Int. J. Electrochem. Sci., 6 **(2011)** 988 - 996

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Effect of Water on the Aging of Activated Carbon Based Electrochemical Double Layer Capacitors During Constant Voltage Load Tests

Dario Cericola[1] , *Patrick W. Ruch*[2] , *Annette Foelske-Schmitz*[1] , *Daniel Weingarth*[1] , *Rüdiger Kötz*[1,*]

[1]Electrochemistry Laboratory, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland
[2]IBM Research GmbH, Säumerstrasse 4, CH-8803 Rüschlikon, Switzerland
[*]E-mail: ruediger.koetz@psi.ch

Received: 8 February 2011 / *Accepted:* 24 February 2011 / *Published:* 1 April 2011

The effect of water contamination in 1 mol L^{-1} Et_4NBF_4 dissolved in acetonitrile or in propylene carbonate as electrolyte on the capacitance fading of activated carbon based electrochemical double layer capacitors has been investigated during constant voltage load tests at 2.75 V and 3.5 V cell voltage. For a cell voltage of 2.75 V, water contamination in the PC based electrolyte led to a fast initial cell capacitance decrease. This cell capacitance loss was predominantly due to a capacitance fading on the negative activated carbon electrode. For the AN based electrolyte a similar but less pronounced effect is observed at 2.75 V. For both electrolytes tested at 3.5 V, no influence of deliberately introduced water contamination on the capacitance loss was identified. The cause for capacitance fading at the higher cell voltage, therefore, appears to be independent on the water contamination. Post mortem X-ray photoelectron spectroscopy and surface area analysis of the negative electrode aged at 2.75 V did not provide evidence for a corresponding loss of surface area or electrode passivation. These results point toward water reduction on the negative electrode as the primary cause for capacitance loss of electrochemical double layer capacitors in water-contaminated electrolytes near nominal working voltage. The formation of trapped hydrogen within micropores of the activated carbon electrodes is proposed as the main aging mechanism in this case.

Keywords: Supercapacitor, capacitance fading, activated carbon, aging, non-aqueous electrolyte

1. INTRODUCTION

Water has commonly been considered detrimental to the performance of activated carbon based electrochemical double layer capacitors (EDLCs) utilizing organic electrolyte with acetonitrile (AN) or propylene carbonate (PC) solvents. Manufacturers typically use electrolyte solutions with a guaranteed water content of 20 ppm or less. However, the information contained in the scientific literature concerning the influence of water on the capacitor performance is scarce.

Zuckerbrod et al. [1] studied the effect of water on large EDLCs, where the drying conditions for the cell components were varied. It was demonstrated that higher drying temperatures led to reduced water contents of the components. These authors found a significant effect on the capacitor cycling stability when drying the cell components at about 120 ºC or 190 ºC compared to room temperature drying. For EDLC cells dried at different temperatures above 120 ºC the differences were rather small.

Another investigation of the effect of water on symmetric and asymmetric capacitors utilizing a graphite positive electrode was performed by Wang and Yoshio [2]. For the capacitor using graphite, water contaminations in the electrolyte resulted in a significant initial capacitance loss, which was mainly attributed to the exfoliation of the graphite. However, also for a symmetric capacitor utilizing AC on both electrodes a similar but smaller effect was observed.

In a divided cell where the anode and cathode compartments were separated, Ishimoto et al. [3] discovered an increase in the water content from 11 ppm to 300 ppm in the positive electrode compartment and a decrease to 2 ppm in the negative electrode compartment after constant voltage hold experiments. From this result, it was concluded that water is consumed at the negative electrode to form H_2 and that water is released from the porous AC structure of the positive electrode.

While the determination of the water content of the electrolyte is straightforward, for instance using coulometric Karl Fischer titration, the water content of the activated carbon is more difficult to access. Most of the bulk water is expected to be removed at temperatures above 130 °C under vacuum. However, the behavior of water confined in the micropores (< 2 nm) is known to differ from its bulk properties and the removal of this water is difficult [4].

