Materials Science Forum
ISSN: 1662-9752, Vol. 899, pp 260-265
doi:10.4028/www.scientific.net/MSF.899.260
© 2017 Trans Tech Publications, Switzerland
Submitted: 2016-12-21
Accepted: 2016-12-29
Online: 2017-07-03

Thermal Influence on the Electric Parameters and Microstructures of Activated Powder Double Layer Supercapacitors

Antonio Paulo Rodrigues Fernandez[a], Eguiberto Galego[b], Rubens Nunes Faria[c]

Instituto de Pesquisas Energéticas e Nucleares, IPEN – CNEN/SP, São Paulo – SP, Brazil,

[a] aprfff@gmail.com, [b] egalego@ipen.br, [c] rfaria@ipen.br

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

Abstract. The effect of the working temperature on the capacity, internal equivalent serial resistance (ESR), equivalent parallel resistances (EPR) of some retail available electric double layer capacitors (EDLC) have been investigated. Standard capacities of 1.0 F at a maximum potential of 5.5 V were employed in this study. EPR values have been calculated using the self-discharge curves at temperatures above to the nominal maximum working temperature of the supercapacitors (~70^{o}C). The ESR values were measured during charge using the constant current (1 mAF^{-1}) interrupt method with oscilloscope. Microstructural characterization of the electrode material have been carried out using scanning electron microscopy (SEM) and chemical microanalyses employing energy dispersive X-ray analysis (EDX).

Introduction

Supercapacitors can operate only temporarily under rigorous temperature conditions [1]. It has been reported that the increase of resistance is more pronounced than the deterioration of capacitance after 1000 hours at 70^{o}C [2]. The internal resistance (ESR) increased by a factor of 3 to 4.5 during this thermal treatment with no significant change on the capacitance. However, after 3 months of storage at 90^{o}C and an applied potential of 2.3 V, the capacitance decreased dramatically. It has been shown in these studies that all tested supercapacitors failed due to the increasing internal resistance. Ageing has also been attributed to traces of water and absorbed gases in the electrolyte and the electrodes [1]. Oxidations of the carbon surface, blocking the pore access and/or electrolyte depletion have been attributed to supercapacitor aging. Irreversible transformations occurred in the electrolyte are accentuated by potential and temperature. This electrochemical decomposition of the electrolyte yields gas overpressure in the double-layer [3]. It has also been reported that there is not any direct relationship between aging of supercapacitors and the specific surface area of the activated carbon and several reasons have been found to explain the fading of the electrochemical performance and the macroscopic effects in supercapacitors [4]. This paper further addresses these aspects and reports the results of a work carried out on a study of supercapacitors aging at temperature reaching 125^{o}C. Electrical, compositional and morphological evaluation of the supercapacitors materials has been carried out.

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. Fluorescence was carried out using a commercial equipment only to detect possible impurities on the material once carbon is not analyzed by this technique.

The capacitance (C) and the internal equivalent series resistance (ESR) of the studied supercapacitors were determined using a computerized analyzer. The capacitance was determined

All rights reserved. No part of contents of this paper may be reproduced or transmitted in any form or by any means without the written permission of Trans Tech Publications, www.scientific.net. (#102098648-06/10/17,19:40:01)

using the constant current discharge method based on the discharge curve [4]. 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 [5]:

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

In this study ESR measurements were carried out using an oscilloscope and the interrupt method during supercapacitor charge at a constant current [6]. 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 [7,8]:

$$EPR = \frac{-t}{C \ln\left(\frac{V}{Vo}\right)} \tag{2}$$

where V is the final potential after a long period of self-discharge and Vo is the initial potential of self-discharge. All electrical measurements were carried out at room temperature.

Results and discussion

The variation of the EPR with time at distinct temperatures is shown in Figure 1. It can be seen that the temperature has significant influence on the EPR behavior. As the aging time was increased the EPR values diminished considerably. The supercapacitor showed no electrical properties after 672 h at 125°C. Figure 2 shows the self-discharge curves for the supercapacitor test at this elevated temperature. A striking change in the self-discharge behavior was observed as the aging time was increased. It has been reported that since self-discharge rates are dependent on the rates of ionic transport it is expected that self-discharge will become more rapid as the temperature of the capacitor is increased [9]. Values of the ESR and capacity for these supercapacitors are given in Table 1. The capacity remained unchanged when taking in consideration the measurement error. A dramatic increase in ESR was observed only in the supercapacitor treated for 504 h at 125°C.

