



# Effect of accelerated ageing on the performance of high voltage carbon/carbon electrochemical capacitors in salt aqueous electrolyte



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## ABSTRACT

An accelerated ageing protocol has been developed and validated to determine the factors influencing the life-time of high voltage carbon/carbon electrochemical capacitors (ECs) in aqueous lithium sulfate electrolyte, and to offer solutions reducing ageing of the cells. The study allowed the internal overpressure, increase of equivalent series resistance and corrosion of the positive current collector to be distinguished as the main failures which can appear during operation of these ECs at high voltage. To assure stability during cycling, the capacitor should not operate above 1.5 V at room temperature. Adding sodium molybdate ( $\text{Na}_2\text{MoO}_4$ ) to the electrolyte reduces the corrosion of the positive collector and lowers the equivalent series resistance which remains constant during floating at 1.5 V; additionally, the initial capacitance is enhanced due to a pseudo-faradaic contribution of the molybdate additive. The internal resistance is further lowered when the pellet electrodes are glued to the current collectors with a carbon conductive adhesive.

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## 1. Introduction

Due to the depletion of fossil fuels and increasing  $\text{CO}_2$  emissions, researches have been recently concentrated on the improvement of energy management by developing high performance storage devices. Among various energy storage elements and power deliverers, electrochemical capacitors (ECs) attract a lot of attention [1,2]. Although high power and long cycle life [1,3] are dominant advantages of ECs over accumulators and fuel cells, it is still very important to enhance their energy density and reduce their cost in order to broaden the possibilities of applications.

The maximum energy,  $E$  (J), of ECs is directly proportional to the capacitance,  $C$  (F), and the square of voltage,  $U$  (V), according to formula (1):

$$E = \frac{1}{2}CU^2 \quad (1)$$

The operating voltage is essentially limited by the stability of the combined electrode and electrolyte system, and it can reach 3 V with organic electrolytes [4] and usually less than 1.0 V with  $\text{H}_2\text{SO}_4$  and  $\text{KOH}$  aqueous electrolytes [5,6]. Therefore, organic solutions are preferred for commercial systems, although the aqueous ones demonstrate a better conductivity. However, when using

aqueous electrolytes, the production costs are dramatically reduced, because it is not necessary to eliminate moisture from the various components before closing the capacitors. Consequently, it is interesting to search for better technical solutions which would allow the operating voltage of ECs to be increased while using aqueous electrolytes.

Lately, it has been demonstrated that carbon/carbon electrochemical capacitors can operate efficiently up to 1.6 V in  $0.5 \text{ mol}\cdot\text{L}^{-1}$   $\text{Na}_2\text{SO}_4$  [6,7] and even achieve around 2 V when using  $1 \text{ mol}\cdot\text{L}^{-1}$   $\text{Li}_2\text{SO}_4$  [8,9]. However, the test conditions used in the publications were based on galvanostatic charge/discharge during around 10,000 cycles, and are far below the expected cycle life of these systems, which should be one or two orders of magnitude higher. Since such tests would obviously require extremely long periods of time, it is necessary to develop an alternative methodology which would be sufficient to prove the lifetime stability of the device. Considering some of the envisioned applications of ECs [10,11], floating at an imposed high voltage is usually applied to accelerate the ageing. Such floating tests are currently applied on activated carbon based ECs in organic electrolytes on commercial capacitors [12–14], but they have not been yet performed in presence of salt aqueous electrolytes.

The main failures which can appear during the operation of an EC under critical conditions, such as high temperature and/or high voltage, may be a decrease of capacitance, an increase of equivalent series resistance (ESR) [15] and unsealing of the system due to internal overpressure provoked by electrolyte decomposition and

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subsequent gas evolution. The decline of capacitance appears to be essentially related to a reduction of electrodes accessible surface area for ions, due to a blockage of pores by decomposition products from the electrolyte and/or formation of surface functional groups [15,16]. The ESR increase is generally due to the deposition of electrolyte decomposition products in the separator and on the electrodes surface (ionic contribution) and may be also caused by increased contact resistance between the electrodes and current collectors (electronic contribution) [14,16]. Apart from the effects of ageing, the decrease of capacitance and increase of resistance can be also related to a reduced availability of ions called 'electrolyte starvation'. This occurs if the electrolyte reservoir, e.g., the amount of electrolyte and its concentration, is too small compared to the pore volume of electrodes which can be potentially filled with ions during charging of the capacitor; as a consequence, the performance of the EC decays as a function of state-of-charge [17]. To avoid such situation, the construction of the system must ensure sufficient feeding of electrolyte.

In summary, to know perfectly the state of health (SOH) of an EC, it is necessary to monitor simultaneously the pressure inside the cell, capacitance and ESR at various life times of the system. An EC is usually considered by manufacturers as out of service when the ESR is increased by 100% or the initial capacitance reduced by 20%. It is typical that the ESR reaches the end-of-life limit earlier than capacitance [18].

In the present work, a protocol of accelerated ageing by floating has been developed and validated for carbon/carbon ECs operating in  $\text{Li}_2\text{SO}_4$  electrolyte with stainless steel collectors. The objective is to determine the factors at the origin of the performance decay and to offer improvements for preventing the lifetime reduction. During ageing, the capacitance and resistance have been measured and the internal overpressure has been estimated with help of a sensitive pressure sensor connected to the EC cell.

