A comparison of the aging of electrochemical double layer capacitors with acetonitrile and propylene carbonate-based electrolytes at elevated voltages

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ABSTRACT

The aging behavior of electrochemical double layer capacitors (EDLCs) based on activated carbon electrodes bound with poly(tetrafluoroethylene) (PTFE) was tested in electrolyte solutions based on acetonitrile (AN) and propylene carbonate (PC) at a constant elevated cell voltage of 3.5 V. The aging was quantified in terms of capacitance loss and resistance increase for the full cell and the individual electrodes. It is shown that the enhanced aging rate of symmetric EDLCs in either solvent at elevated voltages is dominated by the aging of a single electrode, and that the polarity of this limiting electrode depends directly on the solvent. In AN, the positive electrode ages much more rapidly than the negative, while in PC the negative electrode exhibits faster aging than the positive. After aging, the electrodes were investigated by nitrogen adsorption and X-ray photoelectron spectroscopy, revealing significant modifications of the electrode surface and providing clear evidence for the deposition of electrolyte degradation products on the electrodes.

1. Introduction

Electrochemical double layer capacitors (EDLCs) are electrochemical devices in which the charge storage is primarily electrostatic and occurs within the electrochemical double layer [1,2]. In order to maximize the specific interfacial area between the electrode and the electrolyte solution, activated carbon is the current electrode material of choice for these systems [3]. EDLCs feature higher specific power upon both charge and discharge but also intrinsically lower specific energy than galvanic cells due to the lack of a bulk contribution to charge storage [4,5].

As both the specific energy and power of EDLCs are directly proportional to the square of the cell voltage [1,2], a promising approach towards the improvement of these two key properties is to increase the operating voltage. For instance, a cell voltage increase to 3.5 V roughly corresponds to a doubling of the specific energy of current EDLC technology based on a nominal voltage of 2.5 V. However, the device lifetime has been shown to decrease drastically with increasing voltage via a power law [6–9].

Currently, the most commonly employed electrolyte solutions for EDLCs consist of quaternary ammonium salts in either acetonitrile (AN) or propylene carbonate (PC) as solvent [4]. The characterization of aged electrodes and gas evolution in these systems has been reported previously for both AN-based [10–15] and PC-based [6,16–20] electrolytes. Modifications of the electrode porosity and surface chemistry due to aging have been identified in either solvent and attributed to the degradation of the respective electrolyte solution [6,10–12,15,20]. However, a clear correlation between the observed phenomena and the loss of electrochemical performance has yet to be established.

In the present work, the aging of EDLC systems based on AN and PC was directly compared by resolving the electrochemical characteristics of the single electrodes at an elevated cell voltage of 3.5 V. The results obtained demonstrate a striking dependence of the aging mechanism on the type of solvent used.

2. Experimental

2.1. Materials and electrochemical cell assembly

The activated carbon investigated in the present work was YP17 (Kuraray Chemical, Japan). Free-standing sheets bound with 10 wt% poly(tetrafluoroethylene) (PTFE, DuPont) were produced according to a procedure described previously [21]. YP17/PTFE electrodes ($\varnothing$12 mm, thickness 500 μm) were punched out of these sheets and incorporated into three-electrode cells using a cellulose-based paper separator (Maxwell Technologies, Switzerland) of 30 μm thickness. The electrode/separator sandwich was compacted using spring-loaded titanium pistons, with carbon-coated aluminum foils (Gaia Akkumulatorenwerke, Germany) serving as current collectors. A piece of YP17/PTFE was positioned at the periphery of

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the electrode stack as a quasi-reference electrode [22]. Thus, all potentials quoted in the present work are given against this quasi-reference electrode (vs. carbon). The fully assembled cells were dried at 120 °C at 10^3 Pa for at least 24 h.

After drying, the cells were filled with the electrolyte solution, 1 mol/L Et_4NBF_4 in AN or in PC (both from Honeywell Specialty Chemicals Seelze, Germany, less than 20 ppm H_2O), inside an argon-filled glovebox containing less than 1 ppm H_2O and O_2. After filling, the cells were hermetically sealed and transferred outside of the glovebox for the aging experiments.

2.2. Aging procedure

The aging was performed at room temperature using a battery cycler (CCCC from Astrol Electronics, Switzerland) to impose a floating cell voltage of 3.5 V for up to 500 h. Every 10 h, three galvanostatic full cell charge/discharge cycles were performed between 0 V and 2.5 V using a specific current of $I/m_{cell} = 0.28$ A/g where m_{cell} is the total active mass of both electrodes. The maximum time taken for discharging from 2.5 V to 0 V under these conditions was close to 4 min. From the measured cell voltage U_{cell} during these cycles, the specific full cell capacitance $C_{cell} = It/m_{cell}(\Delta U_{cell} - 2IR_{cell})$ was estimated, where It is the amount of charge retrieved during the discharge step of duration t, ΔU_{cell} is the total voltage swing of the cell and R_{cell} is the resistance of the cell which was evaluated from the voltage drop during reversal of the current polarity from $+I$ to $-I$ at $U_{cell} = 2.5$ V. Similarly, the specific capacitances of the positive and negative electrode were estimated as $C_{pos} = It/m_{pos}(\Delta E_{pos} - 2IR_{pos})$ and $C_{neg} = It/m_{neg}(\Delta E_{neg} - 2IR_{neg})$, where ΔE_{pos} and ΔE_{neg} are the respective potential swings measured against the carbon reference electrode, R_{pos} and R_{neg} represent the respective resistance at each electrode and m_{pos} and m_{neg} are the according active masses of the dry electrodes upon cell assembly.

