CAUSES OF AGEING OF SUPERCAPACITORS BASED ON ACTIVATED CARBON ELECTRODES AND ORGANIC ELECTROLYTE. IMPROVEMENT OF THE ELECTROCHEMICAL CHARACTERISTICS BY POST-TREATMENTS OF ACTIVATED CARBON

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Introduction

Although the technology of supercapacitors is known since the early seventies[1,2,3], they have recently received a renewed interest[4]. High capacitance prototypes based on activated carbons and organic electrolytes have been developed by several industrial companies[5,6,7,8,9]. The low price and expected good stability of activated carbons are key parameters for their selection, especially for electric vehicles and power quality devices. Besides, organic electrolytes enable to work with a larger potential window than aqueous electrolytes (2.5V vs. 0.7V). This favours the use of this new generation of supercapacitors in systems that often require medium or high voltage. However, a better knowledge of the ageing mechanisms is required, since long life is mandatory in the envisioned applications. In all cases, the ageing process results in macroscopic and electrochemical phenomena, such as gas evolution, electrodes mass increase and damaging, resistance increase and capacitance decrease.

A preliminary study performed in SAFT Laboratories showed that there is not any direct relationship between ageing of supercapacitors and the specific surface area of activated carbon[10]. From a review of patents, several reasons are found to explain the fading of the electrochemical performance and the macroscopic effects: 1) the surface functionality of the activated carbon has a bad influence on the capacitance evolution[11,12], and the leakage current is linked to the presence of acidic surface groups on the activated carbon[13]; 2) few ppm of water in the organic medium reduce significantly the potential window of the electrolyte and could have an influence on the ageing of the capacitor[14]. The adsorbed water and the surface groups could also react when the voltage is higher than 2.5V, giving some gases and fading the electrochemical performance of the capacitor[15]. Another consequence of these gases emissions could be the pore blocking of the separator and activated carbon, explaining the resistance increase[16]; 3) another reason evocated to explain the resistance increase and the electrodes damage is the presence of oxygen[17] and impurities (such as metals[18]). The

binder itself used in the coating layer is also suspected to be a cause of capacitance decrease and resistance increase [19].

In this work, we show that the surface functionality of activated carbon is directly responsible of supercapacitors ageing in organic electrolyte and a specific treatment of activated carbon is proposed to noticeably improve the performance.

Experimental

The experiments have been performed on SAFT 3500F supercapacitor prototypes based on symmetric coated electrodes. A coating process on aluminium has been developed by SAFT enabling to reach very high volumetric capacitance (>40F/cm^3 of electrode) [20]. The electrolyte is a 1 mol.L^{-1} solution of Et_4N^+, BF_4^- in acetonitrile. The electrode components are the activated carbon, a binder (carboxymethylcellulose, CMC), a plastifier (styrene-butyrene rubber) and a percolating agent (carbon black).

Two industrial activated carbons with different physico-chemical properties, named Maxsorb and OPTI, have been selected for our investigations. OPTI is a typical synthetic activated carbon based on a phenolic resin precursor activated by water vapour. Maxsorb is a petroleum pitch activated at 850°C by KOH, as described in references[21,22,23]. These two carbons were characterised by nitrogen adsorption at 77K on an Autosorb 6 (Quantachrome) after degassing at 200°C for 15 hours. Nitrogen adsorption measurements at 77K were also performed on aged and fresh electrodes based on OPTI and Maxsorb, but outgassing only at 140°C in order to avoid the binder (CMC) decomposition.

The oxygen content in the activated carbons outgassed at 200°C has been measured by elemental analysis at the “Laboratoire Central d’Analyse du CNRS” (France). The oxygenated surface groups have been titrated by the Boëhm method[24]. Thermogravimetric analysis (TGA) has been performed on a Setaram 1600 analyser (SETARAM) in order to estimate the amount of water contained in OPTI and Maxsorb.

SAFT supercapacitors were prepared using aluminium current collectors coated with an aqueous solution containing the electrode components (activated carbon, binder, plastifier and percolating agent)[32]. The devices built with Maxsorb and OPTI were aged by the application of a 2.5V constant voltage for 4000 hours and 7000 hours, respectively. Every 250h, electrochemical impedance spectra are recorded with a Solartron SI 1260 analyser (Schlumberger) in the frequency range from 65kHz to 10mHz at open circuit voltage with 10mV amplitude. The capacitance values are estimated at 10mHz from the imaginary part z” of the impedance value ($C=2\pi/(0.01.z”)$). Self discharge tests have been performed with a potentiostat/galvanostat (VMP Biologic, France) every 250 hours of 2.5V constant voltage application.

