# FREQUENCY DOMAIN ANALYSIS FOR ELECTROCHEMICAL SUPERCAPACITORS

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***Abstract***-The paper deals with the problem of creating a non-linear model of the electrochemical supercapacitors and measuring their electrical parameters in wide frequency range. Formalization of the model as a non-linear equivalent circuit enables to explain non-linear behavior of electrochemical supercapacitors such as dependence of their capacity and electrical series resistance (ESR) on the different voltage levels and frequencies. In order to determine the non-linear supercapacitor equivalent circuit parameters we carry out the impedance measurements and then perform fitting of obtained measurement results by means of impedance function, which describes the electrochemical supercapacitor non-linear properties with greater accuracy.

## I. Introduction

The electrochemical supercapacitors are new energy storage devices. They have capacitance of hundred and thousand Farads and can be combined to power modules by series or parallel connection, available either in open or closed design.

The electrochemical supercapacitor consists of two electrodes, separator and current collectors as shown in Figure 1 [1]. The electrodes are immersed into electrolyte. Across the phase boundary between electrodes and electrolyte there are two layers of excess charge of opposed polarity. They are called the electrochemical double layers.

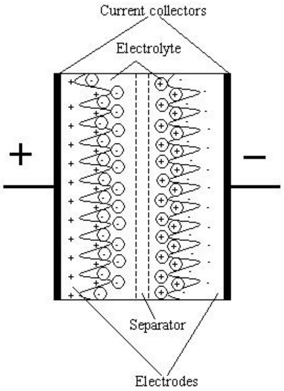

Figure 1. Electrochemical supercapacitor structure

Traditional capacitors have high specific power (power density, W/kg) and low specific energy (energy density, Wh/kg). Conversely, batteries generally have high specific energy but low specific power. The electrochemical supercapacitors bridge the gap between conventional capacitors and batteries. They are now being used in a number of applications. It is important to distinguish two different types of electrochemical supercapacitor applications. In the first place it is the low-power devices such as memory data backup, liquid crystal displays (LCDs) and other electronics with low-current consuming [1-3].

Another application is high-power devices such as hybrid electric vehicle (EV), power electronics and telecommunications, where short, high-power pulses are required. So far the choice of a supercapacitor for particular application is mostly determined by storage capacitance (given for charge/discharge method specified by manufacturer), rated voltage and electrical serial resistance (ESR) usually given at alternative and direct current. These characteristics can give a rough impression of electrochemical supercapacitor performance to a customer, but in many cases it would be more important to know a behavior of a supercapacitor in different operative conditions with various electrical devices.

This problem can be solved by two methods: the first one is a test of an electrochemical supercapacitor with real electrical device. Another method is a digital simulation of a supercapacitor and modeling its behavior in different operative conditions. In particular, for instance, comparative test of supercapacitor behavior is obviously very complicated process for electric vehicle and similar power applications, where the high-current value is needed. The second method is more acceptable in this case because it requires the supercapacitor digital model, which is usually presented by its equivalent circuit.

The main problem that was solved in this paper is a development of the non-linear electrochemical supercapacitor equivalent circuit and definition of its electrical component parameters. By means of supercapacitor equivalent circuit we can perform digital simulation of supercapacitor behavior in various operative conditions using the numerical simulation software such as MathCAD$^{TM}$, MatLab$^{TM}$ and others.

## II. Modeling electrochemical supercapacitors

In order to determine the supercapacitor equivalent circuit it is necessary to measure the supercapacitor impedance spectrum and then to perform fitting of obtained results with chosen equivalent circuit, which more accurately describes the particular supercapacitors properties. Conway's textbook [1] provides a comprehensive overview of the existing supercapacitor equivalent circuits. The usual and simplest supercapacitor equivalent circuit comprises an ideal capacitor in series with a resistor. But, as shown by Conway, such an equivalent circuit is not valid for electrochemical supercapacitors because both the non-Faradaic and Faradaic processes take place during electrical charge storage. In the absence of self-discharge process, the double-layer capacitance $C_{DL}$ corresponds to a non-Faradaic behavior and Faradaic $C_F$ presents a Faradaic behavior, which corresponds to electrosorption of supercapacitor electrodes.

The supercapacitor electrodes are highly porous in order to achieve a large electrode/electrolyte interface while providing a sufficient volume of active material. To create a non-linear model of electrochemical supercapacitors we used physically relevant non-linear transmission-line model of a porous electrode in which the parameters are determined at different voltage levels, as shown in Figure 2.

