Nanostructured porous carbons for electrochemical energy conversion and storage

José L. Figueiredo

Laboratory of Catalysis and Materials - Associate Laboratory LSRE-LCM, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

ABSTRACT

The various methods that have been reported for the synthesis of nanostructured carbons are reviewed, emphasizing sol-gel processing, soft-templating and hydrothermal procedures. Hybrid materials can be obtained by incorporation of nanosized carbon components, such as carbon nanotubes or graphene-derived materials. In addition, the carbon surface chemistry can be tuned by functionalization with surface groups and/or by doping with heteroatoms, in order to suit specific applications. Nanostructured porous carbons can play a decisive role towards the development of efficient and cost-effective electrochemical devices for energy conversion and storage. In this article, we focus on novel electrocatalysts for fuel cells and electrolysers, and electrodes for electric double layer capacitors.

1. Introduction

Activated carbons are widely used as adsorbents and in other industrial applications, due to their large surface areas and high stability, both in acidic and basic media. They are obtained from carbonaceous precursors (such as peat, coal, wood, coconut shell) by carbonization (pyrolysis in the absence of oxygen) and subsequent partial gasification (with steam, carbon dioxide, air, or their mixtures), or by carbonization in the presence of substances that minimize the formation of tars (zinc chloride, phosphoric acid, potassium hydroxide) followed by washing [1,2]. These top-down production routes (named "physical" and "chemical" activation, respectively) lead to a well-developed porous structure with pores of different sizes, which are classified, according to their widths, as micropores (< 2 nm), mesopores (2–50 nm) and macropores (> 50 nm) [3].

The high adsorption capacity of activated carbons stems from their large micropore volumes, which may range from 0.15 to $0.50 \, cm^3 \, g^{-1}$. Unless special activation procedures are used, the volume of mesopores is relatively low ($< 0.10 \, cm^3 \, g^{-1}$), and they account for $< 5\%$ of the adsorption capacity. Macropores are not generated during activation; they are already present in the carbon precursors, thus facilitating the access of reactants during the activation procedure. The volume of macropores in activated carbons can range from 0.20 to $0.50 \, cm^3 \, g^{-1}$. Due to the large dimensions of the macropores, their surface area (and adsorption capacity) is negligible ($< 2 \, m^2 \, g^{-1}$); however, their presence is essential for providing access of the adsorptives to the inner pores where adsorption occurs [2]. The different types of pores are arranged in a hierarchical pattern, with the micropores branching off from the mesopores, and these from the macropores, which in turn open out to the external surface of the particles [1], as shown in Fig. 1. However, the high temperature processes used in the production of activated carbons cannot achieve the fine control of pore size and pore size distribution needed for more sophisticated applications.

2. Nanostructured porous carbons

2.1. Controlling the texture

Nanostructured porous carbons are defined as carbon materials which have their structure and texture controlled at the nanometer scale [4,5]. There are two main routes for the synthesis of nanostructured porous carbons, involving either sol-gel procedures or the use of templates.

The sol-gel procedure involves the polycondensation of hydroxybenzenes (e.g., resorcinol) and formaldehyde, leading to the formation of organic gels (aerogels, xerogels and cryogels, according to the drying method used), which are then converted into carbon gels by carbonization [6]. Their textural properties can be controlled by adjusting the synthesis conditions, such as the pH and the dilution ratio (molar ratio between solvents and reactants). In particular, it is possible to obtain materials with well-developed microporosity together with narrow mesopores of well-defined size [7–9].

The use of templates provides the possibility to control the 3-D structure of the carbon material, in addition to the pore size.
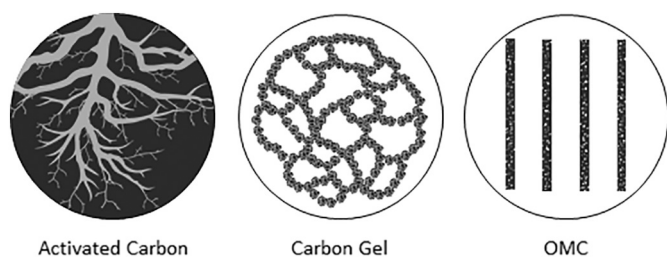
Fig. 1. Schematic representation of the hierarchical porous systems of an activated carbon, a carbon gel, and an ordered mesoporous carbon (OMC).

