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Model of noise sources in supercapacitors

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Abstract. The paper presents detailed model of noise sources in supercapacitors. Noise phenomena observed in supercapacitors may be used as a diagnostic tool for assessment of supercapacitor quality or degradation mechanisms (e.g. corrosion of the electrodes or clogging up the pores) during ageing. Therefore, it is important to consider where noise is generated. The equivalent circuit of noise sources existing in supercapacitor is proposed. Methods of noise sources identification are also considered. Limitations of the proposed model are underlined. Final conclusions show a path of further investigations of random phenomena in supercapacitors.

1. Introduction

We observed a growing demand for the elements storing and delivering electrical energy in a fast way (e.g. miniaturized electronic devices having large computing powers, electrical vehicles or renewable energy sources). Supercapacitors are good candidates to meet these demands. In [1] authors showed classification of different supercapacitors types and possible materials, constructions and technologies for their production. They also clarified position of supercapacitors by comparing their properties to other energy storage systems. The supercapacitors were investigated by various methods. Electrical models describe all important phenomena observed during their usage. Supercapacitor can be modelled by a well-known electric double layer capacitor (EDLC) [1–4]. EDLC assumes an existence of two layers: internal layer (Helmholtz layer) and outer diffuse layer with different charge redistribution mechanisms. These two layers may be modelled by two independent capacitors (C_H, C_{Diff}) and two resistors (R_{ESR}, R_{Diff}), as is shown in figure 1. The Helmholtz layer is responsible for fast charging and discharging with a time constant determined by R_{ESR} and C_H. The second layer is responsible for charge redistribution due to diffusion mechanism with a time constant determined by capacitance C_{Diff} and resistance R_{Diff}. The leakage current of the supercapacitor is modelled by a resistance R_L [3, 4].

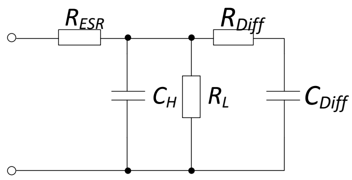

Figure 1. The EDLC supercapacitor model with the specified capacitances C_H and C_{Diff} and resistors R_{ESR}, R_{Diff} and R_L.

New diagnostic methods are required for testing quality of the produced supercapacitors and any new technological changes resulting in reduced production or exploitation costs, or prolonged lifetime. Another possible diagnostic method may utilize noise measurements generated in supercapacitors [4, 5]. The degradation mechanisms may be caused by corrosion phenomena or processes of clogging up the pores, as it was shown by numerous authors [6–8]. We know that these electrochemical processes induce charge flow and therefore generate noise. This phenomenon was observed between the corroding electrodes and used to determine corrosion type or its intensity [9–11]. This method is a novel method for supercapacitors' investigations and therefore noise sources have not been fully investigated. In this paper we propose an equivalent electrical circuit of supercapacitor with noise sources. The proposed circuit was based on physical assumptions and some experimental results.

2. Noise observed in supercapacitors

In our experimental studies the voltage fluctuations during supercapacitor's discharging through the loading resistor were recorded by DAQ card. We have measured voltage across the loading resistor and then the trend component was removed using the procedure based on polynomial approximation. The detailed description of noise measurement equipment can be find elsewhere [4, 5]. Trend removal procedures are presented in the literature [12]. The exemplary discharging curve, using logarithmic voltage axis, for supercapacitor specimen is presented in the figure 2. The curve emphasized a model consisting of more than one time constant (in the case of a single time constant it should be a straight line). It is clearly visible that to about 6000 s the first time constant (determined by capacitance C_H) is dominant and from about 12000 s of discharging the second time constant (determined by the capacitance C_{Diff}) dominates. Between 6000 s and 12000 s both capacitances C_H and C_{Diff} are participating in a process of supercapacitor discharging. These considerations confirm responsibility of the capacitance C_H for fast discharging. At the same time C_{Diff} is responsible for slow discharging by diffusive mechanism. At the end of the recorded discharging process it is clearly seen a noise component due to the used logarithmic scale.

