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**Mini Review** **Open Access**

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# Porosity and Surface Modifications on Carbon Materials for Capacitance Improvement

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**Abstract:** Supercapacitors (SC) are energy storage devices with higher power but lower energy density than Li batteries. SC store energy based on two mechanisms: double layer capacitance (non-Faradaic) and pseudocapacitance (faradaic). Porous carbon materials have been extensively used as electrodes in SC, where their great surface area and pore size distribution have been the main properties for capacitance improvement. Nevertheless, these properties have shown limitations since they cannot be highly increased without losing electric conductivity, which is detrimental for the power requirements of SC. An alternative approach to increase capacitance has been the surface modification of carbon materials by introducing faradaic contributions. In this mini review, the effect of surface area, porosity, surface modification by doping or functionalization, and introduction of electroactive oxides are discussed to show how these factors influences the intrinsic capacitance values of different carbon materials; and some examples from our work are provided. The manipulation of such properties, on carbon materials (porosity and /or surface chemistry) not only are useful for devices such as SC, but also are very useful for a wide variety of Bio-applications (Bio-sensors, labelling and drug delivery, impregnation with microorganisms for its use as biochar, or for bio-fuel cells, etc.)

**Keywords:** Carbon materials, grafting, functional groups, polyoxometalate, tungsten oxide, solar concentration, supercapacitors

## 1 Introduction

Supercapacitors (SC) are high power energy storage devices with lower energy density compared to rechargeable batteries [1-2]. SC cells are assembled using similar configurations as in capacitors and batteries, that is, two electrodes, and a dielectric material or electrolyte solution. Nevertheless, the charge storage mechanism is quite different. In a conventional capacitor, the electrodes are 2 conductive plates separated by a dielectric material, and capacitance is given by the following equation:

$$C = \varepsilon A/d \tag{1}$$

where C is capacitance, $\varepsilon$ is the permittivity constant given for a specific dielectric material, A is the area of the conductive plates, and d is the distance between them. Therefore, when A increases and d decreases the capacitance is increased. In this conventional capacitor, charge is stored due to the ability of the dielectric material to polarize, keeping the electrodes or conductive plates charged, and no charge mobility within the dielectric material is observed as shown in Figure 1a. On the other hand, in SC cells the electrolyte and separator are used instead of the dielectric material, polarization occurs in the electrode-electrolyte interface due to ion mobility in the electrolyte, and the charge is retained by what is known as the double layer (Figure 1b) [3]. This double layer mechanism to store charge has a non-faradaic origin, which is increased as the

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surface area in the electrodes is increased, as can be performed in carbon materials. If we consider for example a carbon material with a BET surface area of 1000 $m^2/g$, a distance of 1 nm for the double layer formed between the positive charges in carbon and the negative charges of the electrolyte (Figure 1b), then the intrinsic capacitance will result in 100 F/g, and cyclic voltammetry will show the typical rectangular profile [4].

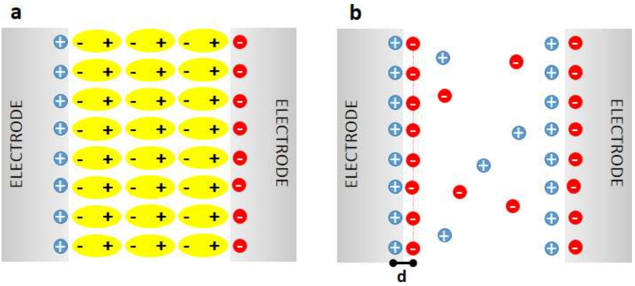

**Figure 1:** Schematic representation of charge storage in a conventional capacitor (a), and in a supercapacitor (b); where d is the distance of charge polarization in the double layer formed at the interphase electrode/electrolyte. Figure adapted from reference [3].

Commercial SC are assembled with carbon materials with great surface area, using a symmetric assembly, that is: 2-carbon electrodes separated by a polymeric or cellulosic membrane impregnated with organic electrolytes, showing a good behavior during numerous charge-discharge cycles. Nevertheless, their low specific energy (≈3-8 Wh/Kg), and the utilization of organic solvents that are not environmentally friendly electrolytes, are the main drawbacks of these commercial devices.

