

Evaluation of nafion based double layer capacitors by electrochemical impedance spectroscopy

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Abstract

In this work some electrochemical characteristics of all solid double layer capacitors prepared by high surface carbon and Nafion polymer electrolyte are reported. Carbon composite electrodes with a Nafion loading of 30 wt.% were prepared and evaluated. Nafion 115 membrane, recast Nafion membrane and 1 M H₂SO₄ solution in a matrix of glass fiber have been used as electrolyte, in the double layer capacitors. The different double layer capacitors (DLCs) have been evaluated by electrochemical impedance spectroscopy. The capacitor with a recast Nafion electrolyte exhibits a proton conductivity of about $3 \times 10^{-2} \text{ S cm}^{-1}$ at ambient temperature, that is higher of that reported for solid electrolytes (10^{-3} to $10^{-4} \text{ S cm}^{-1}$) in the current literature on capacitors. A maximum of specific capacitance of 13 F/g of active materials (carbon + Nafion) corresponding to 52 F/g for a single electrode measured in a three-electrode arrangement has been achieved with the capacitor with recast Nafion. The capacitance of the capacitor with recast Nafion electrolyte, evaluated in low-frequency region below 10 mHz, was practically equivalent at that with sulphuric acid electrolyte. The interpretation of the characteristics of the microporous structure of carbon material of the electrodes by impedance analysis is also discussed.

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1. Introduction

The growing interest in high power and energy density capacitors is connected with the increasing demand of portable power sources and with the potential application, as secondary power supplies, in electric vehicles [1–3]. Generally, double layer capacitors (DLCs) are compact, lightweight, environmentally friendly power devices able to deliver high power on demand. Therefore, they are a good approach in systems requiring high power and remarkable energy. The structure of a DLC, known also as electrochemical capacitor or ultracapacitor or supercapacitor, is similar at that of a battery but the nature of charge storage at the electrodes is different. In DLCs, the electrical storage is purely capacitive, i.e. it is deriving from electric charge separation at the electrode/electrolyte interface and not from electrochemical reactions at the electrode surface. In general, the current generated at the electrode of whatever energy storage system, has to be accounted for either by faradaic reactions, surface charge transfer, or charge separation in the double

layer. Normally, the electrodes of electrochemical capacitors are identical and the electrical charges are accumulated in the double layer by electrostatic forces [1]. On the contrary, in batteries, the faradaic reactions are dominant and the materials, which form the electrodes, take place in the electrochemical reactions, while a minimal double layer effect is present.

Double layer capacitors have several advantages compared to secondary batteries, as longer cycle life (>100,000 cycles), simpler design of device, shorter charging time, more safe, and higher power density [4,5]. The electric power density delivered from capacitors is one of the most remarkable characteristics. In fact, the power density of DLCs generally is larger than that of secondary batteries. Unfortunately, the same is not for energy density that is lower with respect to batteries [6]. Therefore, in most applications, the capacitors have to be considered as secondary power sources, requiring primary electric energy sources, such as fuel cells or batteries [7]. DLCs are especially indicate in applications in which pulse power is required because they allow to utilise primary electric sources of smaller size and to extent the life time of these latter [1,8]. Nowadays, the DLCs are used in the field of consumer electronics such as digital wireless devices and memory back-up systems.

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Moreover, they are also used as auxiliary power sources in small appliances as laptop computers, alarms devices, cellulators and camcorders. The double layer capacitors are also low cost, maintenance-free and long life devices.

In order to apply the electrochemical capacitors as auxiliary systems in hybrid or electric vehicles, they should deliver both high power and sufficient energy. The latter aspect is under study and requires further improvement. From the technological point of view, a commercial DLC is made of two electrodes constituted by carbon of high surface area and of an aqueous or non-aqueous organic electrolyte. In most of the commercial DLCs, tetraethylammonium tetrafluoroborate (ET_4NBF_4) in acetonitrile (ACN) is used as electrolyte, while aqueous solutions containing sulphuric acid or potassium hydroxide are less frequently used [2,9]. The current researches in the field of DLCs are mainly addressed to improve the energy density of the capacitors by proposing new materials and configurations for the electrodes.

