Efficient and sustainable strategies for energy storage are crucial to prevent climate change and exhaustion of natural resources. In this context, supercapacitors are increasingly important components to store energy for stationary, mobile and portable applications. Among different alternatives, conductive carbon-based materials gather matchless availability, relatively low-cost, lightness, enough high stability and enormous versatility to be prepared in different sizes, shapes, conformations, porous textures and compositions, what make them the best candidates to be used as electrodes in these electrochemical devices. After a first monograph two years ago (Boletín 28), the topic of this special issue of the Boletín del Grupo Español del Carbón (Spanish Carbon Group Bulletin) focuses again on supercapacitors. These devices can complement or replace batteries when high power delivery or uptake and/or long cycling stability are required. In addition, they improve efficiencies in supply systems by storing energy when in excess. However, to attain the widespread commercialization and application of supercapacitors, an enhancement in energy density and a cost reduction are necessary, so intense research activity is currently driven towards the development of advanced materials and configurations, as well as cheaper preparation and processing methods.

The design of an optimum morphology and porosity to produce a high and easily-accessible surface area, for both high energy and power densities, is probably the most intense research area to fully exploit the electrochemical double-layer charge storage mechanism. The incorporation of electroactive surface functionalities, metal oxides and/or conductive polymers to promote pseudocapacitance constitutes the most studied strategy to further enlarge the total specific capacitance of carbon electrodes for higher energy densities. Nevertheless, the achievement of high operating voltages will probably lead to a more marked increase in the energy density of supercapacitors. Therefore, research on the enhancement of the electrochemical stability of carbons as well as their combination in asymmetric (with a different carbon electrode) and hybrid (with a pseudocapacitive- or a battery-like electrode) configurations is attracting increasing attention. On the other hand, the development of cheaper and more sustainable preparation procedures, by using abundant and low-cost precursors, and simpler electrode processing routes is the subject of intense research in recent years. Particularly, methods and techniques allowing the direct preparation of binderless, seamless and/or self-standing carbon electrodes could greatly reduce, apart from the electrical resistance, the cost of supercapacitors.

Last May, the collaborative research project on advanced supercapacitors between the Universities of Alicante and Málaga (Spain) and Tohoku (Japan) came to an end. Financed by the Spanish MINECO and Japan Science and Technology Agency (JST), the Project has culminated in fruitful discussion, collaboration and progress on the field of supercapacitors. In particular, the exchange of Japanese and Spanish students has resulted in priceless personal and scientific experience. Personally, this opportunity marked my life in many different ways. I would like to take this occasion to thank all the people who made it possible: Emilia, Diego, Hirotomo, Takashi, Pepe and Tomás. Included within the last planned activities of the Project, last September we met in Málaga for the “2nd Spain-Japan Joint Symposium for Advanced Supercapacitors” (http://web.ua.es/es/spain-japan-workshop). As in the previous edition in 2012, prestigious researchers participated with interesting lectures on some of the aforementioned state of the art topics on supercapacitors. I sincerely want to thank them for their kind acceptance and effort to prepare a contribution to this special issue. Finally, many thanks also to the Editorial Board of this Boletín, especially Olga, for considering me to edit this issue.

Raul Berenguer, Guest Editor
Carbon blacks as active materials for electrochemical double layer capacitors

Abstract

Carbon blacks (CBs) are nowadays the most used conductive additives in electrochemical double layer capacitors (EDLCs) and lithium-ion batteries. Nevertheless, taking into account the appealing properties of CBs, e.g. high conductivity and relatively low cost, also their use as active materials for EDLCs appears of high interest. In this work we present a comparison between the electrochemical behavior of EDLCs containing CBs and the conventional activated carbons (AC) as the active materials. The aim of this investigation is to contribute to the assessment of the advantages and limits related to the use of carbon blacks as alternative active carbonaceous materials for EDLCs.

Resumen

Actualmente los negros de carbón son los aditivos promotores de conductividad más utilizados en condensadores electroquímicos de doble capa (EDLCs) y baterías de ión-litio. No obstante, teniendo en cuenta las propiedades atractivas de los negros de carbón, tales como una elevada conductividad eléctrica y un coste relativamente bajo, su utilización como materiales activos para EDLCs presenta gran interés. En este trabajo, presentamos una comparación entre el comportamiento electroquímico de EDLCs basados en negro de carbón y el de los basados en carbones activados convencionales. El objetivo de esta investigación es contribuir a la evaluación de las ventajas y limitaciones relacionadas con el uso de los negros de carbón como materiales activos alternativos para EDLCs.

1. Introduction

Electrochemical double layer capacitors (EDLCs), also known as supercapacitors, are presently considered among the most important energy storage technologies [1-3]. These devices typically contain electrodes made of activated carbons (AC) and electrolytes containing solvents like propylene carbonate (PC) or acetonitrile (ACN) in which a salt, typically tetraethylammonium tetrafluoroborate (Et₄NBF₄) is dissolved. In EDLCs the charge is stored electrostatically at the interface carbon-electrolyte and, because of this physical storage process, these devices can be charged-discharged in seconds (or less). Furthermore, they display high power (10 kW kg⁻¹) and exceptional high cycle life (>500000 cycles). The energy of these devices is in the order of 5 Wh kg⁻¹ [1-3].

As mentioned above, ACs are nowadays the state-of-the-art electrode materials for EDLCs. These carbonaceous materials, which are typically obtained from carbon-rich organic precursors by carbonization in inert atmosphere followed by a physical or chemical activation, feature high specific surface areas and low cost. In the past many types of syntheses and precursors have been considered for the realization of AC. Huge efforts have been made to tune the pore size distribution, specific surface area and conductivity of ACs suitable for EDLCs [2].

In parallel to the work on AC, also other types of carbonaceous materials have been investigated in the last years, e.g. graphene, [4-5] carbon nanotubes [2], carbide derived carbons [1,2,4], carbon onions [2], carbon fibers and templated carbons [2,4]. All these carbons can be successfully utilized for the realization of EDLCs. However, all these materials are typically more expensive than AC. Furthermore, the use of these carbons for the realization of composite electrodes with mass loadings suitable for commercial devices (>10 mg cm⁻²), appears more complicated with respect to that of AC. Also the specific capacitance of these thicker electrodes is not higher than the one of AC-based electrodes. Taking these points into account, further studies appear therefore needed for the realization of carbons able to fully replace AC in the EDLC technology.

Carbon blacks (CBs) are a well-known class of carbonaceous materials [2, 6-7]. CBs are produced by thermal decomposition or partial combustion of hydrocarbons (oil or gases) in the gas phase. CBs typically display primary particle sizes in the order of 10 nm in diameter, which are fused together in agglomerates with a typical size of 100 nm. The dry powder conductivity of these materials can be in the order of 10¹ to 10² S cm⁻¹ [6-7]. Nowadays, CBs are utilized as conductive additive for composite electrodes used in EDLCs and lithium-ion batteries. In these composite electrodes the weight percentage of CBs is in the order of 5-10%. Nevertheless, it is very interesting to notice that the surface of CBs is considered to be more accessible than that of other high surface area carbons. Furthermore, CBs can be produced in large scale and they may be cheaper than other carbonaceous materials, e.g. graphene. For these reasons, the use of CB as active materials for EDLCs appears certainly of great interest.

In the past only few works have been dedicated to CB-based EDLC. Considering the appealing properties of this material, in the last years we investigated the use of CB as active materials for EDLCs [6-7]. In this manuscript we report some of the most important findings obtained during these studies.
2. Experimental

The carbon black SC3 was supplied by Cabot Corporation, while the activated carbon DLC Super 30 was supplied by Norit. Both samples were used as received.

The morphological and structural characterization of these materials has been carried out as described in references [6-7]. These materials have been used for the realization of composite electrodes as indicated in reference [6-7]. The electrochemical performance of the composite electrodes has been investigated at room temperature using cyclic voltammetry, galvanostatic charge and discharge and impedance spectroscopy. The details about the electrochemical investigation are reported in references [6-7]. All the tests have been carried out using 1 M tetraethylammonium tetrafluoroborate (Et₄NBF₄) in propylene carbonate (PC) as electrolyte.

3. Results and discussion

The properties of CBs can be tuned by controlling the synthesis process and it is possible to realize CBs with high surface area. In this work we will consider the electrochemical behavior of a carbon black with a surface area as high as 1500 m² g⁻¹, which has been produced by Cabot Corporation [6-7]. The behavior of this CB will be compared to that of activated carbon.

Figure 1 compares the SEM images of CB and AC. As shown, both carbons display particles with irregular shape. Nevertheless, these two materials present substantial differences. As a matter of fact, the CB is composed of agglomerations of smaller (primary) nanoparticles, while the AC is composed of particles with sizes in the micro-nanometer range.

As indicated in Table 1, the investigated CB displays higher BET surface area (1805 m² g⁻¹) with respect to the AC (1509 m² g⁻¹). Taking into account the SEM images, such difference might be originated by the agglomeration of the primary particles of the CB, which make the surface of this material more irregular compared to the one of AC. As indicated in the table, the DFT surface area follows the same trend. It is also interesting to notice that the total pore volume (TPV) of CB is higher with respect to that of AC. Another aspect to mention is the fact that, while AC is mainly consisting of micropores, CB display also pores in the mesoporous range. Taking these results into account, CB and AC appear therefore to display rather different properties.