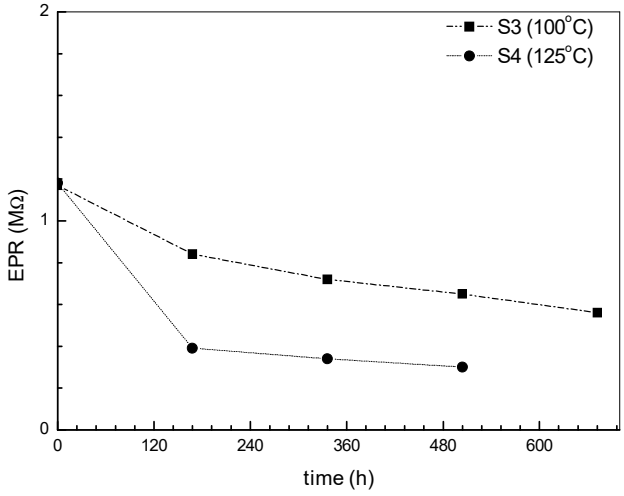

Fig. 1. Variation of EPR with time for the tested supercapacitors at various temperatures.

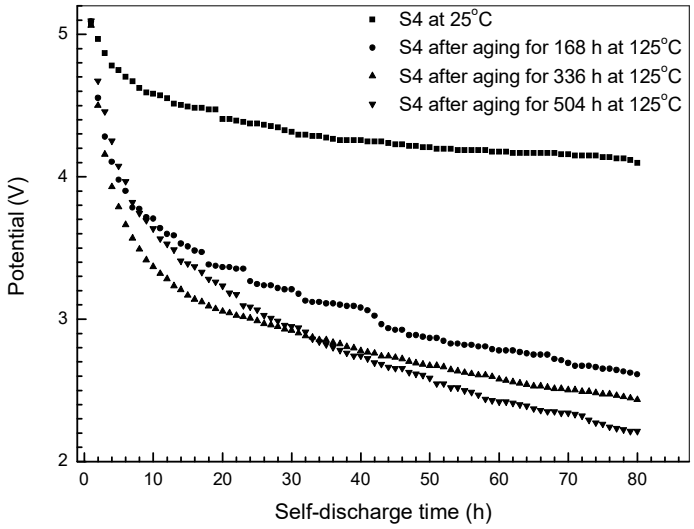

Fig. 2. Potential variation during self-discharge after aging at 125°C.

Considering that the investigated supercapacitors are composed by 2 individual cells to increase the maximum working potential to 5.5 V, it can be inferred that the values of ESR for each cell, assuming even cells, is half of that presented in Table 1. On the other hand, values of capacity per cell should be twice as much for identical cells. Organic electrolytes have a potential window of about 2.7 V and stored energy can be increase four times by this series arrangement.

Table 1. Measured ESR and capacity at various aging times upon distinct temperatures.

Time	T=50°C		T=75°C		T=100°C		T=125°C	
(h)	ESR(Ω)	C (F)	ESR(Ω)	C (F)	ESR(Ω)	C (F)	ESR(Ω)	C (F)
0	9.0±1.0	1.2±0.1	11.6±1.0	1.2±0.1	14.0±1.0	1.1±0.1	11.4±1.0	1.1±0.1
168	8.6±1.0	1.0±0.1	8.3±1.0	1.1±0.1	11.7±1.0	1.1±0.1	10.8±1.0	1.1±0.1
336	11.2±1.0	1.0±0.1	9.2±1.0	1.1±0.1	12.8±1.0	1.1±0.1	11.4±1.0	1.1±0.1
504	10.0±1.0	1.1±0.1	9.3±1.0	1.1±0.1	14.8±1.0	1.2±0.1	19.3±1.0	1.2±0.1
672	10.4±1.0	1.1±0.1	8.2±1.0	1.1±0.1	12.3±1.0	1.1±0.1	- - -	- - -

