The role of oxygen heteroatoms in the surface (electro)chemistry of carbon materials

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Engineering the surface chemistry of carbon-based materials is of crucial importance in tuning their intrinsic properties, including electrical conductivity, wettability, electroactivity, adsorption potential, reactivity, physical and chemical stability. Intense research has recently focused on understanding the role of surface oxygen functional groups when carbon materials are in contact with an electrolyte or solvent in order to tailor and improve them for technological applications. For this purpose, their synthesis method and/or further oxidation treatments should be carefully selected, since they can substantially influence not only the oxygen content, but also the nature of the oxygen moieties, which could be decisive in determining the surface properties of the resulting material. The combined use of different chemical, spectroscopic and electrochemical techniques, provides unique and reliable information about the contribution of a specific oxygen-containing group in the surface (electro)chemistry of carbon-based materials. This paper provides a discussion of the role of oxygen heteroatoms in the surface electrochemistry of a carbon material as they relate to their influence on both its electroactivity and reactivity.

\textbf{KEYWORDS:} Carbon materials, Surface chemistry, Electrochemistry, Oxygen heteroatom, Wettability, Electrical conductivity, Electroactivity, Reactivity

1. Introduction

Carbon materials exhibit unique properties that make them useful in an extraordinary large number of technological applications. The unique (and different) properties that can be found for carbon materials are due to their diversity in structure. From the structure point of view, and focusing only on sp\textsuperscript{2} carbon materials, materials with long-range and short-range orders can be found that explains the large family of carbon materials. The second factor that determines the properties of the carbon materials is the surface electrochemistry, which is determined by the concentration of intrinsic defects and the presence of heteroatoms. Then, the combination of both structure and surface electrochemistry results in an enormous collection of materials with properties that can be tailored for many different applications.

In electrochemical field, the interest in carbon-based materials has been rising along the last decades. Despite the great effort to deepen into the knowledge of carbon surface properties, it remains challenging to interpret the electrochemistry of carbon materials in terms of specific changes in the carbon surface chemistry [1]. Carbon materials, especially those with high surface areas, generally contain surface oxygen groups that can be spontaneously formed by simple exposure to oxygen in air or in a solution. Other functional groups, such as nitrogen or sulphur, are often introduced as heteroatoms to improve the properties of the pristine carbon materials (conductivity, electrocatalytic activity, \textit{etc.}) [2]. In addition, hydrogen atoms are often present in the surface forming C–H bonds and may also be present in certain functional groups (such as carboxylic acids, phenol, \textit{etc.}) [2]. When no other heteroatom is present, oxygen functionalities are the main responsible of the observed electrochemical processes, as the sp\textsuperscript{2} aromatic carbon atoms with π-delocalised electrons are less reactive. Interestingly, they also determine key properties in materials such as wettability or electrical conductivity, among others [1, 3].

To understand the behaviour of carbon materials in electrochemical applications, a deep characterisation of the surface chemistry is necessary [2, 4]. The characterisation of surface oxygen groups is often done by spectroscopic (XPS, FTIR, \textit{etc.}), chemical and electrochemical techniques [5–7]. However, the interpretation of the information is, in many cases, difficult due to the convolution of the contribution of different oxygen functional groups or the overlapping of different reactions. This is a consequence of the surface heterogeneity, and the different chemical nature of the surface oxygen groups. Moreover,
the study of electrochemical properties of carbon materials, is sometimes difficult since the materials might not present enough electrical conductivity. Among the different techniques used to characterise surface chemistry of carbon materials, temperature programmed desorption (TPD) is one of the most employed since it provides valuable information about the surface composition from the analysis of the thermal stability of the oxygen groups and the composition of the evolved gases [6, 8–11]. The combination of spectroscopic and/or electrochemical techniques with TPD experiments provides unique information, but it is not usually encountered in the literature.

In this study we will focus on surface oxygen groups and, specifically, on the contribution of oxygen heteroatoms in the surface electrochemistry of carbon materials. We will pay attention into the role of oxygen functional groups when carbon materials are in contact with an electrolyte or solvent, and will focus on their effect on electrical conductivity, wettability, electroactivity and reactivity with the electrolyte and the solvent. Few examples that illustrate some of the discussed effects will be included throughout the text.

2. Surface Chemistry of Carbon Materials

A strong structure-processing-property correlation can be found in carbon materials [12], in which the adequate choice leads to the development of improved materials for particular applications. There are different approaches facing the modification of physico-chemical properties of carbon materials to enhance their qualities and mitigate their limitations. Tailoring both the surface chemistry and porous texture of carbon materials has been exhaustively investigated to effectively adapt their intrinsic properties (electrical conductivity, wettability, electroactivity, adsorption potential, reactivity, physical and chemical stability, etc.) and applicability. In fact, a better understanding of surface chemistry has allowed to optimise the overall performance of carbon materials and has even broken new grounds of applications, for example, in the field of gas and liquid phase adsorption, gasification reactions, pollutant removal, catalysis, electrochemical energy storage and production, among many others [1, 2, 4, 13–17].

