



Capacitance and surface of carbons in supercapacitors



Belén Lobato, Loreto Suárez, Laura Guardia, Teresa A. Centeno*

Instituto Nacional del Carbón (INCAR-CSIC), Francisco Pintado Fe, 26, 33011 Oviedo, Spain

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ABSTRACT

This research is focused in the missing link between the specific surface area of carbons surface and their electrochemical capacitance. Current protocols used for the characterization of carbons applied in supercapacitors electrodes induce inconsistencies in the values of the interfacial capacitance (in $F\ m^{-2}$), which is hindering the optimization of supercapacitors. The constraints of both the physisorption of N_2 at 77 K and the standard methods used for the isotherm analysis frequently lead to a misleading picture of the porosity. Moreover, the specific surface area of carbons loses their meaning when the supercapacitor operates with organic electrolytes and ionic liquids and the actual surface involved in charge storage has to be assessed by molecular probes suiting the critical dimensions of the ions. In the case of certain carbons such as graphene type-materials, the voltage-driven mechanism may facilitate the access of electrolyte ions to spaces between carbon layers, providing a larger area than that estimated by gas adsorption. Finally, the morphological and porous features of carbons can be extremely modified when they are processed in electrodes. Due to their impact, all these issues should not be neglected and the characterization protocols must be adapted for this specific application of carbons.

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1. Introduction

The great technological implementation of nanoporous carbons stems from the opportunity to be produced with a tailored porosity in a variety of configurations. They are found as powders, fibers, foams, cloths, monoliths, etc. and as a result of their wide spectrum of porous features are able to suit multiple applications in very diverse industrial processes. For many years, they have acted as purification filters, adsorbents for emissions control, catalyst supports, host matrices for active materials, etc. [1]. In the last two decades, nanoporous carbons have also found a niche in electrical energy storage as electrodes in electrochemical double-layer capacitors, EDLC (also known as supercapacitors, SC) [2,3].

All these applications correspond to very different processes but their description essentially relies on porosity parameters such as pore volume, specific surface area and poresize distribution. It follows that the standard textural characterization of carbons for adsorption or catalysis is also applied when they are used in EDLC systems.

The porosity of carbons is generally assessed by the determination of the adsorption isotherm (amount of gas adsorbed at

increasing relative pressure and constant temperature) of small molecules such as N_2 , CO_2 , Ar, etc. There are different methods for analyzing the corresponding isotherms which provide the specific surface area as well as other porous features responsible for their performance [3–6].

In carbon-based SC, electrical energy storage takes place through the electroadsorption of electrolyte ions at the surface of charged carbon electrodes. This mechanism implies that the capacitance (C) is proportional to the extent of the electrochemical double-layer (S) and to the relative permittivity of the solution (ϵ) and reciprocally dependent on the charges separation (d)

$$C = \frac{\epsilon S}{d} \quad (1)$$

Following the simplest approach from Eq. (1), the capacitance is expected to be proportional to the specific surface area of the carbon used in the electrode.

In the case of carbons for supercapacitors, their characterization is carried out routinely with N_2 at 77 K and the most popular approach to evaluate the specific surface rests on the BET method (S_{BET}). The more recent availability of a variety of DFT based-methods in commercial adsorption equipments has boosted their use for the assessment of both the pore size distribution (PSD) and the specific surface area (S_{DFT}). Quite frequently, the average pore

* Corresponding author.

E-mail address: teresa@incar.csic.es (T.A. Centeno).

size from DFT is combined with S_{BET} although they are based on completely different models and S_{DFT} and S_{BET} are often different [7–9].

The lack of a clear linear relationship between C and S_{BET} or S_{DFT} encouraged studies on the specific role of carbon porosity in the formation of the double layer and a variety of interpretations were proposed. Among others, it has been argued that porous carbons often have a significant proportion of narrow micropores inaccessible to ions of electrolyte and, therefore, the entire surface is not used for charge accumulation [10,11]. This hypothesis seems reasonable but it results puzzling that the capacitance tends to level off in microporous materials with pores mostly above 1.2–1.5 nm in width and negligible ultramicroporosity (<0.7 nm). In this context, the limitation of C in highly porous carbons was ascribed to a space constriction for charge accommodation inside their very thin pore walls. Carbons, being semiconductors, do not feature high charge-carrier density and the space-charge capacitance would be more limited for those with larger surface area [12,13].

It was also suggested that the capacitance corresponds to separate contributions from the surface of the micropores walls (C_{mi}) and the external surface (C_{ext}) [14,15]. The fact that the sets of C_{mi} and C_{ext} values differ between types of carbons [14–19] reveals that this approach does not provide a general description of carbons in SC.

The finding that the double-layer capacitance of the edge orientation of graphite was one order of magnitude higher than that of the basal layer [20] led to conclude that carbons with similar specific surface area but higher ratio of edge/basal orientations would reach higher capacitance [21–23].

