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Engaging Nanoporous Carbons in "Beyond Adsorption" applications: Characterization, Challenges and Performance

Conchi O. Ania^{1*}, Phillip A. Armstrong², Teresa J. Bandosz^{3*}, Francois Beguin⁴, Ana P. Carvalho⁵, Alain Celzard⁶, Elzbieta Frackowiak⁴, Miguel A. Gilarranz⁷, Krisztina László⁸, Juan Matos⁹, M. Fernando R. Pereira¹⁰

¹CEMHTI (UPR 3079), CNRS, Université d'Orléans, 45071 Orléans, France.

²Morgan Advanced Materials, 310 Innovation Blvd., Suite 250, State College, PA 16803, USA.

³Department of Chemistry and Biochemistry, The City College of New York, 160 Convent Ave, New York, NY 10031, USA.

⁴Poznan University of Technology, Institute of Chemistry and Technical Electrochemistry, Berdychowo 4, 60-965 Poznan, Poland.

⁵Centro de Química Estrutural (CQE), Faculdade de Ciências, Universidade de Lisboa, Centro de Química Estrutural – Polo Ciências 1749-016 Lisboa, Portugal

⁶Université de Lorraine, CNRS, IJL, 88000 Épinal, France.

⁷Department of Chemical Engineering, University Autónoma de Madrid, 28049 Madrid, Spain.

⁸Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics, 1521 Budapest, Hungary.

⁹Instituto de Ciencias Químicas Aplicadas, Facultad de Ingeniería, Universidad Autónoma de Chile, 8900000 Santiago, Chile

¹⁰Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE-LCM), Faculdade de Engenharia, Universidade do Porto, 4200-465 Porto

ABSTRACT

This paper addresses the challenges of explaining the behavior of porous carbons in cutting-edge applications related to energy storage, catalysis, photocatalysis, and advanced separation based on reactive adsorption. It is a summary of the outcomes of the extensive discussion which took place during the workshop "Beyond Adsorption-II: new perspectives and challenges for nanoporous carbons," organized as a satellite event to the International Carbon Conference on July 20th 2019 in New York. It is not our intention to provide a tutorial on the applications, characterization or performance testing of porous carbons; we would rather like to focus on the controversy of the results and phenomena, on the explanation of findings, and on raising concerns to the growing carbon-researching scientific community about the importance of understanding the features of nanoporous carbons by choosing an appropriate characterization

technique that will bring meaningful information. We want to emphasize that nanoporous carbons have unique features ensuring them making a marked advance in science and technology. Even though recent studies have shown their potential in various emerging applications, the origin of such performance is not yet well understood. Thus, scientists are encouraged to focus on a precise characterization of porous carbons using a set of complementary techniques for triggering future technological developments.

Keywords: Nanoporous carbons; characterization; energy storage; catalysis; surface chemistry; defects

1. INTRODUCTION

Porous carbons are some of the oldest materials known to human beings. Even though one can say that chars, predecessors of porous carbon, have a much longer history of applications dated from BC times (inks in cave paintings, metal age, Chinese ink, water purification), their important feature is also porosity, although not developed sufficiently. The activation of char with steam, CO₂ or inorganic salts leading to the development of large pore volume was first proposed by engineer and entrepreneur R. Ostrejko at the beginning of 20th century [1]. That invention had monumental consequences affecting humanity, starting from saving lives of numerous soldiers exposed to chemical attacks during WWI (gas masks) [2] and continuing to the recent developments of new energy storage media [3,4], sensors [5] and superlight construction composites [6]. By 2016 the estimated world consumption of porous carbons was about 1.8 Mt [7], with 55% of the share in USA, Japan and the EU together.

Traditionally, porous carbons have been applied as adsorbents for liquid and gas purification processes (currently accounting for over 99% of the share of the world market applications [7]). This is the natural consequence of their high surface area and pore volume. Taking into account also the relatively low cost of their large-scale production, up to now and even in the era of the boom in new materials development, they have no competitors with regards to their adsorption capacity, especially for organic compounds. Their selectivity is another issue which needs to be addressed by chemical modification of their surface [8].

During a vast portion of the last century, activated carbons were the only recognized porous and amorphous allotropes of carbon. They were obtained by physical (steam, CO₂) activation of char or by chemical activation of carbon-rich precursors such as wood or mesophase pitch [9]. Along with graphite, they were considered as very important members of the carbon family, and scientifically deep insights, presenting the state of the art at that time, were published in the popular series "Chemistry and Physics of Carbon," which consisted of 31 volumes. In these books such aspects as porosity development [10], porosity characterization [11] and modeling [12], adsorption in the pore structure [13], and carbon chemistry [14] were discussed in detail. These aspects have been also discussed in many other recent books. Examples are those by Marsh and Rodriguez-Reinoso [9], Serp and Figueiredo [15] and by White [16]. It is important to mention that many features of porous carbon addressed at the time of the "Chemistry and Physics of Carbon" publication are still valid for most of the materials from the carbon family, even though recent years show reinvention of well-established modification techniques, especially those addressing surface chemistry.

That "reinvention" was the consequence of the discovery of carbon nanotubes and graphene and the further explorations of the derivatives of the latter (e.g., graphene oxide and reduced graphene oxide). Especially graphene, and the fact that originally it was the subject of the extensive studies by physicists, changed the destiny of porous carbons. Owing to its unique properties, such as a high electrical and thermal conductivity, graphene started to be applied as a component of mechanical or electronic devices including in the sensing and energy storage fields. Soon thereafter it was discovered that, in fact, for numerous applications of graphene there is a need for chemical modifications of its surface. A few examples include the need to increase the selectivity via specific gas/solid interactions [17], the development of porosity (in supercapacitors [18]) and the generation of defects (as catalysts for oxygen reduction reaction, ORR [19]). And this is exactly the point where a return to the "roots" of amorphous and porous carbons' "history of surface characterization" would have been beneficial.

Nevertheless, the failure of defect-free single- and few-layer graphene sheets in such applications was the motivation for carbon scientists to look at porous carbons from a new perspective and take a position "beyond adsorption." Very helpful in this aspect was also the development of high-resolution microscopy which showed that the pores of amorphous carbons are built of disordered and highly defective graphene layers [20]. And this has opened new perspectives for the old, black porous carbons, which might be considered as "*poor-person's graphene*" and have become the "ugly duckling" of the carbon family.

The great advantages of porous carbons are their porosity and surface chemistry, which can be tuned/tailored to a certain extent to fulfill the requirements of a specific application. The combination of both, along with some level of conductivity, results in a very powerful "tool" that is unique only to this kind of material. Even with this great benefit, porous carbons are often relegated to a second plane and considered as "*second class*" cousins of graphene due to the "underestimation" and lack of full understanding of their surface complexity and function. Some scientific high-impact-factor journals openly do not accept papers on porous carbons considering them as "too narrow in scope", which is also likely related to lack of the "buzzword" of "*graphene*."

In fact, it should be quite the opposite: working with porous carbons and fully employing the complexity of a coexisting confined 3D nanospace and tailored chemistry to explain scientific phenomena/behavior is a much greater challenge than that encountered while working on 2D or 1D materials. What is really needed to improve the flow of scientific findings is some level of consensus in the interpretation and understanding of the complex data collected in the studies focused on the characterization and application of porous carbons. These data often differ from those obtained from studies of other less complex materials and in some cases a direct parallelism should not have been even sought or requested (as by reviewers not fully comprehending the complexity of the porous carbons' surfaces and behavior). Further, the complexity of carbons as the target materials of scientific proposals of high research level and impact should not be considered a weak point; complexity is something that many carbon researchers experience quite often during their career, particularly when researchers of other disciplines intensify their investigations of the capabilities of porous carbons in new fields of application.

The challenges of explaining the behavior of porous carbons in cutting-edge applications related to energy storage, catalysis, photocatalysis, and advanced separation based on reactive

adsorption were extensively discussed during the workshop "Beyond Adsorption-II: new perspectives and challenges for nanoporous carbons," organized as a satellite event to the International Carbon Conference on July 20th 2019 in the City College of New York (New York, NY). It is not our intention to provide a tutorial on the applications, characterization or performance testing of porous carbons; in this paper, we would rather like to focus on the controversy of the results and phenomena, on the explanation of findings, and on raising concerns to the growing carbon-researching scientific community about the importance of understanding the features of nanoporous carbons by choosing an appropriate characterization technique, a technique which will bring meaningful information that can be compared to the results of other researchers working on a similar challenge. The outcomes of the discussion of the workshop in New York are presented below as replies to specific research questions containing suggestions rather than detailed explanations and recommendations. Addressing these problems in depth is a necessary task that we leave to those who would like to take the challenge.

2. DISCUSSION OUTCOMES

2.1. The role of the active surface: Is the surface we characterize the one actually used in the target/performance experiments?