Figure 2 compares the electrochemical behavior of two EDLCs containing composite electrodes having CB and AC as active materials. As shown in Fig. 2a, during tests carried out using a scan rate of 20 mV s⁻¹ the EDLC containing CB (25 F g⁻¹) delivers higher capacitance with respect to the one based on AC (22 F g⁻¹). The higher capacitance of the CB-based device is most likely originated by the higher surface area of CB compared to the AC. Fig. 2b compares the capacitance retention of these two devices during tests carried out at different scan rates. As shown, during these tests the CB-based EDLCs display higher performance compared to the one containing AC. At 200 mV s⁻¹, the CB-based EDLC retains more than 90% of its initial capacitance, which is more than 10% higher than the retention of AC-based EDLCs. This higher retention is originated by several factors. First of all, it is reasonable to suppose that the presence of mesopores in the CB might have a positive effect during the test at high scan rates since it might allow the ions an easier entrance into the...
pores of the carbon and thus a faster formation of the double layer. Secondly, as the particles of the CB are smaller than those of the AC (see Fig. 1), it is also reasonable to suppose that the path-length in CB is shorter than in the case of AC. Such different path-length might have a positive influence during test at high current densities. Finally, it is well known that the conductivity of the composite electrodes has a strong impact on the performance, especially during test carried out at high current densities. Since CB-based electrodes display higher conductivity compared to AC-based electrodes (17 mS cm\(^{-1}\) vs. 12 mS cm\(^{-1}\)) it is reasonable to suppose that also this parameter might have a positive influence on the performance of CB at high rate. Fig. 2c shows the evolution of the imaginary part of the complex capacitance vs. the frequency. From these measurements it was possible to define the time constant of the investigated systems. As already reported in literature, this constant indicates the frontier between capacitive and resistive behavior of a system and the lower the time constant, the faster is the system [8]. As indicated in the figure, the time constant of CB is 2 s, while the one of AC is 4 s. Taking this difference into account, it is evident that CB displays a combination of properties which makes this material particularly suitable for high power applications. Fig. 2d compares the energy and power delivered by the two investigated EDLCs in a Ragone-like plot. These values have been obtained from galvanostatic charge-discharge experiments carried out at current densities ranging from 2 to 80 A g\(^{-1}\). From this comparison it is evident that the use of CB allows the realization of EDLCs with improved performance compared to AC. Thus, CB appears a very interesting carbonaceous material for the realization of high performance EDLCs.

Since one of the strengths of EDLCs is the high cycling stability, in order to assess the advantage and limits related to the use of a new material, also this point needs to be carefully investigated. With this aim, we carried out float tests in which we kept the two EDLCs at 2.7 V for 500 h at a temperature of 20°C. As shown in Fig. 3a, the stability of the AC-based EDLCs is significantly higher compared to the one of the CB-based system. As a matter of fact, at the end of the test the AC-based EDLCs was able to keep more than 90% of its initial capacitance, while...
the EDLCs containing CB as active material retained less than 50%. As shown in Fig. 3b, the decrease of capacitance observed in CB-based EDLCs was most likely originated by the cracking observed in both electrodes of these devices. These cracks might indicate a breakage of the big CB agglomerates, which may cause a loss of contact between the CB particles. Such process could explain the strong fade observed for this device. Nevertheless, further investigations are certainly needed to elucidate the origin of these cracks.

4. Conclusion

Carbon black is a promising active material for the realization of EDLCs. CBs are largely available, they might be cheap and their properties can be conveniently tuned depending on the synthetic process. In this work we showed that CB with high surface area are suitable candidates for the realization of high power devices. At a current density of 2 A g⁻¹, CB-based EDLCs display average energy and power densities of 23.2 Wh kg⁻¹ and 2.8 kW kg⁻¹, respectively. These values are higher than those delivered by “conventional” AC-based EDLCs tested in analogous conditions. Nevertheless, the stability of CB-based EDLCs, due to the occurrence of cracks in the electrodes, appears lower than that of AC-based devices. Therefore, improving the stability of CB-based EDLCs appears to be the main challenge to introduce these promising materials in the EDLCs technology.

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References

Abstract

The template carbonization technique enables the production of porous carbons and carbon-based composites with precisely designed, controlled pore structures. The resulting templated carbons are therefore useful to investigate and understand the relation between carbon nanostructure and electrocapacitive properties. In this short review paper, we introduce our works on electrochemical capacitance using zeolite-templated carbons and carbon-coated anodic aluminum oxide.

1. Introduction

An electrochemical capacitor is an electric storage device which can be repeatedly charged and discharged. Compared with secondary batteries, the capacitor has several advantages such as higher power density and longer cycle life, though its energy density is much lower than those of the secondary batteries. There are mainly two strategies in the development of the capacitor electrode materials; focusing on the increase of (i) the power density and (ii) the energy density. In this short review, we introduce our previous works regarding these two strategies, using uniform porous materials prepared by the templated carbonization technique.

2. Electrochemical properties of zeolite-templated carbons

Our group has developed the templated carbonization technique which allows to produce carbon materials having well-tailored nanostructures [1-4]. When a zeolite, a microporous inorganic crystal, is used as a template, an ordered microporous carbon, zeolite-templated carbon (ZTC) can be produced [1, 4-6], according to the scheme shown in Figure 1.

Figure 1. A synthesis scheme of ZTC together with TEM images of zeolite Y and ZTC. Scale bars in the TEM images are 10 nm. Black, blue, and red spheres in the models correspond to carbon, hydrogen, and oxygen atoms, respectively. Reprinted with permission [4]. Copyright 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

ZTC consists of single-layer graphene nanoribbon (Figure 1), and its graphene framework is fully exposed without any stacking. In addition to both faces of the basal plane of the graphene (theoretical surface area is 2627 m² g⁻¹), the contribution of the edge sites to surface area is significant, and thus ZTC has very high surface area of 3000-4000 m² g⁻¹ [7]. Accordingly, ZTC shows a high electric double-layer capacitance [8-10]. A valuable advantage of ZTC is its excellent rate performance [8-10]. The three-dimensionally arrayed and interconnected
pores realize a fast ion-transfer despite its small pore size (1.2 nm). Many people believe that mesoporous, macroporous, or hierarchical porous carbons could be good electrode materials for high-power supercapacitors. However, the introduction of such large pores seriously decreases the packing density of the electrode layer, resulting in a low volumetric capacitance. ZTC is able to achieve both a good rate performance and a high volumetric capacitance, the latter of which comes from the fact that ZTC does not possess unnecessary meso- nor macropores. Figure 2 shows the volumetric capacitance versus current density for ZTC and reference activated carbons (MSC30 and A20) [9]. It is found that ZTC shows a high volumetric capacitance and a good rate performance.

![Figure 2. Volumetric capacitance versus current density for ZTC and activated carbons (MSC30 and A20). Reprinted with permission [9]. Copyright 2011 American Chemical Society.](image)

We have prepared also a binderless thin-film electrode consisting of ZTC, formed directly on a current collector film [11]. The obtained film electrode exhibits a high area capacitance (10–12 mF cm⁻²), compared with other microcapacitors. In addition, the film electrode is free from inter-particle resistance, and ultrahigh rate capability is achieved: the formation of double-layer capacitance could be confirmed at an ultra-high scan rate of 10000 mV s⁻¹.

ZTC has another interesting feature as a pseudocapacitive material. ZTC has a very large amount of edge sites [6], which is about 10-times larger than conventional activated carbons, and a large number of oxygen functional groups can be easily introduced into the edge sites by electrochemical oxidation [12]. By tuning the oxidation condition, it is possible to introduce electrochemically active quinone groups with a high selectivity [8]. Figure 3 shows cyclic voltammogram of ZTC in 1M H₂SO₄ electrolyte. In an acidic electrolyte, ZTC is significantly oxidized and a large amount of quinone groups are introduced into the edge sites, without serious damage to its nanographene framework [8]. Thus, ZTC exhibits very high capacitance (ca. 500 F g⁻¹).

Despite its high capacitance and excellent rate capability, ZTC unfortunately suffers from intense hydrogen evolution at a negative potential range in an acidic electrolyte. To take advantage of the ability of ZTC, we constructed an asymmetric capacitor in which ZTC and an ultrastable KOH-activated carbon are used as a positive electrode and a negative one, respectively [13]. The latter was prepared by KOH activation of Spanish anthracite [14]. The asymmetric capacitor can be operated with the working voltage of 1.4 V, and exhibits an energy density that is comparable to those of conventional capacitors utilizing organic electrolytes, thanks to the large pseudocapacitance of ZTC. Thus, ZTC is advantageous to construct asymmetric capacitors, as a high-capacity positive electrode in acidic electrolytes.

3. Investigation of the effect of N- and B-doping by using a model porous material

It is well known that doping of heteroatoms, such as B, N, and P, into porous carbons is an effective way to enhance the electrochemical capacitance.

![Figure 3. Cyclic voltammogram of ZTC measured between –0.1 and 0.8 V vs. Ag/AgCl in 1M H₂SO₄ at 25 °C, together with illustrations which represent the structure change of ZTC by electrochemical oxidation (during the first positive-direction scan) and the subsequent redox reaction of quinone/hydroquinone conversion.](image)

![Figura 3. Voltamgrama cíclico del ZTC, registrado entre –0.1 y 0.8 V vs. Ag/AgCl en H₂SO₄ 1M a 25 °C, junto con ilustraciones de la oxidación electroquímica del ZTC (durante el primer barrido hacia potenciales positivos) y de la reacción redox subsiguiente quinona/ hidroquinona.](image)
So far, many research groups have indeed reported a positive effect of such heteroatom doping in both aqueous and organic electrolyte solutions [4]. However, heteroatom doping usually alters the pore structure of a carbon matrix, and this makes it difficult to assess the sole effect of heteroatom doping, because the pore structure is also one of the crucial factors affecting electrochemical capacitance. To acquire better understanding about the effect of the heteroatom doping, we have prepared model porous materials by uniform carbon coating on anodic aluminum oxide (AAO), as shown in Figure 4 [15]. Carbon-coated AAO thus prepared has uniform-sized cylindrical mesopores with a diameter of 16 nm, and is free from any other pores, such as ultramicropores and micropores. In addition, it is possible to introduce B or N into the carbon layer. Thus, a series of mesopores completely coated with pure-, N-doped, or B-doped carbon layer were prepared, and their electrochemical properties were systematically examined both in aqueous (Figure 5) and organic electrolyte solutions [15]. It was revealed that the improvement in electrocapacitive properties due to the heteroatom doping is caused by its pseudocapacitance, not by other factors, such as the increase in wettability, conductivity, and space-charge-layer capacitance, in a large mesopores.}

Figure 4. Schematic for the synthesis process of the carbon coated AAO: (a) AAO template and (b) carbon-coated AAO. Reprinted with permission [15]. Copyright 2009 American Chemical Society.