In addition, oxygen containing functional groups present on the carbon surface may behave similarly to trapped water and contribute to the cell aging.

In conclusion, the water content of the electrolyte solution must be considered an underestimate of the total water content of an EDLC device.

In the present communication, the water content of AN based and PC based electrolyte solutions was deliberately increased to 1000 ppm and 850 ppm, respectively. Constant voltage load tests were performed using these contaminated electrolytes in symmetric capacitors utilizing activated carbon electrodes and compared to electrolytes with a water content of 30 ppm or lower.

2. EXPERIMENTAL

Electrochemical aging experiments were performed on activated carbon based EDLCs. The used active material was the activated carbon YP17 from Kuraray Chemicals – Japan. Electrodes with a diameter of 12 mm were punched out from a ~500 μm thick sheet of bound electrode material based on 90 wt.% of YP17 and 10 wt.% of polytetrafluoroethylene (PTFE, Sigma-Aldrich) as binder. A dispersion of activated carbon and the binder solution in a 1:1 water/isopropanol mixture was heated and strongly stirred until a dough-like mass was obtained, which then was rolled into a sheet of 500 μm thickness.

The electrochemical cells were prepared by sandwiching two electrodes separated by a 30 μm thick cellulose based separator (Maxwell Technologies, Switzerland) between two spring loaded titanium current collectors. Carbon coated aluminum foil (Gaia Akkumulatorenwerke, Germany) was placed between the titanium current collector and the carbon electrode in order to improve electrical contact. Experiments were performed in a three-electrodes arrangement. Activated carbon was used as quasi-reference electrode [5]. The mean active material loading was 45 ± 5 mg cm^{-2}. Electrochemical cells were assembled in air and then dried at 120 ºC at a residual pressure of 3000 Pa for 12 h. After transferring the cells into an Ar filled glove box (H_2O and O_2 < 1 ppm), they were filled with the electrolyte solutions and hermetically sealed.

The experiments were performed with both pristine and water contaminated electrolytes. The water contamination was obtained by adding high purity water (resistivity > 18 MΩ cm) to the pristine electrolyte solutions. Karl Fischer titration was used to measure the actual water content of the electrolytes (684 KF Coulometer from Metrohm with HYDRANAL® electrolyte from Sigma Aldrich). The pristine electrolytes exhibited water contents of less than 30 ppm . The electrolytes used in the experiments were: Et_4NBF_4 in AN (<30 ppm H_2O), Et_4NBF_4 in AN contaminated with 1000 ppm H_2O, Et_4NBF_4 in PC (<30 ppm H_2O), and Et_4NBF_4 in PC contaminated with 850 ppm H_2O. The pristine electrolytes were provided by Ferro Corporation.

The aging experiments were performed as described previously [7]. Briefly, the cells were galvanostatically cycled (CCCC battery cycler from Astrol Electronics, Switzerland) three times between 0 and 2.5 V (cell voltage) at a specific current of 280 mA g^{-1} in order to evaluate cell and electrode capacitance. After the cycling step, the cells were charged up to 2.75 or 3.5 V followed by holding the cell voltage for 10 h. The cell was then cycled again and the procedure was repeated until an overall holding period of 100 or 500 h was reached.

For the post mortem analysis, the cells were disassembled in air and the electrodes were washed in a Soxhlet apparatus with AN for 6 h in order to remove most of the residual electrolyte prior to the subsequent analysis (as already reported in [7]).

Nitrogen physisorption experiments were performed post mortem on the washed electrodes using an Autosorb-1 (Quantachrome Instruments, USA). The electrode samples were outgassed at 150 ºC at a residual pressure lower than 1 Pa prior to the physisorption analysis. The recorded isotherms were evaluated according to the non-local density functional theory (NLDFT) algorithm implemented in the AS1WIN software package (Quantachrome Instruments, USA) assuming a combination of slit and cylindrical shaped pores.

