Materials Science Forum Vol. 802 (2014) pp 427-432
Online available since 2014/Dec/31 at www.scientific.net
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doi:10.4028/www.scientific.net/MSF.802.427

Submitted: 01.10.2014
Accepted: 06.10.2014

Self-Discharge and Microstructure of Supercapacitors Tested at Room Temperature and at 333 K

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Keywords: supercapacitors self-discharge, energy storage, scanning electron microscopy

Abstract. The microstructure, chemical composition and self-discharge of some retail available supercapacitors have been investigated. Standard capacities of 1.0, 0.47 and 0.1 F at a maximum potential of 5.5 V were employed in this study. Self-discharge were carried out at room temperature and close to the nominal maximum working temperature of the supercapacitors (specified for 343 K). Internal resistance of the supercapacitors were calculated using the discharge curve for room temperature and 333 K. The microstructures of the electrode powder material have been investigated using scanning electron microscopy (SEM) and chemical microanalyses employing energy dispersive X-ray analysis (EDX). A compositional and morphological evaluation of these commercial supercapacitors materials has been carried out.

Introduction

Over the past years, extensive research has concentrated on the study and improvement of supercapacitors materials [1-7]. The electronic devices produced with these materials are used for storing energy over time periods ranging from seconds to several days [7]. The main factor determining the energy storage time of a supercapacitor is its self-discharge rate. This property concerns to the gradual decrease in the electric potential that occurs when the supercapacitor terminals are left unconnected to either a charging circuit or an electric load [7]. The self-discharge and lifetime of supercapacitors are dramatically affected by variations in the temperature. Self-discharge is faster with an increase in room temperature and lifetime is considerably reduced. The temperature inside electronic equipments can vary considerably over the continuously operation, affecting sensitive components. This paper addresses this aspect and reports the results of a work carried out on a systematic study with supercapacitors with nominal capacitance of 1.0, 0.47 and 0.1 F rated at a DC potential of 5.5 V and a specified maximum working temperature of 343 K.

Experimental

The supercapacitors studied in this investigation were acquired in the retail trade market for these electronic materials. The microstructures of the electrode material were investigated using a Hitachi scanning electron microscope with chemical microanalyses employing energy dispersive X-ray analysis. High vacuum was carried out on the electrode material (10^{-6} mbar) prior microstructure investigation to eliminate electrolyte residue evaporation on the microscope chamber.

The capacitance (C) and the internal equivalent series resistance (ESR) of the studied supercapacitors was determined using a computerized analyzer (Arbin BT4 + MITS Pro-Software). The capacitance was determined using the constant current discharge method based on the discharge curve [1]. The supercapacitor was charged at its rated DC potential (V_R) for 30 minutes and then discharged at a constant current (1 mA/F). The period of time t_2-t_1 is measured, during which the potential across the supercapacitor diminishes from 80% to 40% of the charging potential (V_R). In this method the capacitance is calculated using the equation [1]:

$$C = \frac{I\ (t_2\ -\ t_1)}{V_1 - V_2}\ . \tag{1}$$

In this study the rated DC potential of the supercapacitors was 5.5 V but the rated charging DC potential was fixed in 5.0V; thus: $V_1=0.8V_R=4V$ and $V_1=0.4V_R=2V$. ESR was determined by discharging the fully charged supercapacitor at 1 mAF^{-1} for 10s and reducing the current to zero. The resistance was calculated using this initial potential (V_i) and the potential after 5 s of null current (V_f) with the expression [1]:

$$ESR = \frac{V_f - V_i}{I} \ . \qquad (2)$$

The internal equivalent parallel resistance (EPR) was determined after charging the supercapacitors to V_o for 30 minutes and allowing the self-discharge using the equation [8]:

$$EPR = \frac{-t}{C \ln\left(\frac{V}{Vo}\right)} \ . \qquad (3)$$

where V is the final potential after a long period (t) of self-discharge.

Results and discussion

Energy dispersive X-ray analysis on the supercapacitors showed that carbon is the main element of the electrodes. Fig. 1 shows the EDX spectrum of the analyzed matrix material of the electrode. Fig. 2 shows the micrograph of the analyzed region (circle) of the carbon-based matrix material. A small region of impurity can also be observed in this micrograph. Fig. 3 shows the EDX spectrum of this impurity isolated region. Aluminum, oxygen and silicon were the main constituents of this discrete region. Oxygen has been detected since the high superficial area electrode material has been exposed to air. Fluorine and tin have also been detected in small impurity inside the matrix carbon-based electrode material, as shown in Fig. 4. The micrograph of the analyzed impurity region (circle) is shown in Fig. 5. Fluorine presence has been attributed to the type of electrolyte employed in these supercapacitors [9].

