ELECTROCHEMICAL CHARACTERISTICS AND MICROSTRUCTURE OF ACTIVATED CARBON POWDER SUPERCAPACITORS FOR ENERGY STORAGE

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ABSTRACT

In recent years, extensive investigations have concentrated on the study and improvement of supercapacitors electrode materials. The electric devices produced with these materials are used for stored energy over time periods ranging from seconds to several days. 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. Self-discharge is attenuated with a decrease in room temperature and lifetime is enhanced. 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 rated at a DC potential of 5.5 V and 10.0 F at 2,7 V. The specific capacitance, internal resistance and self-discharge of commercial activated carbon electrode supercapacitors have been investigated. Specific capacitances were measured in this study using cyclic voltammetry (CV). Specific capacitances of 44.4 and 66.7 Fg-1 were determined for distinct carbon electrodes supercapacitors. Self-discharge were carried out at room temperature and close to the freezing point. Internal resistances of the supercapacitors were calculated using the discharge curve at room temperature. The microstructures of the electrode material have been investigated using scanning electron microscopy (SEM).

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

INTRODUCTION

In recent years, extensive investigations have concentrated on the study and improvement of supercapacitors electrode materials [1-7]. The electric 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 attenuated with a decrease in room temperature and lifetime is enhanced. 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 rated at a DC potential of 5.5 V and a 10.0 F at 2.7 V.

EXPERIMENTAL

Two types of activated carbon electrode supercapacitors were studied in this investigation. A disc-type 1F supercapacitor was composed by 4 electrodes in a serial disposition (2 cells) in order to achieve a maximum nominal working potential of 5.5 V and each electrode containing an active carbon mass of 0.09 g. As each electrode has intrinsically an electrical double layer the nominal specific capacitance of this disc-type supercapacitor was accounted as 44.4 Fg^{-1} (4X1F/0.09g). A tubular-type 10F supercapacitor was composed by 2 electrodes in serial disposition with a maximum nominal working potential of 2.7 V and a mass of 0.3 g each. The nominal specific capacitance of this tubular-type supercapacitor was computed as 66.7 Fg^{-1} (2X10F/0.3g). The electrochemical characteristics of the carbon electrodes were investigated using a digital Arbin analyzer. The specific capacitance was determined using the cyclic voltammetry (CV) curves and equation (1):

$$Cs = \frac{\int_{Vi}^{Vf} i(V)dV}{2v(Vf - Vi)} \qquad (1)$$

The specific capacitance was also determined using the constant current discharge method based on the discharge curve [8,9] (galvanostatic charged/discharged at 1 mAF^{-1} using the equation (2):

$$C_s = \frac{I \, \Delta t}{\Delta Vm} \qquad (2)$$

ESR was determined by discharging the fully charged carbon electrodes at 1 mAF^{-1} 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 (3) [1]:

$$ESR = \frac{V_f - V_i}{I} \qquad (3)$$

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 (4) [10]:

$$EPR = \frac{-t}{C \, \ln\left(\frac{V}{Vo}\right)} \qquad (4)$$

where V is the final potential after some time of self-discharge (t).

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.

RESULTS AND DISCUSSION

Figure 1 and 2 show the cyclic voltammetry curves at room temperature for the 1F/5.5V and 10F/2.7V supercapacitors at distinct scan rates. The later supercapacitor shows better performance than the former with curves resembling an ideal supercapacitor. This behavior is more striking as the scan rate is increased and shows that the ESR and EPR values of the 1F supercapacitor is substantially higher than those of the 10 F supercapacitor.

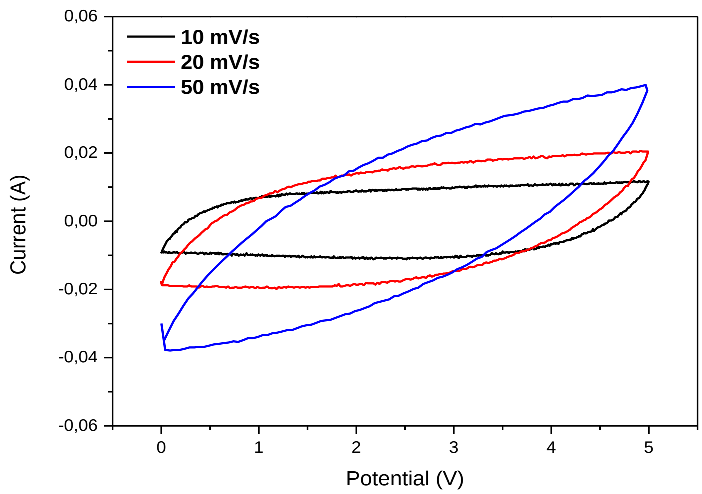

Figure 1. Cyclic voltammetry curves at distinct scan rates of the 1F/5.5V disc-type supercapacitor.