Chemical analysis of the aged and washed electrodes was performed using X-ray photoelectron spectroscopy (XPS, ESCALAB 220iXL from Thermo Scientific, USA, formerly V.G. Scientific) by means of monochromatized Al Kα (1486.6 eV) radiation. The binding energies were calibrated with respect to the Ag $3d_{5/2}$ level at 368.2 eV and the base pressure in the analysis chamber was always smaller than 10^{-6} Pa.

3. RESULTS AND DISCUSSION

3.1. Constant voltage tests at 3.5 V

Recently, we published accelerated aging tests on activated carbon based EDLCs utilizing organic electrolytes at a cell voltage of 3.5 V [6,7]. These tests were performed with electrolyte solutions containing less than 30 ppm of H_2O. The results of the aging tests at 3.5 V using electrolyte solutions with strongly varying water contents are shown in Figure 1 for the cell capacitance and in Figure 2 for the single electrode capacitance. The data was normalized to 100% for the initial capacitance which was 23±3 Fg^{-1} of active material in all the cases. The rate of cell capacitance loss at a cell voltage of 3.5 V was found to be independent of the water content.

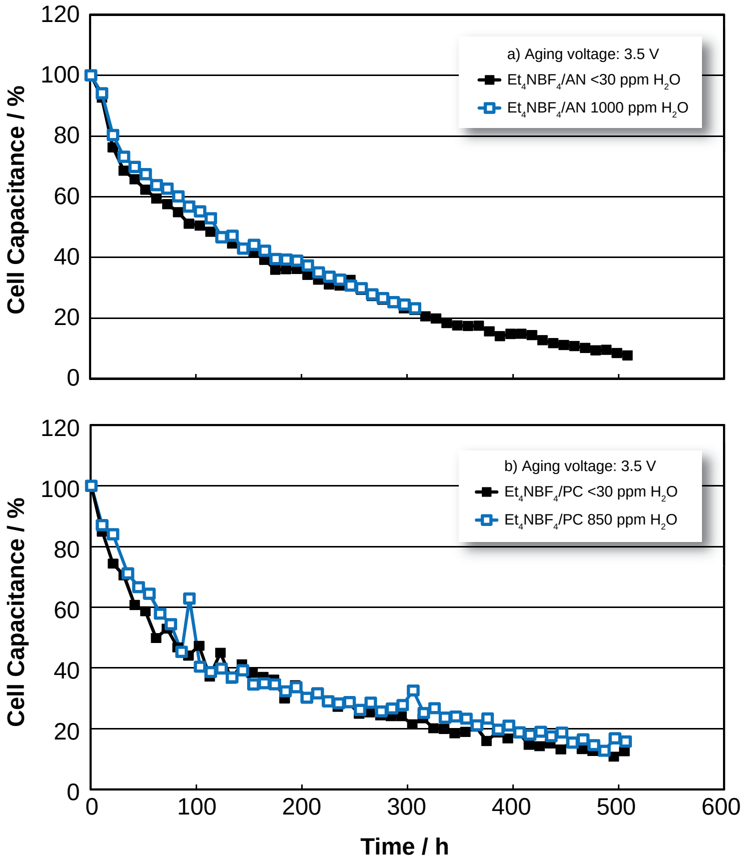

Figure 1. Loss of specific cell capacitance during aging at 3.5 V in AN based electrolytes (a) and PC based electrolytes (b). Full symbols represent the electrolytes with <30 ppm H_2O, open symbols the electrolyte with 1000 ppm H_2O (AN) and 850 ppm H_2O (PC) respectively.

Also, for the aging of the single electrodes (see Figure 2), contamination with water had no obvious effect on the capacitance fading. The preferential aging of the positive electrode in AN and of the negative electrode in PC, which has been observed previously [6], was confirmed. This independence of the aging behavior on the water content is unexpected. The influence of water on the capacitance fading at cell voltages of 3.5 V appears to be negligible in comparison with other degradation processes. This result may be explained by degradation processes, which become possible at a cell voltage of 3.5 V dominating and disguising a possibly existing effect of water. Alternatively it could be concluded that water has no effect on the capacitor performance at such high voltages. This finding is in contradiction to the postulation of Ishimoto et al. [3] that water-induced side reactions play a major role for the degradation reactions observed at higher voltages.