Exotemplating (also called hard templating or nanocasting) consists in filling up the pores of a solid with a carbon precursor. Endotemplating (also called soft templating) involves the use of supramolecular structures (micelles) around which the carbon precursors aggregate by self-assembly [10,11]. Ordered mesoporous carbons (OMCs) are obtained in both cases, upon carbonization and removal of the template.

In the case of hard-templating, the pore sizes of the OMCs obtained are determined by the pore sizes of the templates used [12,13]. Soft templating offers a simpler, safer and versatile route to obtain OMCs [11,14]. One of the most common recipes starts from resorcinol as carbon precursor and Pluronic F127 as template. In this case, the textural properties of the carbon materials obtained can be adequately controlled by the synthesis conditions, such as the Resorcinol/F127 molar ratio [15].

Hierarchically structured carbons exhibit porous structure on more than one length scale, from micro- to meso- and macropores; these pore levels must be interconnected in such way that the transport properties are improved [16]. Fig. 1 represents schematically the hierarchical porous structures of an activated carbon, a carbon gel, and an ordered mesoporous carbon. It is clear that the pore system hierarchy of the activated carbon (larger pores subdividing into smaller ones, in a tree-like arrangement [1]) is different from that of the nanostructured carbons (small pores branching off from larger pores, in a series-parallel arrangement). In the case of carbon gels, we have microporous nodules which are aggregated into a network, the voids between nodule chains being the large pores (meso/macropores) [17]; in the OMC, the micropores are present in the walls of the aligned mesopores [18].

Table 1 shows relevant textural properties of actual samples of porous carbons, namely: a "physically" activated carbon (AC) [19]; two carbon xerogels, CXG1 with wide pores (average mesopore size = 11 nm), and CXG2 with narrow pores (average mesopore size = 3.6 nm) [20]; and a templated carbon obtained by nanocasting with a mesoporous silica template (average mesopore size = 3.5 nm) [21].

2.2. Biomass-derived carbons

Both the sol-gel and soft templating methods offer flexible bottom-up routes for the production of nanostructured porous carbons with tuned properties. Nevertheless, the harmful nature of the carbon precursors used (hydroxybenzenes) has triggered research on more sustainable alternative syntheses, based on renewable raw-materials. For instance, biomass and carbohydrates can be easily converted into carbon materials by hydrothermal carbonization (HTC) at mild temperatures (typically 180–250 °C) under self-generated pressures [22,23]. However, the carbon materials obtained exhibit, in general, a poorly developed porosity, and additional measures are required to improve the textural properties, such as the use of templates or porogens, or post-synthetic activation procedures. For instance, the HTC of carbohydrates generates non-porous colloidal carbon spheres, but mesoporous carbon gels can be obtained by adding phloroglucinol as crosslinking agent [24]. Another strategy consists in using graphene oxide (GO) or oxidized carbon nanotubes (CNTs) as templates; the acidic functional groups on the surface of the nanocarbons promote the dehydration and condensation of carbohydrates, leading to the formation of HTC monolithic gels. The materials obtained with GO exhibited low surface areas ($93 \, m^2 g^{-1}$) and negligible micropore volumes ($0.02 \, cm^3 g^{-1}$), but the textural properties were improved after thermal treatment at 800 °C ($567 \, m^2 g^{-1}$ and $0.25 \, cm^3 g^{-1}$). Further development of the porous structure was achieved by chemical activation with KOH. For instance, surface areas in the range $1800–2000 \, m^2 g^{-1}$ and micropore volumes between 0.67 and $0.75 \, cm^3 g^{-1}$ were obtained by activation at 700 °C [25]. Fig. 2 schematically describes the procedure using GO, but similar materials are obtained by using oxidized CNTs.

2.3. Controlling the surface chemistry

Another important property of carbon materials which can be modified and finely tuned is their surface chemistry. Indeed, the unsaturated carbon atoms at the edges of the graphene layers and at structural defects are highly reactive, and can form various types of functional groups; in addition, it is possible to incorporate heteroatoms (N, B, …) into the graphene layers. Functionalization and heteroatom-doping can be achieved during the synthesis of the carbon material, or by post-synthesis treatments. In any case, the surface properties will be modified, namely the hydrophobicity, acidity-basicity, and surface charge. The most important surface groups are those of oxygen, nitrogen, sulphur, boron and phosphorus. The methodologies used for their incorporation into carbon materials, as well as the methods used for their qualitative and quantitative assessment, have been described in previous papers [15,26–29]. Fig. 3 shows schematically different types of surface groups containing oxygen, nitrogen and sulphur.

