

Carbon Nanomaterials-based modified electrodes for Electrocatalysis

Electrodos modificados con base en Nanomateriales de Carbono para Electrocatálisis

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Abstract

Since their discovery, carbon nanomaterials have been attracting considerable experimental and theoretical interest because of their unique structures and properties which make them suitable and very attractive for a great number of applications in several research fields. Additionally, the possibility of chemical modification/functionalization broadens their utility and gives rise to favourable electrocatalytic properties with regard to several electrochemical processes.

This paper aims to provide an overview of the work developed by our research group regarding the use of carbon-based nanomaterials as electrocatalysts. Firstly, the sensing performance of carbon-based nanocomposites containing magnetic nanoparticles (Fe_3O_4 and MnFe_2O_4) or polyoxometalates (POMs) in oxidative electrocatalysis for detection/sensing of several biomolecules are reviewed. Then, the application of carbon-based electrocatalysts for oxygen reduction reaction is also presented.

Resumen

Desde su descubrimiento, los nanomateriales de carbono han atraído un considerable interés experimental y teórico debido a sus estructuras y propiedades únicas, que los hace adecuados y muy atractivos para un gran número de aplicaciones en varios campos de investigación. Además, la posibilidad de modificación química/funcionalización amplía su utilidad y da lugar a propiedades electrocatalíticas aún más favorables respecto a varios procesos electroquímicos.

Este documento tiene como objetivo proporcionar una visión general del trabajo desarrollado por nuestro grupo de investigación sobre el uso de nanomateriales basados en el carbono como electrocatalizadores. En primer lugar, se muestra el rendimiento de detección de nanocompuestos basados en el carbono que contienen nanopartículas magnéticas (Fe_3O_4 y MnFe_2O_4) o polioxometalatos (POMs) en electrocatalisis oxidativa para la detección/oxidación de varias biomoléculas. A continuación, se presenta también la aplicación de los electrocatalizadores a base de carbono en la reacción de reducción de oxígeno.

1. Introduction

Due to the structural diversity of the various carbon allotropic forms and the ease of tuning their chemical, electronic and crystalline properties, carbon materials are attractive for a wide range of electrochemical applications, such as sensing, electrocatalysis, fuel cells, batteries and supercapacitors [1-3].

Since the conception of carbon paste electrode in the late 1950s [4], which remains one of the most

popular electrode material for electroanalysis, and the development of electrodes based on *classical* carbon materials (glassy carbon, pyrolytic graphite and highly pyrolytic graphite (HOPG) and carbon black), the field of carbon electrochemistry has experienced a robust development over the last decades with the emergence of multidimensional carbon nanomaterials, including fullerenes, carbon nanotubes (CNTs), graphene and its derivatives, carbon nanofibers (CNFs) and diamond/carbon nanoparticles [3].

In comparison with other material electrodes, carbon-based electrodes present many important advantages, namely low cost production, high surface areas, a wide working potential window in both aqueous and non-aqueous media, high electrocatalytic activities for different redox-active chemical and biological systems and chemical inertness. Furthermore, the richness of their surface chemistry enables the functionalization of these carbon platforms *via* strong covalent or noncovalent methods with a variety of surface modifiers, which broadens the utility of carbon electrodes and improves their electrochemical performance [3,5].

Nanostructured materials, in particular, carbon-based nanomaterials such as carbon nanotubes and graphene, have also attracted considerable interest in the field of modified electrodes, with hundreds of papers and many patents published every year covering this topic [6-8], owing to their unique physical, chemical and electrochemical properties. They present, besides the advantages referred above, low residual current and readily renewable surfaces, providing an important and feasible platform for electroanalysis [9]. Also, their properties, such as fast electron transportation, high thermal conductivity, excellent mechanical strength and high surface area, suggest their ability to detect analyte molecules and to promote a fast electron transfer between the electrode and the analyte, which make them promising electrocatalysts [9]. In fact, several reports showed the good electrocatalytic activity of pristine graphene/CNT and graphene/CNT-based hybrid nanocomposites on the electrochemical sensing of several biomolecules (e.g. dopamine (DA), ascorbic acid (AA), uric acid (UA), glucose, hydrogen peroxide and DNA) [10-13]. Actually, higher sensitivities, lower limits of detection, wide linear responses, and faster electron transfer kinetics are generally achieved with CNT- or graphene-based sensors, comparing with traditional carbon electrodes.

