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Capacitance Improvement Based on Cell Design

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ABSTRACT

In the present work we show results related with the influence of the type of binder used to elaborate active electrodes made of activated carbon (DLC), for the assembly of supercapacitor cells. A Nafion 5%w solution and/or Kinar Flex (Polyvinylidene fluoride, PVDF) were used as binders at different concentrations, using DLC carbon as the active material to make the electrodes by aerography, and carbon paper as support and current collector. Thickness of the electrodes was controlled by the weight of active material (DLC carbon). Cyclic voltammetry technique was used to characterize these electrodes in a 3-electrode cell assembly, using as counter electrode a Pt mesh, a SSE reference electrode, and a 0.5M H₂SO₄ solution as the electrolyte. The electrodes made with binder were assembled in a symmetric supercapacitor cell and for comparison a similar cell was constructed with binder-free electrodes. These cells were electrochemically characterized by galvanostatic cycling, showing capacitance values of 38F/g for binder-free electrode symmetric cell, and a stable behavior during 7000 charge-discharge cycles.

Key words: Supercapacitor, Design, Binder Free, Electrochemical Capacitor, Electrodes.



1. Introduction

An electrochemical supercapacitor also called supercapacitor or ultracapacitor can be defined as a device that stores electrical energy in the electrical double layer that is formed at the interface between an electrolytic solution and an electronic conductor [1]. Supercapacitors are designed to bridge the gap between batteries and capacitors to form fast charging energy-storage devices of intermediate specific energy [2]. The use of supercapacitors is growing along with demand for specific requirements for different applications, ranging from small sizes with limited energy content, to levels of hundreds of kW in various vehicles (passenger hybrids cars, hybrid buses and trains) and for electric applications. The variety of applications also determines the need to clarify the measurement procedures to determine the properties of supercapacitors (SC) of the properties for supercapacitors, which may vary when they are used in different operating conditions.

An ideal SC can be represented with a first-order electric equivalent circuit, as described in Figure 1. It is comprised of four ideal circuit elements, which include a capacitor $C1$, a series resistor $R1$, a parallel resistor $R2$ and a series inductor $L1$. $R1$ represents the equivalent series resistance (ESR) and accounts for the power loss during charge and discharge. $R2$ is the parallel resistance responsible for the energy loss due to capacitor self-discharge. This model is the simplest one and also the most adequate for low and medium power applications. In high power applications the non-ideal behavior of electrochemical capacitors cannot be neglected, depending on temperature, current, power, frequency, in case of alternate current systems, and also on SC category [3].

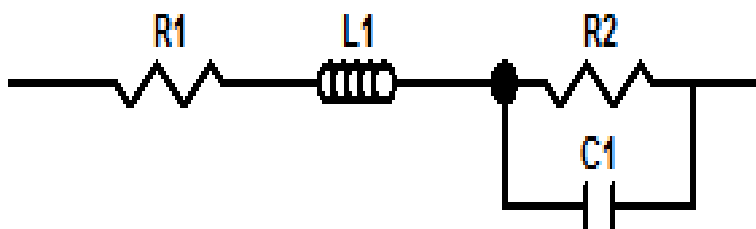


Figure 1. First order electric equivalent circuit of a capacitor

There have been many studies of materials for electrochemical capacitors, and testing for small laboratory devices and prototypes as well for a wide range of commercial products. Many of the materials testing laboratory and small devices have involved the use of cyclic voltammetry, galvanostatic cycling and AC impedance test [4], [5], [6]. In these tests, small currents, limited potentials intervals and/or AC frequencies are used. To test larger prototypes and commercial devices, regularly DC tests similar to those used with batteries are used[7]. In this case we are using cyclic voltammetry, galvanostatic cycling, electrochemical impedance spectroscopy, for our electrodes characterization.

On the other hand, one of the challenges of today is the portability of energy: lighter devices, more compact and more flexible for energy storage are required by a number of devices that can be used on different items from cloth to space applications, in which the cost per weight and volume is very high [8]. A number of recent studies, initiatives and products have been reported and proposed for the development of flexible energy devices based on different chemistries, including supercapacitors [9-14].

