

In situ generation of highly active sites by chemical vapor deposition of C₂H₄ over the LaMn_{0.7}Co_{0.3}O₃ perovskite for the oxygen reduction reaction

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Abstract

The LaMn_{0.7}Co_{0.3}O₃ perovskite was used as a substrate to deposit carbon *via* Chemical Vapor Deposition (CVD) to form composites active for the oxygen reduction reaction (ORR). The presence of carbon material is important to improve the electrical conductivity of the metal oxide. The composites were characterized by different physicochemical methods. During the CVD process and regardless of the time of carbon deposition, the perovskite structure is decomposed into other crystallite structures including MnO, Co, La₂O₃ and La(OH)₃. In addition, carbon nanotubes are formed over the metal oxides due to the presence of cobalt in the perovskite, especially after 20 min of CVD carbon deposition. The electrocatalytic activity towards ORR was assessed using a rotating ring-disk electrode in an alkaline liquid medium. The strong interactions between the carbon material and the metal-based compounds through C-O-M covalent bonds, which are highly active sites for ORR, considerably improve the catalytic performance. Moreover, new crystal phases are formed, which lead to the formation of the MnO/Co heterointerfaces that are also important sites for ORR. However, it was demonstrated that the presence of lanthanum-based compounds limits the number of active sites available for the ORR due to La segregation on the surface of the samples. Finally, the presence of carbon defects in the carbon nanotubes, especially the edge sites, can also produce a synergistic effect with the other active sites, enhancing the overall ORR reaction.

Keywords: Oxygen reduction reaction, Chemical Vapor Deposition, carbon nanotubes, C-O-M covalent bonds, Co/MnO heterointerfaces.

1. Introduction

Recently, perovskite metal oxides with the formula ABO_3 have attracted huge interest in developing materials for electrochemical applications. Indeed, since their composition can be easily modulated, it is possible to modify their physicochemical properties and, consequently, their electroactivity [1]. Especially, these materials can be used as potential electrocatalysts for the oxygen reduction reaction (ORR) occurring at the cathode of alkaline anion exchange membrane fuel cells (AAEMFC) [2]. Similar to proton exchange membrane fuel cells (PEMFC), Pt-based materials are commonly used for this reaction, which limits the development of these devices due to the high cost and low abundance of Pt [3, 4]. Moreover, working under alkaline conditions offers some advantages such as a less corrosive environment and faster kinetics [5].

Among the diverse possibilities, lanthanum-based perovskite oxides ($LaBO_3$ where B is a 3d transition metal) have been reported as promising electrocatalysts for ORR [6–9]. La^{3+} is beneficial for the ORR performance due to the lack of 4f electrons, which enhances the electronic conductivity [10]. Moreover, it favours the formation of symmetrical structures that avoid the distortion and rotation of the BO_6 octahedron, which is important for the ORR performance [10]. In this context, Celorrio *et al.* [11] also reported better performance in a perovskite $AMnO_3$ containing La^{3+} in the A-site position; higher activity was attributed to the formation of a symmetrical BO_6 octahedron. This effect was ascribed to the similar distance between the B-O bonds in the octahedron when combined with the La^{3+} cation, unlike with other cations such as Y^{3+} , Ca^{2+} , or Sr^{2+} [11]. Regarding the 3d transition metals, a partial substitution of the B cation with another 3d transition metal cation can lead to improved electrocatalytic performance. This results from a synergy generated between both cations, changes in the morphology and better electrical conductivity due to the presence of two redox pairs [12]. In this sense, the $LaMn_{1-x}Co_xO_3$ perovskite was reported to have excellent ORR electroactivity due to the generation of different catalytic species including the increase of oxygen vacancies (O_c), the presence of the Mn^{3+}/Mn^{4+} and Co^{2+}/Co^{3+} , and the generation of a larger concentration of Mn^{4+} species [13–16]. These species improve electrical conductivity, oxygen adsorption and the disproportionation reaction of peroxide, resulting in improved ORR performance.

Generally, perovskite-based materials are synthesized as nanoparticles and, subsequently, supported or mixed with carbon-based materials to prepare functional electrocatalysts [9, 13–

15]. These strategies enhance the electrocatalytic performance by increasing the active surface area and enhancing the electrical conductivity of the composite consisting of metal oxide and carbon material. Moreover, the interactions developed between the metal oxide and carbon materials favour electron transfer, enhancing the ORR performance [14]. As a matter of fact, Li *et al.* [17] reported that the C-O-M bonds enhance the ORR kinetics by facilitating oxygen adsorption. Meanwhile, Hu *et al.* [18] suggested that, apart from the formation of small and well-dispersed perovskite nanoparticles, the strong chemical interactions formed between both compounds were responsible for improved ORR performance. Lie *et al.* [19] also reported the importance of the formation of C-O-M covalent bonds at the interphase of both compounds, which can effectively improve ORR kinetics.

The easiest and fastest approach to prepare composites containing metal oxide and carbon material is *via* physical mixing of both compounds, which can lead to the formation of strong interactions between them. Interestingly, it was reported [20] that the number of these interactions can be increased and enhanced by increasing the temperature during mixing. This results in better ORR performance due to the formation of covalent bonds between both compounds. Among the various alternatives, two post-synthesis approaches can be employed to enhance interactions between these components. The first approach is the hydrothermal method, which combines temperature and pressure to strengthen interactions, resulting in the formation of covalent bonds. The second approach involves moderate-temperature treatment, where a physically mixed sample is thermally treated at approximately 400-500 °C. This treatment provides the necessary energy to facilitate the development of covalent bonds [20]. However, the *in situ* preparation of metal oxide over the carbon material was reported to favour the number of C-O-M covalent bonds formed between both phases, leading to great electrocatalytic behaviour [17–19, 21].

Alternatively, the preparation of carbon material over metal oxide is also expected to benefit the ORR performance. In this sense, the hybrid materials could be synthesized *via* Chemical Vapor Deposition (CVD), using a metal oxide as a substrate and an organic gas as a source of carbon [22–27]. From the literature, two different scenarios could occur to the perovskite structure during carbon deposition. On the one hand, the metal oxide containing 3d cations such as Fe, Co, or Ni can catalyse the formation of carbon nanotubes from the organic gas, maintaining the perovskite structure stable during this process [23–25]. On the other hand, other studies reported that 3d transition metals exsolve from the perovskite structure to catalyse the formation of carbon nanotubes [22, 26, 27]. This would lead to the decomposition of the

perovskite structure and the formation of other crystal phases. In each scenario, the formation of strong interactions between both phases is expected to increase the catalytic activity towards ORR.

Interestingly, the appearance of other crystal phases can lead to improved electrocatalytic performance due to the formation of new catalytic sites. In this sense, the decomposition of the $\text{LaMn}_{0.7}\text{Co}_{0.3}\text{O}_3$ perovskite could possibly result in (hydr)oxides containing Mn^{n+} , La^{3+} , or Co^{n+} . Regarding La-based compounds, La_2O_3 was previously demonstrated to form C-O-La covalent bonds which enhance the ORR performance by favouring oxygen adsorption and the desorption of the surface-adsorbed hydroxide [28]. García-Rodríguez *et al.* [29] demonstrated that La^{3+} in the $\text{La}(\text{OH})_3$ or La_2O_3 phases can stabilize low crystallinity metal (hydr)oxides and generate lattice defects from the absence of lattice oxygen that are catalytic active sites.

Meanwhile, previous studies [26] reported that using a manganese-containing perovskite structure as a substrate for synthesizing composites with carbon material can result in the leaching of Mn^{2+} cations from the perovskite structure. This process can lead to the formation of the MnO crystal phase [26]. According to Ryabova *et al.* [30], Mn-based materials need to have a positive potential of the interfacial $\text{Mn}^{4+}/\text{Mn}^{3+}$ redox couple to have a good ORR performance. This explains the excellent activity of the Mn_2O_3 phase due to the presence of these cations in their structure and the remarkable positive potential of this redox couple but, *a priori*, this does not seem to be the case for the MnO phase. However, Mishra *et al.* [31] obtained good ORR performance by ball-milling different amounts of MnO with activated charcoal material. It was concluded that the ORR activity is influenced by the surface morphology, particle size, electrical conductivity, and electrochemical surface area (ECSA). These features can be optimized by supporting an optimum MnO loading over the activated charcoal. In the case of Co-based compounds, previous studies showed that Co atoms exsolve from the perovskite structure due to the reduction of the perovskite surface by ethylene [22][27]. Thus, metallic Co can be formed over the metal oxide; the Co nanoparticles in turn promote the formation of carbon nanotubes by developing active sites from the C atoms resulting from the decomposition of ethylene [26]. Similar to the metallic alloy reported by Li *et al.* [26], Co metal nanoparticles could facilitate the charge transfer between the metal oxide and the carbon nanotubes. However, the interaction between the MnO and Co can lead to highly active sites due to the formation of MnO/Co heterointerfaces [32–35]. Niu *et al.* [33] reported that the Co atoms lead to the modification of the electronic structure of pristine MnO, leading to the formation of catalytically active sites on the surface for ORR. Guo *et al.* [34] stated that these

heterointerfaces are important for ORR because they provide extra electrons for the reaction, promoting the charge transfer. Meanwhile, Wang *et al.* [35] suggested that each component has its role: metal Co improves the electrical conductivity, whereas MnO promotes the adsorption of oxygen-containing intermediates. Thus, these heterointerfaces facilitate electron transfer and lower the reaction energy barrier.

To sum up, in order to reach optimal ORR performance, the ideal electrocatalyst should have the $\text{LaMn}_{0.7}\text{Co}_{0.3}\text{O}_3$ perovskite structure covered by a layer of carbon material to mitigate the poor electrical conductivity of the metal oxide, enhancing the ORR performance. Moreover, the formation of the C-O-M covalent bonds can positively participate in the ORR performance. However, the $\text{LaMn}_{0.7}\text{Co}_{0.3}\text{O}_3$ perovskite structure could be destroyed during the Chemical Vapor Deposition procedure. Thus, apart from the C-O-M covalent bonds, the electrocatalysts could have other highly active sites, such as the MnO/Co heterointerfaces, which are important for great ORR performance.

In this work, we propose the development of composites by generating carbon material over $\text{LaMn}_{0.7}\text{Co}_{0.3}\text{O}_3$ perovskite oxide *via* Chemical Vapor Deposition (CVD) using ethylene as a carbon source. Various deposition durations were applied to the substrate so as to increase the carbon content. The perovskite structure might be decomposed after the CVD process to form different crystal phases with strong interactions with the carbon material. The various composites were characterized by different physicochemical techniques. The electrocatalytic activity in ORR was measured by linear sweep voltammetry using a rotating ring-disk electrode (RRDE). For comparative purposes, the pure metal oxides were also mixed with carbon black to prove that the CVD approach not only increases the electrical conductivity but also facilitates the formation of other active sites.