After more than 4000 hours of application of a 2.5V permanent voltage, the aged electrodes were taken apart in a glove box, transferred in a Kumagawa extractor under argon in order to be washed with acetonitrile during one week for the elimination of the adsorbed species. Then, the electrodes are vacuum dried (139°C, one week) in order to eliminate the remaining acetonitrile and stored in a glove box. All the steps, including the transfer steps, have been performed in an oxygen-free atmosphere (vacuum or ultra pure argon).

X-ray photoelectron spectroscopy (XPS) analyses of each component of the electrodes (binder, plastifier, percolating agent and OPTI or Maxsorb), and of fresh and aged electrodes were performed using an ESCALAB 250 (VG Scientific) after a secondary vacuum outgassing at 200°C. Successive layers were removed under inert atmosphere from the surface of the active material using adhesive tape and analysed by XPS in order to investigate the variation of the electrode composition as a function of depth, from the interface to the aluminium foil.

We have proposed two types of treatments in order to modify the surface functionality of the pristine OPTI and Maxsorb carbons. The first treatment is a two hour oxidation by perchloric acid at 150°C, followed by activated carbon washing with water until neutral pH value, and finally carbon drying at 120°C during 24 hours. In the second kind of treatment, the active surface groups are reduced. After a temperature increase under nitrogen atmosphere, the carbon is treated at 700°C under nitrogen/hydrogen mixture during two hours. Nitrogen adsorption, TGA, XPS and elemental analysis have been performed on these treated carbons after exposure to air during almost two months in order to be compared with the original carbons. Supercapacitors based on these modified carbons have been also built in the same conditions as described before.

Results and Discussion

The amount of oxygen in OPTI and Maxsorb determined by elemental analysis is 1.7% and 6.2 %, respectively, and the pH in water 8.5 and 3.5 for OPTI and Maxsorb, respectively. Generally activated carbons contain oxygenated surface groups, which presence and nature are linked to the activation process[25]. The acid/base titration performed on the two carbons (table 1) shows that the quantity and the nature of each oxygenated surface groups is very different. These amounts are related to the amount of oxygen and macroscopic pH of the activated carbon.

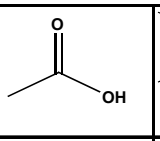
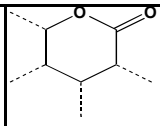
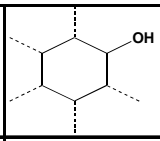
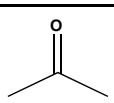
carbon					bases
OPTI	0.04	0	0.88	0.1	0.33
Maxsorb	0.60	0	2.17	0	0.12

Table 1. Surface groups concentration (meq/g) of OPTI and Maxsorb.

The TGA of the activated carbons shows that the amount of water trapped is higher in Maxsorb than in OPTI (fig. 1), confirming the more hydrophilic character of Maxsorb which results from a higher amount of acidic surface groups in Maxsorb. Besides, mass spectrometry on the evolved gases during the TGA experiment shows that the constant mass decrease above 300°C is due to CO_2 emission. Actually, CO_2 is related to the decomposition of the acidic surface groups of Maxsorb.

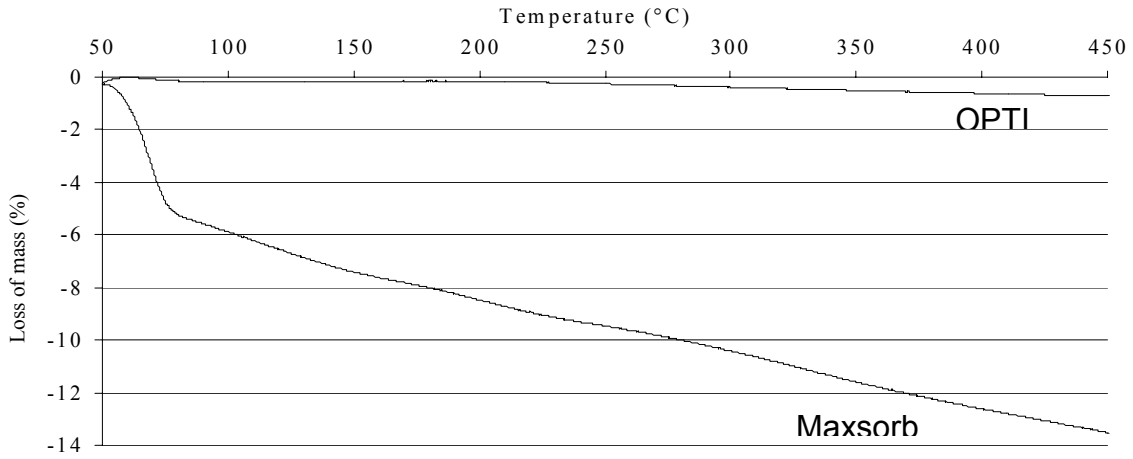


Figure 1. TGA of Maxsorb and OPTI.