Our works shows a systematic study on electrode fabrication in order to reduce resistance (R), with capacitance values (C) as high as possible. Also, an evaluation of different current collectors in a lab-scale assembly was carried out as well as a prototype thin-cell was characterized, where the electrolyte was considerably reduced.

2. Experimental

2.1 Electrode Fabrication

Two series of electrodes were prepared using DLC (activated carbon from NORIT) as active material with Kinar Flex (PVDF polyvinylidene fluoride, Arkema) or Nafion solution (5wt%, Aldrich reagent) as binders in different concentrations. First, a suspension (ink) made of active material and binder was obtained, followed by their deposition on to the surface of the current collector by an aerography process, and finally a drying procedure was followed at room temperature for 24 hours. This impregnation technique produced well distribution of the active material on the surface of carbon paper (2 cm X 2 cm) used as supporting material and current collector, making their performance just a function of the used binder in each electrode. In order to obtain the series of electrodes based on Nafion (N-Elect), the ink was prepared by ultrasonication in an open vessel for 1 hr of a suspension made with the active material (DLC), 2 ml 2-propanol, and varying the concentration of Nafion (1, 2, 3, 4 and 5wt%). In the case of Kinar Flex based electrodes (KF-Electr), the active material was stirred for 24 hours with different amounts of Kinar Flex (3, 4, 5, 10 wt%) in acetone.

The electrodes were characterized electrochemically by cyclic voltammetry in a three-electrode cell, using as reference electrode a saturated sulfate electrode (SSE), a platinum mesh as the counter electrode, and our fabricated electrodes as the working electrode. Impedance spectroscopy was carried out at open potential circuit (OPC)

2.2 Lab-Supercapacitor Assembly

A lab-scale assembly was used to evaluate different current collectors using an excess of electrolyte. For this assembly two acrylic plates and four Teflon screws were used as mechanical support of the 2-electrode cell. Figure 2 shows the components for this supercapacitor assembly, where two identical electrodes separated by a filter paper to avoid electric contact are pressed with the acrylic plates, immersed in 0.5 M H₂SO₄ electrolyte, and sealed with a plastic bag to avoid electrolyte evaporation.



Figure 2. Lab-assembly supercapacitor.

In this cell assembly a stainless steel mesh as current collector coupled to a carbon paper support, and a carbon cloth current collector and support were evaluated. A binder-free suspension made from 0.1 g DLC and 2 ml of 2-propanol was ultrasonicated for 1 hr and deposited by aerography on the surface of 4 cm² electrodes before the assembly.

The electrochemical devices were characterized by galvanostatic cycling at a constant current that was setup to obtain a complete discharge of the supercapacitor cell in 100 s. Cyclability test were carried out by 7000 charge-discharge cycles and the capacitance was calculated according to eq. (1).

$$C = \frac{I \cdot t}{\Delta V} \quad (1)$$

where C is the capacitance I is the applied constant current, t is the discharge time (≈ 100 s) and ΔV is the potential window.

2.3 Prototype Cell

A portable prototype with a thin and flat configuration cell package is shown in Figure 3. In this case it is possible to assess the electrolyte contribution (ionic source depletion) to the cell performance, since it is restricted by the cell design. The cycling stability through the retained capacitance was investigated in 7000 charge-discharge galvanostatic cycles, using a current that permits a 100s discharge time.

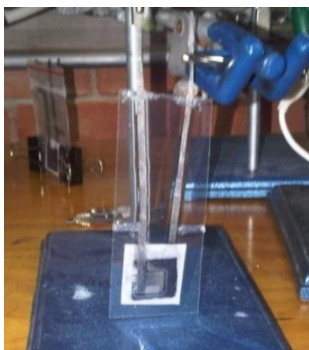


Figure 3. Prototype thin-supercapacitor cell.

3. Results and Discussion

ELECTRODE EVALUATION

The influence of binders on the electrode performance for supercapacitor applications was investigated electrochemically by cycling voltammetry analysis for the two series of electrodes earlier described: N-Elect and KF-Elect, prepared with Nafion and Kinar Flex respectively. All experiments were carried out in 0.5 M H₂SO₄ at 25 °C.

