



# Aging of electrochemical double layer capacitors with acetonitrile-based electrolyte at elevated voltages

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## ABSTRACT

Laboratory-scale electrochemical capacitor cells with bound activated carbon electrodes and acetonitrile-based electrolyte were aged at various elevated constant cell voltages between 2.75 V and 4.0 V. During the constant voltage tests, the cell capacitance as well as the capacitance and resistance of each electrode was determined. Following each aging experiment, the cells were analyzed by means of electrochemical impedance spectroscopy, and the individual electrodes were characterized by gas adsorption and X-ray photoelectron spectroscopy. At cell voltages above 3.0 V, the positive electrode ages much faster than the negative. Both the capacitance loss and resistance increase of the cell could be totally attributed to the positive electrode. At cell voltages above 3.5 V also the negative electrode aged significantly. X-ray photoelectron spectroscopy indicated the presence of degradation products on the electrode surface with a much thicker layer on the positive electrode. Simultaneously, a significant decrease in electrode porosity could be detected by gas adsorption.

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## 1. Introduction

Electrochemical double layer capacitors (EDLCs) are a particular class of electrochemical capacitors in which the charge storage ideally occurs entirely via electrostatic forces at the electrode/electrolyte interface [1,2]. Compared to redox processes commonly encountered in the bulk of battery electrodes, the electrochemical double layer can be both charged and discharged efficiently at high rates and with high reversibility. EDLCs are therefore characterized by higher specific power than galvanic systems due to the restriction of charge storage to the electrode surface. However, the specific energy of EDLCs tends to be lower than that of batteries by roughly one order of magnitude [3,4]. An increase in the specific energy of EDLCs would represent a major development in performance improvement and in widening the application field of these devices.

A possible strategy to improve both the energy and power density of EDLCs is to increase their operating voltage due to the scaling of these properties with the square of the cell voltage [2,5]. However, a pronounced increase in the aging rate has been found for EDLCs above their nominal voltage of typically 2.5–2.7 V [6–9].

There have been a number of studies concerned with the reasons behind the aging of EDLCs. These investigations have dealt with the most commonly employed EDLC systems consisting of activated carbon electrodes in electrolyte solutions of quaternary ammonium salts in acetonitrile (AN) or in propylene carbonate (PC).

In order to account for aging phenomena at elevated voltages, deviations from the idealized capacitive double layer charging mechanism, where the rigid double layer (Helmholtz layer) is represented by a parallel plate capacitor, must be considered. Although ionic charge transfer in the form of ion insertion into the electrode bulk has been proposed as a possible aging mechanism [10,11], it appears as though this effect is minor for microporous electrodes compared to the effects of electronic charge transfer on aging [12,13]. The electrolyte decomposition associated with electron transfer may result in gaseous, solid or soluble degradation products. It has been suggested that the rate of degradation is enhanced by an increase in the number of oxygen-containing functional groups of the activated carbon in both PC-based [14] and AN-based [15,16] electrolytes.

In Et<sub>4</sub>NBF<sub>4</sub>/PC, the main gaseous degradation products at elevated cell voltages from 2.6 V up to 4 V have been identified as propene, CO<sub>2</sub>, ethene, CO and H<sub>2</sub> at the negative electrode as well as CO<sub>2</sub> and CO at the positive electrode [17,18]. Gas evolution has been shown to result in a significant pressure increase [19] and may lead to a loss of electrode cohesion [18] and a loss of ions from the electrolyte [6]. On the other hand, it has also been demonstrated that solid electrolyte degradation products in Et<sub>4</sub>NBF<sub>4</sub>/PC are already formed at 2.3 V (60 °C) and may adhere to the electrode

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surface in the form of solid deposits [6,18,20], which could result in an electronic insulation of the electrode and a loss of porosity. In fact, through in situ monitoring of the pressure evolution in EDLCs, Hahn et al. [19] found that most irreversible charge loss must be associated with degradation processes other than gas evolution.

In  $\text{Et}_4\text{NBF}_4/\text{AN}$ , the main gaseous decomposition product at 2.5 V and 70 °C has been found to be  $\text{CO}_2$  [21], presumably from the reaction of acetonitrile with trace water [22], and ethene due to primarily thermal degradation of the cation  $\text{Et}_4\text{N}^+$  [21]. Kötzt et al. [23] found that the amount of irreversible charge contribution to degradation processes other than gas evolution was even higher in the AN-based electrolyte compared to the PC-based electrolyte. Indeed, both Azaïs et al. [15,16] and Zhu et al. [24,25] measured a marked decrease of the electrode specific surface areas due to aging at voltages between 2.3 V and 2.8 V, in particular for the positive electrode, and attributed this to the blockage of pores by solid electrolyte degradation products generated from the AN-based electrolyte. In addition, changes in the chemical composition of the electrodes were found via X-ray photoelectron spectroscopy (XPS) [16,25] and nuclear magnetic resonance (NMR) [16], and attributed to either the solid degradation products or the functionalization of the electrode surface. Recently, Ruch et al. [26] compared the aging of activated carbon electrodes in acetonitrile as well as in propylene carbonate based electrolytes at 3.5 V and found the aging rate for the single electrodes to depend critically on the solvent, although degradation products could be identified on the electrodes in either electrolyte.

In summary, it appears as though the electrochemical modification of activated carbon electrodes either through the deposition of solid electrolyte degradation products or surface functionalization represents the most important aging pathway for EDLCs at elevated voltages in both PC-based [18] and AN-based [15,16,24,25] electrolytes. While the above findings provide important insights into the various electrochemical processes which occur during aging of EDLCs, a direct correlation of the physicochemical changes undergone by the single electrodes with their actual electrochemical performances in these electrolytes as a function of increased cell voltage has not yet been given.

