

Pseudo capacitive processes and lifetime aspects of electrochemical double-layer capacitors

R. Kötz, M. Hahn, O. Barbieri, F. Campana, A. Foelske, A. Würsig, P. Novák, R. Gallay*.

Electrochemistry Laboratory, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland

* Maxwell Technologies SA, CH-1728 Rossens, Switzerland

Introduction

A smart route towards higher energy density and power density of electrochemical double layer capacitors (EDLC) is to increase the cell voltage. As the square of the voltage is proportional to the capacitors energy and power an increase of the cell voltage from 2.5 V to 3.2 V will result in a 100% improvement. Using aprotic electrolytes cell voltages of above 3 V are realistic as can be seen in modern Lithium ion batteries. Therefore, extending capacitor cell voltage to above 3 volt seems to be practical in principle.

However, as one might expect, upon increase of the electrode potential towards more positive and more negative values the probability for other than capacitive charge storage processes to occur increases significantly. It has been shown by Besenhard et al. /1/ that intercalation of the ions of the typical TEABF₄ salt used in EDLCs is possible in graphite. Ion intercalation/insertion is most probably also the basis of the so called Nanogate capacitor described by Okamura et al. previously at this seminar /2/.

In addition, it is known from lithium ion batteries (LiB) that at potentials of about 1 V vs. Li/Li⁺ electrolyte decomposition occurs, which in the case of the LiB results in the desired formation of the solid electrolyte interphase (SEI) protecting the negative electrode. In an EDLC with a nominal voltage of 4 V the negative electrode will be exposed to potentials comparable to 1 V vs. Li/Li⁺. Therefore electrolyte decomposition may be another faradaic reaction becoming important when trying to increase energy and power density of EDLCs.

Finally the positive electrode of a carbon based EDLC with a nominal voltage of close to 4 V will reach a potential of 5 V vs. Li/Li⁺ which is rather high and may well lead to anodic destruction of the solvent and/or the carbon, especially in the presence of impurities such as H₂O.

In the present paper we present new means of how to determine charge induced dimensional changes and volatile products of possible decomposition reactions. The possible correlation of these processes with lifetime measurements will be discussed.

Experimental

The dilatometer for the measurements of charge induced dimensional changes has been described before /3,4/. Therefore only a brief description of the cell

used for DEMS (Differential Electrochemical Mass Spectroscopy) and for the pressure measurements is given.

Differential Electrochemical Mass Spectrometry (DEMS)

The measurement cell (DEMS cell) used for on-line gas analysis is shown in Fig. 1. Two electrodes, each with a geometric electrode area of ca. 12 cm², were vacuum dried (24 h, 120°C, < 0.01 mbar) and then mounted inside an argon-filled glove box on the two opposing parts of the titanium cell body. The cell was then filled with the electrolyte, 1 M TEABF₄ in PC. A polypropylene sealing placed between the two cell body parts determined the electrolyte gap.

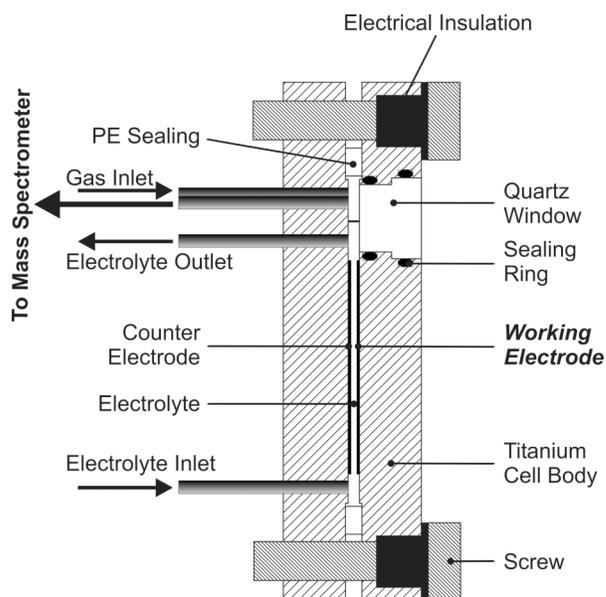


Figure 1: MS cell used for headspace analysis of the gases evolved during cyclic voltammetry.

All measurements were performed in sealed cells outside the glove box at room temperature. A 0.15 mm thick PTFE-bound activated carbon film supported on a 0.03 mm thick aluminum foil was used as the electrode material. The same material was characterized in previous work [5].

