Assessment of Supercapacitor’s Quality by Means of Low Frequency Noise

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Abstract

Low frequency noise is a well-known tool for quality and reliability assessment of electronic devices. This phenomenon is observed in different electrochemical devices as well (e.g., smart windows, electrochemical corrosion processes). Thus, we can assume that the same tool can be used to asses quality of supercapacitors.

Their quality is usually determined only by capacitance and/or equivalent series resistance (ESR), or impedance. Degradation of supercapacitors’ is indicated by a change of capacitance and ESR and is measured by the established methods, determined by industrial standards. We propose to extend these methods by using low frequency noise measurements which should be in our opinion more sensitive to any changes degrading supercapacitors’ structures. This task is quite difficult because capacitance of the tested specimen is at least about a few or even a few dozens of Farads. It means that we can measure 1/f noise at very low frequency range only. This method is a new one and should be helpful in developing more advanced and economically efficient supercapacitors.

We discuss requirements for the measurement set-up and its possible configurations. Next, the prepared measurement set-up consisting of current/voltage sources, a switching unit, a data acquisition board and a computer controlling the process is described. Some experimental noise measurements are presented as well.

Introduction

Supercapacitor is an electric device that is capable to store relatively high energy in comparison to its mass. On a Ragoon plot those devices are placed between batteries and electrolytic capacitors [1]. As the supercapacitor can be charged and discharged very fast with relatively high current, thanks to its low series resistance, they can be used in various applications requiring fast delivery and retrieval of electric power. This quality, combined with high number of charging-discharging cycles, predestinates it for applications requiring peek energies of high dynamics (e.g., electric vehicles, embedded systems, distributed sensors systems).

Growing market of supercapacitors and increasing popularity of their applications require development of new methods of their quality and reliability assessment. Commonly used methods for supercapacitors testing are: galvanostatic cycling with potential limitations (GCPL), cycling voltammetry (CV), impedance spectroscopy, and accelerated aging [2-7]. All those methods are based on observation of current and voltage during forced charging/discharging of the supercapacitor at selected bias conditions.

Supercapacitor’s quality is usually derived from its capacitance, equivalent series resistance (ESR), equivalent distributed resistance (EDR) and impedance. Degradation of supercapacitor is indicated by change of capacity and ESR and is measured by well-known methods. It is commonly accepted that the capacitance should not drop by more than 20% or the ESR value should not be more than twice the initial to consider the specimen as a good one.

Very sensitive and promising method of assessment of devices systems quality and reliability is investigation of low frequency noise (flicker noise). It’s widely used for semiconductor devices, sensors of various characters, electrochemical units, chemical reactions as corrosion, and other random phenomena [8-13]. It’s sensitive to structure impurities, any defects or degradations. The detailed procedure is not obvious, as those devices are commonly used as elements for noise suppression from the circuit and therefore 1/f noise can be dominant at very low frequency range only.

Supercapacitor operation and equivalent circuit

One of commonly used types of supercapacitors are electric double layer capacitor (EDLC). It comprises of two electrodes made of porous material, like activated carbon with ion permeable separator and electrolyte solution between them. The charge is stored by non-Faradic mechanism in a form of so-called Helmholtz layer and diffusion layer. Helmholtz layer is formed in electrode-electrolyte interface by charges in conducting electrode material and ions in electrolyte. Diffusion layer is an effect of thermal moves of ion particles and its limited mobility, and is formed near the electrode-electrolyte interface.

Typically supercapacitor is charged and discharged by a constant current with voltage limitation. During charging, the voltage increase is observed over capacitor contacts. Voltage limitation is required to prevent supercapacitor against overvoltage which could result in electrolyte degradation. When the supercapacitor is charged and left with open terminals, a relatively slow voltage drop with exponential-like character is observed. When discharging supercapacitor, charges flow out of the device structure and voltage decrease is observed. When the voltage reaches near zero volts, the discharging process should be finished. When the supercapacitor is discharged and left open-circuit the voltage restored by increasing to some value. A voltage curve observed during charging, discharging and open-contacts is shown in Fig. 1.

