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Temperature distribution of supercapacitors prepared by various technologies

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Abstract

Supercapacitors, also known by different names such as electrostatic double-layer capacitors (EDLCs) or ultra-capacitors, are electrical storage devices still in development. These devices require fast and reliable methods of assessing their state-of-health. Thermographic imaging is a method which can be applied with this aim due to its popularity, and the high negative impact of overheating on a supercapacitor's parameters. Moreover, thermographic imaging can be easily used to identify any hot spots, present during charging and discharging while in use. These devices are comprised of porous carbon electrodes and an electrolyte, and during the charging/discharging process, extensive heat may be generated and dissipated there. We have observed temperature fluctuations and were able to identify the inhomogeneity of the tested structures. The electrical parameters (capacitance C and equivalent serial resistance ESR) were measured to determine deterioration of the specimen as requested by the industrial standard. X-ray examination of the samples was performed to identify the shape of the applied metal charge collectors. Both techniques indicated areas where eventual overheating took place due to their electrodes' shape, suggesting their further optimisation. The proposed method is much less accurate than the calorimetric methods, determining energy flows, but is still sufficient to identify problems with heat dissipation in the developed specimens. Finally, some conclusions about the ability to apply this method in practice to monitor supercapacitors during use were presented.

Keywords: Electrical double-layer capacitor, supercapacitor, thermography, overheating, state-of-health;

1. Introduction

Supercapacitors, also known as electrostatic double-layer capacitors (EDLCs) or ultra-capacitors, are electrical storage devices which can be used to deliver or store electrical energy in a fast way when compared with other electrochemical power sources [1, 2]. These devices have numerous potential applications, especially for electric vehicles or distributed electrical power sources (e.g., wind power stations, solar cells). Unfortunately, their technology is still too expensive to be popularised more extensively, and the applied materials may be polluting the natural environment. Moreover, these devices are sensitive to overvoltage or even more so to overheating, inducing a decrease of their charging/discharging abilities [3, 4]. Therefore, their detailed studies help to determine how to avoid the enumerated perils. We can reduce overheating by proposing different constructions or by incorporating local temperature sensors as well as temperature-responsive materials, as described elsewhere [5]. This issue is critical because it may reduce charge storage performance or even the hazard of fire. The methods proposed to solve these problems were presented elsewhere [6, 7]. Some of the techniques apply changes in the electrolytes to absorb the emitted heat or modified construction to accelerate ventilation. These solutions are rather expensive or induce some irreversible reactions to protect the device before overheating. Therefore, we propose to focus on construction issues only. The tested samples applied the technology which is commonly used in commercial EDLCs, utilising an organic electrolyte and carbon porous electrodes [8].

We consider how two different shapes of the metal terminals determine the temperature distribution observed during a fast and repeated charging/discharging process. The results help us to avoid eventual overheating at the investigated structure. Next, we propose how to monitor overheating by low-cost methods. The studies were performed by measuring the temperature distribution of the samples having different electrodes shapes. The as-prepared and aged by charging/discharging specimens were investigated.

2. Experimental set-up

All of the specimens were prepared using the same materials but two different shapes of the metal collectors. The collectors, covered by a porous carbon layer, had the terminals: narrow, of about 1/3 of the electrode width (Fig. 1a), or wide (the same size as the width of the electrode – Fig. 1b). Two terminals were used to attach to the current source charging the EDLC or to the loading resistor during discharging. Two small terminals situated on the left side of the pouch (Fig. 2a) or two full terminals located on both (left and right) sides of the pouch (Fig. 2b) were applied. Both pouch cells had a similar capacitance due to almost the same active areas of the applied carbon electrodes. Thus, equal current densities were used for both specimens during charging and discharging. The prototype pouch cells used flat electrodes. In commercial supercapacitors, the electrodes are rolled up and placed into a metal container to protect the cell against mechanical damage and to secure higher capacitance density per volume of the developed device.