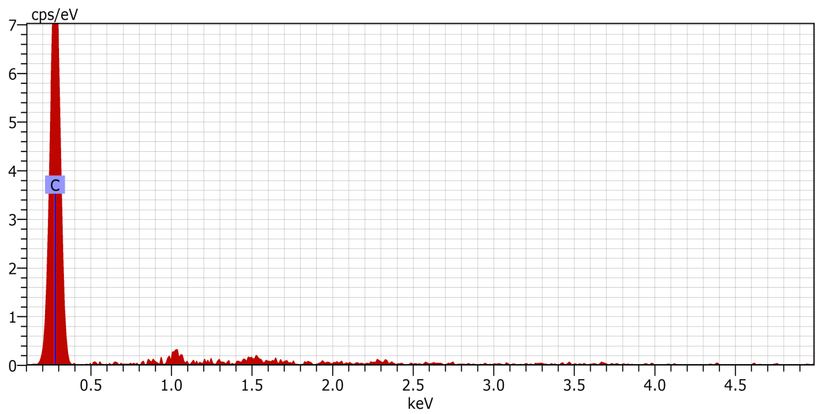

Fig. 1. Energy dispersive X-ray spectrum of the matrix material (0.47 F).

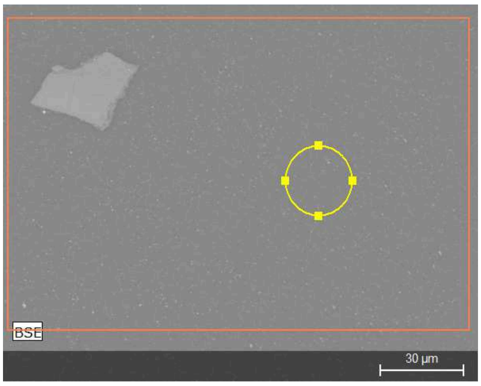

Fig. 2. SEM micrograph of the carbon-based matrix material (0.47 F).

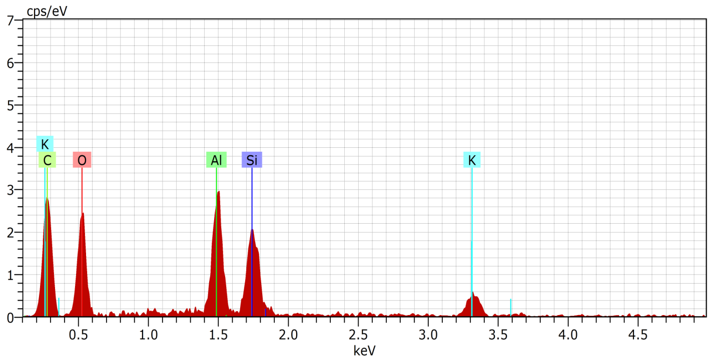

Fig. 3. Energy dispersive X-ray spectrum of impurity found on electrode material (0.47 F).

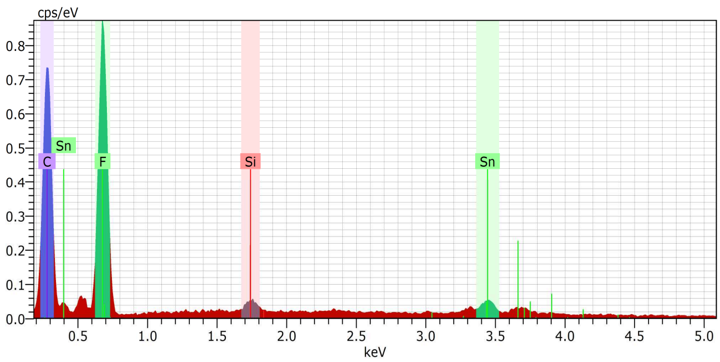

Fig. 4. Energy dispersive X-ray spectrum of the electrode material (1.0 F).

Fig. 5. SEM micrograph of the impurity found on the 1.0 F supercapacitor.