Other types of supercapacitor are made with electrodes containing metallic oxides of ruthenium or manganese, which have the characteristics to furnish an additional pseudo-capacitance (based on faradaic processes) that improves the capacitance performance [10,11]. New alternative materials for supercapacitors are the conductive polymers, which, differently by carbons, have the whole mass capable to store and discharge electric current by faradaic processes [12,13]. Recently, carbon nanotubes have been proposed as new materials for DLCs [14,15]. The carbon nanotubes, having accessible meso-pores to the electrolyte and low resistivity, could be able to give higher capacitance than the activated carbons. But this potential capability has not yet been proved in practical DLCs devices.

Currently, many research efforts in the field of DLCs are mainly addressed to improve the device performances and to reduce the costs. These two objectives should be achieved using more appropriate materials for the electrodes as well as electrolytes with high stability and ion conductivity. At this regard, to realise a practical DLC device with electrolytes significantly cheaper consisting of polymers or gels is strongly wished [16,17]. Moreover, it is expected that the use of these materials should give some advantages, such as a reduced corrosion respect to capacitors which use aqueous electrolytes, and, less moisture-sensitive materials with respect to non-aqueous organic electrolyte. Previously, we have demonstrated that Nafion is an appropriate polymer electrolyte for the realisation of an all-solid DLC of interesting capacitance performance [18]. In fact, with this polymer electrolyte we have obtained a capacitance of 13.2 F/g. This value is comparable with that we have recorded for the capacitors having a solution of 1 M H_2SO_4 as electrolyte. In this work, our configuration of all-solid DLCs is studied by electrochemical impedance spectroscopy. With this technique the capacitance performance is evaluated and the dynamic processes occurring at the interface of carbon composite materials and solid electrolyte are studied.

Moreover, the EIS is used to determine the characteristics of DLCs for the pulse power applications.

2. Experimental

The following procedure was used for the preparation of the electrodes. The active layer of electrodes was prepared, by mixing at first an ink suspension containing 65 wt.% of carbon Black Pearls 2000 (Cabot 1546 m^2/g BET), 5 wt.% of graphite fibers and 30 wt.% of Nafion 1100 and by spreading, subsequently, the suspension on a carbon paper substrate (Toray TGPH090). The so obtained electrodes were thermally treated, following our standardised procedure, to improve the mechanical strength and the stability of the material. The thermal treatment consisted of two steps; (1) 80 °C for 1 h, (2) 160 °C for 20 min. Successively, the electrodes were washed in water and exchanged with 1 M H_2SO_4 solution for at least 4 h at 70 °C to be sure that all cations were exchange with protons. Finally, the free acid is removed from electrodes by several washing with distilled water.

The electrolytes used in this work were (1) commercial Nafion 115 (membrane N115), (2) recast Nafion membrane (NRG50) prepared from 5 wt.% Nafion 1100 solution (Aldrich) and (3) porous glass fibre matrix impregnated with 1 M H_2SO_4 (FVH $_2\text{SO}_4$). The thickness of the three swelled membranes were 160, 50 and 200 μm , respectively.

Each DLC was realised by assembling face to face a membrane and two electrodes. The membrane and electrodes assemblies (MEAs) were prepared by hot-pressing procedure at 200 kg cm^{-2} and 130 °C for 3 min. The porous matrix containing 1 M H_2SO_4 electrolyte was assembled with the electrodes directly in the test cell. Further details on preparation of electrodes, membranes and MEAs are reported in a previous paper [18].

The electrochemical impedance spectroscopy measurements were performed at ambient temperature using a test cell in DLC configuration. The electrochemical cell was connected at an EG&G PAR model 273A potentiostat/galvanostat and at a Solartron 1255 frequency response analyser (FRA) that was interfaced to an IBM PC via a National Instruments IEEE-488 GPIB card. The EG&G PAR—M398 Electrochemical Impedance Software was used for the impedance measurements between 100 kHz and 10 mHz. The amplitude of the ac voltage was 20 mV rms. All the EIS measurements were carried out at ambient temperature in a single cell composed of two graphite end plates containing MEAs of area 4 cm^2 .