During measurement an argon stream (ca. 5 ml/min) was purged through the head space of the cell. Any evolved gases are taken up by this argon stream, of which a small part is pumped off via a capillary into a quadrupole mass spectrometer (QMS 200 Prisma, Pfeiffer Vacuum, Germany). Details of the experimental set-up and the data analysis were published elsewhere [6, 7]. The sensitivity of the headspace method was found to be a factor 10 to 100 higher than that of a previously used DEMS set-up, where the volatile species were pumped off through a membrane located directly behind the working electrode [8].

The ion currents of all relevant mass signals up to $m/z = 44$ were recorded (mass spectrometric CVs, MSCVs) simultaneously with the cell current. CO₂ (molecule

peak $m/z = 44$) and propene ($m/z = 41$) were unambiguously identified by their characteristic fragmentation patterns. The signal $m/z = 2$ was attributed to both, hydrogen being directly formed in the MS cell and to hydrogen being a secondary fragment of other gases.

Since the MS cell was not equipped with a reference electrode, the same voltammetric runs were carried out with a second (reference) cell with only 0.8 cm^2 electrode area. With this coin type reference cell, a 0.3 mm thick glass fiber separator was placed between the two EDLC electrodes, and the half cell electrode potentials were measured against a small stripe of the EDLC electrode material contacted by an aluminum wire and positioned at the separator's edge. The open circuit potential of this pseudo reference was determined to be 3.05 V vs. Li/Li^+ and showed a drift stability of $< 20 \text{ mV}$ per day. Almost identical current densities were obtained with both cells during the first cycle.

Pressure Measurement

The set-up used to measure the pressure changes upon constant voltage charging and cycling is sketched in figure 2.

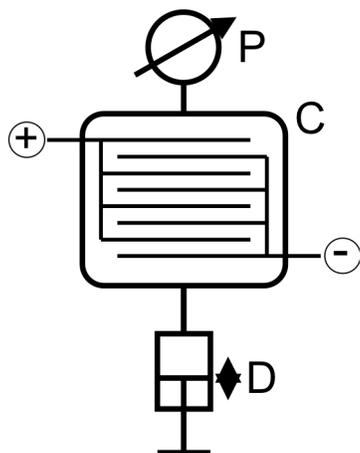


Figure. 2:

Schematic of the set-up used to determine the pressure changes during charging. P: pressure transducer; C: cell case containing the D-size electrode coil; D: motor driven dispenser for periodic injection/ removal of a small liquid volume.

A D-size electrode coil (350 F rated capacitance) was mounted inside a thick-walled plastic (PEEK) case C. Electrical contacts to the outside were made with pure ($> 99.99 \%$) aluminum. Prior to measurement the cell was vacuum dried (24 h , $120 \text{ }^\circ\text{C}$, $< 0.01 \text{ mbar}$), then cooled down in argon atmosphere, and transferred to a glove box. Inside the glove box, the cell was connected to a pressure transducer P ($0 \dots 6 \text{ bar}$) and a purpose made motor driven dispenser D. The assembly was filled with about 40 ml of the argon saturated electrolyte solution, 1 M TEABF_4 in propylene carbonate or acetonitrile, then discharged from the glove box, and finally placed into a temperature chamber held at $25 \text{ }^\circ\text{C} \pm 0.1 \text{ }^\circ\text{C}$.

The initial cell pressure was increased to around 2 bars by adding some electrolyte solution by means of the dispenser. Then, after a settling period of several hours the actual experiment was started by applying a voltage between the two electrodes.

During the experiment the elasticity of the set-up was determined by periodic injection / removal of a tiny electrolyte volume ΔV (about 0.005 ml). The corresponding pressure change ΔP was recorded as an extra hump on the otherwise smooth pressure curve. From the ratio $(\Delta V/\Delta p)_p$ the volume change was calculated according to $V_p = \int_{p_0}^p (\Delta V/\Delta p)_p dp$. In the case of gas evolution, the amount of gas was further computed as $n = (pV)/(RT)$.

Results and Discussion

Dimensional changes

Charge induced dimensional changes of activated carbon based EDLC electrodes in organic electrolyte were reported previously from our laboratory. The dimensional changes were interpreted in terms of ion insertion into graphitic domains of the active electrode material.

