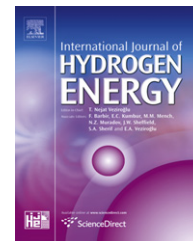


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Carbon xerogels as electrochemical supercapacitors. Relation between impedance physicochemical parameters and electrochemical behaviour

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ARTICLE INFO

Article history:

Received 25 August 2011

Received in revised form

22 December 2011

Accepted 31 January 2012

Available online 25 February 2012

Keywords:

Electrochemical supercapacitors

Porous electrodes

Electrochemical impedance spectroscopy

Interfacial area

ABSTRACT

The electrochemical behavior of carbon xerogels was studied with the aim of analyzing the performance of the materials used as electrochemical supercapacitors (SC) and to relate with physicochemical parameters. These materials have areas involving 1500–2000 m²/g measured with the BET equation and a range of pore size distributions.

Conventional electrochemical techniques were used as cyclic voltammetry (CV), which allowed electrochemical characterization of different materials, and chronopotentiometry (CD), in order to determine the charge storage capacity of the xerogel at different currents or discharge rates.

Experimental results using electrochemical impedance spectroscopy (EIS) were interpreted with a physicochemical model that permitted identifying different parameters of the electrode, which explain the differences in the behavior of materials.

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1. Introduction

The electrochemical supercapacitors (SC) are devices through which electric charges are stored in the electrical double layer (EDL) for each of the high surface area carbon porous electrodes involved. On the other hand, in the batteries, the charge storage process is essentially faradaic, since electron transfer takes place that changes the chemistry of electroactive compounds. The differences in the processes that occur in each of these devices generate features that are opposed, making them suitable for use in different technologies or working in a complementary manner in a single system [1]. The most striking differences between them are: i) The SC can

store a much smaller amount of energy than the batteries (~10 Whkg⁻¹ for SC in aqueous electrolyte and 150–250 Whkg⁻¹ for a lithium-ion battery). ii) The power densities of the SC are even nine times higher than those of lithium-ion batteries, namely, 6.4 vs. 0.7 kWkg⁻¹ [2,3]. iii) A device based on charge and discharge of the EDL involves an entirely reversible process allowing a number of charge–discharge cycles of several orders of magnitude higher than batteries, in which cycle to cycle are produced changes that gradually degrade electrodes irreversibly [1].

In this work, we have synthesized and chemically activated carbon xerogels with high area and a range of pore size distribution. This allowed evaluating the behavior of each

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doi:10.1016/j.ijhydene.2012.01.154

material as SC and their relationship with physicochemical properties of the carbons. Carbon gels are porous materials interesting for use in this area due to its structural characteristics that can be selected by adjusting the conditions used in the synthesis and subsequent processing of materials [4–6].

While this work can be framed within a specific application, it focuses on discussing basic aspects of electrochemistry that are often neglected, incurring in wrong definitions or assigning a determined behavior to erroneous factors. In this context, there is a very detailed discussion about electrochemical interface area, which is important parameters for all basic electrochemistry areas, especially for electroanalytical chemistry and electrocatalysis discussions.

2. Experimental

Carbon xerogels were used, which were impregnated with PTFE TE-3893[®] (an aqueous dispersion of a fluoropolymer resin): i) M1 10% PTFE; ii) M2 30% PTFE; iii) M3 15% PTFE; iv) M4 10% PTFE. Moreover, as comparative parameter was used carbon Supra 30 DLC (Norit[®]) 10% PTFE, designated S30. In all cases a minimum quantity of PTFE were used in order to bring about a minimum change on the properties of the as-prepared carbon material.

The electrodes were prepared by introducing those carbon xerogels impregnated with resin inside a steel pillbox in which had previously placed a Ni wire skeleton, then applying a pressure of 2100 kgcm⁻².