In any application of porous carbons, the detailed evaluation of their porosity is a must. Recent advances in experimental techniques and modeling suggest such gases as argon and nitrogen [21], oxygen [22], hydrogen [23] or even CO₂ [24] to be used as probes defining both the extent of the carbon surface and also a pore volume(s) and pore size distribution. It has become a widespread habit within the scientific community to report the pore size distribution (PSD) of materials (unfortunately, this is not exclusive for porous carbons) instead of the experimental gas adsorption isotherms (the only real experiment). Surprisingly, more and more often the reviewers (allegedly experts on the topic) demand to shift these isotherms to the supplementary material, to limit the discussion to PSD. For those trained in gas adsorption, the strategy should be quite opposite, as the determination of the PSD is not straightforward; in fact, an erroneous application of the available methods might result in important errors often unnoticed by the researcher. Even though advanced non-local density functional theory (NLDFT) [25] and/or quenched-solid density functional theory (QSDFT) [26] models are readily available, still some papers report pore size distributions calculated using classic approaches such as Horwath-Kawazoe and BJH. The former leads, unfortunately in almost every case, to a predominant size of micropores of 0.5 nm. Another common mistake is the application of the BJH approach to the desorption branch of the isotherm, which, in the case of an isotherm with a well-pronounced hysteresis loop and a low number of points recorded in a desorption branch, may lead to an artificial peak on the PSD suggesting some kind of "homogeneity" of the mesopore sizes, a feature which very often does not exist in the specific carbon studied.

The application of CO₂ to determine the narrow microporosity of carbons should be also approached with caution. While gases such as N₂, O₂ or H₂ are not supposed to react with the carbon surface at the measurement conditions (very low temperature), CO₂ adsorption is measured at temperatures close to ambient (ca. 0 °C). Recent studies on CO₂ sequestration have addressed the method of enhancing CO₂ adsorption on carbons through the introduction of basic or even polar oxygen groups, which provide specific or even chemical interactions [27]. This suggests that the surface groups existing on the carbon material (often not determined before the measurement) might affect the amount of CO₂ adsorbed, and thus lead to an overestimation in

the pore volume and erroneous PSD [28]. Therefore, CO₂ as a probe of carbon porosity, even though it has certain advantages related to its accessibility to ultramicropores, should be used with caution when carbons of rich surface chemistry are studied.

Rich surface chemistry of carbon brings another concern related to the determination of porosity. For this, outgassing to high vacuum is very important and, unfortunately, it is often done at 350 °C. One should be aware that the carbon surface groups, such as carboxylic or sulfonic groups, start to decompose at much lower temperature (~ 200 °C) [8], and applying 350 °C and (high) vacuum will certainly lead to their removal. Thus, the porosity measured will not represent the actual porosity of the carbon, particularly for its application at ambient conditions. A few examples are illustrated in references [28] and [29], showing the impact of the outgassing at temperatures between 25-350 °C on the determination of the pore volumes, surface areas (errors of up to 35 % are estimated) and on the adsorption capacity from solution. The PSDs calculated for functional group-rich carbons (Figure 1), and the retention of a pollutant (e.g., phenol) sensitive to the surface chemistry of porous carbon (Figure 2) can be markedly affected. Regrettably, the outgassing conditions are often omitted from the publications. Therefore, it is important to analyze the carbon surface as close as possible to the conditions of the target application, particularly when there is a risk of its partial thermal degradation. For such, an outgassing temperature sufficient to remove the adsorbed water (ca. 120 °C) is recommended.

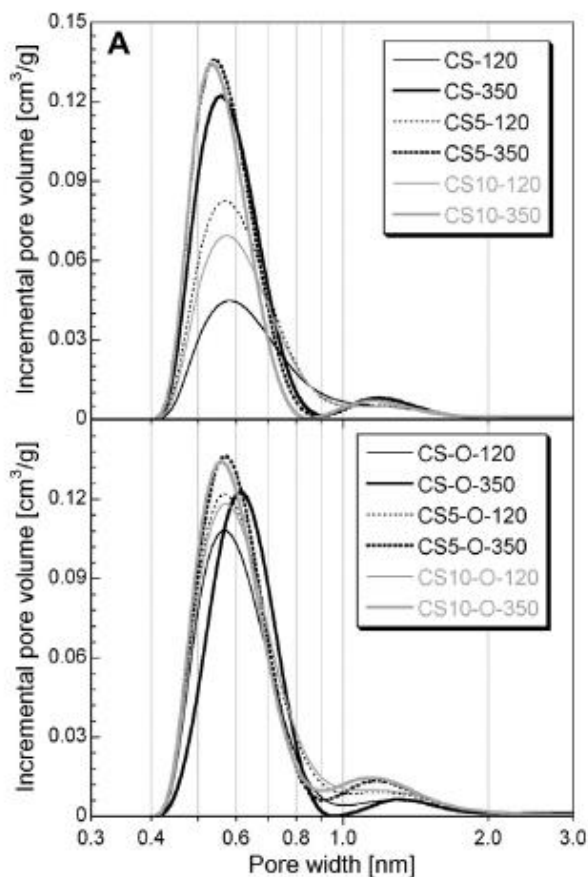


Figure 1. Pore size distributions calculated from N₂ adsorption isotherms for a series of carbons outgassed at 120 and 350 °C (numbers in the labels of the samples represent the outgassing temperature). Adapted with permission from ref. [28]. Copyright 2014, Elsevier.

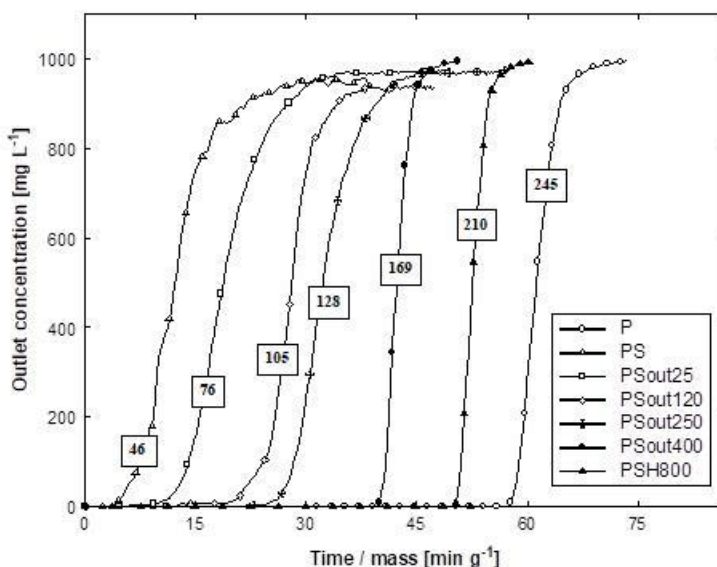


Figure 2. Phenol breakthrough curves on a series of hydrophilic nanoporous carbons (series PS) outgassed at different temperatures (represented by “outT” in the labels of the samples, where T is the outgassing temperature). The corresponding hydrophobic carbons (samples P and PSH — PS thermally treated at 800 °C to remove the surface groups— are included for comparison). Boxes indicate phenol uptake in terms of mg adsorbed per gram of adsorbent [mg g⁻¹]. Reprinted with permission from ref [29]. Copyright 2010, Elsevier.

Differences between the measured surface features and those existing in the carbon material when it is used for a target application apply also to surface chemistry. Nowadays, the most common and often required technique to evaluate carbon surface chemistry is XPS. In this technique, a dry carbon surface is exposed to high vacuum before being measured. Therefore, groups seen on the surface might be markedly different from those present when the carbons are used, for instance, in aqueous phase where protonation and dissociation certainly take place. In such cases, characterization approaches in solution (e.g., titration, electrochemical) are more reliable and provide a complementary view. In addition, those who use XPS to analyze carbon surfaces often experience difficulties in interpretation complexity upon collecting the results and in finding more questions needing to be answered than existed before collecting XPS data. One important observation is that in many cases, the deconvolutions of the core energy level spectra depend on the “deconvoluter”..., and also on the surface features he/she “wishes” to see. These quite common approaches make it very difficult to compare the results or interpretation from different laboratories. So far, in many published works, the deconvolutions are made using the best fit accommodating many contributions and even ignoring C 1s peak asymmetry or chemical/physical principles such as doublets; the often-encountered examples are the studies reporting the wrong deconvolution of S 2p core energy level spectra (and many others). In this respect some more rigorous rules of data analysis are needed, as for instance imposing the same

FWHM, or specific differences in the peaks positions (not too close to each other), and reporting the goodness of the fit.

The last, but not least, aspect of carbon surface characterization is a troublesome reporting of surface area calculated by the BET method with up to 4 or even 5 digits after the decimal point. Unfortunately, it is even more common in high impact factor journals (general audience/general reviewers) than in those focused on an adsorption discipline. For some reason, researchers do not always understand the accuracy of "calculating BET" and even using this term as an equivalent of an isotherm measurement indicates little or no understanding of the basis of this characterization method. No digits after decimal point should be reported. Again, reporting the experimental adsorption isotherms provides more information about the porosity of the carbon (including its surface area) than reporting the BET value without a critical eye.

2.2. Can defects be considered as "natural" features of the nanoporous carbons' surfaces?

It was in the late 1980s that the previously overlooked importance of the surface chemistry of carbon materials was first considered in depth. Since then, particularly for its role in emerging applications, e.g., as catalysts, including electro- and photocatalysts, sensors, energy and gas storage devices, drug delivery vehicles, etc., the significance of the various physical and chemical defects became the focus of intense research. Vacancies in the graphitic regions as well as the unsaturated carbon atoms and unpaired electrons at the edges represent defects, i.e., different energy states, even in the absence of non-carbon atoms. Oxygen, nitrogen, sulfur, to mention only the most frequently incorporated heteroatoms to carbon, introduce further heterogeneities owing to their different physical and chemical properties, e.g., size and number of electrons, thus modulating the electronic properties of the carbon materials. The effects depend on the species, topology, chemical form, concentration, and distribution of the defects. The chemical environment generated by these heteroatoms is different. While O decorates the edges of the graphitic layers, N and S are also able to substitute the carbon atom within the graphene-like sheet [30-32]. In spite of the continuous development and expanding variety of characterization techniques, revealing the influence of these defects on the performance of the carbon materials is not a straightforward task. The contribution of 1D and 2D carbon structures to this field cannot be neglected here, as they made it possible to separate experimentally the influence of the pore confinement from the effect of the defects.

