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Electrical characterization and modelling of round spiral supercapacitors for high power applications

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Abstract

Our laboratory research project consists on the study of accelerating cycling and ageing of supercapacitors under railway and electrical traction constraints. Electrical model parameters according to physical and electrochemical phenomena represent an important key to investigate aging indicators of supercapacitors and give precious information on its state of health. These kinds of studies need a powerful techniques and instrumentations.

Nowadays several electrical characterization methods exist. We have chosen to use two complementary methods: impedance spectroscopy and direct current charge/discharge methods. The present work describes the metrology defined to electrical characterization of supercapacitors. Electrical modelling based on simple tortuous pore impedance is explained. Some electrical parameters of the model defined for winded supercapacitors are investigated for different temperatures and different voltages. Finally, we have assessed the electrical model under full charge/discharge at high currents levels.

Keywords

Supercapacitor, characterization, Impedance Spectroscopy, Constant Current charge/discharge, modelling

Introduction

Supercapacitors are electrical energy devices with high power density and high expected reliability. They express more temperature stability than other energy storage devices. As a consequence cycles are possible with high charge/discharge currents. Nowadays they become an attractive alternative storage device for several applications. They may be used as the only energy and power device or in combination with other energy supplies like batteries [1], fuel cells [2]...

Some electrical applications like railway [3], [4] and electrical traction systems present high dynamics constraints. In such case, accurate electrical modelling with adaptive characterization methods are necessary. Consequently, we have proposed Impedance Spectroscopy technique [5] in combination with Direct current method.

Impedance spectroscopy technique provides a powerful tool of analysis and investigation of dynamics behaviour of supercapacitor according to dynamic constraints [6]. In addition charge/discharge method allows assessing model validity under high current constraints.

Some mathematical transformations are necessary to find a representative equivalent electric circuit. More Impedance spectroscopy allows detecting the state of charge of the supercapacitor at any working point.

Ideally, electrical parameters of any electrical model must reflect physical and electrochemical phenomena of supercapacitor. It may be allows observation and comprehension of the evolution of the state of health of supercapacitor under current or power cycling and with ageing.

In this paper we use impedance spectroscopy technique to characterize supercapacitors. We define its metrology [7] and we present and we discuss it. It responds to practice requirements in time of measurements, precision and covering different properties of the supercapacitor under test. On the other hand we propose electrical model based on homogenous porous electrode impedance.

A supercapacitor with carbon/carbon electrodes and organic electrolyte is characterized using impedance spectroscopy method at different voltages. Correlation between impedance spectroscopy measurements and full charge discharge at high current level (100 A, 200A, 400A) is investigated.

Measurement techniques

Impedance spectroscopy method

Impedance spectroscopy technique consists to excite the system under test with small alternative signal (voltage or current) and to measure the other part (current, voltage).

In fact the operating mode for characterization of supercapacitor is the potentiostatic mode, it consists to apply DC voltage V to the system which must be regulated and controlled during the impedance measurement. An alternative sinus AC voltage $U(\omega)$ with small amplitude and with pulsation ω (frequency f) is superposed to DC voltage V already stabilized.

$$U(\omega) = U_0 e^{i(\omega t + \alpha)}$$

We measure the alternative current

$$I(\omega) = I_0 e^{i(\omega t + \delta)}$$

We calculate the impedance

$$Z(\omega) = dU(\omega) / dI(\omega) = Z_0 e^{i\varphi}$$

Where the impedance amplitude is calculated as a ratio between the alternative voltage amplitude and the alternative current amplitude, and the phase of the impedance is calculated as a difference between alternative signals arguments.

By varying the frequency of the alternative AC voltage signal we obtain a spectrum of impedance versus frequency. Numerous representations of the impedance spectrum exist: BODE diagram, complex plane diagram (NYQUIST plot) ...

The alternative AC voltage magnitude is optimized according to some constraints:

- Minimization of noise on alternative voltage and current signals.
- No violating of the linearity of the system response region in the U/I characteristic.
- Characteristics of supercapacitor in particular its low impedance.
- Technical hardware specifications of the impedancemeter (maximal current, maximal voltage...)