The oxygen groups are acidic, with the exception of ether and carbonyl groups, which are neutral and may form basic structures, such as quinone and pyrone groups. The most important nitrogen groups are basic: pyridine (N6), pyrrole (N5) and quaternary nitrogen (NQ). The π electrons on the basal planes also contribute towards the basicity of carbon materials [28]. The presence of these groups is of paramount importance in determining the surface interactions and, therefore, the properties of the carbon materials towards adsorption and catalysis. In aqueous media, the surface groups can be protonated or deprotonated, originating a surface charge. The point of zero charge (PZC) is defined as the value of pH at which the net surface charge is zero. The surface will be negatively charged when pH > PZC, thus attracting cations; conversely, the surface will be positively charged when pH < PZC, thus attracting anions [28]. Therefore, the PZC is a convenient parameter to explain the behaviour of carbon materials in contact with aqueous solutions, in particular when electrostatic interactions are involved.

3. Applications in energy conversion and storage

3.1. Fuel cells and electrolysers

Hydrogen is expected to play a major role, as an energy carrier, in the development of efficient and competitive solutions for the production and storage of electricity from renewable energy sources. Fig. 4

Table 1
Textural properties of typical porous carbons: activated carbon (AC), carbon xerogels (CXG1 and CXG2) and templated carbon (TC): BET surface area; mesopore surface area; and micropore volume. Data from [19–21].

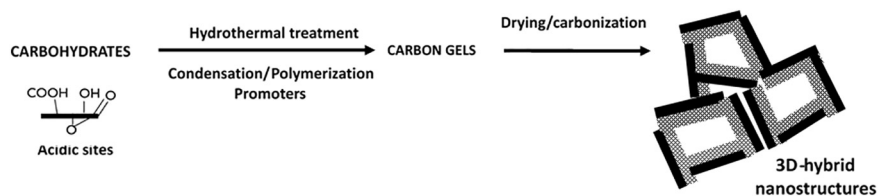| Sample	S_{BET} [$m^2 g^{-1}$]	S_{meso} [$m^2 g^{-1}$]	V_{micro} [$cm^3 g^{-1}$]
AC	1357	116	0.520
CXG1	717	311	0.124
CXG2	792	462	0.157
TC	1120	819	0.134

Fig. 2. Schematic procedure for the synthesis of 3D-hybrid nanostructures from the GO-assisted HTC of carbohydrates.

shows a conceptual system based on renewable energy, using water electrolysis and fuel cells. When there is an excess of electric energy, hydrogen is produced by electrolysis of water and stored on-site. The stored hydrogen can then be used to generate electricity in fuel cells, or used directly as a fuel [30].

The fuel cell (FC) is an electrochemical device with two electrodes (anode and cathode) separated by an electrolyte, the electrode surfaces being covered with a thin layer of an electrocatalyst. The FC generates electricity by oxidizing the fuel (e.g., hydrogen) at the anode (HOR) and reducing oxygen at the cathode (ORR). The components of the electrolyser are similar to those of the fuel cells. In the electrolyser, electric

energy is converted into chemical energy based on the electrochemical splitting of water, either in acid or alkaline electrolytes. Hydrogen is produced at the cathode (HER), and oxygen is released at the anode (OER).

The electrochemical processes involved in acid medium are:

- the cathodic Hydrogen Evolution Reaction (HER) in the electrolyser:

