New approach to supercapacitor testing and dynamic modelling

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Abstract—**Energy storage systems undergo an intense application in both stationary and vehicle applications. Supercapacitors in particular present interesting proprieties due to its high power characteristics. To study and analyze its dynamic behavior it is necessary to apply test procedures, such as electrochemical impedance spectroscopy. However, the classical way in which these tests are carried out are not easily applicable to high capacitance supercapacitors, due to the high currents involved. We present a new approach to test these types of supercapacitors and develop a simple and precise dynamic model, which is experimentally validated.**

Keywords- supercapacitors, dynamic modelling, EIS, testing

I. INTRODUCTION

Among the available energy storage technologies, supercapacitors exhibit high power densities, which make them especially suitable as part of hybrid energy power systems, either in stationary or vehicle applications. Supercapacitors present an extremely high surface due to its micropore electrodes and therefore present capacitances in the order of thousands of Farads [1]. This high capacitance, combined with a very low series resistance allow its use as power boosters, accepting or supplying very high power loads during shorts periods of time (seconds to minutes, depending on the current load). Moreover, and as an important difference with batteries, supercapacitors accept deep discharges and are able to withstand high number of cycles due to its charge separation phenomena, instead of chemical phenomena. These special characteristics are a challenge for the testing of supercapacitors, due to their large operation currents.

Existing test procedures are time or frequency domains tests. Time domains tests are usually applied to calculate the equivalent series resistance (ESR), time constant and to validate the capacitive behavior by investigating the charge/discharge symmetry through voltamogram plots. This time domain approach has been used by some authors, such as Lajnef [2], [3] or Michel [4], but not as the unique approach, but as a complement to frequency domain tests.

Frequency domain tests, such as electrochemical impedance spectroscopy (EIS), need the application of a small ac excitation signal (either current or voltage). This excitation signal will cause the system to react, generating an ac voltage (if the excitation signal is current) or ac current (if the excitation signal is voltage). The ac excitation signal can be applied with a fixed (not usual) or variable frequency, which in the variable case can be programmed as a sweep. Obtained the ac voltage and current over a wide range of frequencies, it is possible to calculate the complex impedance of the system under test.

II. STATE-OF-THE-ART

A. *EIS test procedure*

Normally, EIS tests are carried out with impedance analyzers. These equipments control the test by generating the ac excitation signal and recording the resulting voltage or current ripple to calculate the complex impedance. However, impedance analyzers are equipments more focused to test passive elements, which can be correctly characterized with a typical value of 60 mA current threshold of the impedance analyzer. This current limit is inadequate for active elements, such as batteries, fuel cells or supercapacitors, due to the high operation currents. Therefore, another equipment, named potentiostat, is

978-1-4244-8218-4/10/$26.00

used with the impedance analyzer as interface to boost the current. However, commercial potentiostats usually allow a maximum of 100 A. This current booster allows testing commercially available fuel cells and batteries, as well as low capacitance supercapacitors.

Up to now, other authors have tested supercapacitors smaller than 3000 F; therefore, commercial impedance analyzers and potentiostats presented no current limitations. For example, Lajnef [2] carried out voltage control (potentiostatic) EIS tests in a 10 mHz to 1 kHz frequency interval for a 2600 F supercapacitor. Dougal [5] also conducted potentiostatic EIS tests with 20 mV ac voltage ripple for a 100 F supercapacitor. And Buller [6] applied a galvanostatic EIS tests to a 1400 F supercapacitor between 10 μHz and 6 kHz.

Recently developed high capacitance supercapacitors (3000 F onwards), which allow higher power loads, need the order of hundreds of amperes alternating current to obtain a millivolt voltage ripple. Smaller currents would result in a large superimposed noise to the ac voltage ripple, which would hinder obtaining clear results. Therefore, currents larger than 100 A are needed to carry out EIS tests satisfactorily and commercial potentiostats are inadequate for its high operation currents.