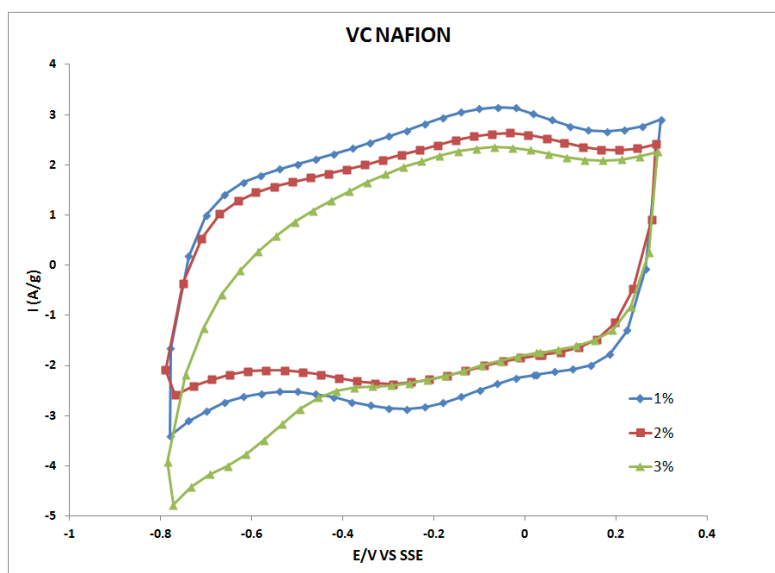


Figure 4.- Electrode Cyclic voltammetry response of N-Elect at different binder concentration, 0.5 M H₂SO₄ and scan rate 20 mVs⁻¹.

Figure 4 shows the cyclic voltammetry carried out at 20mV/s for all electrodes of N-Elect series with different amounts of Nafion, where a potential range from -0.8 to 0.3 V was used to avoid electrolyte decomposition. For 1 and 2 wt% Nafion concentrations, the voltamperometric profile almost remained a rectangular form, typical response of charge accumulation on the double layer. For binder concentrations higher than 2 wt% (3, 4 and 5 wt%) an inclination of the voltammogram profile is observed on the cathodic limit and is related with the increase of electrode

resistance. The capacitance values calculated from the voltamogram integer as we seen in eq. 1 for low-resistance electrodes are 245 F/g for 1% Nafion electrode and of 202 F/g for 2% Nafion electrode. Therefore, the 1 wt% Nafion electrode resulted in the best performance with higher capacitance value and lower resistance, determined by cyclic voltammetry.