Measurements of pore size distribution and surface area of carbon powder (Black Pearls 2000) were made using a gas adsorption analyser (Carlo Erba Instruments—Sorpomatic 1990) based on nitrogen adsorption at 77 K. The sample was degassed at 200 °C for 3 h under vacuum before the analysis. The total surface area and pore size distribution of micropores was calculated by the Dubinin method, and the total

adsorbed volume (cm^3/g) is obtained by the Horvath–Kawazoe (HK) method.

3. Results and discussion

In the Nyquist impedance plot, the imaginary part of impedance is plotted as a function of its real component in the frequency range from 10 kHz to 10 mHz. The appearance of inductive effects at higher frequency ($>2\text{ kHz}$) in the experimental data reduces the useful frequency range. Thus, the experimental points above 2 kHz, which appeared disturbed for the presence of parasitic effects, which could be due at the electric wires, at the capacitor connectors and/or at noise and oscillation of potentiostat determined by coupling of EG&G and the Solartron 1255, have been removed from the plots. The impedance plots of the capacitors made with the different electrolyte are shown in Fig. 1. The trend of the curves shows clearly that a non-ideal behaviour of the different capacitors is present and that the shape of the plots is similar for all samples in the range of the frequency studied (2 kHz–10 mHz). The internal resistances evaluated at 1 kHz are 91 m Ω for N115, 45 m Ω for NRG50 and 27 m Ω for FVH₂SO₄ electrolyte (see insert in Fig. 1). The larger resistance for Nafion 115 membrane is evidenced by a more remarkable dependence of impedance by frequency, whereas the capacitors with NRG50 and that with H₂SO₄, show lower resistances and similar impedance plots. The decreasing frequency in Fig. 1 is into the direction from bottom to upper side. At intermediate frequencies the impedance is less frequency dependant and the behaviour of the devices approaches at a pure capacitor independently of electrolytes even if a vertical line is never reached. At lower frequency, the experimental points seem to show the appearance of semicircles, which should be likely due at diffusional effects of the electrolyte in the electrodes. The non-vertical slope of the impedance plot at low-frequency of electrochemical

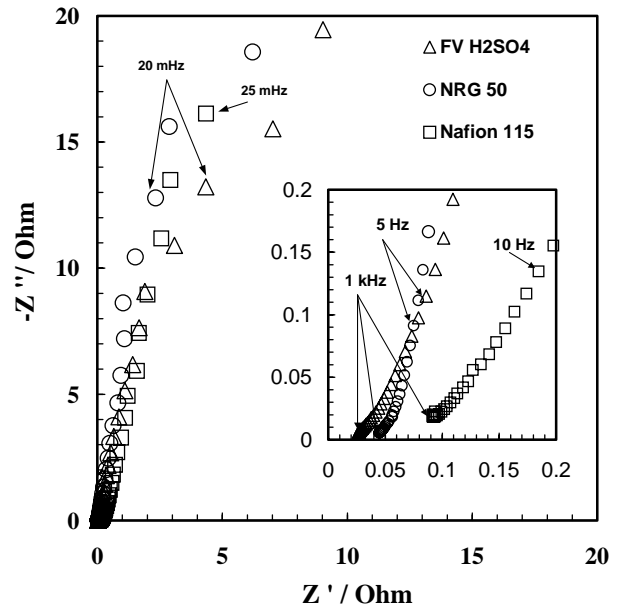


Fig. 1. Nyquist ac impedance plot for the DLCs with the different electrolytes.

capacitor, may be attribute at different causes as, the high microporosity of carbon, and the low mobility of the proton inside the electrodes, or the combination of both. In literature, this deviation is often attributed at the increase in electronic resistance of carbon materials or of contact between the different components of the complete capacitors [19–22]. A further possible explanation of the high resistance shown by the capacitors with the decreasing frequency, not always taken into consideration, could be connected with the higher impedance exhibits from the electrolytes [23,24]. In Fig. 2 is shown the impedance diagrams, in Bode coordinates, of the capacitors with the different electrolytes. Also in Bode diagram, the non-ideal behaviour of the capacitor is well shown. At the high frequency, the low shift of the phase angle