Carbon-based nanomaterials have also been presented as effective electrocatalysts that fulfill the requirements for several electrochemical reactions of massive importance in energy conversion systems, such as oxygen reduction reaction (ORR), oxygen

evolution reaction (OER), hydrogen oxidation reaction (HOR) and hydrogen evolution reaction (HER) [14]. Concerning ORR electrocatalysis, significant progress has been achieved using carbon nanomaterials as support for Pt nanoparticles, as well as for non-precious metal catalysts, which promote an enhancement of the electrochemical stability, activity and durability of the supported catalysts [2,5]. Moreover, several works have also been reported showing the ORR electrocatalytic activity of carbon-based materials as standalone catalysts, such as activated carbons [15] and heteroatom doped graphene [16].

This paper intends to provide an overview of the recent work developed by our group on carbon-based electrocatalysis. The first part will be focused on the sensing performance of carbon-based nanocomposites containing polyoxometalates or magnetic nanoparticles for the detection of several biomolecules, namely AA, DA, UA, acetaminophen (AC), caffeine (CF) and theophylline (TP). In the second part, our latest results on carbon-based electrocatalysts for ORR will also be presented.

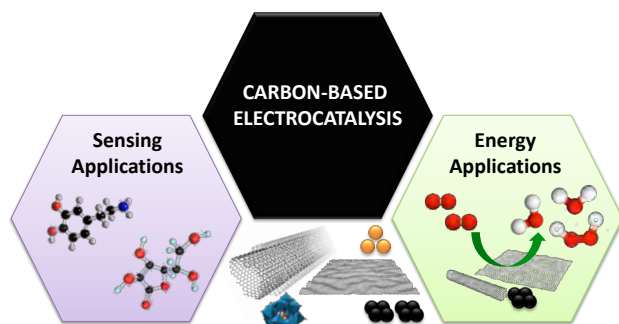


Figure 1. Electrochemical applications of carbon-based electrocatalysts addressed in this work.

Figura 1. Aplicaciones electroquímicas de electrocatalizadores a base de carbono tratados en este trabajo.

2. Carbon-based electrocatalysts for sensing applications

Today, electrochemical and electrocatalytic sensing represents one of the key topics in current science and technology. Taking advantage of the electroactivity of some drugs and biomolecules, the application of electrochemical sensors for biological analysis has been growing rapidly, mainly due to the simplicity, accuracy, precision, low cost and rapidity of the electrochemical techniques. In order to develop electrochemical sensors with higher selectivity and sensitivity, the chemical modification of electrode surfaces has been a major focus of research. The modified electrodes present lower overpotential values and improved mass transfer kinetics, decreasing the effect of interferences and avoiding surface fouling [17].

In this context, recently we reported the preparation of different hybrid materials and their application as electrode modifiers for subsequent use in oxidative electrocatalysis. One set of these materials were based on N-doped carbon nanotubes (N-CNT) and magnetic nanoparticles namely, magnetite (Fe_3O_4) and manganese(II) ferrite (MnFe_2O_4) [10,12]. In both cases, the pristine N-CNT nanomaterial with a multiwall bamboo-like structure was prepared by catalytic chemical vapor decomposition and then functionalized with the magnetic nanoparticles formed *in situ* by coprecipitation in the presence of