Figure 5. Capacitance of carbon-coated AAOs versus current density in 1M H₂SO₄ at 25 °C. Reprinted with permission [15]. Copyright 2009 American Chemical Society.

4. Summary
ZTC, an ordered microporous carbon, achieves both a high volumetric capacitance and an excellent rate performance at the same time, due to its three-dimensionally interconnected ordered pores. In addition, its nanographene-based framework contains a large amount of active edge sites which can be functionalized with electrochemically active quinone groups. We have demonstrated that carbon-coated anodic aluminum oxides are good model mesoporous materials for the understanding about the effects of the heteroatom-doping. Thus, by using the model porous carbon materials prepared by the templated carbonization technique, we can reveal the relation between carbon nanostructure and electrocapacitive properties.

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References
Abstract

Supercapacitors are energy storage devices that will replace or boost batteries in multiple applications. For their widespread utilization and commercialization, however, markets demand a reduction in their cost and an enhancement of their energy density. In this overview, the main challenges and research activities towards the development of cheap and high-performance carbon-based electrodes for supercapacitors are identified and analyzed.

1. Supercapacitors: markets, forecasts and research

Supercapacitors, or electrochemical capacitors, are electric devices that store energy electrochemically in conductive materials, in the presence of a suitable electrolyte (see the main types in Fig. 1), by two different mechanisms, namely, the electrostatic adsorption of ions (charges) on a polarized surface and the reversible redox reactions of surface electroactive species [1]. The first mechanism (pure capacitive) is predominant in the so called electrochemical double layer capacitors (EDLCs) and it is characteristic of high surface area carbon materials. The second one (based on pseudocapcitance) prevails in the so called active or redox electrodes (also called pseudocapacitors), like metal oxides/hydroxides (RuO$_2$, MnO$_2$, VO$_2$, Co$_3$O$_4$, Fe$_3$O$_4$, Ni(OH)$_2$, Co(OH)$_2$, etc.) and conductive polymers (polyaniline, polypyrrole, etc.). Both mechanisms involve highly reversible and fast charge and discharge processes that make these materials distinct from the battery-like electrodes. Nevertheless, carbon materials usually contain electroactive surface functionalities that can participate in pseudocapacitive processes, and active materials usually display high surface areas to adsorb electrolyte ions, so they contribute to their total specific capacitance. The third type of electrode for supercapacitors is then the combination of previous ones in the form of composites, typically, a redox material finely dispersed on the large surface of a carbon. A simplified classification of electrode materials for supercapacitors is shown in Fig. 1.

As previously mentioned, the characteristic features of supercapacitors involve that they can be charged and discharged very quickly (within few seconds to milliseconds) and several times (usually more than 100000 cycles) without significant capacitance loss. Hence, these devices can complement or replace batteries when high power delivery or uptake, intermittent energy with variable power demands, and/or long cycling stability are required. This is mainly the case of electric vehicles, when accelerating and braking, and modern multifunctional portable electronic devices (Laptops, Mobile phones, Tablet PCs, Cameras, etc.), which require different

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**Figure 1.** Taxonomy of materials, configurations and electrolytes for supercapacitors (special attention is paid to carbons).  
**Figura 1.** Taxonomía de los materiales, configuraciones y electrolitos para supercondensadores (con especial atención a los materiales carbonosos).
power profiles depending on the function (Fig. 2a). In addition, supercapacitors exhibit excellent low temperature performance and improve efficiencies in supply systems (such as internal combustion engines, renewable energy systems, batteries and fuel cells) by storing energy when in excess or not needed. As a consequence, apart from automotive and portable electronic devices, supercapacitors find potential application in energy harvesting, renewable energy, electrical grids, wireless sensors and Radio Frequency IDentification (RFID) [2].

As a result, great efforts and multiple research activities are currently driven towards the development of advanced materials and configurations for enhanced energy densities, as well as cheaper preparation and processing methods. Some of these currently most important research lines are analyzed in the following sections.

2. Design of morphology and porosity of carbon materials

The study of the relationship between supercapacitor performance and the texture/morphology/dimensions of carbons constitutes a research topic determinant for the optimization of these systems. Fig. 1 includes a possible general classification of carbon materials used as electrodes in EDLCs. It is mainly based on the type of carbon surface curvature that governs the double layer formation, which in turn, depends on the morphology (particle shape and size) and pore texture (micropore and mesopore volume and pore size distribution) of carbons. Apart from the double layer formation, both features determine the extent and accessibility of the specific surface area of carbons and, therefore, the significance of the double-layer charge storage mechanism.

Graphene and 2D derivatives are the only carbon materials showing (theoretically) no curvature. Their morphology optimizes the double-layer formation, so that the theoretical normalized capacitance of graphene is among the highest of carbon materials (0.21 F/m²) [7]. Carbons with spherical, cylindrical and tubular shape (endothedral carbons), like carbon blacks, onions, gels, nanotubes (CNTs), nanofibers (CNFs), etc. display positive surface curvature and mainly external surface area from inter-particle pores [8]. On the other hand, the inner sidewalls of CNTs and the intra-particle pores of carbons (independently of their particle shape) show negative surface curvature [8]. The last is mainly the case of porous carbons (endothedral carbons), like activated, templated, carbide-derived carbons or activated carbon fibers (Fig. 1). Nevertheless, most of carbons show both types of curvatures because of their morphology and porosity. In general, exohedral carbons display lower power density and normalized capacitance (F/m²) than endohedral ones. On the contrary, the presence of micropores and mesopores remarkably increase the specific surface area of endohedral carbons and, thus, they lead to higher specific capacitances (F/g) and energy densities. Particularly, micropores showing diameters in the range of desolvated ions facilitate higher normalized capacitances (F/m²) than mesopores, whereas this last type of pores facilitates faster ion diffusion for enhanced power densities.

Apart from all these effects on surface area, the morphology and porosity of carbons determine another important characteristic of carbon electrodes, that is, their conductivity. Thus, the smaller the dimensions or the higher the porosity of carbons (for enhanced extent and accessibility of their surface area) usually results in higher inter- and intra-particle resistances, respectively, causing an overall decrease in their conductivity.
conductivity when used as electrodes. Hence, this compromise relationship must be taken into account on the design and engineering of carbons for their use in supercapacitors. Considering all these properties and effects, it is quite difficult to choose which carbon material is generally the best electrode candidate for supercapacitors. In addition, the manufacture cost of carbons and that of their processing into electrodes are also crucial factors for the choice.

Up to now, the highest performance devices already on the market have been high surface-area activated carbon supercapacitors with organic electrolytes (mainly based in acetonitrile). At present, while research is concentrated on finding less-toxic and high-performance organic and ionic liquid electrolytes, the supercapacitor industry moves towards safer aqueous electrolytes. Independently of the electrolyte, graphene is considered the carbon material that will gather the best combination of high energy and power densities, as well as suitable flexibility to be used in stretchable supercapacitors [5-7]. Therefore, for the next future, market forecasts in supercapacitor are strongly focused in graphene [5,6]. Similar perspectives are predicted for the application of graphene in batteries, so that analysts expect that a great part of graphene production will be managed by the energy storage sector (Fig. 2b) [4]. Although the prices of graphene are still very high, it is expected that they will fall as applications and supply volumes emerge. In this sense, the high versatility of graphene and the continuous multi-billion-dollar R&D investment suggest that the so-called ‘killer application’ (in which graphene exhibits a crucial advantage) will be found [4].

From the scientific point of view, however, the theoretical specific capacitance of graphene (550 F/g) is still far to be achieved. This is mainly caused by the strong tendency of graphene layers to stack [7]. Hence, most research activities on graphene-based electrodes are focused on new preparation, modification and assembling routes to avoid graphene stacking [7]. In parallel to graphene, carbon nanotubes (CNTs) are considered attractive potential candidates for future supercapacitors. However, they show lower theoretically-achievable surface area, less expectation for cost reduction and considerable stacking problems too, so their popularity among manufactures seems to have progressively decreased in the last years. On the other hand, because of their high conductivity and electrochemical stability, exohedral carbons (like carbon blacks, carbon onions, etc.) are nowadays used as conductive additives in electrode pastes, but they could be also potential candidates as electrode materials for high power supercapacitors [8]. Besides the high price, their wider usage is highly limited by their low surface area and, therefore, low energy density. Considering all the mentioned drawbacks of graphene, CNTs and exohedral carbons, much research work is being carried out on porosity development by suitable activation treatments [9]. By using this strategy the capacitance and energy density provided by these materials has been successfully increased. However, the overall utility of this strategy should be reconsidered if degradation of their exceptional structure and conductivity (power density) occurs. On the other part of the wide spectrum of carbon materials, activated carbons are comparatively much cheaper and can exhibit much larger surface areas (above 3000 m²/g) because of their well-developed porosity (endohedral curvature). Nevertheless, their amorphous and highly defective structure and their large porosity make them to display low conductivity and electrochemical stability, while their intricate (randomly connected) pore system causes poor ionic transport [1]. As a result, these materials rarely show high power density and their energy density is commonly much lower than that expected form their high surface area [1]. In order to solve these problems, the optimization of the pore size distribution with an adequate proportion of micropores (for optimum charge storage) and mesopores (to favor micropore’s accessibility), by carefully controlling the activation process, is the preferred strategy. Although more expensive, another approach is the utilization of activated carbon fibers, which show a lower interparticle resistance and a better exposed microporosity [1].

For the best design of pore texture, two new families of endohedral carbons have emerged and greatly developed as electrodes for electrochemical capacitors in last decade. These families are carbide-derived and templated carbons. Manufactured by the chlorination of metallic carbides (such as TiC, SiC, etc.) at temperatures of 800–1200 °C, carbide-derived carbons exhibit average pore widths below 2 nm and very narrow pore size distributions (S_{mes} over 1600 m²/g) [1]. On the other hand, templated carbons are produced by filling the pores of an inorganic sacrificial template (zeolites, silica or scaffolds) with a carbon precursor, followed by carbonization and subsequent removal of the template. The use of the template results in a well-defined pore diameter, high surface areas and three-dimensionally interconnected pore networks. Thus, templating is considered the best technology for pore design and engineering hierarchical architectures, giving rise to the highest specific capacitances (among carbons) and fast ion diffusion [1,10]. Due to the high control on the pore texture, both types of carbons show unequalled relevance from a research point of view. Nevertheless, because of their high cost, low carbon yields, as well as safety and environmental concerns associated with production, these materials have limited commercial potential.