2. Experimental

2.1. Materials and reagents

Nitrate precursors were used for the preparation of the perovskite metal oxide: $\text{La}(\text{NO}_3)_3\text{O}_3 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich, 99 wt.%), $\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (Sigma Aldrich, 98 wt.%), and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich, 98 wt.%). Moreover, the following reagents were also used: ethylenediaminetetraacetic acid (EDTA - Sigma Aldrich, ACS reagent), citric acid (Sigma Aldrich, 99 wt.%), ammonia solution 28 % (NH_3 - VWR Chemicals, analytic reagent), 2-

propanol 100 % (VWR), Nafion® 5 wt.% solution (Quintech), potassium hydroxide (KOH - Supelco, 85 wt.%), $K_3[(Fe(CN)_6)]$ (Merck, ACS reagent), $K_4[(Fe(CN)_6)] \cdot 3H_2O$ (Thermo scientific, 100 wt.%), KH_2PO_4 (VWR Chemicals, 99.8 wt.%), K_2HPO_4 (Merck, 99 wt.%). Commercial Vulcan XC72R carbon black (Vulcan) (Cabot Corporation) was used as benchmark carbon material. Furthermore, a commercial catalyst made of 20 wt.% Pt/Vulcan (Sigma-Aldrich) was employed as the reference material for ORR.

All solutions were prepared with ultrapure water ($18 M\Omega cm^{-1}$, prepared at the laboratory using a Veolia water system). The gases used for the experiments were: N_2 (99.999%), O_2 (99.995%), and ethylene (C_2H_4) (> 99.5%) from Air Liquide.

2.2. Synthesis procedure

The $LaMn_{0.7}Co_{0.3}O_3$ perovskite was synthesized using a sol-gel method that has been modified [36]. This sol-gel method employs two chelating agents for the synthesis of the metal oxide: citric acid and EDTA. In this case, the molar ratio used was 2:3:2 for EDTA, citric acid, and the sum of metal cations. The sol complex was adjusted to pH = 9 through a dropwise addition of a 28% NH_3 solution. Then, the mixture was heated at 80 °C and kept for 6 h under stirring. The product was dried overnight at 150 °C in an oven and calcined at 500 °C for 1 h under atmospheric air pressure. After this, the material was ball-milled in a Fritsch planetary mill (Mono Mill P6) using an agate jar with 1 cm diameter agate balls. The milling conditions were 24 cycles at 400 rpm for 1 min and 15 s of pause between them [37]. Finally, the material was calcined again at 700 °C for 6 h under air at atmospheric pressure to form the perovskite structure. The obtained sample was named P.

Ethylene was used to deposit carbon over the metal oxide *via* chemical vapor deposition (CVD, similar to a procedure [38]). For this purpose, a stainless-steel tubular oven was used. Firstly, the temperature was set at 685 °C under an N_2 atmosphere with a flow rate equal to 0.025 mol min^{-1} . Then, the P sample was placed in a quartz boat and introduced into the oven under a reverse flow system to maintain a protective inert atmosphere over the sample. After temperature stabilization, the atmosphere was changed to a gaseous mixture containing 80% C_2H_4 and 20% N_2 with a flow rate of 0.066 mol min^{-1} and 0.016 mol min^{-1} , respectively. The contact time with this gaseous mixture varies from 0 to 30 min. Then, still at 685 °C, the atmosphere was reset to N_2 using the same flow rate. Finally, the temperature was increased up to 900 °C and kept for 2 h. The as-prepared materials were named P_CVDx, where x

indicates the contact time (in minutes) with C₂H₄. The sample that had no contact with C₂H₄ and was only treated at 900 °C for 2 h is named CVD_0 hereafter.

Moreover, the P and CVD_0 samples were mixed physically with Vulcan in an equal weight ratio using an agate mortar to prepare the P+Vul and CVD_0+Vul samples, respectively.

2.3. Characterization techniques

The materials were characterized by diverse physicochemical techniques. The crystal structure was analysed by X-ray diffraction (XRD) using a Bruker D8 Twin-Twin diffractometer (Billerica, USA) with a Cu K_α radiation source in the 2θ range of 10-80° with a step of 0.02°. The morphology of the materials was characterized by scanning electron microscopy (SEM) using a FEG-ESEM XL-30 microscope (FEI, Eindhoven, Netherlands) at 15 kV under a high vacuum. Prior to analysis, the samples were coated with a thin layer of gold to prevent charging of the surface *via* sputtering (Balzers, SCD004, Sputter coater). The samples were also examined by transmission electron microscopy using a TECNAI G2 TWIN microscope (FEI, Eindhoven, Netherlands) operating at 200 kV. A small amount of crushed sample was first dispersed in ethanol and deposited on 200 mesh carbon-coated Cu-grids (S160, AGAR).

The surface chemistry of the materials was examined by X-ray photoelectron spectroscopy (XPS) with a VG-Microtech Multilab 3000 equipment (Thermo-Scientific, Waltham, MA, USA) with an Al K_α radiation source (1253.6 eV). The raw XPS data was deconvoluted to identify the different species using the XPSPEAK41 software. The fitting was done with a combination of Lorentz-Gaussian functions and using a Shirley line as a background.

The textural properties of the materials were characterized by N₂ adsorption-desorption measurements at -196 °C using ASAP 2420 equipment (Micromeritics, Norcross, GA, USA). Previously, the samples were degassed under high vacuum (2×10^{-4} Pa) for 5 h at 30 °C, followed by 2 h at 270 °C. The Brunauer-Emmett-Teller (BET) method was applied to calculate the specific surface area, A_{BET} [39]. The carbon material contents of the samples was assessed by thermogravimetric analysis (TGA) with a Sensys Evo TG-DSC equipment (Setaram, Caluire-et-Cuire, France). The sample was heated to 800 °C under an air atmosphere at a heating rate of 5 °C min⁻¹ and kept at that temperature for 2 h until reaching a constant mass. The possible mass gain produced in the oxidation of the metal oxides was omitted to quantify the carbon content because it should be low, as metal oxides were used for the CVD carbon deposition.

Finally, Raman spectra of composites prepared *via* CVD were obtained using a Jasco NRS5100 spectrometer (Jasco Corporation, Tokyo, Japan) with a 3.9 mW solid-state laser (green) at 532 nm. This technique was applied to identify the presence of carbon defects in the composites.

2.4 Electrochemical characterization

To electrochemically characterize the samples, an ink was prepared by sonicating 19.9 mg of the sample with 5.15 mL of a solution containing 70 vol% water, 27 vol% isopropanol, and 3 vol% Nafion[®]. The electrochemical measurements were done in a three-electrode cell in 0.1 M KOH solution at 25 °C using an Autolab PGSTAT30 potentiostat (Metrohm, Netherlands). A rotating ring-disk electrode (RRDE) was used as the working electrode. The disk was a glassy carbon (GC) of 5 mm, whereas the ring was made of Pt. A Pt sheet electrode was used as a counter-electrode, whereas the reference electrode was an Ag/AgCl electrode (3 M KCl). All the electrodes were provided by Metrohm. In all cases, the electrolyte was a solution of 0.1 M KOH. To convert the potential measured to standard relative hydrogen reversible (RHE) potentials, the Nernst equation [40] was used:

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.209 + 0.0591\text{pH} \quad (\text{Eq. 1})$$

Before electrochemical measurements, a layer of 590 $\mu\text{g cm}^{-2}$ material was deposited over the glassy carbon disk electrode. The measured currents were divided by the geometrical surface area of the GC to determine the current densities. Then, cyclic voltammetry (CV) tests were performed after bubbling the electrolyte for 20 min with either N₂ or O₂. On the one hand, the N₂ atmosphere is used to characterize the electrochemical properties of the materials including redox processes and stability. On the other hand, the O₂ atmosphere is used for the characterization of the oxygen reduction reaction. The window potential was chosen from 0.0 to 1.2 V (vs. RHE), and the sweep rate was set at 10 mV s⁻¹.

The catalytic activity towards ORR was analyzed by linear sweep voltammetry (LSV) tests at 1600 rpm at 2 mV s⁻¹ from 1.0 to 0.0 V (vs. RHE) in an O₂-saturated solution. To quantify the concentration of hydrogen peroxide formed during the measurements, the ring was kept at 1.5 V (vs. RHE). Thus, the number of electrons exchanged (n_{e^-}) was calculated from the oxidation of the hydrogen peroxide according to [41]:

$$n_{e^-} = \frac{4I_{\text{disk}}}{I_{\text{disk}} + I_{\text{ring}}/N} \quad (\text{Eq. 2})$$

where I_{ring} is the current measured at the ring, whereas the I_{disk} is the one at the disk. N is the collection efficiency of the ring, which has a value of 0.265. This was experimentally determined by performing linear sweep voltammetry measurements in a 1 M KNO_3 solution containing 0.1 M $\text{K}_3[\text{Fe}(\text{CN})_6]$. The LSVs were conducted at different rotation speeds (400-2025 rpm) with a scan rate of 5 mV s^{-1} from 1.4 to 0.0 V (vs. RHE) under an N_2 -saturated solution. The limiting current detected in the disk results from the reduction process of Fe^{3+} to Fe^{2+} . Simultaneously, the ring kept at high potential produces the oxidation of Fe^{2+} to Fe^{3+} which also generates a limiting current. Therefore, the N parameter is determined according to the following equation:

$$N = \frac{-I_{\text{disk}}}{I_{\text{disk}}} \quad (\text{Eq. 3})$$

The N value is calculated from an average of the different values determined at different rotation speeds.

Moreover, the Tafel values for the different samples were determined by plotting the potential vs. the logarithm of the current density of the ORR data. The slope obtained in the kinetic-limited region (close to the onset potential) is the Tafel value.

To determine the ElectroChemically active Surface Area (ECSA) of the composites prepared via CVD, CVs were performed at different scan rates. Firstly, 30 μL of the 1 mg mL^{-1} ink previously prepared was deposited on a glassy carbon electrode of 3 mm diameter. Then, CVs were realized at different scan rates ranging from 2 to 400 mV s^{-1} in a 0.1 M phosphate buffer solution (PBS, $\text{pH} = 7.2$) containing a redox probe (*i.e.* 10 mM $\text{K}_3\text{Fe}(\text{CN})_6$ / 10 mM $\text{K}_4\text{Fe}(\text{CN})_6$). Finally, the Randles-Sevcik equation was used to estimate the ECSA [42]:

$$I_p = 2.687 \times 10^5 A C n^{3/2} (Dv)^{1/2} \quad (\text{Eq. 4})$$

where I_p is the peak current (A), A is ECSA (cm^2), C is the concentration of the electroactive species (mol cm^{-3}), n is the number of exchanged electrons, D is the diffusion coefficient of the redox probe ($\text{cm}^2 \text{s}^{-1}$) and v is the scan rate (V s^{-1}). According to the literature, the D value for the diffusion of $\text{Fe}(\text{CN})_6^{3-/4-}$ in water at 25°C is $7.6 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$ [43]. To obtain the ECSA, both the anodic and cathodic intensities were plotted against the square root of the scan rate. In each case, the ECSA value was determined by calculating the average between the anodic and cathodic slopes.