There is no method which could provide a full picture about the overall features of the defects. For some reason, the use of electron spin resonance (ESR) spectroscopy and the widening varieties of solid-state NMR techniques is still limited [33,34]. Interestingly, although several of the traditional and emerging applications of carbon materials take place in a liquid medium, the characterization of the surface chemistry is performed mainly in vacuum or gas phase-related methods, like XPS, FTIR or Raman spectroscopy. Extension of the general characterization to the application conditions including the medium is often neglected. Most of the cutting-edge methods give only local information, probing only about a few nm² of the material. Surface analytical methods, such as XPS, provide information only about the upper few nm of the theoretically flat sample. Other methods have a deeper information depth (FTIR), though gathering quantitative information is very difficult. The challenges of two of the most frequently

used methods addressing defects in a broad sense of this word, Raman scattering and XPS, are discussed below in detail.

Raman scattering is a powerful technique for detecting defects in carbon structures, and this is the reason why it has become so popular. It nevertheless suffers from disadvantages which are serious enough to deserve mention here, and which justify further studies. Worse, poor applications of its use can lead to erroneous or misinterpreted results, frequently encountered in the literature. First, nanoporous carbons have, by definition, a low density, and are often analyzed as fine powders; therefore, there is very little material in the laser beam. It is then tempting to increase the power of the laser to increase the signal-to-noise ratio, often low, while these materials are also thermally insulating, so that they heat up a lot and then either degrade or are modified under the beam. Spectra obtained with a power greater than 2 mW with a green laser are then generally unreliable. It must also be verified that the obtained spectra are reproducible, because a natural heterogeneity of the samples can never be ruled out. Ignoring this point could lead to accepting and discussing spectra that do not correspond to the reality of the materials as a whole. This practice is unfortunately almost impossible to detect in scientific manuscripts (perhaps open access policies to research would correct this?).

When the appropriate experimental conditions of acquisition are used, which is a practice that, in itself, deserves a monograph of good practices, the spectra of nanoporous carbons are still difficult to interpret. Indeed, most often the spectra appear very similar from one material to another, regardless of the material synthesis conditions and precursors. In particular, it is hardly possible to compare directly spectra of materials obtained under markedly different conditions. It has indeed been demonstrated that, for example, under visible light the position of the G band may remain unmodified for carbons with different nanotextures (in terms of percentage of sp^3 carbons in the sp^2 network) or different nitrogen levels [35,36]. It is therefore wiser under these conditions to study the evolution of the spectra in a series of materials for which only one parameter has been varied at a time (e.g. pyrolysis temperature, heteroatom level, particular post-treatment) and to observe the widening of the bands rather than their position and intensity ratio.

In this regard, the significant fraction of defects in nanoporous carbons leads to such broadening of the bands that they overlap very widely. It is therefore difficult to try to draw firm conclusions from the D/G intensity ratios obtained on the first order of the spectrum, these intensities being only apparent since they are the result of contributions from 4 to 5 individual bands, depending on the deconvolution method proposed by the authors. The first order of the Raman spectra of nanoporous carbons is better represented by Sadezky's 5-band model [37], as shown in Figure 3, which corresponds to a material obtained by pyrolysis of a phenolic resin at 900 °C. While the overall profile of the spectrum suggests *a priori* that D and G intensities are similar, the deconvolution indicates that the D1/G ratio measured from the bands centered on 1355 and 1588 cm^{-1} , respectively, is in fact much greater than 1.

The result of the deconvolution of the overall Raman profile is often not unique and it is a major problem in the interpretation of the Raman spectra. It indeed strongly depends on the Lorentzian or Gaussian functions (or combination of both in various proportions) used to describe the profile of the individual contributions. As a result, excellent fits of the first order as a whole can most often be obtained for different combinations of band positions and widths; this is even more problematic when the signal/noise ratio of the spectrum is low. From there, any discussion of the variations of the D1/G intensity ratios can be wrong, including the general trends themselves.

Many authors often forget that nanoporous carbons are not graphitizable, and correspond to stage 2 of the amorphization trajectory of carbons [35,36], for which the D1/G ratio is proportional to the square of the size of the coherent domains along the aromatic layers (i.e., L_a^2). In other words, the higher is the D1/G ratio, the smaller are the domains, and therefore the more disordered is the nanotexture. An opposite conclusion would be obtained with graphitizable carbons, for which the D1/G ratio is proportional to $1/L_a$.

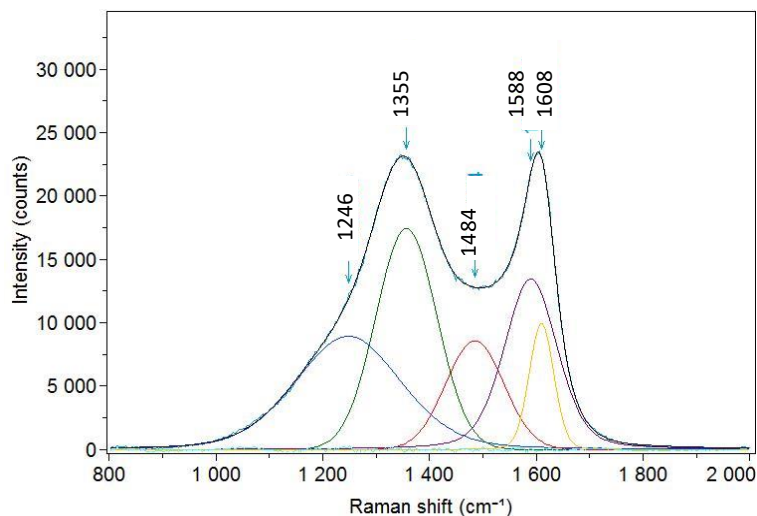


Figure 3. First-order spectrum of a nanoporous carbon derived from a tannin-based resin pyrolyzed at 900 °C, obtained with a laser of wavelength 532 nm and power of 1.8 mW.

In general, it therefore seems safer in the state of current knowledge to refer to the width of the bands, which is the most significant in terms of concentration of defects. A discussion on the evolution of the positions of the bands is also possible, but risks leading to misinterpretations if one does not have a full collection of spectra acquired at several wavelengths (i.e., not only under visible light but also under UV) [36]. The first order and the second order give information on the structural order perpendicular to the c-axis, and on the stacking order along the c-axis, respectively [38]. Thus, if one only deals with the first order, the G band (centered at about 1580 cm^{-1} with a green laser) is broader if there are more structural defects in the sp^2 network, i.e., if the material is less graphitic. The D1 (around 1350 cm^{-1} with the same laser) corresponds to the in-plane defects and widens if L_a decreases, whereas the D3 (around 1500 cm^{-1}) corresponds to the out-of-plane defects and widens if the number of sp^3 atoms in the sp^2 network increases. The D4 band is also usually present in nanoporous carbons and is at the origin of a shoulder centered at about 1200 cm^{-1} . Its origin is not clearly established but there is consensus that it is linked to the presence of disorder and impurities in the sp^2 network. Finally, the D2 (around 1610 cm^{-1}) can serve as an indicator of the surface-to-volume ratio of crystallites. However, all these considerations are futile if doubts remain about the way to deconvolute the Raman spectra, on which work of rationalization remains to be done.

Regarding the role of heteroatoms as a source of defects in the carbon structure, it is very important to say that their presence non-trivially influences the relative proportions of carbon atoms in sp^2 and sp^3 configurations. This is particularly the case of O and N, and therefore it is

not recommended to try to determine such proportions by comparison with spectra of model materials progressively enriched in one heteroatom or the other. It then seems much preferable to quantify these defects by XPS studies, or even by FTIR provided that the number of surface functionalities is sufficient, which might be the case when the surface area is high enough.

Defects and disorder in carbon materials have been suggested to play a pivotal role in several adsorption and reaction processes, with a particular emphasis, in recent years, on ORR. Their identification and quantification are still significant challenges to elucidate the involved catalytic mechanisms [39]. Among the different analytical tools available to quantify the type and number of defects, Raman spectroscopy is the most used due to its non-invasive nature and simplicity [40], as was discussed in detail above.

Active Surface Area (ASA) and X-Ray Photoelectron Spectroscopy (XPS) are alternative techniques that can present some advantages, but are seldom used in this context. The concept of ASA was originally proposed by Walker and co-workers [41]. Briefly, starting from a sample with a clean carbon surface (previously outgassed at high temperature, usually 950 °C), oxygen is then chemisorbed in conditions such that gasification can be neglected (generally at 300 °C) leading to the formation of surface oxygen complexes. The amount of chemisorbed oxygen is subsequently measured by TPD-MS. ASA is then calculated considering the amounts of CO and CO₂ released in TPD (usually between 300 and 950 °C) and the area of an edge carbon site where one atom of oxygen is adsorbed [42]. ASA has the advantage of being a chemical method that directly measures the number of accessible defects on the carbon surface. A direct relationship between the number of defects determined by ASA and Raman spectroscopy has been established [43,44], and a good correlation between ASA and the capacitance of carbon materials was observed [45,46]. However, it should be pointed out that this method should not be applied to soft carbons (e.g., biomass-derived) where the outgassing treatment at 950 °C may provoke the collapse of the porosity.