Surface chemistry of carbon materials can be suitably modified using different covalent and non-covalent strategies, including the incorporation of one or multiple foreign species or heteroatom doping, as well as the creation of intrinsic defects and edges [4, 18]. In this short review, we will only dedicate to broaden the knowledge about the relevance of oxygen functional groups in surface chemistry of carbon materials and how do they affect their surface electrochemical properties. This is a small, but highly important, part of the rich surface chemistry of carbon materials that can serve as a guide in the design of high-performance carbon-based materials with optimised properties for already existing or novel technological applications.

2.1 Role of oxygen functional groups when carbon material is in contact with an electrolyte/solvent

As it is well-known, the incorporation of single/multiple foreign heteroatoms into the structure of carbon materials considerably alters their surface chemistry and electronic properties, as well as their elemental composition, performance, and subsequent applications, which can be fine-tuned according to the final interest [19]. Generally, heteroatom-doped carbon materials can be synthesized from the carbonisation of suitable heteroatoms-rich precursors [20, 21], although they can also be generated by subsequent modification of the pristine carbon material with reactive compounds containing the desired heteroatoms, for example by subjecting them to distinct chemical and thermal treatments [22–28]. The most common heteroatoms found in carbon materials include nitrogen (N) and oxygen (O), but other interesting doping candidates like phosphorus (P), sulphur (S), fluorine (F), boron (B), chlorine (Cl), selenium (Se), bromine (Br) and iodine (I) atoms can also be found as dopants [29, 30]. In particular, heteroatom doping is one of the most popular strategies for engineering the surface adsorption properties and catalytic performance of carbon-based materials by inducing local structural distortions, electronic density redistribution and specific intrinsic defects across the conjugated lattice of carbon atoms. For instance, in graphene-based materials, doping with P or S atoms provides an electron-donating environment for the adjacent carbon atoms, while N and O are known to act as electron-acceptor dopants [31]. Interestingly, these atoms can not only act as active sites by themselves for catalytic applications, but also may promote the performance of other catalytic species [26] or neighbour carbon atoms [32, 33] or even be the anchoring points for the coordination of other active species [34]. The presence of electrochemically active heteroatoms can boost the performance of the materials in electrical energy storage systems, associated with a higher mass or electron transfer rate due to their induced-pseudocapacitive interactions [13], while also improving electrooxidation resistance [35]. In addition, the hydrophilicity and thus the wettability of carbon-based materials can be also promoted by the incorporation of these heteroatoms [8, 36]. Not only single-atom doping, but also co-doping or multi-doping with different heteroatoms have been found as promising strategies to synergistically enhance the applicability of carbon materials. For example, it has been reported that doping with two heteroatoms with considerably different charge density and electronegativity, such as N and P, could be beneficial for enhancing electron donor-acceptor properties and catalytic performance of the adjacent carbon atoms [37].

Among all these heteroatoms, nitrogen and oxygen-related species are by far the most studied. Of particular interest, oxygen atoms can be found naturally present in the structure of all carbon materials exposed to environmental conditions. Nonetheless, different experimental routes have been developed for preparing oxygen-containing
carbon-based materials, both during the manufacturing process or through post-treatments. Here, oxidative treatments of carbon materials in the gas or liquid phase (i.e., the so-called dry and wet oxidation, respectively), together with further heat treatments, have been conventionally used as efficient procedures [38–40]. A wide variety of oxygen functional groups (OFGs) can be identified and sorted according to their acidity or basicity in: carboxylic acids, anhydrides, lactones and phenols as acid groups and carbonyls, quinones and ethers as slightly basic groups [41, 42].

Fig. 1 shows a schematic illustration of some surface oxygen functionalities that may be present throughout the structure of carbon materials.

The nature and concentration of oxygen functionalities incorporated are determined not only by the starting materials, but also by the oxidizing conditions used in the preparation method (e.g., temperature, duration of the treatment, oxidant concentration and oxidizing power, etc.). In terms of chemical oxidation, wet oxidation (e.g., by using a solution of an oxidizing agent) [23, 43–45] is known to lead to higher incorporation of acid groups, whereas dry oxidation (e.g., usually by air treatment) generates higher amounts of basic and neutral groups [39, 44, 46]. Otherwise, during the physical and chemical activation of carbon materials, not only is the surface area increased, but also oxygen groups are introduced. It has been observed that the oxygen content goes through a maximum or decreases with the degree of activation [36]. However, all these methods lack of selectivity and the nature of the surface oxygen groups can be modulated through posterior heat treatments [39, 47]; in addition, these methods generally need for high volumes and quantities of reagents. Alternatively, electrochemical techniques have become increasingly popular in the recent years since they offer an extra level of control, accuracy and selectivity to straightforwardly modifying the surface chemistry of carbon materials by proper choice of the electrochemical oxidation conditions [48, 49]. In this case, the electrode potential or the applied current, the duration of the treatment, the electrolyte and the carbon material used are decisive in the nature of OFGs, allowing a major control in the selective modification of the carbon surface. Other alternative oxidation strategies can be found in literature, as plasma electrolytic oxidation, also known as microarc oxidation, but are less employed so far [50].