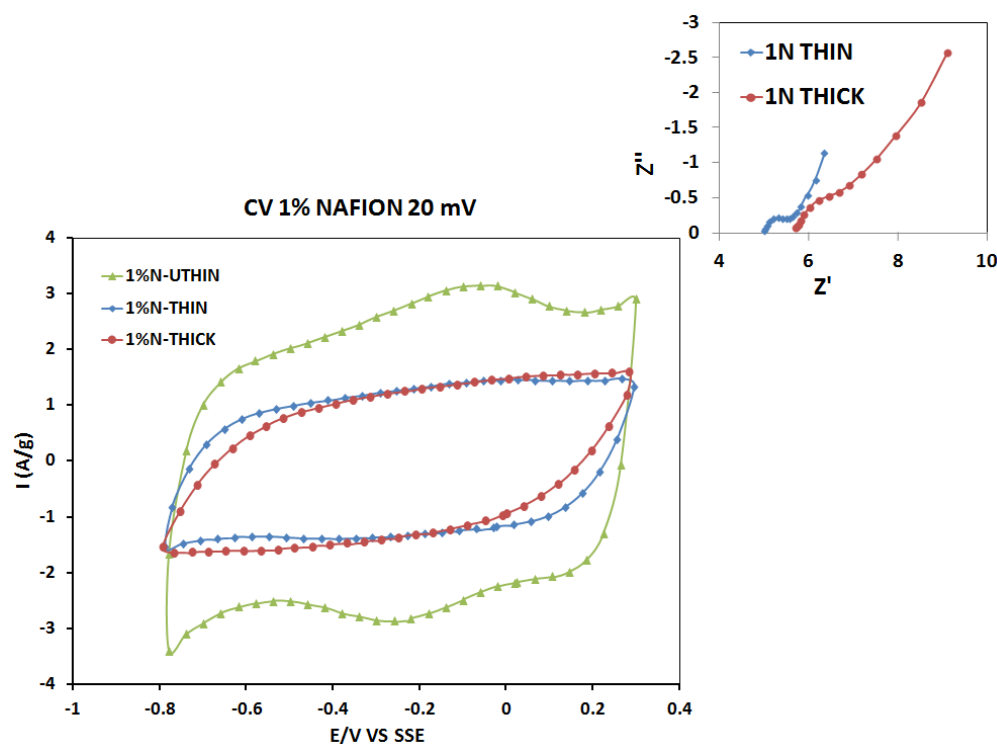


Figure 5. Cyclic Voltammetry of Nafion 1% electrodes with different thickness carried out at 20 mv/s and in the inset electrochemical impedance of these electrodes are shown.

Thickness of electrodes in supercapacitor cells is a parameter that needs to be improved due to variation in resistance, which is an important parameter to take into consideration for these high power devices. Therefore, the electrode thicknesses of 1% Nafion formulation was varied and are labeled as 1%N-Thick, 1%N-Thin, and 1%N-Ultrathin. Figure 5 shows the voltammograms of these electrodes, where the capacitive profile is observed with higher current range for the 1%N-Ultrathin electrode. The inclination or deviation from the rectangular profile is related with resistance in the electrode and these phenomena increases with the thickness increase of the electrode. In the inset of figure 5 the electrical response from Electrochemical Impedance Spectroscopy (EIS) of two prepared electrodes: 1N-thin and 1N-thick electrodes are shown as an example. Series resistance is very similar in both electrodes (about $1.25 \Omega\text{cm}^{-2}$, because the area in the electrode is 4cm^2), demonstrating the low resistance of the electrodes using this fabrication method. On the axis cut the charge transfer resistance can be detected, showing a

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lower value for 1%N-thin electrode than for 1%N-thick electrode. In addition, at very low frequency range it is observed that the species diffusion in 1N-thin electrode is greater than 1N-thick electrode. The behavior observed in these two electrodes can be related with a better porosity distribution in 1%N-thin that makes the surface of the electrode more accessible to the electrolyte. Also, it is observed a combined charge mechanism in 1N-thick electrode due to the appearance of a non-defined Warburg semi-infinity diffusion at low frequencies, which has been observed in electrochemical systems occurring incomplete charge transfer process in non porous medium.

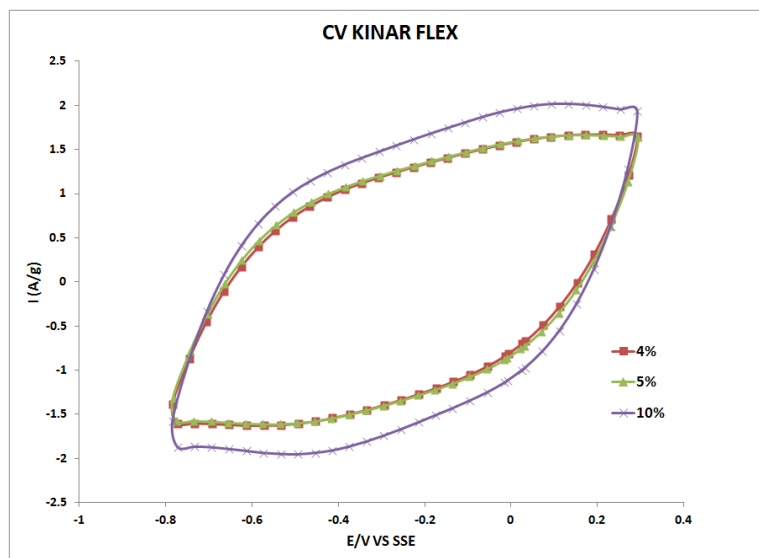


Figure 6.- Cyclic Voltammetry of KF-Electr series in 0.5M H₂SO₄ electrolyte using a scan rate 20mVs⁻¹