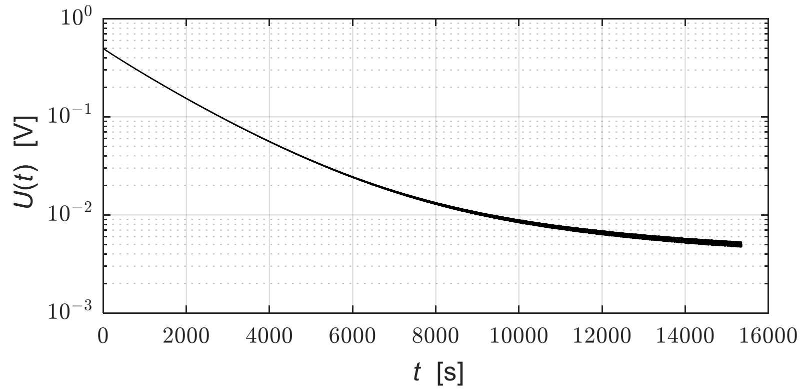

Figure 2. Voltage $U(t)$ observed at the terminals of supercapacitor when discharged through the loading resistor.

After an operation of trend removal, we obtain a random signal (voltage fluctuations) caused by noise generation phenomena in the supercapacitor structure. In some cases, during ageing of supercapacitor we observed slow undulations of the determined random signal (figure 3 b) or more intense noise (figure 3a). These undulations may be caused by clogging up pores in the carbon electrodes or corrosion reactions taking place at the surface of metal collector, to which the electrodes are attached [6–8]. The consequence of corrosion may be delamination of carbon layer, which was observed by us after opening supercapacitor specimens, preceded by a damage of the specimen after ageing. Similar damage results (decrease of capacitance, increase of R_{ESR}, delamination of the electrodes) were observed for ageing mechanisms induced by floating (keeping at constant voltage) or cycling (charging/discharging with intense current).

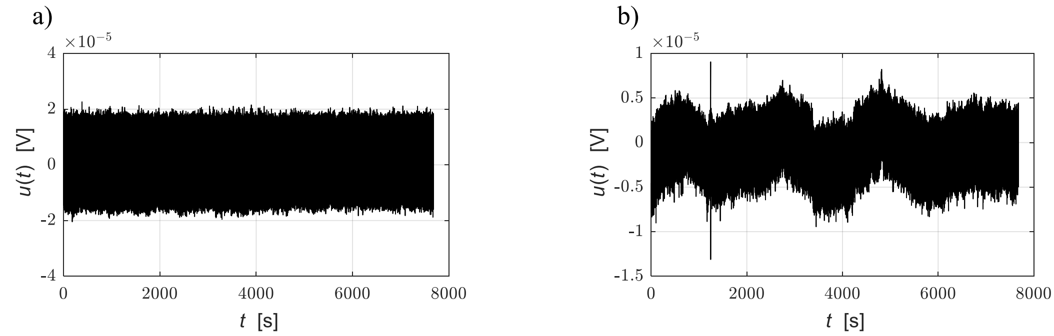

Figure 3. Voltage fluctuations $u(t)$ observed across the supercapacitor terminals after detrending operation: a) without slow undulations, the supercapacitor was charged to 0.5 V b) with slow undulations, the supercapacitor was charged to 2.7 V.

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Figure 4 presents an impact of slow undulations and noise intensity on the estimated power spectral density of voltage fluctuations, especially on intensity of $1/f$ noise. During our investigations we also observed a change of thermal noise level, which may be caused by change of resistances in the model presented in the figure 1. Sedlakova et al. [3] show that R_{Diff} is time-dependent parameter of the presented model. It is obvious that during supercapacitor ageing [13, 14] all parameters presented in the model (figure 1) may change their values, even permanently.

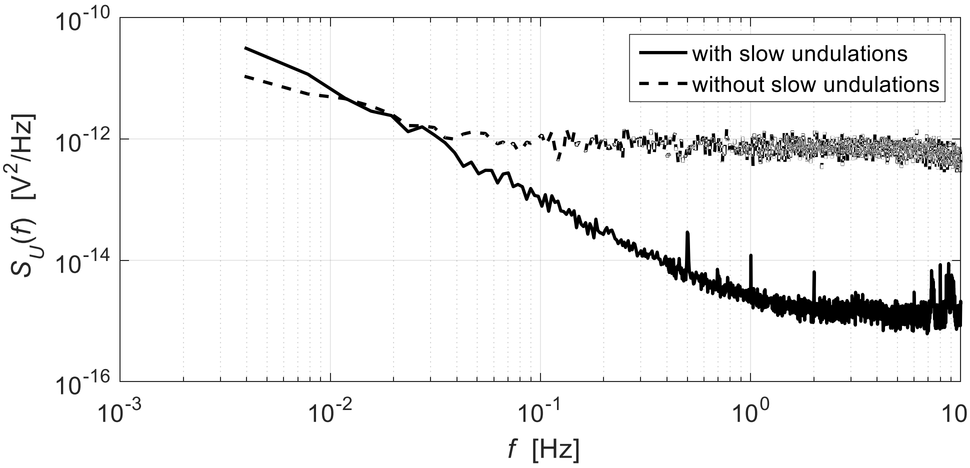

Figure 4. Power spectral densities $S_u(f)$ of voltage fluctuations observed during discharging of the tested supercapacitor through the loading resistor, there are visible changes caused by different charging voltage.