Measured values of capacitance and equivalent series resistance of the supercapacitors at room temperature are presented in Table 1. Some deviation from the nominal capacitance has been found for the measured values of these particular supercapacitors. Measurements carried out in various supercapacitors showed much less discrepancy between measured and nominal capacitance. Carbon based electrode material have high specific superficial area and are prone to this variations. The equivalent series resistance measured at room temperature varied considerably as the supercapacitor nominal capacitance changes. The best measured value of ESR was exhibited by the 0.47 F supercapcitor, since the ideal value would be zero, that is, null series resistance. The worst value was exhibited by the 0.1 F supercapacitor.

Table 1. Measured capacitance and equivalent series resistance at room temperature.

Nominal Capacitance	1.0 F	0.47 F	0.1 F
C [F]	0.90±0.10	0.57±0.10	0.18±0.10
ESR [Ω]	19.9±2.5	5.7±2.4	29.5±10.3

Fig. 6 shows the self-discharge curves for the carbon based supercapacitors at room temperature. A very distinct profile is found for each supercapacitor. The higher the capacitance the higher the potential after long term self-discharge. Fig. 7 shows the self-discharge curves for the carbon based supercapacitors at 333 K. Again, a very distinct profile is found for each supercapacitor. The higher the capacitance the higher the potential after long term self-discharge but considerably lower than that at room temperature. Self-discharge curves for the supercapacitors of 1.0 F and 0.47 F were overlapping at room temperature whereas at 333 K they were far apart. Thus, the former is the less susceptible to self-discharge with increasing temperature. The calculated values of the equivalent parallel resistance at room temperature and at 333 K using the self-discharge curves are presented in Table 2. The equivalent parallel resistance measured at room temperature varied considerably as the supercapacitors temperature changed. The equivalent parallel resistance measured at room temperature varied considerably as the supercapacitors temperature changed.

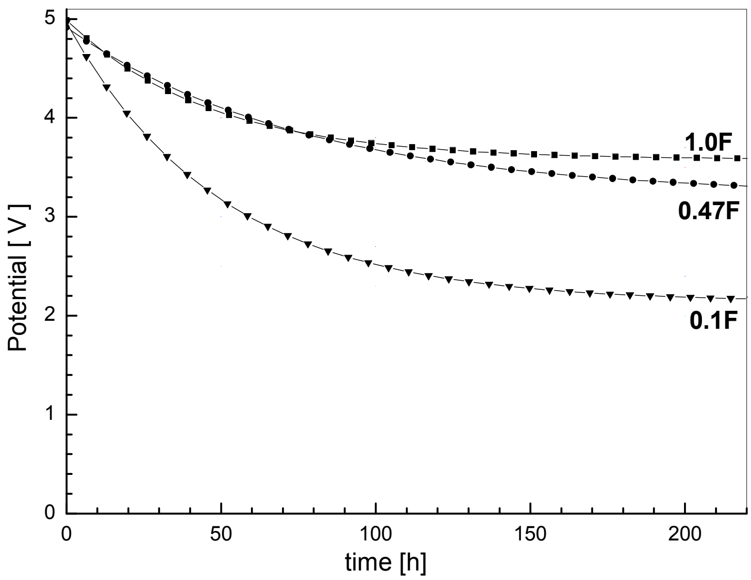

Fig. 6. Self-discharge curves for the carbon based supercapacitors at room temperature.

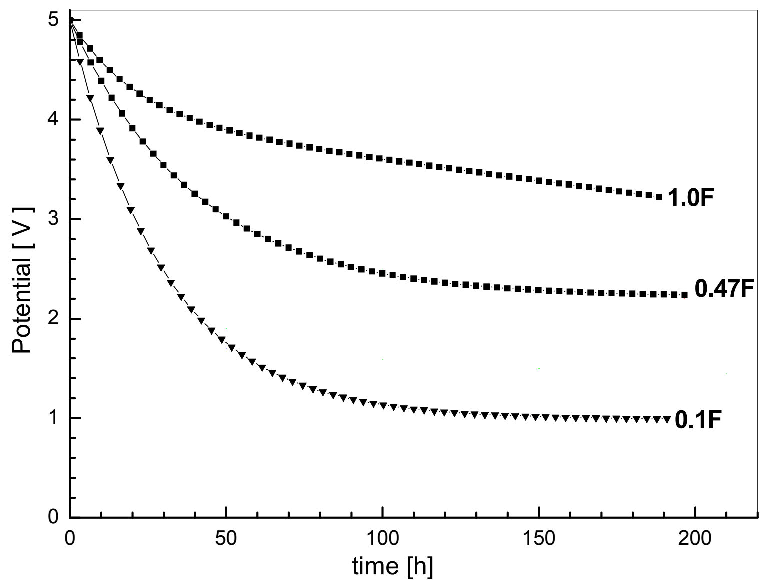

Fig. 7. Self-discharge curves for the carbon based supercapacitors at 333 K.