Finally, carbon gels (including xero-, aero- and cryogels; sometimes called polymer-derived carbons) are a unique family of exohedral materials with a well-developed porous system [1,11]. These carbons are prepared from organic gels (such as resorcinol formaldehyde) with much more control of the pore size distribution than in the case of activated carbons. In addition, they gather advantages of both exohedral and endohedral materials and can be prepared at relatively low cost (mainly in the case of xerogels). As a result, their specific capacitance outperforms that of the activated carbons so they are considered the most promising alternatives to these conventional materials.

3. Functionalization of carbon materials

The role of surface chemistry of carbon materials, i.e. carbon-bonded functionalities containing
active materials like MnO₂ seems to be one of the possibilities, the combination of CNTs with different price of the electrode is expected. Among different electrodes. Moreover, a marked increase in the rate performance and cycling stability of the carbon the active additives usually reduce the surface area, increase in the overall specific capacitance, however, pseudocapacitance contribution [16,17]. Despite the polymers to form carbon composites with an extra carbons with active metal oxides or conducting materials. The first type of combination is obtained by mixing carbons or redox active materials (see Fig. 1). The first type of combination is obtained by mixing active materials (in the case of composite electrodes) of carbons. Specially, the increase in total capacitance by faradic reactions and effects on electrochemical stability are very important for the energy density of supercapacitors [1]. In spite of such a huge influence and the abundance of related studies, however, little is unambiguously known respect each of these functionalities. This must be mainly due to two factors, namely, (i) the lack of selectivity of current preparation methods and post-functionalization techniques to introduce exclusively the desired surface groups; and (ii) the strong difficulty to assess the sole effects of these groups, while simultaneously affecting the nature and physical properties of carbon materials. In this sense, fundamental research on selective functionalization methods [12,13] and careful systematic studies controlling all the involved parameters are highly demanded.

Particularly, in recent years the benefits from carbon functionalization with N- and P-containing surface groups have been claimed in several papers [14,15]. Nevertheless, the mechanisms of pseudocapacitance and induced stability are still uncertain. On the other hand, the influence of the various functionalities of carbons on their pseudocapacitance and electrochemical stability in non-aqueous electrolytes constitutes less explored topics, despite these aspects could be significant for battery-competing present and future high-energy supercapacitors. Finally, a present challenge under intense study is to optimize the profit of different redox reactions in both the positive and negative potential ranges (in two electrode cells) for the usage of maximum potential pseudocapacitance of carbons. This can be done by balancing the mass of the electrodes and/or the utilization of different optimized carbons for the positive and negative electrodes in an asymmetric configuration [1].

4. Combining carbons with other carbons or redox materials. Composites and configurations

Another important approach to increase the energy density of carbons is their combination with other carbons or redox active materials (see Fig. 1). The first type of combination is obtained by mixing carbons with active metal oxides or conducting polymers to form carbon composites with an extra pseudocapacitance contribution [16,17]. Despite the increase in the overall specific capacitance, however, the active additives usually reduce the surface area, rate performance and cycling stability of the carbon electrodes. Moreover, a marked increase in the price of the electrode is expected. Among different possibilities, the combination of CNTs with different active materials like MnO₂, seems to be one of the most studied and successful composites.

In the second approach, a carbon electrode is externally connected to a different carbon electrode (asymmetric configuration) or a pseudocapacitive- or battery-like electrode in the so called hybrid or asymmetric-hybrid configuration. In this case, however, the objective is not only to introduce pseudocapacitance or faradic capacity (like in batteries), but also to greatly expand the operating voltage [17,18]. Among the proposed hybrid devices, the lithium ion capacitor (LIC) has attracted most attention because of its wide operating voltage (3.8 – 4.0 V), high energy (> 20 Wh/kg) and cycling life in between those of LIBs and EDLCs [18,19]. These devices use a graphite anode for Li⁺ insertion/extraction and AC as positive electrode and their related research is mainly focused on the control of the optimal potential window of both electrodes and the careful selection of the electrolyte.

5. Reducing the manufacturing costs

The utilization of a given carbon material and, therefore, the cost of supercapacitors will rely on the demanded performance for specific applications. Thus, it is expected that different carbon materials will occupy different applications and market niches. Graphene, carbon aerogels and activated carbons are currently considered the main materials to govern these niches. Nevertheless, as the performance of these materials is being progressively optimized by fundamental research, the widespread commercialization of supercapacitors demands greater efforts on a reduction of their manufacturing costs [6]. For a given electrolyte and type of current collectors, the decrease in supercapacitor price can be addressed by using low-cost carbon precursors and simpler and cheaper preparation procedures and electrode processing methods.

Because of their abundance, biomass and natural polymers have been identified as the currently most viable precursors for carbon-based supercapacitors, from both economic and sustainability points of view [20]. In the case of activated carbons and carbon gels, this is already a fact. Remarkably, the valorization of lignin (the second most abundant polymer in nature and substantial by-product of paper and pulp industry and bio-refineries) into different carbons materials for supercapacitors is recently receiving a growing interest [21]. In the case of graphene, however, this approach becomes conceptually more complex. Nevertheless, the preparation of graphene-like materials from natural resources recently constitutes a research subject of increasing attention [22,23].

As for the preparation of carbons showing excellent performance, simpler procedures and approaches without the need of expensive catalysts, templates, reagents and/or excessive temperatures are highly demanded. Furthermore, the simplification of existing methods by reducing the number and length of necessary steps would be desirable. Among different alternatives, the high versatility, simplicity and low-cost of sol-gel [11], electrospinning [24] or hydrothermal carbonization [25] techniques make them very attractive for the production carbons for supercapacitors.

Most of carbons display a small particle size so that, for their usage as electrodes, they necessarily have to be processed in the form of carbon pastes or slurries by the aid of an appropriate binder (usually from 5 to 15 wt%). This binder normally blocks (decreases) the surface, reduces the electrochemical stability and strongly increases the electrical resistance of the electrode. As a result, the utilization of a conductivity promoter (usually carbon black) becomes necessary.
Because of both additives, the total weight and price of the carbon electrodes increase. Moreover, they have to be finely dispersed throughout the fine carbon particles, increasing the time, complexity and cost of the whole process. Hence, the main consequence of pasting is that a carbon electrode is more expensive and shows much lower performance than that expected from the corresponding carbon material. Taking into account all these drawbacks, the preparation of binderless carbon electrodes is the subject of intense research. Among different strategies, the preparation of 3D seamless and/or self-standing architectures (like monoliths, fabrics, webs, nets, etc.) or the deposition of carbon particles directly on current collectors have been found promising approaches [26].

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References

Design of hybrid asymmetric capacitors in aqueous electrolyte using ZTC and ultraporous activated carbons

Diseño de condensadores asimétricos híbridos en electrolito acuso mediante ZTC y carbones activados utraporosos

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Abstract

The use of two different materials as electrodes allows the construction of asymmetric and hybrid capacitors cells with enhanced energy and power density. This approach is especially well-suited for overcoming the limitations of pseudocapacitive materials that provide a huge capacitance boost, but in a limited potential window. In this work, we introduce the concepts and protocols that are required for a successful design of such systems, which is illustrated by the construction of an asymmetric hybrid cell where a zeolite-templated carbon and an ultraporous activated carbon have been combined.

Resumen

La combinación de dos electrodos de distintos materiales permite la construcción de celdas de supercondensadores híbridos y asimétricas, obteniéndose notables mejoras en cuanto a su energía y potencias específicas. Esta estrategia de montaje es especialmente útil en el caso de usar un material pseudocapacitivo, cuya capacidad es notoria, pero limitada a un rango de potencial reducido. En este trabajo, introducimos los conceptos y protocolos necesarios para un correcto diseño de estos sistemas, lo que ilustramos con un ejemplo de la construcción de una celda híbrida asimétrica que combina un electrodo de carbón nanomoldeado con zeolitas y un carbón activado ultraporoso.

1. Introduction

Supercapacitors are electric energy storage systems that show superior power and durability characteristics when compared to secondary batteries, although they lack of sufficient energy density to replace them. This energy density is especially low for aqueous electrolyte supercapacitors, which are greener than their organic counterparts, but can only work at voltages under the potential window stability of water. In order to expand the number of applications where they could serve alone or paired with a battery, it is necessary to implement strategies for increasing their energy density.

There exist some controversy about the use of the terms “hybrid” and “asymmetric”, an issue that has been tried to clarify in the recent literature [1]. The combination in a single device of a supercapacitor electrode that stores charge through the formation of an electrical double-layer and a pseudocapacitive electrode that stores energy through fast surface redox reactions was proposed by Conway in the last decade of the twentieth century [2]. These hybrid devices show an expanded energy density thanks to the higher capacitance of the pseudocapacitive element in aqueous electrolyte, though it comes at the price of lower power density and durability.

On the other hand, two different porous carbon materials with different electrochemical behavior can be paired together in a cell, given rise to what it is called “asymmetric” device. In this configuration, the resulting cell can benefit from the combination of two materials that have a better performance in a specific role, either as positive or negative supercapacitor electrode. In such a way, extended operational voltages or capacitances can be achieved. When the carbon electrodes are made using the same material, but different amounts (i.e. electrode weight or thickness) are placed in the positive and negative electrodes, the obtained cell is also named “asymmetric”, and the reasons for unbalancing the mass of the electrodes are again the same, i.e. obtaining an enhanced cell performance than that achieved using symmetric mass of the electrodes [3].

In this work, we report the development of a supercapacitor cell combining both hybrid and asymmetric strategies. An ultraporous activated carbon obtained through the activation of an Spanish anthracite, which stores energy through the formation of the electric double layer, and a zeolite-templated carbon (ZTC), which is easily functionalized with electroactive surface oxygen groups that stores energy through redox reactions, are used as the carbon electrodes, and two different approaches for selecting the mass ratio between them have been studied.