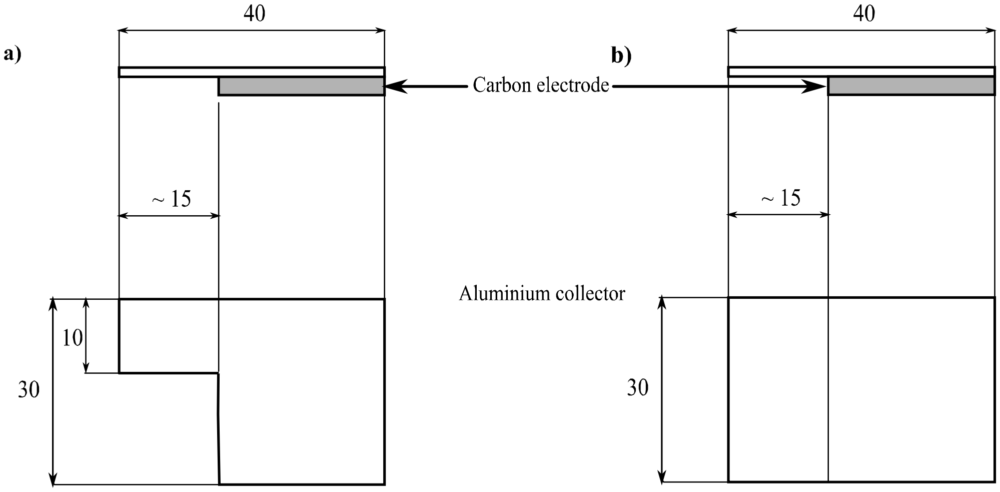

Fig. 1. The shapes of aluminium collectors covered by carbon porous electrodes and applied in the investigated samples with narrow (a) or wide (b) terminals.

All experimental studies were performed by applying the developed measurement set-up comprised of a thermographic camera, VIGOcam v50, and a multichannel potentiostat galvanostat, Atlas-Sollich. A detailed description of the prepared set-up is available elsewhere [9]. The cells were painted before the measurements with Graphite 33 paint from Contact Cheme, to reduce reflections. The camera recorded thermograms with a resolution 384 x 288 pixels at a sampling frequency of 1/60 Hz. The samples were repeatedly charged and discharged up to a nominal voltage of 2.7 V by a current per unit mass of the electrode I = 4 A/g. The period of the charging/discharging repeated process was about 17 s. The detailed procedure of the measurements and the developed set-up is available elsewhere [10]. The same wide contact clamps to the EDLC terminals were used to allow current flows. Next, the recorded pictures were analysed by estimating selected statistical parameters, separately for each pixel. We used at least 100 images to determine the average temperature of each pixel.

The industrial standard assumes that the specimen is destroyed when its equivalent serial resistance (ESR) has increased by more than 100% or its capacitance C has decreased at least 30% [11]. Therefore, we aged the specimens by the repeated charging/discharging procedure to reach one of these conditions. It required more than 25,000 cycles of continuous charging/discharging — this procedure was needed to record a series of thermogram pictures and their further processing. We applied the Matlab software to perform the necessary computations.

