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Investigations on the Aging Effect of Supercapacitors

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ABSTRACT

In this paper, the degradation processes of commercial supercapacitors aged at 2.7 V and 65 °C for 2000 h were studied. The crystallinity, thermal stability, and specific surface areas of the carbon electrodes of the supercapacitors were measured. Significant changes and degradations in the carbon electrodes were observed for the aged supercapacitors. New functional groups were also found on the surface of the electrodes. The degradation of the lattice structures and the reduction in the specific surface area were as well observed for the aged supercapacitors. It was suggested that the aging of supercapacitors significantly changed the electrode surface which affects considerably electrical properties and functionality of supercapacitors. We have also performed experiments which suggest that the aging effect on the electrode is not uniformly distributed through its length.

INTRODUCTION

Supercapacitors (SCs), also called ultracapacitors, are short-term energy storage devices. SCs are suitable either for industrial purpose, backup power, quick charge or regenerative power and applications such as pitch control in wind turbine, solar system, and transportation [1-3]. SCs have higher specific energy than regular electrolytic capacitor and higher specific power than regular lithium-ion batteries or fuel cells [9, 13, 14]. SCs are characterized by the capability of delivering high specific energy in a short amount of time and a high cycling life time. The life of a regular SC is > 100 000 cycles [4, 7, 8]. The difference in cycling life is ascribed to the fact that SCs store energy in an electrostatic way, in comparison to batteries which store energy through oxidation/reduction processes. The specific capacitance of a SC can reach 150F/g [6, 7] and the energy density can reach 6.5 Wh/kg [12]. The operating voltage of a SC varies according to the electrolyte as for the aqueous electrolytes the voltage is around 1 V and the non-aqueous the voltage can be to 4 V approximately [5, 8]. It has been shown that during the cycling the SCs performance degrades as a result of the equivalent series resistance (ESR) increases and the capacitance decreases. This degradation is ascribed to the physical changes such as gas evolution, mass increases and degradation of the carbon coat on the current collectors [4]. According to numerous related references, the causes of the electrochemical decline of SCs are addressed to the electrolyte decomposition and to the presence of contaminations in the carbon electrodes such as metals, water and oxygen. The surface functional groups formed on the carbon surface lead to the decrease of the capacitance and the increase in the leakage current [4, 9, 11]. At voltages above 2.5 V, the surface functional groups will react with water and generate gases that affect the SCs's performances. Degradation is influenced by temperature, high voltage, and number of cycles [4, 5]. Up to now, only limited investigations have been performed to understand the physical and chemical behaviors of the SCs during aging processes [4].

The objective of this work is to study the aging of commercial supercapacitor using Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and Surface area analyzer.

MATERIAL AND METHODS

Commercial SCs, model BCAP3000P MaxwellTM Technologies 3000 F | 2.7 VDC, were used for this study. The aging process of the SCs was conducted at 65 °C and constant voltage 2.7 V for 2000 h by Maxwell's Technologies, Inc. San Diego, CA. In table 1 are presented the parameters of the SCs given by Maxwell.

Aged and new SCs were opened in a glove box under N₂ environment. Then, the electrodes of the SCs were extracted and unrolled. Rectangular samples (2X5 cm) were cut from the edge and the central part of the anodes. To remove the quaternary tetraethyl ammonium tetrafluoroborate (TEATFB –used as the electrolyte in the SCs) the samples were washed using anhydrous acetonitrile (solvent in the SCs) for one week. To ensure complete removal of the TEATFB, FTIR was employed to analyze the anhydrous acetonitrile by comparing with the FTIR spectrum of fresh anhydrous acetonitrile. After that, the clean samples were dried in a Lindberg vacuum oven with a Veeco-Vs-9 mechanical pump at 100 °C for 24 h at a pressure of 10 mTorr. The samples were stored in an N₂ environment to protect and avoid possible hydration and oxidation according to reference [4]. Carbon samples have been scratched from the aluminum current collectors before proceeding with the measurements. The samples were analyzed using four different techniques: Raman spectroscopy, TGA, FTIR, and Surface analyzer.

The Raman spectra were used to study the crystallinity of the activated carbons. Spectra were acquired using a Renishaw inVia dispersive micro-Raman spectrometer (1 - μ m laser spot) with an excitation source at 514 nm, employing laser excitation with about 10mW power and Leica microscope equipped with 50x objectives.

The presence of the surface groups on the samples has been studied by thermogravimetric analysis. TGA was performed using a Perkin Elmer STA6000 at high resolution ramp of 10 °C/min and the accuracy of 1 °C. The measurements were performed in nitrogen environment (20 mL/min) for the temperature interval from 22 to 1000 °C.