In order to design good SC cells, it is highly recommended to use cheap and non-toxic materials, high power density, and the main issue is the energy density increase [4]. The following general equations describe power and energy density in SC:

$$P = V^2/4R, \quad E = CV^2 \tag{2}$$

where V is the operational voltage window, R is the resistance, and C is the capacitance of the SC cell. High power cells are achieved by increasing the operational voltage window (V), and by decreasing all contributions to the total resistance value; that is: electrolyte conductivity, porosity characteristics in carbon, binders used in electrode fabrication, adhesion of electrode material to current collectors, etc. On the other hand, to increase energy density there are two main strategies: 1) increase the operational voltage window by the correct electrolyte selection using asymmetric assemblies, and 2) increase the capacitance by increasing the surface area and by controlling porosity in carbon electrodes, or by introduction of pseudocapacitance effects. The second strategy related with high surface carbon materials, porosity control, and pseudocapacitive effects will be the main focus for discussion in this mini review.

## 2 Porous carbons

Amorphous carbon has a disordered structure that consist mainly of $sp^2$ carbons, with up to 10 % of $sp^3$, and almost no sp carbons [5], and their properties depend on the preparation method. From a crystallinity point of view, amorphous carbons are considered to have local crystalline properties with no long range order, where this disorder and defects decreases electric conductivity. Within this group of carbons, we can find activated carbons, which are low cost materials and are well known due to their high surface area and micro-meso porous properties [6–9]. These carbons have been widely used as electrode materials for charge storage among other applications, and have been normally obtained from pyrolysis of a carbon precursor, followed by a physical or chemical activation procedure [10]. A great diversity of precursors used to produce carbons and activated carbons, come from natural sources, known as biomass [10–17]. Industrially produced activated carbons come from wood, mineral carbon, coconut shell, and animal bones [14–17]. Nevertheless, the available great amount of agroindustrial waste has led to proposed alternative materials to obtain these activated carbons, and decrease solid waste [18].

Pyrolysis temperature has been one of the main parameter involved in the structural, and physicochemical properties of carbons. At lower temperatures, between 873 K and 1173 K, structural disorder has been promoted, resulting in carbons with higher surface area. At pyrolysis temperatures higher than 1173 K, carbon porous structures start to collapse, losing surface area and porosity, and electric conductivity is promoted due to more graphitization degree. Therefore, porous carbons with sufficient electric conductivity give way to charge storage on the double layer, like in supercapacitors, while carbons with a more ordered structure (graphitized) have been typically used for Li intercalation [19]. In Figure 2 we show simulated carbon structures with different degree of graphitization, from very amorphous carbon structure (Fig. 2a) to a more graphitized structure (Fig. 2c). As observed in the figure, highly amorphous carbon structures show higher calculated surface area (2198 $m^2/g$ and 1950 $m^2/g$) than for carbons with a higher degree of graphitization (815 $m^2/g$)

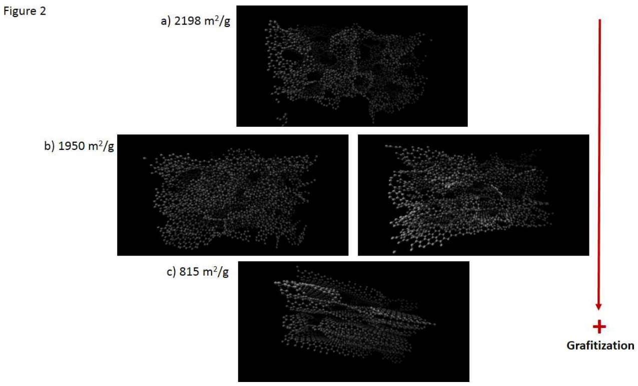

**Figure 2:** Simulated carbon structures using Tersoff potential implemented in LAMMPS software and applying a heating-quench technique in order to obtain nanoporous samples with different degrees of amorphicity. From these structures the surface areas were computed using a Connolly based algorithm. a) Highly amorphous nanoporous carbon with slight graphitic regions. b) Amorphous nanoporous carbon with disordered graphitic regions. c) Nanophorous carbon with a high degree of graphitization.