$$2H^+ + 2e^- \rightarrow H_2 \text{ (HER)} \tag{1}$$

- the anodic Hydrogen Oxidation Reaction (HOR) in the fuel cell:
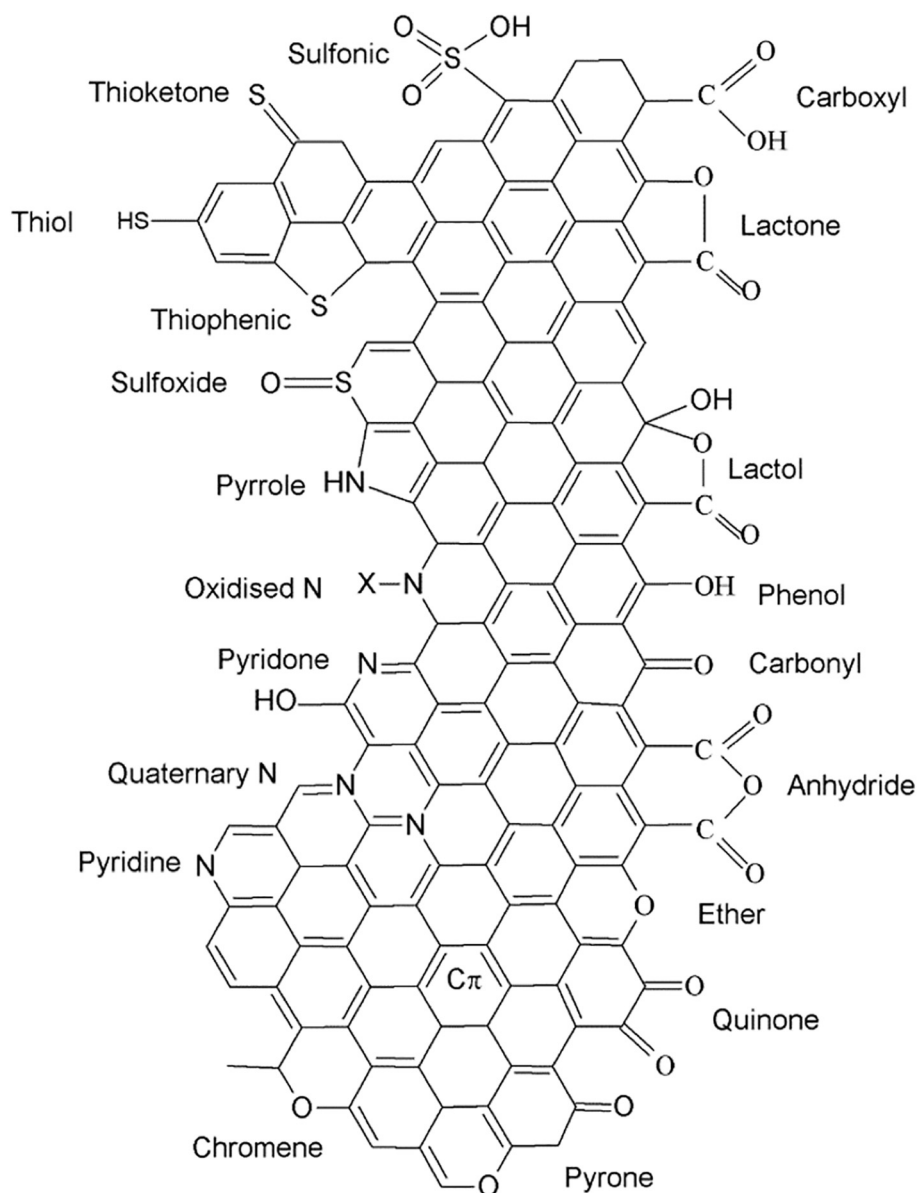

Fig. 3. Schematic representation of oxygen, nitrogen and sulphur functional groups on the carbon surface. Adapted from references [27,29].
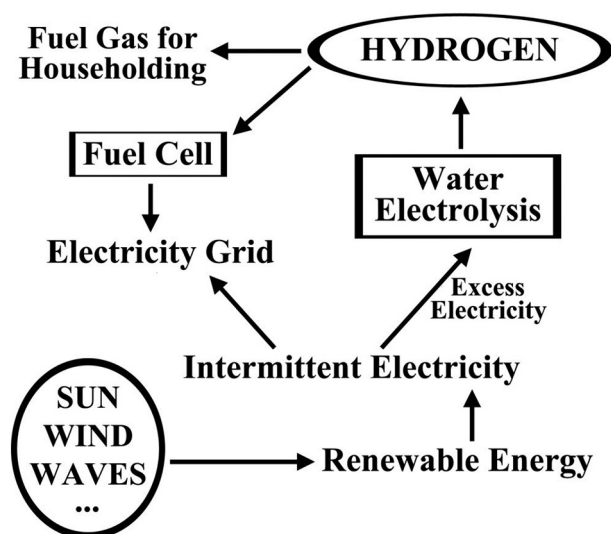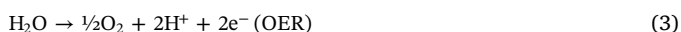
Fig. 4. Conceptual system based on hydrogen as an energy carrier, using water electrolysis and fuel cells.
Reprinted from [30] with permission from *Química Nova*.