N-CNT. The Fe_3O_4 @N-CNT modified electrodes were then used for the voltammetric determination (by cyclic and square wave voltammetry) of AA, DA and UA while the MnFe_2O_4 @N-CNT ones for AA, CF and AC. Cyclic voltammetric results showed that for most of the biomolecules, the modification of GCE with N-CNT leads to a decrease in the oxidation potentials, more significant to DA, AA and UA, and to an increase in peak currents. These effects outcome from the combination of the high electrical conductivity of N-CNT and the possible interactions between the biomolecules and the CNTs surface, through π - π interactions and/or hydrogen bonds between their hydroxyl or amine groups and nitrogen atoms from N-CNT [10]. However, much more noteworthy results were obtained for GCE modification with the nanocomposites Fe_3O_4 @N-CNT and MnFe_2O_4 @N-CNT: larger decrease in over-potentials and increase in peak currents which are decisive aspects for the application of modified electrodes in electrocatalysis. Square wave voltammograms also presented significant changes in peak potentials and currents upon electrode modification as can be observed, as an example, in Fig. 2.

For N-CNT/GCE the most distinctive changes were observed for UA in which the i_p is almost 13 times higher when compared to bare GCE; for DA the i_p increase is of the same magnitude, but for AA the i_p increase is about 2 times. At the Fe_3O_4 @N-CNT/GCE, the same distinctive changes are also observed for UA where the i_p is ≈ 30 times higher when compared to bare GCE; for AA and DA peak currents increase approximately 3 and 7 times, respectively [10]. Similar results were obtained for the MnFe_2O_4 @N-CNT/GCE where the more significant results were observed for AA with a decrease in overpotential of ≈ 0.200 V and an increase in peak current of $\approx 520\%$. Then, SWV was used to study the electrochemical behaviour of the modified electrodes towards a mixture of 3 different biomolecules [12]. The major outcome of these modifications was the possibility of the simultaneously determination of the biomolecules since all peaks could be resolved (Fig. 2d, red). At the bare electrode only one broad peak was observed what makes impossible their determination.

The second set of materials reported by us was based on single-walled carbon nanotubes (SWCNT), graphene flakes (GF) and/or N-doped few layer graphene (N-FLG), and POMs ($\text{PMo}_{12}\text{O}_{40}$, $\text{PMo}_{11}\text{O}_{39}$, $\text{PMo}_{11}\text{VO}_{40}$ and $\text{PMo}_{10}\text{V}_2\text{O}_{40}$) [11,18]. POMs are a well-known class of discrete early transition metal-oxide clusters with a variety of sizes, shapes, composition and physical and chemical properties. One of their most important properties is their ability to undergo reversible multi-valence reductions/oxidations, leading to the formation of mixed-valence species, which brings about favourable electrocatalytic properties with regard to several electrochemical processes. The preparation of POM@SWCNT and POM@GF modified electrodes revealed to be easy to perform giving rise to stable and reproducible electrodes. Their voltammetric features were studied and showed that all POM peaks were much better resolved and had higher current intensities compared with the analogous POM-modified electrodes (Fig. 3), which suggested faster electron-transfer kinetics, which was associated with the exceptional electronic properties of SWCNT and GF.