2. Specifications of a supercapacitor

The most relevant parameters of a supercapacitor cell are the specific energy that it can store and the power it can deliver. The most widely accepted test in the research community for determination of these parameters is galvanostatic discharge of a cell previously charged at the same constant current up to the cut-off voltage, though there are other tests that can be used for more industrial-oriented measurement of energy and power. The amount of stored or delivered energy by a two electrode cell supercapacitor can be calculated as follows:

\[ E = \frac{1}{m} \cdot \int V \cdot dQ \]  \hspace{1cm} (1)

where \( E \) is the specific energy in Jules per gram, \( V \) is the difference of potential between the positive and negative electrodes of the device (volts) and \( Q \) is the charge feed to or recovered from the cell. On the other hand, the specific capacitance of a cell, \( C \), represents the amount of charge the cell is able to store per each volt of difference between their electrodes:

\[ C = \frac{Q}{m \cdot V} = j \cdot \frac{t_{dis}}{V} \]  \hspace{1cm} (2)
In this equation, $t_{dis}$ stands for the discharge time of the process, while $j$ represents the specific current (A g$^{-1}$) applied during the discharge of the cell. Note that energy and capacitance are usually measured during the discharge process, since this is the electrical charge that can be delivered by the cell. It is possible to find that the discharge energy or capacitance of a cell is lower than the charge ones, since part of the charge delivered to the cell during the charge will be wasted in irreversible processes (oxidation or reduction of the electrode surface, electrolyte decomposition, degradation of the collectors...), and as heat dissipated by the Joule effect due to the cell electrical resistance. The ratio of the charge recovered from the cell and the charge employed in charging the cell is called Coulombic efficiency. A similar energy efficiency ratio can be defined for energy delivered from and supplied to the cell. While most supercapacitor devices work under an energy efficiency of 100%, coulombic efficiency should be close to 100% for avoiding undesirable reactions that could compromise the cell stability.

In a purely capacitive electrode, the charge and discharge process are related to the electric double layer formation inside the pores of the system, and if we assume that the capacity value of the electric double layer formation inside the pores is invariant with respect to the mass ratio of the electrodes. It results in the next expression:

\[ \frac{1}{C_+ (m^+ + m^-)} = \frac{1}{m^+ \cdot C^+} + \frac{1}{m^- \cdot C^-} \]  

where $C^+$, $m^+$ and $C^-$, $m^-$ are the specific capacitance and the mass of the positive and the negative electrode, respectively. Snook et al. proposed that it is possible to maximize capacitance for a given m$^+/m^-$ ratio [6], and this optimum value can be calculated by equating to zero the first derivative of Eqn. 7 with respect to the mass ratio of the electrodes. It results in the next expression:

\[ \left( \frac{m^+}{m^-} \right)_{c_{max}} = \frac{C^-}{\sqrt{C^+}} \]  

The other approach that can be taken for enhancing the energy of the cells in asymmetric systems is to maximize the operational voltage by taking advantage of the full potential windows where each electrode are electrochemically stable [3]. In order to do so, both the stability limits as well as the open circuit potential of the electrodes must be carefully determined [7]. The potential window that is able for safe operation of each electrode, denoted as $\Delta E_{+}^{*}$ and $\Delta E_{-}^{*}$ for the positive and the negative electrodes, is estimated as the difference between the positive/ negative potential limits and the open circuit potential. Subsequently, capacitance is measured for each electrode on their maximized potential window. Note that all these measurements must be carried out in a three electrode system in order to control the potential that the electrode is facing in every moment.

Figure 1a presents a scheme of a three-electrode cell like the one used in the next section of this work. That, the working electrode has been prepared from the carbon material to be analyzed using a standard formulation with 5% of binder (PTFE) and 5% of conductivity promoter (carbon black). The counter electrode consists in a platinum wire, which provides the required current by oxidizing or reducing water; since excess of electrolyte is used in the cell, water decomposition will not cause relevant changes in concentration. The counter electrode is placed a few centimeters away from the working one in order to avoid any product to diffuse between them and modify the working electrode response. Finally, an external reference electrode is employed for following the potential of electrodes, providing a precise control of the potential of the working electrode during the experiment.
maximum ones.

while fixing the value of the potential window to the amount of charge stored in each electrode.

Finally, the value of the mass ratio of electrodes that en este trabajo.

la celda de dos electrodos asimétrica híbrida empleadas Figura 1. in this work.

Figure 1. Esquema de (A) la celda de tres electrodos y (B) la celda de dos electrodos asimétrica híbrida empleadas en este trabajo.

Finally, the value of the mass ratio of electrodes that maximizes the voltage can be obtained by equating the amount of charge stored in each electrode while fixing the value of the potential window to the maximum ones.

\[ Q^+ = Q^- \cdot m^+ \cdot C^+ \cdot \Delta E^+ = m^- \cdot C^- \cdot \Delta E^- \]  

(8)

\[ \frac{m^+}{m^-} C_{max} = \frac{C^- \cdot \Delta E_m^-}{C^+ \cdot \Delta E_m^+} \]  

(9)

4. Optimization of hybrid asymmetric cell consisting of ZTC and ultraporous activated carbon in aqueous electrolyte

Zeolite Template Carbons (ZTC) are a family of porous nanostructured carbon material that are obtained by carbon filling of the pore systems of zeolite (a template). After removal of the zeolite, a negative carbon replica of the zeolite structure is obtained. This ordered microporous carbon material is then known as ZTC. These nanostructured materials are very promising for energy storage applications [8]. Using optimized synthesis routes, ZTC consisting of single-layer graphene nanoribbon forming a micropore solid with a narrow pore size distribution centered at 1.2 nm can be obtained. This ZTC has a very high micropore volume (1.56 cm³ g⁻¹) and a surface area of 3600 m² g⁻¹. Thanks to the three-dimensionally ordered structure, micropores are highly interconnected through straight channels, enhancing ion-mobility and therefore providing an outstanding rate performance [9]. Since ZTC structure provides a large amount of edge sites, a huge number of surface oxygen groups can be easily introduced by chemical or electrochemical treatments [10]. Electrochemically functionalized ZTC shows a notorious reversible redox peak in its cyclic voltammogram at potentials over 0.5V vs the reversible hydrogen electrode, which is connected to the fast reduction and oxidation reactions of quinone-type surface groups, and given the large contribution of these redox reactions to the overall capacitance of the electrode, it can be considered as a pseudocapacitive electrode. Although ZTC shows a remarkable behavior as positive electrode in 1M H₂SO₄, it shows a lower capacitance and a low overpotential for the hydrogen evolution reaction at a negative potential range. Thus, the capacitance (and therefore, the stored energy) of symmetric ZTC-ZTC supercapacitor cells is ruled out by the negative electrode.

To take full advantage of the unique properties of ZTC as positive electrode, we decided to pair it in an asymmetric capacitor in which an ultraporous KOH-activated carbon will be used as the negative electrode. The production of this kind of activated carbons has been researched in detail at the beginning of the century [11]. The ultraporous activated carbon used in this work has been prepared using an Spanish anthracite as the carbon precursor, temperature of 750º C and a KOH:coal mass ratio of 3. The resulting activated carbon shows a BET surface area of 3100 m² g⁻¹ and micropore volume of 1.10 cm³ g⁻¹. These activated carbons show high capacitance values in organic and aqueous electrolyte [12], and have been successfully used for the construction of durable supercapacitor symmetric cells and hybrid symmetric cells where this reaction starts to be significant, -0.55V.

\[ \text{Reduction peak appears, a feature that is found in subsequent cycles at the same potential. This current peak is associated to hydrogen evolution reaction, and therefore the maximum potential that can be applied on negative polarization is set to the value where this reaction starts to be significant, -0.55V.} \]

In a similar manner to AC, ZTC was investigated as

In order to establish the potential window and the capacitance for each material, an electrode sheet was prepared by mixing active material (ZTC or AC) with binder (PTFE; PTFE 6−J, Du Pont−Mitsui Fluorochemicals Co. Ltd.) and carbon black (Denka black, Denki Kagaku Kogyo Kabushiki Kaisha). The weight ratio of active material:PTFE:carbon black was 90:5:5. 10 mg of each mixture was formed into a circular-shaped sheet (13 mm in diameter and 0.2 mm in thickness) by pressing inside a stainless steel circular mold. A working electrode was prepared by sandwiching the electrode sheet with a stainless steel mesh as a current collector. Before the measurements, the working electrodes thus prepared were vacuum-impregnated in an aqueous electrolyte, 1 M H₂SO₄, at 40 ºC for 3 h. A spiral platinum wire and a commercial Ag/AgCl (in 3M KCl) were employed as counter and reference electrodes, respectively. The stability window of each electrode has been established by cyclic voltammetry (CV) using a scan rate of 5 mV s⁻¹. It can be seen that the AC electrode shows a purely capacitive behavior, showing a boxy-shape of the CV (Fig. 2a). When the potential of the electrode surpasses -0.5V vs Ag/AgCl, a reduction peak appears, a feature that is found in subsequent cycles at the same potential. This current peak is associated to hydrogen evolution reaction, and therefore the maximum potential that can be applied on negative polarization is set to the value where this reaction starts to be significant, -0.55V. In a similar manner to AC, ZTC was investigated as
positive electrode using CV. A wide hump of slightly irreversible behavior is found on the 0.2-0.4 V range of potential (Fig. 2b). As commented before, the formation of this redox couple in sulfuric acid is the consequence of electrooxidation of the edge sites of ZTC, which readily occurs when the material is submitted to positive potential in this media, generating CO-type surface oxygen groups [10]. When the applied potential reaches values higher than 1.0V, an oxidation peak is obtained, which is related the oxygen evolution reaction occurring on the ZTC surface. Therefore, 1.05V is selected as the upper limit of the safe potential window of operation of ZTC.

Figure 2. Cyclic voltammograms of (A) KUA in negative potential range, (B) ZTC in positive potential range, (C) capacitance-optimized KUA-ZTC cell increasing the operational voltage from 1.4 to 1.8 V and (D) ZTC electrode used in the capacitance-optimized KUA-ZTC cell before and after a durability test. Scan rate: 5 mV s⁻¹.

