017**, *29*, 40–52. [\[CrossRef\]](#)
27. Carrillo-Rodríguez, J.C.; Garay-Tapia, A.M.; Escobar-Morales, B.; Escorcia-García, J.; Ochoa-Lara, M.T.; Rodríguez-Varela, F.J.; Alonso-Lemus, I.L. Insight into the performance and stability of N-doped Ordered Mesoporous Carbon Hollow Spheres for the ORR: Influence of the nitrogen species on their catalytic activity after ADT. *Int. J. Hydrogen Energy* **2021**, *46*, 26087–26100. [\[CrossRef\]](#)
28. Chernyak, S.A.; Ivanov, A.S.; Maslakov, K.I.; Egorov, A.V.; Shen, Z.; Savilov, S.S.; Lunin, V.V. Oxidation, defunctionalization and catalyst life cycle of carbon nanotubes: A Raman spectroscopy view. *Phys. Chem. Chem. Phys.* **2017**, *19*, 2276–2285. [\[CrossRef\]](#)
29. Claramunt, S.; Varea, A.; López-Díaz, D.; Velázquez, M.M.; Cornet, A.; Cirera, A. The Importance of Interbands on the Interpretation of the Raman Spectrum of Graphene Oxide. *J. Phys. Chem. C* **2015**, *119*, 10123–10129. [\[CrossRef\]](#)
30. He, X.; Liu, X.; Nie, B.; Song, D. FTIR and Raman spectroscopy characterization of functional groups in various rank coals. *Fuel* **2017**, *206*, 555–563. [\[CrossRef\]](#)
31. Li, Y.; Zhong, J.; Yang, X.Z.; Lan, G.J.; Tang, H.D.; Liu, H.Z. Simple synthesis of semi-graphitized ordered mesoporous carbons with tunable pore sizes. *New Carbon Mater.* **2011**, *26*, 123–129. [\[CrossRef\]](#)
32. Alwin, E.; Kočí, K.; Wojcieszak, R.; Zieliński, M.; Edelmannová, M.; Pietrowski, M. Influence of High Temperature Synthesis on the Structure of Graphitic Carbon Nitride and Its Hydrogen Generation Ability. *J. Mater.* **2020**, *13*, 2756. [\[CrossRef\]](#) [\[PubMed\]](#)
33. Guan, D.; Shi, C.; Xu, H.; Gu, Y.; Zhong, J.; Sha, Y.; Hu, Z.; Ni, M.; Shao, Z. Simultaneously mastering operando strain and reconstruction effects via phase-segregation strategy for enhanced oxygen-evolving electrocatalysis. *J. Energy Chem.* **2023**, *82*, 572–580. [\[CrossRef\]](#)
34. Thommes, M.; Kaneko, K.; Neimark, A.V.; Olivier, J.P.; Rodriguez-Reinoso, F.; Rouquerol, J.; Sing, K.S.W. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure Appl. Chem.* **2015**, *87*, 1051–1069. [\[CrossRef\]](#)
35. Chen, A.; Yu, Y.; Li, Y.; Wang, Y.; Li, S.; Xia, K. Synthesis of macro-mesoporous carbon materials and hollow core/mesoporous shell carbon spheres as supercapacitors. *J. Mater. Sci.* **2016**, *51*, 4601–4608. [\[CrossRef\]](#)
36. Chao, B.; Konggidinata, M.I.; Lin, L.; Zappi, M.; Gang, D.D. Effect of carbon precursors and pore expanding reagent on ordered mesoporous carbon for resorcinol removal. *J. Water Process Eng.* **2017**, *17*, 256–263. [\[CrossRef\]](#)
37. Guo, J.; Yao, Y.; Yan, X.; Meng, X.; Wang, Q.; Zhang, Y.; Yan, S.; Zhao, X.; Luo, S. Emerging Carbon-Based Catalysts for the Oxygen Reduction Reaction: Insights into Mechanisms and Applications. *Front. Mater.* **2025**, *12*, 303. [\[CrossRef\]](#)