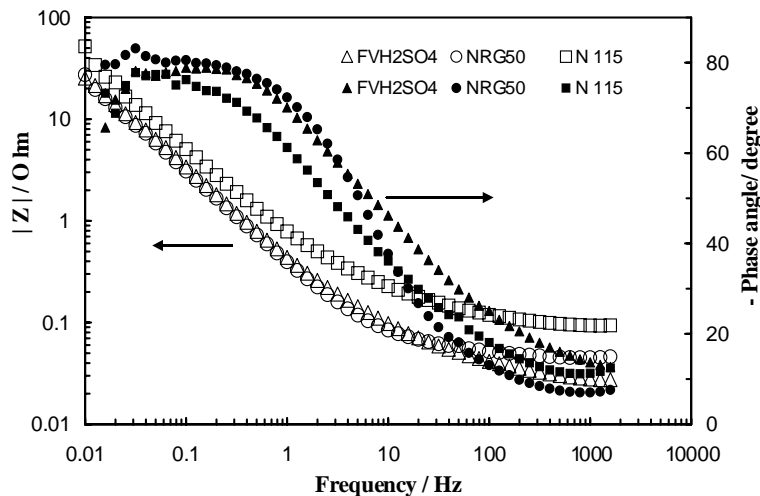


Fig. 2. Bode diagram of the capacitors with the different electrolytes.

is controlled from the ionic resistance of the electrolyte (Nafion membrane or sulphuric acid) and the capacitance is very low, while when the frequency decreases (<10 Hz) the phase shift approaches at $\approx -80^\circ$, and, the DLCs are very similar at a ideal capacitor. From the shape of the curves, substantial differences, between the capacitors with liquid electrolyte respect to that with Nafion electrolyte are not evidenced.

The ac impedance measurements of DLCs permit to make a correlation between the porous structures of electrodes and the dependence of the capacitance by the frequency. The observed responses of the DLCs are generally modelled by simple series RC circuit. However, the RC model is inadequate to describe the response of DLCs under high rate power discharge and for those applications which do not require a full discharge from full charge state. In such circumstance Miller [8] has suggest the use of ac impedance approach to assess the pulse power performance of capacitors [25]. This consist, in the evaluation from the Bode diagram of the particular frequency, f_0 , at which a capacitors reaches the -45° phase angle (the point at which the real and imaginary component of impedance are equal) and determining the characteristic response time, T_0 , by the reciprocal of this frequency. The imaginary component (Z'') at f_0 is used to calculate the available energy using the equation $E_0 = \frac{1}{2}CV^2$, where $C = -(1/2\pi f_0 Z'')$ and V the rated voltage of the capacitor. The pulse power performance, definite by the gravimetric “figure-of-merit” is simply the available energy density (E_0/mass) divided by the characteristic response time T_0 . Following this approach for the studied capacitors, response times of 0.25 s for Nafion 115, 0.16 s for NRG50 and 0.090 s for FVH₂SO₄ electrolyte have been calculated for the respective capacitors. These values indicate that the capacitor with H₂SO₄ delivers the fastest response, i.e. this capacitor has the best pulse power performance, respect to

those with Nafion electrolytes. The evaluation of the characteristic response times of the capacitors can be made also plotting the real and imaginary components (in absolute value) as function of the frequency (see Fig. 3). The abscissa value, corresponding at the intersection point of the two components of the impedance, gives the characteristic frequency value (f_0). In Fig. 3, for convenience, only the experimental points relative at the capacitor with NRG50 electrolyte has been reported. The tangent at the data points of imaginary impedance allows the evaluation of the capacitance, while the tangent at the points of real impedance, drawn parallel to the abscissa axis, gives the value of the equivalent series resistance (Fig. 3). In the same figure, it is possible to observe as both the components of impedance are increasing with the decreasing frequency. The same characteristic trends have been recorded in the capacitors with the other investigated electrolytes, then their behaviour was like-ideal capacitor at very low-frequency and like-ideal resistor at higher frequency (1–2 kHz, see Fig. 3). Similar evaluation of DLCs characteristics has been reported and discussed in previous publications by Conway [5] and Burke [26].

