Short communication

Effect of electrode mass ratio on aging of activated carbon based supercapacitors utilizing organic electrolytes

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ABSTRACT

The accelerated degradation of carbon based supercapacitors utilizing 1 M Et_4NBF_4 in acetonitrile and in propylene carbonate as electrolyte is investigated for a constant cell voltage of 3.5 V as a function of the positive over total electrode mass ratio. The degradation rate of the supercapacitor using acetonitrile as a solvent can be decreased by increasing the mass of the positive electrode. With a mass ratio (positive electrode mass/total electrode mass) of 0.65 the degradation rate is minimum. For the capacitor utilizing propylene carbonate as a solvent a similar effect was observed. The degradation rate was smallest for a mass ratio above 0.5.

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1. Introduction

Carbon based supercapacitors, also called electrochemical double layer capacitors (EDLC) or ultracapacitors, store the energy in the electric field of the electrochemical double layer, which forms at the electrode electrolyte interface. EDLCs are characterized by high specific power but relative low specific energy, when compared to batteries. The concept of an asymmetric or hybrid design has been developed in order to improve the specific energy of today's EDLCs and was also implemented in some technical devices. Such asymmetric devices utilize typically one activated carbon electrode (capacitive electrode) in combination with a battery electrode (faradaic electrode) such as $Ni(OH)_2$ [1] or other [2]. Due to the different specific charges of the capacitive and the faradaic electrode it is important to balance the mass of both electrodes. The optimized electrode mass ratio to achieve maximum specific energy for hybrid devices was calculated by Zheng [3]. Asymmetric hybrid capacitors were recently reviewed by Naoi and Simon [2] and classified by Conte [4].

Another strategy to increase the specific energy of carbon/carbon capacitor is to increase the cell voltage, however the aging increases dramatically due to the degradation of the electrolyte [5,6]. Different authors used ionic liquids as electrolytes which guarantee high cell voltage [7,8] however the low con-

ductivity limits the specific power of the device. An alternative which allows to use the regular electrolytes is to optimize the cell construction by varying the relative masses of the two electrodes.

The electrode potentials of both electrodes of a discharged carbon/carbon EDLC are equal and correspond to the immersion or open circuit potential (OCP) of the respective electrolyte / electrode material combination. During charging of the EDLC only the cell voltage is controlled and the electrode potentials shift according to the respective electrode capacitance to more positive and negative values, away from the OCP. The stability limit of the capacitor is reached as soon as one of the electrodes reaches the potential of a faradaic degradation process. The potential of the other electrode, however, may still be far from any limiting degradation potential. As a consequence the available potential window of the active material/electrolyte combination may not be fully utilized by the positive or the negative electrode.

In order to overcome this problem and to optimize carbon based EDLCs the concept of different electrode mass for the positive and negative electrode was utilized, eventually resulting in an asymmetric design as far as the electrode mass is concerned. This approach allows to affect the extend of the potential windows of both electrodes by changing the relative capacity of the electrodes.

It could be shown that optimization of activated carbon based supercapacitors for maximum cell capacitance or energy [8,9] resulted in devices with loading of activated carbon on the two electrodes slightly different. Arbizzani et al. [8] as well as Wen et al. [10] found a positive over negative electrode mass ratio of about 1.5

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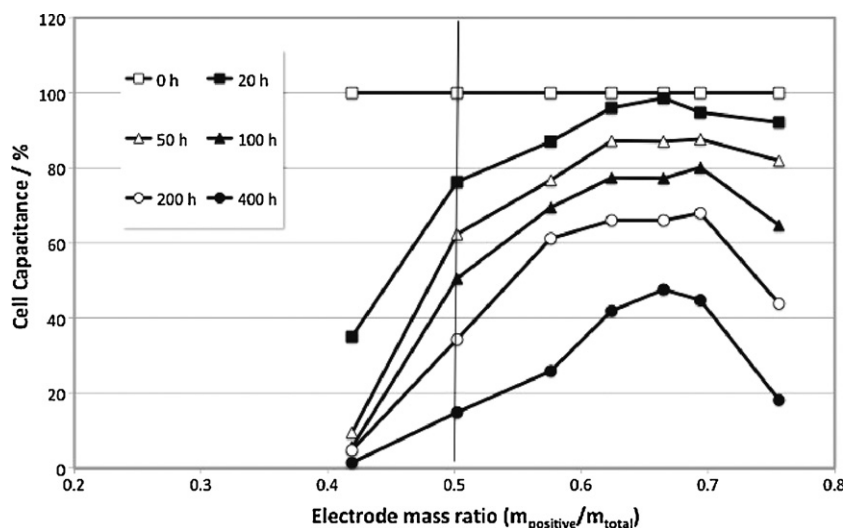*E-mail address:* ruediger.koetz@psi.ch (R. Kötz).