The nitrogen adsorption isotherms are both of type I for Maxsorb and OPTI, indicating essentially microporous materials, however with a narrower pore size distribution for OPTI than for Maxsorb. The values of specific surface area are close to 1600m²/g and 2500m²/g, respectively for OPTI and Maxsorb.

This section deals with the ageing effects on the electrochemical performance. The values of initial gravimetric capacitance of OPTI and Maxsorb are 100F/g and 110F/g, respectively. As demonstrated by Endo et *al.*[26], these values are not directly related with the specific surface area. The initial selfdischarge after 70 hours in open circuit is lower for OPTI than for Maxsorb. Yoshida et *al.*[27] have demonstrated that the leakage current of an organic medium supercapacitor (i.e. the selfdischarge) is linked to the amount of carboxylic groups. Figure 2 shows that the capacitance loss with the floating time at 2.5V is higher for Maxsorb than for OPTI.

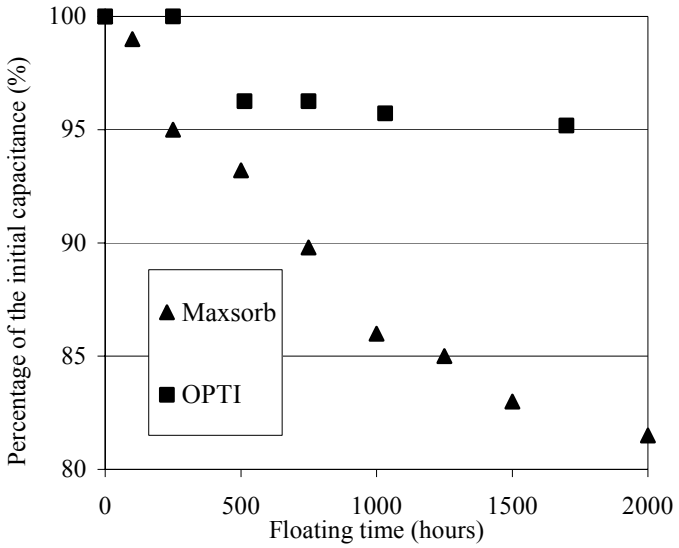


Figure 2. Effect of a 2.5V floating on the capacitance of Maxsorb and OPTI.

The XPS analyses of OPTI (table 2) and Maxsorb (table 3) show that the fresh electrodes contain sodium and a high oxygen content both due to the binder (cellulose). The positive and negative aged electrodes are qualitatively and quantitatively very different. The positive electrodes contain more nitrogen than the negative ones and no sodium. The negative electrodes contain more fluorine than the positive ones and the same quantity of sodium as the fresh electrode. One must note that, taking into account the migration of Et_4N^+ and BF_4^- ions, just the opposite trend should be observed for the amount of nitrogen and fluorine in the two electrodes. Moreover, only the aged negative electrodes contain a small amount of boron. This fact might suggest the decomposition of BF_4^-, as fluorine appears to be involved in different groups. A concentration gradient of all the detected elements (Na, N, F) was observed from the electrolyte/electrode interface toward the aluminium support, generally with a decrease in the depth. The lower oxygen amount at the surface could be attributed to a partial dissolution of the binder in the electrolyte. This means that the decomposition reactions of the electrolyte and the binder mainly take place on the electrode surface. Hence, capacitors from OPTI and Maxsorb seem to age by the same mechanism probably due to similar redox decomposition reactions of the electrolyte. Moreover, taking into account the difference floating time, we could not evidence any remarkable difference between the two carbons which could explain different ageing rates.

Element	raw powder	fresh electrode	negative aged electrode		positive aged electrode	
			surface	inside	surface	inside
B	0	0	0	0.3	0	0
Na	0	1.1	0.8	0.3	0	0
F	0	0	2.2	0.6	0.7	1
N	0	0	0.9	0	12.5	4
O	4	17.7	9.2	19.8	13.2	18.6

Table 2. Elements detected by XPS (atomic percent) analysis of Maxsorb powder, fresh electrodes and aged electrodes (floating time : 4000h).