$$H_2 \rightarrow 2H^+ + 2e^- \text{ (HOR)} \qquad (2)$$

- -the Oxygen Evolution Reaction (OER) at the anode of the electrolyser:

$$H_2O \rightarrow \tfrac{1}{2}O_2 + 2H^+ + 2e^- \text{ (OER)} \qquad (3)$$

- and the Oxygen Reduction Reaction (ORR) in the fuel cell cathode:

$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \text{ (ORR)} \qquad (4)$$

The reaction rates of the HER and HOR are very fast on platinum-based catalysts. In contrast, the kinetics of OER and ORR are much slower. These processes tend to be faster in alkaline media, using an anion exchange membrane instead of the proton exchange membrane (PEM) used in acidic conditions, opening the possibility for using less costly platinum-free electrodes [31]. In such conditions, the reactions in the electrolyser are:

$$H_2O + e^- \rightarrow \tfrac{1}{2}H_2 + OH^- \text{ (HER)} \qquad (5)$$

and

$$2OH^- \rightarrow \tfrac{1}{2}O_2 + H_2O + 2e^- \text{ (OER)} \qquad (6)$$

The reverse reactions occur in the alkaline fuel cell anode (HOR) and cathode (ORR), respectively.

3.1.1. Electrocatalysts for fuel cells

So far, the most efficient catalysts for the fuel cell reactions are based on Pt, but their high cost, limited supply and poor stability limit the widespread commercialization of these devices [32–34]. Carbon nanomaterials recently emerged as a promising class of electrocatalysts, since they exhibit high surface areas without compromising their electronic conductivity, and can be doped or functionalized in order to present active sites for the hydrogen/oxygen reactions. This offers the possibility to develop a new generation of carbon-based electrocatalysts without the use of precious metals. In particular, the excellent performance of N-doped nanostructured carbons for the ORR has been reported [35].

In order to investigate the effect of the type and content of nitrogen, N-doped CNTs with surface areas in the range 350–364 $m^2 g^{-1}$ and surface nitrogen contents from 0.2% to 4.8% were prepared and tested as catalysts for ORR in alkaline medium [36]. Pyridinic, pyrrolic and quaternary nitrogen groups were identified in these samples. The onset potentials (E_{on}) ranged from 0.806 to 0.837 V (vs RHE), approaching

the value of Pt/C (0.841 V). The two best catalysts exhibited average numbers of electrons transferred per O_2 molecule (n_{O2}) of 3.3 and 3.1, respectively, while n_{O2} = 4.0 for Pt/C. However, the best catalyst exhibited higher durability and methanol tolerance than Pt/C. The correlation between ORR performance data and catalyst composition suggested that the $N_{pyridinic}/N_{quaternary}$ ratio plays a more relevant role than the total N content for this reaction. In fact, the catalysts with the best performance (in terms of E_{on} and n_{O2}) exhibited the highest $N_{pyridinic}/N_{quaternary}$ ratios (5.6 and 3.9 respectively), while their nitrogen contents were quite different (3.1 and 0.8%) [36].

In a more recent work, porous carbons were prepared by using an ionic liquid as structural directing agent and porogen, and their activities were assessed for the ORR in alkaline media [37]. The ionic liquid (IL) used was 1-butyl-3-methylimidazolium methanesulphonate, [bmim][MeSO$_3$], which also served as a precursor for double-doped (N,S) porous carbons. The following samples were prepared: HTC, by hydrothermal carbonization of glucose; HTC-IL, by hydrothermal carbonization of glucose in the presence of [bmim][MeSO$_3$]; ITC, by ionothermal carbonization of glucose (i.e., carbonization of glucose dissolved in the ionic liquid under self-generated pressure); and Carb-IL by direct carbonization of the IL. Only Carb-IL contained nitrogen and sulphur (3.2 and 0.5 wt%, respectively, as determined by XPS). All four materials were found to be active for the ORR in alkaline medium, with onset potentials in the range 0.80–0.89 V, but Carb-IL was the best catalyst, with n_{O2} = 4.0 in the whole potential range investigated (0.5 to 0.2 V) [37].