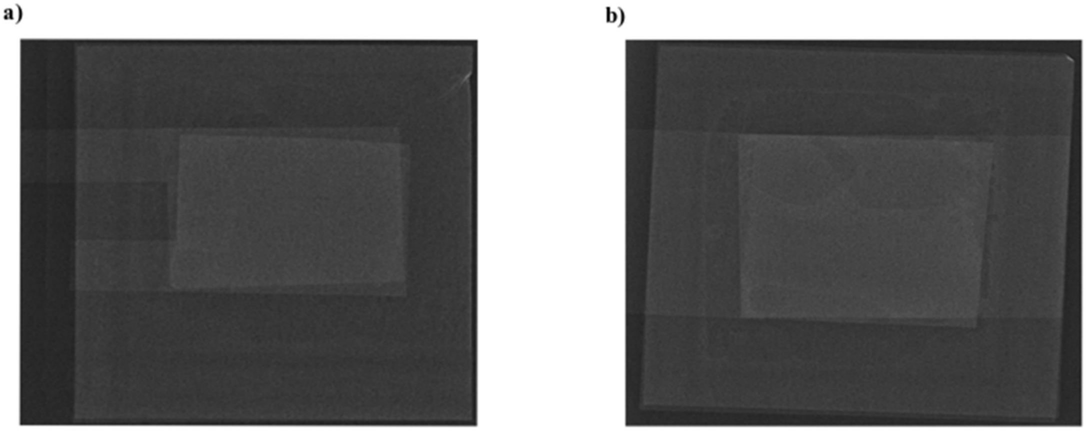

Fig. 2. X-rays of the investigated supercapacitor pouch cells: (a) with narrow terminals situated on the left side, (b) with wide terminals located on the left and the right sides. A separator is placed between the electrodes to avoid their touch, and the square pouch cell protects the sample against the destructive influence of the atmosphere.

3. Experimental results and discussion

The specimens dissipated heat when charged and discharged repeatedly. The emitted energy is due to current flow through the resistances of the tested EDLCs, especially the ESR. Therefore, we can expect higher temperatures in the aged samples when the ESR increased. The issues of energy emission in the EDLCs was presented in a few papers [12, 13]. The proposed models apply RC elements to determine energy dissipation in the considered constructions. The models predicted temperature saturation within the structure after about 1-2 h of continuous charging/discharging. Our experimental studies showed quite similar behaviour. Temperature saturation was reached after about 2.5 h of applying constant charging/discharging. The temperature increased exponentially to saturation with visible ripples of about 0.3°C, and synchronised with the charging/discharging cycle [9]. The amplitude of the observed surface temperature ripples was even a few times lower than for commercial supercapacitor (Maxwell BCAP350 F), as reported elsewhere [13]. Temperature variates due to the superposition of two processes: (a) an irreversible Joule heat generation by a current flowing through the supercapacitor ohmic series resistance, and (b) a reversible heat generation caused by a change in entropy of the system (rearrangement of ions during charging/discharging determining entropy – a measure for disorder [14]).

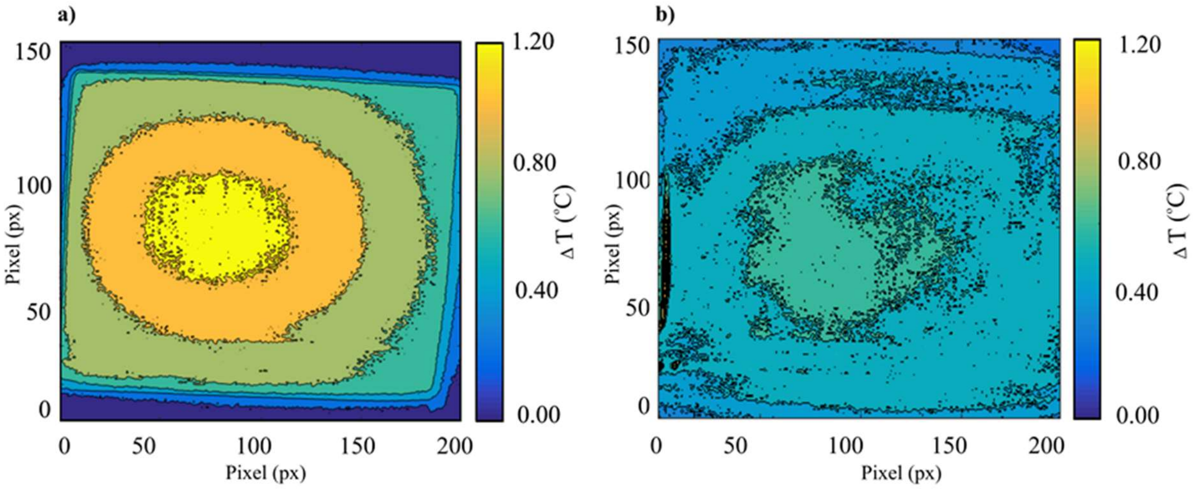

Fig. 3. Distribution of temperature increase observed in the tested as-prepared EDLC specimens at a current density of 1 A/g and having the terminals as presented in: (a) Fig. 1a, (b) Fig. 1b; the samples were characterized by the parameters: C = 2.75 F, ESR = 0.465 Ω (left), and C = 7.88 F, ESR = 0.318 Ω (right).