Estrade-Szwarczkopf [47] was the first to report that the C 1s line shape broadening of the XPS spectrum, with a peak centered at 285.2 eV, is due to the presence of defects and that broadening is in direct proportion to their concentration. Since then, several authors have been using XPS to quantify the number of defects in carbon materials. Recently, Ganesan et al. [48] investigated defect concentration on nanographitic structures by Raman and XPS. Although a good correlation in estimating defect density was obtained between the two techniques, the authors concluded that the estimation of surface defects on the carbon materials studied was more accurate when done using the XPS analysis. Relative to XPS, Raman spectroscopy probes very deeply inside carbon materials and shows saturation in estimating defects due to the contribution of the structurally intact deeper layers. Nevertheless, the use of XPS to determine the number of defects is still not very popular, and further studies are needed. XPS has the additional advantage of allowing the simultaneous quantification of the heteroatoms and their bonding environment in carbon materials.

The main challenge is the quantification of the different types of defects on the carbon surface, since only part of them can be active for a specific reaction. For example, for the ORR, DFT simulations have shown that the armchair edges are inactive, contrary to the zigzag edges which were shown to be active, in both cases with or without the presence of O-containing species [49,50].

Although the intense, and increasingly concerted, experimental and computational investigations into defect-performance relationships have led to great advances, there still remain several challenges to tackle. Despite approaching these properties using multiple-technique characterization, particularly in the case of 1D and 2D carbon materials, the control of the type, concentration, distribution and location of the defects during the synthesis still constitutes a major hurdle. This may call for new, more controllable synthesis strategies, preferentially up-scalable. The formation of new edge sites or the introduction of vacancies, heteroatoms, etc., may result in further collateral changes, such as to the hydrophilic/hydrophobic properties or morphology (surface area or pore size distribution), thus preventing a clear recognition of the consequence of the intended modification. The role of nitrogen incorporation is still debatable. In the oxygen reduction reaction (ORR), for instance, it is still not convincingly clarified whether all the N-functionalities have a benevolent influence, or only pyridinic and/or graphitic ones are effective [51,52].

In highly porous systems, what is the combined outcome of confinement and defects in electrocatalysis, energy storage or photocatalytic applications? At this moment only a limited number of thorough pioneering studies exist on carbon materials with deliberately combined dopants [52-54]. The probability and consequence of possible interactions is therefore still to be discovered.

2.3. What are carbon requirements for metal-ion batteries?

A lithium-ion battery (LIB) in its early version developed by Sony in 1991 combines a low-temperature carbon [55] as an anodic material and LiCoO_2 as a cathodic material. Later, graphite, owing to its staging effect at potential ca. 0.1 V vs. Li^+/Li , has been adopted as an anode host, enabling the battery to be charged at voltage ca. 3.7 V. Before battery operation, lithium must be transferred from the cathodic material (LiCoO_2 in the first versions) to be intercalated/inserted into the carbonaceous substrate. During this step, a part of lithium from LiCoO_2 is firstly irreversibly consumed to form a solid electrolyte interphase (S.E.I.) at potential ca. 0.8 V vs Li^+/Li , and then lithium is reversibly intercalated/inserted at a lower potential. In the case of graphite, the reversible capacity reaches theoretically 372 mAh g^{-1} , which corresponds to the first stage graphite intercalation compound LiC_6 . The very low specific surface area of graphite results in a low irreversible capacity and consequently in a low amount of additional LiCoO_2 needed to form the S.E.I.

Considering the great success of the LIB, and subsequent market pressure to enhance its specific energy for applications e.g., to electric vehicles, as well as to develop alternative technologies of lower cost, as for example the sodium ion battery (NIB), intensive efforts have been devoted for approximately 25 years to enhance the capacity of electrode materials. As far as the anode of metal-ion batteries is concerned, various carbons have been investigated including, among others, hard and soft carbons, carbon nanotubes, graphene, Hundreds/thousands of papers claim outstanding, excellent (with many other such enthusiastic adjectives) properties, while ignoring totally the main scientific/technical requirements that carbons should display to be applicable as active anodic materials in a secondary battery. They are: a high reversible capacity at low potential (to ensure a high voltage of the battery), a high first cycle coulombic efficiency (i.e., low irreversible capacity) to reduce the amount of cathodic material from which lithium is

irreversibly extracted to form the S.E.I. with creation of a residual dead mass, and a long cycle life (i.e., high coulombic efficiency during the next cycles).

Unfortunately, many authors/papers do not take into consideration the above listed requirements, and make claims about good anodic properties of carbons based only on the reversible capacity, while ignoring the first cycle coulombic efficiency and the amplitude of potential increase during the oxidation step. First cycle reversible capacity values comparable to graphite, or even higher, can be easily found in the literature for porous carbons [56-58], with “record” values as high as ca. 1000 to 1250 mAh g⁻¹ [59-62]. However, as these materials display a very high specific surface area (S_{BET} up to 2400 m² g⁻¹), the first cycle irreversible capacity reaches very high values ranging from ca. 900 mAh g⁻¹ up to even 2590 mAh g⁻¹ [56]. This means that, when applied in a full cell, a huge amount of cathodic material should be consumed to form the S.E.I., causing an enormous dead mass in the battery. Moreover, as the S.E.I. development is favored by the active sites on the carbon surface, it still develops in the next cycles, and the reversible capacity progressively decreases upon cycling. Another well-illustrated feature in all the above-mentioned references is the steep potential increase during lithium deinsertion (which would correspond to the discharge of a Li-ion cell where such a material would be used as anode) from the electrode. The voltage of the cell would continuously and rapidly decrease from e.g., 3.7 V to 0.7 V: hence, such a cell would be a poor battery.

Other non-adequate materials for secondary battery anodes are carbon nanotubes (SWCNTs and MWCNTs) and graphene. Figure 4a shows for example the galvanostatic characteristics of a half-cell with a MWCNTs working electrode and a lithium counter/reference electrode [63]. The reversible capacity reaches 447 mAh g⁻¹, which is effectively much higher than the theoretical capacity of graphite. More impressive values of reversible capacity (up to 1830 mAh g⁻¹) are even claimed in the literature for carbon nanotubes and graphene processed in specific conditions [64,65]. However, the potential of the oxidation branch, which represents the discharge of such an anode in a LIB, shifts continuously from 0 to 3 V (Figure 4a). In addition, in Figure 4a, the irreversible capacity is at the level of 505 mAh g⁻¹ and increases with cycling. The first cycle irreversible capacity even reaches higher values of 657 mAh g⁻¹ for graphene/SWCNTs composites [66], 700 mAh g⁻¹ for ball-milled SWCNTs [64], 1000 mAh g⁻¹ for graphene/MWCNTs hybrid materials [67], and 3030 mAh g⁻¹ for so-called porous graphene [65]. In the case of carbon nanotube electrodes, it has been demonstrated that the irreversible capacity increases linearly with the mesopore volume (the mesopores are formed by the entanglement of nanotubes) [68].

Hence, when making claims about a carbon for metal-ion batteries, it is not sufficient to focus only on the reversible capacity value. First, the claimed capacity should be delivered at a low potential as close as possible to 0 V vs M⁺/M, and be constant during cycling. Second, the irreversible capacity should be very low. Such criteria cannot be fulfilled by high surface area materials (> 10 m² g⁻¹) which contain a high number of active sites for electrolyte decomposition (S.E.I. formation); indeed, for graphite samples ball-milled in various conditions, a proportional dependence of irreversible capacity on active surface area value has been demonstrated (Figure 4b) [69]. Hence, provided that carbon electrodes can be charged/discharged at a low potential vs M⁺/M, appropriate anodic materials for metal-ion batteries should be searched among low specific surface area carbons (<10 m² g⁻¹) with a small amount of active sites. In that

sense, coating of the active material with pyrolytic carbon is an appropriate strategy to reduce both the active surface area and S.E.I. development (Figure 4b) [69].

