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ELECTRIC AND THERMAL CHARACTERIZATION OF INORGANIC SUPERCAPACITORS

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Abstract: *Supercapacitors represent an alternative for the actual storage devices being able to provide high power density. The present paper is focused on characterizing the inorganic aqueous stacked supercapacitors. DC charge / discharge method was used to determine the dependency between the electric series resistance, capacitance and temperature. Electric impedance spectroscopy method was used to determine the variation with frequency of the real and imaginary part of the impedance. Based on the experiments an electric model was developed. The results of the simulations are compared with the experiments and the results are interpreted and discussed.*

Key words: *supercapacitor, capacitance, electric series resistance, electric model.*

1. Introduction

Supercapacitors are electrochemical double layer capacitors (EDLC) with short time constants. Supercapacitors are suitable for multiple applications, especially because of their high power density, high capacitance in a small volume, long life cycle and reduced electric series resistance (ESR).

The supercapacitors store the electric charge between the electrodes, at the level of the surface-electrolyte interface. Because the electric layers are thin and the contact surface is large, the capacity of the supercapacitor can reach increased values and high power density and lifetime [3]. The ideal operating principle is based on not including faradic reactions [3]. Unfortunately, because of the impurities from the electrolyte, chemical reactions, which increase the value of the ESR and reduce the lifetime of the device, can appear.

The internal structure of a supercapacitor is illustrated in Fig. 1.

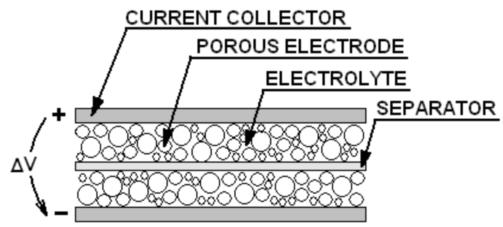

Fig. 1 *EDLC Internal Structure [11]*

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As it can be seen in Fig. 1, a supercapacitor is composed of a current collector, two porous electrodes, electrolyte and a separator, which allows the ion transfer and avoids the physical contact between the electrodes [8]. There are tree types of pores: micropores (<2nm), mesopores (between 5 nm and 50 nm) and macropores (between 5 μm and 50 μm) [6]. As it was demonstrated in [2] and [5], the optimal pore size is 0.7 nm for aqueous electrolyte and 0.8 nm for organic electrolyte.

Lately, the landscape of the short time storage devices is continuously researched by industry and also by academic institutions. Multiple types of supercapacitors such as organic, inorganic, hybrid and pseudo-capacitors have been developed lately. The type of the supercapacitor is given by the electrolyte and by the type of the electrode material.

The performances of the supercapacitors are limited by the decomposition voltage of the electrolyte. For organic electrolyte the breakdown voltage is maximum 3.5 V and for inorganic one is 1.2 V.

There are manufacturers that prefer inorganic electrolytes to organic ones because of the increased power density and high efficiency. Also, the inorganic supercapacitors use aqueous electrolyte to reduce the risk of explosion at high temperatures.

The state of the art emphasizes that inorganic stacked supercapacitors are used in high voltage applications 400 V, 300-350 Wh and high power (megawatts) [1], [9], [10].

2. Objectives

The aim of the present paper is to characterize the inorganic aqueous stacked supercapacitors. As sample, an ECOND aqueous stacked inorganic 14 V / 40 F supercapacitor was used. The ECOND sample used in the experiments is a cycled one and consists in 20 cells, each of them having 0.7 V and 800 F.

The focus was oriented on an electric and thermal study of the tested supercapacitor in order to determine the variation of its internal parameters. Direct current (DC) charge / discharge and electric impedance spectroscopy (EIS) measurements were made. The two corresponding test benches are described in the paper. The DC charge / discharge and EIS experiments are illustrated and interpreted.

Based on the experiments an electric model was developed. The results of the simulation of the model are compared with the results of the experiments and the conclusions are taken.

3. Experimental Methods, Results and Discussions

Lately, the manufacturing technology of the supercapacitors was improved in order to increase their performances. The testing procedure of the supercapacitor was developed in accordance with the specifications of the IEC 62391 standard emitted in 2006.

In order to determine the behaviour of the storage device and to characterize the ECOND inorganic supercapacitor, DC charge / discharge and electric impedance spectroscopy methods were implemented and measurements on the chosen sample were made.

3.1. DC Charge / Discharge

DC charge / discharge method was the first method used for characterizing the inorganic aqueous stacked ECOND supercapacitor.

The test bench used for DC charge / discharge measurements is illustrated in Fig. 2.

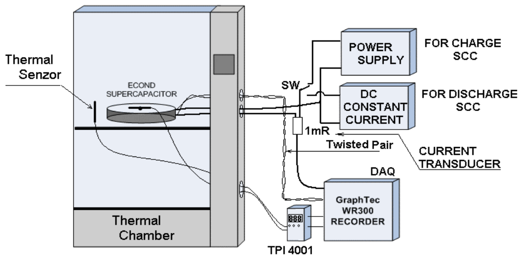


Fig. 2 *DC charge/discharge test bench*

The configuration used for DC charge / discharge experiments consists in: Thermal Arraycorder WR300 Graphtec, Climats Thermal Camera, ARDETEM TPI 4001 AR Thermocouple, DC charge / discharge source and SONY Tektronix Arbitrary Waveform Generator.