Now that the chemical nature of the oxygen functional groups as well as the methods for their introduction in carbon materials have been briefly discussed, the following sections analyse from a fundamental point of view the role of OFGs when carbon materials are in contact with an electrolyte or solvent, paying special attention to electrical conductivity, wettability, electroactivity and reactivity.

2.1.1 Water wettability and electrical conductivity

Carbon materials can have very different wettability properties, from highly hydrophobic to hydrophilic character, being these differences mainly determined by the nature and concentration of OFGs. It is well-known that the electrical double layer of carbon materials is dependent on surface area, but surface chemistry and electrical conductivity are also relevant parameters [3, 36]. While the microporous structure of carbon materials presents a hydrophobic behaviour, the presence of OFGs generates polarity, which favours the interaction between water molecules and the surface of carbon materials, thus increasing the wettability [51]. However, OFGs also influence the electrical conductivity. Since the electrical conductivity is favoured by the electron delocalization, the presence of strong electron-withdrawing groups, such as CO$_2$-type groups, has a significant negative effect in this parameter.

Several studies have evidenced that the concentration of OFGs plays an important role in wettability in aqueous electrolytes. For example, Bleda-Martinez et al. reported that low oxygen concentrations result in very low double layer capacitance (DLC) values even for materials with large surface area as a consequence of the highly hydrophobic behaviour of the surface [8]. Fig. 2(a) shows the cyclic voltammograms (CVs) of a purified activated carbon (AC) (black...
The post-treated material in H₂ at 850 °C for 3h (blue line) and the reoxidised material in air at 450 °C for 12h (red line). As it can be observed, the reduced AC presents a negligible DLC, measured using the same experimental method as for the other materials, due to the small amount of OFGs and the incorporation of many C–H bonds. The DLC value of the reoxidised sample is almost recovered although it remains slightly lower than the original AC; this is because porosity slightly decreases after the aggressive procedure applied before the thermal treatment in H₂.

As mentioned before, OFGs have a strong influence in electrical conductivity. An example to illustrate this effect is shown in Fig. 2(b). In this case, Tabti et al. studied the anodic electrooxidation at different currents of activated carbon cloths (ACCs) [52]. The CV of the pristine ACC (black line) has a typical rectangular shape due to DLC with a small and wide redox peak that corresponds to electroactive surface oxygen groups. The electrooxidation of the ACC produced important changes in the voltammograms depending on the applied current and, thus on the amount of OFGs. In the sample modified with the lower current (blue line), in which the oxygen content is increased from 4 to 14 wt%, the knee of the CV is wider (i.e., less rectangular shape) and a broad peak with the peak potential on the vicinity of 0.7 V vs. RHE is observed. On the negative scan, the potential peak is shifted to 0.3 V vs. RHE, which indicates the increased irreversibility of the redox process. Moreover, the capacitance value obtained (143 F g⁻¹) is higher than for the original ACC (137 F g⁻¹), despite the lower BET surface area of the sample. When capacitance is expressed with respect to the surface area, the effect of the presence of OFGs is more evident (from initial 0.118 F m⁻² to 0.155 F m⁻² in the oxidised sample). However, when the sample is oxidised at higher current density (red line), thus incorporating more OFGs, the voltammogram profile appears tilted what indicates a higher resistance in the sample as a consequence of the loss of the electrical conductivity after the severe oxidation process. This fact can be attributed to the presence of electron withdrawing groups and to diffusivity problems of the ions into the porosity, which shows how high concentrations of electron withdrawing groups produce an important decrease of the performance of the carbon material as electrodes for capacitors.

### 2.1.2 Electroactivity

It is well-known that the incorporation of OFGs on the surface of carbon materials results in a significant increase in capacitance values in aqueous solutions [8, 36, 53, 54]. This effect is related to two different factors. On one hand, as explained in the previous section, OFGs improve wettability of the carbon materials and facilitates the penetration of ions into the microporosity, which increases the double-layer contribution to the capacitance [8]. On the other hand, the existence of electrochemically active oxygen functionalities positively promotes the capacitance through electron transfer reactions (i.e., the so-called pseudocapacitance) [36].