Fig. 1. Cell capacitance as a function of electrode mass ratio r after various times of accelerated constant voltage test at a cell voltage of 3.5 V, electrolyte 1 M Et_4NBF_4 in acetonitrile.

to result in optimized supercapacitor performance in ionic liquid electrolyte and in KOH electrolyte, respectively.

The optimization of the electrode mass ratio in carbon/carbon supercapacitor leads to the full utilization of the electrochemical stability window and therefore to a larger cell voltage and specific energy. It is known that the aging is strongly affected by the cell voltage because the potential of one electrode is too positive or negative [11]. However the effect of the electrode mass balance on the aging of carbon based EDLCs has not been investigated at the best of our knowledge.

In the present study we investigate the effect of electrode mass ratio for activated carbon based supercapacitors using 1 M Et_4NBF_4 in acetonitrile (AN) and propylene carbonate (PC) as electrolyte on the stability during accelerated constant load aging tests. This is in contrast to previous studies where the electrode mass ratio was tuned for optimized capacitance or energy.

2. Experimental

The supercapacitors used in the investigations utilized activated carbon (AC) (YP17, Kuraray Chemical – Japan) electrodes. Self-supporting electrode sheets based on 90% YP17 and 10% poly(tetrafluoroethylene) PTFE (from a 60% (w/w) aqueous dispersion – Sigma Aldrich) as binder were prepared. A dispersion of YP17 and the proper amount of PTFE was vigorously stirred and heated until a dough-like mass was obtained which was then repeatedly rolled into sheets of different thicknesses (from 200 to 500 μm). Cells based on Ø12 mm electrodes separated by a Ø13 mm separator (cellulose based 20 μm thickness Maxwell Technologies – Switzerland) were assembled in air. The aging experiments were performed in a three-electrode arrangement with an activated carbon quasi reference electrode [12].

The mass ratio r is defined as the ratio of the positive electrode mass to the total electrode mass (r = mass$_{pos}$/(mass$_{pos}$ + mass$_{neg}$)). When changing the mass ratios of the electrodes the total electrode mass was attempted to be kept constant to 35 ± 5 mg cm^{-2}.

Assembled cells were dried at 120 °C for 24 h at 20 mbar and then transferred, filled and hermetically sealed in an Ar filled glovebox (H_2O and O_2 < 1 ppm). The electrolytes used were 1 M Et_4NBF_4 in acetonitrile and propylene carbonate provided by Honeywell Specialty Chemical Seelze – Germany with a water content of less than 30 ppm.

The aging experiments followed a measurement protocol, which was described in detail before [11]. Basically the protocol consists of consecutive periods where the voltage of the cell was hold at 3.5 V for 10 h and short periods (less than 1 h) where the cell was cycled three times between 0 and 2.5 V at the specific current of 280 mA g^{-1}. From these cycles the cell capacitance, electrode capacitances and the internal resistance of the cells were determined.

3. Results

3.1. Et$_4$NBF$_4$ in acetonitrile

In a recent study we demonstrated that the aging of symmetric activated carbon based capacitors is dominated by the aging of one electrode only [6,11]. For capacitors using AN as the solvent, capacitance fading during accelerated aging tests at a cell voltage of 3.5 V is caused by the aging of the positive electrode, while for PC based capacitors it is dominated by the aging of the negative electrode. Most likely, the preferentially aging electrode is exposed to potentials beyond its stability limit.

Therefore it would be straightforward to reduce the potential excursion of the particularly aging electrode by increasing its mass and thus the absolute capacity of that electrode.