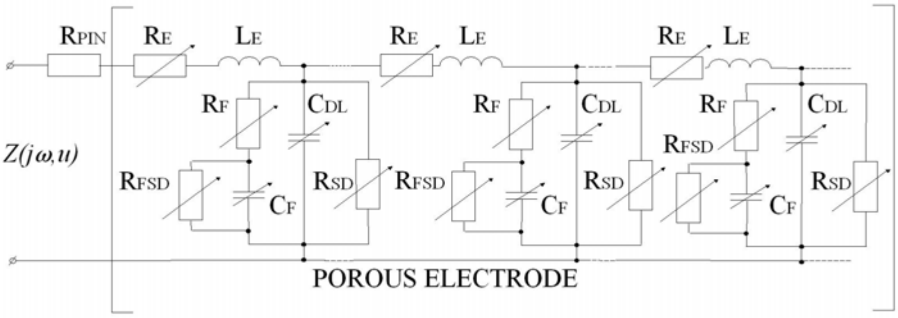

Figure 2. Non-linear electrochemical supercapacitor equivalent circuit

In this non-linear equivalent circuit the distributed double-layer capacitance $C_{DL}$ is in parallel to serial connection of distributed Faradaic capacitance $C_F$ and Faradaic resistance $R_F$. The supercapacitor equivalent circuit also includes the pin resistance $R_{PIN}$, the distributed electrode resistance $R_E$ and parasitic distributed electrode inductance $L_E$. The electrochemical supercapacitor self-discharge is represented by distributed Faradaic and non-Faradaic self-discharge resistances $R_{FSD}$ and $R_{SD}$ respectively. The next equation gives the impedance function of such an equivalent circuit.

$$Z(j\omega,u) = R_{PIN}(u) + \sqrt{\frac{R_E(u) + j\omega L_E}{\left( \frac{1}{R_F(u) + \frac{1}{j\omega C_F(u) + \frac{1}{R_{FSD}(u)}}} + \frac{1}{R_{SD}(u)} + j\omega C_{DL}(u) \right)}} cth\left[ \sqrt{(R_E + j\omega L_E)\cdot\left( \frac{1}{R_F(u) + \frac{1}{j\omega C_F(u) + \frac{1}{R_{FSD}(u)}}} + \frac{1}{R_{SD}(u)} + j\omega C_{DL}(u) \right)} \right] \quad (1)$$

Here ω is an angular frequency and *u* is a voltage level to which electrochemical supercapacitor was charged.

## III. Methodology

The impedance measurements were performed for the commercial samples of the electrochemical supercapacitors model HE0120C-0027A with a nominal 120 Farad and a rated voltage 2.7 Volt manufactured by Ness Capacitor Co., Ltd (South Korea). These electrochemical supercapacitors are based on an activated carbon with organic electrolyte. The impedance data was collected with our multi channel measurement system controlled with digital signal processor (DSP) and personal computer. The hardware and the control software were specially designed for impedance measurements.

The impedance measurements were performed under potentiostatic conditions in frequency range of 1mHz to 1kHz with amplitude of measurement signal of 10 mV. The experimental impedance data were measured at different voltages of 0V to 2V. The obtained experimental results were fitted to Equation (1) with the complex non-linear-least-squares data fitting computer program (LEVM) developed by Dr. J. Ross Macdonald [4] as shown in Figure 3.

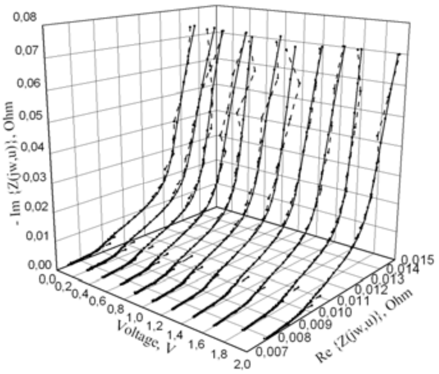

Figure 3. Experimental impedance data (solid line) and non-linear fit results (dash line)

As shown in Figure 3 the experimental impedance spectra were correctly fitted by impedance function of porous electrodes Equation (1). The set of parameters representing the fitting results of impedance data are shown in Table 1.