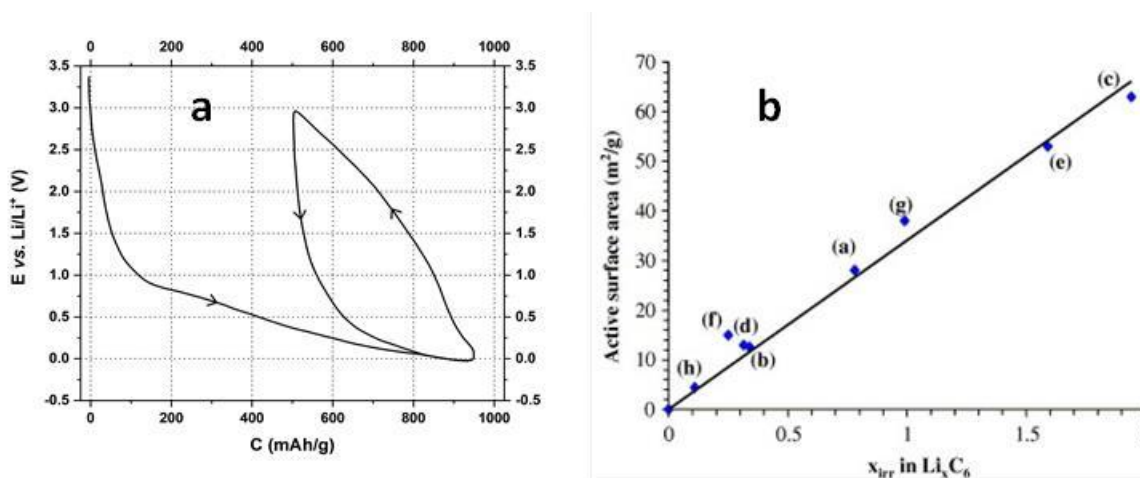


Figure 4. (a) Galvanostatic charge/discharge of a MWCNTs electrode vs Li counter/reference electrode in $1 \text{ mol L}^{-1} \text{ LiPF}_6$ in EC/DEC; adapted from [63]; (b) Relation between the active surface area and the irreversible capacity x_{irr} of graphite samples ball-milled in various conditions, or ball-milled and subsequently coated by pyrolytic carbon: (a) 10 h in vacuum; (b) 10 h in vacuum + pyrolytic carbon deposition; (c) 10 h under H_2 ; (d) 10 h under H_2 + pyrolytic carbon deposition; (e) 10 h under O_2 ; (f) 10 h under O_2 + pyrolytic carbon deposition; (g) 20 h in vacuum; (h) 20 h in vacuum + pyrolytic carbon deposition. Reprinted with permission from ref [69]. Copyright 2005, Elsevier.

Besides, it is necessary to point out that an important component, also of a carbonaceous type, is a conductivity percolator introduced in a small amount to the electrode formulation. The most commonly used is carbon black. Carbon nanotubes and graphene can be also beneficial for this purpose. Yet, still the influence of their surface area/mesopore volume should be kept in mind as a possible detrimental factor; therefore, these additives should be introduced at a low level, generally below 5 wt.%.

2.4. What are carbon requirements for electrochemical capacitors?

Nanoporous carbons with high surface areas are the key components of electrochemical capacitors (ECs), often called supercapacitors or electrical double-layer capacitors (EDLCs) [70]. These devices present high power storage of moderate specific energy, and commercially available ones are commonly based on charging an electrical double-layer in the porosity of a high surface area carbon material (generally activated carbon). Why porous carbons? Because they are generally inexpensive (especially activated carbons), display a high conductivity (good for the power of ECs), an adaptable porosity and may be found under various morphologies (powders, fibers, films, nanotubes, graphene, ...).

As the charges are stored electrostatically, contrary to a battery where redox reactions are involved, ECs are fast energy storage systems characterized by a low time constant. The negative counterpart of this charge storage mechanism, which involves the surface of the electrode

material, is the low specific energy of the system. Consequently, most of the research work is dedicated to enhance the specific energy of traditional EDLCs and also to design new concepts of ECs based on the use of porous carbons.

The energy stored in ECs depends on two factors: the capacitance of the cell C and the voltage U ($E = \frac{1}{2} CU^2$). The main factor controlling the capacitance of an electrode is its specific surface area ($C = \epsilon S/d$, where ϵ is electrolyte dielectric constant, S surface area of the electrode/electrolyte interface, d the distance between ions and the electrode surface), which is generally measured by nitrogen adsorption/desorption at -196 °C. The general trend is an increase of capacitance with the specific surface area, yet without any proportionality dependence. As far as gas adsorption data have been manipulated to tentatively establish correlations, it is necessary to mention the increase of normalized capacitance when the average pore size of carbon decreases [71,72] and the puzzling use which is made of this property. Indeed, it is often traduced in the fact that capacitance is higher in carbons having pores around 0.7 nm, which is not necessarily accurate, in particular when the porosity of the electrode becomes saturated with ions at high voltage [73,74]. On the contrary, increasing the surface area of the carbon material without any control of the pore size is not a good strategy, because the density of the material is generally lowered, which leads to low values of volumetric capacitance (thus low values of volumetric energy). There are abundant examples in the literature of this, particularly those reporting the use of the so-called hierarchical carbons featuring a lot of mesopores.

Another important issue that is necessary to mention is the mismatch between the most frequent practice of scientists for reporting data (essentially referring data to the mass of materials, e.g., specific capacitance, energy and power) and industrial interests, mainly centered in volumetric parameters, because the common objective is to reduce the size of the devices. The consequence of this is that, while plenty of publications report about “fantastic” values in gravimetric basis, most of the materials would be completely useless materials in practice, due to their low density. One of the best examples in this category is graphene; therefore, only attempts trying to use the advantages of graphene while aiming to enhance its density are of interest; an interesting development of such strategy is given in [75].

The second parameter controlling the energy is the voltage, which depends on the stability window of the electrolyte in the presence of the porous carbon electrodes. For this reason, organic electrolytes are generally preferred, enabling achievement of voltages up to 2.7-2.85 V with activated carbons. The stability window is strongly influenced by the surface functionalities of the carbons (i.e., active sites such as oxygenated functionalities, free electrons and free edges sites, also called dangling bonds) [76], since they are able to trigger decomposition reactions of most organic electrolytes. Therefore, for EC applications, a specific post-treatment of the carbon materials is necessary to reduce the concentration of active sites. In this regard, the operating voltage in organic electrolytes has been recently noticeably enhanced by producing high surface area “graphene mesosponges” displaying very few edge sites [77]. While it demonstrates clearly how active sites are undesirable for enhancing the voltage and the life span of ECs, the electrodes made from graphene mesosponges are limited by a low density (ca. 0.16 g cm^{-3}) compared to traditional materials such as activated carbons (electrode density ranging from 0.5 to 0.7 g cm^{-3}). Future efforts should then be focused on developing high density carbons with a reduced number of active sites.

It must also be indicated that many papers mention voltage limits determined by cyclic voltammetry, very often at very high scan rate; in such case, the redox peaks due to electrolyte oxidation/reduction might be dramatically reduced, leading to an overestimation of voltage. The only reliable determinations should be based either on long galvanostatic cycling or potentiostatic floating [78] that requires shorter recording times. The latter can be even more shortened by increasing the temperature up to 60 – 70 °C.

High energy EDLCs can be also developed by employing ionic liquids (ILs) as electrolytes, as it is often claimed in the literature that they exhibit a larger potential window than organic electrolytes. What is important to bear in mind is that most of such studies on the electrochemical stability window of ILs are inferred using platinum or glassy carbon (non-porous) support electrodes. However, when nanoporous carbon electrodes are used, the potential window is dramatically reduced due to the presence of active sites. The maximum reachable voltage is only very slightly superior to the values obtained with organic electrolytes [79]. Consequently, the criteria to enhance the voltage of ECs operating in ILs are the same as for organic electrolytes.

2.5. Can we compare the performance of porous carbons as electrocatalysts in oxygen reduction?

Research on development of oxygen reduction catalysts for fuel cells can be considered as one of the cutting-edges of energy-related scientific exploration. So far the best performing catalyst has been platinum supported on Vulcan carbon black; however, it is expensive, and thus an intensive search for its substitutes has intensified recently. Carbon materials and especially graphene or carbon nanotubes have been intensively explored for this application, owing to their high electrical conductivity and the possibility of introducing catalytic N- or S-based centers to the carbon matrix [80-82]. Quite recently, the search expanded and nanoporous carbons have been also included in that quickly advancing quest. Similarly to their other applications, there are reports in the literature indicating the importance of the porosity [83-88] and oxygen adsorption on the nanoporous carbons [89-92] for achieving an efficient ORR. The latter is usually described by the electron transfer number, kinetic current density, and onset potential. The problem with erroneous reporting of the electron transfer number (sometimes the reported value is greater than 4!, the theoretical one) and recommendations about how to address the experimental and computational limitations have been recently addressed in the work of Qiao et al [93], who strongly support the use of rotating ring disc electrodes (RRDE) made of gold (not platinum) for the determination. Despite their popularity, Ring Disc Electrodes (RDE) do not provide reliable information about the electron transfer number ($n > 4$).

Reporting of onset potential values also remains questionable, and this issue has important implications as the allegedly expert reviewers frequently demand to provide a direct comparison with “record” (but perhaps biased) onset potential values reported in the literature, or else causing the rejection of valuable works. In 2015 Botz and coworkers stated [94] that the onset potential intrinsically depends on the experimental conditions, and that there is no agreement about the measuring procedure, which make the comparison of the results very difficult. Even though generally it is accepted that it is a potential at which the reaction starts, there are various approaches to find/report these values. For instance, Wouters et al. [95] indicated that it is a potential at which the slope of the voltammogram exceeds a threshold value (e.g. 0.1 mA cm⁻²); some reports use the "tangent" method (Figure 5) [96] and many others just report the value at which the potential starts to decrease without further explanation, leaving the reader to judge by

him/herself. Generally, the values obtained using the last approach are more positive than those evaluated using the tangent method, which might lead to wrong conclusions about the superiority of some carbons over others. Therefore, until a consensus on the reporting of the onset potential is found and accepted by the scientific community, it would be a good practice to include in any reported data and plots the data obtained for Pt/C. It would also be advisable to clarify in the manuscript the method chosen for the estimation of onset potential value.