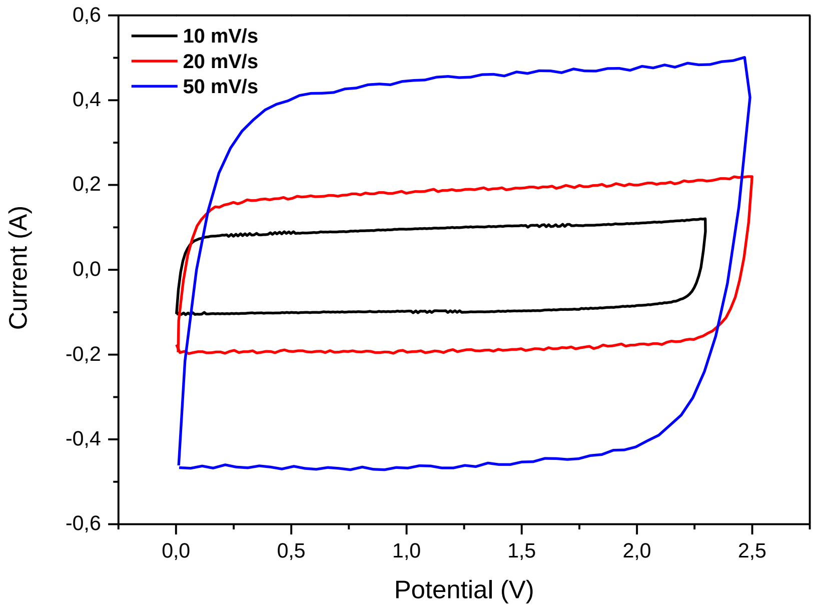

Figure 2. Cyclic voltammetry curves of the 10F/2.7V tubular-type supercapacitor.

Table 1 gives the values of the calculated specific capacitance using the cyclic voltammetry curves (equation 1) and the mass of active material in a single electrode. As expected the specific capacitance decreased as the scan rate was increased. The 10F/2.7V supercapacitor showed higher specific capacitances and a considerably smaller variation as the scan rate was increased.

Table 1. Calculated specific capacitance using the cyclic voltammetry area.

Rate	Capacitor 1F/5.5V		Capacitor 10F/2.7V	
(Vs^{-1})	CV integral	Cs (Fg^{-1})	CV integral	C_s (Fg^{-1})
10	0.0816	75.2	0.4326	115.2
20	0.1235	55.2	0.8933	119.2
50	0.1565	28.0	2.0316	108.4

Figure 3 shows the charge/discharge curves at room temperature for the 1F/5.5V and 10F/2.7V supercapacitors. Both supercapacitors show almost linear behavior on charge and discharge.

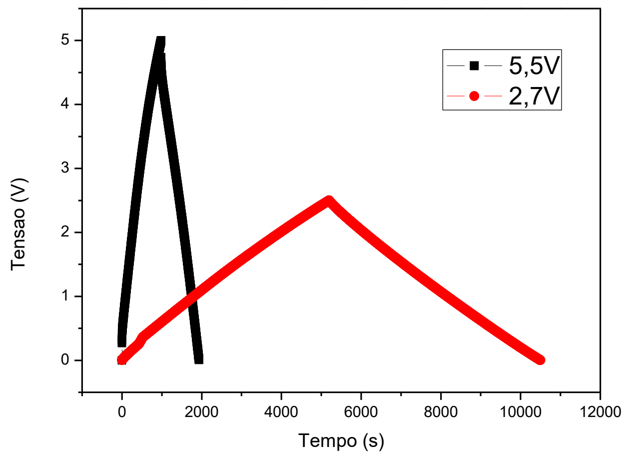

Figure 3. Galvanostatic curves for the 1F/5.5V and 10F/2.7V supercapacitors.