The surface chemical groups formed on the activated carbons were characterized with FTIR spectroscopy, Thermo-Nicolet AVATAR 360 FTIR system. Sixteen interferograms in transmission mode with 4 cm⁻¹ resolution were collected. The samples were baseline corrected.

The available surface areas of the samples were measured by Micrometrics ASAP 2020 Surface Area and Porosity Analyzer using the nitrogen adsorption/desorption isotherms at 77 K. The samples were prepared by degassing under vacuum for seven hours.

Table 1. Supercapacitor parameters given by Maxwell.

	CAP (F)	ESR (mΩ)
New	3195	0.25
Aged	2625	0.48
% Change	17.8	47.9

RESULTS AND DISCUSSIONS

During the opening process of the aged SCs, it was noticed that the aged ones were at high pressure, confirming the gas generation as reported in reference [4].

Raman spectroscopy was used to study the crystallinity of the activated carbons taken from new and aged SCs. Two dominant Raman shifts at 1350 and 1590 cm^{-1} are observed and ascribed to the D- and G-bands, respectively [14]. In this research, the full width at half maximum (FWHM) of the D- and G-bands was analyzed to study the crystallinity of the samples. The Raman mapping of the electrodes are shown in figure 1. The red color indicates the broadening of the FWHM of the G-band. The brighter the color is, the more broadening the FWHM of the band is. As can be notice from figure 1 (b) and (d), the samples from the aged SCs have a broadening of the FWHM of the G-band, which indicates a decrease in crystallinity of activated carbon after the aging process.

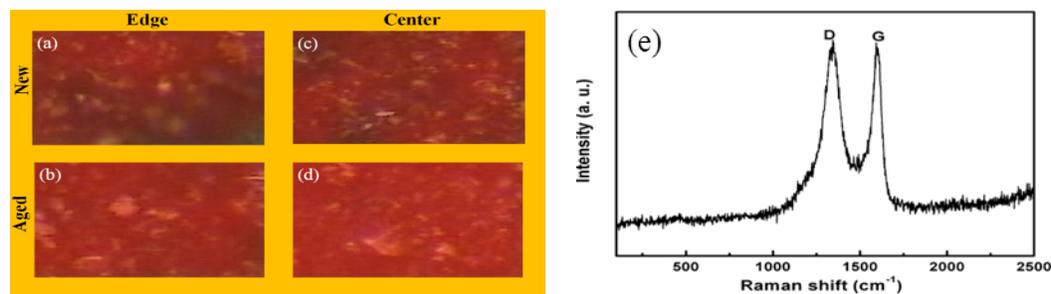


Figure 1. (a) to (d), Raman mapping of FWHM of G-bands. (e) Typical Raman spectrum of activated carbon taken from SCs.

Surface Analyzer was used to study the influence of the aging effects on the carbons electrodes. In table 2 are presented the results of the specific surface area for new and aged electrodes at the edge and center part.

Table 2. Specific surface area [m^2/g] of new and aged electrodes.

	New electrodes		Aged electrodes	
	Edge	Center	Edge	Center
Surface Area [m^2/g]	630	722	331	705

From the results for the specific surface area it can be concluded that the specific surface area of the samples obtained from the edge of the aged electrodes have a significant reduction compared to the samples of the edge of the new electrodes. This reduction is approximately 50 % while for the center samples there were not significant differences. This specific surface area reduction could be due to the decomposition of the electrolyte.

TGA results of the weight losses of the activated carbons in function of temperature are shown in figure 2. It can be noticed that weight loss of the activated carbon samples in the new electrodes started about $310\text{ }^\circ\text{C}$, while for the aged electrodes it started at about $250\text{ }^\circ\text{C}$. The total

weight lost for the new electrodes was approximately 2.8% and does not depend significantly on the picking place of the sample (edge or center). The total weight loss of the edge samples decrease by 7.5 % and for the center samples by 6.7 %. The higher mass decreases in the aged samples are attributed to gas emission, which is due to the decomposition of the surface functional groups on the activated carbons [4].

