

Carbon blacks as active materials for electrochemical double layer capacitors

Negros de carbón como materiales activos para condensadores electroquímicos de doble capa

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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 (Et_4NBF_4) 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 10^{-1} to 10^2 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 (Et_4NBF_4) 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 $1500 \text{ m}^2 \text{ g}^{-1}$, 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 ($1805 \text{ m}^2 \text{ g}^{-1}$) with respect to the AC ($1509 \text{ m}^2 \text{ g}^{-1}$). 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

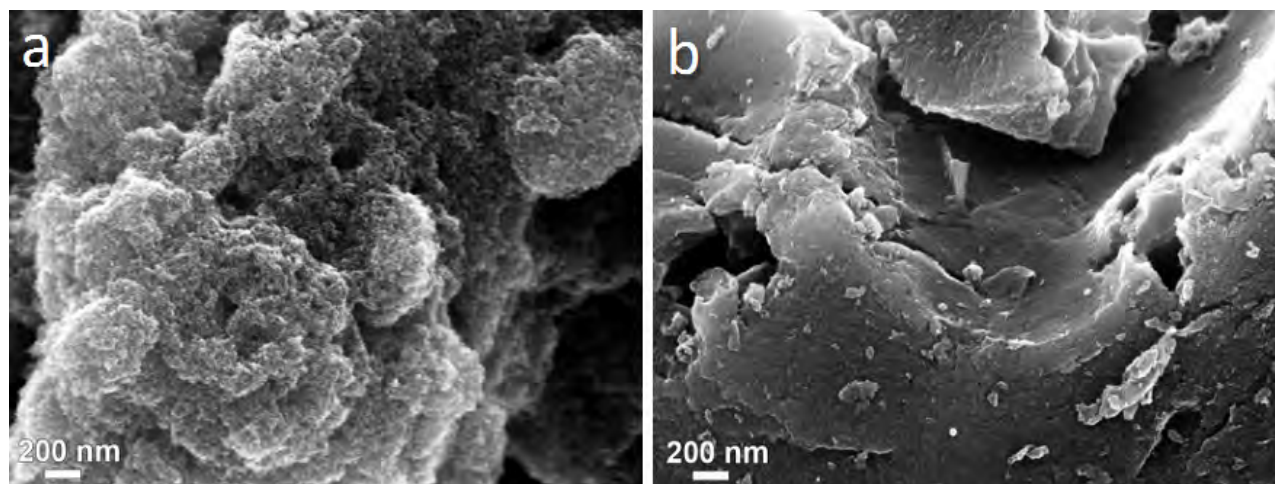


Figure 1. SEM images of CB (a) and AC (b).

Figura 1. Imágenes SEM del negro de carbón (CB) (a) y el carbón activado (CA) (b).

Table 1. Comparison of specific surface area and pore characteristics of CB and AC.

Tabla 1. Comparación del área superficial específica y propiedades texturales del negro de carbón (CB) y el carbón activado (AC).

sample	BET-area [$\text{m}^2 \text{ g}^{-1}$]	DFT surface area [$\text{m}^2 \text{ g}^{-1}$]	TPV [$\text{cm}^3 \text{ g}^{-1}$]	$V_{\text{micro}}/V_{\text{meso}}$
CB	1805	1344	2.49	0.8
AC	1509	1133	0.90	6.5