Carbons obtained after pyrolysis do not have all their porosity available, due to gasification products entrapped on the carbon structure. Therefore, an activation process is needed to generate and liberate the pores to obtain high specific surface on carbons [20, 21]. The most effective activation has been a chemical activation with dehydrating agents, such as: $H_3PO_4$, $ZnCl_2$, KOH, or NaOH [10, 20, 22]. Specific surface areas up to 3000 $m^2/g$ have been obtained with KOH activation [23]. Nevertheless, it is well known that a surface area between 1000 $m^2/g$ and 2000 $m^2/g$ has been useful for practical application for charge storage on the double layer [24]. Therefore, chemical activation gives higher carbon yield with higher surface areas, and the appropriate requirements of micro-meso porosity for applications in SC cells [22, 25, 26]. Nevertheless, it is believed that the disordered pore structure in these activated carbons has been responsible for the limited capacitance values obtained with very high surface area [20, 24, 27–30]. Therefore, the design of carbons with controlled porosity, with similar specific surface areas or even less, are needed to further improve capacitance values, as well as the cycling rate [26, 28, 31–33]. It has been very important to consider that when trying to control the porosity properties in a carbon material, if the porosity has been highly increased the electric conductivity will decay resulting in low volumetric capacitances [23, 34]. Carbons obtained from templetes [31], carbides [35], or aerogels from carbon gel precursors [36–38] have been some examples where the porosity has been highly tuned. In Figure 3, we show cyclic voltammograms profiles of carbon aerogels prepared in our lab with different pore sizes and BET surface areas calculated from $N_2$ isotherms. We can observe a rectangular-shape voltammetric profile for all aerogels, which is related to a capacitive behavior due to charge storage in the double layer formed at the electrolyte-electrode interphase. In addition, we observe that as the pore size decreased, the surface area increased, as well as the current interval of the voltamogram profile, resulting in an improved specific capacitance. Therefore, higher surface area and smaller pore size results in higher capacitance values, in good agreement with previous publications [31–35]. The inset on Figure 3 shows the porous microstructure of the aerogel with the lowest pore size diameter and higher surface area (ACP-100)

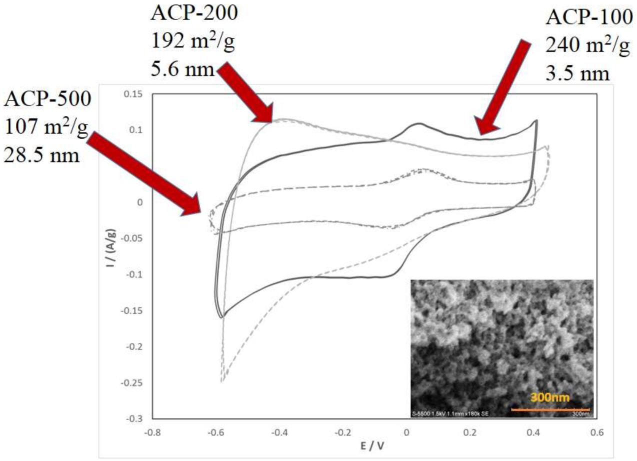

**Figure 3:** Cyclic voltamogram profiles of carbon aerogels with different BET surface areas and pore size, obtained at 20 mV/s in 0.05M $H_2SO_4$ as electrolyte. Figure adapted from reference [9]. SEM image of sample ACP-100 can be observed on the inset.