3. Results and discussion

3.1. Structural characterization

The identification of the crystal structure is essential to understanding the electrocatalytic behaviour of the materials towards ORR. Therefore, the materials were characterized by X-ray diffraction; the results are shown in Figure 1. As expected, the P sample displays diffraction peaks at 23° , 33° , 40° , 47° , 53° , 58° , 68° , and 78° , which can be indexed to a cubic perovskite phase ($\text{LaMnO}_{3.17}$ (Pm3m), PDF code: 04-017-7968). Meanwhile, the CVD_0 sample exhibits partial decomposition of the perovskite structure during the thermal treatment at 900°C , resulting in the formation of additional crystal phases. In the case of the remaining perovskite structure, it can be deduced that a lattice enlargement occurs from the shift of the peak at 2θ values close to 32° (Figure S.1a). This enlargement is caused by the presence of cations with a large ionic radius in the structure that result from the chemical reduction of the $3d$ transition metal to lower valence values [16]. Moreover, the $3d$ metal cations exsolved from the structure can also lead to the formation of the cubic MnO (MnO (Fm3m), PDF code: 04-005-4310) with peaks at 2θ close to 35° , 41° and 59° and the cubic metallic Co (Co (Fm3m), PDF code: 00-015-0806) with one peak at 44° . Regarding the La^{3+} cation, it can be found in two main crystal structures: La_2O_3 and $\text{La}(\text{OH})_3$. On the one hand, the peaks at 2θ values close to 26° , 29° , 30° , 39° , 46° , 52° , 55° , and 56° can be indexed to hexagonal La_2O_3 (La_2O_3 (P-3m1), PDF code: 04-005-4229). On the other hand, the peaks at 16° , 27° , 28° , and 49° can be indexed to hexagonal $\text{La}(\text{OH})_3$ ($\text{La}(\text{OH})_3$ (P6₃/m), PDF code: 04-005-8587). Moreover, a LaCoO_3 structure is also detected by the diffraction peak around 31° , as shown by an asterisk in Figure 1.

On the contrary, under the ethylene flow and high temperature, a higher amount of Co atoms seems to exsolve from the perovskite structure, leading to its complete decomposition [22]. This results mainly in the formation of the La_2O_3 , $\text{La}(\text{OH})_3$, and MnO crystal structures. Interestingly, the peak intensity from the $\text{La}(\text{OH})_3$ crystal structure increases with the carbon deposition duration in the composites. This suggests that longer interaction times between metal-based compounds and the ethylene flow favours the crystallinity of $\text{La}(\text{OH})_3$ phase since the peaks increase in intensity (Figure S.1a). The intensity of the peak related to the MnO structure ($\sim 41^\circ$) seems constant with the carbon deposition duration in the carbon-containing composites (Figure S.1b), but no peak related to the metal Co phase is detected (Figure S.1c). This suggests the formation of small, well-dispersed Co nanoparticles over the other metal

oxides, similarly to previous studies [22, 26]. This can lead to the formation of Co/MnO heterointerfaces, which are highly active sites for ORR [32, 33, 35]. Indeed, these heterointerfaces enhance the electrical conductivity and promote the adsorption of oxygen-containing intermediates [35].

A peak at 2θ close to 41° is also observed (Figure S.1b); this peak is related to the carbon structure, and its intensity increases with carbon deposition duration. This indicates that more graphitic structures seem to form due to the presence of the crystal phases resulting from the decomposition of the perovskite structure.

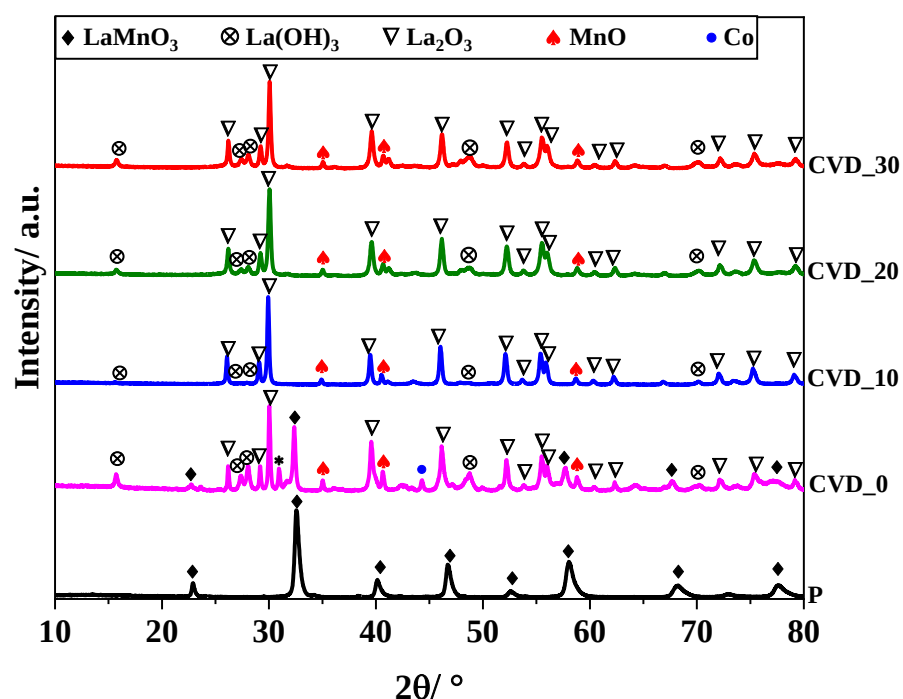


Figure 1. XRD patterns of the samples with different CVD times. (black line —) P; (magenta line —) CVD_0; (blue line —) CVD_10; (olive line —) CVD_20; (red line —) CVD_30. The asterisk (*) points to the LaCoO_3 structure.

The crystallite size of the main crystal structures was calculated using the Scherrer equation [44] (see Supporting Information, Table 1). As expected, the crystallite size of the LaMnO_3 increases for the CVD_0 sample compared to the P sample, from 18 nm to 28 nm, due to the sintering of nanoparticles caused by the thermal treatment. In the case of the CVD_0 sample, large crystallite sizes for the MnO and Co crystal phases are also detected, with values of 41 and 45 nm, respectively. The crystallite size of the MnO decreases by increasing the duration of the CVD treatment. This implies that the formation of carbon material over the metal oxide

might prevent the particles from sintering. Meanwhile, in the carbon-containing composites, the crystallite size of the La_2O_3 phase tends to decrease, while the $\text{La}(\text{OH})_3$ phase increases with longer carbon deposition durations. Interestingly, the CVD_20 sample displays the lowest crystalline size for the La_2O_3 and the largest one for the $\text{La}(\text{OH})_3$. This might imply that the $\text{La}(\text{OH})_3$ phase is formed to the detriment of the La_2O_3 phase, which could strongly impact the ORR activity.

3.2. Morphology and textural properties characterization

The morphology can also play an important role in the electrocatalytic performance of the different materials. Indeed, a porous structure that can provide a higher amount of accessible active sites is preferred. To get insight into those properties, the surface morphology of the samples was characterized by SEM, and the results are displayed in Figure 2. The main objective was to observe any possible change in the morphology resulting from the CVD treatment. Firstly, the pristine perovskite (P) (Figure 2a) displays polyhedral particles with an average size of around 60 nm; those particles are agglomerated into larger structures. Voids between the particles can also be observed; those voids probably result from the decomposition of nitrate precursors and chelating agents during the calcination process [45]. They provide porosity to the material and increase the surface area available for the reaction. Secondly, Figure 2b shows the CVD_0 metal oxide after thermal treatment at 900 °C. One can observe that the sample underwent sintering, leading to larger particles (100 to 360 nm). Thus, not only would the interaction of the perovskite with ethylene under the CVD process change the morphology of the metal oxides, but also the post-thermal treatment. In the CVD_10 sample (Figure 1c), irregular particles that are well covered by a layer of carbon material are barely distinguishable. Small carbon nanotubes (inset Figure 3c) can even be observed emerging from the aggregates. In this case, Co nanoparticles catalyse the growth of carbon nanotubes through the deposition of reactive carbon atoms on their surface. Indeed, Co-based catalysts are commonly used in industry for the synthesis of carbon nanotube materials [46]. Hence, longer contact times between the perovskite and ethylene flow might favour the increase in the amount of carbon nanotubes within the composite samples. This is evident in the CVD_20 sample (Figure 3d), where higher amounts of isolated carbon nanotubes with an average diameter of 30 nm can be detected among small aggregates of metal oxide material. In the case of the CVD_30 sample, carbon nanotubes with a larger average diameter (around 55 nm) can be

observed. This might explain the increase in crystallinity of the carbon phase observed by XRD analysis.