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

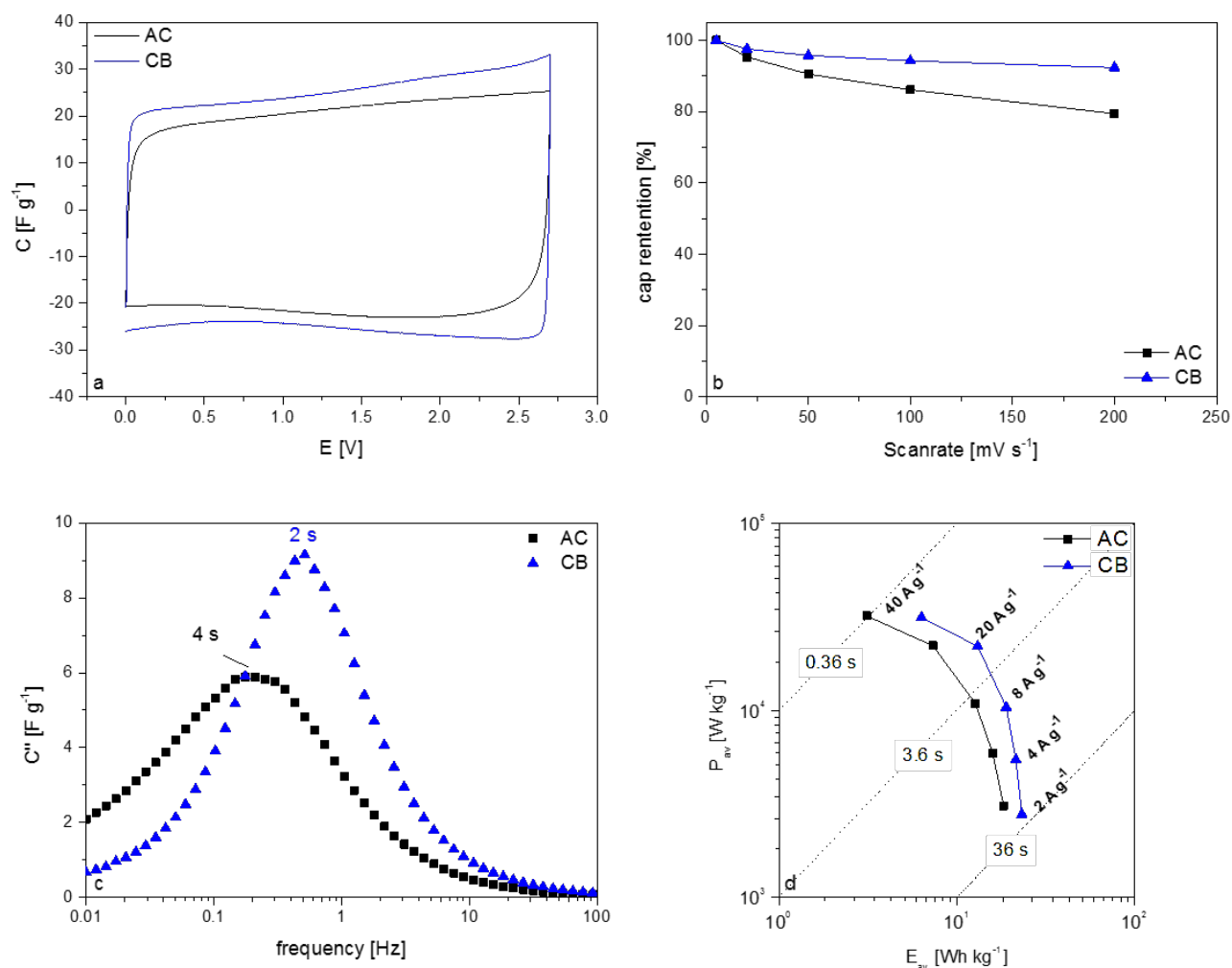


Figure 2. (a) Cyclic voltammety of EDLCs containing CB and AC as active material at a scan rate of 20 mV s^{-1} ; (b) Capacitance retention of EDLCs containing the investigated materials; (c) Evolution of the imaginary part of the complex capacitance vs. frequency of EDLCs containing CB and AC as active material. (d) Ragone plot for EDLCs based on the investigated active materials. Both average energy and power are referred to the total mass of active material.

Figura 2. (a) Voltametría cíclica de los supercondensadores (EDLCs) con negro de carbón (CB) y carbón activado (AC) como materiales activos a 20 mV s^{-1} ; (b) Retención de la capacidad de los supercondensadores con los materiales investigados; (c) Evolución de la parte imaginaria de la capacidad frente a la frecuencia de los supercondensadores con los materiales investigados; (d) Diagrama de Ragone de los supercondensadores con los materiales investigados. Tanto la energía como la potencia están referidas a la masa total del material activo.

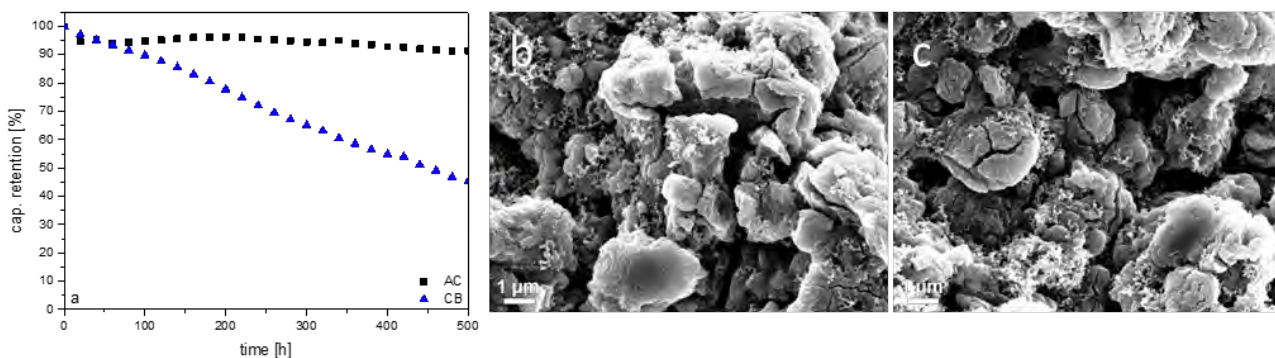


Figure 3. Capacitance retention of CB-based and AC-based EDLCs during float test carried out at 2.7 V for 500 h (a); SEM images of the positive (b) and negative (c) CB electrodes at the end of the float test.

Figura 3. Retención de la capacidad de los supercondensadores (EDLCs) basados en negro de carbón (CB) y carbón activado (AC) durante ensayos tipo floating llevados a cabo a 2.7 V durante 500 h (a); Imágenes SEM del electrodo positivo (b) y negativo (c) de negro de carbón al final del ensayo tipo floating.

the EDLCs containing CB as active material retained less than 50%. As show 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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