2.3. Post-mortem analysis of aged electrodes

The aged cells were disassembled in air and the electrodes washed in a Soxhlet reactor for at least 6 h using AN as the extraction solvent in order to remove residual electrolyte. Afterwards, the electrodes were stored in a desiccator at 10^3 Pa until separate pieces of each electrode were used for further analysis.

The aged electrodes were characterized by nitrogen adsorption at 77 K using an Autosorb-1 (Quantachrome Instruments, USA). Prior to the measurements, the samples were dried at 150 °C for at least 24 h under a vacuum better than 1 Pa. The specific surface areas and micropore volumes were determined using non-local density functional theory (NLDFT) as implemented in the AS1WIN software package provided by Quantachrome Instruments, USA, by assuming a mixed slit/cylindrical pore shape.

A chemical analysis of the aged electrodes was performed via X-ray photoelectron spectroscopy (XPS) with an ESCALAB 220iXL (Thermo Scientific, USA, formerly V.G. Scientific) using Al K_α (1486.6 eV) radiation. Apart from the washing procedure described above, no further sample preparation was performed prior to the XPS measurements.

3. Results and discussion

3.1. Aging at 3.5 V float voltage

The initial specific full cell capacitance was 23 F/g in PC and 25 F/g in AN, with a rapid loss of capacitance occurring in both systems over time (Fig. 1). In the first 100 h, the relative capacitance loss of the full cells was 34% in PC and 51% in AN. After 500 h, the
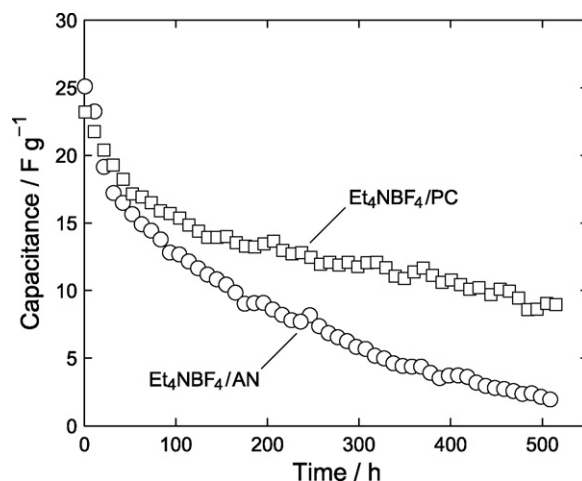

Fig. 1. Capacitance loss of YP17/PTFE full cells in 1 mol/L solutions of Et_4NBF_4 in AN and in PC, respectively, held at a constant float voltage of 3.5 V. The cell capacitance is normalized to the total active mass of both electrodes.

capacitance was reduced by 98% (AN) and 61% (PC) compared to the initial value.

When comparing the leakage currents during the aging experiments of the present study with those conducted on commercial EDLCs (BCAP0350 from Maxwell Technologies, Switzerland) at the same voltage [23], values close to 20 μA/F at 3.5 V after 100 h are found in both cases, suggesting that the aging processes observed in the present work are also relevant for commercial devices.

From the evolution of the single electrode capacitances in AN (Fig. 2a), a dramatic dependence of the aging rate on the electrode polarity is evident. While the specific capacitance of the negative electrode, initially at 88 F/g, was close to 95 F/g after 500 h, the positive electrode experienced a pronounced loss from initially 117 F/g to 37 F/g after 100 h and to only 4 F/g after 500 h. Thus, it is clear that the aging of the entire cell at 3.5 V in AN was dominated by the aging of the positive electrode.

Due to the significant capacitance loss of the positive electrode, the potential excursion of this electrode (ΔE_{pos}) increased progressively with the extent of aging (insets in Fig. 2a). Accordingly, the potential excursion of the negative electrode (ΔE_{neg}) was reduced and centered at more negative potentials. The observed capacitance increase of the negative electrode during aging in AN can thus be understood, since the capacitance of activated carbon is known to increase with increasing polarization relative to 0 V [24].

For the aging behavior of the single electrodes in PC, precisely the contrary was observed (Fig. 2b). In this case, the aging of the full cell was dominated by the rapid capacitance loss of the negative electrode, which dropped down to 46 F/g after 100 h and to 22 F/g after 500 h compared to the initial value of 105 F/g. The capacitance of the positive electrode, initially 83 F/g, increased to 105 F/g in the same total time period. Analogous to the behavior of the negative electrode in AN, this increased capacitance of the positive electrode in PC can be explained by the narrowing and shift of its operating potential window to more positive potentials (inset in Fig. 2b).

The dependence of the aging on both the electrode polarity and the solvent is also clearly reflected in the resistance changes at each electrode (Fig. 3). In both electrolytes, the increase in the electrode resistance was more pronounced for the electrode which experienced the greatest capacitance loss. Thus, the resistance of the positive electrode in AN increased from 0.45 Ω cm^2 to 28 Ω cm^2 after 500 h. In PC, the resistance of the negative electrode increased from 1.2 Ω cm^2 to 15 Ω cm^2 in the same time period.

The increased electrode resistances can be attributed to increased contact resistances, which may occur between individual