One problem inherent in impedance experiments is the balance between the improvement in the data quality obtained by increasing the number of frequencies uses and the number of cycles collected at each frequency and the increase of the time required for the full experiment. This problem is mainly observed when low frequencies are used. The THALES software of the IM6 impedancemeter offers a partial solution by dividing the frequency range into two: high frequency range ($f > 66$ Hz) and low frequency range ($f < 66$ Hz).

At high frequencies we calculate impedance as the mean value of impedances calculated for numerous cycles (10 cycles) at the same frequency to increase the quality of data measurement. At low frequencies although the precision is respected the time of measurement is limited at one cycle at each frequency. The total time impedance measurement is realistic for our laboratory uses.

The frequency spectra are chosen in the range between 10 mHz and 50kHz which corresponds to typical time constants in most high power applications.

DC voltage applied to supercapacitor is sufficiently stabilized before starting impedance spectroscopy measurements.

Limitation in high frequencies for low impedance supercapacitors

Some errors appear in low impedance supercapacitors at high frequencies. They are caused by the coupling effects between current feeding and potential sensing lines [8]. They diminish at low frequencies but become dramatic at high frequencies. In practice the use of one twisted wires for current feeding lines and second one for potential sensing lines can help to minimize such errors on measurements.

In spite the careful taking on connections, errors on measurements are minimized but not eliminated. Some complementary methods to spectroscopy measurement exist in literature like High current interrupt method [9].

We have proposed a solution represented in Fig. 1. We have separated voltage sensors from power source according to Ampere's law. Theoretically the electromagnetic field in the exterior of the cylinder is equal to zero.

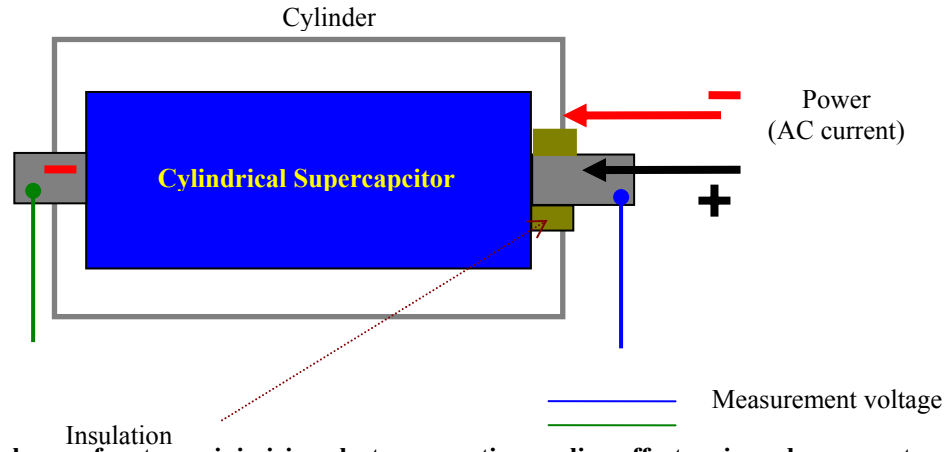


Fig. 1 Basic scheme of system minimizing electromagnetic coupling effect on impedance spectroscopy measurements

Supercapacitors, instrumentation

The two testing methods (impedance spectroscopy and constant current charge/discharge) were applied to two supercapacitors B, and F based on activated carbon and organic electrolyte developed for power applications. B is supercapacitor rated 2600 F of capacitance and 2.5 V of voltage, F is rated 2600 F of capacitance and 2.7 V of voltage.

Impedance spectroscopy measurements are realised with Zahner IM6+PP240 impedance analyzers [10][11]. THALES software ensured the data acquisition and the control function with good quality [12].

We have developed a constant charge/discharge test bench for supercapacitors characterization in our laboratory.

Measurements results and modelling

Impedance Spectroscopy results and discussions

Two supercapacitors E (2600F, 2.5V) and F (2600 F, 2.7 V) are tested with impedance spectroscopy method.

Figure 2 illustrate an example of complex plane plot of impedance spectroscopy behaviour of supercapacitors E at different temperatures at voltage of 2 V in the frequency range from 10 mHz to 1 kHz.

In contrast figure 4(a, b) represent the behaviour of E and F supercapacitors at different DC voltages at a temperature of 25° C in the frequency range from 10 mHz to 1 kHz.