Element	raw powder	fresh electrode	negative aged electrode		positive aged electrode	
			surface	inside	surface	inside
B	0	0	0.5	0.1	0	0.4
Na	0	1.6	1.7	0.4	0	0.3
F	0	0	5.6	0.6	0.8	0.9
N	0	0	1.5	1.1	16.6	1.5
O	5.4	22.0	19.3	21.3	13.8	23.6

Table 3. Elements detected by XPS (atomic percent) analysis of OPTI powder, fresh electrodes and aged electrodes (floating time : 7000h).

Fresh and aged electrodes were washed and dried using the previously described treatment, and analysed by nitrogen adsorption in order to determine the influence of ageing on the electrode porosity (Table 4). Because of the electrodes composition (binder/plastifier/percolant/activated carbon = 4/4/5/87), their BET specific surface area is lower than for the pristine powders (Table 4). Nevertheless, all isotherms are still of type I (exclusively microporous materials). After ageing, the specific surface area decreases for all the electrodes, indicating that the pores are blocked by the

decomposition products from the electrolyte. This fact can be easily correlated with the capacitance loss of the capacitors based on both activated carbons and it confirms that the electrolyte decomposition is more important in the case of Maxsorb, because of its high concentration of acidic surface groups. The decrease of specific surface area is more important for the positive electrode than the negative one (Table 4). This result fits well with previous observations that the decrease of the electrolyte potential window in presence of small amount of water is more important on the positive side than on the negative one[8]. This could be the reason for the higher decrease of porosity of the positive electrodes.

Materials	BET specific surface area (m^2/g) Maxsorb	BET specific surface area (m^2/g) OPTI
Powder	2500	1600
Fresh electrode	2350	1400
Negative	1650	1130
Positive	1280	980

Table 4. Specific surface area of OPTI and Maxsorb fresh and aged electrodes (7000h for OPTI and 4000h for Maxsorb).

In order to confirm that the surface functionality has an important impact on the ageing of supercapacitors, the OPTI and Maxsorb activated carbons have been heat treated under hydrogen at 700°C in order to reduce the active surface groups without noticeably modifying the porosity. After this treatment, the pH of both carbons is neutral, and the amount of oxygen in treated OPTI and Maxsorb is 0.4% and 0.5%, respectively. The absence of an important weight loss on the TGA curves at 100°C confirms that the two treated carbons are quite hydrophobic. On the contrary, when OPTI is treated by perchloric acid, the oxygen ratio increases to 10.8% whereas it was 1.7% in pristine OPTI. XPS and elemental analyses demonstrate the grafting of perchlorate groups on the carbon surface.

Figure 3 shows that the capacitance of a supercapacitor based on Maxsorb thermally treated under hydrogen does not vary noticeably with floating. On the contrary, when OPTI is oxidized by perchloric acid, the ESR increases (Figure 4), whereas the capacitance drastically decreases with floating (Figure 5). These results confirm unambiguously that the oxygenated surface functionality of activated carbons is strongly involved in the ageing mechanisms of supercapacitors in organic medium.

Conclusion

We have demonstrated that the ageing of supercapacitors is tightly related with the electrolyte decomposition on the active surface of the activated carbon. Since the phenomena are different for both electrodes, and since they were not observed when electrodes are dipped in the electrolytic solution without the application of a polarization, this suggests that redox processes are responsible for the electrolyte decomposition, and consequently for the ageing of supercapacitors. Precluding surface functional groups on carbon and moisture seem to be important requirements for a good cycle life of supercapacitors. The pore blocking by the decomposition products has a noticeable influence on the resistance increase and capacitance decrease. An easy way for

improving the supercapacitor performance is to treat the activated carbons under reducing atmosphere (i.e. hydrogen) at 700°C. This treatment enables to keep the porosity and to eliminate drastically the surface functionality of the activated carbons.