Fig. 1 shows the result of several accelerated aging tests for the activated carbon based supercapacitor in 1 M Et_4NBF_4 in AN for different mass ratios r for different aging times. The optimum mass ratio for highest stability is around 0.65. During 400 h of aging at 3.5 V the capacitance of the cell with r = 0.65 decreases to 50% of its initial value (from 21.5 to 10.5 F) while the capacitance for mass ratio r = 0.50 is only 15% of its initial value (the capacitance is reduced from 25 to 3.5 F). This corresponds to a reduction of the capacitance fading from 54 mF h^{-1} to 28 mF h^{-1} by increasing r from 0.50 to 0.65 and results in a significant capacitance gain after accelerated aging at 3.5 V.

The fundamental effect leading to this result is visualized in Fig. 2 where the specific capacitance of the individual electrodes is plotted during the aging experiment for supercapacitors with r = 0.5 (a), and r = 0.65 (b). The results reproduced in Fig. 2a are in accord with the data published earlier for a device with r = 0.5 [6,11] tested in AN based electrolyte. It is clear from Fig. 2b that the increased mass of the positive electrode reduces the degradation process of this electrode while that of the negative electrode is increased. As a result both electrodes age at a similar rate and because the
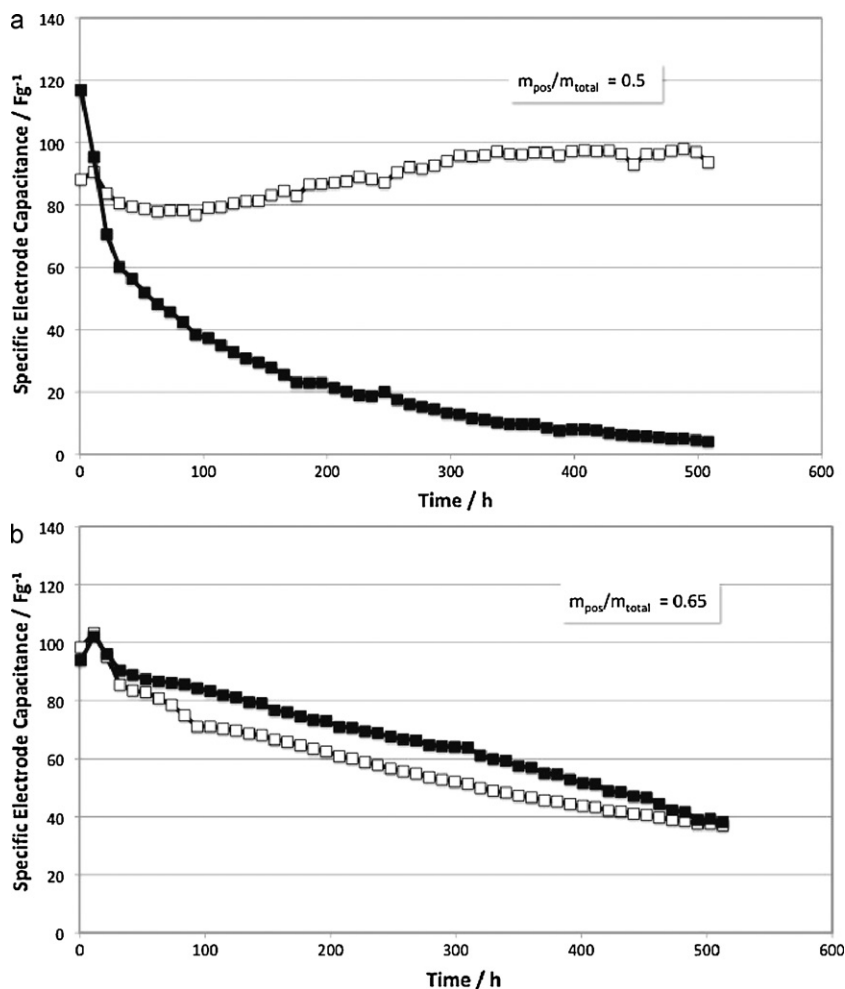
Fig. 2. Specific capacitance of the single electrodes during accelerated aging tests in 1 M Et$_4$NBF$_4$ in AN for mass ratio r = 0.5 (a) and mass ratio r = 0.65 (b). Full squares: positive electrode, open squares: negative electrode.

cell capacitance is determined by the less capacitive electrode the cell capacitance fading is significantly mitigated using an oversized positive electrode (r = 0.65).