The DC charge / discharge procedure developed by INRETS LTN for characterizing the supercapacitors was used. In order to obtain a proper DC characterization of the inorganic supercapacitor the voltage and discharging current were varied and tested at different temperatures. As threshold voltage, the nominal 14 V voltage was chosen. Also, the supercapacitor was discharged at the threshold current 50 mA / F, 100 mA / F and 300 mA / F.

The DC charge / discharge procedure consists of four phases. In the fist phase the inorganic supercapacitor is charged at 5mA / F until it reaches the chosen threshold voltage. In the second phase the supercapacitor is stabilized for 30 minutes. In the third phase the supercapacitor is discharged for Δt=5 seconds at the chosen values of the current (50 mA / F, 100 mA / F and 300 mA / F). The value of the voltage is stored (U_1) and it will be used to determine the ESR. In the fourth phase is monitored the relaxation process of the inorganic supercapacitor. After the first 5 seconds of the relaxation process the value of the voltage is stored (U_2).

The value of the ESR is determined by using the formula:

$$ESR = \frac{U_2 - U_1}{I_{mean}} = \frac{\Delta U_{cap}}{I_{mean}} . \qquad (1)$$

Where:

$$I_{mean} = \frac{1}{\Delta t} \int_{\Delta t} i(\tau) d\tau \qquad (2)$$

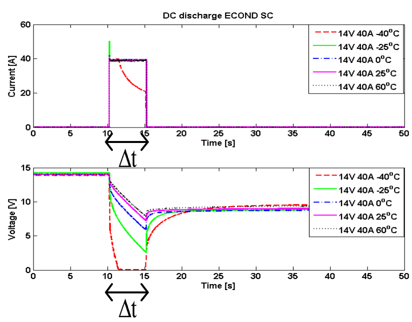
$$I_{mean} = \frac{1}{\Delta t} \sum_k (\frac{i(\tau_k + \Delta\tau) + i(\tau_k)}{2}) \cdot \Delta\tau \qquad (3)$$

Where k is the sampling index and $\Delta\tau$ is the sampling period for the discharging process.

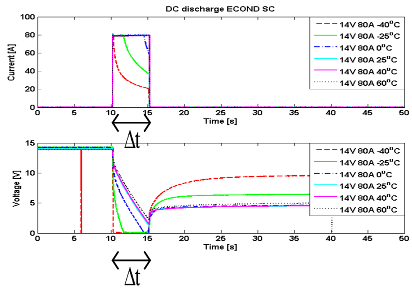
To determine the value of the capacitance of the inorganic supercapacitor the following formula was used:

$$C = \frac{I_{mean} \cdot \Delta t}{\Delta U_{cap}} . \qquad (4)$$

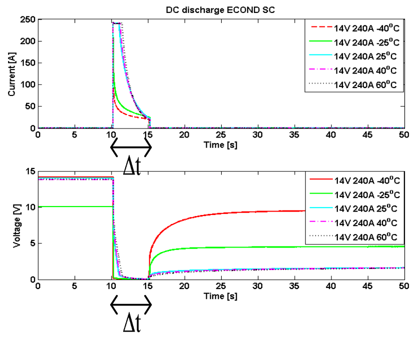
For testing the sample, the measurements were made at the nominal voltage (14 V) and the discharging current and temperature were varied. The experimental results are illustrated in Fig. 3.



a)



b)



c)

Fig. 3 *DC discharge measurements at a). 40* A *b). 80* A *c). 240* A

As it can be seen in Fig. 3, the discharging process, the relaxation process and the internal parameters of the tested supercapacitor are dependent with temperature. In Fig. 4 and Fig. 5 is emphasized that at high temperatures, the performances of the tested supercapacitor are more increased than at low temperatures.

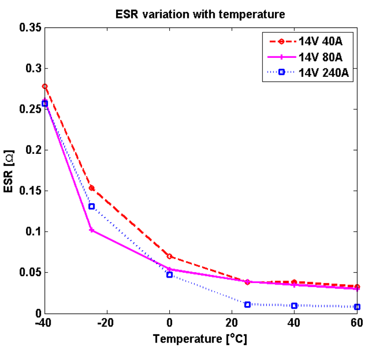


Fig. 4 *ESR variation*

The results illustrated in Fig. 4 demonstrate that the value of the ESR is increased at low temperatures and decreases while increasing the operating temperature.