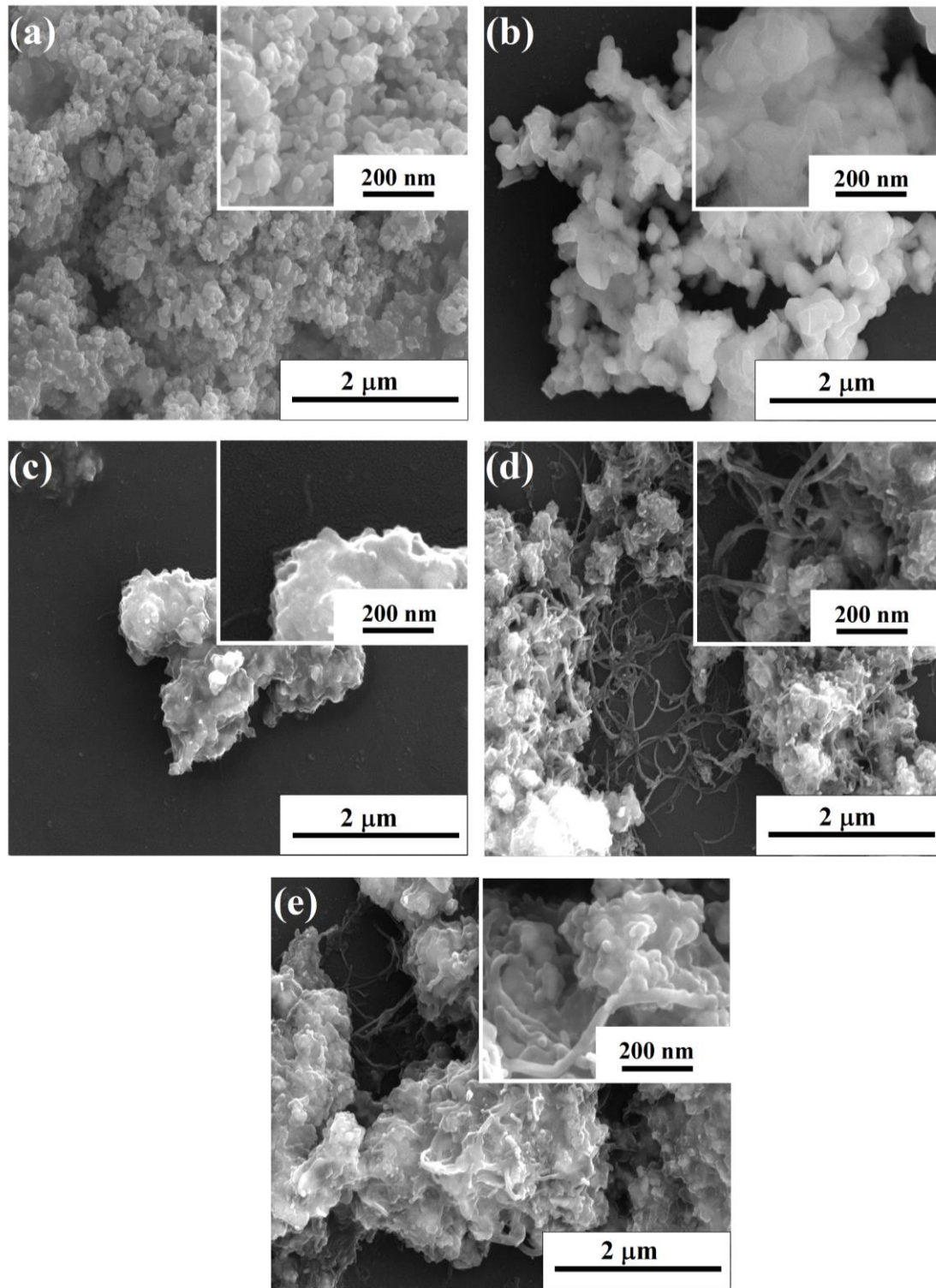


Figure 2. SEM images for the different composites with different durations of carbon deposition: (a) pristine $\text{LaMn}_{0.7}\text{Co}_{0.3}\text{O}_3$ perovskite (P); (b) CVD_0; (c) CVD_10; (d) CVD_20; and (e) CVD_30.

For a more in-depth analysis of the microstructure of the composites, the CVD_20 and CVD_30 samples were selected for characterization using TEM. Figure 3 shows the TEM images of the samples at different magnifications. From Figures 3a and 3d, it can be observed that both samples are composed of aggregates with various sizes and carbon nanotubes with different diameters. The tube diameter might change due to the formation of multiple walls, which is ascribed to the different sizes of the catalyst particles formed at high temperatures [47]. Also, the increase in the tube diameter could be related to the coating of the carbon nanotubes with carbon during the CVD treatment.

Figure 3b displays a magnification of the CVD_20 sample, where it can be seen that not only carbon nanotubes with a bamboo-like shape but also amorphous carbon are present. This non-ordered carbon material is associated with carbon defects (white arrows). In the case of the CVD_30 sample, the observations suggest a higher proportion of carbon nanotubes and less amorphous carbon. Generally, the carbon nanotubes have a bamboo-like shape with different diameters ranging from 15 to 30 nm. However, one can also observe carbon defects (white arrows) related to broken walls and lattice fringes.

Concerning the carbon defects, their identification or quantification is important because they play an important role in ORR as active sites. The carbon defects can break the integrity of the π conjugation, producing charged sites that can promote the O_2 adsorption for its further reduction [48]. Therefore, Raman spectroscopy was used to detect carbon defects in the carbon-containing CVD-based samples. Surprisingly, the Raman spectra of the CVD_10 and CVD_20 samples were impossible to exploit because of the strong background of the fluorescence emission of the samples masking the Raman signal (Figure S.2) [49]. Considering the laser wavelength used for the Raman analyses, the material that might interfere with their determination is La_2O_3 , which has a strong photoluminescence emission at around 520 nm [50]. Therefore, the increase of $La(OH)_3$ to the detriment of La_2O_3 might explain why it was possible to obtain Raman spectra for the CVD_30 sample. The bands associated with information about carbon defects are typically the G and D bands, which are related to graphitic carbon and carbon defects, respectively [51]. The I_D/I_G ratio is generally used to determine the number of carbon defects. The greater this value, the more defects the carbon material has. The existence of carbon defects observed by Raman spectroscopy in the CVD_30 sample agrees with TEM images. However, the unsuccessful determination of the Raman spectra for the other samples leads to find an alternative method to obtain information about carbon defects. The alternative method involved electrochemical measurements and will be discussed later.

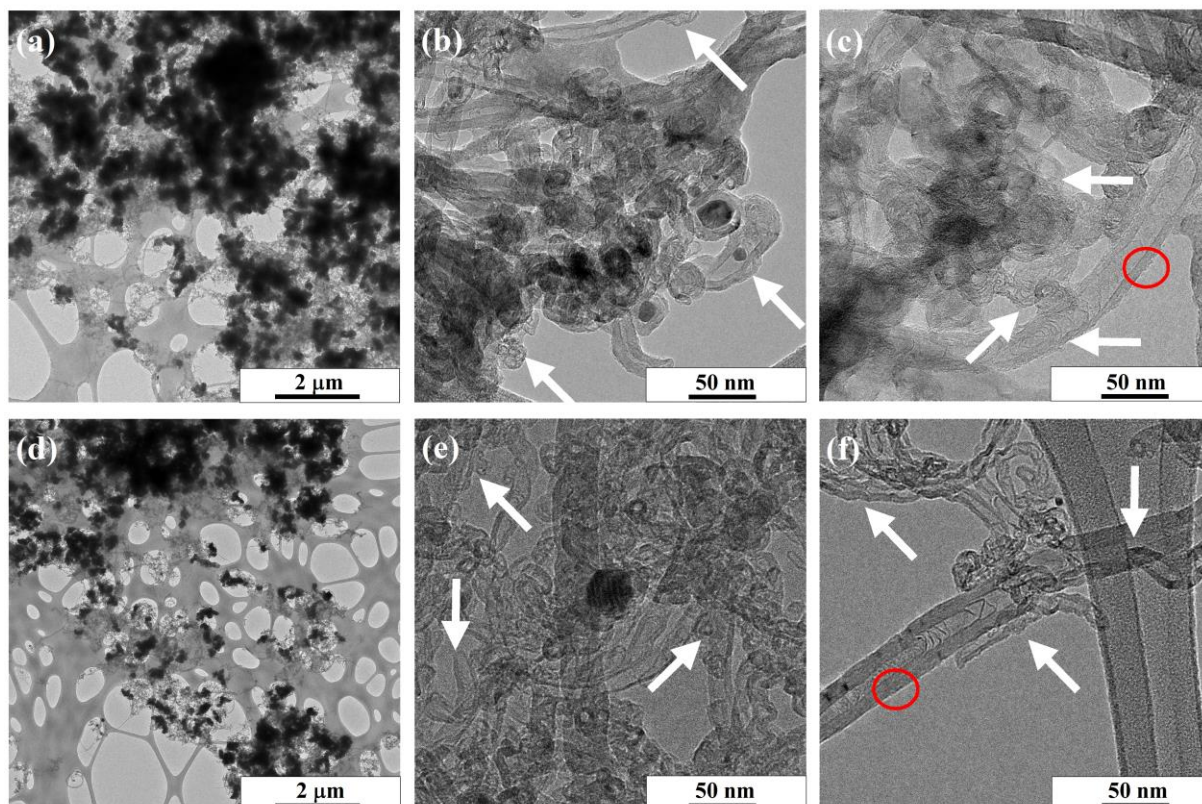


Figure 3. TEM images for the different composites: (a, b, and c) CVD_20 and (d, e, and f) CVD_30. The white arrows indicate carbon defects, whereas the red circles indicate the multi-walled carbon nanotubes.

Apart from the morphological changes, the various durations of the carbon deposition process can induce other significant changes that need to be studied. Firstly, it is important to determine the carbon content in the different composites by TGA experiments (Figure S.3a). It can be observed that the pristine perovskite is almost stable over the whole temperature range. Meanwhile, the carbon-containing samples start to lose weight from ~ 350 °C, which is ascribed to the combustion of the carbon material. This combustion is certainly catalysed by the metal-based compounds. From the data of mass loss at 800 °C, a carbon weight ratio of 30 wt.% was determined for sample CVD_10. The value increases to 40 wt.% after 20 min CVD but remains constant after that duration (Table 1). This suggests that longer deposition times only affect the morphology, but not the overall carbon content of the composites.

Regarding the textural properties, N_2 adsorption-desorption isotherm measurements were performed at -196 °C and the results are shown in Figure S.3b. According to IUPAC classification, all materials exhibit a type II isotherm profile indicative of non-porous or

macroporous materials [39]. The A_{BET} values nevertheless increase with the carbon deposition duration due to carbon material primarily contributing to the surface area of the composites (Table 1). The adsorption isotherms of the CVD_20 and CVD_30 samples almost overlap, which is in line with the similar C contents determined by TGA. The slight difference in A_{BET} between these samples might be ascribed to the less agglomerated structure observed by TEM in the CVD_30 sample. Thereby, the ORR activity is expected not to be strongly influenced by the surface area of the composites because the differences between them are not that significant.

Table 1. Physicochemical characterization of the samples by XRD, TGA curves and nitrogen adsorption-desorption isotherms.

Sample	Crystallite size ^a					Carbon material content ^b	A_{BET}^c
	LaMnO ₃	La ₂ O ₃	La(OH) ₃	MnO	Co		
	nm	nm	nm	nm	nm		
P	18	- ^d	- ^d	- ^d	- ^d	0	- ^e
CVD_0	28	25	26	41	45	0	- ^e
CVD_10	- ^d	29	15	34	- ^d	30	50
CVD_20	- ^d	21	38	30	- ^d	40	75
CVD_30	- ^d	27	23	29	- ^d	40	80

^a Crystallite size determined using the Scherrer equation for the detected crystal phases.