Electroactivity of OFGs has been reported in aqueous and organic electrolytes. We can find interesting examples in the literature that analyse in detail electroactivity of OFGs in aqueous electrolyte and their dependence with the pH; some examples are those found in references [8, 36, 55]. Similarly, some studies have demonstrated the electroactivity of OFGs in aprotic solvents (for example, references [56] and [57]), thus motivating their use in rechargeable batteries and electrochemical capacitors. Fig. 3 includes examples of CV obtained in aqueous acid electrolyte and in organic electrolyte that allow us to observe the redox processes in both media.

However, even though each surface oxygen group plays a different role in the electrochemical response [38, 58], it is difficult to unravel the origin of the pseudocapacitance in correlation to a specific type of oxygen functionality, taking into account the surface heterogeneity of carbon materials and the important number of different OFGs that can be present in the carbon surface (see as an example Fig. 1). Although this is still an important issue which is not completely understood,
significant research effort has been done to get detailed information about the nature of the electrochemically active OFGs. Some studies that have obtained interesting conclusions combine electrochemical and surface chemistry techniques that permit to correlate to some extent the electroactivity with the chemical nature of the OFGs.

In this sense, temperature programmed desorption (TPD) is a very useful tool to characterise the surface chemistry of materials [6, 9–11, 39]. TPD experiments provide information of the nature and amount of oxygen-containing functional groups by monitoring and quantifying the gases desorbed (mainly as CO and CO$_2$) from the sample when applying a temperature program. In these experiments, the decomposition temperature is correlated to a specific type of oxygen group. It is generally accepted that CO desorption mainly comes from the decomposition of phenol groups and neutral or basic surface groups like ethers (600–700 °C) and carbonyls or quinones (800–900 °C). CO desorption at higher temperatures (i.e., above 1000 °C) is assigned to the decomposition of pyrone type groups [9, 59]. The evolution of CO$_2$ mainly occurs at lower temperatures due to the decomposition of acid groups, such as carboxylic acids (200–500 °C) and lactones (600–800 °C) [39, 47]. Moreover, acid anhydrides give rise to both CO and CO$_2$ (400–600 °C) (molar ratio 1 : 1) [39]. This means that CO-type groups seems to be more stable than CO$_2$-type species [36]. Based on these analyses, the total oxygen content can be calculated as CO + 2CO$_2$.

Anon, we summarize the results obtained by Bleda-Martínez et al. [36] trying to identify the nature of electroactive oxygen groups. In this study an important number of carbon materials were used that covered the effect of the structure, porous texture, and surface chemistry on the total capacitance in aqueous acidic electrolyte. Fig. 4 plots the specific capacitance values versus the specific content of CO-type groups (both calculated dividing by the BET surface area). The results show an excellent correlation between both parameters (except for some deviations from some specific samples), thus demonstrating that CO-type groups are the main responsible for the observed redox processes in carbon materials. These results are in agreement with other published studies [3, 55, 56, 58]. Then, the

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Fig. 3 Cyclic voltammograms of (a) activated carbon cloths (ACCs) in 0.5 M H$_2$SO$_4$ and (b) activated carbon fibers (ACFs) in 1 M TEMA-BF$_4$/PC solution. Scan rate=1 mV s$^{-1}$.

Fig. 4 Specific capacitance vs. CO content divided by BET surface area. Reprinted with permission from ref 36. Copyright 2005 Elsevier.
higher the incorporation of CO-type oxygen groups, the higher the electroactivity of the carbon materials, which directly points out the source of pseudocapacitance in OFGs like ethers, carbonyls, phenols, pyrone-containing or quinone groups. These last groups are composed by two carbonyl groups or two phenol groups in the reduced form and will be the subject of detailed discussion later. Although other OFGs like anhydrides [8], have been also proposed to contribute to pseudocapacitance, the main contribution in most of cases is due to CO-type groups.

Then, the next question to answer is if all CO-type groups are electroactive and if some insights can be obtained about the specific chemical nature of the electroactive OFGs. For this purpose, we have collected and analysed previously published data of capacitance measured in acidic conditions and CO-type groups as determined from TPD. The data correspond to a chemically activated carbon with a high porosity development (BET surface area around 3000 m$^2$ g$^{-1}$) and which surface chemistry was modified by different chemical treatments [8], activated carbon cloths (BET surface area between 1000–800 m$^2$ g$^{-1}$) which surface chemistry was modified by electrochemical oxidation at constant current conditions [52], and a zeolite templated carbon (ZTC) (BET surface area around 4000 m$^2$ g$^{-1}$) which surface chemistry was modified by cyclic voltammetry [60]. From the charge of the redox process observed in the CV of the materials, calculated subtracting the contribution from the double layer charge, we have estimated the amount of electroactive OFGs. This information has been compared to the total amount of CO evolved from the TPD. In this approach, we have not deconvoluted the CO TPD profile to avoid any misunderstanding in the assignation of a CO peak to a specific type of OFGs.