Such ion insertion processes giving rise to pseudo capacitance are to be discussed from two points of view. First, such processes will increase the charge capacity (in As/kg) as has been demonstrated by Okamura et al. /9/ with the so called "Nanogate" capacitor introduced in 2002 by JEOL. Further more, the significantly increased voltage window will add to the energy density resulting in capacitors with claimed energy density of > 20 Wh/kg /2/.

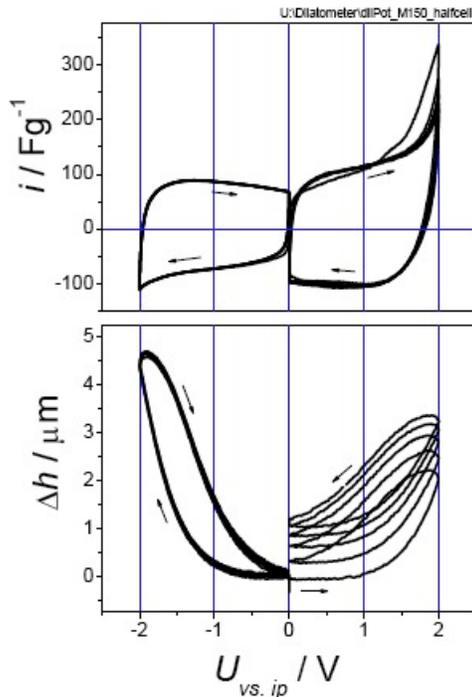


Figure 3: Top: EDLC half cell CVs (1st to 5th cycle) for the extended negative (0 to -2 V) and the extended positive potential range (0 to 2 V). Scan rate: 10 mV/s. Bottom: Simultaneous dilatation record. 1M TEABF₄ in AN, activated carbon.

Secondly, however, such periodic insertion and extraction reactions may eventually result in active material / electrode degradation as is known from batteries. Figure 3 shows the dimensional changes of a commercial EDLC electrode upon potential excursions with a potential window of 4 V measured in a AN based electrolyte. The same charge-specific expansion was observed in the

PC based electrolyte. For highly graphitic materials, in contrast, expansion in PC was found to be much stronger than in AN. This striking difference may be attributed to the different extent of solvent co-intercalation.

Gas evolution

DEMS In addition to ion insertion processes described above other faradaic reaction such as electrolyte or carbon decomposition will have to be considered when the potential window of an EDLC is extended to above 3 V. At around this voltage cyclic voltammograms usually show a clear increase in current during the forward scan with no counterpart during the backscan. Similarly, a significantly increased leakage current is found for the corresponding voltage-hold experiment. In order to clarify the origin of this charge transfer current we have applied in-situ DEMS (Differential Electrochemical Mass Spectroscopy) for the *in situ* identification of volatile reaction products as a function of the electrode potential.

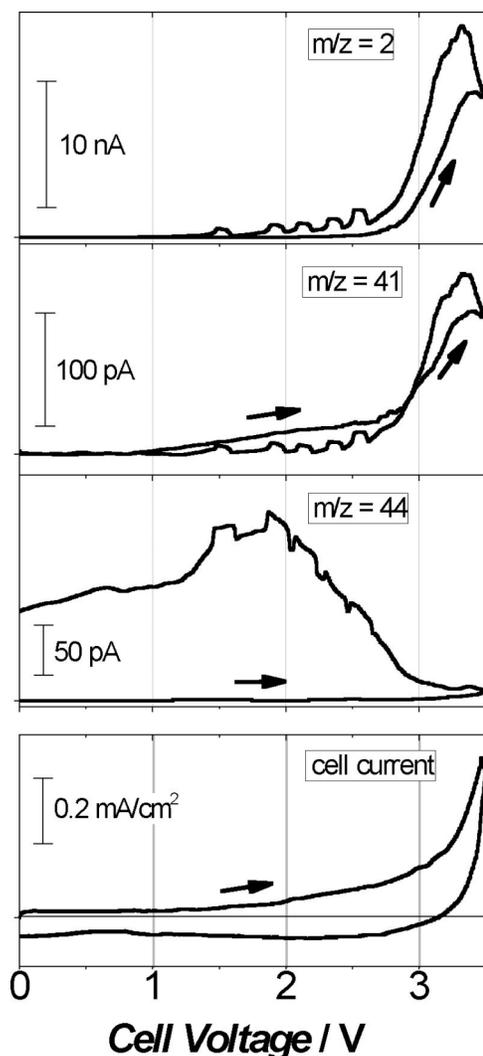


Figure 4: First cycle of the CV (bottom) and simultaneous gas evolution as detected by on-line mass spectroscopy (MSCV). The set-up used is shown in Fig. 1. Scan rate: 0.1 mV/s. 1M TEABF₄ in PC.