^b Carbon content determined from the TGA curves.

^c A_{BET} : BET surface area determined from nitrogen adsorption-desorption isotherms at -196 °C.

^d Not determined because the crystal phase was not detected by XRD, indicating that this was not formed in the composite.

^e Not measured because the pure metal oxide without the carbon phase, the value is not comparable or expected to be negligible.

3.3. Surface chemical composition

XPS spectroscopy was employed to characterize the surface chemistry of the different samples. This technique is important to quantify and identify the different elements on the surface that could participate actively in the ORR. Firstly, the quantification of the metal cations, carbon, and oxygen is summarised in Table S.1. Generally, as expected, the concentration of the metal cations on the surface decreases with the carbon deposition. However, the CVD_20 sample has

a slightly higher concentration of carbon than the CVD_30 sample. This fact suggests a higher degree of heterogeneity of the sample and a higher number of isolated carbon nanotubes available, which agrees with the SEM images.

Figure S.4 displays La 3d, Mn 2p, Co 2p, and O 1s spectra for the different samples. In the CVD-based samples, the La spectrum displays two peaks at around 834.6 and 851.7 eV related to La 3d_{5/2} and La 3d_{3/2}, respectively (Figure S.4a). Meanwhile, in the perovskite sample, these contributions appear at 833.4 and 850.2 eV, similar to previous studies [36, 52]. These contributions also show a multiplet structure. The spin-orbit splitting of 16.8 eV for all the samples indicates the presence of lanthanum in a trivalent state [53]. However, the multiplet splitting energy value differs between the CVD-based samples and perovskite oxides. The perovskite oxide has an energy value of around 4.2 eV, indicating the presence of La³⁺ in a perovskite structure [36]. The energy value of 3.8 eV in turn indicates the presence of La(OH)₃ structure [52], which agrees with the XRD results. To get deeper insight into the different contributions of La 3d, the La 3d_{5/2} spectra were deconvoluted, which resulted in three peaks: the empty c4f⁰ (~834 eV), the c4f¹L anti-bonding (~836 eV) and c4f¹L bonding (~838 eV) orbitals of lanthanum [29, 54, 55]. The c indicates the presence of a core hole, 4f⁰ the absence of electrons in this orbital and L the transfer of one electron from the ligand to the 4f orbital [54]. Hence, the concentration of the different contributions can provide information about the electron transfer from the ligand atoms to the 4f orbital, *i.e.*, it can indicate the degree of interaction between La³⁺ and 3d metal cations. For the perovskite, the values were 39.4%, 25.9% and 34.7% for the 3d_{5/2} cf⁰, 3d_{5/2} cf¹ antibonding and 3d_{5/2} cf¹ bonding orbitals, respectively. As expected, in the CVD-based materials, the destruction of the perovskite structure leads to a worse interaction between La³⁺ cations and the 3d transition cations as the 3d_{5/2} cf⁰ contribution increases up to ~46% of the total 3d_{5/2} peak, whereas the cf¹L antibonding contribution decreases to ~19% [54, 55]. This agrees with the formation of La₂O₃ and La(OH)₃ crystal phases detected by XRD.

Meanwhile, the Mn 2p spectra show two asymmetrical peaks at about 641 and 653 eV; those peaks are related to the Mn 2p_{3/2} and Mn 2p_{1/2} signals, respectively, indicating different oxidation states [9, 36]. Concerning the energy values of the spin-orbit splitting, the perovskite oxide has an energy value of 11.6 eV, which is typical for the perovskite structure [36, 56]. On the contrary, the composites have an energy value close to 11.9 eV which was reported for the MnO structure [57]. The spectra were deconvoluted into three peaks related to different oxidation states: Mn²⁺ (640.9 and 652.6 eV), Mn³⁺ (642.1 and 653.8 eV), and Mn⁴⁺ (643.2 and

654.9 eV) [34, 58]. The Co 2p spectra also show two asymmetrical peaks at about 779 and 795 eV associated with Co 2p_{3/2} and Co 2p_{1/2} signals, respectively [34, 59]. Moreover, the energy value of spin-orbit splitting of 15.6 eV suggests a mixture of Co²⁺ and Co³⁺ species [34]. Despite the spectra for the composites being a bit noisy, all of them were successfully deconvoluted into three contributions: Co⁰ (778.5 and 794 eV), Co²⁺ (780 and 795.6 eV), and Co³⁺ (779.4 and 795 eV) [34, 60]. The presence of Co⁰ species agrees with the formation of metal Co nanoparticles.

Finally, the O 1s spectrum of the perovskite shows two peaks at 528.8 and 530.8 eV, whereas in the CVD_0 sample, only one peak at 530.9 eV can be distinguished. In the carbon-containing samples, this peak progressively shifts towards higher binding energies on increasing the carbon deposition time, suggesting the generation of an O species. In the metal oxides, the O 1s spectra are deconvoluted into three peaks: lattice oxygen (O_L) (~529 eV), chemisorbed oxygen species or OH⁻ (O_C) (~530.8 eV), and adsorbed H₂O molecules (O_w) (~532 eV) [13, 15]. Meanwhile, in the carbon-containing samples, the O 1s spectra are separated into five contributions: O_L (529.7 eV), O_C (530.9 eV), O-C=O (531.8 eV), C-O-M (533 eV), and C-O and C=O (533.6 eV) [17, 19, 28, 61]. The C-O-M (M = Mn, Co, La) indicates the covalent bonds formed on the interface between carbon and metal-based materials.

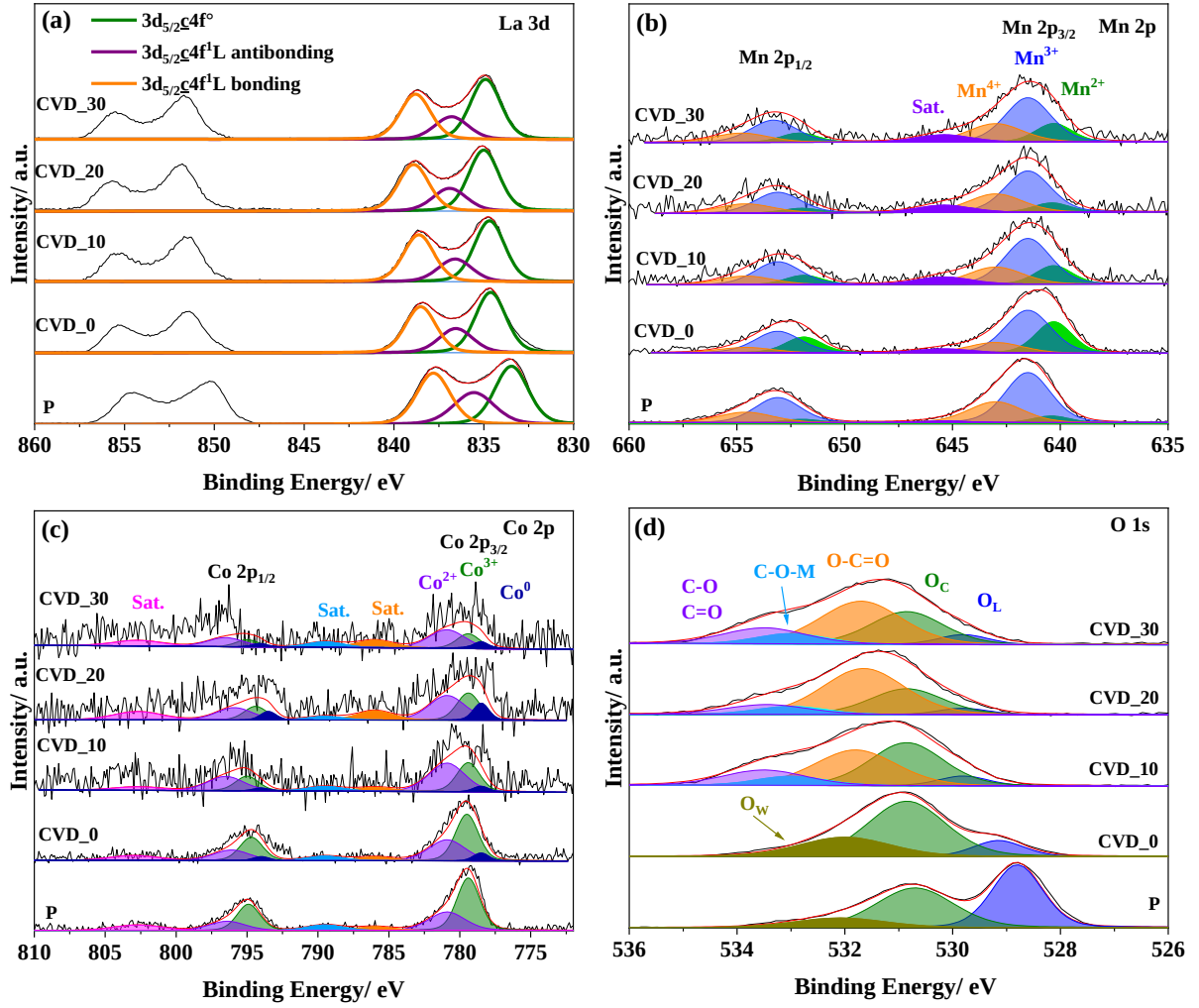


Figure 4. Deconvolution of X-ray photoelectron spectra at (a) La 3d, (b) Mn 2p, (c) Co 2p and (d) O 1s spectral regions for all the samples.

Table 2 summarizes the data obtained from the deconvolution of the XPS spectra and also shows the atomic ratio between the different cations. Similarly to previous studies [34, 58], a lanthanum segregation on the surface of the samples can be detected; this segregation increases in the CVD-treated samples compared to the P sample. This observation agrees with the formation of the lanthanum (hydro-)oxides. Data also show that the $\text{Co}/\text{B}_{\text{Total}}$ ratio is close to the nominal value of 0.3 in all materials, regardless of the presence of carbon. The $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio is around 0.5 in almost all materials except for the CVD_0 sample. This suggests that the carbon deposition significantly modifies the surface chemistry of the MnO oxide, leading to the formation of oxidized species such as Mn^{3+} and Mn^{4+} to the detriment to Mn^{2+} species. However, the CVD_0 sample has a composition more suitable for the MnO crystal phase, featuring low concentrations of Mn^{4+} species and high concentrations of Mn^{2+} species.