Fig. 3 shows the micrographs of the analyzed regions of the electrode material. Energy dispersive X-ray analysis on the supercapacitors showed that carbon is the matrix element of the electrodes with minute impurities, some from the separator material. Fig. 4 shows the micrographs of regions containing minor impurities. The EDX spectrum of impurity region with the peaks corresponding to Fe and C elements is shown in Fig.5. Fe and C were the main constituents of this discrete region. Oxygen has been detected possibly due to the activation processing to achieve the electrode material high superficial area. Fluorine and tin have also been detected in small impurity inside the matrix carbon-based electrode material. Fluorine presence has been attributed to the type of electrolyte employed in these supercapacitors [10]. $TEABF_4$ is a very common organic electrolyte and the preferred choice of supercapacitor manufacturers. Fig. 6 shows the fluorescence spectrum of the analyzed electrode material and the semi-quantitative results are given in Table 2. Apart from Si and Fe already shown by EDX S, K, Cu, Ni and Zn were also detected using X-ray fluorescence. The former shows a punctual analysis of a small impurity region and light elements (C and O) peaks only indicate the presence of these elements whereas the latter, although showing a more representative analysis with larger region (area) of material, the light elements were not computed. This must be taken in consideration since C is the main component on the electrode.

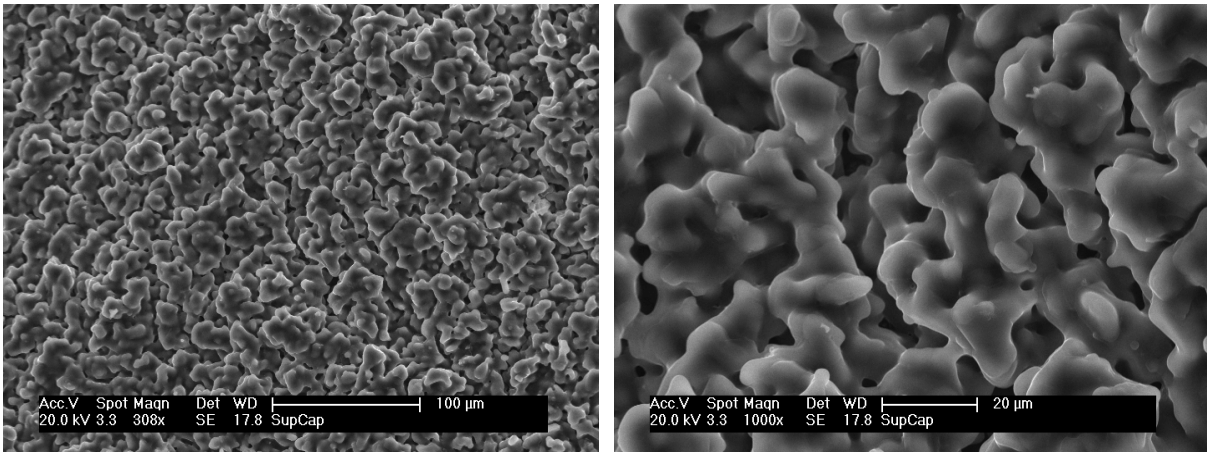

Fig. 3. SEM micrographs of the carbon-based matrix material.