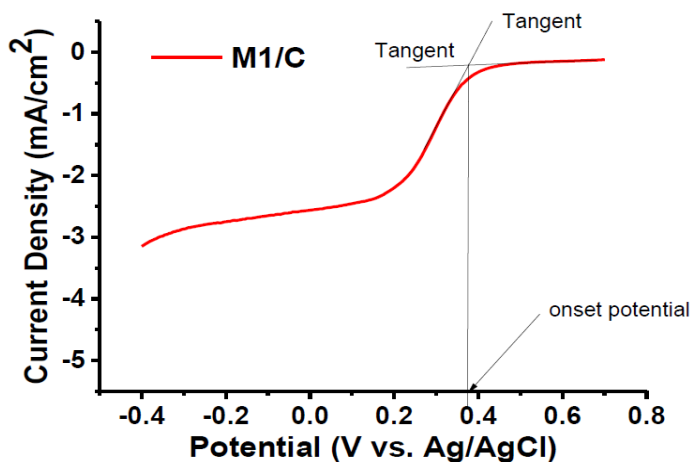


Figure 5. The determination of onset potential. Reprinted with permission from Ref. [96]. Copyright 2015, Royal Society of Chemistry.

Another issue of concern in the electrocatalytic applications of porous carbons is the interpretation of the data related to their porosity. Conventional fundamentals of electrocatalysis have been developed for rather nonporous materials, and their extension to highly porous materials often raises questions and doubts from the traditional electrocatalysis community on the validity of results/interpretations. It is true that in porous materials the mass transfer plays a non-negligible role, and such electrochemical concepts as ECSA (electrochemical active surface area) or the trend in kinetic current (or its values compared to other catalysts) might need revision. We hope that the promising results on porous carbons as noble metal-free ORR catalysts might stimulate the electrocatalysis community to address those challenges.

2.6. Does the traditional active site definition represent the actual nanoporous carbon active sites?

For many years, porous carbons have been used in catalysis either as supports or as catalysts on their own. For the latter, there are plenty of examples in the literature reporting the excellent performance of porous carbons in various catalytic reactions (some at industrial scale) including electrocatalysis, oxidative dehydrogenation, advanced oxidation of pollutants, photocatalysis, and many others [15,97,98]. The market value of porous carbons in the field of catalysis is expected to rise in the near future due to the rapid advance in several areas such as the development of fuel cells, the need of selective and less expensive catalysts, and the development of applications where metal-free catalysts can be substitutes for noble metal-based ones, due to constraints related to availability and cost of the latter [97].

The catalytic activity of porous carbons has been attributed to the presence of heteroatoms (with particular attention to N- and O- containing groups) [99,100], defects and edges [101-103], and pore confinement [104-108]. Recent computational approaches have provided complementary insights in underlying mechanism and the role of specific active sites. Nevertheless, attribution of the individual contribution of each of these active sites is still under debate for most of the reactions catalyzed by porous carbons, due to the difficulty to synthesize materials containing only one type of active sites (an identified surface group, pores of a certain size, defects of a certain nature) and the puzzling effect of impurities.

Comparison of the activity of catalysts is usually conducted using global activity indicators. IUPAC's recommended standardized methods for this purpose including the evaluation of kinetic parameters such as the turnover number (TON) and turnover frequency (TOF) (number of molecules reacting per active site in unit time for specified reaction conditions —temperature, initial concentration, extent of the reaction), that serve to characterize (photo)catalytic ($N \gg 1$) or stoichiometric/photoassisted ($N > 1$) mechanisms of the process [109]. Evaluation of these parameters in homogeneous catalysis does not pose any problem, as the catalytic sites are well described. However, extending turnover calculations to heterogeneous systems, and particularly to metal-free carbon catalysts finds an important limitation in the realistic measure (identification and quantification) of the catalytic active centers. In such cases, it has become a common practice to use other intrinsic parameters of the catalyst (such as surface area or mass) as substitutes of the active sites [15, 110, 111]. Thus, it is not surprising that obtained values are typically much lower than those of metallic catalysts for the same catalytic reaction [112], leading to a misinterpretation of the comparative performance in favor of the metallic catalysts [113-115].

In (photo)catalysis based on nanoporous carbons, the situation is even more complex; the determination of turnover, quantum yields (aka quantum efficiency, number of events per absorbed photons, only applied to monochromatic light) and photonic efficiencies (number of reactant molecules transformed, or of product molecules formed per incident photons) suffer from lack of consensus and collective understanding, with little progress (if any, it may have been backwards) in the past two decades [116,117]. This is mainly due to the difficulties associated with measuring the number of photons absorbed by dispersed solid particles (light scattering applies to all solid catalysts). For strong light absorbing catalysts such as porous carbons, the uncertainty associated with discriminating the fraction of light reaching the carbon surface and the pores, from that absorbed by the carbon matrix itself (i.e., the accurate incident flux) becomes a challenge [104, 118].

Standard descriptors that are reasonably well-defined and understood for homogenous catalysis and some heterogeneous catalysts, fail to describe the activity of unconventional catalysts where the active sites are not clearly identified. Thus, it is important to find more adequate alternatives to such catalysts, and to propose new standard protocols and descriptors that enable one to account for the catalytic activity of porous carbons. Such descriptors must be chosen carefully; those based exclusively on intrinsic properties can underestimate the catalytic activity, since the active sites may not be equally accessible; different types of active sites may contribute unevenly to the global activity; and topology can be quite different even for carbons with similar porosities and compositions. In addition, individual contributions of different active sites may depend on the catalytic reaction conditions (pH, temperature) and may be subjected to aging and/or

deactivation just as much as conventional catalysts (it should be recalled here that even so-called true catalysts suffer from deactivation, as proven in the extensive literature published on this topic).

Standardization of the catalytic sites activity may require to consider global (lumped) or apparent activity obtained in ad hoc activity tests more related to the final application than to the intrinsic properties. This is a challenging approach since no universal reaction tests can be defined and various groups have different roles and activity in different reactions. Alternatively, the use of global multi-parametric indexes reflecting the joint contribution of relevant properties of the catalyst for a certain reaction should be considered. These indexes would consider properties at a bulk material level, and not necessarily at a molecular level.

For these reasons, surface area of the catalyst must not be considered a reliable descriptor to normalize the activity (despite the fact that it is often used for this purpose). Rather than surface area, the confinement state of the target molecules inside the porosity of the carbons should be considered, as it is well-known that the strength of the interactions with the catalyst's surface changes dramatically upon adsorption and accommodating of the dimensions with the size of the nanopores [104, 108, 119]. Information about other important parameters such as the mass, density, geometrical area (e.g., dimensions of electrodes, irradiated area of photocatalysts), porosity, composition (among others) are essential to compare performances in certain cases, although they do not give information about the catalytic activity itself. Indeed, the key remains in the quantification and identification of the active sites. In this regard, the usefulness of several descriptors proposed by different authors will be further analyzed below.

In heterogeneous photocatalysis, the quantification and identification of the active sites has been a long-discussed issue [104, 116, 120], and two descriptors have been proposed for adequately standardizing and comparing data of different photocatalysts: i) pseudo-quantum yields (based on an incident photon flux emitted by an irradiation source), as they represent a lower limiting value of true quantum yields (provided that the photon flux is measured by chemical actinometry on the same cell used for the photocatalytic tests, rather than estimated by a radiometer); ii) photonic efficiencies (number of reactant molecules transformed, or product molecules formed per incident photons in the photocatalytic cell). The estimation of photonic efficiencies (number of reactant molecules transformed, or product molecules formed per number of photons incident inside the front window of the photocatalytic cell) could be considered more adequate for standardizing and comparing heterogeneous photocatalysis data. Particularly, the relative photonic efficiencies (values are normalized per the photonic efficiency of a so-called standard process measured in similar conditions) are extremely useful parameters as they are independent of the photoreactor geometry and of other operating constraints (loading, irradiation source, extent of the reaction). The use of these descriptors is still quite rare.

Addressing the role of surface groups in catalytic reactions is always challenging [111]. In the case of the ORR, Zhao et al. [121] defined a descriptor based on the electronegativity and electron affinity of species in doped nanocarbons to correlate it with the catalytic activity. Zou et al. [122] found the adsorption energies of O, O₂ and OH also to be good descriptors of the performance of metal-free B- and N-doped nanocarbons catalyzing ORR, although in the case of graphene nanoribbons an important edge effect was also found. A similar approach was proposed by Zhu et al. [123] for the definition of a descriptor for the activity of graphitic carbon nitride in the hydrogen evolution reaction. A descriptor for active sites was based on the number of

electrons occupying the outermost p orbital and electronegativity, and then correlated to the catalytic activity. Another example is the Pore Influence Factor (PIF), a descriptor of the catalytic activity of metal-free carbons for ORR proposed by Barrera et al [92]. It combines the effects of the number of dissociating groups (affecting hydrophilicity), ECSA (electrochemically active surface area) and the volume of ultramicropores (affecting the strength of O₂ adsorption) on the electron transfer number. Also, for the hydrogen evolution reaction (HER) the Gibbs free energy of hydrogen adsorption (ΔG_{H^*}) has been suggested as a suitable descriptor correlating the catalytic activity of doped carbons [124]. In photocatalytic applications, it has been found that certain sulfur-, nitrogen- and oxygen-containing groups in carbons favor the charge transfer reactions triggered upon light stimulation of the carbons, with no direct correlation with the amount of heteroatoms but rather the nature of the groups and their ability to absorb and harvest light of adequate wavelengths [104, 106-108, 125-127].