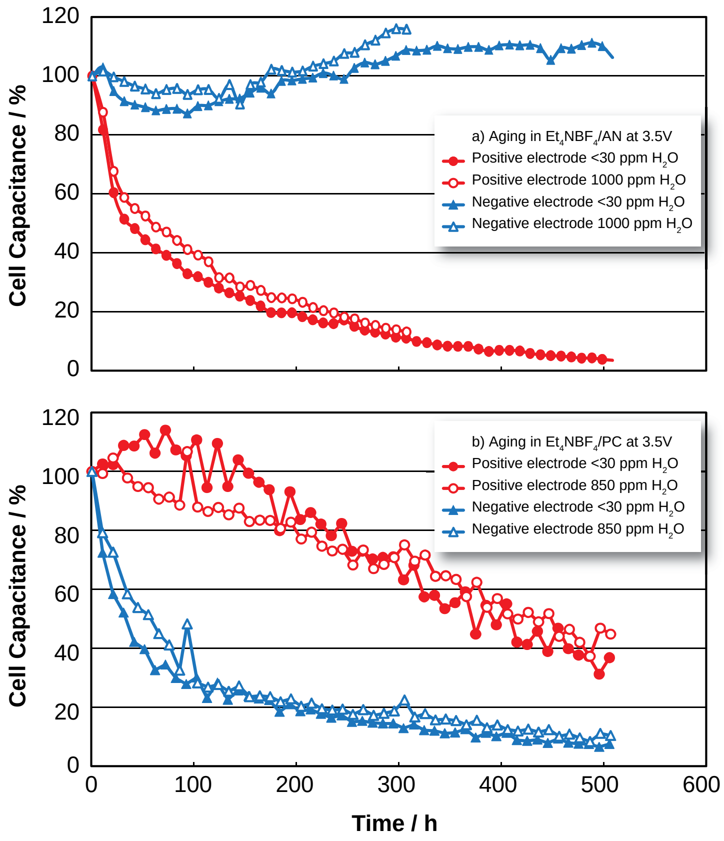

Figure 2. Capacitance loss of the individual electrodes during aging at 3.5 V in AN based (a) and PC based (b) electrolytes. Full symbols represent electrolytes with <30 ppm H_2O, open symbols the electrolyte with 1000 ppm (AN) and 850 ppm (PC) respectively. Circles represent positive electrodes and triangles the negative electrodes.

3.2. Constant voltage tests at 2.75 V

The influence of water contamination on the aging at a lower cell voltage of 2.75 V was also investigated. In this case, the higher concentration of water leads to a significant reduction of cell as well as electrode capacitance during the initial 50 h to 100 h of testing (Figures 3 and 4). Figure 3 suggests that the impact of water appears to be more pronounced in the PC based electrolyte where the cell capacitance is reduced by 20 % during the first 100 h of testing. For AN the reduction is in the order of 10 %.

The result for the PC based electrolyte is in good agreement with the results published by Wang and Yoshio [2] for a similar electrolyte system (1.5 M $TEMAPF_6$ / PC) for cycling tests between

0 V and 2.5 V. These authors also investigated the initial capacitance loss as a function of water concentration in the electrolyte. For a concentration of 850 ppm they found an initial loss of about 10% during cycling, which compares qualitatively well to the 20 % observed in our experiment for a higher cell voltage and different experimental conditions. The investigations show, that the effect of water is limited to the first hours of the constant voltage or cycling test, while the rate of capacitance loss for the rest of the tests is unaffected by the water content.