B. Dynamic models

Known the complex impedance calculated with the EIS tests, this complex impedance can be fitted to an electric circuit, which is the model used. Most authors model the supercapacitor as the connection of a variable number of RC networks. There is no defined criterion of which should be the number of networks involved. For example, Lajnef [2] considers different time constants (RC networks) for the entire frequency interval. Zubieta [7] considered a three time-constants circuit, whilst Buller [6] does not reveal this information. Other authors, such as Dougal [5] modeled a variable order selection model, so that the number of RC network varied depending on the load characteristics. In general, the models presented include a too high number of elements (especially capacitors), which increase the model complexity.

III. PROPOSED EIS PROCEDURE

A. Experimental procedure

In this work we propose an experimental EIS test procedure, which allows testing high capacitance supercapacitors. To do so the equipment used includes an impedance analyzer, a programmable dc power source, a dc electronic load and a control and acquisition system (dSpace system). No potentiostat is used due to the current limitation it presents for the supercapacitor under test: Maxwell Boostcap 3000 F 2.7 V.

The first decision which must be taken is under which mode the EIS tests should be carried out: galvanostatic or potentiostatic. Either option is suitable; however, storage systems allow an easier current control, rather than a voltage control. Therefore, in this work the EIS tests are conducted in galvanostatic mode. Even if current is the control variable, the ultracapacitor voltage must be carefully monitored, to avoid over-voltage.

For other electrochemical systems, such as batteries or fuel cells, a small amplitude ac current component is normally superimposed to a dc operation level. However, supercapacitors charge and discharge very quickly, with voltage varying between rated voltage (2.7 V) and half of its rated value. This voltage variation is not acceptable during EIS tests, as the test conditions (voltage, temperature, current, etc.) must be kept constant to guarantee linearity during the test. To avoid this voltage variation, we propose to apply only the ac level, with no superposed dc current. This test procedure guarantees that the voltage at the beginning and end of the test will be the same due to the fact that the energy stored during half of the period of the ac current signal will be discharged during the other half. The ac current amplitude is set at 150 A, as that is the current at which a reasonable ac voltage ripple is obtained. The EIS tests are carried out for different voltage levels, to observe the dependency of the model parameters with voltage. The ac signal frequency is variable from 0.1 Hz to 1 kHz, as it allows studying the supercapacitor behavior in a wide frequency interval.

The impedance analyzer controls the EIS test, which is the equipment which generates the ac excitation signal with variable frequency and monitors current and voltage to calculate the impedance. Due to the fact that there is no commercial impedance analyzer or potentiostat that can work under 150 A we propose to use the impedance analyzer to control other equipments which can work at high currents: a programmable dc electronic load and power source. The impedance analyzer is programmed to generate the ac excitation signal, whose positive semi-cycle is sent to the electronic load and negative semi-cycle is sent to the power source. As seen in Figs. 1 and 2, with this setup the combined control of the electronic load and power source is able to generate a complete 150 A ac current signal. A real-time acquisition and control system (dSpace) is the interface between the impedance analyzer and the power source and electronic load.