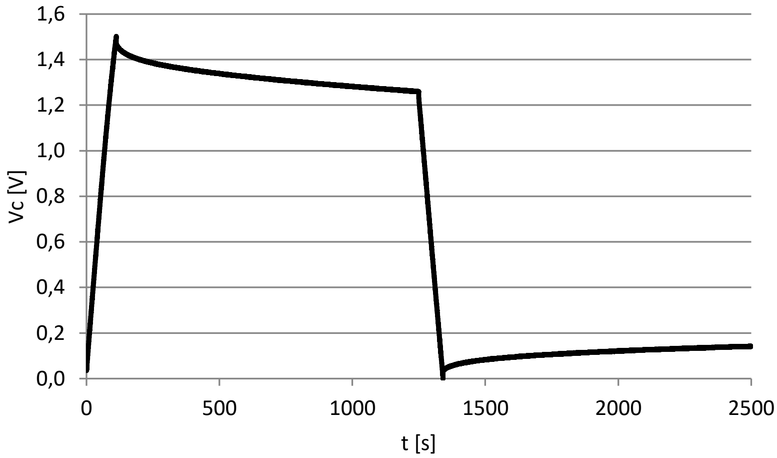

Fig. 1 Voltage between supercapacitor's terminals during charging, discharging and at open-circuit stage

Supercapacitor is well modeled by equivalent circuit described in [7, 14]. The model comprises of two branches of RC elements connected as shown in Fig. 2. The ESR represents equivalent series resistance. In commercially available devices its value is below a few hundred mΩ, depending on the applied technology. Capacitor C_H represents capacitance of Helmholtz layer. It is available during fast charging/discharging processes. The second branch represents charges redistribution by diffusion [14, 15]. Capacitor C_D represents capacity of diffusion layer while resistance R_D determines how fast a mechanism of diffusion is. Resistance R_L represents leakage current.

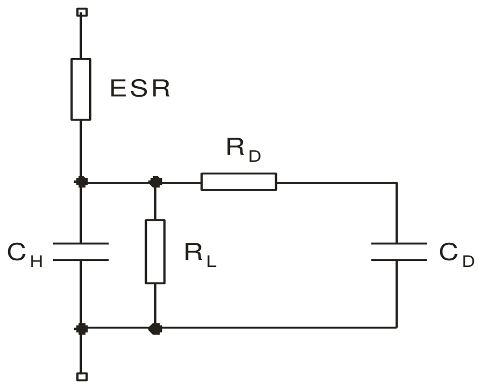

Fig. 2. Supercapacitor's equivalent circuit

During supercapacitor's charging, when voltage is applied to the contacts, first the C_H capacitor is charged because the ESR is relatively low. Subsequently, the capacitor C_D is charged with time constant equal $R_D \times C_D$. ESR value can be neglected in this process, as it is significantly lower than resistance R_D. When a voltage across the capacitor C_H riches its nominal value and the charging process is finished, the charges stored in the C_H flow through the resistor R_D to the capacitor C_D and voltage drop is observed because a collected charge is divided between C_H and C_D.

When the supercapacitor is discharged, the reverse mechanism occurs. First, the charges from C_H are removed in discharging process, while C_D discharges much slower because of high value of R_D. For high enough discharge current the voltage between supercapacitor's terminals reaches zero even when some charges rest inside C_D. When supercapacitor is open-circuited, charges remained in capacitance C_D flow through the resistance R_D to the capacitance C_H and a voltage increase is observed between open-circuit supercapacitor's terminals.

Voltage applied to the supercapacitor's terminals induces ions migration within vicinity of electrodes surface. As the electrode material is porous, and pores have different sizes, ions penetrate pores at various speed and fluctuations in voltage between the terminals, when charged by a constant current, should be observed. The reverse phenomena occurs during discharging process.

Also during charge redistribution within supercapacitor's we should observed some voltage fluctuations between the terminals. Ions move into and out of pores and changes in local capacitance, which depends on charge and distance between the ions layer and surface of electrode, results in voltage changes. Fluctuations during charge redistribution should be of lower intensity than those during charging-discharging, as charges flow is much lower and decline when the structure is closer to an equilibrium state.