Figure 6 shows the voltammetry response of KF-Electr series as a function of binder concentration. The voltammograms show the typical charge storage mechanism (rectangular profile) of carbonaceous materials controlled by double layer adsorption. Nevertheless, the observed inclination in all electrodes indicates the higher resistance contribution compared to N-Electr series. The use of 10 wt% Kinar Flex showed a moderate current range increase and the electrode resistance is lower than the other concentrations. Capacitance values were obtained from these profiles, resulting in 120F/g for 4%-KF, 121F/g for 5%-KF, and 149F/g for 10%-KF.

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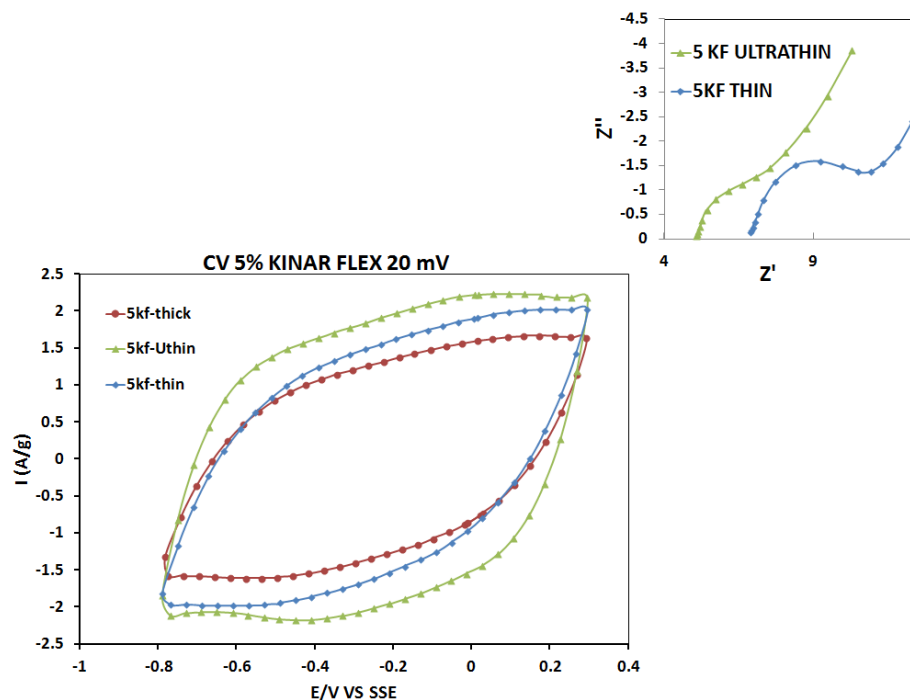


Figure 7. Cyclic Voltammetry of 5%-KF with different thicknesses and electrochemical impedance spectroscopy on the inset.

As for the N-Electr series, variation of the thickness was carried out for 5 and 10%-KF electrodes and the cyclic voltammetry and electrochemical impedance spectroscopy (EIS) results are shown in figures 7 and 8. In general, the voltammograms resistance evidenced by the inclination of the profile varied with the film thickness in both concentrations of Kinar Flex used. The resistance decreased as the electrode went from thick to ultrathin.

The EIS results of 5KF electrodes was carried out for the thin (5KF-Uthin) and thick electrode (5KF-thin). The calculated series resistance values (ESR) detected on EIS were very similar in both electrodes, indicating the similar setup operation conditions where the experiments were carried out. 5KF-Uthin electrode showed a lower charge transfer resistance than 5KF-thin electrode [15]. The lower charge transfer resistance is due to the better ion-electron interaction at the porous interface of the thin electrode. The semiconductor nature of thick electrode controls the transfer mechanism at very low frequency, indicating the presence of a non-diffusion process on the electrode surface.