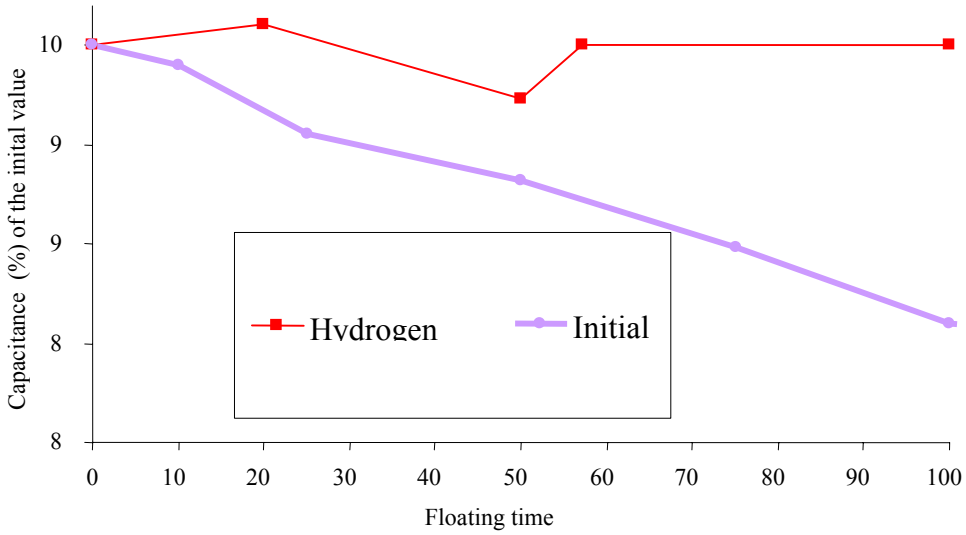


Figure 3. Dependence of capacitance with the floating time for supercapacitors based on as-received Maxsorb and Maxsorb treated at 700°C under hydrogen flow

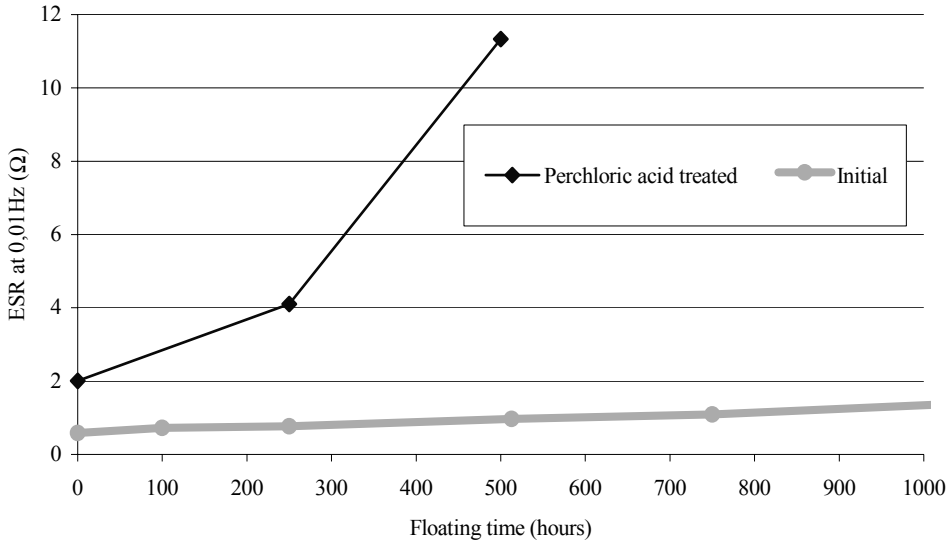


Figure 4. Evolution of the ESR for supercapacitors based on as-received OPTI and OPTI treated by perchloric acid.

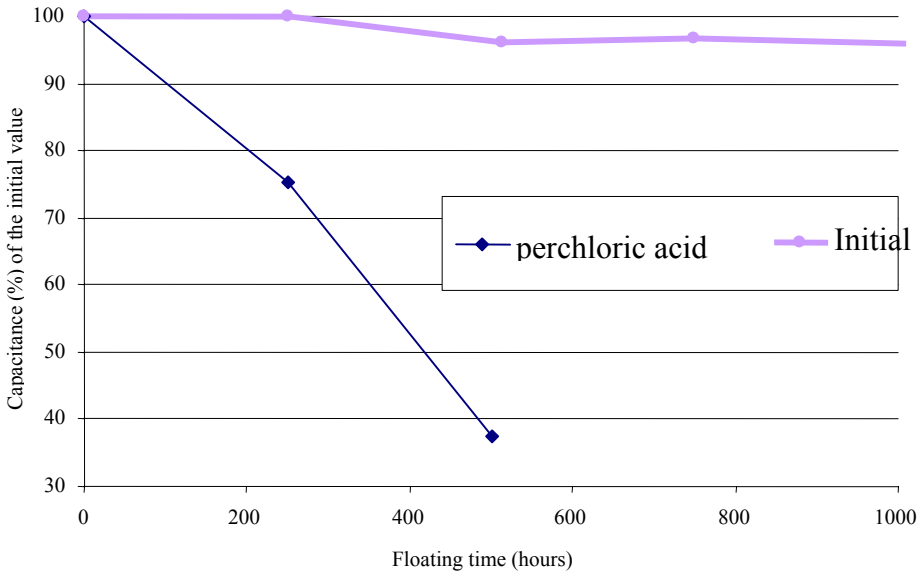


Figure 5. Evolution of the capacitance for supercapacitors based on as-received OPTI and OPTI treated by perchloric acid.

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