Figure 4 shows the cyclic voltammogram together with the MSCVs of H_2 ($m/z = 2$), propene ($m/z = 42$) and CO_2 ($m/z = 44$) for the PC based EDLC electrolyte. The DEMS results clearly demonstrate that at EDLC voltages above 2.8 V volatile products are formed indicating PC decomposition with H_2 and propene generation at the negative electrode and CO_2 generation presumably at the positive electrode. The rather slow response of the CO_2 signal may be explained by CO_2 accumulation in pores with a slow release of the gas.

Pressure measurements A quantitative analysis in terms of the amount of gas evolved is difficult on the basis of the DEMS measurements. If gas is evolved in significant amounts the pressure inside the capacitor will rise, eventually leading to mechanical destruction of the housing (or opening of a safety valve). While the absolute pressure increase is valuable information by itself it depends very much on the design of the cell, in particular on the available "dead volume". Only in combination with a measurement of the compressibility a design independent quantity, the absolute amount of evolved gas, can be determined.

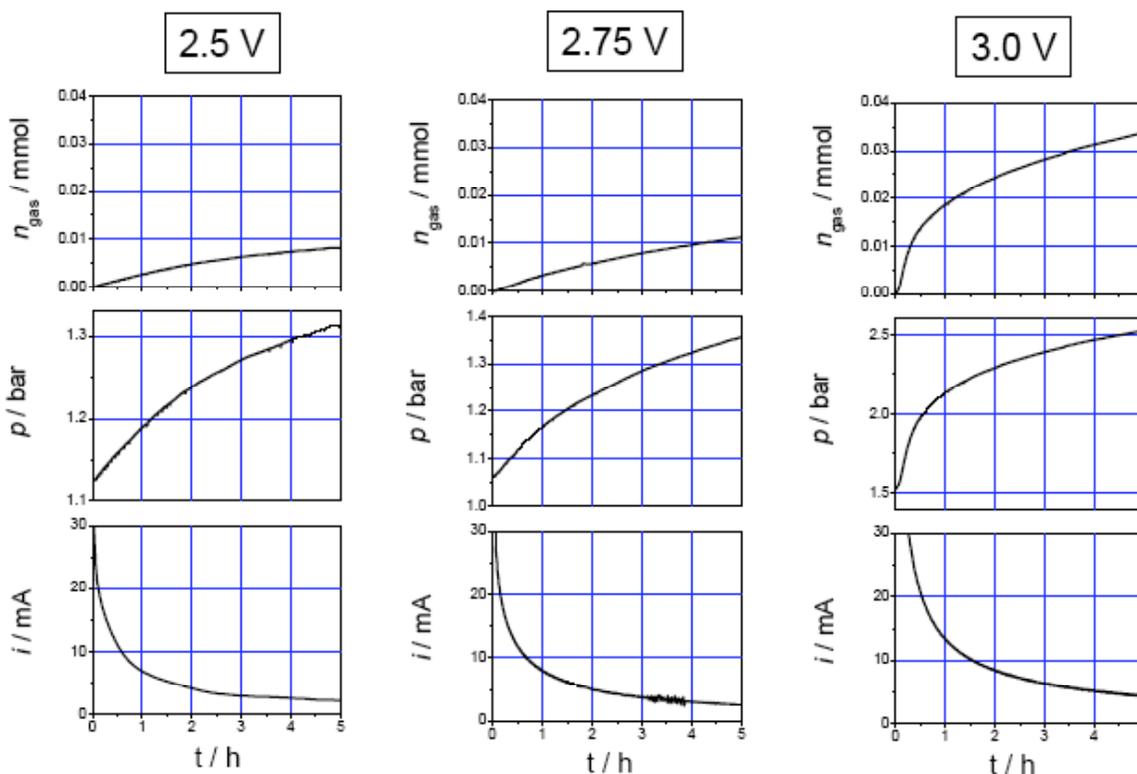


Figure 5: Pressure increase as a function of time monitored at constant cell voltages of 2.5 V, 2.75 V and 3.0 V. 1 M TEABF₄ in PC

Figure 5 shows the evolution of leakage current, pressure and calculated amount of gas as a function of time for a 350 F electrode coil in 1 M TEABF₄ in propylene carbonate. After cycling the cell the scans were stopped at 2.5 V, 2.75 V and 3 V

cell voltage. For several hours the pressure variation was detected at these constant potentials.