After determining the potential limits of each electrode, galvanostatic charge discharge (GCD) experiments at a current density of 1000 mA g⁻¹ were carried out in order to determine the capacitance of the electrodes. Specific capacitance was calculated from the GC discharge curves as described before, while the potential cut-offs employed were the open circuit potential of the electrodes (which was found to be 0.22 V and 0.24 V for AC and ZTC, respectively) and the potential limits determined by CV. This way, capacitances values of 310 and 400 F g⁻¹ were measured for AC and ZTC electrodes, respectively.

4.2. Asymmetric cell constructed using a mass ratio optimized for maximizing capacitance

First, the mass ratio of the ZTC and AC electrodes were set in order to maximize the capacitance of the resulting hybrid asymmetric cell. By the precise knowledge gained about the capacitance of each electrode in the intended operational potential window, it is possible to use equation n. 7 to estimate the amount of each electrode:

\[
\left( \frac{m_1}{m_2} \right)_{\text{op}} = \frac{C_1}{C_2} = 0.88
\]  

In consequence, the expected cell capacitance for the asymmetric 2-electrode cell is 88 F g⁻¹ in an operating voltage of 1.6V. Such a supercapacitor cell was constructed using the scheme depicted in Figure 1.b. To prepare the positive electrode, a ZTC sheet with a diameter of 10 mm was attached to a gold current collector by using a conducting adhesive (colloidal graphite suspension, Hitasol GA−715, Hitachi Chemical Co., Ltd.). The ZTC-attached current collector was then dried with an infrared lamp for 1 h and vacuum-impregnated in 1 M H₂SO₄ at 40 ºC for 3 h. Prior to the construction of the cell, this electrode was submitted to cyclic voltammetry in that electrolyte in order to generate the CO-type surface oxygen groups that enhances the capacitance of ZTC. The negative electrode was simply prepared by attaching an AC sheet onto the current collector, following with the same vacuum-impregnation step as the case of ZTC. An asymmetric capacitor was constructed by using ZTC and AC as a positive and negative electrodes with active mass of 8.6 and 9.8 mg, respectively, using a sandwich type configuration, where ZTC and AC electrodes were separated by a membrane filter separator (membrane filter, Nylon 0.45 µm, TR−200140, Tracer). In addition, the potential of ZTC electrode was tracked during the course of either CV or GC experiments by the auxiliary reference electrode.

Fig. 2c shows the CV results of the asymmetric ZTC/AC capacitor loaded at 1.4, 1.6 and 1.8 V. While the supercapacitor seems to be stable at 1.4V, it is not possible to safety operate it at 1.6V, as demonstrated
by the formation of a large irreversible oxidation peak at a voltage of 1.5V. Capacitance retention after 200 cycles at 500 mA g⁻¹ showed a declining of 20% in capacitance. Thanks to the use of the external reference electrode, it was possible to measure the potential of ZTC and AC electrodes when the cell was loaded at 1.6V, being 1.03 and -0.57 V (vs. Ag/AgCl) in this case. Thus, it was proposed that AC was gradually degraded in this configuration. Further polarization to 1.8 V resulted in a serious drop of the capacitance. At this cell voltage, the potential of ZTC reached 1.23 V (vs. Ag/AgCl), which is far above the upper limit potential of ZTC (1.1 V). This result is further confirmed by the malfunction of the capacitor when working at 1.8 V after 50 GCD cycles. Therefore, a new cell was mounted and operated at 1.4V for 5000 cycles at 500 mA g⁻¹, showing an initial capacitance of 90 F g⁻¹ (in close agreement to the expected cell value), and a capacitance retention of 85% [15]. Cyclic voltammetry was again recorded after the durability test (Fig. 2.d), showing a similar capacitance and shape of the CV curve, with an increase in the irreversibility of the redox processes associated to the pseudocapacitive behavior of ZTC. Energy values of 24.5 Wh kg⁻¹ were found for the cell, clearly higher than the ones achieved in the symmetric ZTC/ZTC and AC/AC systems, which showed 15.3 and 20.8 Wh kg⁻¹, respectively.

4.3. Asymmetric cell constructed using electrode mass ratio optimized for maximizing voltage

It is also possible to design the cell attending to the maximizing voltage criteria. As detailed in the previous section, the voltage-optimized electrode mass ratio can be obtained if the operating potential windows and the capacitance of the electrodes are accurately determined. For the ZTC-AC system, the voltage-optimized electrode mass ratio is determined to be:

\[
\left( \frac{m^e}{m^i} \right)_{C_{\max}} = \frac{310 \cdot (0.23 - 0.55)}{400 \cdot (1.05 - 0.23)} = 0.74
\]

which comes from direct substitution on Eqn. 9. Using this mass ratio, the expected two-electrode cell capacitance is 81 F g⁻¹, working in a voltage of 1.6 V. The asymmetric two electrode cell system is mounted as in section 4.2, but this time the active mass of the electrodes were set to be 8.0 and 10.8 mg for ZTC and AC electrodes, respectively. The resulting cell was characterized using GCD experiments at 0.45 A g⁻¹ using a voltage of 1.5V (Figure 3a).

Tracking separately the potential of each electrode allowed to check that, upon full charge, the ZTC electrode was reaching a potential of 0.98V, while AC was reaching a potential value close to its limit, 1.02V. The coulombic efficiency of the system was close to 100%, which points out that the contribution of irreversible redox reactions, like those causing electrode or electrolyte degradation, is negligible in this cell. A durability test conducted under such conditions confirmed that the cell could be safely operated on such a high voltage, showing full capacitance retention (Fig. 3b). This configuration resulted in energy density of 26.8 Wh Kg⁻¹. This better value of energy density in spite of the lower capacitance value of the voltage-optimized cell is not surprising when one consider that voltage contribution to energy density is larger than the capacitance one. Thus, the 8% loss of capacitance is compensated by the 15% gain of energy density due to the larger working voltage.
increase of CO-type evolving groups comes together with a massive formation of CO₂-evolving groups (ca. 4 mmol g⁻¹). This evolution is connected to the presence of carboxylic acid and anhydrides moieties, with the first of them being well-known as electron-withdrawing groups [16,17]. In consequence, a drastically drop in the electrical conductivity of the electrode is expected. Apart from that, the wasted electrode showed an amount of oxygen as measured by TPD larger than 24% in weight basis, which probably hinders the ion accessibility to the surface of the pore system. Such a large amount of surface oxygen groups has been previously reported as the origin of a deterioration of the ordered structure of ZTC [10], so the negative effect of the declining on electrical conductivity is expected to be increased by the destruction of the structure and blockage of the pore system of ZTC.

As conclusion, voltage-optimized approach seems to be better suited for the construction of cell with electrodes of slightly different specific capacitances, as the current case of the ZTC-AC system. For electrodes that shows very different specific capacitances, the capacitance-optimized approach is expected to behave better, since the increase of energy that the increase of voltage can deliver is not expected to improve the increase of energy related to the maximization of cell capacitance.

5. Summary
The design of hybrid asymmetric supercapacitor cells is a simple, yet powerful technique for achieving larger energy density through a wise combination of materials of outstanding electrochemical behavior either as positive or negative electrodes that impeccably complement each other. The mass ratio of the complementary electrodes can be optimized in order to maximize capacitance or voltage. These two approaches have been identified in this work, and for a correct implementation, careful electrochemical characterization using a three-electrode system must be carried out. The design of hybrid asymmetric systems following capacitance-optimized and voltage-optimized approaches have been illustrated by design of a ZTC-AC supercapacitor cell. In this system, energy densities can be expanded from 15-20 Wh kg⁻¹ of the symmetric systems up to 26 Wh kg⁻¹ of the asymmetric ones by implementing the aforementioned design strategies.

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References
Thesis Review. Synthesis of fibrous activated carbons and monoliths for hydrogen storage

M. Kunowsky

OBJECTIVES AND NOVELTY

For a future energy sector, hydrogen is considered a clean alternative to other fuels. As an ideal secondary energy carrier it can be produced from renewable energy sources (e.g., solar, wind, biomass, etc.), and converted very efficiently to electricity in fuel cells, emitting only water. However, one of the main obstacles which impedes the introduction of this technology is the absence of efficient storage solutions. This is strongly related to the low density of hydrogen, which exists as a supercritical fluid under normal conditions. In order to use hydrogen as a fuel, a number of different technologies are considered today. Among them, the high pressure storage in adsorbent materials is a promising technology. The adsorbents for such kind of application require very specific features, depending on the thermophysical storage conditions.

The overall research objective of this study was the synthesis and characterization of activated carbon fibers and nanofibers, as well as monoliths, in order to obtain suitable materials for hydrogen storage. The specific objectives of the research were:

- Identify the optimal parameters of activation, in order to synthesize activated carbon fibers (ACFs) with suitable hydrogen storage characteristics.
- Produce larger amounts of ACFs by up-scaling of the activation process.
- To study the synthesis of activated carbon nanofibers (ACNFs).
- To optimize the density of the ACFs and ACNFs by synthesizing monoliths from them.
- Measure the adsorption of H2 on selected samples and evaluate their total storage capacities.
- Estimate the capacities of H2 storage systems by taking into account the technical specifications of state-of-the-art H2 storage vessels.

The main contribution of this work was the identification of the activation parameters for the synthesis of activated carbon fiber materials with tailored properties for hydrogen storage application. H2 adsorption measurements on ACFs confirm and consolidate results previously reported in the literature. Despite this, exceptionally high hydrogen adsorption amounts were measured for an ACNF at 298 K and 20 MPa. The total H2 storage capacity was established as a useful tool for material characterization. In addition, formulas have been developed for calculating the capacities of H2 storage systems. These formulas provide the opportunity to evaluate the performance of tanks and adsorbents for H2 storage via physisorption.

RESULTS

The research work presented in the Ph.D. Thesis deals with the synthesis of advanced activated carbon materials, in order to use them for hydrogen storage application. A total number of 90 samples were investigated, comprising activated carbon fibers (ACFs), activated carbon nanofibers (ACNFs), as well as activated carbon monoliths from different precursors.