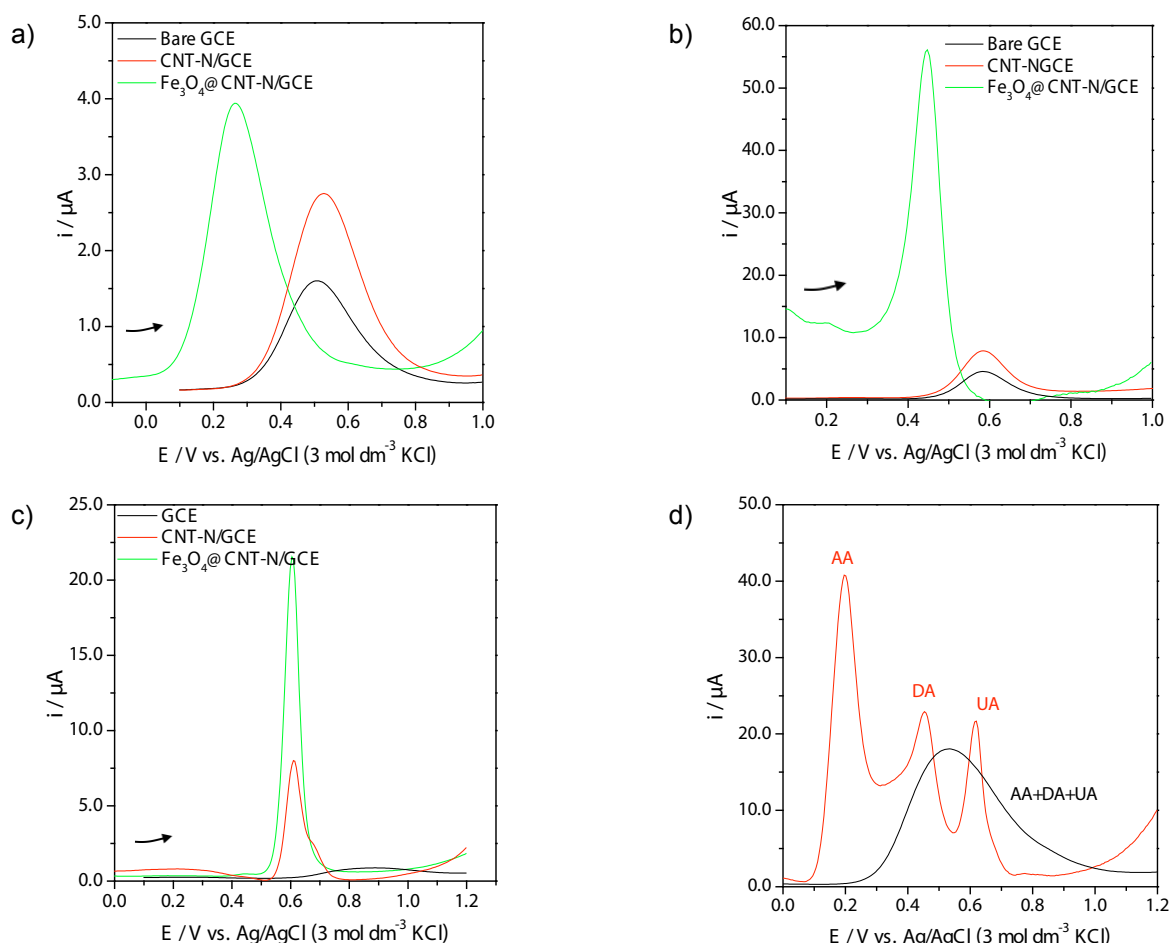


Figure 2. SWV responses of: 0.5 mM AA (a), 0.5 mM DA (b) and 0.5 mM UA (c) at bare GCE, N-CNT/GCE and Fe₃O₄@N-CNT/GCE; and 5 mM AA, 0.05 mM DA and 0.05 mM UA (d) at Fe₃O₄@N-CNT/GCE (red) and GCE (black); in pH 2.5 H₂SO₄/Na₂SO₄ buffer solution. Reprinted from J Colloid Int Sci, 432, Diana M. Fernandes *et. al*, page 211, Copyright (2014), with permission from Elsevier.

Figura 2. SWV respuestas de: AA 0,5 mM (a), DA 0,5 mM (b) y UA 0,5 mM (c) al GCE desnudo, N-CNT/GCE y Fe₃O₄@N-CNT/GCE; y AA 5 mM, DA 0,05 mM y 0,05 mM UA (d) Fe₃O₄@N-CNT/GCE (rojo) y GCE (negro); en pH 2.5 H₂SO₄/Na₂SO₄ solución tampón. Reimpreso de J Colloid Int Sci, 432, Diana M. Fernandes *et. al*, pág 211, Copyright (2014), con permiso de la Elsevier.