## 3 Surface modifications of carbons

Porosity properties, as well as surface area in carbon materials have shown a strong relevance in their capacitive properties. Nevertheless, introduction of pseudocapacitive processes has been usually more helpful than increasing considerably carbon porosity, due to electric conductivity loss, as mentioned before. Introduction of heteroatoms (N, O, S), functional groups, and/or transition metal oxides can result in higher capacitance due to pseudocapacitance contributions. Incorporation of heteroatoms have been introduced intrinsically when using biomass rich in a particular heteroatom. For example, seaweed has shown high nitrogen content, and has been proven that when pyrolyzed to produce carbon, the resulting carbon has been doped with nitrogen, showing a voltammetric profile with pseudocapacitive contributions [16]. In Figure 4 we show a cyclic voltammogram of a carbon obtained from a brown seaweed (Macrocistis pyrifera) collected on the California coast. A rectangular profile typical of a double layer charge storage can be observed, with very wide peaks around 0.55 V/0.14 V, related with faradaic contributions from nitrogen doping, confirming previous observations. The inset on Figure 4 shows a type IV $N_2$ isotherm for such carbon, with hysteresis between adsorption and desorption, that is typically related to mesoporous materials. Even though the BET surface area for this carbon was low (430 $m^2/g$) compared to other carbons [16], its intrinsic capacitance was high (around 200 F/g average) due to the pseudocapacitance contribution from nitrogen doping. This is a typical example on how this type of pseudocapacitive contribution has been more effective in improving capacitance than only increasing surface area.

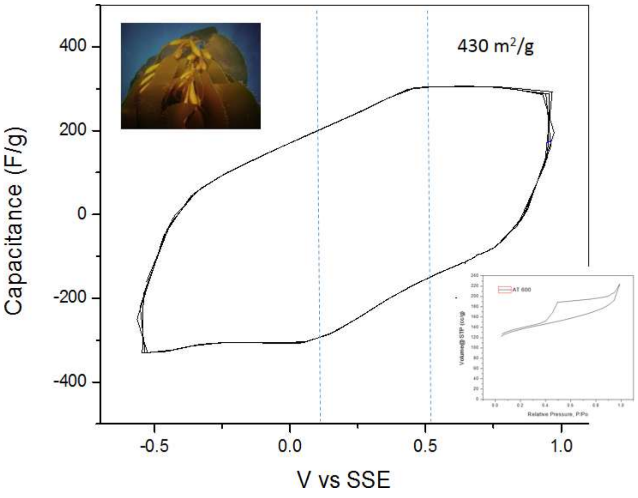

**Figure 4:** Cyclic voltammetry profile of a carbon obtained from pyrolysis at 650 °C of a brown seaweed from the coast of California. This electrochemical characterization was performed at 20 mV/s, using as electrolyte 0.5M $H_2SO_4$ solution. $N_2$ isotherm from where BET surface area was calculated can be observed on the inset.

Another way to introduce pseudocapacitive effects to carbon has been through incorporation of oxygen-based functional groups, such as: hydroxyls, ether, epoxy, aldehyde, carbonyls, carboxylic, lactone groups. Aside from the pseudocapacitance contributions of some of these groups, their presence has been very important because it changes the wettability properties of the carbons, which has been important when using aqueous electrolytes. These groups can be introduced to carbon by oxidation, using acidic treatments that usually result in a cocktail of functional groups [39]. If the interest is to selectively introduce or graft a particular oxygen-based functional group, the diazonium chemistry has been a good alternative where no significant destruction of carbon occurs, compared to traditional oxidative treatments [39–41]. It has been shown that the introduction of antraquinone to carbon, resulted in a large faradaic contribution from the redox activity, aside from the double layer of the carbon [42]. Another example is the grafting of OH groups performed in our group. In Figure 5 we show the schematic reaction for the diazonium chemistry used to graft this hydroxyl group, the $N_2$ isotherms performed to calculate the BET surface area, and the ATR spectra showing the presence of the C-O stretching mode on the grafted carbon (DLC-OH). The phenolic group grafting involved the in-situ generation of the diazonium cation from the amine group reduction with sodium nitrite, giving the aryl group that permitted carbon modification, and nitrogen evolution, as confirmed from the ATR spectrum (DLC-OH). This grafting procedure takes place in the microporosity of the carbon, as previously reported elsewhere [42], and is confirmed in our results by the decrease of the starting point of the isotherm on the grafted carbon (DLC-OH). Both isotherms are Type I, which is related to microporous materials. BET surface area was calculated for these two carbon materials, giving values of 1673 $m^2/g$ for the un-grafted carbon (DLC) and 1045 $m^2/g$ after grafting (DLC-OH), confirming again less area after grafting the phenolic groups.