Despite Mn^{3+} species being the catalytic sites for ORR [6], an adequate concentration of Mn^{4+} species can enhance the oxygen adsorption *via* favouring the $\text{O}_2^{2-}/\text{OH}^-$ exchange step, which could be a rate-limiting step in ORR [13, 58, 62]. Moreover, Mn^{4+} can facilitate the chemical disproportionation of peroxide species due to its higher oxidative ability than Mn^{3+} , improving the ORR performance [62]. Opposite to the $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratio, the $\text{Co}^{3+}/\text{Co}^{2+}$ ratio follows a decreasing tendency with the carbon deposition duration. This is in line with the formation of metal Co nanoparticles dispersed over the material covered by carbon material to avoid further passivation.

Regarding the chemisorbed oxygen (O_C) species, these increase abruptly in the CVD_0 sample whereas in the carbon-containing sample, they decrease with the carbon deposition duration. These species can also be related to the oxygen vacancies and their increase might indicate the formation of Co/MnO heterointerfaces [15, 32]. The oxygen vacancies come from the charge transfer structure between the Co/MnO heterointerfaces of the composite [32]. The O_C species are important for enhancing electrical conductivity and these can participate actively in the ORR. Furthermore, these species can enhance the binding affinity with oxygen intermediates, improving the ORR performance [35]. The slight decrease in the O_C species might be attributed to the removal of Co nanoparticles from the metal oxides during the growth of the carbon nanotubes. This can lead to the reduction of Co/MnO heterointerfaces in the composites. However, as expected, the amount of C-O-M covalent bonds increases with the time of carbon deposition. This might benefit electron transfer and, as a consequence, the oxygen adsorption and regeneration of surface hydroxide, accelerating the ORR kinetics [17, 19, 28].

Table 2. Experimental atomic ratios of the cations of the samples and deconvolution data obtained from Figure 4.

Sample	$\text{B}_{\text{Total}}/\text{A}^{\text{a}}$	$\text{Co}/\text{B}_{\text{Total}}^{\text{b}}$	$\text{Mn}^{4+}/\text{Mn}^{3+}$	$\text{Co}^{3+}/\text{Co}^{2+}$	$\text{O}_\text{C}/\text{O}_\text{L}^{\text{c}}$	$\text{O}_{\text{C-O-M}}/\text{O}_{\text{Total}}^{\text{d}}$
P	0.51	0.24	0.50	1.80	0.98	- ^e
CVD_0	0.30	0.26	0.29	1.41	5.31	- ^e
CVD_10	0.30	0.21	0.45	0.65	6.25	0.074
CVD_20	0.33	0.35	0.54	0.70	5.77	0.075
CVD_30	0.32	0.25	0.50	0.51	4.75	0.084

^a $\text{B}_{\text{Total}}/\text{A}$: B_{Total} is the sum of Mn and Co species and A is La^{3+} species.

^b $\text{Co}/\text{B}_{\text{Total}}$: Co is the concentration of Co^{n+} species.

^c O_C/O_L : O_C is related to chemisorbed oxygen species, whereas O_L is the lattice oxygen species.

^d O_{C-O-M}/O_{Total} : O_{C-O-M} covalent bond species created by the interaction between metal cations and carbon through oxygen, whereas O_{Total} is the total oxygen contained in the sample.

^e Not determined due to the absence of carbon.

3.4 Electrochemical characterization

The carbon content in metal oxide/carbon composites has been previously reported to affect their electrochemical properties, including electrical conductivity, available electrochemical surface area, and activity toward ORR [14, 17, 19, 21]. Therefore, the carbon content and other changes in the physicochemical properties of the composites are expected to generate different electrochemical properties.

The samples were first electrochemically characterized by cyclic voltammetry measurements in 0.1 M KOH medium saturated either with N_2 or O_2 . The results are depicted in Figure 5. The P and CVD_0 samples display low double-layer capacitance due to the poor electrical conductivity and low surface area of the metal oxides. The P sample displays several peaks related to redox processes of the 3d transition cations (inset of Figure 5a). In the anodic scan, two peaks can be detected at around 0.7 and 1.0 V vs. RHE; those peaks are certainly related to the Mn^{2+}/Mn^{3+} redox pair and to the formation of MnOOH species, respectively [11, 30, 58]. However, one cannot discard the contribution of the Co^{2+}/Co^{3+} redox process starting at around 0.9 V vs. RHE [63]. Meanwhile, the cathodic scan indicates the Mn reverse processes at around 0.5 and 0.8 V vs. RHE [11, 30]. In the case of the CVD_0 sample, no redox contributions can be distinguished. This might be related to the decrease of Mn species on the surface and to the sintering of the particles.

However, the composites show an increase in pseudocapacitive currents, confirming the strong interaction between both phases. This leads to better electrical conductivity and an increase in accessible active sites. Two main contributions related to Mn redox processes are detected at around 1.0 and 0.5 V vs. RHE in the anodic and cathodic currents, respectively [31, 64]. The higher contribution of the anodic peak might be associated with the Co^{2+}/Co^{3+} redox process [63]. The possible formation of the Co/MnO heterointerfaces could enhance electron transfer between the Co- and Mn-based compounds. As a result, the redox processes observed in the CVD-containing carbon materials may indicate a strong interaction between these phases and the subsequent formation of heterointerfaces. Regarding the carbon deposition duration, it can be observed that the voltammetric peaks are strongly influenced: the redox response clearly increases with the CVD treatment duration. The CVD_30 sample exhibits the largest

voltammetric charges that might be ascribed to the adequate carbon concentration and greater interaction between both components. Moreover, the higher concentration of graphitic carbon structures might favour the electrical conductivity [65].

On the contrary, the CVs in the O₂-saturated atmosphere show a sharp cathodic peak related to the oxygen reduction process at different potentials, depending on the presence of the carbon and the number of catalytic active sites. The pure metal oxides display this peak at around 0.6 and 0.5 V vs. RHE for the P and CVD_0 samples, respectively. Improved behavior is evidenced for the composites, where the reduction peak is located around 0.80 V vs. RHE, especially for the CVD_30 sample. The catalytic activity will be discussed later in detail *via* linear sweep voltammetry curves.

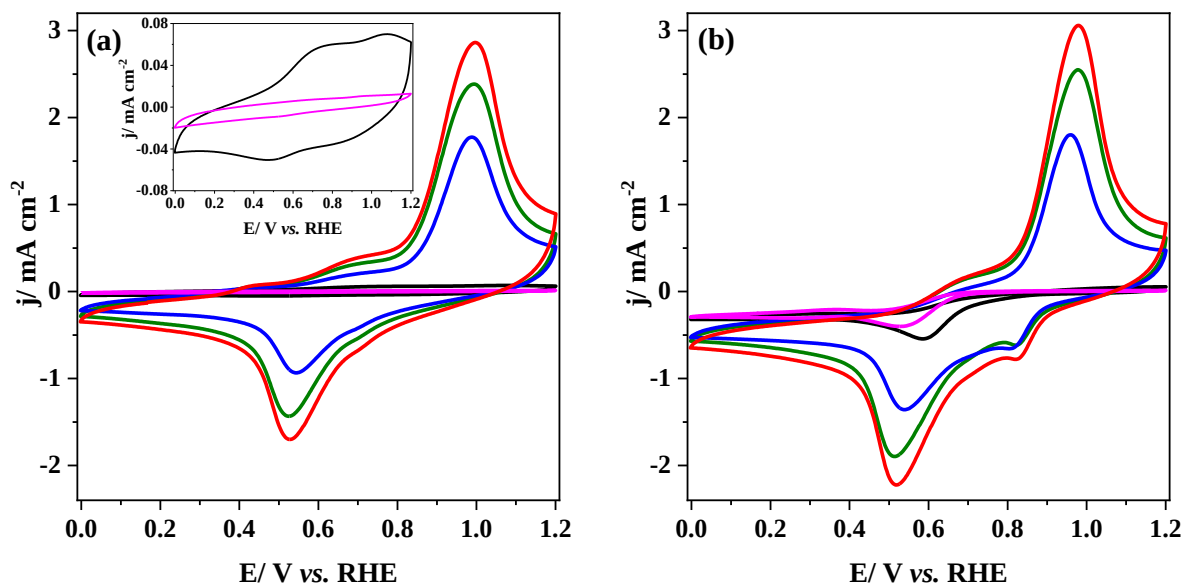


Figure 5. Voltammograms of the samples in 0.1 M KOH medium saturated with either (a) N₂ or (b) O₂. Scan rate: 10 mV s⁻¹. (—) P; (—) CVD_0; (—) CVD_10; (—) CVD_20; (—) CVD_30. Inset Figure (a): magnification for the P and CVD_0 samples.

As was previously mentioned, some carbon defects including edge sites and topological defects, are highly active sites for the ORR [66]. Generally, carbon defects can be detected by Raman spectroscopy, but in this case, it was not possible due to the fluorescence interfering with the Raman baseline. Moreover, Raman spectroscopy detects all carbon defects regardless of their ORR activity, and this could lead to a misunderstanding if the carbon materials do not have the same origin. To solve this issue, electrochemical measurements with a redox probe can be used to identify edge sites, *i.e.* a type of carbon defect with high activity in ORR [55]. Especially, the zigzag edge sites are known to display high activity due to the fast electron

transfer and the stronger adsorption energy to oxygen molecules [48]. In general, the edge sites can be detected using the $\text{Fe}(\text{CN})_6^{3-/4-}$ couple redox probe, which is surface-sensitive: indeed, this redox process is favoured by the presence of edge sites exposed to the electrolyte solution [42]. Figure S.5. displays the plots of the anodic and cathodic peak currents against the square root of the scan rates. From the slope, the ECSA values were calculated by applying the Randles-Sevcik equation (Eq. 4) and these values are shown in Table 3 [67]. The carbon-containing CVD samples have similar values ($\sim 5.8 \text{ m}^2 \text{ g}^{-1}$), suggesting that the main difference in the ORR performance might be ascribed to the other catalytic sites. However, one cannot discard a synergistic effect between all active sites that could positively influence the ORR performance.

The electrocatalytic activity in ORR was measured by linear sweep voltammetry measurements using RRDE equipment at 1600 rpm in an O_2 -saturated medium. The results are depicted in Figure 6, and Table 2 summarizes the main electrochemical parameters. As expected, the poor electrical conductivity and low surface area of the pure metal oxide materials lead to a double-plateau profile, which could be characteristic of two-reduction processes (Figure 6a). The first reduction process is related to the reduction of O_2 into peroxide, whereas the second one corresponds to the reduction of remaining O_2 and peroxide species into hydroxide. However, in the case of the P sample, the double-plateau profile might be associated with the blockage by adsorbed species to the surface-active sites, resulting from the low surface area of metal oxides [68]. This might hinder the diffusion of the reactants and the products through the surface. The CVD_0 sample exhibits a lower onset potential, indicating that the degradation of the perovskite structure and the particle sintering result in poorer ORR performance. Meanwhile, the carbon-containing composites show a significantly better performance in terms of onset potential and limiting current density. Concerning the number of electrons through which the ORR reaction occurs, the P sample displays a 4-electron pathway, whereas the CVD_0 sample seems to undergo a combination of 4- and 2-electron pathways (Figure 6b). In the case of the composites, the reduction pathway is close to the 4-electron pathway, *i.e.*, the direct reduction of oxygen to hydroxide.