Fluctuations phenomena at low frequency range should intensify when some area of electrodes are at verge of charging/discharging ability. We can assume that when some pores are blocked or almost blocked the gathered charge can be removed (or stored) in a more slowly rate and low frequency fluctuations of that process should be generated.

Degradation of supercapacitor can be identified by decrease of electrical capacitance or increase of ESR. Capacitance drop is usually a results of excluding some porous area of electrode, when the pores are blocked by products of electrolyte decomposition. That degradation is irreversible. Pores can be also blocked by respectively large ions which exclude these pores from contribution to the supercapacitor terminal capacitance. These blocking processes are reversible and after some relaxation time can be restored.

Variation of active area of porous carbon electrode should modify intensity of low frequency fluctuations. We expect that the most intense 1/f-like noise is generated when the pores are at the verge of charging/discharging ability because such processes are rather very slow and will increase random components at very low frequency range. When the pores are blocked completely the area is excluded from further charging/discharging ability and any noise generation as well. Thus, the 1/f-like noise should be potentially an interesting indicator of any process of pores blocking at its very preliminary stage.

Noise measurements

Measurements of noise require stable conditions and low noise measurement set-up. In a case of supercapacitors, when very low frequency noise is considered, time of voltage fluctuations recording should be relatively long. Estimation of power spectral density requires operation of averaging, prolonging data acquisition process, even up to a few hours.

To ensure stable measurement conditions, noise should be observed during one of operating modes of supercapacitors: charging, discharging or charge redistribution. Charge redistribution process, in both cases when supercapacitor is charged or discharged, run dynamically at the beginning, then, after relatively short time, decrease strongly. Low intensity of this process generates low intensity noise. Additionally this process could be monitored only to a small extend.

Charging and discharging of supercapacitor is a more promising stage to record fluctuations. This process can be fully controlled and its duration could be shortened or extended by increasing or decreasing charging/discharging current. It should be mentioned, that during supercapacitor charging a stabilized current or voltage source, with overvoltage and overcurrent protection, should be used to prevent its eventual degradation. Those sources require advanced electronic circuits and can generate intense harmonic interferences. Then supercapacitor's inherent noise could be overwhelmed by inherent noise or interferences generated in these circuits. Similar limitations are present during discharging process with a stabilized current/voltage source.

Supercapacitor could be discharged through a constant load resistance. For our purpose, a low noise metalized resistor should be used. It reduces inherent noise in that circuit. Time of discharging could be set by a loading resistor value. Increasing this resistance increases a discharge time and reduces discharge current. A compromise should be made between measurement time and discharging current, correlated with 1/f noise intensity. Too low current results in low intensity of voltage fluctuations measured across the loading resistance. The discharge time could be estimated by:

$t=-RC\ln(V/V_0)$,

where V_0 is an initial voltage between the terminals of the charged supercapacitor, R is the loading resistor and C is the capacitance. Voltage V is observed at the end of discharging stage.

Measurement set-up

The proposed measurement set-up for low frequency noise of supercapacitor comprises of: (1) controllable current source with a voltage control, (2) a switching unit with a set of relays to connect/disconnect the tested supercapacitor to the elements of the bias circuit, (3) loading resistor and (4) data acquisition card. The block diagram of the measurement set-up is shown in Fig. 3.