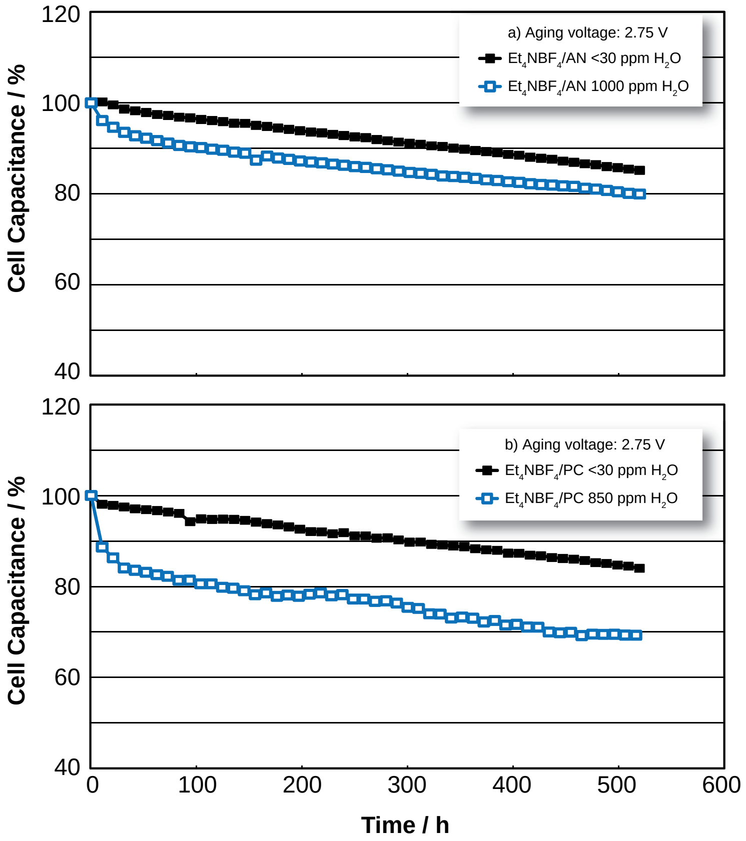

Figure 3. Loss of specific cell capacitance during aging at 2.75V for AN based (a) and PC based (b) electrolytes. Full symbols represent the electrolytes with <30 ppm H_2O, open symbols the electrolytes with 1000 ppm H_2O (AN) and 850 ppm H_2O (PC) respectively.

For the capacitance loss of the single electrodes it is evident that, for both electrolytes, the impact of H_2O on the capacitance fading is most pronounced at the negative electrode (see Figure 4) while the positive electrode is not significantly affected.

The observed difference between the effect of water at the positive and negative electrode is in agreement with the results obtained by Ishimito et al. [3], who found that the water content of the electrolyte in a divided cell increased at the positive electrode and decreased at the negative electrode for a cell voltage of 4 V. Water is likely to be consumed at the negative activated carbon electrode while being remarkably stable at the positive activated carbon electrode. The enhanced capacitance fading of the negative electrode at higher degrees of water contamination is therefore likely to be linked to the degradation of water at this electrode.