The process of charging/discharging degraded the sample by increasing the ESR and decreasing the capacitance [15, 16]. Capacitance and ESR were measured during the fifth cycle of repeated charging/discharging at the current I = 1 A/g which is lower than the applied during aging (I = 4 A/g). Similar processes induced by charging/discharging are also observed in other electrochemical systems, such as batteries [17].

The temperature of the as-prepared specimens increased by about 1°C on the pouches' surfaces (Fig. 3). We observed quite a similar temperature distribution in both cases. The higher temperature was present in the specimen with smaller terminals (Fig. 3a). The highest temperature was in the central part of the pouch. Faster energy exchange (lower thermal resistance) at the edges of the pouch explains this result.

We observed more severe changes of temperature after aging the specimens (Fig. 4). The temperature increased a few degree Celsius, and is a few times more intense than in the as-prepared samples. We suppose that this is due to the higher ESR values. Moreover, its maximum shifted to the pouch edge for the specimen with small terminals (Fig. 4a). We suppose that this is a result of some local changes in the specimen structure (e.g., electrode delamination or even a tiny bit of electrolyte leakage). The leakage increases locally series resistance due to lower content of the electrolyte between the electrodes and inside their porous structures and therefore induces higher temperatures. The same effect can be explained by limited charging ability and change of entropy, responsible for temperature decrease during discharging as described elsewhere [14]. We observed similar changes after dismounting some of the tested samples. The specimen change may be induced by the narrow shape of the terminals, where the density current is higher. Therefore, this area is more vulnerable to a more marked increase in ESR and overheating.

The recorded thermogram pictures were used to estimate a few selected statistical parameters, such as temperature variance, skewness, and kurtosis. An overview of the observed results can be found elsewhere [9]. The results are quite similar to the presented results of temperature increase but required more computations. Therefore, we didn't consider it in the presented studies. We focused on the informative parameter (temperature increase), which can be monitored even by low-cost sensors.