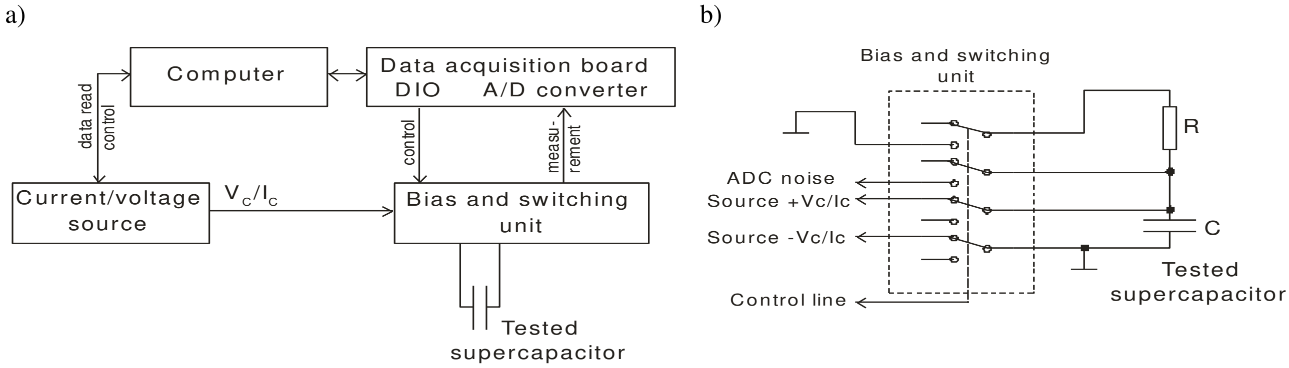

Fig. 3. Block diagram of the prepared measurement set-up (a) and switching unit circuit (b)

Programmable current source with voltage control is used for charging/discharging supercapacitor before noise measurement. Relays are used to switch supercapacitor between current source and a part of the system (load resistor and data acquisition card) used during noise measurements. That separation is required to cut off a loading resistor and data acquisition card during charging supercapacitor. Otherwise a charging current will be bypassed by this resistor and internal resistance of data acquisition card and it would complicate estimation of supercapacitor parameters based on the registered charging/discharging current and voltage. Additionally, that separation prevents introduction of eventual distortions induced by current loops.

Data acquisition card should provide dynamic and resolution of the recorded signals to measure AC (noise) and DC components in voltage ranging from nominal voltage of the tested supercapacitor to nearly zero voltage. In our laboratory system a data acquisition card having resolution of 24-bits and a voltage range of +/-10 V was used.

Before starting noise measurements the tested supercapacitor is charged by a constant current during potentiostatic cycle. That allows to spread charges within its structure. Next, the relays are switched and the supercapacitor is disconnected from current/voltage source and the loading resistor and data acquisition card is connected to record voltage during discharging.

Time records of voltage recorded during discharging comprise of a slowly (exponentially) changing intense trend component, that is a result of voltage drop on a loading resistor, and additive noise. Before estimation of power spectral density of noise component the DC component has to be removed. In order to extract noise component form the recorded data the trend component should be determined and removed. In our case a trend curve is close to an exponential decaying curve. We have applied a polynomial approximation using the fifth order polynomial. We have used MATLAB scripts, the functions: *polyfit* (determination of polynomial coefficients approximating the trend in a least-squares sense) and *polyval* (computes polynomial values). The determined trend component was subtracted from the recorded data due to identify noise component.

Experimental results

In our experimental studies, commercially available supercapacitors, type DRL 2.7V 10F with a nominal capacitance 10 F and a nominal voltage 2.7 V, were used. A loading 1 kΩ resistor was used. A discharging curve of the tested supercapacitor initially charged to a voltage of 2.7 V is shown in Fig. 4. Exemplary time record of voltage fluctuations and its histogram after trend removal are presented in Fig. 5.

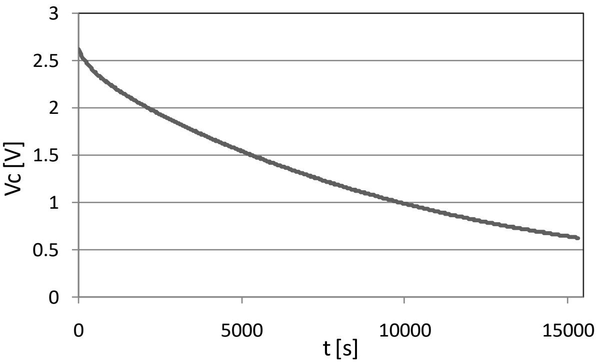

Fig. 4. Discharging curve of the tested supercapacitor, type DRL 2.7V 10F, through the loading resistance of 1 kΩ