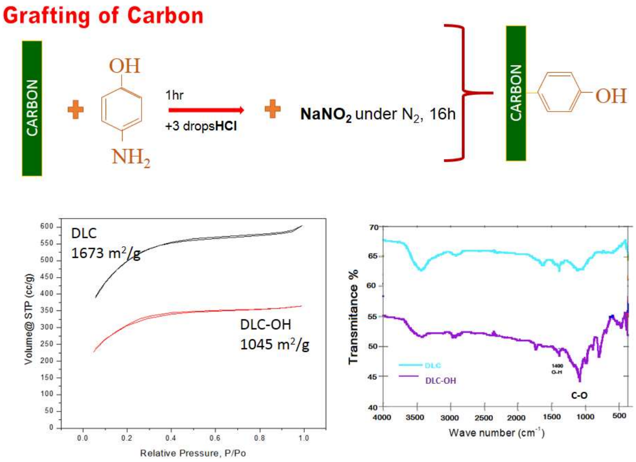

**Figure 5:** Schematic illustration of the diazonium chemistry reaction to graft hydroxyl groups to a Norit carbon (DLC). $N_2$ isotherms of un-grafted (DLC) and grafted carbons (DLC-OH), from where BET surface areas were calculated are also shown.

We evaluated the electrochemical performance of these carbons by cyclic voltammetry on different aqueous electrolytes: a) 0.5 M $H_2SO_4$, and b) 0.5 M $LiClO_4$. In Figure 6a we show the cyclic voltammetry profiles using an acid based electrolyte, where we can clearly detect the typical capacitive behavior for the un-grafted carbon (DLC), while in the modified carbon with OH groups (DLC-OH) the electroactive behavior of the functional group through its faradaic contribution was revealed, improving the capacitance value of DLC (100 F/g) up to an average value of 250 F/g. In this case, it was clear that the BET surface area decrease did not result in a penalized capacitance value, but instead on a pseudocapacitance contribution that ended on a higher total value of capacitance. On the other hand, when using a neutral aqueous electrolyte (Fig. 6b), the faradaic contribution of the hydroxyl groups was not revealed, and only a capacitive behavior was observed. The main contribution of the introduction of this functional group to carbon in its electrochemical behavior was the ionic diffusion improvement in this neutral electrolyte (0.5 M $LiClO_4$), which was related with the voltammetry profile change to a more rectangular behavior. Therefore, incorporation of oxygen-based functional groups, phenolic groups in this case, helped to improve wettability of the carbon, improving ionic diffusion, and improving capacitance values by introduction of pseudocapacitance effects.

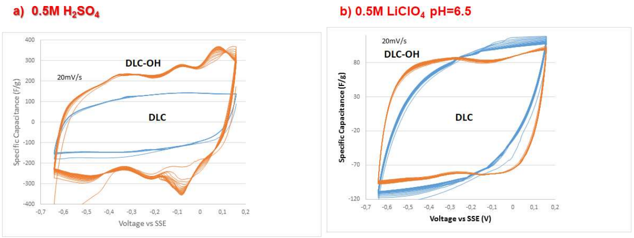

**Figure 6:** Electrochemical performance for un-grafted (DLC) and grafted carbons (DLC-OH) performed by Cyclic voltammetry at 20 mV/s using an acidic aqueous electrolyte (a), and a neutral electrolyte (b).

Metal oxides with pseudocapacitance to obtain hybrid, nanocomposite, or composite materials with carbons, has been an effective way to improve capacitance values of carbon materials [4, 43]. In our group, we have worked with polyoxometalate nanocomposites with carbon nanotubes [44–47], nanofibers [48], aerogels [49], and some activated carbons. These molecular metal oxides have shown to be very interesting because of their reversible multielectronic redox reactions, which have resulted very useful for energy storage. For example, a nanocomposite prepared with oxidized multiwall carbon nanotubes (MWCNT) decorated with PMo12O40 as the polyoxometalate (POM), showed a cyclic voltammetry profile with contribution from the double layer formed at the interphase MWCNT/electrolyte, and the pseudocapacitance contribution of POM through its 3 reversible redox multielectron reactions (Figure 7). Both contributions, double layer and pseudocapacitance, added up to give an intrinsic capacitance for this nanocomposite material (MWCNT/POM) of up to 232 F/g, higher than for the reported nanocomposites with activated carbon [50]. Symmetric supercapacitor cell has been assembled with this MWCNT/POM hybrid, obtaining up to 30 F/g [45]. Another example for this type of nanocomposites has been an activated aerogel carbon (Activated AG) prepared also in our lab with the same POM, where its electrochemical characterization by cyclic voltammetry is shown also in Figure 6. For the activated carbon AG we obtained a BET surface area of 334 $m^2/g$, and an intrinsic capacitance of 78 F/g. When POM was introduced, the surface area decreased almost 60 $m^2/g$ to give 274 $m^2/g$. Nevertheless, the capacitance value increased up to 94 F/g, showing that the pseudocapacitive contribution of POM was more effective than increasing surface area in the bare carbon (244 $m^2/g$, 59 F/g). This shows again the effective contribution of pseudocapacitance to improve carbon capacitance values.