38. Wang, C.; Yang, F.; Xu, C.; Cao, Y.; Zhong, H.; Li, Y. Sulfur-doped porous graphene frameworks as an efficient metal-free electrocatalyst for oxygen reduction reaction. *Mater. Lett.* **2018**, *214*, 209–212. [\[CrossRef\]](#)
39. Klingele, M.; Pham, C.; Vuyyuru, K.R.; Britton, B.; Holdcroft, S.; Fischer, A.; Thiele, S. Sulfur doped reduced graphene oxide as metal-free catalyst for the oxygen reduction reaction in anion and proton exchange fuel cells. *Electrochem. Commun.* **2017**, *77*, 71–75. [\[CrossRef\]](#)
40. Macias, E.M.; Valenzuela-Muñiz, A.M.; Alonso-Núñez, G.; Sánchez, M.H.F.; Gauvin, R.; Gómez, Y.V. Sulfur doped carbon nanohorns towards oxygen reduction reaction. *Diam. Relat. Mater.* **2020**, *103*, 107671. [\[CrossRef\]](#)
41. Wang, H.; Bo, X.; Zhang, Y.; Guo, L. Sulfur-doped ordered mesoporous carbon with high electrocatalytic activity for oxygen reduction. *Electrochim. Acta* **2013**, *108*, 404–411. [\[CrossRef\]](#)

42. Zhang, X.; Wang, Y.; Du, Y.; Qing, M.; Yu, F.; Tian, Z.Q.; Shen, P.K. Highly active N,S co-doped hierarchical porous carbon nanospheres from green and template-free method for super capacitors and oxygen reduction reaction. *Electrochim. Acta* **2019**, *318*, 272–280. [\[CrossRef\]](#)
43. Li, J.C.; Qin, X.; Hou, P.X.; Cheng, M.; Shi, C.; Liu, C.; Cheng, H.M.; Shao, M. Identification of active sites in nitrogen and sulfur co-doped carbon-based oxygen reduction catalysts. *Carbon* **2019**, *147*, 303–311. [\[CrossRef\]](#)
44. Xing, X.; Liu, R.; Anjass, M.; Cao, K.; Kaiser, U.; Zhang, G.; Streb, C. Bimetallic manganese-vanadium functionalized N,S-doped carbon nanotubes as efficient oxygen evolution and oxygen reduction electrocatalysts. *Appl. Catal. B Environ.* **2020**, *277*, 119195. [\[CrossRef\]](#)
45. Lin, H.; Chen, D.; Lu, C.; Zhang, C.; Qiu, F.; Han, S.; Zhuang, X. Rational synthesis of N/S-doped porous carbons as high efficient electrocatalysts for oxygen reduction reaction and Zn-Air batteries. *Electrochim. Acta* **2018**, *266*, 17–26. [\[CrossRef\]](#)
46. Rambabu, G.; Turtayeva, Z.; Xu, F.; Maranzana, G.; Emo, M.; Hupont, S.; Mamlouk, M.; Desforges, A.; Vigolo, B. Insights into the electrocatalytic behavior of nitrogen and sulfur co-doped carbon nanotubes toward oxygen reduction reaction in alkaline media. *J. Mater. Sci.* **2022**, *57*, 16739–16754. [\[CrossRef\]](#)
47. Kundu, J.; Kwon, T.; Lee, K.; Choi, S. Exploration of metal-free 2D electrocatalysts toward the oxygen electroreduction. *Exploration* **2024**, *4*, 20220174. [\[CrossRef\]](#)