Before explaining the results obtained from the above approach, we should make few remarks about the experimental method used for ZTC oxidation. The ZTC material is synthesised using a zeolite Y as a hard template, which is filled with the carbon precursor, then it is thermally treated and, subsequently, the template is removed [61–63]. This process results in an ordered carbon material made up of three-dimensional buckybowl-like nanographenes with a large number of edges sites and structural distortions, and a tailored pore network that gives rise to a very homogeneous porosity and unique features [61] (Fig. 5(a) includes a proposed structure for ZTC). This material has a uniform and well-defined nanopore size of 1.2 nm and high specific surface area (up to 4000 m$^2$ g$^{-1}$) [62]. Here, the entire carbon material (edge sites and graphene surface) is fully exposed, so it is of great interest to incorporate a large number of functional groups into ZTC, such as OFGs. However, this material has an extremely fragile structure with numerous edge sites and reactive defects, which is susceptible to degrade by traditional chemical oxidation treatments due to the fast kinetics of the oxidation process in presence of high concentration of reactants, making impossible the incorporation of
OFGs without destroying the structure using the classical oxidation methods [48]. By contrast, electrochemical methods allow a slower and more controlled oxidation and modification of the surface chemistry of ZTC and this can be achieved by adjusting the experimental method and conditions, i.e. galvanostatic anodic oxidation or by cyclic voltammetry [48, 60].

Among the different electrochemical techniques, the potentiodynamic oxidation is of high interest for this specific material [60]. Leyva-Garcia et al. conducted an in-depth study of mass change during the potentiodynamic electrochemical oxidation in aqueous H₂SO₄ solution of ZTC material, using an electrochemical quartz crystal microbalance [60]. In this study, the CVs were done up to different positive potential limits. At the lower positive potential limits, most of the OFGs generated were of CO-type and the CVs showed a high reversibility of the redox processes which intensity increased with increasing the positive potential limit. However, when harsher electrochemical oxidation conditions were used, the CVs showed an increase in the irreversibility of the redox process, which could have twofold origin. On the one hand, the presence of a high number of electron-withdrawing groups could make this redox process more difficult to occur and, on the other hand, it is possible that non-electroactive oxygen groups are generated. Furthermore, these hard conditions also produced the degradation of the ZTC structure due to electrochemical gasification reactions.

Once the materials and the need of using specific oxidation methods and conditions have been presented, in the next paragraphs we will discuss the results obtained about electroactivity of CO-type groups using electrochemical data from CV and chemical information from TPD for the three materials explained before. Fig. 6 plots the percentage of electroactive groups (obtained from the redox process observed in the CV experiments and assuming a one-electron transfer mechanism and dividing by the total amount of CO-type groups measured from the TPD) and the total amount of CO-type groups (obtained from TPD measurements). Red points correspond to the samples prepared by chemical oxidation methods, blue triangles correspond to electrochemically oxidized activated carbon cloths and yellow points correspond to electrochemically oxidized ZTC.

Interestingly, chemical oxidation of a porous carbon with a high surface area produces an almost constant amount of electroactive groups which number is lower than 12% independently of the degree of oxidation. Electrochemical oxidation of activated carbon cloths seems to generate a somewhat higher number of electroactive groups. Taking into account that both porous carbons have similar structures (i.e., short range order materials with slit shaped pores), the results suggest that electrochemical oxidation allows a better control of the nature of OFGs generated. The electrochemical oxidation allows a more precise control of the oxidation conditions by, for example, adjusting the potential, selecting the proper electrolyte and electrode support, etc [48]. The results obtained for ZTC are certainly remarkable. Electrochemical treatment permits to control the degree of oxidation through an adequate selection of the electrolyte and the oxidation conditions [48, 60]. Interestingly, electrochemical oxidation performed at carefully controlled potentiodynamic conditions allows to achieve up to 60% of electroactive OFGs [60]. The observed differences among the classical porous carbons and the ZTC are consequence of the different structure.

Considering the structure shown in Fig. 5(a) for the pristine ZTC, it contains a large concentration of edge sites that can be easily oxidized to hydroxyl groups and these hydroxyl groups can be converted into quinone electroactive groups through further oxidation steps provided that enough armchair sites are available. The mechanism through which these species can be formed might be similar to the mechanism proposed for the oxidation of phenol to quinone species in ortho position [64]. Fig. 5(b) depicts the proposed oxidation mechanism for phenol to quinone in ortho position and the scheme also adds the reduction reactions proposed for quinone species in acidic and alkaline conditions [65]. Thus, it can be understood that a controlled oxidation of ZTC affords the generation of a high amount of electroactive quinone groups, what is not possible in classical porous carbons in which the concentration of sites with adequate geometry for the formation of these functional groups is much lower.