Regarding kinetic data analysis, most classic catalytic reactions based on non-porous catalysts are well-described upon apparent first-order rate expressions, with experimental data mainly fitted to Langmuir–Hinshelwood or Eley-Rideal models that consider that the catalytic reaction occurs with the species adsorbed on the surface [128-131]. For porous catalysts, the analysis of the kinetic data must be done carefully, as the common assumption of a first order kinetics may not apply. This is often the case when the catalytic reaction and the adsorption of reactants or products occur simultaneously on the catalysts surface, and the overall reaction rate represents both contributions. In these cases, the use of simplified forms of first-order models is discouraged, as it may lead to miscalculation of rate constants.

Engineering aspects of the photocatalytic reactors (geometry, catalyst loading, monochromatic irradiation), often disregarded in the literature, are also important for reporting overall photocatalytic efficiencies and performance. Indeed, the volumetric rate of photon absorption of the process, a key descriptor for scaling up, is a parameter strongly dependent on the geometry of the reactor [132,133]. There is still a number of open questions regarding the correlation between porosity, surface density of adsorbed molecules and the volumetric rate of photon absorption that deserve further attention. The impact of the porosity on the dynamics of fluids upon the absorption of photons still remains unclear, although it has been well-described for non-porous photocatalysts [132,133].

Quantification and identification of catalytic active sites is complex and not straightforward, due to the difficulties to identify and estimate both the nature and amount of such centers. This is particularly important for metal-free porous carbon catalysts. Indeed, the uncertainty in the attribution of the activity to individual sites and the evaluation of carbon surface reactivity is a long-standing discussion. For instance, Radovic et al. [134] proposed to use the oxygen chemisorption capacity in air at 102 °C and 0.1 MPa as an index of the reactivity of chars in gasification reactions, and for allowing the evaluation of the amount of active sites in the char, differentiating the concepts of active surface and total surface areas.

Based on the complexity of the systems, the following aspects should be considered for the correct quantification of the active and accessible surface groups to fairly compare catalyst activities:

a) Characterization techniques. The most used methods to quantify surface groups on carbon materials are elemental analysis, chemical/potentiometric titrations, Temperature-Programmed Desorption (TPD) and X-ray Photoelectron Spectroscopy (XPS). Elemental analysis allows to

determine the content of the heteroatoms in the bulk, which is useful to validate the total content derived by the other techniques. The main problem is that, in most papers, the oxygen content is calculated by difference from a CHNS analysis, and the errors can be quite significant. The direct quantification of oxygen by dedicated equipment should be preferentially used. In addition, it is recommended to carefully dry the samples before an elemental analysis, as the humidity retained in the pores may interfere with the measurements. Boehm titration [135] is frequently used to quantify surface groups, but the method suffers from several drawbacks; namely the fact that not all the surface groups are quantified (e.g., only about half of the total oxygen obtained by elemental analysis is determined in porous materials), and that being initially developed for O-containing groups, it fails to characterize other heteroatoms [136]. Moreover, Boehm titration should not be used for carbons containing a marked amount of ash/inorganic matter. By analogy with Boehm titration, methods to identify the different basic sites with acids of increasing strength have been proposed [137], but they suffer similar limitations. Potentiometric titration [138,139], although able to provide the amount and strength (in terms of their pKa values) of acidic groups, is not able to strictly assign them to specific functionalities, and the problem becomes more important when besides oxygen other heteroatoms are present on the carbon surface. In the case of TPD and XPS, a deconvolution methodology allows one to quantify the different oxygenated surface groups. XPS is a surface technique that only measures the topmost few atomic layers (usually below 10 nm), which may not be representative of the bulk material for porous solids [111]. In any case, XPS has proved to be a suitable technique for non-microporous carbons like carbon fibers, graphite, CNTs, graphene and mesoporous carbons. The deconvolution of the C 1s and O 1s peaks is used to quantify the different surface groups, with the C 1s peak being usually more informative. As deconvolutions can be complex, it is highly recommended to confirm that the total amount of oxygen calculated from the C 1s deconvolution peaks (Cox) is in agreement with the total oxygen content (Oox) of the sample. This is often neglected, and a simple validation test is to confirm that Cox/Oox is close to one [140]. Moreover, as indicated above, XPS suffers from the strong influence of the “deconvoluter” and his/her approach to the deconvolution problem. TPD combined with a deconvolution procedure is also very useful [141,142]. To avoid misinterpretations it is advisable to select the TPD operational conditions to minimize secondary reactions during the experiments (e.g., low heating rates, usually below 10 °C/min, and high flow rates, usually above 25 cm³/min) [143,144]; the deconvolution methodology should follow strict rules (for example, those described in [141, 145]); and temperatures above those used to synthesize the carbon material should not be considered, since the CO and CO₂ released will result not from the surface group decomposition but from the pyrolysis of the material.

b) Number of active sites under the reaction conditions. The surface groups should be quantified before and after reaction to confirm that the active sites remain stable on the carbon surface (i.e., to discriminate if such active sites are truly catalytic ones). This is especially important for reactions involving oxygen, such as the case of oxidative dehydrogenation of alkanes, where the activity may change during reaction due to the modification of the active sites [114, 146]. The challenge is to use *in-situ* measurements to follow the surface groups during reaction. FTIR and *quasi-in-situ* XPS are the most promising techniques [147], although FTIR will always present additional difficulties for black materials like carbons. An interesting alternative was proposed by Su et al. [148] in which *in-situ* chemical titration is used to identify the accessible active groups on the surface. These authors were able to show that, although the carbon catalysts

undergo a rearrangement of their surface chemical structure under reaction conditions, the intrinsic activity per active site did not change, as expected.

2.7. Can advances in water treatment be reached by focusing on hybrid technologies for enhanced pollutants degradation and carbon regeneration?

Liquid phase end-uses are by far the largest application of nanoporous carbons, accounting for 66 % of the share of the total consumption worldwide [7], and water treatment is the largest individual market of porous carbons. Despite being a mature technology, there are still several important aspects on the use of porous carbons in water treatment that deserve attention, which include i) the need to deal with the spent carbon adsorbent when it has reached its saturation limit (that might become a hazardous waste), and ii) to face the occurrence of emergent pollutants, a new threat to the aquatic environment that covers a number of compounds such as pharmaceuticals, personal care products, endocrine disruptors, perfluorinated compounds, pesticides... and derivatives and degradation products. Wastewater treatment plants (WWTPs) should be crucial barriers against new pollutants, but most of these compounds are resistant to conventional biological treatment by activated sludge, and thus are not efficiently removed, ending up in recipient waters at trace levels [149-151]. The actual challenge in wastewater treatment is to develop cost-effective and efficient end-of-pipe technological solutions to upgrade existing infrastructures, as new investments are often limited by the economic constraints of different countries. Furthermore, these solutions should be able to remove/degrade the emerging pollutants without generating secondary sources of pollution or wastes.

Adsorption on porous carbons is commonly implemented as an end-of-pipe technology in the final stage of WWTPs (tertiary treatment), but it can also be positioned in early steps of the water treatment plants, allowing the preservation of the secondary biological reactor. Alternatives based on hybrid systems conjugating simultaneous adsorption on porous carbons with other existing processes at the WWTP have recently started to receive attention (Figure 6), e.g., based on carbons added to the biological reactor, ultrafiltration membrane modules or membrane biological reactor (MBR) systems, advanced oxidation processes, e.g., the Fenton reaction, photocatalysis, etc. [152,153]. For instance, solutions based on carbons added to the secondary active sludge reactor generating mixed liquid-suspended solids were found effective for the removal of emerging pollutants [152, 153]. MBR systems seem especially appropriate to be coupled to porous carbons, since they produce suspended solids-free effluents, thus reducing the competitive adsorption of organic matter on the carbon adsorbent [154-156]. However, there are many technological and engineering issues to be solved, related to the decantability and disposal of the carbon-biomass slurry (where pollutants and/or metabolites of uncertain toxicity might be adsorbed), and the recuperation and reusability of the carbon.

Most studies at lab-scale tackle the challenge by classical experimental approaches typically conducted in synthetic solutions (i.e., ultra-pure water) and mainly based on reporting the influence of experimental parameters on the retention capacity (e.g., adsorbent physicochemical features —surface area, microporosity, composition, solution temperature, pH). These classic approaches are of importance in mechanistic studies, in screening of adsorbents, and in evaluating the potential new materials synthesized from novel precursors and using new synthetic recipes compared to commercially available carbons. However, it is necessary to direct research efforts towards more realistic scenarios using real wastewaters, and evaluating the influence of parameters that would define the performance in real cases with complex water

matrices, reflecting realistic levels of water hardness, organic matter or competitive adsorption [157-162].