The trend of the curves of the specific capacitance (F/g) with the frequency for the different tested capacitors is shown in Fig. 4. The capacitance is calculated by the expression $C = -(1/2\pi f Z'')$. The values of specific capacitance (F/g) were evaluated per mass unit of carbon + Nafion material in the capacitor. The curves of capacitance seem to show more step changes and never they reach a plateau, even at frequency as low as 10 mHz. Clearly, these results are indicative of a resistive behaviour caused by microstructure of carbon that produces a difficult access of electrolyte inside of carbon electrodes. Several papers [14,20–22,27,28] have evinced that the microstructure of the carbons reduce the availability of part of surface area at electrical charging in double layer. These considerations are supported by pore

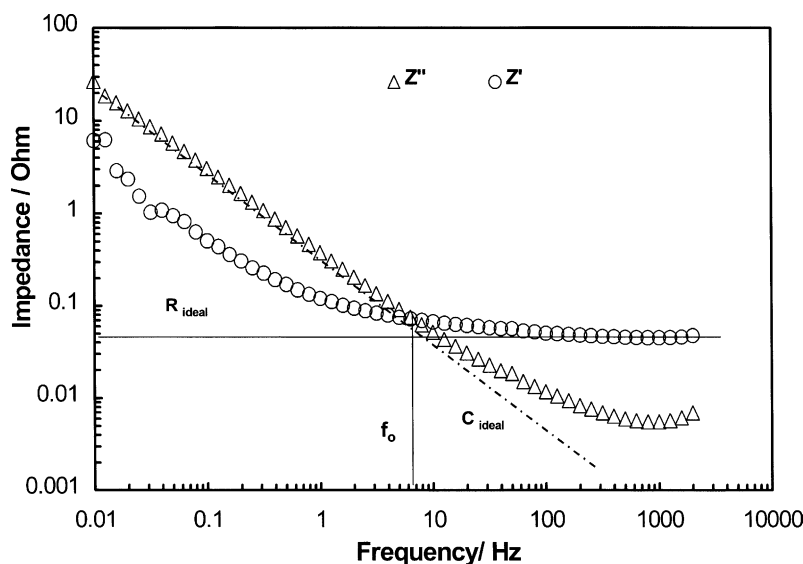


Fig. 3. Impedance plot of the capacitor with cast Nafion electrolyte (NRG50).

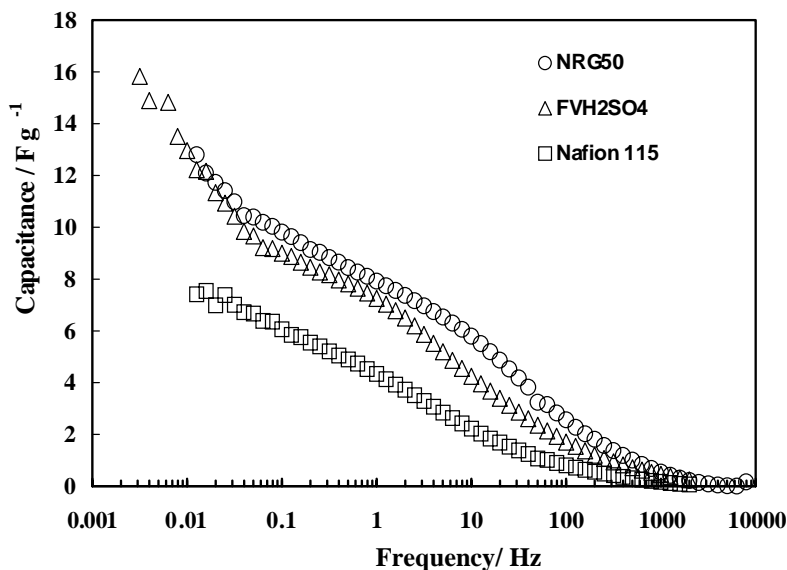


Fig. 4. Specific capacitance, expressed as F/g of active materials (carbon + Nafion), as function of the frequency for the different capacitors.