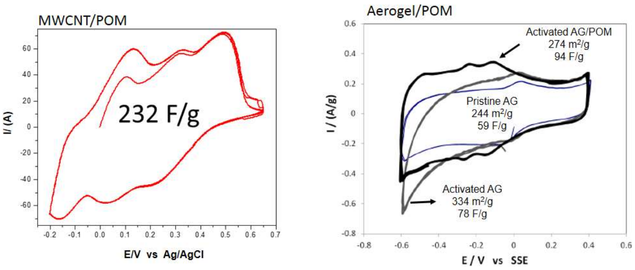

**Figure 7:** Electrochemical performance evaluated by cyclic voltammetry of different POM nanocomposites, performed at 20 mV/s in 0.05M $H_2SO_4$ as the electrolyte. MWCNT/POM is a nanocomposite based on oxidized multiwalled carbon nanotubes, and a Mo-based POM (left); Aerogel/POM nanocomposite compared to its activated AG, and the pristine AG (right, figure adapted from Ref. 9).

Other oxides with pseudocapacitance may be used to increase the capacitance performance of carbon electrodes. In Figure 8 we show the XRD pattern, and cyclic voltammetry for a tungsten oxide ($WO_3$) synthesized from tungsten at 1273 K using a green approach with a solar concentration oven [51]. This $WO_3$ has a triclinic and monoclinic mixed structure with a crystal size of 40 nm, and its rectangular voltammetry profile with some bumps resembles the typical pseudocapacitive material, as ruthenium [52] and manganese oxides [53–56]. Even though, the capacitance of the bare oxide was only 4 F/g, when it was incorporated in 1.5 % to a Norit activated carbon (DLC) during electrode fabrication, the voltammetric profile indicated a more rectangular shape profile with less ionic resistance, and improved capacitance value (Figure 9) for this composite electrode. This hybrid, nanocomposite, or composite approach that we have shown are excellent strategies to increase capacitance values [3, 43].

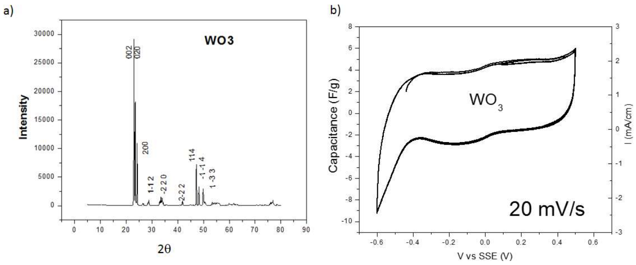

**Figure 8:** Powder XRD pattern obtained for $WO_3$, and its electrochemical performance evaluated by cyclic voltammetry at 20 mV/s in 0.05M $H_2SO_4$ electrolyte.