2.1. Synthesis of carbon Xerogels

Carbon xerogels used in this work were constructed as follows. First, an organic xerogel (OX) was synthesized using an RF solution through a microwave radiation treatment, according to a procedure described elsewhere [7]. Subsequently, several materials were obtained: i) M1 is an OX prepared with an RF solution (pH = 6.5) and activated with KOH in a microwave oven ($T = 700\text{ }^{\circ}\text{C}$ for $t = 6\text{ min}$). ii) M2 was synthesized in the same way as for M1, being activated in a horizontal furnace during 2 h iii) M3 is an OX prepared with an RF solution (pH = 5.8). Then, it was stabilized heating at 800 °C in N₂ atmosphere to obtain a carbon xerogel, which was then activated with KOH in the same way as that for M2. iv) M4 was obtained equally to M3 but RF solution with pH = 6.5.

2.2. Electrochemical system

The electrochemical experiments were performed using a cell of three electrodes in 6M KOH aqueous solution. As working electrode teflonated carbon xerogels were used; the counter electrode was a nickel mesh and as the reference electrode was used Hg/HgO/6M KOH (+0.098 vs. NHE). In the text, the potentials are referred to the electrode employed as reference. All experiments were performed at room temperature.

2.3. Characterization

The textural characterization of the samples was carried out through physical adsorption of N₂ at 77K, using a Micromeritics

model TriStar II. The volume of micropores, V_{mic} (cm³g⁻¹), was achieved by applying the Dubinin-Radushkevich (DR) method [8] to the N₂ adsorption isotherms. From the volume of the micropores and the average size of the pores (L_p) can be obtained the surface area of micropores ($S_{\text{mic}} = 2V_{\text{mic}}/L_p$) applying Stoeckli equation [9]. The BET area was also evaluated using the N₂ adsorption isotherms [10]. The structure of the samples was assessed using a transmission electron microscope (TEM). The images were taken with a JEOL JEM-2000 EX II.

The conductivity measurements of carbons were carried out at atmospheric pressure, using an apparatus made in the laboratory, which is a modification of the van der Pauw technique [11].

3. Results and discussion

3.1. Carbon characterization

3.1.1. Transmission electron microscopy (TEM)

Fig. 1A and B show images of one of the xerogels with and without Teflon, respectively. Fig. 1A clearly exhibits the structure of a typical amorphous xerogel, whereas the 1B shows the loss of the porous structure characteristic of the material due to masking by the homogeneous deposition of polymer on the surface.

3.1.2. Textural characterization

Fig. 2 shows the isotherms performed with N₂ at 77K for different electrodes. Usually, measurements are made with the carbons in his pristine state. Although we found that the addition of 10% PTFE slightly changes the features of those isotherms, the fact that for the construction of the electrodes is required to apply pressure to the carbons impregnated with Teflon leads to a decrease of the textural characteristics of the materials. For this reason, it was necessary to obtain the isotherms of the electrode materials. These were classified into two groups. Thus, M2 and S30 samples exhibit a type I isotherm, which correspond to the presence of predominantly microporous materials (but also have small mesopores), while M1, M3 and M4 reveal hysteresis cycles, showing isotherms of type I-IV, being characteristic of micro-mesoporous materials [12].

Table 1 shows a summary of the parameters calculated by means of the isotherm measurements, which are related to the porosity and surface area of materials. These are: i) the area calculated by BET equation (S_{BET} in m²g⁻¹); ii) the volumes represented by mesopores and micropores in cm³g⁻¹; iii) the average size of micropores, L_p in nm. Moreover, in the last column is placed the solid conductivity measurement, σ , expressed in Scm⁻¹.

3.2. Electrochemical measurements

3.2.1. Cyclic voltammetry (CV) and potentiometry (CD charge and discharge)

VC was conducted by performing triangular potential sweeps at $v = 1.10^{-3}$, 3.10^{-3} , 5.10^{-3} and 1.10^{-2} V^{-1} . Potential limits were set to show only the region of purely capacitive behavior.

Fig. 3 shows voltammograms for all the carbons utilized, made at $v = 1.10^{-2}\text{ V}^{-1}$. For these electrodes a clear deviation

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