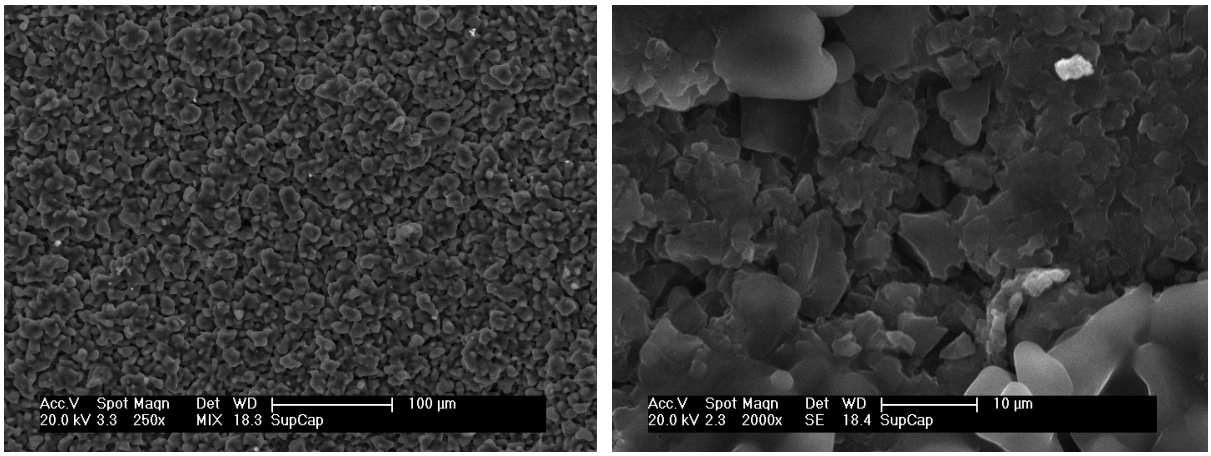

Fig. 4. SEM micrographs of the electrode material with impurities (white spots).

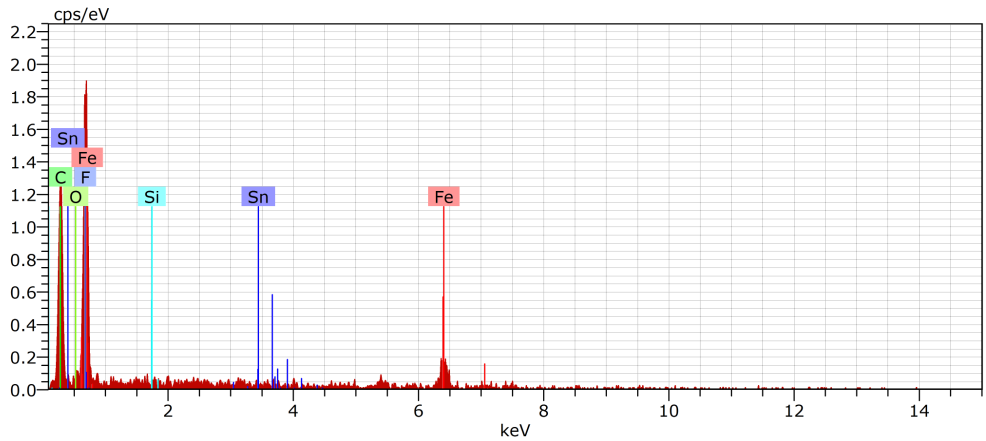

Fig. 5. Energy dispersive X-ray spectrum of impurity in the electrode material.

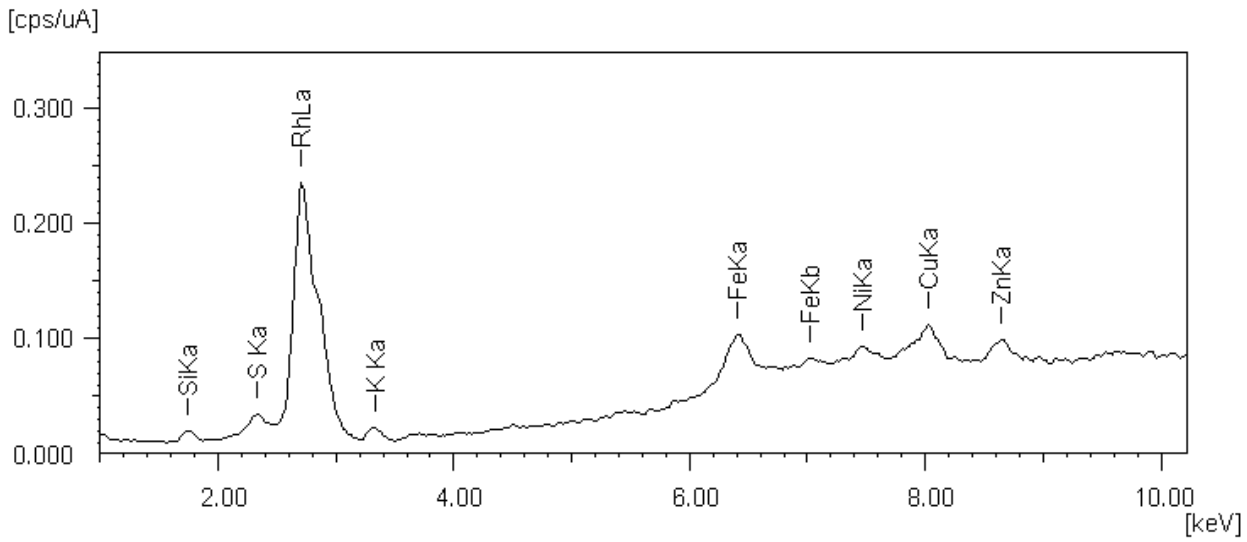

Fig. 6. Fluorescence spectrum of the electrode material.