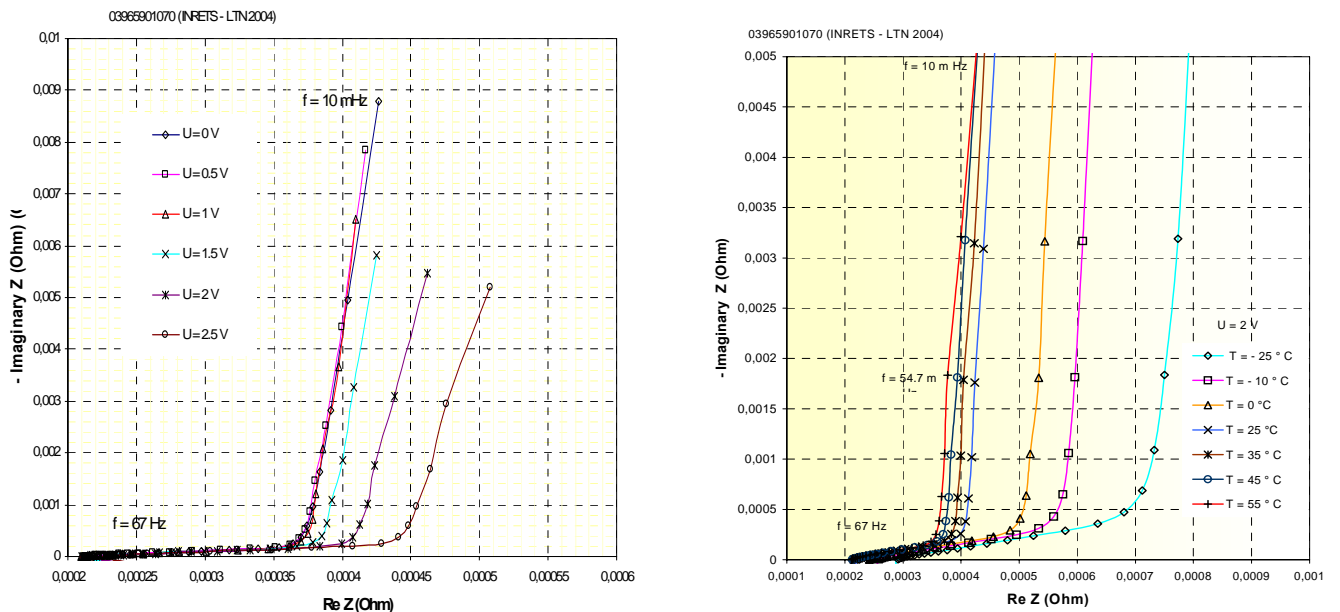


Fig. 2 Complex plot of Impedance spectroscopy measurements data for B (2600F, 2.5V) supercapacitor at different voltages ($T = 25^{\circ}\text{C}$) and at different temperatures ($U = 2\text{V}$)

Simple Pore Model of cylindrical supercapacitor

Fig. 3 gives frequency behaviour of a supercapacitor with homogenous porous electrode at stabilized voltage. We consider pore size accessible with uniform dimensions, and inaccessible pores behaving like a resistance contributing in self discharge. As consequence the impedance of the electrode is equivalent to cylindrical pore impedance in parallel with resistance.

The structure of supercapacitor can be decomposed to three elements [13], [14] : inductor L , series resistance R_s , and complex pore impedance $Z_P(j\omega)$ (cf. Fig. 4, Fig. 5)