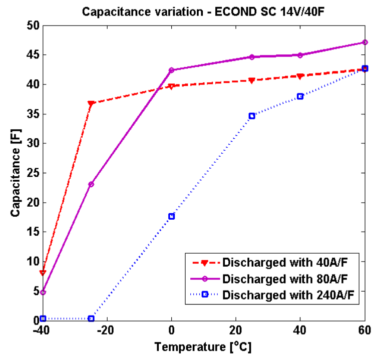


Fig. 5 *Capacity variation*

Fig. 5 demonstrates that the value of the capacitance increases while increasing the temperature. Thus, the results of the DC charge / discharge experiments demonstrate that at high temperatures the performances of the tested inorganic ECOND supercapacitor are better than at low temperatures, the performances drastically varying with the temperature range.

3.2. Electric Impedance Spectroscopy

In order to completely characterize the behaviour of the inorganic supercapacitor, electric impedance spectroscopy (EIS) method was applied. EIS method is a technique used to identify the variation of the devices and to analyze their behaviour [7]. EIS experiments provided data to determine the dependency between the real and imaginary part of the measured impedance and also, the dependency with the frequency and temperature [9].

The test bench used for EIS measurements is illustrated in Fig. 6.

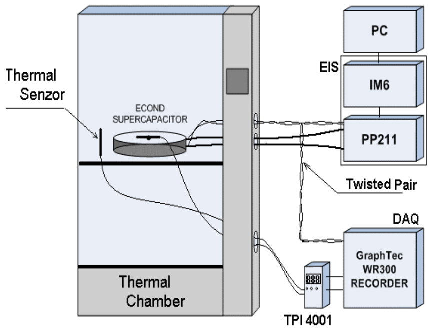


Fig. 6 *EIS test bench*

The configuration used for EIS experiments consists in: Zahner Electrik PP211 device, Thermal Arraycorder WR300 Graphtec, Climats Thermal Camera and ARDETEM TPI 4001 AR Thermocouple.

The measurements were made in the frequency range 1 mHz-100 Hz-1 kHz with 5 point / decade and with a 100 mV alternative signal applied at the terminals of the tested ECOND supercapacitor. The inorganic supercapacitor was charged at its nominal voltage (14 V) and the Thales software maintained the nominal voltage during the measurements. The experimental results are illustrated in Fig. 7.

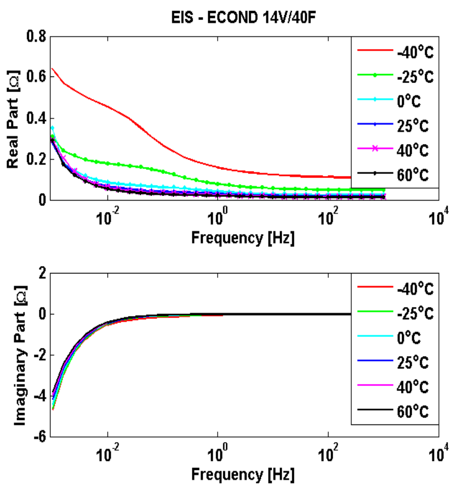


Fig. 7 *EIS Measurements*

4. Electric Model

Based on the DC charge / discharge and EIS experiments, an empirical electric model for the supercapacitor tested at a temperature of 25 ^{o}C was developed and it is illustrated in Fig. 8.

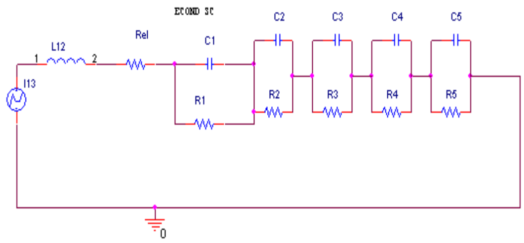


Fig. 8 *Electric model*

The determined model (Fig. 8) was simulated in PSpice environment with the same constraints as the experiments: 14 V nominal voltage, 40 A discharging current, 5 seconds of discharging.

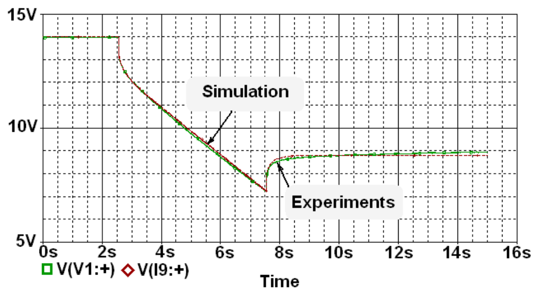


Fig. 9 *Simulation vs. Experiments*

As it can be seen in Fig. 9, the simulation results fit the experimental ones, thus validating the developed model.

5. Conclusions and Future Work

In order to completely characterize the behaviour of the ECOND aqueous stacked inorganic supercapacitors, electric and thermal experiments were made.

As experiments demonstrated, the variation of the capacitance and of the ESR is dependent with voltage, frequency and temperature [4].

The experiments illustrated that the performances of the inorganic supercapacitors are increased while they are operating at high temperatures. Operating at high temperatures is safer for inorganic supercapacitors than for organic ones, being no risk of explosion.

Based on the experiments, an electric model was developed and validated.

As future work, it has to be done a comparison between the characteristics of the organic and inorganic supercapacitors. Also, a mathematical model has to be determined and a comparison between the mathematical and electric model has to be made.

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