From the diagrams in fig. 5 it is evident that already at a cell voltage of 2.5 volts an increase in pressure of about 0.2 bars is observable during 5 hours. At 3.0 V the pressure increase in the same time is about 1 bar. Together with the DEMS results there is no doubt that gaseous degradation products are generated especially at cell voltages > 2.5 V.

When estimating the number of electrons consumed for one gas molecule we obtain about 50 electrons per molecule. This result clearly indicates that there must be additional contributions to the measured leakage current than the pressure increase measured in the above experiment.

Lifetime measurements

In general there are two accepted procedures for EDLC life time estimation. One is the constant current cycling resulting in the maximum number of achievable charge/discharge cycles and the other is the constant voltage hold measurement resulting in the lifetime of the device. In both cases the end of life criteria is a 20 % loss of capacitance and/or a 100 % increase of the internal resistance. All of our measurements so far show that the criteria for the internal resistance is never reached before the capacitance criteria is met. Capacitance fading is definitely the more severe degradation criteria.

The two processes discussed above, ion insertion and solvent electrolysis, may have important consequences for the life time determining measurement procedure. If dimensional changes are an important degradation process this should be reflected in cycle tests. If gas evolution at elevated potentials is most important, this effect should be clearly visible in constant voltage hold experiments. A comparison of both degradation test methods shows that at least during the first few thousand cycles the cycle test is less demanding. However, for some samples a strong increase in degradation may be observed for the cycle test, which is not observed in the constant voltage hold experiments.

Conclusions

In order to increase energy and power of an EDLC an increased cell voltage of > 2.5 V would be very desirable. However, upon increase of the cell voltage the probability and importance of non-capacitive electrode processes such as ion insertion with dimension changes and gas evolution reactions will increase. We have demonstrated that such processes occur. While constant voltage hold experiments appear to be most severe in terms of thermodynamics in some instants cycle experiments reveal degradation caused by dimensional changes. In other words, the two different test methods for the EDLC lifetime address dynamic (cycling) and static (constant voltage) fatigue processes in a different way.

Acknowledgement

Financial support of this work by the Swiss CTI (project # 5807.2 KTS-NM), by Maxwell Technologies SA (Rossens, CH), and by the Swiss National Science Foundation (project # 200020-103715/1) is gratefully acknowledged.

References

- ¹ J.O. Besenhard, H.P. Fritz: *J. Electroanal. Chem* 53, 329 (1974)
- ² H. Nakamura, M. Okamura: 13th International Seminar on Double Layer Capacitors and Hybrid Energy Storage Devices, Deerfield Beach, FL, Florida Educ. Seminars Inc., Boca Raton, FL, p. 215 (2003)
- ³ M. Hahn, O. Barbieri, M. Campana, R. Gallay* and R. Kötz, Proceedings of the 14th International Seminar on Double Layer Capacitors and Hybrid Energy Storage Devices, Dec 6-8, 2004, Deerfield Beach, USA, pp 40-48
- ⁴ M. Hahn, O. Barbieri, F.P. Campana, R. Kötz, R. Gallay, *Appl. Phys. A* (2005), in press
- ⁵ M. Hahn, M. Baertschi, O. Barbieri, J-C. Sauter, R. Kötz, R. Gallay, *Electrochem. Solid-State Letters*, A33 (2004) 7
- ⁶ M. Hahn, A. Würsig, R. Gallay, P. Novák, and R. Kötz, *Electrochem. Commun.* 5, 925-930 (2005).
- ⁷ A. Würsig, Dissertation, ETHZ, Nr. 16059, 2005
- ⁸ R. Imhof, P. Novak, *J. Electrochem. Soc.*, 145 (4) (1998) 1081
- ⁹ M. Takeuchi, K. Koike, T. Maruyama, A. Mogami, M. Okamura, *Electrochemistry* 66, 1311 (1998)