Table 2 gives the values of the calculated specific capacitance using these curves (equation 2) and the mass of active material of a single electrode. Again, the 10F/2.7V supercapacitor showed a much higher specific capacitance of 141.6 Fg^{-1}. This value is higher that exhibited by cyclic voltammetry measurement at any scan rate. Conversely, the 1F/5.5V supercapacitor showed inferior values of specific capacitance (42.4 Fg^{-1}) than those found with cyclic voltammetry at 10 and 20 Vs^{-1} (72.2 and 55.2 Fg^{-1}, respectively).

Table 2. Calculated capacitance using the galvanostatic cycles.

Nominal capacitance (F)	ΔV (V)	Δt (s)	Calculated C_s (Fg^{-1})
1	5.0	951.457	42.4
10	2.5	5312.01	141.6

The parameters values for the calculation of the ESR for the investigated supercapacitors are given in Table 3 and 4. As expected, the 10F/2.7V supercapacitor shows a much better performance than the 1F/5.5V supercapacitor showing an ESR of 0.4 Ω per electrode contrasting to that of almost 4.4 Ω per electrode exhibited by the supercapacitor with smaller capacitance. The difference is very significant (almost 10 times) and this was quite visible in the cyclic voltammetry curves.

Table 3. Calculated ESR for the 1F supercapacitor.

V_f (V)	1.019	3.015	4.018
V_{min} (V)	0.999	3.000	4.000
i (A)	0.001	0.001	0.001
ESR (Ω)	20	15	18
ESR_{mean}= ~4.4 Ω per electrode			

Table 4. Calculated ESR for the 10F supercapacitor.

V_f (V)	1.010	2.005	3.008
V_{min} (V)	1.000	2.000	3.000
I (A)	0.010	0.010	0.010
ESR (Ω)	1.0	0.5	0.8
ESR_{mean} = 0.4 Ω per electrode			

Figure 4 and 5 show the self-discharge curves for the both supercapacitors at room temperature and close to the freezing point. The parameters values obtained from these curves for the calculation of the EPR are given in Table 5 and 6. The 1F/5.5V supercapacitor showed much higher EPR values (5.5 MΩ per electrode) than those exhibited by the 10F/2.7V supercapacitor (200 kΩ per electrode). An exceeding high value was observed for the 1F/5.5V supercapacitor at temperatures close to freezing point (59.5 MΩ per electrode).

Figure 6 shows the micrographs of the composite material composing the electrodes of these supercapacitors. No significant morphological differences have been noticed using SEM at these standard magnifications.

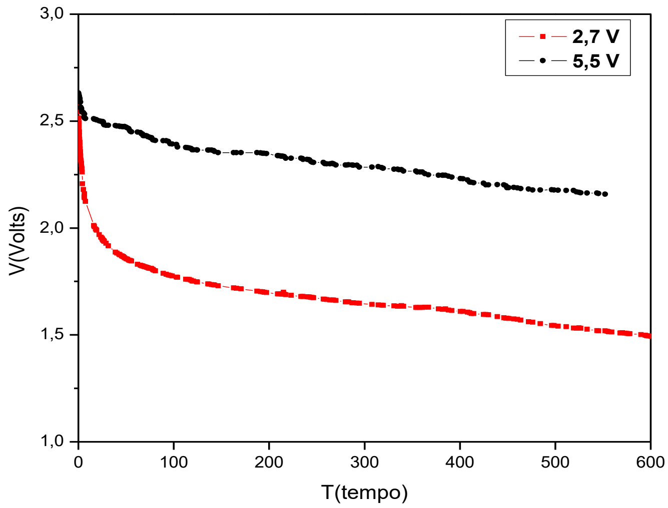

Figure 4. Self-discharge curves for the carbon based supercapacitors at room temperature.