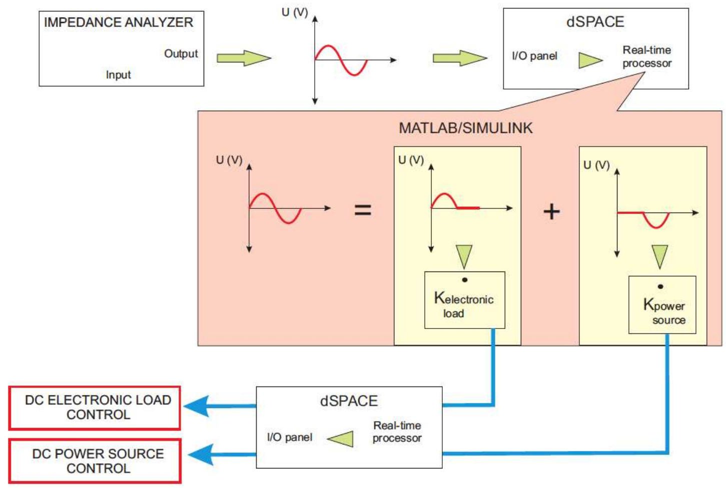


Fig. 1: EIS control for supercapacitor testing

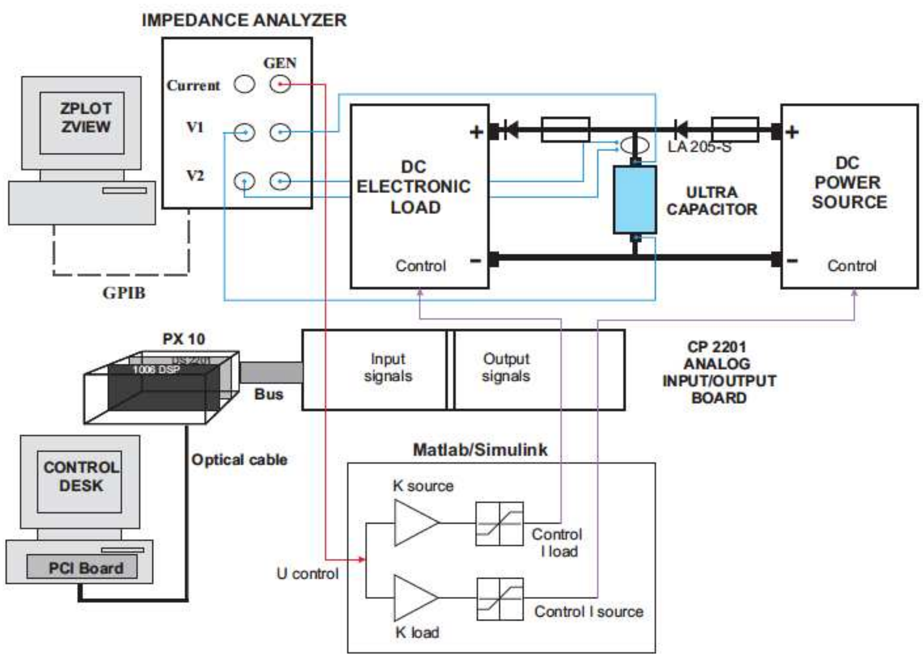


Fig. 2: EIS experimental setup diagram

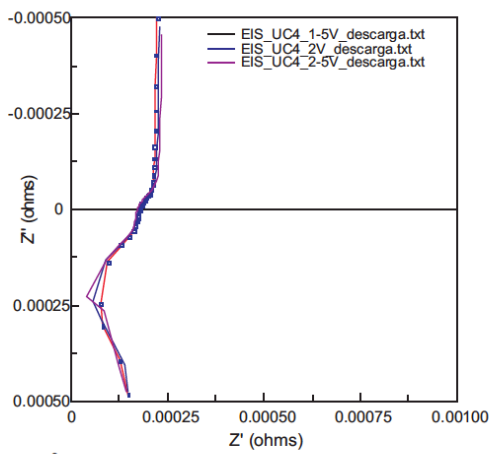
B. Results

The graphical representation of the EIS tests are the Nyquist plots (Z' and Z" real and imaginary part of the impedance) shown in Fig. 3. The supercapacitor capacitive behavior is restricted to a small interval (from 0.1 Hz to 31.6 Hz). For the lower frequencies of this interval the Nyquist plot is practically a vertical line, which is the representation of a capacitance in series with a resistance, whose value (0.25 mohms) is identified as the intersection between the curve and the abscissa axis. In literature, this part of the curve is not totally vertical due to the contact resistance between components, high electrode porosity or low proton mobility inside the electrodes [8].

From 1 Hz to 31.6 Hz the complex impedance changes to a 45º slope due to diffusion phenomena at the electrode pores. This diffusion phenomenon can be represented by a Warburg impedance, which is the series connection of RC networks. In this work, the diffusion has been represented with two RC networks, avoiding the use of higher number of networks, which complicates the modelling and requires more computational work. From 31.6 Hz onwards, the supercapacitor behavior is totally inductive.