Table 1. - Set of parameters representing the fit results of impedance data

| Voltage (V) | $R_{PIN}$ (mΩ) | $R_E$ (mΩ) | L (nH) | $R_F$ (mΩ) | $C_{DL}$ (F) | $C_F$ (F) | $R_{FSD}$ (Ω) | $R_{SD}$ (Ω) |
|---|---|---|---|---|---|---|---|---|
| 0 | 7.499 | 4.147 | 15.0 | 32.605 | 62.781 | 31.793 | 4.959 | 31.749 |
| 0.2 | 7.561 | 4.119 | 15.0 | 34.633 | 63.968 | 30.987 | 4.463 | 29.155 |
| 0.4 | 7.541 | 4.131 | 15.0 | 32.068 | 63.071 | 31.656 | 5.651 | 157.666 |
| 0.6 | 7.606 | 3.899 | 15.0 | 31.892 | 63.454 | 31.876 | 4.382 | 38.402 |
| 0.8 | 7.404 | 4.545 | 15.0 | 33.302 | 63.694 | 31.452 | 9.301 | 144.067 |
| 1 | 7.499 | 4.147 | 15.0 | 32.605 | 62.781 | 31.793 | 4.959 | 126.694 |
| 1.2 | 7.405 | 4.565 | 15.0 | 33.588 | 65.194 | 32.619 | 6.820 | 169.877 |
| 1.4 | 7.439 | 4.904 | 15.0 | 34.813 | 65.831 | 31.339 | 4.831 | 164.508 |
| 1.6 | 7.497 | 4.931 | 15.0 | 31.842 | 63.933 | 32.175 | 4.704 | 100.033 |
| 1.8 | 7.793 | 5.145 | 15.0 | 33.732 | 64.417 | 31.349 | 12.978 | 154.637 |
| 2 | 7.808 | 5.542 | 15.0 | 34.013 | 66.402 | 31.799 | 4.273 | 148.904 |

As shown in Table 1 the most significant value changes for the distributed electrode resistance $R_E$, the distributed double-layer capacitance $C_{DL}$ and the distributed self-discharge resistance $R_{SD}$ are observed at the bottom of Table 1. This corresponds to the non-linear electrochemical processes that take place in the electrochemical supercapacitor with the increase of the operated voltage. But some electrical parameter values are not influenced by the voltage changes, for example, the parasitic distributed electrode inductance $L_E$. The inductance $L_E$ is not changed by the non-linear electrochemical process and as a result is a linear component.

By means of the parameter set presented in Table 1 we can obtain the interpolation functions as an Equation System (2) for each supercapacitor parameter. These interpolation functions are theoretical representation of the non-linear electrochemical laws that describe the non-linear behaviour inside the voltage range. For the Equation System (2) we limit the polinom to the sixth power. The higher polinom power is the closer it approches to the real experimental results.

$$\left.\begin{array}{l}
R_{PIN}(u)=7.496+0.9761u-4.6013u^{2}+9.5988u^{3}-10.153u^{4}+5.0732u^{5}-0.9361u^{6}\\
R_{E}(u)=4.1527-0.4481u+1.6326u^{2}-4.0377u^{3}+5.7011u^{4}-3.2953u^{5}+0.6598u^{6}\\
R_{F}(u)=32.655+32.695u-177.63u^{2}+336.41u^{3}-287.73u^{4}+114.27u^{5}-17.152u^{6}\\
C_{DL}(u)=62.814+8.62.83u-20.571u^{2}-1.6896u^{3}+38.193u^{4}-30.505u^{5}+6.9885u^{6}\\
C_{F}(u)=31.764-9.9092u+48.886u^{2}-92.789u^{3}+84.606u^{4}-36.856u^{5}+6.1299u^{6}\\
R_{FSD}(u)=24.693+330.59u-840.87u^{2}+1293.8u^{3}-907.1u^{4}+261.8u^{5}-21.609u^{6}\\
R_{SD}(u)=4.8074+26.818u-215.32u^{2}+572.06u^{3}-643.42u^{4}+321u^{5}-58.535u^{6}
\end{array}\right\} \qquad (2)$$

According to the supercapacitor impedance function we can replace each supercapacitor parameter in Equation (1) by corresponding interpolation function from Equation System (2). In this case we determined the supercapacitor impedance function as a continuous surface depending on voltage *u* and angular frequency $\omega$. This impedance surface is shown in Figure 4.

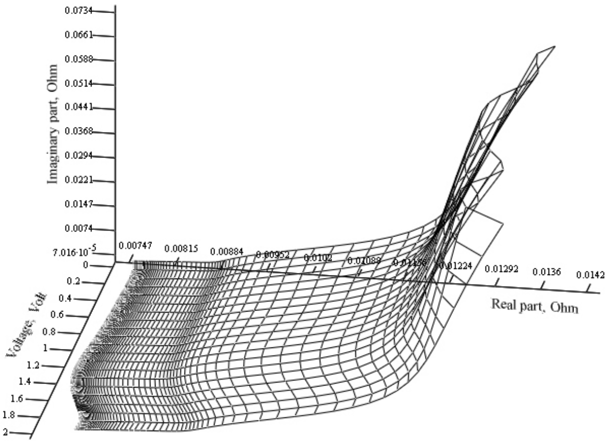

Figure 4. Supercapacitor impedance surface

The theoretical supercapacitor electrical serial resistance and capacitance as functions of voltage and frequency are shown in Figure 5 and Figure 6.