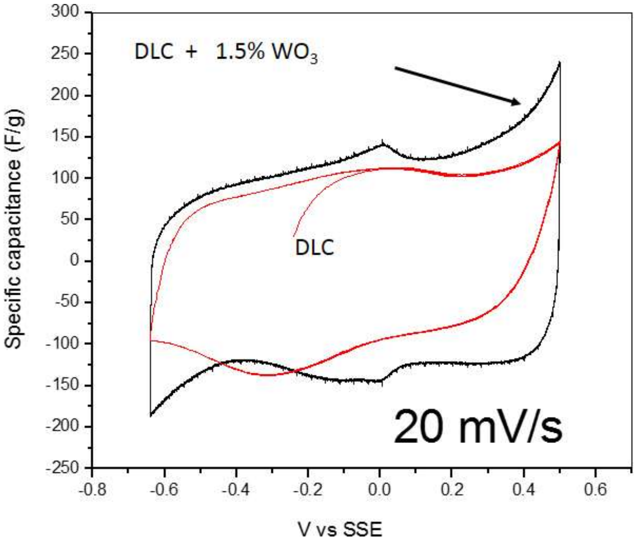

**Figure 9:** Comparison of the electrochemical performance by cyclic voltammetry at 20 mV/s in 0.05M $H_2SO_4$ electrolyte of a bare Norit activated carbon (DLC) electrode, and a composite electrode of DLC with 1.5% of $WO_3$.

## 4 Conclusions and closing remarks

The examples from our work provided in this minireview confirmed that surface modifications performed on carbon materials had more impact on obtaining higher intrinsic capacitance values in aqueous electrolytes, than increasing their surface area. For example, pristine carbon AG (ACP-100) with higher surface area and smaller pores resulted in higher capacitance values. Nevertheless, nitrogen doping of carbon as for carbon obtained from a brown seaweed, was more efficient in improving capacitance than only increasing surface area, as in carbon aerogels (AG). In addition, incorporation of O-based functional groups by a grafting technique using a diazonium chemistry, was a very efficient way to improve wettability of the carbon, improving ionic diffusion, and capacitance values. Finally, the hybrid, nanocomposite, or composite approach, as for the introduction of POM or $WO_3$ to carbons, showed as in many other cases in the literature, an excellent strategy to increase capacitance values. Nevertheless, we must point out that cyclability in SC cells must be studied with all of this approaches. In addition, we must point out that all these properties studied on carbon materials (porosity, surface area, functionalities, etc) are not only useful within the supercapacitor field. There have been many studies related for example with biosensors [57], labelling and drug delivery [58], biochar for soils [59], or for bio-fuel cells [60].

## 5 Experimental procedures

### 5.1 Simulated Carbon Structures

The nanoporous carbon samples calculated in this work were generated using a thermal procedure of heating-quenching, thermalization, and the Tersoff [61] potential implemented in LAMMPS [62] software. We report here hexagonal supercells with densities of 0.71, 0.85 and 1.37 g/cm$^3$ which were generated using three different quenching rates, being these 74.00x10$^{12}$ K/s for the 0.71 g/cm$^3$ sample, 23.68x10$^{12}$ K/s for the 0.85 g/cm$^3$ sample, and finally 68.08x10$^{12}$ K/s for the 1.37 g/cm$^3$ sample. Each supercell has 6400 carbon atoms, and were constructed by the 20x20x4 replication of a hexagonal unitary cell with the P63/*mmm* space group. The thermal procedure applied for each supercell consisted in the linear heating of the cell from 300 to 4000 K in 50,000 simulation steps of 1 fs, followed by the quenching rates depicted earlier; all the samples were quenched to 300 K. After this, a constant temperature molecular dynamics was applied for 0.5 ns in order to reach thermal equilibration. During all simulations, the volume was kept constant by an isothermal-isobaric NVT canonical ensemble, and the Nosé-Hoover thermostat [63-64] was used.

## 5.2 Materials

**Carbons**

Carbon aerogels (AG) were synthesized following the procedure previously reported by our group [49]. Briefly, a resorcinol (99 % purity)/formaldehyde (37.4 %; methanol stabilized) molar ratio of 0.5, and molar ratios of resorcinol/catalyst (Sodium carbonate) of 100, 200, and 500 were used. All reagents in solution were stirred, aged at 358 K for 96 hours, followed by a solvent exchange with acetone during three days, and dried by supercritical drying with $CO_2$ to obtain the corresponding precursor gels (RF). Finally, a pyrolysis procedure at 1123 K for 30 min was performed to obtain the different carbon aerogels. Chemical activation of carbon AG obtained with a moral ratio of resorcinol/catalyst of 100 was performed with a solution of KOH in ethanol, using a mass ratio of 5/1 of KOH/AG. The mixture was dried at 383 K, then heated at 1123 K for 3 hours using a heating rate of 278 K/min. The AG was washed with a 10 % HCl solution and deionized water, and finally dried at 383 K for 6h (Activated AG).

