Supercapacitor calendar ageing and post mortem analysis

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The physical origin of the activated carbon supercapacitor ageing is attributed to different phenomena as the oxidation of the carbon surface, the closing of the pores access, or/and to the ionic depletion in the electrode due to electrolyte starving [1]. When a double-layer capacitor is opened, after an ageing period under large stress, the oxidation of the separator may be observed. A brown coloration appears on the surface, especially on the side exposed to the positive electrode [2].

The electrolyte undergoes irreversible transformations, which are accentuated by voltage and temperature. The electrochemical decomposition of the electrolyte generates a gas overpressure in the double-layer capacitor package (for example generation of H2 in the case of acetonitrile, CO2 in the case of polypropylene carbonate).

Azaïs et al [3] have studied the causes of supercapacitors ageing in an organic electrolyte. The activated carbon electrodes have been characterized before and after prolonged floating (4,000–7,000 h) at an imposed voltage of 2.5V. After ageing, the positive and negative electrodes have been studied by XPS and NMR on the nuclear spin of 19F, 11B and 23Na. Decomposition products have been found in the electrodes after ageing.

This paper investigates supercapacitor post mortem analysis after calendar ageing. The studied supercapacitors are based on activated carbon and organic electrolyte. Industrial supercapacitors are tested and opened in the aim to analysis the causes of their ageing. The supercapacitors are aged under constant voltage and constant temperature. The protocol of calendar ageing consists to put supercapacitors inside a climatic chamber. The temperature is regulated and fixed at constant value. Supercapacitors are polarized at constant DC voltage.

Experimental results have shown that the energetic performances of supercapacitors decrease according to the ageing time. The capacitance and consequently the energy stored decrease when the series resistance increases. To elucidate ageing processes in the electrodes, the supercapacitors ageing are analyzed. The experimental methods were SEM and nitrogen porosimetry (BET). Experimental results show that the specific activated carbon surface decreases according to the ageing. The electrodes are not completely inert, and their ageing is due to chemical and electrochemical reactions at the carbon. Moreover, the ageing procedures are much stronger at the positive pole.

To quantify the supercapacitor ageing, the equivalent series resistance (ESR) and the equivalent capacitance (C) are measured using the DC characterization. In order to study the impact of the ageing process on supercapacitors, an aged and a new supercapacitor were opened and analyzed. The specific surface area of the activated carbon and pore size distribution were measured. The activated carbon surface was analyzed using SEM.

The studied supercapacitor is aged at 2.9V, the temperature is fixed at 65°C. The first results show that after 1200 hours, the activated carbon specific area of the aged supercapacitor is in order of 460 m^2/g, for the new supercapacitor the specific area is in order of $858 m^2/g$. The physical origin of the ageing is attributed to different phenomena as the oxidation of the carbon surface, the closing of the pores access. When the supercapacitor is opened, after the ageing period under large stress, the oxidation of the separator was observed. A brown coloration appears on the surface, especially on the side exposed to the positive electrode. Figure 1 represents the pore size distribution for activated carbon. The curve in red represents the pore size distribution for the new supercapacitor and in green for the aged one.

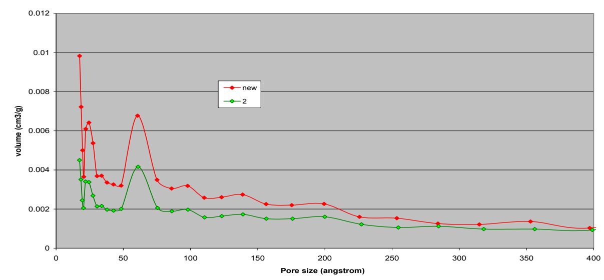

Figure 1: Pore size distribution for activated carbon aged in red, new in green

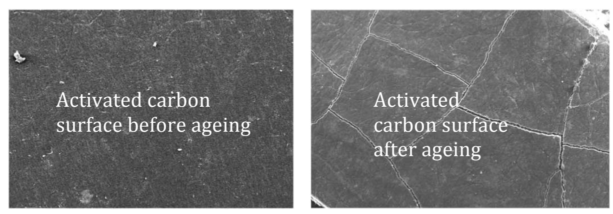

Figure 2: Activated carbon surface before and after calendar ageing

The calendar ageing of supercapacitor causes the degradation of the activated carbon surface as shown in figure 2.

The calendar ageing can also causes a modification of the electrode/electrolyte interface. The deposition of solid electrolyte degradation products within the porosity of activated carbon electrodes must be viewed as a critical parameter, which strongly deteriorates the performance of the supercapacitor.

More results and analysis will be given in the final paper.

1 Kurzweil P. and M. Chwistek M., Electrochemical stability of organic electrolyte in supercapacitors: Spectroscopy and gas analysis of decomposition products. Journal of Power Sources 2008; 176: 555-567

2 Kurzweil P., Frenzel B., Gallay R., Capacitance Characterization Methods and Ageing Behavior of Supercapacitors. Proc. 15th International Seminar On Double Layer Capacitors, Deerfield Beach, USA 2005, 14.

3 Azaïs Philippe, Duclaux L., Florian P., Massiot D., Lillo-Rodenas M.A., Linares-Solano A., Peres J.P., Jehoulet C., Béguin F., Causes of supercapacitors ageing in organic electrolyte. J. of Power Sources 2007; 171: 1046-1053