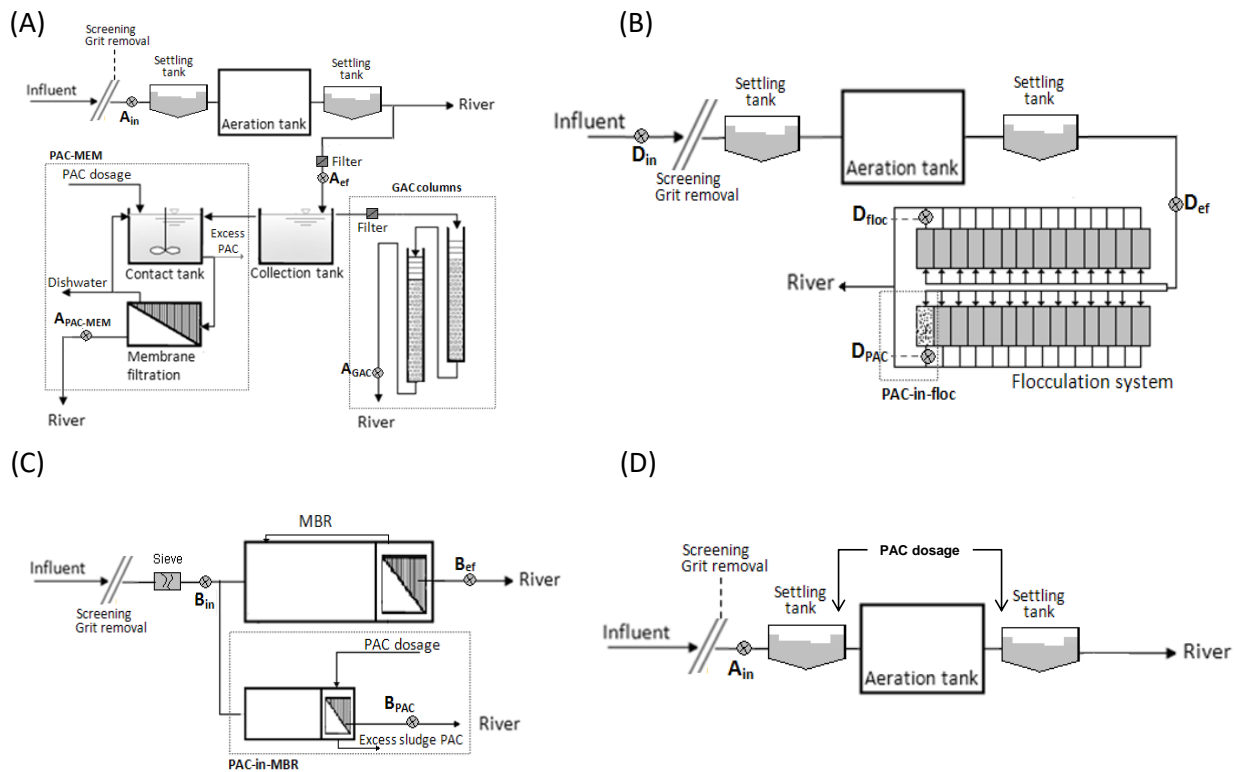


Figure 6. Schematic diagrams of full scale WWTPs with conventional activated sludge coupled with various advanced technologies for the removal of emerging pollutants: (A) post-treatment adsorption of granular porous carbon and coupling powdered carbon with membrane filtration; (B) carbon added to flocculation system; (C) carbon added to a membrane biological reactor; (D) carbon added to the biological reactor. (A-C are adapted from [154]).

Besides screening carbons with diverse porosity and surface chemistry, it is necessary to use statistical tools to perform multivariate analysis to identify the critical descriptors (Key Performance Indicators, KPIs, and Key Operating Conditions, KOCs) needed to adapt the requirements of the porous carbons based on the characteristics of the existing infrastructures and to estimate the overall costs (capital expenditure, CAPEX, and operational expenditures, OPEX) of the upgrading of the WWTPs. Most of these KPIs (carbon density, mechanical properties, particle size, decantability, hydrophobicity, toxicity) and KOCs (residence time, flow rate) are scarcely addressed in the scientific literature, despite their importance in the process engineering. For instance, high density adsorbents are typically preferred, which prevents the use of certain precursors for the preparation of carbons for water treatment applications (such as graphene-derived porous carbons). High abrasion resistance is also required for granular carbons (to minimize attrition) but not for powder carbons. Decantability and wettability should be also reported, as the carbon must present a good dispersion within the effluent to assure the adsorption in the operating conditions of the WWTP (typically flow rates and contact times in plants are very different from those tested in lab-scale). It should also be pointed out that in

hybrid systems, the porosity of the carbons might not be fully used (i.e., partial saturation) for which carbons with high surface areas will not necessarily improve the overall process performance.

The recuperation of a carbon adsorbent for further reuse and its reactivation are other crucial aspects, as upgrading of WWTP must not only comply with measures aiming to guarantee the quality of the water resources, but also should assure a feasible economic restructuring of the plants. Thermal reactivation of spent carbons is generally carried out off-site in the carbon manufacturer's facilities (by heating or steaming). Its main drawbacks are the economic costs associated to the energy consumed and the transportation to the reactivation factory. Thus, to boost the development of hybrid systems based on porous carbons, actions must be taken to improve the regeneration of the porous carbons or to extend their lifetime. The combination of adsorption and/or advanced oxidation processes (e.g., ozonation, the Fenton process, electrochemical oxidation, photocatalytic reactions) appear to be promising alternatives to lower the cost of the reactivation of the carbon, as they enable on-site regeneration [163-165]. Most of these processes have been explored for the degradation of recalcitrant pollutants in water, achieving mineralization (i.e., complete degradation). Moreover, even though complete reactivation of the carbon is not yet fully achieved, the carbon is returned to a reusable quality, which is the key to extend the reusability of carbon adsorbent and on-site (even if partial) reactivation.

3. Perspectives

The scientific challenges presented above are among the most critical facing the nanoporous carbon community today; yet, the discussion in New York during the Workshop Beyond Adsorption II (July 2019) centered on the lack of consensus on or even awareness of many of these issues by the carbon science community at large. And while scientific communities often undergo cycles of fragmentation and recombine, the duration of these cycles is solely a function of a community's ability to recognize synergies in seemingly disparate topics and to make connections to parallel but complementary lines of inquiry.

Porous carbons, of which nanoporous carbons are the most important industrially, are a multi-billion-dollar worldwide industry, with projections for impressive growth in the next years [166, 167]. As discussed above, these materials are unique in their potential to achieve high efficiency in clean energy production and storage, emissions control, catalysis and purification. Emerging market forces are driving innovations in mobility, communications/connectivity, artificial intelligence, agriculture, and medicine, which are in part enabled by further development of low-cost nanoporous carbons.

The same or similar market forces are driving innovations in nanocarbons, such as CNTs and graphene. Although these materials are still in their infancy commercially speaking, successful early applications involve optimal incorporation with other material systems, e.g., polymers, ceramics, and semiconductors. As has been discussed here, developers of these materials, to enable more wide-spread applications, are encountering many of the same issues that have been previously addressed in the development of nanoporous carbons. We suggest that the so-called "2D" (nanocarbons) community and the "3D" (porous carbons) community might make a concerted effort to find synergies for mutual benefit.

The history of heterogeneous catalysis development provides a rough precedent. Work in the 19th and early 20th centuries to develop heterogeneous catalytic materials was characterized by the measurement of macroscopic material and performance parameters, while employing the methods of synthetic chemistry and engineering science as they were developed [168-170]. Catalytic sites were hypothesized and specific site information was inferred from macroscopic measurements. With the development of high-vacuum techniques, the field of surface science emerged in the mid- to late-20th century, and shed considerable light on the identity of adsorbate species and the nature of defect sites giving rise to catalytic activity. Although the conditions under which pristine surfaces are studied are often not directly applicable to the conditions under which industrial catalysis is carried out, the work has generated sufficient corroborating and supporting evidence to enable interpretation of phenomena on actual (three-dimensional) catalysts [171]. Today, catalyst development routinely makes use of surface science data, while catalytic studies on pristine surfaces are supported by findings from two centuries of industrial catalyst research.

Carbon science has a long history of extraordinary achievement, and the pace of new discovery and the importance of carbon materials have only grown with time. New discoveries are attracting new communities into the field. The authors strongly encourage these new investigators to consider the established science and on-going work in adjacent but related areas of the science. Work on nanoporous carbons will proceed in addressing some formidable challenges in coming years, and will be greatly strengthened by incorporation of nanocarbons and nanomaterial concepts through greater collaboration. It is, after all, the greater community of carbon scientists who is best positioned to advance the science and application of carbon materials to the problems of society.

Finally, we want to emphasize that nanoporous carbons have unique features ensuring them making a marked advancement in science and technology. Nowadays, their porosity can be designed to some extent, and recent developments in instrumentation combined with sophisticated surface modifications targeting specific features, can help to better explain and quantify the phenomena taking place in their pore system. To use these to a full extent, we stress that a precise and thorough description of the physicochemical, porous and structural properties of nanoporous carbons is essential to completely understand their properties. This necessarily implies the use of complementary techniques, a consensus in characterizing carbons and in describing the performance parameters, along with interdisciplinary collaboration. Although an explanation of the origin of porous carbon behavior is still controversially discussed by the scientific community, we would like to underline that pushing their emerging applications to a higher technological level can only occur through a precise characterization of the carbon material and through the understanding of basic phenomena, revisiting old works in other disciplines beyond carbon science. Even though materials science has recently become a very competitive discipline, scientists are encouraged to step aside in their endeavors and to focus on building solid knowledge considering even opposite findings for the good of future technological developments and for the future and advancement of the society, in general.

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