Then, their electrocatalytic properties were evaluated and with the exception of PMo₁₁, all presented electrocatalytic behaviour towards AA oxidation. Nevertheless, the best results were obtained for PMo₁₁V@GF and PMo₁₀V₂@GF with catalytic efficiencies (CAT) of 666% and 274%, respectively ($CAT=100\% \times [i_{p(POM, substrate)} - i_{p(POM)}] / i_{p(POM)}$, where $i_{p(POM)}$ and $i_{p(POM, substrate)}$ are the catalytic currents of the POM in the absence and presence of substrate). Additionally,

the PMo₁₁V@GF modified electrode was also applied towards the DA oxidation. This was able to detect and measure the amount of DA in the presence of AA with a detection limit (DL) of 0.88 $\mu\text{mol dm}^{-3}$ (LR = 2 – 300 $\mu\text{mol dm}^{-3}$).

The same PMo₁₁V was also immobilized onto N-FLG. The electrocatalytic and sensing properties of PMo₁₁V@N-FLG modified electrodes were evaluated towards AC and TP and showed that peak current increased linearly with AC concentration in the

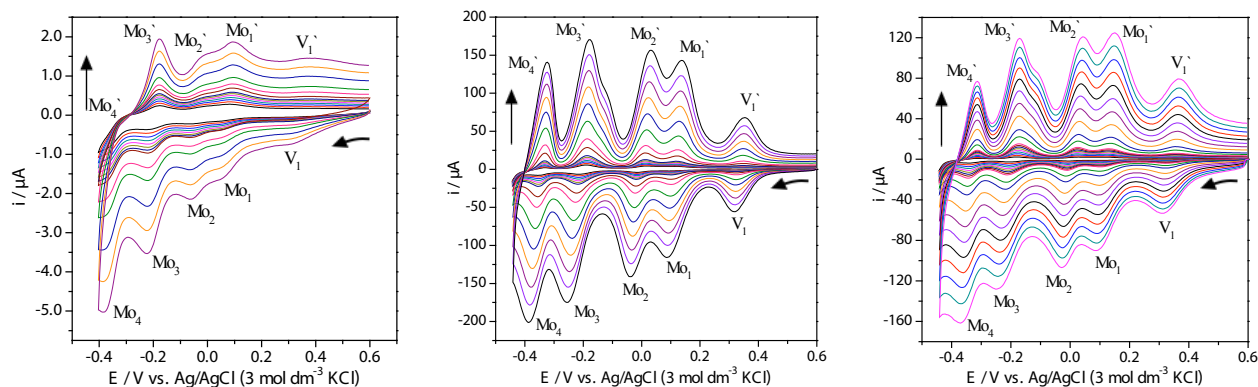


Figure 3. CVs at different scan rates of PMo₁₁V (a), PMo₁₁V@SWCNT (b) and PMo₁₁V@GF (c), in pH 2.5 H₂SO₄/Na₂SO₄ buffer solution. Reprinted with permission from Fernandes, D.M., *et. al* ChemElectroChem (2015) 2, 269. Copyright©2015 Wiley-VCH Verlag GmbH & Co. kGaA, Weinheim.

Figura 3. CVs a diferentes velocidades de barrido de PMo₁₁V (a), PMo₁₁V@SWCNT (b) y PMo₁₁V@GF (c), en pH 2.5 H₂SO₄/Na₂SO₄ solución tampón. Reimpreso con permiso de Fernandes, D.M., *et. al* ChemElectroChem (2015) 2, 269. Copyright©2015 Wiley-VCH Verlag GmbH & Co. kGaA, Weinheim.

presence of TP, showing two linear ranges: 1.2 – 120 and 120 – 480 $\mu\text{mol dm}^{-3}$, with different AC sensitivity values, 0.022 and 0.035 $\mu\text{A}/\text{mmol dm}^{-3}$, respectively (DL = 0.75 $\mu\text{mol dm}^{-3}$) [11].

The importance of carbon materials in these hybrids is in great part associated with the fact that they allow a much higher amount of electroactive species to be deposited at the electrode surface due to their nanostructures which constitutes an outstanding advantage when developing superior modified electrodes [18].