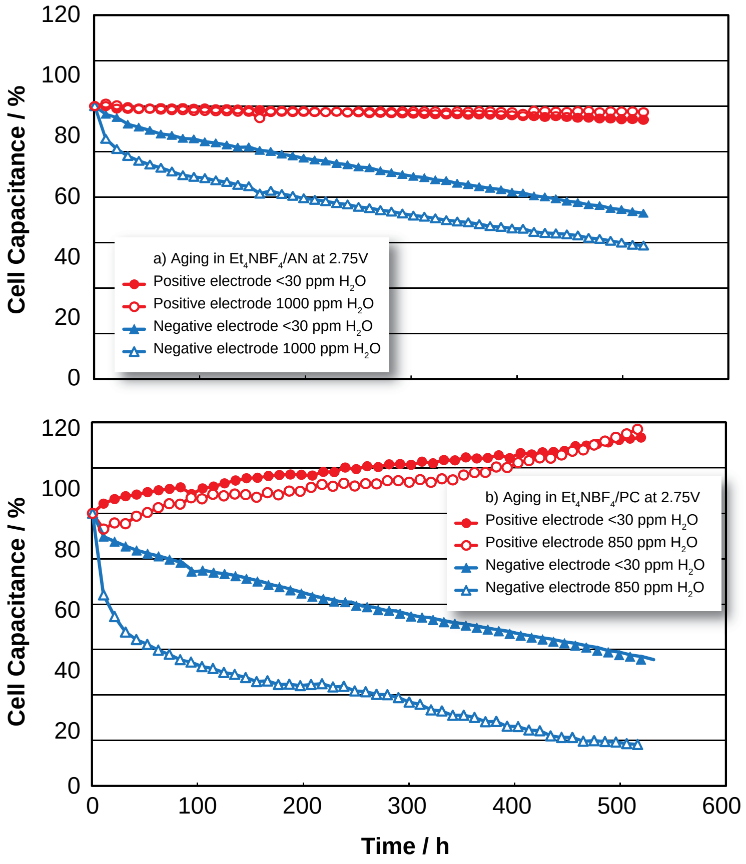

Figure 4. Capacitance loss of the individual electrodes during aging at 2.75 V in AN based (a) and PC based (b) electrolytes. Full symbols represent the electrolytes with <30 ppm H_2O, open symbols the electrolytes with 1000 ppm H_2O (AN) and 850 ppm H_2O (PC), respectively. Circles represent positive electrodes and triangles the negative electrodes.

3.3. XPS and surface area analysis

In order to gain more insight into the water-induced processes XPS analysis was performed on the negative electrode after 100 h of aging with and without water contamination in the electrolyte. The C1s spectra obtained from the negative electrodes aged in the pristine and the water contaminated electrolytes do not show significant differences (see Figure 5). The features visible around binding energies of 295 eV originate from C-F bonds of the PTFE binder used in the electrodes.

Surface area determination by nitrogen physisorption also indicated no significant dependency on the water content. The NLDFT surface area of the electrode in pristine PC based electrolyte after 100 h of aging was 1158 m^2g^{-1} compared to 1117 m^2g^{-1} for the H_2O-contaminated electrolyte. For the AN based electrolyte, the NLDFT surface area was reduced from 1165 to 1117 m^2g^{-1}. The measured specific surface areas are roughly within the limits of measurement uncertainty.

The XPS and nitrogen adsorption measurements can be interpreted to indicate the absence of both surface passivation and pore clogging due to degradation products. Both of these phenomena have previously been found to lead to capacitance fading in EDLC systems with low water contents, but at significantly higher cell voltages [6,7]. Alternatively, the results may indicate that all degradation products are removed by the washing procedure employed in the present work.