3. Noise model

In the figure 5 we propose an equivalent noise model of the investigated supercapacitor. This model was established by considering experimental data measured during supercapacitor's discharging through the loading resistor $R_0 = 200\ \Omega$. Each of the resistor from the model is a source of white noise induced by thermal noise. Thermal noise, having constant spectrum, can be seen in the figure 4 at the frequency range from about 1 to 10 Hz. The mean square value of voltage fluctuations per bandwidth of the observed noise is given by following equation:

$$\overline{e_{nT}^2} = 4kTR, \tag{1}$$

where: $\overline{e_{nT}^2}$ is the mean square value of thermal voltage fluctuations, k is Boltzmann constant, T is an absolute temperature of the resistor R. It is obvious that contribution of thermal noise sources in the measured fluctuations (figure 5) are not equal. The resistor R_{ESR} has very small resistance (typically below 1 Ω), while the resistor R_{Diff} can be a few hundred times bigger than R_{ESR} and additionally it can be time dependent [3]. The combination of both thermal noises generated by the resistors R_L and R_{Diff} determines the observed noise at higher frequencies due to their high values when compared with the resistance R_{ESR}. We have observed that after ageing white noise component increased more than the $1/f$ noise at the same time. This effect can be explained by an increase of the resistance R_{Diff} due to ageing processes.

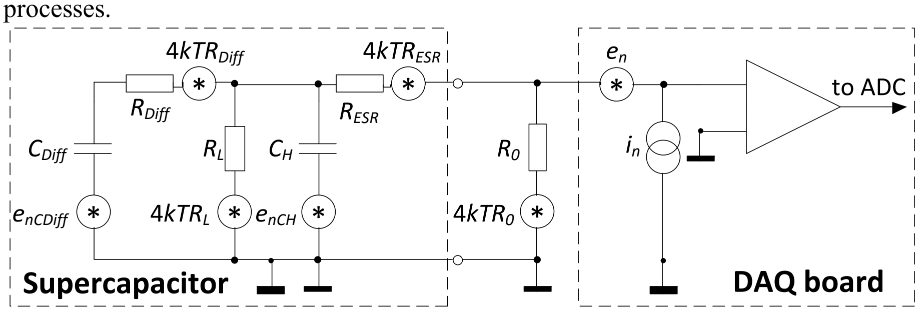

Figure 5. The proposed noise model of supercapacitor during discharging through the loading resistor R_0.

The $1/f$ noise is represented by the sources e_{nCH} and e_{nCDiff}. Those sources can indicate quality or state of the carbon electrodes and may contain information about history of supercapacitor ageing. The fundamental problem of measuring $1/f$ noise is its low frequency range and high-pass filter structure formed by capacitors and resistors included in proposed model (figure 5). For the investigated specimens we experimentally determined a value of the cut-off frequency of high-pass filter to about 1 to 4 mHz. Power spectral densities presented in the figure 4 are in the frequency range from 4 mHz to 10 Hz, therefore they are not attenuated by high-pass filter composed from these elements.

The DAQ card is equipped with an input amplifier which has its inherent noise sources (voltage e_n and current i_n). We have applied low-noise card to guarantee the noise level at least ten times (20 dB) smaller than the measured noise. The contribution of loading resistor R_0 is also non-negligible and therefore we have applied metallic low-noise resistor.

4. Conclusions

The proposed noise model of supercapacitor may help to investigate processes occurring in a supercapacitor structure during ageing. Noise measurements can be a non-destructive diagnostic tool for supercapacitor assessment. There is necessity for accurate noise model of a supercapacitor to explain the observed noise measurement results and to correlate changes in noise intensity with ageing processes. These phenomena need more in-depth investigations and are very promising for studying new materials and technologies used for supercapacitors' construction. The presented model explains measurement results and suggest that ageing induce changes in $1/f$ noise intensity and also in resistance R_{Diff} of the proposed model.

Acknowledgments
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