48. Chen, C.; Levitin, G.; Hess, D.W.; Fuller, T.F. XPS investigation of Nafion[®] membrane degradation. *J. Power Sources* **2007**, *169*, 288–295. [\[CrossRef\]](#)
49. Sun, Y.; Wu, J.; Tian, J.; Jin, C.; Yang, R. Sulfur-doped carbon spheres as efficient metal-free electrocatalysts for oxygen reduction reaction. *Electrochim. Acta* **2015**, *178*, 806–812. [\[CrossRef\]](#)
50. Wang, B.; Hu, J.; Zhang, L. Nitrogen and sulfur co-doped hierarchical porous carbon as functional sulfur host for lithium-sulfur batteries. *Mater. Today Commun.* **2021**, *27*, 102312. [\[CrossRef\]](#)
51. Wen, Y.; Zhu, H.; Hao, J.; Lu, S.; Zong, W.; Lai, F.; Ma, P.; Dong, W.; Liu, T.; Du, M. Metal-free boro and sulphur co-doped carbon nanofibers with optimized p-band centers for highly efficient nitrogen electroreduction to ammonia. *Appl. Catal. B Environ.* **2021**, *292*, 120144. [\[CrossRef\]](#)
52. Li, F.; Sun, L.; Luo, Y.; Li, M.; Xu, Y.; Hu, G.; Li, X.; Wang, L. Effect of thiophene S on the enhanced ORR electrocatalytic performance of sulfur-doped graphene quantum dot/reduced graphene oxide nanocomposites. *RSC Adv.* **2018**, *8*, 19635–19641. [\[CrossRef\]](#)
53. Park, J.E.; Jang, Y.; Kim, Y.; Song, M.; Yoon, S.; Kim, D.; Kim, S. Sulfur-doped graphene as a potential alternative metal-free electrocatalyst and Pt-catalyst supporting material for oxygen reduction reaction. *Phys. Chem. Chem. Phys.* **2014**, *16*, 103–109. [\[CrossRef\]](#) [\[PubMed\]](#)
54. Yang, S.; Zhi, L.; Tang, K.; Feng, X.; Maier, J.; Müllen, K. Efficient synthesis of heteroatom (N or S)-doped graphene based on ultrathin graphene oxide-porous silica sheets for oxygen reduction reactions. *Adv. Funct. Mater.* **2012**, *22*, 3634–3640. [\[CrossRef\]](#)
55. Fan, M.; Zhu, C.; Yang, J.; Sun, D. Facile self-assembly N-doped graphene quantum dots/graphene for oxygen reduction reaction. *Electrochim. Acta* **2016**, *216*, 102–109. [\[CrossRef\]](#)
56. Perazzolo, V.; Durante, C.; Pilot, R.; Paduano, A.; Zheng, J.; Rizzi, G.A.; Martucci, A.; Granozzi, G.; Gennaro, A. Nitrogen and sulfur doped mesoporous carbon as metal-free electrocatalysts for the in situ production of hydrogen peroxide. *Carbon* **2015**, *95*, 949–963. [\[CrossRef\]](#)
57. Perazzolo, V.; Grądzka, E.; Durante, C.; Pilot, R.; Vicentini, N.; Rizzi, G.A.; Granozzi, G.; Gennaro, A. Chemical and Electrochemical Stability of Nitrogen and Sulphur Doped Mesoporous Carbons. *Electrochim. Acta* **2016**, *197*, 251–262. [\[CrossRef\]](#)
58. Flyagina, I.S.; Hughes, K.J.; Pourkashanian, M.; Ingham, D.B. A Theoretical Study of Molecular Oxygen Chemisorption on N, B, or O Doped Carbon Edge Sites. *Fuel Cells* **2014**, *14*, 709–719. [\[CrossRef\]](#)