3.2. Et$_4$NBF$_4$ in propylene carbonate

On the bases of the arguments forwarded above it would be straightforward to optimize the PC based capacitor by increasing the mass of the negative electrode. Our previous investigations [6] have shown that for this system the negative electrode dominated the accelerated aging process and most probably reaches potentials beyond the stability regime. However, as is clearly demonstrated in Fig. 3, the aging process is accelerated for all mass ratios below r = 0.5 for the PC based electrolyte. For mass ratios r above 0.5 the degradation process appears to be reduced similar to the situation for AN as a solvent. While for a mass ratio of r = 0.45 the cell capacitance decreases to 10% after 400 h, for a mass ratio of 0.55 the capacitance reduces only to 30% after 400 h.

This result indicates that in the case of PC as a solvent the dominating aging of the negative electrode in the carbon/carbon supercapacitor cannot be avoided by an increased mass of the negative on the expense of the positive electrode. As is evident from Fig. 3 only an increased mass of the positive electrode reduces the capacitance fading of the cell. The origin of the improved capacitance fading with respect to the single electrode capacitance is visible in Fig. 4. As previously reported the capacitance fading of the negative electrode dominated the cell aging for r = 0.52 in PC

based electrolyte [6]. For r = 0.65 (Fig. 4b) the capacitance fading is still dominated by the negative electrode but the capacitance loss of the negative electrode during the first 20 h is significantly reduced when compared to the capacitor with r = 0.4 (Fig. 4a). In addition the aging of the positive electrode is also reduced. The capacitance evolution for both electrodes plotted in Fig. 4b is in good agreement with those published earlier [6] for a cell with r = 0.52

The dependence of the aging on the electrode mass ratio is certainly related to the different potentials experienced by the electrodes. For the optimized mass ratio in AN as well as in PC based electrolyte the potential of the positive electrode is 1.65 V and for the negative −1.85 V respectively, vs. the carbon quasi reference electrode. When r is greater than the optimal value (either of AN on PC based devices) the electrode potentials are more negative than in the case of the optimal r due to the oversized positive electrode, and no pronounced shifts are observed with the aging time. The evolution of the electrode potentials in the cases of r smaller than the optimal values is significantly different. The electrode potentials are more positive at time zero, than in the case of the optimal r and tend to drift towards more negative values and than stabilize within the first 50 h of aging. The driving force for the potential drift may be an irreversible charge consumption on the positive electrode at high potentials, which mechanism has not been clarified yet.