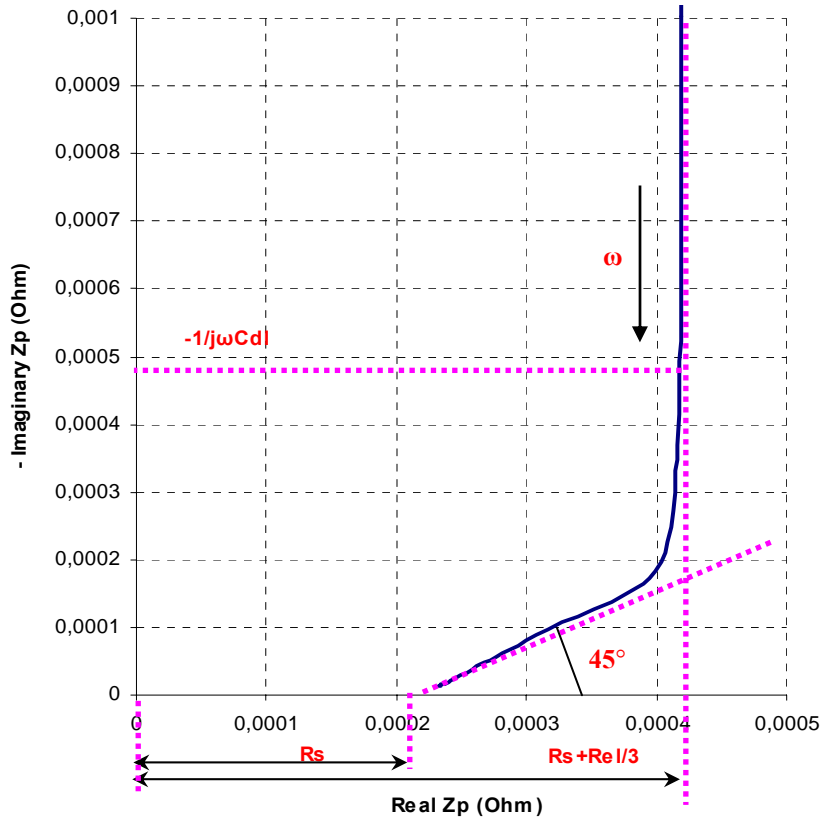


Fig. 3 Complex plane plot of a porous ideally polarizable electrode in series with R_s

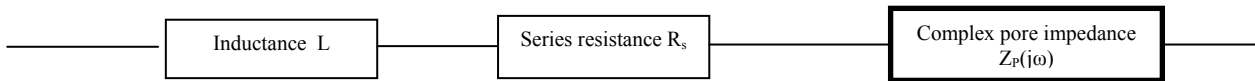


Fig. 4 Equivalent circuit for supercapacitor at constant voltage

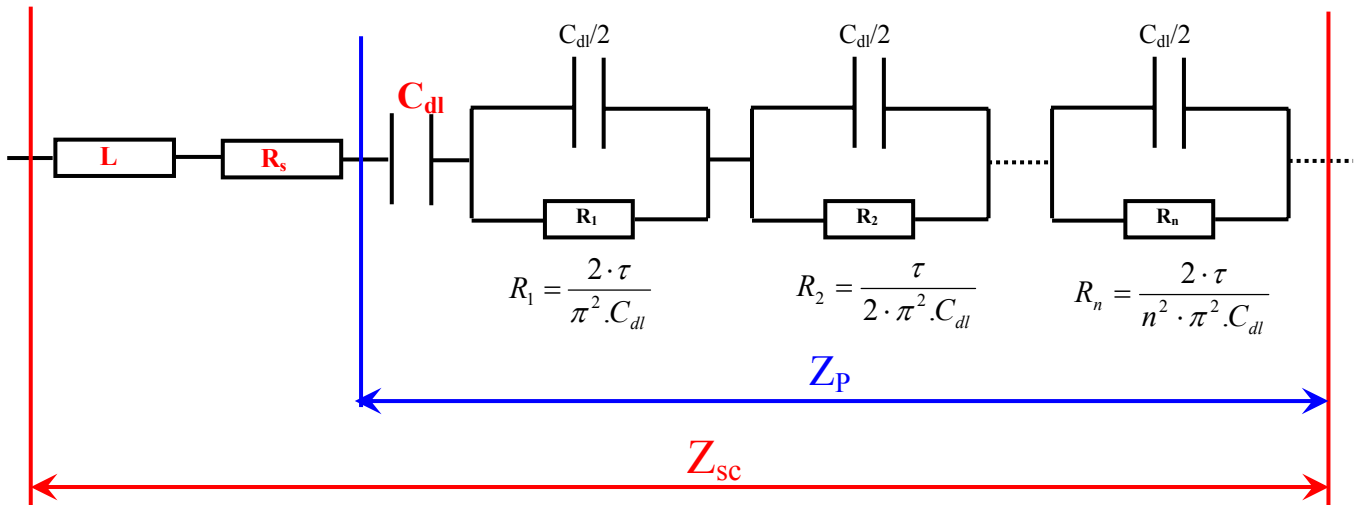


Fig. 5 Equivalent circuit of Z witch depends to four parameters

The mathematical expression of $Z_p(j\omega)$ can be given by

$$Z_p(s) = \frac{\tau}{C_{dl}\sqrt{\tau \times s}} \times \coth \sqrt{\tau \times s}$$