In the present work, the aging behavior of activated carbon electrodes in 1 M solutions of  $\text{Et}_4\text{NBF}_4$  in acetonitrile was investigated systematically as a function of the cell voltage. The loss of electrochemical performance was quantified on an individual electrode basis and correlated with structural and chemical changes of the aged single electrodes using cyclic voltammetry, nitrogen adsorption and XPS. The results highlight the limitations of current EDLC systems based on acetonitrile with respect to cell voltage and the polarity of the single electrodes.

## 2. Experimental

### 2.1. Materials and electrochemical cell assembly

The activated carbon investigated in the present work was YP17 (Kuraray Chemical, Japan). Free-standing carbon sheets were produced from a slurry consisting of 25 wt% YP17 in a 1:1 mixture by mass of isopropanol and distilled water. Under constant stirring, a suspension of 35.5 wt% poly(tetrafluoroethylene) (PTFE) in water (TE 3554-N, DuPont) was added until an equivalent of 10 wt% PTFE was obtained with respect to YP17. In order to achieve precipitation of PTFE, acetone was added to the suspension in a 2:1 mass ratio with respect to YP17. After 15 min of vigorous stirring, the suspension was heated at 150 °C until a dough-like mass was obtained. The moist dough was kneaded repeatedly and rolled into flat sheets of ca. 500  $\mu\text{m}$  thickness. Finally, the self-supporting sheets were left to dry under ambient conditions overnight before being dried at 120 °C under a vacuum of  $10^3$  Pa for at least one week. The elec-

trode thickness of 500  $\mu\text{m}$  is rather large compared to electrodes in commercial devices, but was chosen in order to alleviate the post-mortem analysis.

From the YP17/PTFE sheets,  $\varnothing 12$  mm electrodes were punched out and incorporated into three-electrode cells using a cellulose-based paper separator (Maxwell Technologies, Switzerland) of 30  $\mu\text{m}$  thickness. Carbon-coated aluminum foils (Gaia Akkumulatorenwerke, Germany) served as current collectors between the YP17/PTFE electrodes and the spring-loaded titanium pistons which were used to compress the electrode/separator stack. The total electrode mass varied between 40 and 60 mg, and the positive to negative electrode mass ratio varied between 0.96 and 1.07. A third electrode consisting of YP17/PTFE was used as a quasi-reference electrode against which all potentials are quoted [27]. The fully assembled cells were dried at 120 °C at  $10^3$  Pa for at least 24 h prior to the aging experiments.

After drying, the cells were vented with argon, hermetically sealed and transferred to an argon-filled glovebox with less than 1 ppm of  $\text{H}_2\text{O}$  and  $\text{O}_2$ , respectively. Inside the glovebox, the cell volume was filled with the electrolyte solution, 1 M  $\text{Et}_4\text{NBF}_4$  in AN (Honeywell Specialty Chemical Seelze, Germany). The solution was found to contain less than 30 ppm water using Karl-Fischer titration (684 KF Coulometer from Metrohm, Switzerland, with Hydranal® from Sigma-Aldrich as anolyte and catholyte). After filling, the cells were again hermetically sealed and transferred outside of the glovebox for the aging experiments.

### 2.2. Characterization via cyclic voltammetry

Cyclic voltammetry was used to characterize YP17/PTFE in the AN-based electrolyte using an electrochemical workstation (IM6e from Zahner-Elektrik, Germany). Three-electrode measurements were performed at a potential sweep rate of 1 mV/s in successively larger potential windows, whereby excursions to negative and positive potentials were done in separate electrochemical cells to avoid a change of electrode polarity during cycling.

### 2.3. Aging procedure

A battery cycler (CCCC from Astrol Electronics, Switzerland) was used to apply a constant cell voltage ( $U_{\text{aging}}$ ) during aging for up to 500 h. Every 10 h, three galvanostatic charge/discharge cycles were performed between cell voltages of 0 V and 2.5 V (see Fig. 1) using a current of  $I/m = 0.28$  A/g (referred to the total active electrode mass  $m$ ). From the measured cell voltage  $U_{\text{cell}}$  during these cycles, the full cell capacitance was estimated by  $C_{\text{cell}} = It_{\text{d}}/(m(\Delta U_{\text{cell}} - 2IR_{\text{cell}}))$ , where  $It_{\text{d}}$  is the amount of charge retrieved during the discharge step of duration  $t_{\text{d}}$ ,  $\Delta U_{\text{cell}}$  is the total voltage swing of the cell and  $R_{\text{cell}}$  is the resistance of the cell evaluated from the voltage drop during reversal of the current polarity at  $U_{\text{cell}} = 2.5$  V. Similarly, the capacitances of the positive and negative electrode were estimated as  $C_{\text{pos}} = It_{\text{d}}/(m_{\text{pos}}(\Delta E_{\text{pos}} - 2IR_{\text{pos}}))$  and  $C_{\text{neg}} = It_{\text{d}}/(m_{\text{neg}}(\Delta E_{\text{neg}} - 2IR_{\text{neg}}))$ , where  $\Delta E_{\text{pos}}$  and  $\Delta E_{\text{neg}}$  are the respective potential excursions and  $R_{\text{pos}}$  and  $R_{\text{neg}}$  are the resistances at the respective electrode.

Before and after each aging experiment electrochemical impedance spectra were recorded using an electrochemical workstation (IM6e from Zahner-Elektrik, Germany). The spectra were recorded at the cell voltage of 0 V, between 100 kHz and 10 mHz with a perturbation of 5 mV.

### 2.4. Post-mortem analysis of aged electrodes

After the aging experiments, the cells were disassembled in air and the electrodes washed in a Soxhlet reactor for at least 6 h using acetonitrile as the extraction solvent in order to remove residual

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