3. Carbon-based electrocatalysts for energy applications

In order to face the current global energy crisis, fuel cells and metal-air batteries have attracted a lot of attention as sustainable alternative technologies for energy conversion and storage [19]. The operation of these technologies is based in several electrochemical processes, among which the oxygen reduction reaction plays a crucial role in controlling the overall devices performance. Platinum nanoparticles supported on carbon materials (Pt/C) are the most effective known ORR catalysts, leading to low ORR overpotential and large current densities, with selectivity toward a direct 4-electron pathway [20]. Nevertheless, the required high Pt loading (40-80 %) associated with its high cost, scarcity, declining activity and possible Pt-deactivation by methanol crossover have limited the large-scale application of Pt-based electrocatalysts [20,21]. Therefore, research efforts have been devoted to developing alternative ORR electrocatalysts, with a competitive activity with the Pt/C catalysts but more stable and cost-effective [22]. In this context, carbon-based materials, with their versatile properties, appeared as ideal to be applied in ORR as metal-free electrocatalysts itself or as catalyst supports in functional composites.

Several works have reported the application of graphite [23], CNTs [24], GF [25], ordered mesoporous carbons [21] and carbon nanoparticles [20] as metal-free ORR catalysts. In this context, recently we reported the application of two activated carbons (ACs) as ORR electrocatalysts [15].

The ACs were prepared from a sucrose-derived hydrochar [26], which was a valuable green approach considering the availability, low cost and environmental friendliness of the starting material. Both ACs, denoted as SH800 and SC800, exhibited ORR electrocatalytic activity in alkaline and acidic media. In alkaline medium (Fig. 4a), the two ACs showed similar onset potentials ($E_{\text{onset}} \approx -0.20$ V vs. Ag/AgCl), which were only 60 mV more negative than the observed for the state-of-the-art Pt/C electrocatalyst [15]. Moreover, the higher limiting current densities recorded for SH800 [15] showed the advantage of the high surface areas and large pores of this material, as favourable conditions for a high ORR electrocatalytic performance, once increase the number of active sites exposed to the electrolyte [27]. The selectivity of the electrocatalysts showed to be dependent of the applied potential, moving closer to the 4-electron process (direct O_2 reduction) as the potential became more negative. Furthermore, the ACs revealed excellent tolerance to methanol, with the SH800 also exhibiting greater long-term electrochemical stability than the Pt/C electrocatalyst, which are important

advantages considering a possible application in direct methanol fuel cells.

The ACs-based electrocatalysts also showed ORR electrocatalytic activity in acidic medium, which was a key result considering the common inactivity or low ORR activity of carbon materials in acidic medium and an application in proton exchange fuel cells; however, the ORR performance was lower than in alkaline medium, probably due to active sites deactivation [28].