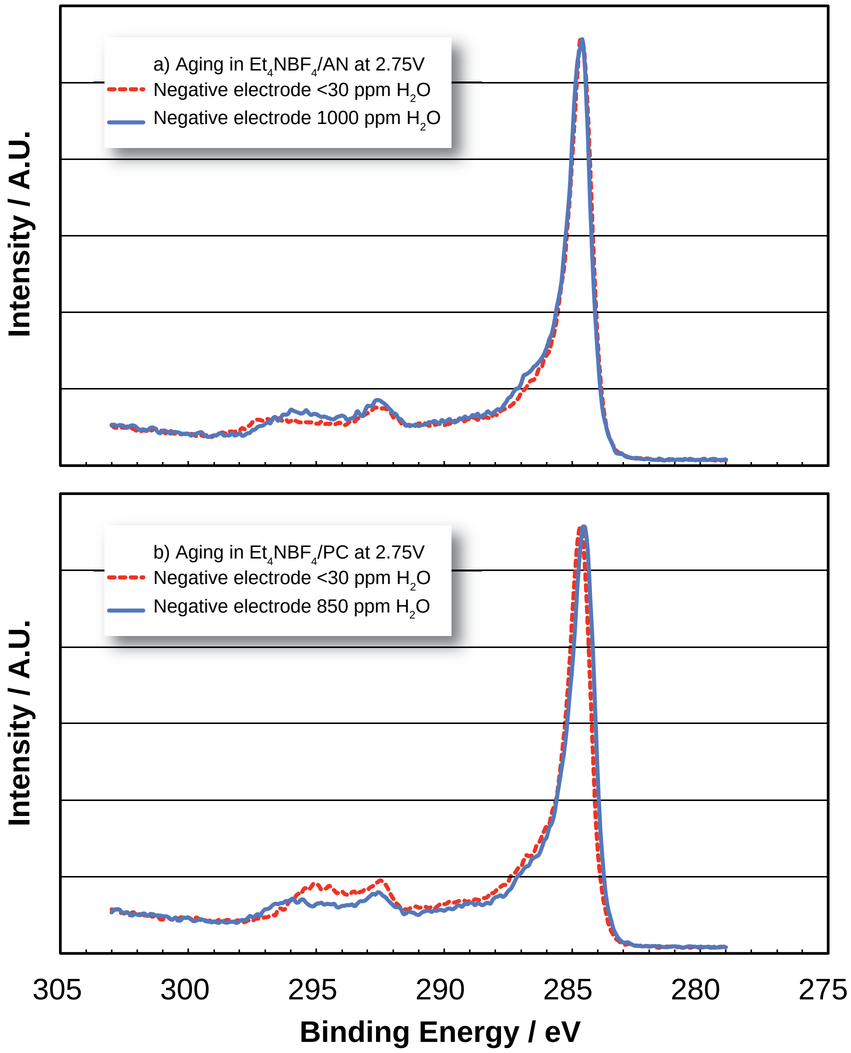

Figure 5. XP spectra of the C1s level of the electrodes recorded after 100 h of aging in AN based (a) and PC based (b) electrolyte with (dashed line) and without (full line) water contamination.

However, there might be another explanation for the observed enhanced capacitance fading of activated carbon negative electrodes in water-contaminated electrolyte solutions. The formation of H_2 gas upon water reduction, which partially blocks the pores and, thus, the accessible surface could lead to the initial capacitance loss.

Such H_2 would not show up in the XPS analysis and would also not be detected in the gas adsorption measurements. Evolution of H_2 into the cell headspace during capacitor operation was indeed found by Hahn et al. [8] and Ishimoto et al. [3]. The presence and trapping of gaseous H_2 within the pores of aged activated carbon electrodes, however, remains to be experimentally confirmed.

4. CONCLUSIONS

The effect of water contamination in the electrolyte of EDLCs on the aging behavior was investigated for cell voltages of 2.75 V and 3.5 V.

At 2.75 V a clear initial loss of capacitance was detected in water contaminated electrolyte for both AN and PC based electrolyte.

The enhanced capacitance fading occurs exclusively at the negative electrode. XPS and surface area analysis did not indicate electrode passivation by surface film formation or an equivalent surface area loss on the negative EDLC electrodes.

At 3.5 V, the effect of water is negligible during aging of the EDLCs. The trapping of gaseous H_2 as a product of water reduction within micropores of the activated carbon electrode is proposed as the main reason for capacitance fading due to water contamination.

ACKNOWLEDGEMENT
We thank the Swiss National Science Foundation (SNSF) for financial support (project number: 200021-117607)

References

1. D. Zuckerbrod, K. Kobayashi, in: Proceedings of the 15th International Seminar on Double Layer Capacitors and Hybrid Energy Storage Devices, Dec. 5-7, 2005, Florida, USA, 101-110
2. H. Wang, M. Yoshio, *J. Power Sources,* 195 (2010) 389
3. S. Ishimoto, Y. Asakawa, M. Shinya, and K. Naoi, *J. Electrochem. Soc.,* 156 (2009) A563
4. H. Ye, N. Naguib, and Y. Gogotsi, *JEOL News* 39 (2004) 38
5. P.W. Ruch, D. Cericola, M. Hahn, R. Kötz, and A. Wokaun, *J. Electroanal. Chem*., 636 (2009) 128
6. P.W. Ruch, D. Cericola, A. Foelske, R. Kötz, A. Wokaun, *Electrochim. Acta*, 55 (2010) 2352
7. P.W. Ruch, D. Cericola, A. Foelske-Schmitz, R. Kötz, A. Wokaun, *Electrochim. Acta,* 55 (2010) 4412
8. M. Hahn, A. Würsig, R. Gallay, P. Novák, and R. Kötz, *Electrochem. Commun.*, 5 (2005) 925.