size distribution of Black Pearls 2000 as obtained from nitrogen adsorption analyser. The analysis shows a large presence of micropores with pore size of $<20 \text{ \AA}$ and volume up to $0.54 \text{ cm}^3/\text{g}$. This volume together with the meso- and macro-pores volume gives a maximum pore volume of $1.87 \text{ cm}^3/\text{g}$ (see Fig. 5). From the figure can be observed that the pore sizes are not uniformly distributed, and its smaller pores are likely responsible of the low electrochemical accessibility at the ion diffusion in the pores, within of time scale of capacitive measurements. To further confirm at these assertions, the capacitance of the capacitor with sulphuric acid increases when the frequency is less than 10 mHz . This is meaning that with this latter electrolyte, at these frequencies, the electric signal is penetrating in the smaller pores. This observation can be surely extended at

the capacitor with the solid electrolyte. Nevertheless, because the capacitor with recast Nafion electrolyte (NRG50) exhibits capacitance very close to that with sulphuric acid, it is probable that water bonded at the sulfonic groups acts as the free acid of H_2SO_4 solution contributing to increase the proton conductivity of the capacitor.

The proton conductivities and specific capacitances of the different capacitors obtained by different methods are shown in Fig. 6. The values of proton conductivity measured by Universal Bridge at 1 kHz [18] are compared with those determined by impedance analysis at the same frequency. The values obtained by the two different methods show slight differences, in particular those obtained by impedance for the different capacitors are underestimated. The same trend is recorded for the specific capacitances, i.e. the values

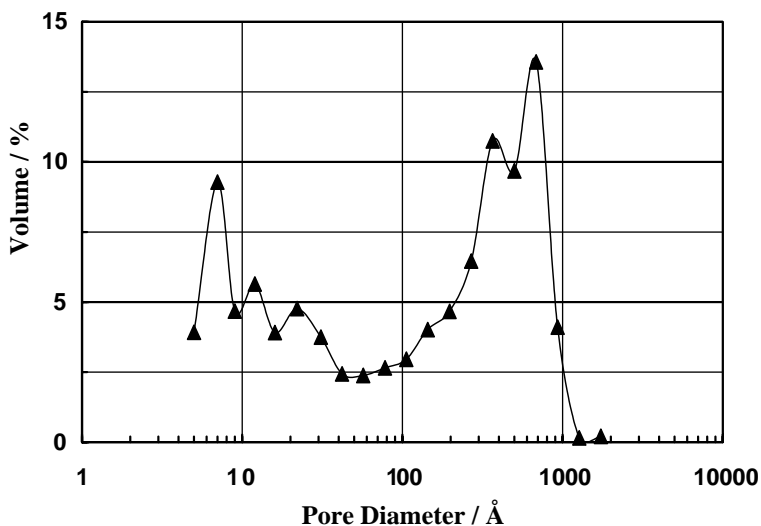


Fig. 5. Pore size distribution of carbon Black Pearls 2000 (BET $1546 \text{ m}^2/\text{g}$).