Table 2. Semi-quantitative X-ray fluorescence analyses of the electrode material.

Analyte	Amount (%)	Standard Deviation	Intensity (cps/μA)
Si	23.96	0.59	0.036
S	20.11	0.43	0.070
K	19.35	0.73	0.032
Fe	14.16	0.28	0.434
Cu	9.29	0.23	0.392
Ni	8.33	0.28	0.253
Zn	4.80	0.22	0.201

Additional reasons for supercapacitors aging have been previously compiled from various sources, including some patents and can be summarized as follows [4]. Oxygen and metals impurities also have been attributed to electrode damage and increased resistance. Surface functionality of the activated carbon has been shown to be detrimental to the capacitance evolution. The leakage current has been associated to the presence of acidic surface groups on the activated carbon. Water in the organic medium reduced the potential window of the electrolyte influencing the supercapacitor aging and yielding gases with fading of the electrochemical performance (for potentials higher than 2.5V) by blocking the separator and carbon pores with increasing internal resistance. The binder used as the coating layer has also been suspect to be a cause of capacitance decrease and resistance increase. It can be also inferred that sufficiently high temperature combined with prolonged exposure time also might cause electrolyte evaporation if sealing is insufficient for increased pressure. Thus, lifetime expectance is dramatically reduced with a small increase in the working temperature of the supercapacitors [11].

Conclusions

The results showed that the capacity is independent of the aging temperature until the electrical fault of the supercapacitors. In the long term at an elevated temperature the ESR of the supercapacitor decreases dramatically. Self-discharge is the most sensitive parameter to the aging process in supercapacitors. The EPR determined using the self-discharge curves is a good indicator of the supercapacitor aging state. The self-discharge rates accelerate strongly with an increase in the

working temperature. The deleterious effect of the temperature on the supercapacitors has been attributed to modifications on the electrolyte interface with the activated highly porous carbon.

Acknowledgements

Many thanks are due to IPEN-CNEN/SP for supporting this investigation.

References

[1] P. Kurzweil, B. Frenzel, R. Gallay, *Electrochemical and spectroscopy studies on rated capacitance and aging mechanisms of supercapacitors*. 2nd European Symposium on Super Capacitors and Applications, Lusanne, 2-3 November, 2006, p. 1
[2] P. Kurzweil, M. Chwistek, R. Gallay, *Capacitance characterization methods and aging behavior of supercapacitors*. Proceedings of The 15th International Seminar on Double Layer Capacitors, Deerfield Beach, Florida, USA, December 5-7, 2005, p. 1
[3] P. Azais, L. Duclaux, P. Florian, D. Massiot, M.L. Rodenas, A.L. Solano, J.P. Peres, C. Jehoulet, F. Beguin: Journal of Power Sources Vol. 171 (2007), p. 1046.
[4] P. Kurzweil and M. Chwistek: Journal of Power Sources Vol. 176, (2008), p. 555.
[5] M. Conte: Fuel Cells Vol. 10 (2010), p. 806.
[6] L.H. Seim: Modeling, Control and experimental testing of a supercapacitor/battery hybrid system –passive and semi-active topologies, Master Thesis, 2011.
[7] Y. Wang: Modeling of ultracapacitor short-term and long term dynamic behavior. Master of Science Thesis, University of Akron (2008).
[8] A. M. Namisnyk, *A survey of electrochemical supercapacitor technology*. Project submitted for the degree of bachelor of engineering, (2003).
[9] Y. Diab, P. Venet, H. Gualous, G. Rojat: IEEE Transactions on Power Electronics Vol. 24 (2) (2009), p.510.
[10] G. Park: Graphite: application to anode and cathode materials for energy storage device. Doctor Thesis, Saga University (2010),.
[11] R.S. Rajan, M. Rahman: Journal of electrical and electronics engineering Vol. 9 (1) (2014), p. 55.