An overall decrease in the EPR has been observed with an increase in the room temperature. The smallest variation in the capacitance with temperature (from 4.2 to 1.7 MΩ) was observed for the 1.0 F supercapacitor. The equivalent parallel resistance should be as high as possible, thus, the best value of EPR was exhibited by the 0.1 F supercapacitor (7.73 MΩ) at room temperature and the worst (1.45 MΩ) by the 0.47 F supercapcitor at 333 K.

Table 2. Equivalent parallel resistance at room temperature and 333 K.

T [K]	**273**			**333**		
Nominal C	**1.0 F**	**0.47 F**	**0.1 F**	**1.0 F**	**0.47 F**	**0.1 F**
C [F]	0.90	0.57	0.18	0.90	0.57	0.18
V [V]	3.46	3.11	1.88	3.22	2.13	0.92
Vo [V]	5.00	4.95	5.07	5.00	5.02	5.00
t [10^6s]	1.40	1.39	1.38	0.68	0.71	0.69
EPR [MΩ]	4.23	5.25	7.73	1.72	1.45	2.26

Conclusions

The results showed that retail trade supercapacitors are based on carbon material and presents some deviation of the nominal capacitance. This has been attributed high specific electrode area required for these materials. Variation on the equivalent series resistance has also been found. The supercapacitor with a capacitance of 0.47 F showed the lowest value of equivalent series resistance. Measured variations on the equivalent parallel resistance at room temperature and 333 K were very significant since the supercapacitors were specified to work at a maximum temperature of 343 K. The highest value of equivalent parallel resistance (7.73 MΩ) was exhibited by the supercapacitor of 0.1 F at room temperature and the lowest (1.45 MΩ) by the 0.47 F supercapacitor at 333 K.

Acknowledgements

Many thanks are due to IPEN-CNEN/SP for supporting this investigation and also to the PIBIC-PROBIC program for a research grant (V. R. S. Visentini).

References

[1] M. Conte: Fuel Cells Vol. 10 (2010), p. 806.
[2] C. Arbizzani, M. Mastragostino, F. Soavi: J. Power Sources Vol. 100 (2001), p. 164.
[3] E. Frackowiak, F. Béguin: Carbon Vol. 39 (2001), p. 937.
[4] A. Burke: J. Power Sources Vol. 91 (2000), p. 37.
[5] D. Qu, H. Shi: J. Power Sources Vol. 74 (1998), p. 99.
[6] J. Gamby, P.L. Taberna, P. Simon, J.F. Fauvarque, M. Chesneau: J. Power Sources Vol. 101 (2001), p. 109.
[7] B.W. Ricketts, C. Ton-That: J. Power Sources Vol. 89 (2000), p. 64.
[8] Y. Wang: Modeling of ultracapacitor short-term and long term dynamic behavior. Master of Science Thesis. University of Akron 2008.
[9] G. Park: Graphite: application to anode and cathode materials for energy storage device. Doctor Thesis. Saga University 2010.

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10.4028/www.scientific.net/MSF.802

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10.4028/www.scientific.net/MSF.802.427

DOI References

[1] M. Conte: Fuel Cells Vol. 10 (2010), p.806.
http://dx.doi.org/10.1002/fuce.201000087
[2] C. Arbizzani, M. Mastragostino, F. Soavi: J. Power Sources Vol. 100 (2001), p.164.
http://dx.doi.org/10.1016/S0378-7753(01)00892-8
[3] E. Frackowiak, F. Béguin: Carbon Vol. 39 (2001), p.937.
http://dx.doi.org/10.1016/S0008-6223(00)00183-4
[4] A. Burke: J. Power Sources Vol. 91 (2000), p.37.
http://dx.doi.org/10.1016/S0378-7753(00)00485-7
[5] D. Qu, H. Shi: J. Power Sources Vol. 74 (1998), p.99.
http://dx.doi.org/10.1016/S0378-7753(98)00038-X
[6] J. Gamby, P.L. Taberna, P. Simon, J.F. Fauvarque, M. Chesneau: J. Power Sources Vol. 101 (2001), p.109.
http://dx.doi.org/10.1016/S0378-7753(01)00707-8
[7] B.W. Ricketts, C. Ton-That: J. Power Sources Vol. 89 (2000), p.64.
http://dx.doi.org/10.1016/S0378-7753(00)00387-6