IV. SUPERCAPACITOR DYNAMIC MODEL

The complex impedance values obtained from the Nyquist plots allow to fit the plot to a particular equivalent circuit. The user selects the circuit topology. In our case, we have decided to reduce the number of RC networks presented by other authors and to simplify the model. To do so, the Nyquist plot was fitted to the circuit presented in Fig. 3, which includes a series inductance, capacitance and two RC networks. The series inductance is not considered in the final simulation, but taken into account at this point improves the fitting of the rest of parameters. For each voltage tested, there is a set of parameters. These parameters are then processed with a statistical software (Statgraphics) to obtain the relationship between each parameter and the voltage. Obtained an equation for each parameter, the model was implemented in Matlab/Simulink and experimentally validated, as shown in Fig. 4.



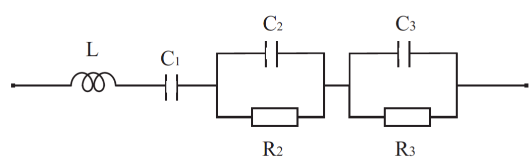


Fig. 3 Nyquist plot obtained after the EIS tests and supercapacitor equivalent circuit

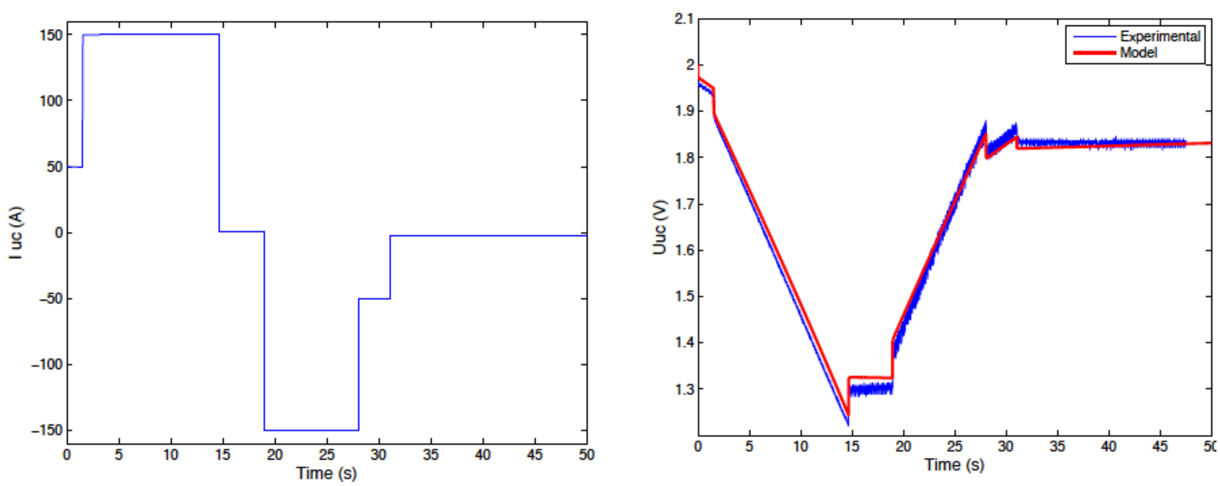


Fig. 4 Experimental validation during an abrupt current load

V. CONCLUSIONS

In this work we have presented a novel approach to supercapacitor EIS testing procedure for high capacitance supercapacitors ($C \geq 3000$ F). The classical frequency domain tests carried out with and impedance analyzer and potentiostats were found to be inadequate due to the high currents needed to carry out the electrochemical impedance spectroscopy tests (EIS). Therefore, we propose to eliminate the potentiostat and substitute it by a controlled combination of electronic load and power source, in order to generate the ac current needed for the test.

Moreover, the results of these EIS tests were fitted to a simple circuit, able of reproducing the internal phenomena which takes place in the supercapacitor. The model presented is simpler than the one presented by other authors, but is able to reproduce the supercapacitor dynamics.

VI. REFERENCES

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