59. Maouche, C.; Zhou, Y.; Li, B.; Cheng, C.; Wu, Y.; Li, J.; Gao, S.; Yang, J. Thermal treated three-dimensional N-doped graphene as efficient metal free-catalyst for oxygen reduction reaction. *J. Electroanal. Chem.* **2019**, *853*, 113536. [\[CrossRef\]](#)
60. Friedman, A.K.; Shi, W.; Losovyj, Y.; Siedle, A.R.; Baker, L.A. Mapping Microscale Chemical Heterogeneity in Nafion Membranes with X-ray Photoelectron Spectroscopy. *J. Electrochem. Soc.* **2018**, *165*, H733–H741. [\[CrossRef\]](#)
61. Chen, S.; Luo, T.; Chen, K.; Lin, Y.; Fu, J.; Liu, K.; Cai, C.; Wang, Q.; Li, H.; Li, X.; et al. Chemical Identification of Catalytically Active Sites on Oxygen-doped Carbon Nanosheet to Decipher the High Activity for Electro-synthesis Hydrogen Peroxide. *Angew. Chem. Int. Ed.* **2021**, *60*, 16607–16614. [\[CrossRef\]](#)
62. Kim, D.W.; Heo, S.; Lee, J.S.; Lim, S.Y. Metal-Free, NH₃-Activated N-Doped Mesoporous Nanocarbon Electrocatalysts for the Oxygen Reduction Reaction. *Electrochem. Commun.* **2021**, *129*, 107092. [\[CrossRef\]](#)
63. Wütscher, A.; Eckhard, T.; Hiltrop, D.; Lotz, K.; Schuhmann, W.; Andronescu, C.; Mühler, M. Nitrogen-Doped Metal-Free Carbon Materials Derived from Cellulose as Electrocatalysts for the Oxygen Reduction Reaction. *ChemElectroChem* **2019**, *6*, 514–521. [\[CrossRef\]](#)
64. Zhu, M.; Xie, P.; Fan, L.F.; Rong, M.Z.; Zhang, M.Q.; Zhang, Z.P. Performance Improvement of N-Doped Carbon ORR Catalyst via Large Through-Hole Structure. *Nanotechnology* **2020**, *31*, 335717. [\[CrossRef\]](#) [\[PubMed\]](#)

65. Tang, H.; Chen, W.; Wang, J.; Dugger, T.; Cruz, L.; Kisailus, D. Electrocatalytic N-Doped Graphitic Nanofiber–Metal/Metal Oxide Nanoparticle Composites. *Small* **2018**, *14*, 1703459. [[CrossRef](#)] [[PubMed](#)]
66. Jia, N.; Weng, Q.; Shi, Y.; Shi, X.; Chen, X.; Chen, P.; An, Z.; Chen, Y. N-doped Carbon Nanocages: Bifunctional Electrocatalysts for the Oxygen Reduction and Evolution Reactions. *Nano Res.* **2018**, *11*, 1905–1916. [[CrossRef](#)]
67. Jiang, T.; Jiang, W.C.; Li, Y.L.; Xu, Y.S.; Zhao, M.Y.; Deng, M.Y.; Wang, Y. Facile Regulation of Porous N-Doped Carbon-Based Catalysts from Covalent Organic Frameworks Nanospheres for Highly-Efficient Oxygen Reduction Reaction. *Carbon* **2021**, *180*, 92–100. [[CrossRef](#)]
68. Mena-Durán, C.J.; Alonso-Lemus, I.L.; Quintana, P.; Barbosa, R.; Ordoñez, L.C.; Escobar, B. Preparation of metal-free electrocatalysts from cassava residues for the oxygen reduction reaction: A sulfur functionalization approach. *Int. J. Hydrogen Energy* **2018**, *43*, 3172–3179. [[CrossRef](#)]
69. Seredych, M.; Bandoz, T.J. Confined Space Reduced Graphite Oxide Doped with Sulfur as Metal-Free Oxygen Reduction Catalyst. *Carbon* **2014**, *66*, 227–233. [[CrossRef](#)]