Since quinone groups are considered as the responsible for the electroactivity observed in OFGs-containing carbon materials, we should briefly explain the main properties of quinone species. Quinone-containing molecules have been a subject of research for a long time and important fundamental studies of their electrochemical properties can be found in the literature. Here we will use the results published in references [64] and [65]. In acidic conditions (see blue pathway in Fig. 5(b)), the second reduction reaction is very fast and...
usually overlaps with the first reduction one electron reaction, thus resulting in one peak in the cyclic voltammetry. Reversible potentials for hydroquinone-quinone systems are strongly dependent on the composition of the molecule. For example, at pH=0, \( E^0 = 0.78 \) V for 1,2 benzoquinone and \( E^0 = 0.21 \) V for 2,5 Dimethyl-1,4-benzoquinone; but we can find values between these two values for molecules with different functional groups and structures. The redox potential shifts to lower values with increasing pH and the two one-electron reactions occur at different potentials or the second may not be observed or be irreversible (see red pathway in Fig. 5(b)); this effect can occur because of the instability of the two radicals and two anions in the molecule. Similar situation is found in aprotic solvents in which the potential and the observation of the two reactions will depend on the electrolyte and solvent used. Here, electroactive redox processes could be discerned in presence of cations that strongly stabilize the above species.

The properties of the quinone-containing molecules are in very good agreement with the electrochemical properties observed for OFGs-containing carbon materials: i) the redox process observed in acidic conditions are wide because \( E^0 \) depends on composition and local structure; ii) the redox potential shifts to lower values with increasing pH and it is not observed in high pH conditions; iii) redox processes are observed in organic electrolytes.

In summary, it can be concluded that an appropriate selection of the surface chemistry and structure of the carbon material may allow us to achieve materials with a high concentration of electroactive quinone/hydroquinone oxygen functional groups. Other OFGs either are not electroactive or their oxidation/reduction occurs at very high or very low potentials [64, 66].

### 2.1.3 Reactivity with the electrolyte and the solvent

This is a very important issue in many applications. For example, in fuel cells, the interaction between the electrolyte and the electrode are responsible for the oxidation and corrosion of the cathode [67–69] although it can also affect the anode if there is a non-correct distribution of hydrogen in the positive electrode [69]. In the field of supercapacitors, reactions with the electrolyte are the main responsible for the electrodes ageing and supercapacitor degradation [70–75]. There are many examples in the case of Li-ion batteries (or metal-ion batteries in general) because of the well-known solid electrolyte interphase (SEI) which has a great and determining influence in the battery performance [76–78].

Therefore, it is very important to study the fundamental electrochemical processes and reactions that occur when exposing carbon-based electrodes to both aqueous and organic electrolytes, since this will allow us to improve or design new materials or to use the most appropriate working conditions for the device.

#### 2.1.3.1 Reactivity of carbon materials with aqueous electrolytes

When potentials above 0.207 V vs. NHE are applied in aqueous electrolytes, the oxidation of carbon to carbon dioxide is thermodynamically favoured according to the global reaction (1) [67]:

\[
C(\ ) + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-
\]

which may occur through different steps like:

\[
C(\ ) + H_2O \rightarrow C(OH) + H^+ + e^-
\]

\[
C(OH) \rightarrow C(O) + H^+ + e^-
\]

\[
C(O) + H_2O \rightarrow C(OOH) + H^+ + e^-
\]

\[
C(O) + H_2O \rightarrow CO_2 + 2H^+ + 2e^-
\]

The last reaction (5), where the CO2 molecule is released, is highly irreversible for carbon materials and requires a high overpotential [67, 79], what allows to extend the stability of carbon-based electrodes to higher potentials. Carbon-based electrodes can react with H2O-based electrolytes at both potentiostatic and potentiodynamic conditions [80–83]. However, the corrosion rates observed in potentiodynamic conditions are quite higher than those produced when a constant potential is applied, what can be related to the oxidation/reduction cycle of OFGs [68]. On the one hand, at potentiostatic conditions, only the fraction of the carbon material that has a low enough activation energy gets oxidised, but when an oxide layer is formed, because of the above mentioned irreversibility of the gasification reaction (5), the oxidation/corrosion rate decreases. The oxidation rate of the carbon support in dynamic conditions increases with increasing both the positive and negative potential limits. When carbon material is subjected to high potentials, surface oxygen groups are formed according to reactions shown above. Subsequently, under cathodic conditions, the surface oxygen groups can be reduced to produce CO or CO2 and, possibly, H2 [84]. The oxidation rate in potentiodynamic conditions is higher because the time at high potentials is not long enough to build up a high coverage of oxygen-containing species that are formed at constant potentials and, when the potential moves to low values, reduction reactions such as those indicated in (6) and (7) can generate new carbon active sites or C(H) species that can participate in a new oxidation/reduction cycle.