$$\text{We put } K_1 = \sqrt{\tau}/C_{dl} \text{ and } K_2 = \tau/C_{dl},$$

$$Z_p(s) = \frac{K_1}{\sqrt{s}} \times \coth \frac{K_2}{K_1} \sqrt{s}$$

The inverse transformation of $Z_p(s)$ in the time domain is given by [14]

$$Z_p(t) = \frac{k_1^2}{k_2} + \frac{2k_1^2}{k_2} \sum e^{-\frac{n^2 \pi^2 k_1^2}{k_2^2} t}, \quad Z_p(t) = \frac{1}{C_{dl}} + \frac{2}{C_{dl}} \sum e^{-\frac{n^2 \pi^2 \cdot C_{dl} \cdot 2}{2\tau \cdot C_{dl}} t}$$

$$R_n = \frac{2 \cdot \tau}{n^2 \cdot \pi^2 \cdot C_{dl}} \text{ And } Z_p(t) = \frac{1}{C_{dl}} + \frac{2}{C_{dl}} \sum_{n=1}^{\infty} e^{-\frac{2}{R_n \cdot C_{dl}} t}$$

with $\tau = C_{dl} \cdot R_{el}$

Where C_{dl} (average double layer capacitance) is the capacitance at low frequencies, Tau (τ) depends on C_{dl} and the electrolyte resistance filled in pore R_{el} . $Z_p(j\omega)$ is approximated by a n. RC circuits which are fully described by two parameters (C_{dl} , and τ), it describe in-pore diffusion. So for the totally model of supercapacitor we need to identify four parameters (L , R_s , C_{dl} , R_{el})

Analysis

According to the physic's theory of Gouy, Chapman and Stern [15],[16],[17] on double layer capacitor, the capacity C_{dl} is equivalent to two parallel capacities. We note V the voltage on the extremities of the double layer. The dependency of C_{dl} to the voltage is expressed by

$$C_{dl} = \left(\frac{1}{C_3} + \frac{1}{C_2 \cosh(C_1 \cdot V)} \right)^{-1}$$

We have defined the parameters of the capacity C_{dl} (C_3 , C_2 , C_1) for B supercapacitor at different temperatures Table. 1) Simulated curves of the double layer capacity C_{dl} and values of C_{dl} calculated from impedance spectroscopy measurements show a great agreement (cf. Fig. 6)

The accessibility of the electrolyte within pores depends on molecular electrolyte dimensions and pore size, it varies with temperature. The electrolyte resistance may be a good indicator for electrolyte-pore accessibility. Its behaviour can reflect supercapacitor's dependency of supercapacitor to temperature. We note T is the supercapacitor temperature ($^{\circ}$ K). The dependency expression of the electrolyte resistance R_{el} to temperature can be given by

$$R_{el} = r_3 + r_2 \times \exp(r_1 \times T)$$

We have defined the function's factors (r_1 , r_2 , r_3) for B supercapacitor at different voltages (cf. Table. 2) Simulated curves of electrolyte resistance R_{el} and values of R_{el} calculated from impedance spectroscopy measurements show a great agreement (cf. Fig. 7)

By using the expression of C_{dl} defined above, we have compared constant current discharge measurement voltage with model simulated voltage. We observe a good concordance between model and constant current discharge Table. 3. Time discharge is limited by our test bench. To enhance the assessment of the validity of our modelling, we have done other experiences in Cegely Laboratory. Model is assessed to full charge/discharge measurements of supercapacitor at high currents levels (100A, 200A, 400A).