Regarding the synthesis of activated carbon fibers (ACFs), it turned out that the carbonization temperature of the original carbon fiber had a high impact on the porosity development, a detail which previously had not been taken into account. Other activation parameters (activation time and temperature, nitrogen flow, mixing method, etc.) were also studied. By combining different carbonization temperatures of the precursors on the one hand and different amounts and types of activating agents on the other hand, samples with a wide range of porosity development were prepared. Thus, ACF samples with BET surface areas over 3000 m2g−1 and very selective porosity distributions were synthesized. In particular, some samples revealed very narrow distributions of micropores and Vm(CO2) values of around 0.8 cm3g−1 which are particularly interesting for the storage of hydrogen at room temperature. In addition, two scale-up activations were successfully carried out, in order to synthesize large amounts of ACFs with suitable properties for hydrogen storage applications. The amount of sample produced was approximately an order of magnitude higher compared to the laboratory scale activations. The degree of activation was slightly higher for the scale-up activations. Therefore, higher porosity and lower yields than on laboratory scale were obtained. In both scale-ups, the produced ACFs reached BET surface areas of around 2300 m2g−1, high Vm(CO2) up to 0.8 cm3g−1 and packing densities around 0.6 g cm−3.

Activated carbon nanofibers (ACNFs) were produced from a type of carbon nanofiber (CNF) of amorphous nature. Surprisingly, CO2 was more effective when compared with other activating agents (H2O, alkali hydroxides). When CO2 was used as activating agent, a suitable porosity for storing H2 was developed and better activation yields were obtained. BET surface areas up to 2000 m2g−1, Vm(CO2) of 0.6 cm3g−1 and packing densities near 0.5 g cm−3 were reached.

Monoliths were produced from activated carbons, ACFs, and ACNFs, reaching high densities up to 0.7 g cm−3. These were higher than the bulk densities and the densities of the original compressed fibers and close to their packing densities. Furthermore, the porosity of the monoliths generally decreased in comparison with their precursors. The density increased with the amount of binder used for the monolith synthesis. In addition, a commercial high-density AC-monolith (ATMI Co.), which was produced from PVDC, was investigated, increasing its porosity by physical activation with CO2.

Because of hydrogen’s low heat of adsorption in comparison with other gases, its adsorption is favored at high pressures and/or at low temperatures. Both of the scenarios were investigated in the scope of the Thesis for selections of ACFs, ACNFs, and monoliths, covering a wide range of porosity. At liquid
nitrogen temperature (77 K) and up to pressures of 4 MPa, hydrogen adsorption isotherms were measured in a gravimetric equipment. In Figures 1 and 2, the maximum $H_2$ adsorption amounts were plotted against the total volume of micropores, $V_{DR}(N_2)$, taking into account pore sizes < 2 nm. In Figure 1, the hydrogen adsorption amounts are expressed in gravimetric terms. Although different kinds of ACF and ACNF materials were measured, a linear tendency with $V_{DR}(N_2)$ can be observed, confirming results from the literature. In contrast, on a volumetric basis a linear correlation can only be adumbrated for small pore volumes (< 0.6 cm$^3$g$^{-1}$) and is clearly absent in the case of high pore volumes (see Figure 2). Here, the density of the adsorbent gains in importance. Thus, maximum amounts are obtained for optimum combinations of porosity and packing densities. The maximum $H_2$ excess adsorption values on gravimetric and volumetric basis at 77 K and 4 MPa were 5 wt.% and 30 g l$^{-1}$, respectively.

For measurements at room temperature (298 K) and high pressures up to 20 MPa, a volumetric device was used, and measurements of a significantly larger number of samples was performed, including ACFs, ACNFs, and different kinds of monoliths. In Figures 3 and 4, the maximum $H_2$ adsorption amounts obtained under these conditions are plotted against the volume of narrow micropores, $V_{DR}(CO_2)$, with pore sizes < 0.7 nm. On a gravimetric basis (see Figure 3), the values are more dispersed than the results obtained under cryogenic conditions (compare Figure 1); however, the results confirm that the narrow microporosity is the key porosity parameter which determines $H_2$ adsorption at room temperature, confirming previously reported results. Surprisingly, an exception was observed in the case of the ACNF materials: For these samples, the adsorption of $H_2$ was higher than expected from their porosities (see elevated tendency in Figure 3). This characteristic may be due to the presence of some very narrow microporosity in the CNFs. Such very narrow micropores may be accessible to $H_2$ at room temperature, but not to $CO_2$. The different kinetic molecular diameters of both gases (0.24 nm for $H_2$ vs. 0.33 nm for $CO_2$) could be the reason. This could also explain that at 77 K no exceptional high adsorption was measured for the CNF-based samples, because at such low temperature the kinetic adsorption energy of $H_2$ is much lower than at room temperature, so that both gases present similar accessibilities. The room temperature results on a volumetric basis are plotted in Figure 4. The values are even more dispersed that at 77 K (compare Figure 2), and no tendency can be found, due to the important impact of the adsorbents’ densities. Interestingly, some “clusters” can be observed for different materials (see circles in Figure 4). For example, in the case of the ATMI-based monoliths, exceptionally high volumetric $H_2$ adsorption amounts were obtained. This can be contributed to their significant increase of narrow micropores upon activation, and their sustained high densities. In the case of the ACNFs, it can be observed that relatively low volumetric values are reached, due to their low densities. However, upon monolith synthesis, their densities can be substantially increased, so that significantly higher volumetric $H_2$ adsorption amounts are obtained (see arrows in Figure 4). The maximum excess adsorption values that were obtained at 298 K and 20 MPa were 1.3 wt.% and 7.5 g l$^{-1}$, respectively.

The total storage capacity is an extremely important parameter, because it accounts for the total number of gas molecules which is present in a given adsorption tank system. The molecules can either be adsorbed

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**Figure 1.** Maximum hydrogen adsorption amounts on a gravimetric basis, obtained at 77 K and up to 4 MPa, plotted against the total volume of micropores < 2 nm.

**Figure 2.** Maximum hydrogen adsorption amounts on a volumetric basis, obtained at 77 K and up to 4 MPa, plotted against the total volume of micropores < 2 nm.

**Figure 3.** Maximum hydrogen adsorption amounts on a gravimetric basis, obtained at 298 K and up to 20 MPa, plotted against the volume of narrow micropores < 0.7 nm.

**Figure 4.** Maximum hydrogen adsorption amounts on a volumetric basis, obtained at 298 K and up to 20 MPa, plotted against the volume of narrow micropores < 0.7 nm.
in the porous structure of the adsorbent, or exist as a compressed gas phase in the void space (see schematic diagram in Figure 5). The latter contribution appears to be particularly important at high pressures and temperatures. The established formulas strongly depend on the appropriate selection of the material densities. For ACFs, a maximum value of 16.6 g l⁻¹ was reached at 298 K and 20 MPa. The monolith synthesized from this sample reached a higher total H₂ storage capacity of 17.6 g l⁻¹. ACNFs also reached high values up to 17.4 g l⁻¹. At 77 K and 4 MPa, maximum values of around 39 g l⁻¹ were reached.

In order to calculate the capacity of whole H₂ storage systems, formulas were developed which can be applied to any adsorbate, considering various operating conditions and for different combinations of tanks and adsorptive properties. In addition, a dimensionless property κ was introduced which identifies if the storage capacity of an empty tank system can be increased by filling it with adsorbent material. Calculations for a number of existing H₂ containers were performed, assuming their filling with ACF samples that were synthesized in the scope of the Thesis. In all cases, the volumetric system storage capacities increased for storage tanks filled with adsorbent. The gravimetric system storage capacity also increased in the case of storage conditions of 77 K and 4 MPa. Only at 298 K and 20 MPa the gravimetric capacity of the empty vessel was higher compared to the tank filled with adsorbent.

CONCLUSIONS

The main contribution of this work was the identification of the activation parameters for the synthesis of activated carbon fiber materials with special properties for hydrogen storage. H₂ adsorption measurements on ACFs confirm and consolidate previously reported results in the literature. Despite this, exceptionally high amounts of hydrogen were adsorbed on ACNFs at 298 K and 20 MPa. The total H₂ storage capacity is found to be a useful tool for material characterization. In addition, formulas have been developed with the aim to calculate the storage capacities of whole H₂ storage systems. These formulas provide the opportunity to evaluate the performance of tanks and adsorbents for storing H₂ through physisorption. Future research should focus on further characterization of fiber precursors that were carbonized at different temperatures, in order to optimize this activation parameter. In particular, the study of the influence of surface groups, which was not subject of this study, could be interesting.

The scale-up of the activation process could be extended to furnaces with continuous feed; thus, substantially increasing the quantity of produced adsorbent. Similar to the activation process, also the washing step could be improved, e.g. through automatication. The exceptionally high amount of H₂ adsorbed in ACNFs at room temperature and the provided hypothesis (high development of a very narrow porosity) should be further investigated. The total storage capacity of H₂ on a volumetric basis should be established as a standard characterization tool for H₂ storage in porous materials. In gravimetric terms, precise packing densities must be used, in order to avoid unrealistic and overestimated values. The proposed formulas to estimate the capacity of H₂ storage systems should be used, in order to evaluate and/or design tank systems specialized for the storage of gases by physisorption.

RELATED PUBLICATIONS


Full Thesis can be downloaded from www.ua.es
RESEÑA. Profesor Dr. D. Juan de Dios López González (1924-2015)

Don Juan de Dios López González falleció en Granada el pasado 28 de mayo, a los 90 años de edad, después de una breve enfermedad. Para los investigadores españoles que trabajan en materiales de carbón y adsorción ha sido un referente y se puede afirmar que tanto el Grupo Español del Carbón como el Grupo Ibérico de Adsorción que conocemos en la actualidad no serían los mismos sin su importante contribución.