In figure 8 the electrical response from EIS is shown for the two prepared electrodes: thin and thick electrodes at very high binder concentration (10KF-Uthin and 10KF-thin electrodes respectively). The influence of high binder concentration does not affect significantly the series resistance of the electrochemical systems, but it clearly affects the electron transfer mechanistic processes in both electrodes. Thin electrode (10KF-Uthin) shows a simple electronic transfer formed by a charge transfer resistance and diffusion process due to low-porosity concentration. In the case of thick electrode (10KF-thin), it is shown a more complex mechanism to transfer electrons at intermediate

frequencies. It is probably due to charge transfer resistance coupled to adsorption process as a function of thick semiconductor material (carbon) and low-porosity degree. This combined process produces a change in the response of the electric properties of ion-electron interaction in this kind of material.

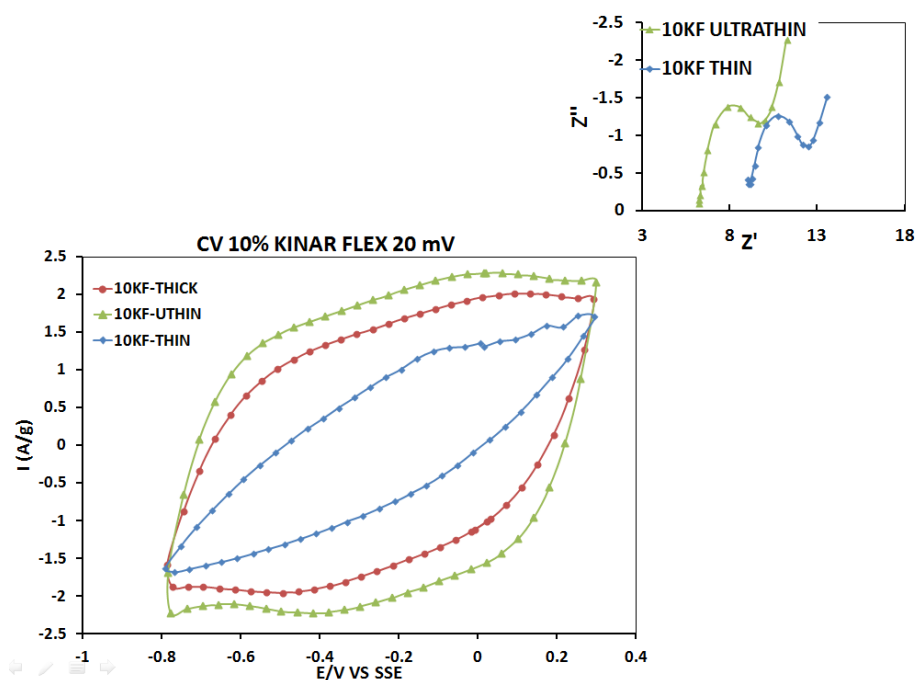


Figure 8. Cyclic Voltammetry of 10%-KF with different thicknesses and electrochemical impedance spectroscopy on the inset.

LAB AND PROTOTYPE SUPERCAPACITOR ASSEMBLY

Binders are normally used in supercapacitors to promote stability performance over 5,000 charge/discharge cycles, but the use of binders also affects the capacitance and resistance of the electrochemical devices, as shown previously. A Lab-assembly has been carried out with bind-less electrodes in order to evaluate different current collectors and a prototype has been developed to evaluate the electrolyte limitations due to design and the results are shown in Figure 9.

Lab assemblies shown in figure 9 using stainless steel mesh as current collector and carbon paper as support (Lab mesh-paper) resulted in 50% less specific capacitance ($\approx 21\text{F/g}$) than when using carbon cloth as current collector and support (Lab Cloth, 38F/g). This result could be associated to the extra component (stainless steel mesh) resulting in a higher contact resistance with the carbon paper. Carbon paper is so hydrophilic that the electrolyte migrates to the metal connections by capillarity, destroying them when long cycling is carried out. Therefore, since the extra

resistance introduced by the stainless steel mesh to prevent contact oxidation cannot be eliminated, the carbon cloth has shown its excellent properties as a current collector and support for electrode materials assembled in a supercapacitor cell. In addition, the inset on Figure 9 shows the cycling stability of this Lab cell through 7000 charge-discharge cycles.