## 2. Experimental

All electrochemical investigations were realized with two- and three-electrode cells assembled in a Teflon vessel with stainless steel (316L grade) current collectors. The electrodes were composed of 85 wt.% active material (activated carbon DLC SUPER 30, NORIT®) further named AC, 10 wt.% polyvinylidene fluoride as binder (PVdF, Kynar HSV900) and 5 wt.% carbon black (C65, Timcal). The electrodes were prepared in the form of pellets (1 cm diameter, thickness ca. 0.3 mm and mass 8–10 mg), pressed under  $4.87 \text{ kg cm}^{-2}$ . Glass microfiber paper (GF/A, Whatman™) of thickness 260  $\mu\text{m}$  was used as separator. The electrolyte was  $1 \text{ mol L}^{-1}$  lithium sulfate (Sigma Aldrich,  $\geq 99\%$ ). In some experiments,  $0.1 \text{ mol L}^{-1}$  sodium molybdate (Sigma Aldrich,  $>99.5\%$ ) has been added to the  $\text{Li}_2\text{SO}_4$  solution, in order to reduce the corrosion of current collectors. The gas evolution was measured with a digital pressure sensor KELLER 35X Ei (pressure range 0–3 bars; total error band of 0.05%) connected to the Teflon cell. The pressure values were recorded using the READ30 software.

A multichannel VMP3 potentiostat/galvanostat (Biologic Instrument, France) was used to carry out the accelerated ageing, consisting of repeated two-hour potentiostatic periods (called 'floating') at maximum voltages of 1.5 V, 1.6 V, 1.7 V and 1.8 V and at temperatures of 24 °C (RT), 35 °C and 40 °C. Each two-hour period was preceded with five galvanostatic ( $1 \text{ A g}^{-1}$  referred to the average active mass of both electrodes) charge/discharge cycles. The capacitance and ESR were estimated from the 5<sup>th</sup> discharge. The ESR was determined as the voltage difference measured with and without current (so-called Ohmic drop) divided by the applied current. Each series consisting of galvanostatic cycling and floating period presented in Fig. 1 was repeated 60 times, i.e. for a total floating

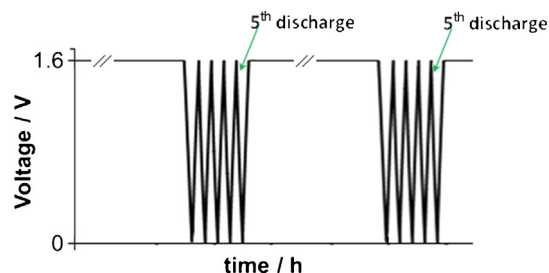


Fig. 1. Scheme of the accelerated ageing protocol. The fifth discharge cycle of each series was considered to estimate the capacitance and ESR values.

time of 120 hours. To stabilize the wetting of fresh electrodes, cyclic voltammetry (10 cycles) at a scan rate of  $10 \text{ mV s}^{-1}$  was applied to all systems before starting floating. The relative capacitance  $C/C_0$  and resistance  $R/R_0$  ( $C_0$  and  $R_0$  are the initial values of capacitance and resistance, respectively) were plotted in order to determine the end-of-life of the capacitors.

The electrochemical impedance spectra (EIS) were recorded in the frequency range 1 mHz to 100 kHz, before ageing and after 60 series of accelerated ageing, using an AUTOLAB 4.9/FRA potentiostat.

Nitrogen adsorption isotherms were recorded at 77 K on the pristine powder and on the powder of fresh and aged electrodes using Micromeritics' ASAP 2020 Accelerated Surface Area and Porosimetry analyzer; the samples were degassed at 100 °C for 36 hours. The specific surface area was determined by application of the BET equation. The Quenched Solid Density Functional Theory (QSDFT) [19] was used to calculate the pore size distribution, the total, micro- and mesopores volume. All porous texture data were referred to the mass of active material.

## 3. Results and discussion

### 3.1. Effect of ageing conditions

Fig. 2 shows the plots of cell voltage and internal overpressure values versus time for an AC/AC electrochemical capacitor in  $1 \text{ mol L}^{-1}$   $\text{Li}_2\text{SO}_4$  aged under the conditions defined in the experimental part. The pressure increases with time to attain approximately 95 mbar after 1 hour of floating at 1.8 V. The magnification presented in Fig. 2 (b) shows that the pressure already increases during the initial galvanostatic charge/discharge cycles. During the galvanostatic charge, the pressure is first stable at low voltage and it increases when the voltage exceeds 1.4 V, then it slightly declines during the galvanostatic discharge when the voltage is lower than this value. With the assumption that the system really ages when gas is generated, it can be seen that even galvanostatic cycling above a given voltage can reduce the life-time of the EC by loss of electrolyte and/or electrode cohesion. Furthermore, the pressure does not return back to its initial values during discharge, which suggests that during long time galvanostatic cycling it would be necessary to remove gases or to favor their recombination into water, using for example an absorptive glass mat separator (AGM) as applied in valve-regulated lead-acid (VRLA) batteries [20].

Due to the relatively important pressure increase demonstrated at 1.8 V with lithium sulfate electrolyte, we decided to carry out the investigations at a lower voltage value of 1.6 V, and to estimate the capacitance from the 1<sup>st</sup> galvanostatic discharge just after each floating period and from the 5<sup>th</sup> one before the next floating period (Fig. 3). Whatever the floating time, the capacitance measured from the 1<sup>st</sup> discharge just after floating is always higher than when estimated from the 5<sup>th</sup> discharge. It seems that a prolonged period at high voltage promotes better packing of ions, especially in the

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