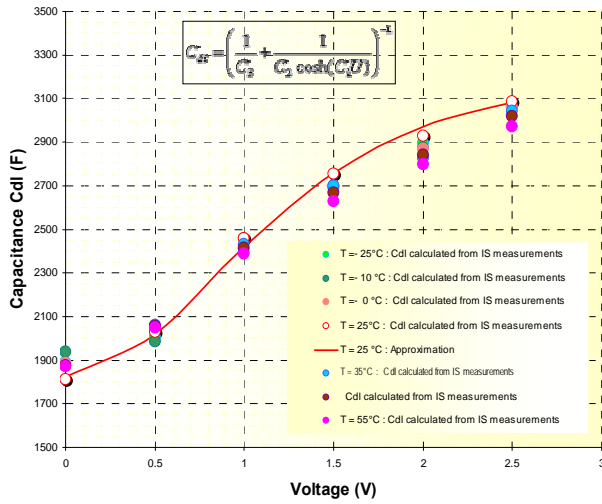


Fig. 6 Behaviour of capacitance C_{dl} with voltage at different temperatures

T (°C)	C ₁ (F)	C ₂ (F)	C ₃ (F)
-25	1.19	4387	3331
-10	1.1	4414	3403
0	1.48	4881	3082
25	1.5	4250	3190
35	1.35	4771	3108
45	1.42	4800	3108
55	1.39	4897	3053

Table. 1 Approximation function of C_{dl} parameters at different temperatures

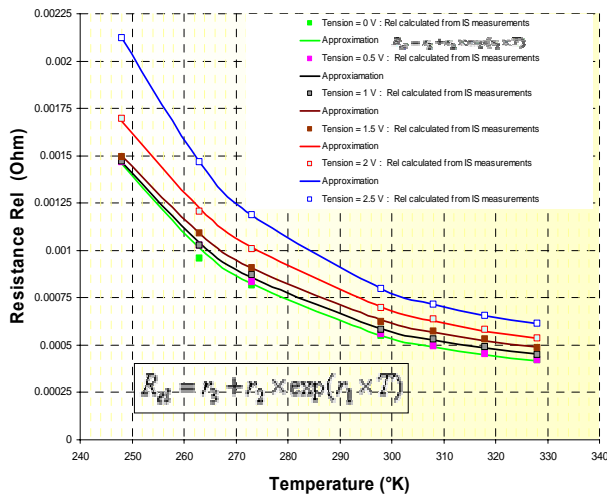


Fig. 7 Behaviour of electrolyte resistance R_{el} with temperature at different voltages

Voltage (V)	r ₁	r ₂	r ₃
0	-0.035	6.483	0.000356
0,5	-0.035	6.542	0.000361
1	-0.033	3.908	0.000377
1,5	-0.031	1.884	0.000387
2	-0.03	2.144	0.000421
2,5	-0.035	9.45	0.000517

Table. 2 Approximation function of electrolyte resistance R_{el} at different voltages

Temperature (°C)	Current (A)	Discharge time (s)	Max ((V _{measured} -V _{simulated})/V _{nom}) (%)
-25	500	3	0.4
	300	5	0.5
-10	500	3	0.2
	300	5	0.4
0	500	4	0.2
	300	5	0.2
25	500	4	1.2
	300	5	0.6
35	500	3	0.4
	300	5	0.8
45	500	3	0.4
	300	5	0.8
55	500	3	0.2
	300	5	0.4

Table. 3 Difference between of measured voltage and model voltage in the time domain under constant current discharge for B supercapacitor at different temperatures

Assessment of electrical model

Constant current charge/discharge method is the most straightforward method. It requires the application of a current step charge/discharge to the supercapacitor from initial stabilized voltage. The voltage response as function of time is measured by four wires method. In practice we have applied full charge/discharge current to the supercapacitor B between 0V and 2.5 V with three current's level (100A, 200A, 400A) and full discharge between 2.7V and 0V for F(2600F, 2.7V) supercapacitor with two current level (300A, 500A) at ambient temperature (25 °C). Comparison between measurements and simulations is represented in Fig. 8. It shows differences less than 2 % in the worst case.