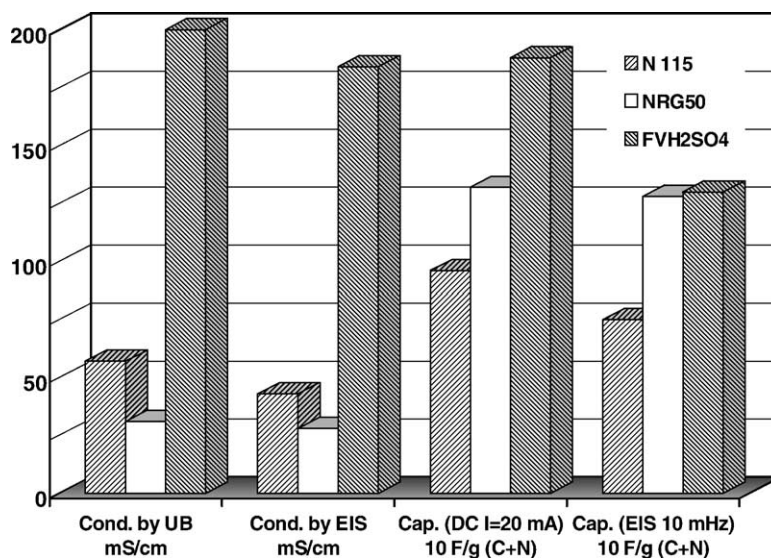


Fig. 6. Comparison of proton conductivities of capacitors obtained by universal bridge (at 1 kHz) and by impedance. Specific capacitances in F/g active materials (carbon + Nafion) obtained by dc charge/discharge (discharge at $I = 20$ mA) and by impedance ($f = 10$ mHz).

calculated by impedance measurements at 10 mHz, are generally lower than that obtained by dc charge–discharge measurements. Before to take in consideration the differences between the capacitance in dc and the ac current measurements, we should consider their time characteristics. A relationship that connects the charge (or discharge) time measured during dc charge (or discharge) tests with the frequency (f) measured during EIS analysis is the following: $t_{dc} = 0.25/f$. This derived by the fact that in a single period of ac measurement there are two charging and two discharging phases. For the capacitance are compared the values obtained by galvanostatic dc charge/discharge measurements at 20 mA of discharge current (5 mA/cm^2) with those by impedance calculate at 10 mHz of frequency by the expression $C = -(1/2\pi fZ'')$. The maximum difference of the capacitance is in the order of 20% for the all capacitors. The probable reasons of these differences are the same already discussed in the text and connected with the characteristics of carbon composite electrodes. Moreover, it is clear that the results obtained by ac impedance and by dc charge/discharges tests, are likely dependents on time scale of capacitive measurements.

4. Conclusions

Electric double layer capacitors made with Nafion electrolyte and sulphuric acid electrolyte have been realised and evaluated by electrochemical impedance spectroscopy (EIS). The Nyquist impedance plots, relative at the different samples, evidence small differences in the profile of the curves and show a non-ideal behaviour of the capacitors even at the low frequencies. In the high frequency region the electrolyte resistance is the controlling factor of

the characteristics of the devices, and as consequence the capacitor with higher resistance exhibit lower specific capacitance. The impedance analysis have evidenced that the capacitor with the acid solution has a faster response time, likely due to its higher proton conductivity with respect to that of recast Nafion membrane (NRG50) and Nafion 115 (N115).

The impedance analyses have evidenced as a large microporosity of carbon can produce an additional proton and/or electronic resistances in the electrodes of the capacitors. As a consequence the specific capacitance derived by ac impedance does not reach a plateau even at very low-frequency (10 mHz) and a difference in capacitance, in the order 20% for all capacitors, drawn by impedance and by dc charge/discharge measurements has been found. This has been interpreted as the low electrochemical accessibility of the pores, within of time scale of capacitive measurements, and is attributable at the difficult penetration of electric signal in the smaller pores. Moreover, it is also shown, as the impedance plots of different capacitors do not reveal remarkable differences because, very likely, inside the electrodes the water adsorbed in the Nafion makes the same function of sulphuric acid electrolyte.

A specific capacity of about 13 F/g was achieved in the capacitor having recast Nafion electrolyte in our all-solid configuration, which was equivalent to that of a capacitor with sulphuric acid. This encouraging result presses us to study the optimisation of these capacitors through the determination of the appropriate amount of Nafion electrolyte in carbon electrodes and in the choice of carbons at high surface area and low resistivity. The high ion conductivity (about $3 \times 10^{-2} \text{ S cm}^{-1}$) at room temperature of Nafion electrolyte in capacitor configuration is indicative for being able to realise high rate response devices.

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