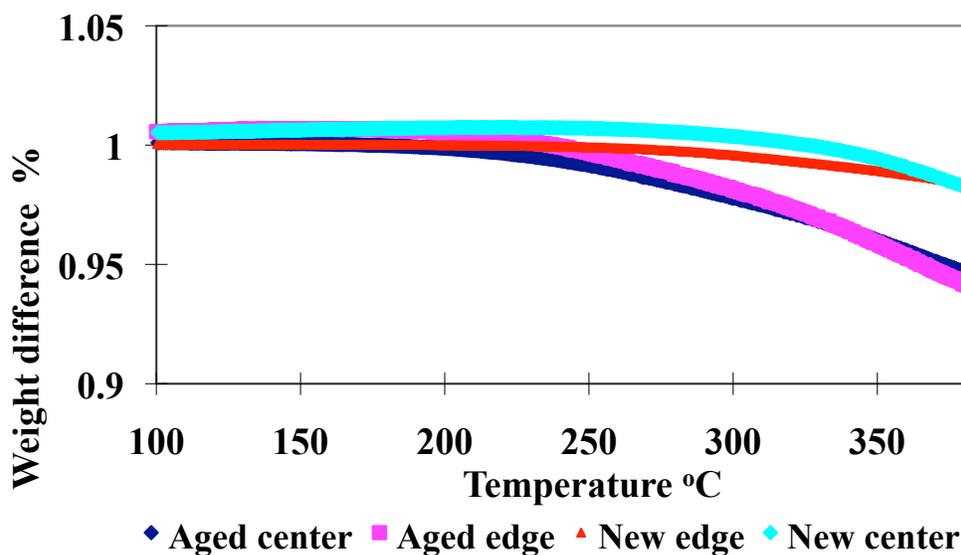


Figure 2. TGA of the samples.

FTIR was used to characterize the surface functional groups formed on the activated carbons. In figures 3 are presented the results of the FTIR spectra of the samples. The dominant peaks of the spectra are summarized in Table 3. As indicated by Table 3, the samples from the edge and center areas of aged SCs give nearly the same peaks as those taken from the new SCs. However, the samples of the aged ones have a peak at approximately at 2360 cm^{-1} , which does not appear in the spectra for those taken from the new SCs. This peak corresponds to -CN bond, which is attributed to the decomposition of electrolyte during the aging process.

The results of the FTIR of the samples taken from new SCs were blue shifted compare to those taken from aged SCs. This blue shift could be due to the chemical reaction happened in the aging process. This chemical reaction is still under investigation.

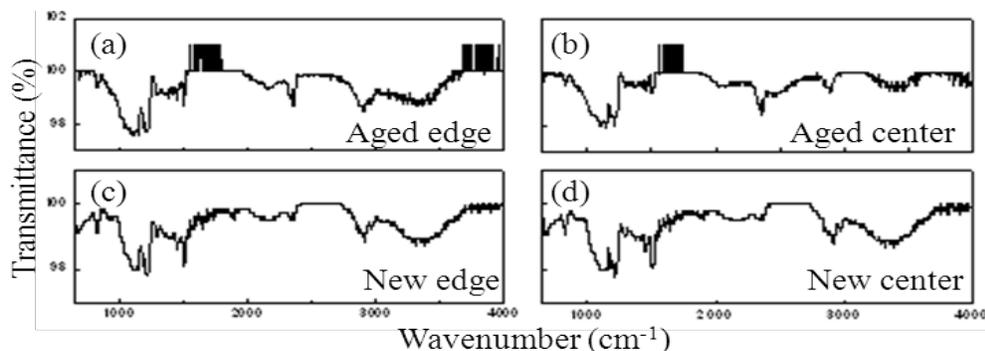


Figure 3. FTIR spectra of the samples.

Table 3. Surface functional groups formed on the activated carbon samples.

		New electrodes		Aged electrodes	
Wavenumber (cm ⁻¹)	Chemical groups	Edge	Center	Edge	Center
762	-CH ₂ -	✓	✓	✓	✓
892	 rings	✓	✓	✓	✓
1100	Ar-COOR	✓	✓	✓	✓
1250	-CONH-, Ar-COOR	✓	✓	✓	✓
1290	Ar-COOR	✓	✓	✓	✓
1380	 or multi-member rings	✓	✓	✓	✓
1460	 or multi-member rings	✓	✓	✓	✓
1510	-COO-,  -NH	✓	✓	✓	✓
1580	-COO-,  -NH	✓	✓	✓	✓
2360	-CN			✓	✓
2870-2970	-CH ₂ , -CH ₃ , -NH ₃ ⁺ , -NH ₂ ⁺ , C=C	✓	✓	✓	✓

CONCLUSIONS

By using the four techniques for characterization of the supercapacitor it can be concluded that there were significant differences in the results obtained for the new and aged electrodes. The edge and the center samples of the new electrodes did not present significant differences in the results obtained. Also there were significant differences in the results obtained from the edge and the center of the aged electrodes. During the aging process, the decomposition of the electrolyte causes the formation of chemical groups (-CN) on the surface of activated carbons, and the decreases in crystallinity and surface area of activated carbons. As a result, the capacitances of

the aged supercapacitors decrease and ESRs increase. TGA and Surface analyzer showed a marked aging effect at the edge area rather than central area.

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