Previous authors established that the 4-electron pathway in metal oxide-based materials proceeds *via* a direct cyclic mechanism involving four steps: (i) surface hydroxide displacement ($\text{O}_2^{2-}/\text{OH}^-$ exchange), (ii) surface peroxide formation, (iii) surface oxide formation, and (iv) surface hydroxide regeneration. The rate-limiting step could be either the first or the last one, depending on the filling of the e_g orbital of the $3d$ metal cations [6].

Meanwhile, the 2-electron pathway involves the reduction of O_2 to HO_2^- to be further reduced to OH^- . The latter pathway is commonly observed in carbon materials. Additionally, a Pt/C commercial catalyst was analysed as a reference, demonstrating superior ORR performance with higher onset potential, current limiting density, and selectivity towards the 4-electron pathway.

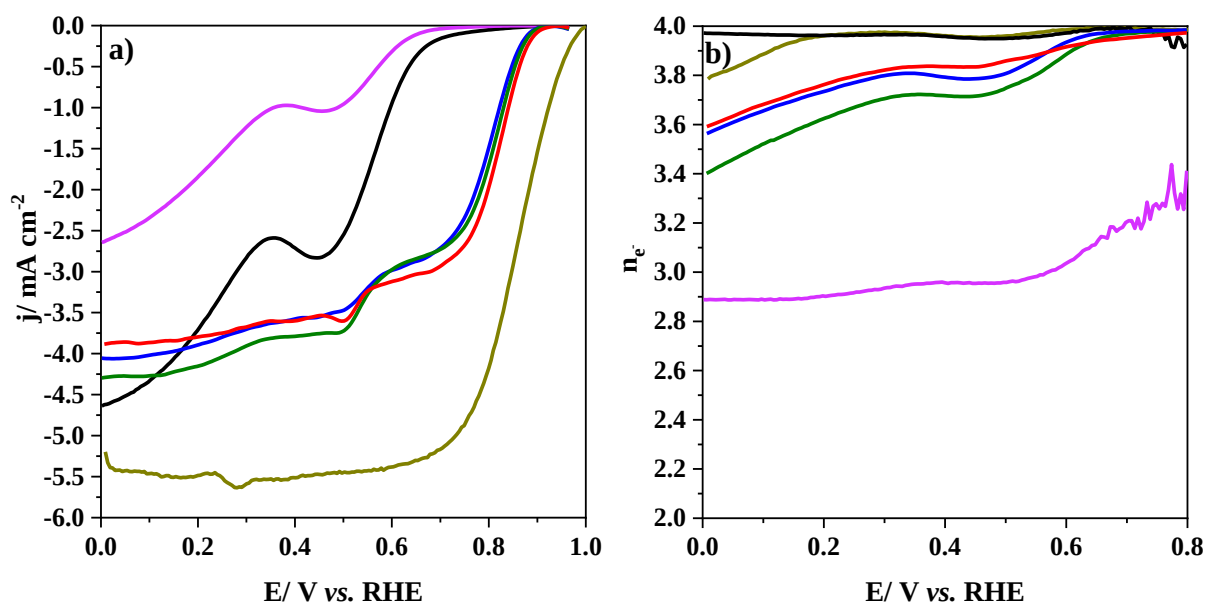


Figure 6. (a) LSVs for the samples in 0.1 M KOH saturated with O_2 at 1600 rpm; (b) Number of electrons exchanged in ORR at increasing potential. (—) P; (—) CVD_0; (—) CVD_10; (—) CVD_20; (—) CVD_30; (—) 20 wt.% Pt/Vulcan.

Although the differences in carbon-containing composites in the ORR are not huge, it is important to discuss them since they are influenced by the concentration of active sites. The CVD_30 sample exhibits the best ORR performance in terms of onset potential (0.9 V vs. RHE), half-wave potential (0.83 V vs. RHE), and number of electrons exchanged ($n_e = 3.84$). This might be ascribed to the small crystallite size of the MnO phase and presumable Co phase (Table 1), which could lead to well-dispersed Co/MnO heterointerfaces. These are assumed to enhance the ORR activity by facilitating charge transfer and providing extra electrons for the reactions [35]. Moreover, increasing the carbon deposition duration leads to the formation of more graphitic carbon structures that improve electrical conductivity. Furthermore, the slightly higher A_{BET} of the CVD_30 seems to be enough to facilitate the accessibility of O_2 to the active sites. Interestingly, this composite has the lowest O_C/O_L ratio (Table 2), indicating lower oxygen vacancies, which are important to enhance the electrical conductivity and facilitate the

$\text{O}_2^{2-}/\text{OH}^-$ exchange [58, 62]. However, the higher concentration of C-O-M covalent bonds might mitigate the low concentration of oxygen vacancies because these also improve electron transfer and greatly affect the $\text{O}_2^{2-}/\text{OH}^-$ exchange [17, 19, 28]. A synergistic effect between the above-mentioned species and edge site defects cannot be discarded; the latter could significantly enhance the ORR performance.

Surprisingly, the CVD_20 sample has a slightly lower ORR catalytic activity than the CVD_30 sample despite containing more specific active sites. Indeed, according to XPS data (Table S.1), the CVD_20 sample contains more Co^{n+} species on the surface; therefore, more Co/MnO could be formed on the surface of the composite. This also could explain its higher $\text{O}_\text{C}/\text{O}_\text{L}$ ratio compared to the CVD_30 sample. Moreover, this sample also contains slightly higher amounts of edge site defects, which could improve the ORR catalytic activity. In the present case, it seems that these sites are not that essential to the ORR activity compared to the C-O-M covalent bonds, which have a strong catalytic behaviour. As can be observed in Table 3, their progressive formation with the carbon deposition duration directly affects E_onset , $E_{1/2}$ and the Tafel slope. In the case of the current-limiting density, the CVD_20 sample displays the highest value with -3.80 mA cm^{-2} (vs. -3.60 mA cm^{-2} for the CVD_30 sample); this can be ascribed to the higher number of active sites. Interestingly, this sample has the lowest number of electrons exchanged despite having slightly higher number of active sites ($n_{e^-} = 3.72$ at 0.4 V vs. RHE). This could be attributed to the large crystallite size of $\text{La}(\text{OH})_3$ (38 nm) with poor inherent ORR behaviour. Therefore, the $\text{La}(\text{OH})_3$ crystal phase might interfere with the performance of the surrounded active sites and be responsible for the low selectivity towards the 4-electron pathway.

Tafel slope values can provide information about the kinetics of the ORR reaction, with small values close to 60 mV dec^{-1} being desirable. In this sense, the poor electrical conductivity of the metal oxides leads to sluggish kinetics for the electron transfer processes. For the CVD_0 sample, the formation of the Co/MnO heterointerfaces facilitates the charge transfer, decreasing the Tafel slope value from 150 to 109 mV dec^{-1} . In both metal oxides, *i.e.*, P and CVD_0 samples, the electron transfer determining step is the first electron transfer (120 mV dec^{-1}) [69]. The composites exhibit an improvement of the kinetics due to better electrical conductivity and the presence of species that favour the electron transfer, including the C-O-M covalent bonds, Mn^{4+} species, Co/MnO heterointerfaces, and oxygen chemisorbed species. In this case, the electron transfer determining step of the composites is the formation of HO_2^- (60 mV dec^{-1}) [69].

Table 3. *Electrochemical properties of the samples measured by LSVs.*

Sample	ECSA	$E_{\text{onset}}^{\text{a}}$	$E_{1/2}^{\text{b}}$	n_{e}^{c}	$j_{\text{lim}}^{\text{d}}$	Tafel slope ^e
	m ² g ⁻¹	V vs. RHE	V vs. RHE	-	mA cm ⁻²	mV dec ⁻¹
P	- ^f	0.74	0.57	3.96	-2.36	150
CVD_0	- ^f	0.65	0.56	2.96	-1.00	109
CVD_10	5.70	0.88	0.80	3.79	-3.58	61
CVD_20	5.96	0.89	0.81	3.72	-3.80	56
CVD_30	5.85	0.90	0.83	3.84	-3.60	54
Pt/Vulcan	- ^f	0.98	0.86	3.96	-5.51	60

^a E_{onset} : onset potential at -0.1 mA cm⁻².^b $E_{1/2}$: half-wave potential.^c n_{e} : number of electrons exchanged at 0.4 V vs. RHE.^d j_{lim} : limiting current density at 0.4 V vs. RHE.^e Tafel slope.^f Not measured because these materials were not prepared by CVD carbon deposition method.

To further confirm that the increase in catalytic activity is related not only to the formation of highly active sites but also to the strong interactions formed between the carbon material and the metal oxide during the CVD process, the P and CVD_0 samples were physically mixed with Vulcan carbon black. Thus, using an agate mortar, both compounds were mixed in an equal weight ratio. Firstly, the materials were electrochemically characterized by CV under N₂ atmosphere and the results are shown in Figure S.6 together with the CVD_30 sample. As expected, the CVD_30 sample exhibits the largest double-layer capacitance of all three samples (Figure S.6a). This observation might be associated with the better accessibility of the electrolyte to the electroactive sites and to the formation of C-O-M covalent bonds between the

metal-based compounds and the carbon materials during the CVD treatment. These covalent bonds facilitate the electron transfer during the redox processes. These effects can also be detected when the metal compounds are mixed physically with the Vulcan support, but at a lower degree. This also might be related with the different nature of the carbon materials. The P+Vul sample exhibits larger double-layer capacitance than the P sample. In addition, it shows a pseudocapacitive current related to Mn redox processes. In the anodic scan, two peaks can be detected; those peaks are related to the $\text{Mn}^{2+}/\text{Mn}^{3+}$ redox process (0.65 V vs. RHE) and to the formation of MnOOH species (0.95 V vs. RHE), respectively [30, 58]. Meanwhile, the cathodic scan shows the reverse $\text{Mn}^{3+}/\text{Mn}^{2+}$ redox process at 0.5 V vs. RHE [58]. On the contrary, the CVD_0 sample mixed with Vulcan displays mainly two redox contributions at around 1.0 and 0.6 V vs. RHE in the anodic and cathodic currents, respectively. These pseudofaradaic currents were previously detected in MnO-based materials [70]. Similar to the previous discussion, the $\text{Co}^{2+}/\text{Co}^{3+}$ redox process contribution cannot be discarded around 1.0 V vs. RHE [63].