3.1.2. Electrocatalysts for electrolysers

The high potentials of both the oxygen (OER) and hydrogen evolution (HER) reactions and the lack of stability of the electrode materials are the main hurdles to overcome, and research efforts are currently focused on the development of non-precious metal based electrocatalysts [30].

Promising catalytic activities for the Hydrogen Evolution Reaction (HER) were obtained with Mo_2C anchored on two different carbon supports, CNTs and a carbon xerogel (CXG) [38,39]. Table 2 summarizes some results obtained with these electrocatalysts for the HER in acid and alkaline media [38,39], where **b** (mV dec^{-1}) is the slope of the Tafel plot, J_0 (mA cm^{-2}) is the exchange current density, and η_{10} (mV) is the overpotential at 10 mA cm^{-2}.

The advantages and challenges of alkaline water electrolysis are discussed in a recent review [40].

3.2. Supercapacitors

Supercapacitors, or electrochemical double layer capacitors (EDLCs), are promising devices for clean and sustainable energy storage. The charge storage in such devices is based on the electrostatic adsorption of electrolyte ions on the electrode surface; therefore, the surface area is the primary factor influencing the electrode capacitance [41–43]. On the other hand, pore accessibility and conductivity are additional key factors to enable the storage of large amounts of energy and to achieve high operation rates. Thus, nanostructured carbons with hierarchical micro-mesoporosity are required for this application. In particular, it has been established that carbon electrodes should present

Table 2
Performance of different electrocatalysts for HER in acid and alkaline media (potentials vs RHE).
Data from references [38,39].

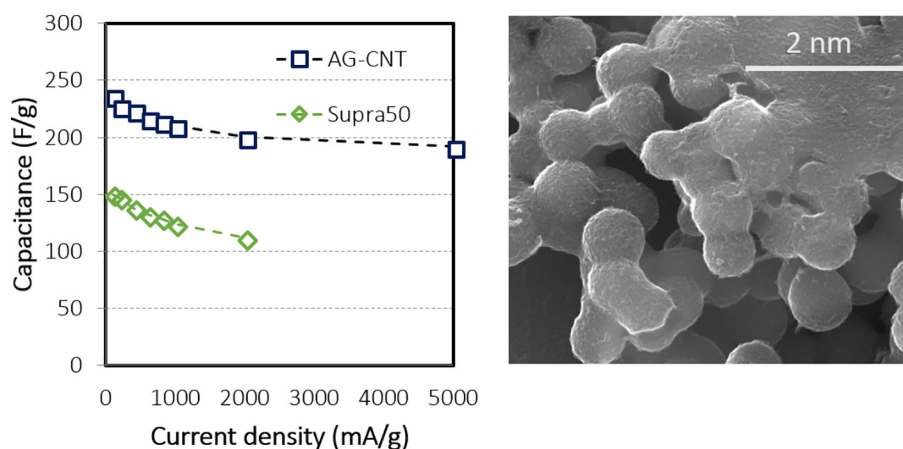| Electrocatalyst	Electrolyte	b (mV dec^{-1})	J_0 (mA cm^{-2})	η_{10} (mV)
Mo$_2$C/CNT [38]	0.1 M HClO$_4$	251	1.43	250
Mo$_2$C/CXG [38]	0.1 M HClO$_4$	264	1.69	170
Mo$_2$C/CNT [39]	8.0 M KOH	74	5.2×10^{-5}	280
Mo$_2$C/CXG [39]	8.0 M KOH	71	8.7×10^{-5}	304

Fig. 5. Electrochemical performance of an activated glucose-derived/CNT hybrid carbon gel (AG-CNT) at different current densities, and corresponding SEM micrograph. The performance of a commercial activated carbon (Norit Supra DCL 50) is included for comparison [48].

micropores of about 1 nm width (for ion storage), together with mesopores (for enhanced transport of ions) [43]. Besides electrostatic adsorption, the energy density of supercapacitors can be enhanced by promoting reversible faradaic reactions between the electrode surface and the electrolyte (pseudocapacitance) [41]. In this case, it has been shown that the surface chemistry of the electrode plays a major role, especially in acidic media [44]. Hybrid supercapacitors, combining electrostatic and electrochemical storage mechanisms as well as enhanced molecular diffusion, can be obtained by coating the non-porous conductive surface of graphene or CNTs with porous and/or redox active species [45]. On the other hand, the manufacture of such high-performance energy storage devices requires a deep understanding of the phenomena occurring at the surface of the electrodes during operation. Current research not only focuses on the development of novel carbon electrodes for EDLCs, but also on their thorough electrochemical characterization [45].

