Surface & Coatings Technology 350 (2018) 307–312

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Nanostructured porous carbons for electrochemical energy conversion and storage

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ARTICLE INFO

Keywords:
Nanostructured porous carbons
Textural properties
Surface chemistry
Energy
Electrocatalysts
Supercapacitors

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.

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https://doi.org/10.1016/j.surfcoat.2018.07.033
Received 30 April 2018; Received in revised form 15 June 2018; Accepted 9 July 2018

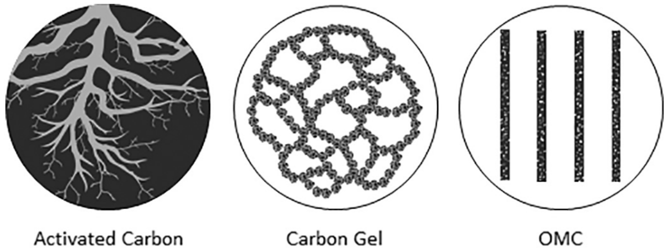

Fig. 1. Schematic representation of the hierarchical porous systems of an activated carbon, a carbon gel, and an ordered mesoporous carbon (OMC).

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.

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

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