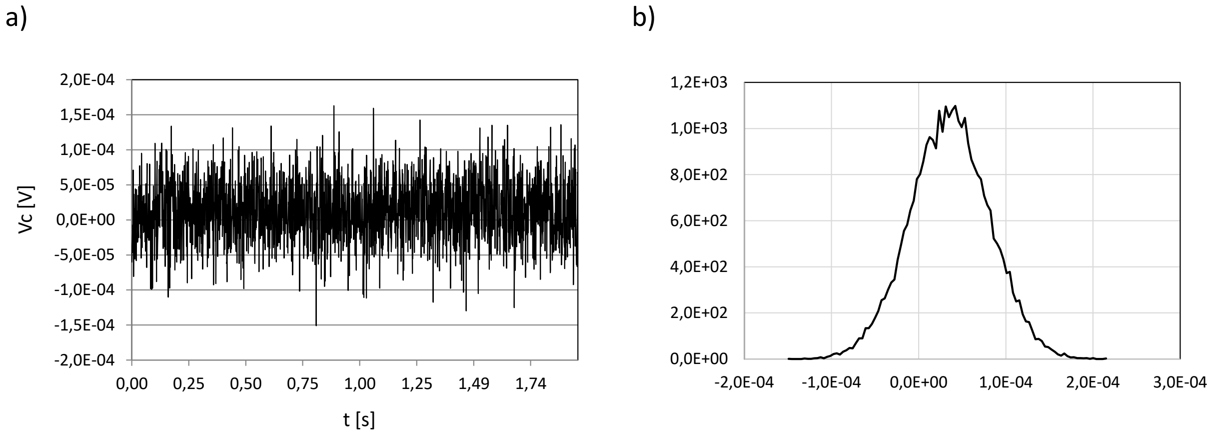

Fig. 5. Exemplary time record of voltage fluctuations after removing trend component (a) and its histogram (b)

The determined voltage noise record after detrending was divided into sub-records and power spectral density S(f) was estimated using Welch estimation method. Power spectra were normalized to the square of a discharging current I at given sub-record, and averaged to reduce estimation random error. This normalization makes the observed noise intensities independent from bias conditions. Exemplary power spectrum density function is shown in Fig. 6. Flicker noise (1/f – like noise) is dominant at the frequencies below 1 Hz.

The investigated supercapacitor was aged by floating at elevated voltage. The procedure of testing was as follow: (1) supercapacitor was charged to the given voltage and (2) kept at this value by potentiostatic cycle for 2 hours, then (3) 5 cycles of discharging-charging to the nominal voltage were applied to stabilize its structure. This procedure was performed to ensure the same condition for noise measurement at different floating voltages and different floating times. Temporary changes of supercapacitor parameters should settle during cycling charging-discharging with nominal current/voltage value. The 5th discharge cycle is used to estimate capacitance and ESR by standard procedure. After the 5th charging, the supercapacitor is charged again and noise measurements began.

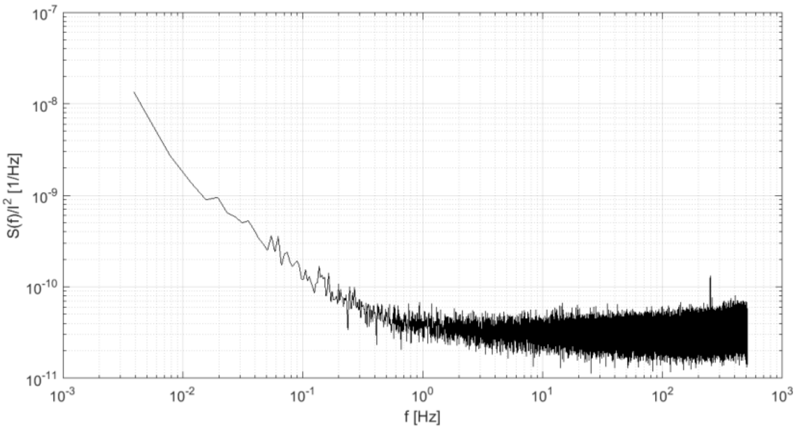

Fig. 6. Power spectral density S(f) of current fluctuations normalized to the square current I given for each sub-record separately