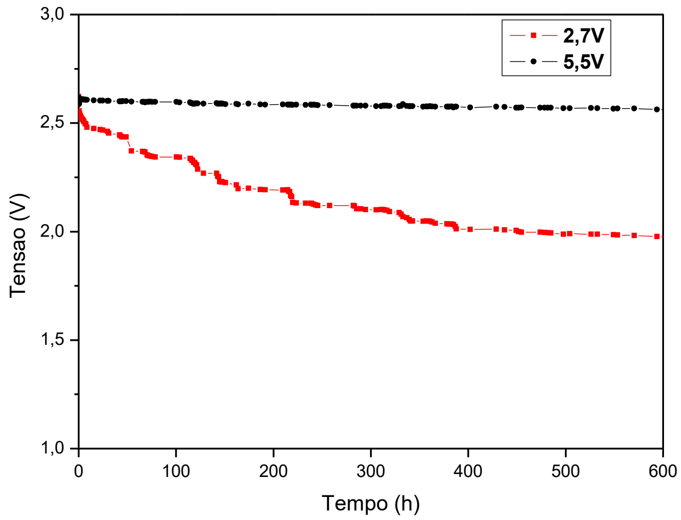

Figure 5. Self-discharge curves for the carbon based supercapacitors at 333 K.

Table 5. Calculated EPR for the supercapacitors at freezing point.

	10F – 2.7V	1F – 5.5V
t (s)	2.172 x 10^6	2,442 x 10^6
C (F)	10.0	1.0
V_0 (V)	1.909	2.559
V (V)	2.622	2.612
EPR (MΩ)	**0.7**	**119**

Table 6. Calculated EPR for the supercapacitors at room temperature.

	10F – 2.7V	1F – 5.5V
t (s)	2.183 x 10^6	2.193 x 10^6
C (F)	10.0	1.0
V_0 (V)	1.491	2.158
V (V)	2.624	2.632
EPR (MΩ)	**0.4**	**11.0**

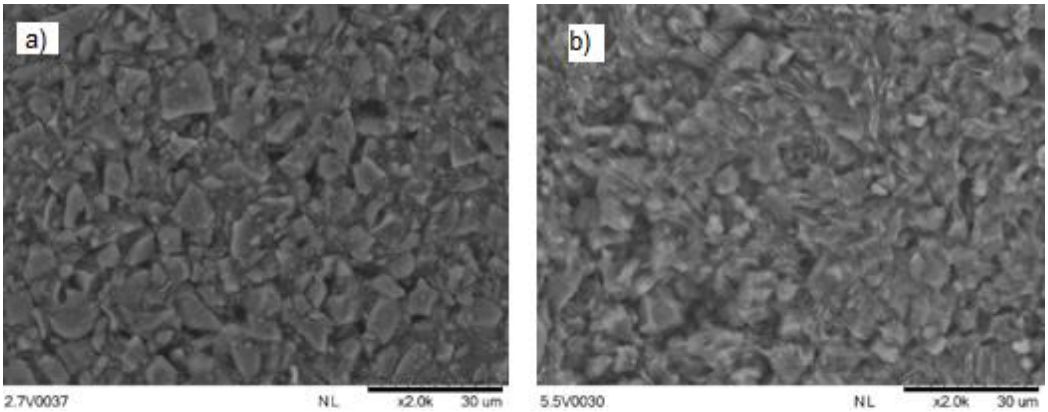

Figure 6. SEM micrographs of the 1 F (a) and 10F (b) supercapacitors.

CONCLUSION

The results showed that the performance of commercial supercapacitores with distinct specific capacitance can differ considerably. A tubular-type 10F/2.7 V showed much better electrochemical characteristics than a disc-type 1F/5.5 V supercapacitor. The former showed a cyclic voltammetry loop shape close to ideal and good equivalent series resistance (0.4 Ω per electrode) whereas the latter exhibited an improved equivalent parallel resistance (11MΩ per electrode). Temperature had a remarkable influence in the equivalent parallel resistance of the disc-type 1F/5.5V supercapacitor. Specific capacitance of the electrode active material was much superior in the tubular-type 10F/2.7V supercapacitor.

ACKNOWLEDGEMENTS

Many thanks are due to IPEN-CNEN/SP for supporting this investigation and also to the PIBIC-PROBIC program for a research grant (T.C. Gonsalves). The authors wish to thank the Federal Institute of Education, Science and Technology of Rondônia Campus Porto Velho Calama for their financial support.

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