**Grafting OH groups**

We used an Activated Carbon from Norit (DLC SUPRA 50) to graft phenolic groups, using the diazonium chemistry. We followed the same grafting procedure used previously in our group [65], and summarized is as follows: we dispersed 500 mg of Norit Carbon (DLC) in 50 ml of deionized water, then 4 mmol of 4-aminophenol was added with two drops of HCl, after 1 hour of stirring we added 4 mmol of $NaNO_2$ dissolved in 50 ml of deionized water, and finally the reaction was stirred for 16 hours under nitrogen bubbling. The grafted carbon was recovered by filtration, washed with deionized water, acetonitrile, dimethylformamide, and methanol to remove unreacted reagents, and finally dried at 353 K for 1 hour to obtain the modified Norit carbon with OH groups (DLC-OH).

**Incorporation of Metal oxides**

We incorporated different oxides to different carbon matrices, such as: multiwalled carbon nanotubes (MWCNT), carbon aerogel (AG), and Norit activated carbon. The oxides that we used were a commercial Mo-based polyoxometalate (POM), and a tungsten oxide ($WO_3$) prepared with a green approach [51]. We will first describe the procedures to obtain the hybrid materials from POM and then from $WO_3$. The incorporation of POM to MWCNT has been reported elsewhere [44]. Briefly, in this hybrid we used a Cs salt of the POM, and the nanotubes were strongly oxidized to obtain a high degree of dispersion. Also, POM in its acidic form was incorporated in activated AG synthesized with a resorcinol/catalyst ratio of 100, following a procedure that has been already reported by our group [49], that is: we added the activated AG to a 1.7 mM POM solution, was sonicated for 3 hours, the solid was recovered by filtration, then washed. The obtained suspension was filtered off, washed with a pH=2 sulfuric acid dissolution, and dried at 373 K for 1h. The incorporation of $WO_3$ to Norit activated carbon was performed during the fabrication of the electrode, and is described in detail in the next section.

## 5.3 Characterization Techniques

Physisorption characterization to calculate BET surface area, and pore size was performed in a Quantachrome NOVA instrument. First, we pretreated the samples under vacuum at 393 K for 16 h to clean the surface. Then, we performed nitrogen isotherm measurements at 77 K, and calculated the specific surface area using the Brunauer-Emmett-Teller (BET) theory between 0.02 and 0.3 P/Po and the BJH method to calculate pore size. ATR (Attenuated Total Reflectance) spectra was obtained using a Bruker Infrared spectrometer, model ALPHA between ranges of 4000 $cm^{-1}$ to 375 $cm^{-1}$. SEM was performed using a Bruker HR-SEM model QUANTAX from Hitachi. Powder XRD was performed in a DMAX Rigaku 2200 diffractometer with a graphite secondary monochromator.

Electrochemical characterization by cyclic voltammetry in half cells was used to detect the charge storage mechanism in the different studied materials, and calculate the intrinsic specific capacitance of the materials by dividing the voltammetric current by the used scan rate, and electroactive electrode mass. We used a Biologic VSP potentiostat controlled by EC-Lab® software. The half-cell was arranged with a reference electrode, a platinum mesh as counter electrode, and our different materials as the working electrodes. The working electrodes were fabricated as follows: we mixed in ethanol 60 wt% of our electroactive material, 30 wt% of Super P conducting carbon (TIMCAL), and 10 wt% of Teflon (Sigma-Aldrich) as the binder. We must point out that for $WO_3$ hybrids with Norit activated carbon, we used 1.5 % of the oxide and 58.5 % of the carbon as the electroactive material. The prepared mixtures were heated until a dough was obtained, which was cold-rolled to prepare a film that was dried at room temperature for 24 hours. From the films we cut 1 $cm^2$ squares, and pressed them in a stainless steel mesh current collector (Aisis 316L). Before the electrochemical characterization was performed, the electrolyte was purged with nitrogen for 20 min.

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