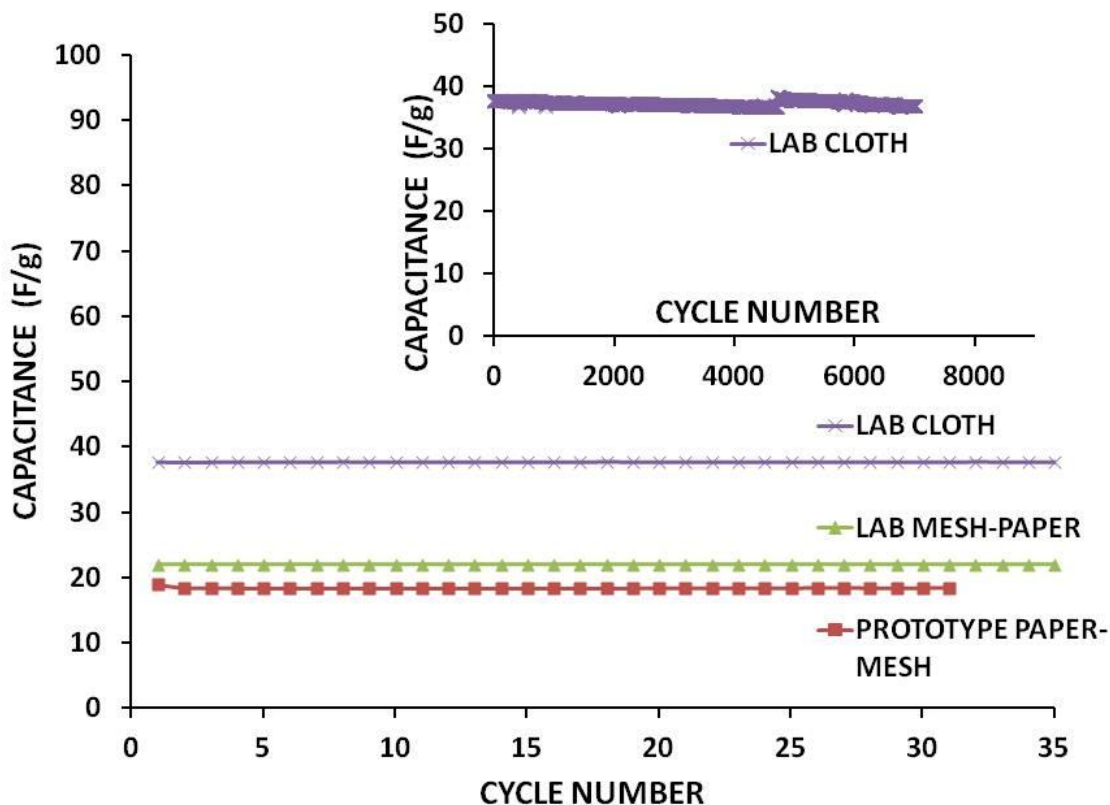


Figure 9. Galvanostatic cycling of Lab and Prototype assemblies using different current collectors using a voltage window of 1.1 V , 0.5M H₂SO₄ as electrolyte, and 6.5 mA discharge current for cloth based electrode and 3.9 mA discharge current for mesh/paper based electrode.

A thin-prototype has been developed to evaluate the electrolyte limitations due to design. In the thin-prototype and the lab assembly using a mesh-paper as current collector and support, differences can be hardly observed in capacitances values during the first 30 charge-discharge cycles. These results suggest that the electrolyte quantity in the prototype is not a limiting factor and the 2F/g difference in both assemblies could be more related with other parameters as pressure that is not studied here.

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4. Conclusions

For conventional electrodes in supercapacitor applications, it is possible to consider the use of 1 wt% Nafion solution as binder for optimum electrode performance, obtaining the maximum specific capacitance and minimum electric resistance contribution, considering the importance of the film thickness in the electrode. The use of carbon cloth as support and current collector for electrode materials resulted in a minimum contact resistance, maximizing the capacitance value up to 38F/g. A prototype design has been proposed and it is also possible to consider the use of carbon cloth in portable devices as current collector, avoiding the ionic source depletion due to reduced amount of electrolyte.

5. Acknowledgements

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