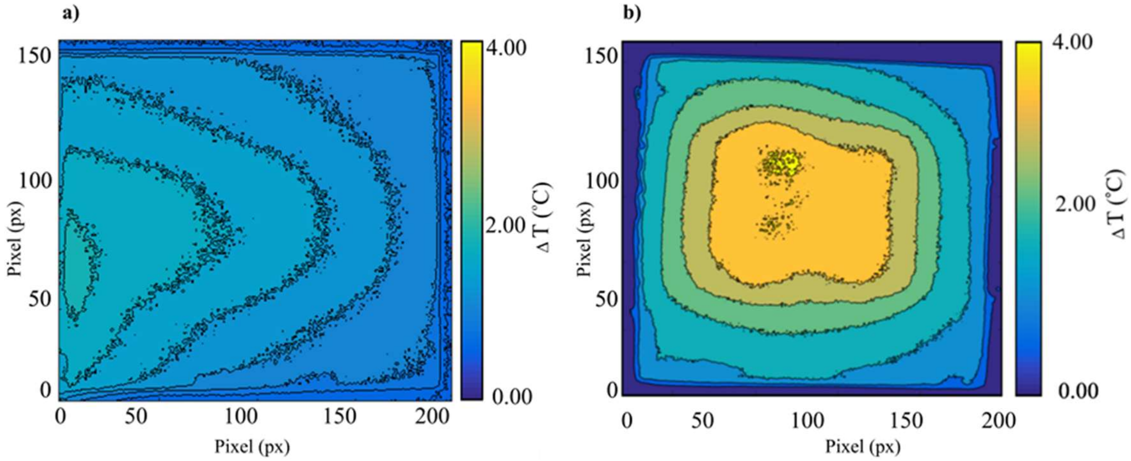

Fig. 4. Distribution of temperature increase observed in the tested EDLC specimens after aging at a current density of 1 A/g and having the terminals as presented in (a) Fig. 1a, (b) Fig. 1b; the samples were characterized by the parameters: C = 1.32 F; ESR = 1.15 Ω (left), and C = 0.49 F; ESR = 3.46 Ω (right).

The recorded heterogenous temperature changes can be used to evaluate the state-of-health of the EDLC. We can include a temperature sensor inside the supercapacitor to monitor eventual overheating at the selected and most vulnerable places, such as the area close to the terminals identified by these experimental studies (Fig. 4a). Similar effects were observed in other specimens. Figure 5 presents the results for another pair of the as-prepared samples using both shapes of the collectors (Fig. 1). We observed similar temperature distribution as in a previous couple (Fig. 3). The samples after aging (Fig. 6) exhibited similar temperature distribution, as observed in a former couple (Fig. 4). The sample with the narrow terminals (Fig. 6a) had a higher temperature at the edge on its right side, where a tiny leakage was identified. We can conclude that the samples with narrow terminals were more fragile because we observed leakages at the edges of the applied pouch.

Even cheaper solutions (e.g., a temperature fuse made of a spring embedded in a wax) can be applied to reduce the risk of premature damage of the applied EDLC. We have to underline that temperature monitoring gives valuable information about the state-of-health of the EDLC, but is not decisive. A few works consider other factors accelerating EDLC aging, such as AC voltage ripples polarising a supercapacitor. These factors work together and accelerate the aging processes [18]. Therefore, any efficient monitoring system should consider a few factors inducing degradation of the EDLCs' structures.

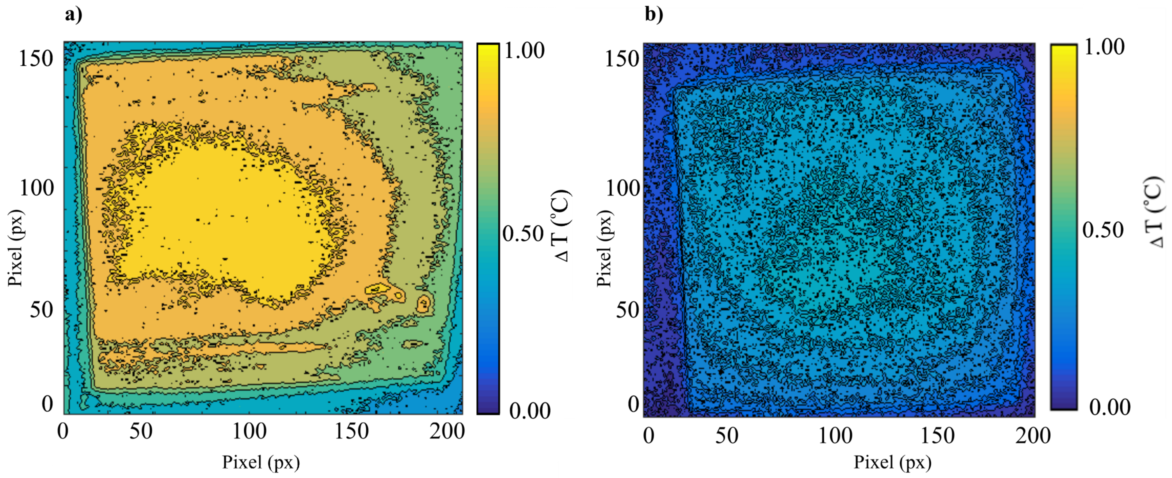

Fig. 5. Distribution of temperature increase observed in the tested EDLC specimens after aging at a current density of 1 A/g and having the terminals as presented in (a) Fig. 1a, (b) Fig. 1b; the samples were characterized by the parameters: C = 2.5 F; ESR = 0.385 Ω (left), and C = 8.84 F; ESR = 0.13 Ω (right).