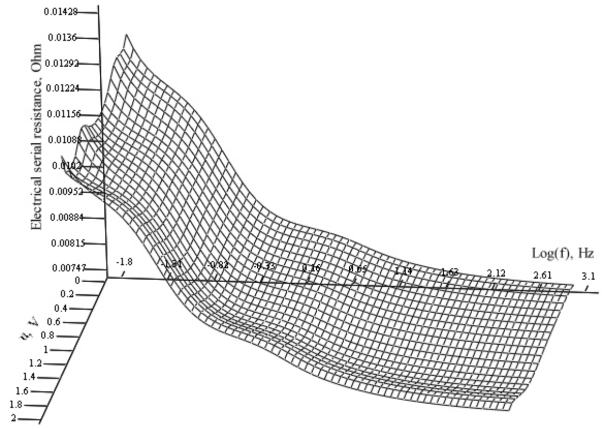

Figure 5. Supercapacitor electrical serial resistance as a function of voltage and frequency

The supercapacitor electrical serial resistance describes the energy losses that are typical of such components. They limit the maximum charge/discharge current values. In fact Figure 5 shows how the charge/discharge current is limited inside voltage and frequency ranges. As shown in Figure 5 the supercapacitor electrical serial resistance is changed about two times inside presented frequency range. Hence, the short charge/discharge current pulses have higher amplitudes than amplitudes of the long charge/discharge current pulses. This phenomenon is very important for the powerful supercapacitor applications.

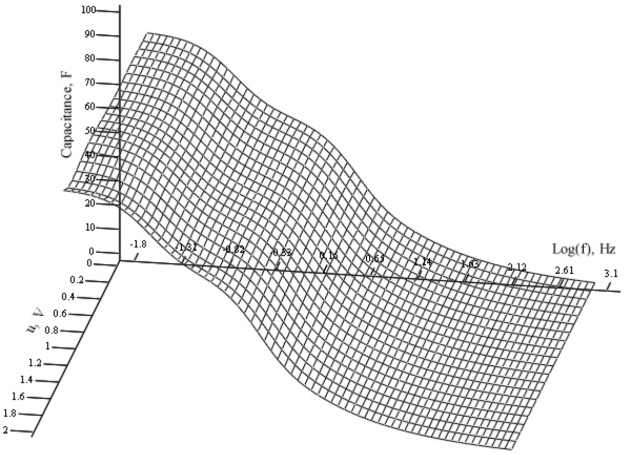

Figure 6. Supercapacitor capacitance as a function of voltage and frequency

As shown in Figure 6 the supercapacitor capacitance is changed about hundred times inside presented frequency rage. This capacitance drop is huge at the frequencies more than 100 Hz. In this case we can make a conclusion that the electrochemical supercapacitor is capable of operating only at the low frequencies. The operation at the high frequencies does not allow using the whole capacitance value.

In fact this limitation restricts the electrochemical supercapacitor application. The customer cannot obtain all accumulated electrical energy from the electrochemical supercapacitor during short period of time. For full discharge of the electrochemical supercapacitor a long period of time is necessary. Moreover the full charge of the electrochemical supercapacitor also requires a long period of time.

The dependence of the capacitance from operation voltage is much smaller than from frequency. It is explained by the small operation voltage range of the electrochemical supercapacitor. But this dependence is also significant because it allows more accurate prediction of the capacitance value.

## IV. Conclusions

1. Measurement and modeling of the electrochemical supercapacitors are becoming increasingly important for manufactures and customers.
2. The representation of the electrochemical supercapacitors as a non-linear equivalent circuit allows determining the real values of capacitance and resistance at various levels of working voltages and currents.
3. The supercapacitor impedance parameters are obtained with the impedance measurements and non-linear fitting the impedance data.
4. The interpolation functions allow researching a behavior of the non-linear equivalent circuit parameters, which are significant for electrochemical supercapacitor parameters such as electrical capacitance and active serial resistance.
5. The modeling approach presented in this paper has significant implications for simulating supercapacitor behavior in different working conditions and applications.
6. This paper explains the difficulties that occur in real application and allows calculating the electrochemical supercapacitor parameters without conducting expensive experiments using the complete and accurate mathematical model.

## References

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