\[
C(O) + 2H_2O + 2e^− \rightarrow CO + 2C(H) + 2OH^−
\]

\[
C(O) + 2H_2O + 2e^− \rightarrow CO + C(\ ) + 2H_2 + 2OH^−
\]

If we consider the oxidation reactions occurring when going to positive potentials and the reduction reactions at negative potentials, then we have the carbon gasification reactions (8) and (9) which are known as electrochemical carbon gasification or electrogasification, also referred to “carbon corrosion”, which is the electrochemical analogue to the well-known thermal steam carbon gasification reaction.
These oxidation/reduction cycles responsible for the carbon gasification have been followed using the electrochemical quartz crystal microbalance [60, 84], showing that this is a powerful technique to study carbon reactivity in electrochemical conditions. Fig. 7(a) shows as an example the mass change of a commercial AC electrode subjected to five cyclic voltammetry at 50 mV s\(^{-1}\). An important mass loss was observed in the cathodic sweep, that corresponds to the formation of CO or CO\(_2\), while for the anodic sweep it can be observed a mass gain because of the formation of the C(O) complexes.

The global reaction that is taking place is the electrogasification. If we accumulate a sufficient number of cycles over time [60], we can observe that the mass loss can reach a nearly steady state (Fig. 7(b)). From this region of constant change of mass with time, a reactivity value can be calculated, as it is usually done for thermal gasification (i.e., \(R = 1/\Delta m (\Delta m/\Delta t)\)). The reactivity value obtained when cycling a carbon sample between \(-0.10\) V and 1.40 V in 1 M H\(_2\)SO\(_4\) solution was 0.75 h\(^{-1}\), which is a value similar to those measured for steam carbon gasification at temperatures near or above 800 °C [85]. This type of study comparing thermal carbon gasification and electrochemical carbon gasification could provide very interesting insights about the fundamentals of carbon materials reactivity.

The previously discussed results show that OFGs play a key role in the stability of the carbon material in aqueous electrolytes. Since oxygen groups in the carbon materials play a main role in the gasification reactions and electrolyte/solvent degradation, one possibility to minimize these processes is to block these sites. As a proof of concept, in the next paragraphs we summarize the results obtained using tailored metallacarboranes as mediators for boosting the stability of carbon-based aqueous supercapacitors [86].

The decomposition of the solvent and the oxidation of the carbon electrodes are important issues that need to be solved for extending the use of aqueous-based electrolytes in supercapacitors. The use of aqueous electrolytes has important economic, safety and power performance advantages compared to organic electrolytes. However, the energy density of these devices depends on the allowable voltage, which is mostly driven by the electrochemical stability window of the solvent and the electrolyte [81]. While voltages higher that 2.5 V can be applied in organic systems, only values below 1.2 V are employed commonly in aqueous based electrolytes due to solvent decomposi-

\[
C(\ ) + H_2O \rightarrow CO + 2C(H), \text{ or } CO + H_2 \\
C(\ ) + 2H_2O \rightarrow CO_2 + 4C(H), \text{ or } CO_2 + 2H_2
\]

Fig. 7 (a) Electrode mass behaviour of a commercial activated carbon (AC) electrode in a solution pH of 12 at 50 mV s\(^{-1}\) for five cyclic voltammograms. Reprinted with permission from ref 84. Copyright 2009 Elsevier. (b) Gravimetric response between \(-0.10\) V and 1.40 V of ZTC at 5 mV s\(^{-1}\) in 1 M H\(_2\)SO\(_4\) solution during 22 cycles of the 4th cyclic voltammetry experiment. Reprinted with permission from ref 60. Copyright 2015 Elsevier.
tion and carbon electrodes oxidation [87]. The development of novel strategies is needed for increasing the allowable voltage in aqueous systems. It has been reported that the use of neutral electrolytes provides a larger potential stability window compared to alkaline media and it is known that the voltage can be expanded by balancing the weight ratio between electrodes [88, 89]. However, in addition to optimizing these factors, the surface chemistry of the carbon electrodes has also to be tailored to improve the performance of the capacitor when working at high voltages.