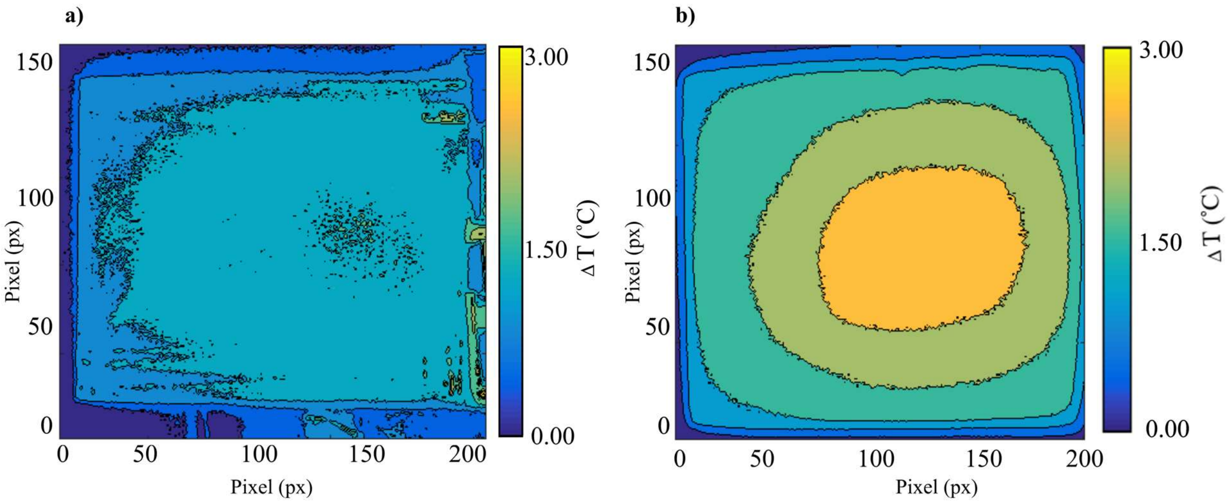

Fig. 6. Distribution of temperature increase observed in the tested EDLC specimens after aging at a current density of 1 A/g and having the terminals as presented in (a) Fig. 1a, (b) Fig. 1b; the samples were characterized by the parameters: C = 1.03 F; ESR = 1.24 Ω (left), and C = 8.58 F; ESR = 0.511 Ω (right).

4. Conclusions

We reported our experimental results of temperature distribution measurements in the investigated pouch samples of supercapacitors. The results suggest that these observations may be utilised to determine the state-of-health of the tested specimen by considering an evaluation of temperature changes during usage. Various statistical parameters of temperature fluctuations may be considered, but temperature increase is sufficient to identify overheated regions and to monitor these areas. The proposed method may be desirable due to limited costs when compared with other means (e.g., electrochemical noise or impedance measurements [19, 20]). The mentioned methods require a more advanced measurement set-ups and additional data processing [21]. Thanks to this, these techniques are more sensitive to any internal degradations in the EDLCs' structures' samples when induced by various factors. This limits the proposed method, based on monitoring a temperature increase only.

We observed that noise intensity is very sensitive to any changes within the electrode-electrolyte interface. Power spectral densities of noise level can change even a few times during aging when the capacitance C or resistance ESR changes tens of percent only. This result can be related to an increase in the resistance of charge transfer determining shot noise level [10] and was predicted by a model of noise sources generated within an electrode-electrolyte interface [22]. This effect can be observed during discharging the spacemen as presented elsewhere [23]. Impedance measurements of supercapacitors confirmed this conclusion for some electrolytes only. Unfortunately, the mentioned techniques require more complicated measurement methods.

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