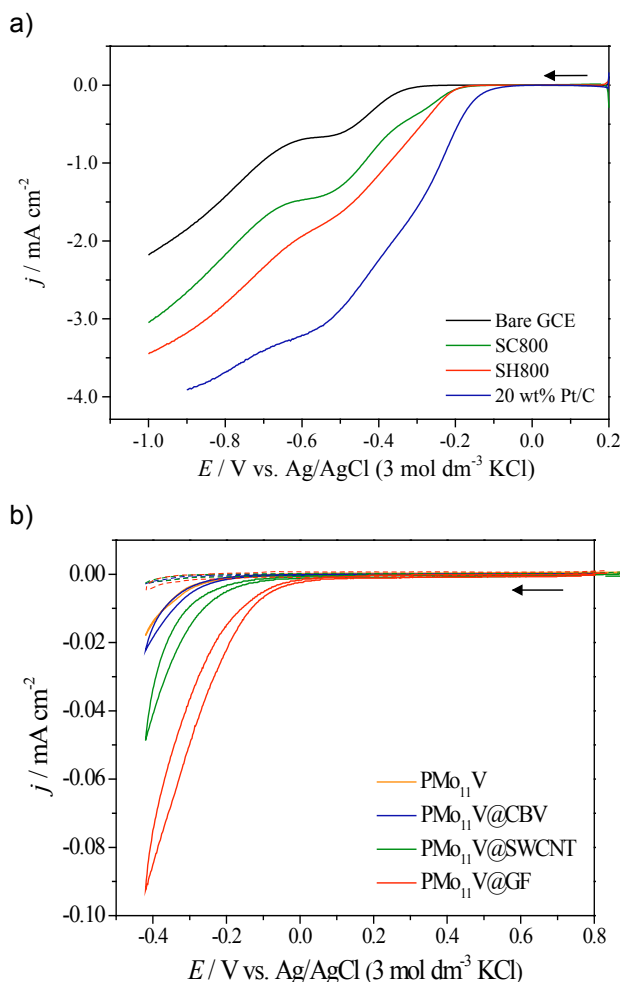


Figure 4. ORR results of (a) ACs in O_2 -saturated solution in alkaline medium and (b) PMo_{11}V and $\text{PMo}_{11}\text{V@carbon}$ -based composites in N_2 - and O_2 -saturated solutions in acidic medium. Reproduced by permission of the Royal Society of Chemistry.

Figura 4. Resultados de ORR de (a) ACs en una solución saturada de oxígeno en medio alcalino y (b) PMo_{11}V y $\text{PMo}_{11}\text{V@carbon}$ compuestos en una solución saturada de nitrógeno y oxígeno. Reproducido con permiso de la Royal Society of Chemistry.

The use of carbon materials as catalyst support also has several advantages: higher electroactive surface area, enhanced conductivities and brings the catalyst particles close to the reactants, improving the catalytic activity and durability [1]. Carbon black is the most commonly used support catalyst due to its low cost, but its susceptibility to oxidation sometimes results in active surface area loss and alteration of the pore surface characteristics. Carbon nanotubes and graphene supports, although more expensive, normally result in high catalyst utilization, owing to their high crystallinity and surface area [1]. Currently, we are studying the application of several composites as ORR electrocatalysts, prepared through the incorporation of a vanadium-substituted phosphomolybdate (PMo_{11}V) into carbon black Vulcan (CBV), SWCNT and GF [29]. At this regard, the ability of POM to mediate

electron, proton and oxygen transfer reactions was an additional value [11]. All composites, designated by $\text{PMo}_{11}\text{V@CBV}$, $\text{PMo}_{11}\text{V@SWCNT}$ and $\text{PMo}_{11}\text{V@GF}$, showed ORR electrocatalytic ability, with a strong dependency between the ORR performance and the carbon-based material employed as support (Fig. 4b).

In comparison with the pristine PMo_{11}V , the composites showed the peak associated with the reduction of oxygen at more positive potentials and with higher current densities, which indicated the advantage of the incorporation of POM into the carbon-based supports; these results were corroborated by the higher electroactive surface coverages obtained for composites-modified electrodes [29]. The $\text{PMo}_{11}\text{V@SWCNT}$ and $\text{PMo}_{11}\text{V@GF}$ composites exhibited the best ORR performances, as consequence of the high conductivity of these SWCNT and GF supports that improved the charge transfer between the modified layer and the GCE electrode and promoted a beneficial synergistic effect with PMo_{11}V .

4. Concluding remarks

In this paper the electrocatalytic applications of several carbon-based electrocatalysts developed by our group in two major areas of high current impact, electrochemical sensing and renewable energy, were overviewed. Firstly, the *carbon-based electrocatalysts for sensing applications* was reviewed: initially, was covered the oxidative electrocatalysis by hybrids based on carbon and magnetic nanoparticles and then those based on carbon and POMs. The last topic, *carbon-based ORR electrocatalysts for energy applications*, addressed the application of our contribution regarding this type of electrocatalysts for one of the reactions that play a key role in several promising energy systems, the oxygen reduction reaction.

Even though the electrocatalytic application of carbon-based electrocatalysts is growing in great part because of the huge advantage of offering higher amount of electroactive species at the electrode surface and less soluble electrocatalysts, there is definitely huge room for improvement and discovery in carbon-based materials research.

5. Acknowledgments

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