Ruiz-Rosas et al. studied the increased stability of carbon materials, used as electrodes in supercapacitors in aqueous electrolytes at high voltages, by adding metallacarboranes with tuned redox potentials [86]. Metallacarboranes are anionic molecules soluble in water, highly resistant to harsh conditions and able to perform electron transfer reactions in a reversible way. These molecules can be strongly adsorbed in carbon materials through the interaction with OFGs and their redox potential can be tuned to obtain a potential compatible with the carbon electrode requirements. In this study [86], the pH of point of zero charge for the AC studied was 8.5; then, the AC is of basic character and, at the conditions used for the adsorption of the metallacarborane, the surface is positively charged what favours the interaction with the metallacarborane anion. In addition, the hydrogen atoms of the metallacarborane are of acidic character and can have a specific interaction with basic sites, what explains the strong interaction observed. A chlorinated derivative of the most studied metallacarborane, the cobaltabisdicarbollide anion (\([\text{Cl}_4\text{Co(C}_2\text{B}_{9}\text{H}_{11})_2]\)^−), was used to modify the electrochemical behaviour of the electrode/electrolyte interface. When this compound was adsorbed on the surface of the carbon material, it exhibited a strong interaction with CO-evolving functional groups. The processes related with the electroactive OFGs and water decomposition reactions were significantly modified by the presence of the metallacarborane. The oxidation current registered at the positive electrode and the potential limit at the negative electrode were both lowered. In addition, the higher cycling life and the lower amounts of surface oxygen groups detected in the used electrode, confirms the effective protection of the carbon material from electrochemical oxidation through the blockage of the oxygen-containing active sites. The authors suggest a parallelism between the use of boron as inhibitor to the well-known gas phase carbon gasification and the blocking of electrochemical oxidation active sites by metallacarboranes species.

### 2.1.3.2 Reactivity of carbon materials with organic electrolytes

Organic electrolytes are usually used in electrochemistry as they show a much wider voltage window. Nevertheless, the electrolyte may also decompose upon application of high voltages or temperature since they exponentially accelerate the electrochemical decomposition of the electrolyte [70, 90]. In the specific case of supercapacitors, tetraethylammonium tetrafluoroborate (TEABF₄) is frequently used as electrolyte and propylene carbonate (PC) or acetonitrile as solvents. The decomposition of the electrolyte at high voltages has been demonstrated by multiple in situ experiments [71–73]. The presence of functionalities and impurities (water, metals and heteroatoms) in the carbon electrodes plays a decisive role in the stability window as they may promote the decomposition of the electrolyte [74].

In the case of oxygen functionalities, it has been reported that their presence results in a faster electrode degradation, mainly due to pore blockage caused by the reaction of the solvent with the functional groups [75]. Propylene carbonate may react with many oxygen-containing compounds as phenols, carboxylic acids and other alcohols to form hydroxyalkyl derivatives producing CO₂ evolution, as shown in Fig. 8. Therefore, the solvent can react with oxygen functional groups of carbon materials if the conditions of potential are appropriate, producing a blockage of the porosity and the evolution of CO₂ molecules. For carbon electrodes in organic electrolyte, it has been observed that purification treatments with different acids and H₂ at high temperature to remove the oxygen groups produce carbon materials with much lower degradation rates under very aggressive conditions due to the decreased reactivity of the carbon/electrolyte system. It must be noted that the presence of inorganic compounds may also have an important contribution catalysing the hydroxyalkylation reactions, which is the main reason why the acid treatment is also required. The effect of OFGs, and of carbon edge sites in general, on carbon material degradation through reaction with the organic electrolyte, is very important for the positive electrodes [91], whereas the basal planes seem to determine the reactivity for negative electrodes [92]. All these results are helpful for the design of improved materials for this application in which the best positive electrode should avoid reactive edge sites either by creating materials without these sites [91] or by introducing heteroatoms which decrease the reactivity, like for example, nitrogen heteroatoms [93].

### 3. General Conclusions

Surface (electro)chemistry plays a key role in the behaviour of carbon materials in different environments and functional groups de-

![Fig. 8](image-url)
termine electrochemical properties. In the specific case of OFGs, they are naturally found and formed in carbon materials and can be easily introduced in any material, thus having a great effect in many properties, especially in the carbon/electrolyte interface. Thus, OFGs favour water wettability but a high concentration may decrease electrical conductivity, being then necessary to incorporate the adequate concentration of OFGs to get a compromise between both properties.

Some specific OFGs functionalities are electroactive in different electrolytes. The experimental results, including the easy electroactivity in acid electrolyte, the wide range of potentials in which the redox process is observed, the non-appearance in alkaline conditions and the observation in aprotic solvents, are all in them of agreement with the quinone/hydroquinone groups as the electroactive OFGs. In addition, the amount of electroactive OFGs that can be generated is especially dependent on the structure of the carbon material because of the structural requirements of these functionalities.

OFGs can be formed through reactions with the solvent/electrolyte and determine carbon reactivity. They play a very important role in different electrochemical energy storage and production devices like fuel cells, metal ion batteries or supercapacitors. Thus, understanding of the dynamics of OFGs formation/decomposition is essential to improve the devices or design new carbon materials. Their blockage, their substitution by other less reactive functional groups or the design of new materials with lower concentration of edge sites can be efficient routes to design more stable and less reactive systems.

We expect that this contribution has shown that the correlation between the nature and amount of the functional groups, exemplified with OFGs, and the performance of the carbon-based materials, is so strong that it is indubitable that the control of the surface chemistry will remain crucial to the development of a new family of advanced carbon materials.

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