The fast aging of carbon/carbon supercapacitors at high voltage hinders the development of high voltage devices. However the use
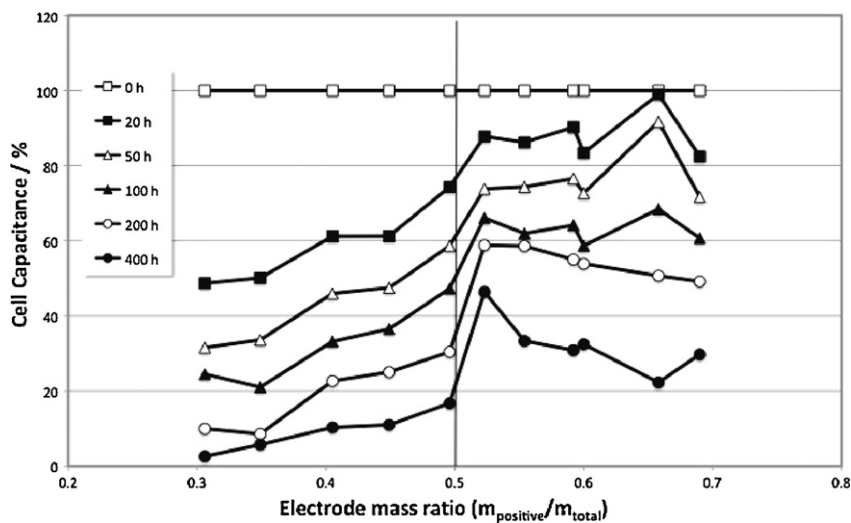
Fig. 3. Cell capacitance as a function of electrode mass ratio **r** after various times of accelerated constant voltage test. Cell voltage: 3.5 V, electrolyte 1 M Et_4NBF_4 in propylene carbonate.
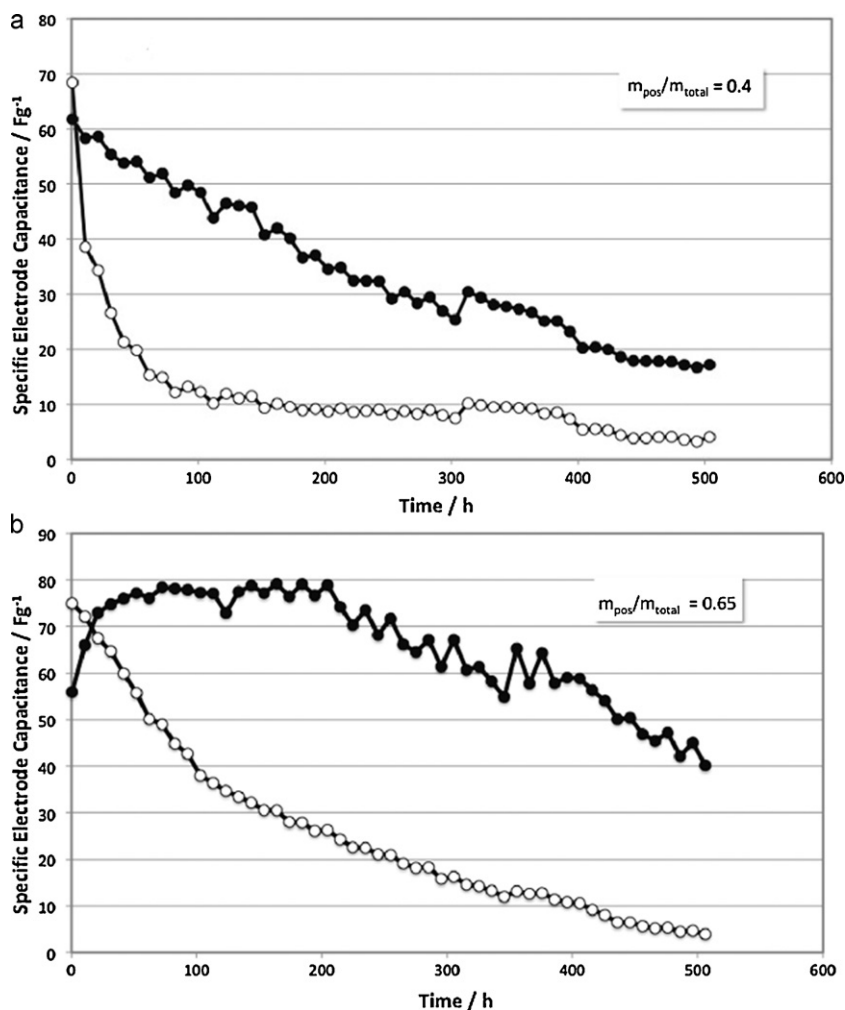

Fig. 4. Specific capacitance of the single electrodes during accelerated aging tests in 1 M Et_4NBF_4 in PC for mass ratio **r** = 0.4 (a) and mass ratio **r** = 0.65 (b). Filled circles: positive electrode, open circles: negative electrode.

of an oversized activated carbon positive electrode clearly increases the lifetime at high cell voltage. This may be a possible strategy to increase the lifetime of an EDLC at high cell voltage, and therefore to achieve stable high energy devices.

4. Conclusions

The aging of carbon/carbon EDLC is clearly a complex balance between cell voltage and electrode masses.

Changing the mass ratio of the electrodes significantly affects the capacitance fading during accelerated constant voltage tests at a cell voltage of 3.5 V significantly. The aging is reduced for an increased mass of the positive electrode for both electrolytes, 1 M Et_4NBF_4 in acetonitrile and in propylene carbonate.

Acknowledgement

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