More recently, it was pointed out that pores with sizes matching the ions dimensions result more effective for charge storage, maximizing the capacitance normalized to the surface area (in F m^{-2}) [8,9,24].

Finally, it was reported that the puzzling interfacial capacitance found for certain highly porous carbon electrode materials may be originated by a quantum capacitance component of graphene layers, in addition to surface area [25].

In order to address such outstanding questions, here we summarize a comprehensive study on the correlations between surface and electrochemical capacitance of a wide variety of carbons tested as SC electrodes under the same conditions. It is found that the standard textural characterization of carbons may be very limited to evaluate their actual porosity involved in charge storage. The protocols must be adapted for eliminating possible inconsistencies between textural parameters and capacitance. In fact, a critical re-examination of current insights and theoretical models will certainly benefit the technological development of supercapacitors with optimal performance.

2. Experimental

2.1. Carbons

This extensive study is based on a wide variety of carbons of different origins and obtained by diverse procedures. They include activated carbons, graphite, nanotemplated mesoporous carbons, carbide derived-carbons, carbon gels, graphene related-materials (graphite oxides, reduced graphite oxides, graphene oxide, etc.). Details on the main structural, textural, chemical and electrochemical characteristics of most of them have been previously reported [18,26–49].

2.2. Characterization of the porous structure

The porosity features of all samples were determined with the

help of the combination of different techniques. In a first step, N_2 adsorption at 77 K (Micromeritics ASAP 2010) was used for routine measurements. The specific surface area was determined by the analysis of the isotherm by the BET equation as well as by diverse DFT models (Micromeritics and Quantachrome software packages). Furthermore, the results were cross-checked by applying Kaneko's comparison plot technique and Dubinin's theory. For certain samples, data from the adsorption of CH_2Cl_2 (293 K), C_6H_6 (293–298 K), CO_2 (273 K), CCl_4 (293–298 K) and 2,5-norbornadiene (273 K) isotherms (gravimetric McBaine type apparatus) were also used [3–6]. The characterization of a selection of carbons was complemented with the adsorption of CO_2 at 273 K (Micromeritics TriStar 3000) and the corresponding analysis by NLDFT approach and Dubinin-Raduskevich equation. For a better assessment, the surface area was also evaluated by immersion calorimetry into 0.4 M aqueous solution of phenol [5,6].

Gas adsorption (DFT models) and immersion calorimetry (293 K) into liquids with different critical dimensions provided the pore size distributions [5,6,38,47].

2.3. Determination of the electrochemical capacitance

The electrochemical capacitance of carbons was assessed in a sandwich-type capacitor, set up with two carbon pellets (8–10 mg, 8 mm diameter, 100–300 μm thickness), separated by a glassy fibrous paper (300 mm thick) and placed in a Swagelock cell. The electrodes were obtained by pressing a mixture of the carbon (75 wt%), PVDF (20 wt%) as binder and carbon black (Super P, 5 wt %). Following another procedure, a mixture of 90 wt% of carbon, 5 wt% of PTFE and 5 wt% of Super-P was rolled and punched into pellets. The electrodes were dried overnight in an oven at 100 °C prior to be tested.

The capacitance was determined by galvanostatic charge-discharge cycles (Autolab-Ecochimie PGSTAT 30) at a constant current density of 1 mA cm^{-2} from 0 to 0.8 V for 2 M aqueous H_2SO_4 and between 0 and 2 V for the organic electrolyte 1 M $(\text{C}_2\text{H}_5)_4\text{NBF}_4$ in acetonitrile ($\text{Et}_4\text{NBF}_4/\text{AN}$). The results were further confirmed by cyclic voltammetry at 1 mV s^{-1} . The values of the gravimetric capacitance (F g^{-1}) are relative to the mass of the carbon under study in a single electrode.

3. Results and discussion

3.1. Specific surface area

Eq. (1) suggests that a large specific surface area (S) of carbons is the most important parameter leading to a high gravimetric capacitance (C). However, as illustrated by Fig. 1a and b, the gravimetric capacitance of a wide variety of carbons in both aqueous (H_2SO_4) and organic ($\text{Et}_4\text{NBF}_4/\text{AN}$) electrolytes does not increase linearly with the specific surface area estimated by the standard BET method.

BET equation is the most widely used approach for determining the specific surface area of supercapacitors carbons but its limitations for microporous materials should be taken into account. This equation was developed to explain the adsorption of multilayers on open surfaces and provides reliable values of the specific surface area from the monolayer capacity and the corresponding molecular cross-sectional area of the adsorbate. On the contrary, this approach results misleading when applied to microporous carbons since BET-surface reflects the area equivalent to the total volume adsorbed [3–5,50].

In spite of the specific weaknesses of each of the methods available for the interpretation of physisorption isotherms [3,4,50], the systematic analysis carried out on a variety of carbons has found

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