3.2.1. The effect of boron on supercapacitor performance

Boron-doped ordered mesoporous carbons were prepared with different amounts of boron by hydrothermal treatment (HT) at two temperatures (50 and 100 °C) and also at 50 °C without the HT [46]. The results of the electrochemical characterization of different series of samples by cyclic voltammetry and electrochemical impedance spectroscopy (EIS) led to the conclusion that substitutional boron (promoted by HT) enhances the conductivity of the electrodes. On the other hand, the boron-oxygen species attached to the carbon surface provided an important pseudocapacitive contribution. The best sample was evaluated as a supercapacitor electrode in a two-electrode cell, exhibiting a specific capacitance of $156 \, F \, g^{-1}$, whereas the undoped carbon only reached $115 \, F \, g^{-1}$. This was ascribed to the higher conductivity (B−C bonding) and wettability (surface groups enriched surface) of the former. Moreover, it compared well with a commercial activated carbon ($162 \, F \, g^{-1}$), in spite of its modest micropore volume. This was explained by the well-developed mesoporosity (enhancing diffusion) and by the occurrence of pseudocapacitive charge storage. Nevertheless, the prepared carbons showed poor cyclability, possibly as a result of the poor stability of the boron species [46].

3.2.2. Supercapacitor performance of activated glucose-derived carbon gels

Activated carbon gels with a cellular morphology, obtained from hydrothermal carbonization of glucose in the presence of GO and subsequent chemical activation, were tested as supercapacitor electrodes [47]. The effect of the chemical activation step (using KOH) on the nanometer-scale morphology, local structure, porous texture and surface chemistry of the resulting carbon materials was investigated and correlated with their electrochemical behaviour. The carbon gels

prepared with lower amounts of activating agent exhibit cellular structures with well-connected, continuous and very thin carbon walls, while higher amounts of KOH lead to broken and thicker walls. The electrochemical performance of the activated carbon gels was studied in a three-electrode cell using $1 \, M \, H_2SO_4$. The results underlined the relevant role of the cellular morphology, which favoured ionic diffusion and electronic conduction. The effect of the nanomorphology and local structure was also made apparent when the carbon gels were tested in a supercapacitor device. Particularly, a symmetric capacitor assembled from a carbon gel with very thin walls and relatively high graphitic character delivered a much higher specific capacitance than that of a commercial activated carbon (223 vs $153 \, F \, g^{-1}$, at $100 \, mA \, g^{-1}$), as well as exhibiting a significantly improved retention of capacitance at high current densities [47]. Similar results were obtained with an activated glucose-derived carbon prepared with CNTs instead of GO, as shown in Fig. 5 [48].

4. Conclusions and outlook

Carbon materials can be produced with a wide range of textures, structures, morphologies and surface chemistries, playing a decisive role towards the development of efficient and cost-effective electrochemical devices for energy conversion and storage. The textural and surface chemical properties of carbon materials can be modified in a controlled way, addressing the needs of the specific applications envisaged. Micro-mesoporous hierarchical carbons can be synthesized by sol-gel, soft-templating and hydrothermal routes. The hazardous compounds traditionally used in these syntheses can be advantageously replaced by carbohydrates and other biomass-derived precursors, with the assistance of nanocarbons such as GO and CNTs. These hierarchical carbons offer more favourable kinetic properties for application in electrochemical devices, when compared with the currently available activated carbons. Composites consisting of nanostructured carbons self-assembled with metal oxides or carbides have been developed as electrocatalysts for the HER. On the other hand, nitrogen-doped and sulphur-doped carbons have demonstrated excellent activities as electrocatalysts for the ORR. This is an extremely active field of research, driven by the need to replace platinum and other noble metals which are hindering the wide-scale implementation of the new energy paradigm based on hydrogen and renewable sources.

Declarations of interest

None.

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