SUPERCAPACITORS TEST METHODS

Zoran STEVIC, Mirjana RAJCIC-VUJASINOVIC, Ilija RADOVANOVIĆ, Daniel MIJAILOVIC, Misa STEVIC

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INTRODUCTION

- There are a number of standard methods for the examination of electrochemical systems that are used for supercapacitor testing [1]. In this paper, the most important standard methods are presented along with their modification proposals, and also some more suitable methods for testing various supercapacitor parameters are presented.

- Depending on the wanted accuracy, possible duration of the test or equipment availability, different electrochemical system testing methods are applied. Comparative analysis of the most suitable dynamic methods for supercapacitor testing is presented in this paper.
Resistance $R_0$ physically corresponds to the resistance of the electrolyte and the electrode material together, and its value is in the order of ohms. Capacitance $C_o$ (order of magnitude $\mu$F) corresponds to the double layer that is formed on the side of the electrolyte. Resistances $R_1$ and $R_2$ (the order of magnitude of tens of ohms) are related to the slow processes of adsorption and diffusion, as well as the capacitors $C_1$ (mF) and $C_2$ (F). $R_3$ is the resistance of self-discharge, so it is reciprocally connected with electricity leakage. Its value is in the order of hundreds of ohms to several kilohms.
\[ \eta(t) = (R_O + R_{23})I \left( 1 - e^{-\frac{t}{\tau_1}} \right) + (R_3 - R_{23})I \left( 1 - e^{-\frac{t}{\tau_2}} \right) \]

whereby:

\[ R_{23} = \frac{R_2 R_3}{R_2 + R_3} \]

Parallel connection R2 and R3

\[ \tau_1 = (R_1 + R_{23})C_1 \]

Time constant of the first phase

\[ \tau_2 = (R_2 + R_3)C_2 \]

Time constant of the second phase
$$i(t) = (I_0 - I_1)e^{-\frac{t}{\tau_1}} + (I_1 - I_2)e^{-\frac{t}{\tau_2}} + I_2$$

whereby:

$$I_0 = \frac{E}{R_0 + R_{123}} \text{ Initial charging current}$$

$$I_1 = \frac{E}{R_0 + R_{23}} \text{ Final first-phase charging current}$$

$$I_2 = \frac{E}{R_0 + R_3} \text{ Final charging current}$$

$$\tau_1 = (R_0 + R_1)C_1 \text{ Time constant of the first phase}$$

$$\tau_2 = (R_0 + R_2)C_2 \text{ Time constant of the second phase}$$
As the response, input current in the time domain is monitored. Common name in electrochemistry is cyclic voltammetry, although the current is being measured, because the voltage at which current peak occurs is essential. In the case of supercapacitor, peaks are not expressed, because of the slow changes of overvoltage.
Excitation voltage can be expressed analytically as:

\[
i(t) = \frac{E_m}{t_1} \frac{C_2}{2} \left( 1 - 2e^{-\frac{t}{\tau_2}} \right) + \frac{E_m}{2R_3} \quad \text{Charge phase}
\]

\[
i(t) = \frac{E_m}{t_1} \frac{C_2}{2} \left( 2e^{-\frac{t}{\tau_2}} - 1 \right) + \frac{E_m}{2R_3} \quad \text{Discharge phase}
\]
In the case that the expensive equipment is not available or it is necessary to quickly determine the certain individual parameters, it is possible to use one of the fastest methods. The experiments show that the potentiostatic method gives good results with a shorter duration of the experiment, and even faster, but also rougher determination of the parameters can be applied electrochemical method. For a reliable determination of the capacitance $C_2$, cyclic voltammetry can be applied, but with a long time experiment. Table 1 shows the overview of the equivalent circuit parameters obtained by various methods for one electrochemical system ($1\text{M }\text{H}_2\text{SO}_4 + 0,1\text{M }\text{CuSO}_4$).

Overview of the measured parameters of the adopted electrochemical system:

<table>
<thead>
<tr>
<th>Method</th>
<th>$R_1$ [Ω]</th>
<th>$R_2$ [Ω]</th>
<th>$R_3$ [Ω]</th>
<th>$C_1$ [F]</th>
<th>$C_2$ [F]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Galvanostatic method</td>
<td>17,3</td>
<td>31,2</td>
<td>210</td>
<td>0,23</td>
<td>33,1</td>
</tr>
<tr>
<td>Potentiostatic method</td>
<td>17,1</td>
<td>30,8</td>
<td>206</td>
<td>0,22</td>
<td>31,8</td>
</tr>
<tr>
<td>Cyclic Voltammetry</td>
<td>-</td>
<td>32,1</td>
<td>-</td>
<td>-</td>
<td>32,2</td>
</tr>
</tbody>
</table>
CONCLUSION

In order to do better investigation of the observed electrochemical systems, the mathematical model is set, equivalent circuit was accepted and the comparative analysis was done for the standard electrochemical test methods (cyclic voltammetry and potentiostatic method), and galvanostatic method is modified. Based on mathematical analysis all the parameters for experimental research are determined.

Series of the experiments has been conducted, both in the physical model and the real electrochemical systems. Based on obtained results, the model and test methods are verified, and also the electrochemical system is optimized. Also, the methods are compared in terms of efficiency and accuracy.
Thanks for watching!