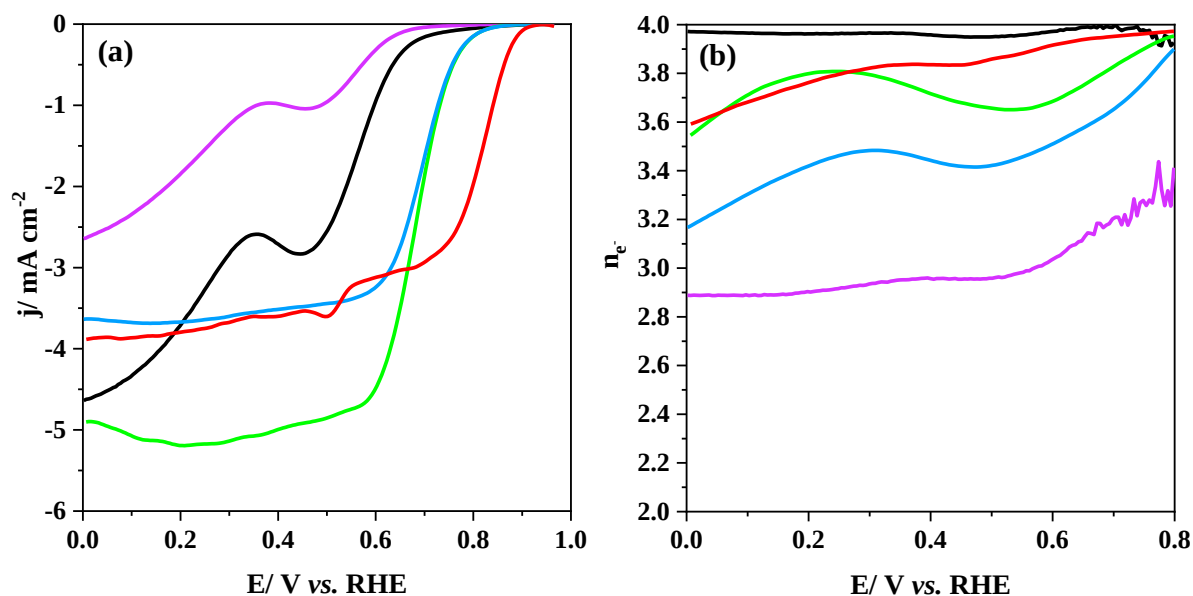


Figure 7. (a) LSVs for the CVD_30 sample and metal oxide mixed physically with and without Vulcan in 0.1 M KOH saturated with O_2 at 1600 rpm; (b) Number of electrons exchanged in ORR at increasing potential. (—) P; (—) P+Vul; (—) CVD_0; (—) CVD_0+Vul; (—) CVD_30.

Figure 7 shows the LSVs comparing the mixed and unmixed samples and Table S.2. summarizes the main electrochemical parameters. As expected, the carbon material significantly enhances the catalytic performance in ORR, especially the onset potential and the limiting current density. In the case of the CVD_0 sample mixed with Vulcan, the number of

electrons exchanged also increases, indicating the importance of the carbon material in the ORR mechanism. The carbon material acts as a co-catalyst producing peroxide, which can be further reduced over active metal oxide sites [71]. However, this positive effect is not observed for the P+Vul sample as the number of electrons exchanged slightly decreases compared to the P sample. This effect may be attributed to the replacement of perovskite, which catalyses the ORR *via* a 4-electron pathway, with carbon sites, which follow a 2-electron pathway [14]. Despite both metal oxides having different crystal structures and surface chemistry, they have the same onset and half-wave potentials, suggesting that the existing active sites in both oxides are equally active for the ORR. The big difference between both samples is the limiting current density being: -4.98 and -3.51 mA cm⁻¹ for P+Vul and CVD_0+Vul, respectively (Table S.2). This indicates that the number of active sites available at the surface of the electrode is lower for the CVD_0+Vul sample. Moreover, this material also contains crystal phases such as La₂O₃ and La(OH)₃, which have poor ORR performance. This indicates the importance of the concentration of B-site cations on the surface, as these are correlated to the active sites for the electrochemical reaction. For this purpose, previous studies investigated [58] approaches such as reducing the La percentage in the La:Mn ratio to increase the concentration of B-sites on the surface to have an optimum concentration of surface-active sites. Therefore, the drop in the ratio from 0.51 in the P sample to around 0.30 in the other samples may explain the difference in current limiting density in the CVD_30 sample compared to the P+Vul sample.

Surprisingly, the limiting current densities of the CVD_0+Vul and CVD_30 samples are similar, suggesting that the number of active sites is kept constant during the carbon deposition, regardless of the presence of the perovskite structure in the former sample. However, the formation of C-O-M covalent bonds during the carbon deposition might favour the electron transfer, enhancing the overall reaction rate. In the case of the physical mixing method, only strong interactions might be formed, but no covalent bonds. Moreover, the decomposition of the perovskite structure leads to an increase in the Co/MnO heterointerfaces, which are highly active for ORR compared to La-based compounds. Thereby, the most important active sites for great ORR performance are especially the C-O-M covalent bonds and the Co/MnO heterointerfaces. The edge site defects formed during the growth of carbon nanotubes cannot be discarded due to their highly electrocatalytic behaviour and the likely synergistic effect between all active sites. In terms of metal cations, further studies could include 3d transition metal-based oxides containing Mn and Co only, as starting material in the CVD treatment, to increase the number of available active sites. This approach would prevent the formation of

La-based compounds, which limit the electrocatalytic activity of the Mn and Co-based electrocatalytic sites.

4. Conclusions

A chemical vapour deposition (CVD) method was employed to prepare active composites for oxygen reduction reaction, using $\text{LaMn}_{0.7}\text{Co}_{0.3}\text{O}_3$ perovskite as substrate and ethylene as carbon source. The carbon deposition over the metal oxide was performed with various durations to observe possible changes in the physicochemical and electrochemical properties. Regardless of the carbon deposition time, the perovskite structure was decomposed into other crystal phases, including $\text{La}(\text{OH})_3$, La_2O_3 , MnO , and Co . Interestingly, the MnO and Co crystallite sizes decreased with the duration of the CVD treatment due to growth hampering by carbon deposition. Therefore, a large number of the MnO/Co heterointerfaces could be formed; these heterointerfaces are highly active for the ORR because they enhance the electron transfer of the reaction and the adsorption of oxygen intermediates. Moreover, the carbon nanotubes formed during CVD due to the presence of Co nanoparticles can enhance the electrical conductivity of the composites. These carbon nanotubes display carbon defects, especially edge sites, which are highly active for the ORR through the enhancement of the adsorption of oxygen. The characterization of the chemical surface by XPS indicated the formation of C-O-M covalent bonds, which can favour the electron transfer as well. On the contrary, the amount of chemisorbed oxygen species tends to decrease with the carbon deposition duration. These species can also enhance the electrical conductivity and facilitate the $\text{O}_2^{2-}/\text{OH}^-$ displacement. The sample subjected to 20 min of CVD carbon deposition shows a slightly higher concentration of C-O-M covalent bonds, chemisorbed oxygen species, and edge sites compared to the sample with 30 min of CVD carbon deposition. However, its activity is slightly lower than that of the sample with 30 min of CVD carbon deposition. Moreover, 20 min of CVD carbon deposition forms the largest crystallite size of the $\text{La}(\text{OH})_3$ phase, which can harm the catalytic activity. In the case of the sample with 30 min of CVD carbon deposition, its greater activity is mainly ascribed to the higher concentration of C-O-M covalent bonds, resulting in a better electron transfer of the reaction. Moreover, longer carbon deposition leads to higher amounts of MnO/Co heterointerface sites and to higher content of carbon nanotubes, which both enhance the ORR kinetics.

Finally, it was demonstrated that the CVD treatment is interesting in preparing composites because not only are C-O-M covalent bonds formed, but also new active phases. Moreover, it

has been demonstrated that La-based species negatively impact the ORR because they are not highly active and reduce the number of available active sites on the surface.

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Author contributions

Jhony Xavier Flores-Lasluisa: Investigation, Methodology, Validation, Writing—original draft, Writing—review & editing, Formal analysis, Conceptualization. Bryan Carré: Investigation, Writing—review & editing, Formal analysis. Joachim Caucheteux: Investigation, Writing—review & editing, Formal analysis. Alexandre F. Léonard: Writing—review & editing, Formal analysis, Conceptualization. Nathalie Job: Methodology, Validation, Writing—original draft, Writing—review & editing, Formal analysis, Conceptualization, Funding acquisition, Supervision. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

The authors declare no conflict of interest.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Supplementary information

Figure S.1: XRD patterns of the samples with different CVD times. (a) zoom in the region 25-34° (b) zoom in the region 38-42°, and (c) zoom in the region 43-47°. (—) P; (—) CVD_0; (—) CVD_10; (—) CVD_20; (—) CVD_30. The asterisk (*) is related to the LaCoO₃ structure; Figure S.2: Raman spectra of the CVD-based composites. (—) CVD_10; (—) CVD_20; (—) CVD_30; Figure S.3. (a) Thermogravimetric analysis (TGA) curves of the samples and (b) N₂ adsorption-desorption isotherms at -196 °C for the samples. (—) P; (—) CVD_10; (—) CVD_20; (—) CVD_30; Figure S.4. XPS spectra obtained from (a) La 3d; (b) Mn 2p; (c) Co 2p; and (d) O 1s for the pristine perovskite and the composited formed at different times of CVD; Figure S.5. Cyclic voltammetry experiments performed at different scan rates for the composites in 10 mM K₃Fe(CN)₆/K₄Fe(CN)₆ in pH 7.0 PBS solution saturated with N₂: (a) CVD_10; (b) CVD_20; (c) CVD_30; and (d) Randles-Sevcik plot obtained from the cyclic voltammetry for samples in the same conditions. (■) CVD_10; (●) CVD_20; (▲) CVD_30; Figure S.6. (a) Cyclic voltammetry of the pure metal oxides, the composites formed with Vulcan and the CVD_30 sample in 0.1 M KOH under N₂ atmosphere and (b) CVs at smaller current density scale to observe only the metal oxides and the composites. Scan rate: 10 mV s⁻¹. (—) P; (—) P+Vul; (—) CVD_0; (—) CVD_0+Vul; (—) CVD_30; Table S.1. Surface composition of the samples determined by XPS; Table S.2. E_{onset} , number of electrons involved in the ORR, limiting current density, and tafel slope obtained from the LSV data of the CVD_30 sample and metal oxides mixed physically with and without Vulcan.

Ethical approval

Not applicable.

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