70. Li, W.; Yang, D.; Chen, H.; Gao, Y.; Li, H. Sulfur-Doped Carbon Nanotubes as Catalysts for the Oxygen Reduction Reaction in Alkaline Medium. *Electrochimica Acta* **2015**, *165*, 191–197. [[CrossRef](#)]
71. Chen, G.; Liu, J.; Li, Q.; Guan, P.; Yu, X.; Xing, L.; Zhang, J.; Che, R. A Direct H₂O₂ Production Based on Hollow Porous Carbon Sphere–Sulfur Nanocrystal Composites by Confinement Effect as Oxygen Reduction Electrocatalysts. *Nano Res.* **2019**, *12*, 2614–2622. [[CrossRef](#)]
72. Jiao, R.; Zhang, W.; Sun, H.; Li, A. N- and S-Doped Nanoporous Carbon Framework Derived from Conjugated Microporous Polymers Incorporation with Ionic Liquids for Efficient Oxygen Reduction Reaction. *Mater. Today Energy* **2020**, *16*, 100382. [[CrossRef](#)]
73. Singh, K.P.; Song, M.Y.; Yu, J.-S. Iodine-Treated Heteroatom-Doped Carbon: Conductivity Driven Electrocatalytic Activity. *J. Mater. Chem. A* **2014**, *2*, 18115–18124. [[CrossRef](#)]
74. Wang, F.; Ma, Z.; Xu, X.; Wang, H.; Li, D.; Zhang, Y.; Zhao, J. Metal-Free B, N Co-Doped Hierarchical Porous Carbon as Electrocatalysts for the Oxygen Reduction Reaction. *ChemistryOpen* **2021**, *10*, 100090. [[CrossRef](#)] [[PubMed](#)]
75. Gong, T.; Qi, R.; Liu, X.; Li, X.; Zhang, H.; Wang, C.; Liu, Y.; Zheng, B.; Xiao, L.; Wang, S. N, F-Codoped Microporous Carbon Nanofibers as Efficient Metal-Free Electrocatalysts for the Oxygen Reduction Reaction. *Nano-Micro Lett.* **2019**, *11*, Article 9. [[CrossRef](#)] [[PubMed](#)]
76. Gao, Y.; Xiao, Z.; Kong, D.; Iqbal, R.; Yang, Q.-H.; Zhi, L. N,P Co-Doped Hollow Carbon Nanofiber Membranes with Superior Mass Transfer Property for Trifunctional Metal-Free Electrocatalysis. *Nano Energy* **2019**, *64*, 103879. [[CrossRef](#)]
77. Lv, Y.; Yang, L.; Cao, D. Sulfur, Nitrogen and Fluorine Triple-Doped Metal-Free Carbon Electrocatalysts for the Oxygen Reduction Reaction. *ChemElectroChem* **2019**, *6*, 741–747. [[CrossRef](#)]
78. Ferrero, G.A.; Fuertes, A.B.; Sevilla, M.; Titirici, M.M. Efficient Metal-Free N-Doped Mesoporous Carbon Catalysts for ORR by a Template-Free Approach. *Carbon* **2016**, *106*, 179–187. [[CrossRef](#)]
79. Alia, S.M.; Ngo, C.; Shulda, S.; Ha, M.-A.; Dameron, A.A.; Weker, J.N.; Neyerlin, K.C.; Kocha, S.S.; Pylypenko, S.; Pivovar, B.S. Exceptional Oxygen Reduction Reaction Activity and Durability of Platinum–Nickel Nanowires Through Synthesis and Post-Treatment Optimization. *ACS Omega* **2017**, *2*, 1408–1418. [[CrossRef](#)]
80. Jaouen, F.; Herranz, J.; Lefèvre, M.; Dodelet, J.-P.; Kramm, U.I.; Herrmann, I.; Bogdanoff, P.; Maruyama, J.; Nagaoka, A.; Dahn, J.R.; et al. Cross-Laboratory Experimental Study of Non-Noble-Metal Electrocatalysts for the Oxygen Reduction Reaction. *ACS Appl. Mater. Interfaces* **2009**, *1*, 1623–1639. [[CrossRef](#)]

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