This experiment accelerates degradation process of the tested specimen induced by elevated voltage at floating. As a result, eventual changes of its electrical parameters (capacity C, equivalent series resistance ESR) should be correlated with low frequency noise intensity and its changes. The observed values of C and ESR of the tested supercapacitor are shown in Fig. 7. Evolution of power spectral density at selected frequency f = 0.01 Hz is presented at Fig. 8.

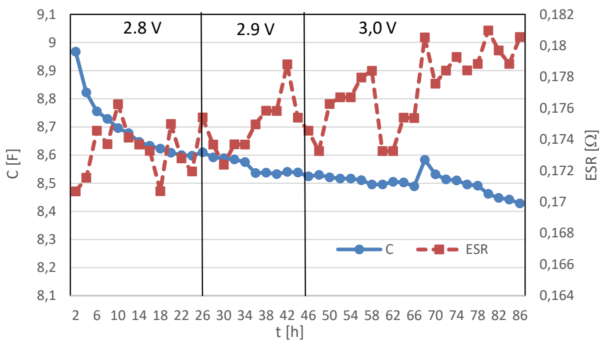

Fig. 7. Evolution of capacitance C and resistance ESR during specimen's aging by floating at increased DC voltages

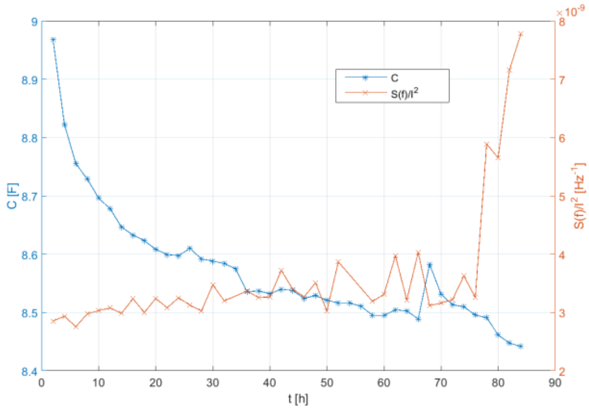

Fig. 8. Evolution of power spectral density S(f) at frequency f = 0.01 Hz and normalized to the square current I given for each sub-record separately during specimen's aging by floating at increased DC voltages

As we expected the changes of electrical parameters follow changes of normalized power spectral density. Final drop of capacitance is accompanied by huge increase of noise intensity. Relative drop of capacitance in the experiment is about

6%, while noise intensity increases over 270%. Then a change of noise is more than 40 times bigger than capacitance changes. Thus we can expect, that noise measurements should be valuable for prediction of any aging changes inside supercapacitor structures. Presented results are very preliminary and more experiments have to be conducted to determine which aging processes are correlated with noise intensity.

Summary

The presented experimental results confirmed that the developed measurement set-up and the proposed methodology of low frequency noise measurements and processing enable identification of 1/f-like noise component in the investigated industrial supercapacitor. Flicker noise was observed at frequencies lower than 1 Hz and it required at least 4 hours of recording voltage across the loading resistance when the specimen was discharged.

In the proposed measurement set-up a time of data recording is determined by the loading resistor. Its value is a compromise between too fast discharging and too low discharging current resulting in low noise component intensity. We have to underline that the data has to be collected sufficiently long time to reduce random error of power spectral density estimation. More experimental work is required to develop algorithms for noise data processing when the measurement are done during other operating modes of the tested specimen. Special attention should be addressed to a problem of charge redistribution inside the specimen. That phenomena is significant at relatively short times comparing to the required observation time because it can be modelled as an exponential process.

Acknowledgment

This research was financed by the National Science Center, Poland, project No. DEC-2014/15/B/ST4/04957, “Charging/discharging mechanism at the electrode/electrolyte interface of supercapacitors”.

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