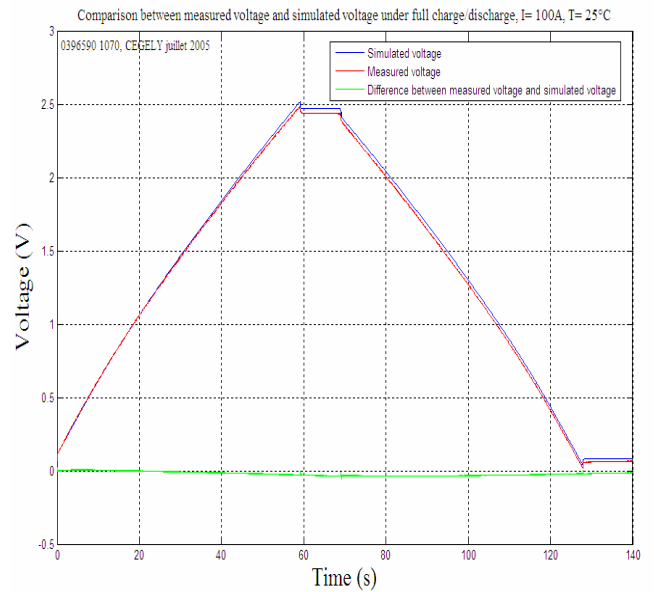
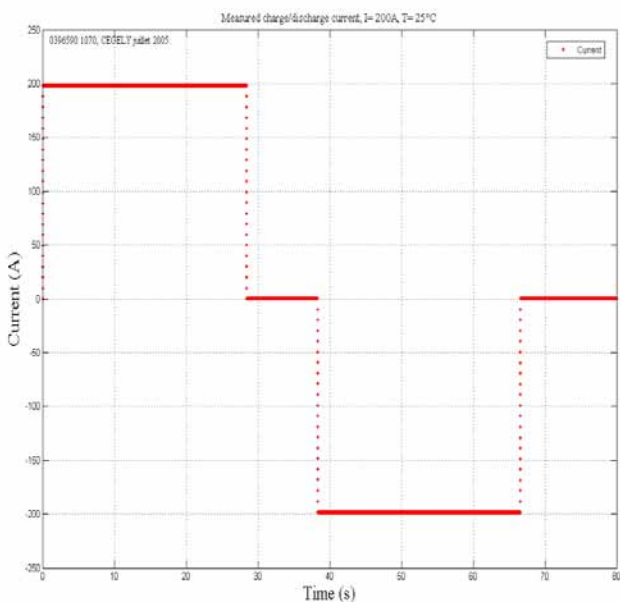
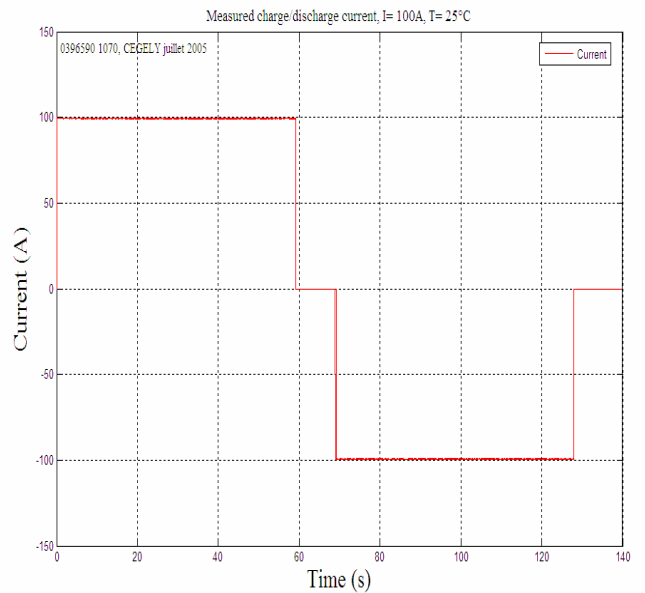
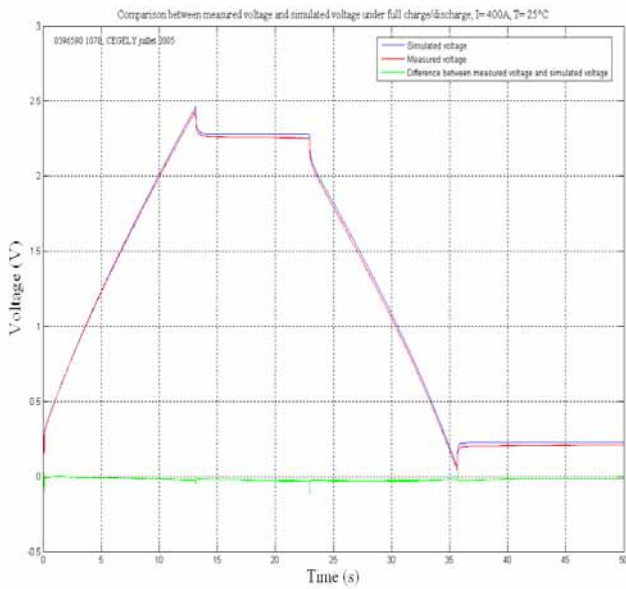
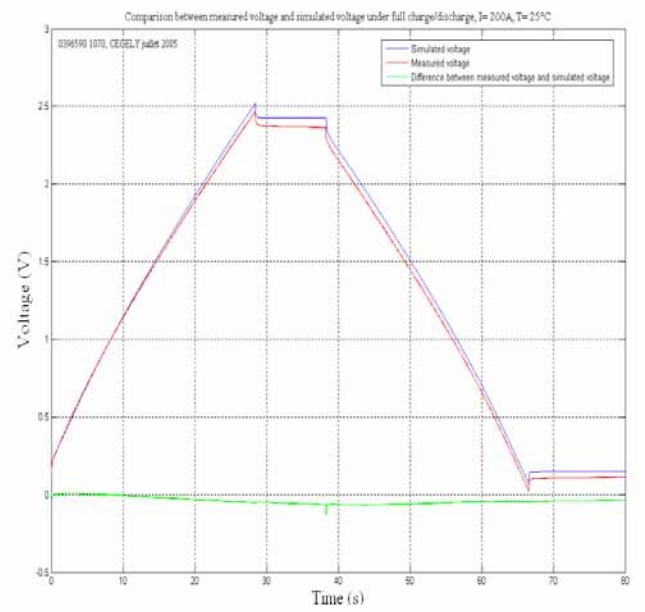
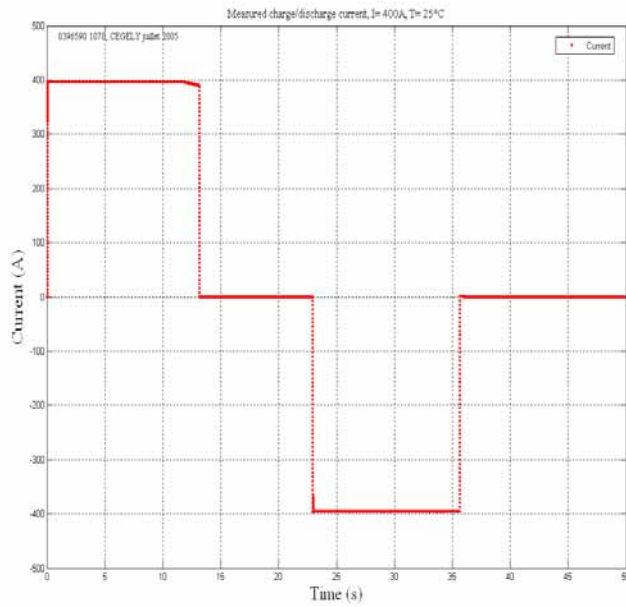


Fig. 8 Comparison between measured voltage and simulated voltage under full charge/discharge with three levels currents (100 A, 200 A, 400 A)

The difference observed between measurements and simulations may be explained by:

- The model proposed is based on the mean value of capacity of homogenous porous electrode with uniform pore size. It gives good approximation and results. In fact the electrode presents a pore size distribution not uniform.
- The model proposed take into account the in pore diffusion or frequency diffusion, but it neglect the pore size diffusion, observed in low frequencies [18][19].
- The precision of our instruments in the order percentage of the difference observed between measurements and simulations.

Conclusions

We proposed in this work a simplified method to avoid effect coupling in spectroscopy measurements. Indeed we have defined a measurement procedure. It is practice and precise.

The electric model gives a good agreement between measurements and simulations. It is based on physical phenomena. It is very interesting to model supercapacitors in good state of health.

We have modelled in-pore dispersion with frequency, a complete model witch takes into a count pore size dispersion will be proposed in our next papers.

The measurement voltage and the model voltage give a good agreement. It introduces the dependency of capacitance C_{dl} , resistance R_{HF} and τ to voltage and temperature.

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