Las estancias en Estados Unidos fueron esenciales para que a su vuelta a Granada él decidiera iniciar las líneas de investigación acerca de los materiales de carbón y adsorción, inicialmente bastante vinculadas. Fue pionero en conseguir en esos primeros años un contrato de investigación con el Ministerio de Agricultura de Estados Unidos, que significó un importantísimo empuje al potencial del departamento y pronto salieron los primeros doctores, aumentando el grupo de forma exponencial. Adicionalmente tuvo la visión de enviar a uno de los primeros doctores a realizar estancias posdoctorales en Inglaterra y Estados Unidos, ejemplo que posteriormente fue seguido por muchos otros de los jóvenes investigadores que iban terminando su doctorado, haciendo cada vez más internacional al grupo de Granada.

D. Juan de Dios era un magnífico investigador pero, más aún, era un extraordinario promotor de la investigación y de investigadores, acertando en las directrices que daba a cada uno de sus discípulos en lo que concernía a su carrera profesional. Él siempre estaba pendiente de cada uno de los miembros del grupo, poniendo los medios necesarios y buscando la forma de ayudar a todos, pero exigiendo siempre una correspondencia en el cumplimiento de la labor encomendada a cada uno. Es por ello que con su dedicación, esfuerzo e interés por la situación de todos lo que le rodeaban surgió de manera natural la “escuela de D. Juan de Dios”, que fue extendiéndose por toda España. Así, muchos de los más de ochenta doctores a quienes dirigió la tesis doctoral fueron distribuyéndose en las Universidades de Salamanca, Extremadura, Alicante, Valencia, Complutense de Madrid, Málaga, UNED, Almería, Jaén, Pamplona, así como en centros públicos de investigación del CSIC, empresas y centros de enseñanza no universitaria. Afortunadamente, el ejemplo de D. Juan de Dios ha sido seguido por muchos de sus discípulos y hoy varios de esos grupos de investigación han alcanzado muy altos niveles de reconocimiento científico a nivel internacional.

Casi toda su carrera universitaria ha estado vinculada a la Universidad de Granada, pasando por todos los cargos posibles, desde estudiante a doctorando (aunque la tesis doctoral la defendió en Madrid por no poder hacerlo legalmente entonces en Granada), Profesor Adjunto, Catedrático, Decano de la Facultad de Ciencias, Vicerrector y finalmente Rector. En su etapa final de Granada realizó una extraordinaria labor como Director del Patronato de la Alhambra, cargo que dejó al marchar en 1981 a la UNED de Madrid. Mencionar aquí que el artículo más citado del Departamento en la UNED sigue siendo uno sobre óxido gráfico publicado en 1995 por D. Juan de Dios y colaboradores en la revista Carbon. También mencionar que su actividad científica se prolongó por más de sesenta años, siendo el último artículo publicado uno sobre intercambio iónico en zeolitas y publicado en J. Colloids & Interface Science en 2007, en colaboración con miembros del Departamento de Química Inorgánica de Granada.

Aunque estuvo en Madrid varios años después de su jubilación (por entonces a los 65 años, en 1989) como Profesor Emérito, siempre estuvo ligado a la Universidad de Granada, en la que fue nombrado Doctor Honoris Causa en 1999; fue poco después, en el año 2000, cuando su esposa Aurora falleció, pero ha estado desde entonces siempre rodeado de sus hijos y nietos (y últimamente un bisnieto).

A él se deben muchas iniciativas de investigación que luego han resultado en grupos de investigación mundialmente reconocidos en los campos de los materiales de carbón, en adsorción/catálisis, etc. De hecho, D. Juan de Dios fue el fundador del Grupo Ibérico de Adsorción en 1975 y en cierta manera el que influyó en la creación del Grupo Español del Carbón constituido algo más tarde (1991). Ambas instituciones han premiado al Profesor López González. Recibió en 1994 el premio GEC en reconocimiento a su extraordinaria labor en la investigación sobre materiales de carbón coincidiendo con el congreso internacional Carbon’94, celebrado en Granada. Por otra parte, el GIA decidió establecer el premio López González a la mejor tesis doctoral en el campo de adsorción realizada en el periodo entre congresos del grupo ibérico; el primero lo entregó personalmente D. Juan de Dios en Baeza el pasado noviembre de 2014.

Si desde el punto de vista científico D. Juan de Dios fue el maestro capaz de formar a un elevado número de discípulos y constituir lo que fue su escuela, más importante aún era su extraordinaria humanidad y caballerosidad. Muchos de los científicos con quienes hemos coincidido a lo largo de muchos años siempre preguntaban por él y destacaban no sólo su capacidad investigadora y creadora de escuela, sino además su carácter encantador, aunque aparentemente se le pudiera percibir como serio y algo tímido. Capaz de cultivar amistades y hacerse querer por mucha gente, tuvo la oportunidad de recibir en el departamento de Granada a renombrados investigadores. Profesores de la talla de G. Wilkinson (Premio Nobel de Química del año 1973), N.N. Greenwood, P.L. Walker, K.S.W.
Sing. J. Rouquerol, etc., lo definían como *gentleman* y persona extremadamente agradable con quien se podía hablar de todo. Y esto, afortunadamente, se ha mantenido así hasta pocos días antes de su fallecimiento, cuando se podía hablar con él de cualquier aspecto de la vida universitaria de Granada, que conocía y recordaba perfectamente. Su pérdida ha sido muy importante para su escuela, pero estará siempre entre nosotros como ejemplo a seguir en todos los aspectos de la vida. Finalmente, enviar desde el Grupo Español del Carbón nuestro más sentido pésame a sus cuatro hijos, nueve nietos y bisnieto.

Francisco Rodríguez Reinoso
RESEÑA. Curso Materiales Nanoestructurados para Conversión y Almacenamiento de Energía (MANACAE-2015)

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Del 17 al 19 de junio de 2015 se celebró en el Instituto de Carboquímica de Zaragoza el curso Materiales Nanoestructurados para Conversión y Almacenamiento de Energía (MANACAE-2015), organizado por el Grupo Español del Carbón (GEC), el Instituto de Carboquímica (ICB) del Consejo Superior de Investigaciones Científicas (CSIC), el Instituto de Nanociencia de Aragón (INA) de la Universidad de Zaragoza y el Departamento de Ingeniería Química y Tecnologías del Medio Ambiente (IQTMA), ambos dos últimos de la Universidad de Zaragoza. El comité organizador estuvo constituido por las doctoras Mª Isabel Suelves Laiglesia y Mª Jesús Lázaro Elorri, representantes las dos del GEC y del ICB, y los doctores Carlos Téllez Ariso y Joaquín Coronas Ceresuela, ambos del INA e IQTMA.

En el curso se impartieron un total de 20 horas que se estructuraron en tres días de ponencias y visitas a instalaciones de investigación del ICB y del INA. En el curso se matricularon un total de 42 personas procedentes de diversas localidades y entidades (ICB-CSIC, Univ. de Zaragoza, Univ. de Alicante, Univ. de Granada, Instituto de Catálisis y Petroleoquímica ICP—CSIC y del Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas CIEMAT), siendo en su gran mayoría estudiantes pre y postdoctorales con interés y/o actividad en el ámbito del desarrollo de materiales para aplicaciones relacionadas con la energía.

En la apertura del curso se contó con D. Miguel Ángel García Muro (Director General de Investigación en Innovación, DGA), D. Jesús Santamaría Ramiro (Subdirector del INA), D. Antonio Monzón Bescós (Director del IQTMA) y D. Victor Orera Clemente (Coordinador Institucional de la Agencia Estatal CSIC Aragón). Tras ella, tuvieron lugar las diversas conferencias con un total de 15 ponentes de diferentes entidades: Univ. Zaragoza (IQTMA e INA), Univ. Alicante (Instituto de Materiales y Departamento de Química Inorgánica) CSIC (ICB, ICP e Instituto Nacional del carbón INCAR) y Centro Universitario de la Defensa de Zaragoza.

En las jornadas se dio una visión general a los materiales basados en el carbono y a los materiales porosos cristalinos con los que hacer frente a los retos energéticos del siglo XXI. Retos que de alcanzarse serán garantía de bienestar y empleo para las generaciones presentes y futuras. En la primera jornada del curso se comenzó presentando la evolución de los materiales carbonosos desde el carbón activo al graeno y se profundizó en la química y aplicaciones del graeno. También se presentó una visión global del estado del arte y líneas actuales de investigación de los materiales carbonosos nanoestructurados profundizado en dos aplicaciones concretas: la conversión catalítica de recursos energéticos y su uso como supercondensadores. También se presentaron nanomateriales fotocatalíticos para combatir la contaminación y
obtener energía así como se mostraron recientes logros y futuros desafíos en electrocatálisis para pilas de combustible de electrolito polimérico.

La segunda jornada se inició de nuevo con materiales de carbono avanzados y novedosos para dos usos de gran interés como son la aplicación en baterías de ion litio y el almacenamiento de gases y aplicaciones espaciales. Además se analizó en detalle una realidad industrial generada de la investigación científica como son los xerogeles de carbono para electrodos de súper-condensadores. A continuación se realizó una presentación general de los materiales porosos cristalinos donde actualmente las zeolitas tienen un papel destacado pero el reto investigador no cesa y actualmente los Metal Organic frameworks (MOFs) se postulan como posible alternativa, por lo que se analizó su preparación y sus futuras aplicaciones. Dentro de los nanomateriales para aplicaciones energéticas se ahondó en materiales laminares como silicatos y calcogenuros metálicos. En la última jornada se presentaron nuevos desafíos como las membranas basadas en MOFs para separaciones en fases gas y líquida, así como se mostraron dispositivos más eficientes para la producción de hidrógeno como son los reactores de membrana y microreactores. Finalmente se expuso la estrategia en el desarrollo de materiales nanoestructurados para craqueo catalítico como vía futura para la producción de biocombustibles de segunda generación. Tras el cierre oficial de las jornadas por parte de D. Luis De Diego Poza (Director del Instituto de Carboquímica) se produjo la entrega de diplomas a los alumnos. En resumen, este curso MANACAE ha sido una exitosa ocasión de acercar los nanomateriales a los futuros profesionales de la ciencia, la docencia y la industria, y esto sin descuidar el debate, la discusión y la camaradería.
Socios protectores del Grupo Español del carbón