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Short communication

Aging and failure mode of electrochemical double layer capacitors during accelerated constant load tests

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A B S T R A C T

Electrochemical double layer capacitors of the BCAP0350 type (Maxwell Technologies) were tested under constant load conditions at different voltages and temperatures. The aging of the capacitors was monitored during the test in terms of capacitance, internal resistance and leakage current. Aging was significantly accelerated by elevated temperature or increased voltage. Only for extreme conditions at voltages of 3.5 V or temperatures above 70 °C the capacitors failed due to internal pressure build-up. No other failure events such as open circuit or short circuit were detected. Impedance measurements after the tests showed increased high frequency resistance, an increased distributed resistance and most likely an increase in contact resistance between electrode and current collector together with a loss of capacitance. Capacitors aged at elevated voltages (3.3 V) exhibited a tilting of the low frequency component, which implies an increase in the heterogeneity of the electrode surface. This feature was not observed upon aging at elevated temperatures (70 °C).

1. Introduction

Electrochemical double layer capacitors (EDLCs) or supercapacitors penetrated the market during recent years mainly in the area of backup power such as for wind turbines, UPS, the door locks of the Airbus 380 or in the Toyota Prius for backup of the electric breaks. A noteworthy market break through within the automotive industry is still in the future.

In many applications, the voltage of the system is significantly higher than the voltage of a single supercapacitor cell. Therefore, many capacitors have to be connected in series to form a module. For the reliability and safety of a module, it is rather important to know the aging behavior of the capacitor and especially its mode of failure. For the operation of a module, it is of utmost importance to know whether the capacitor end-of-life is characterized by a short circuit or an open circuit state, for instance. For the performance of a module, voltage balancing is a major issue [1] along with possible uneven temperature distribution across the module. In addition, it would be helpful to predict the time and mode of capacitor failure on the basis of performance data.

Approaches for testing supercapacitor lifetime and performance are based on either cyclic, varying, or constant load patterns [2]. For the former, the effect of high currents of varying sign can be evaluated, while for constant voltage tests the current is low and determined by side reactions (leakage current). In both cases, the aging behavior is determined by the loss of capacitance and by the increase of internal resistance. In general, the end-of-life criteria are defined as either 20% capacitance loss or 100% increase in internal resistance.

In this publication, we have investigated the aging of commercial EDLCs under accelerated degradation conditions in order to learn about the way these capacitors fail. The tests were ended either when the capacitor developed an abrupt loss of performance or when one of the standard end-of-life criteria was exceeded.

2. Experimental

The EDLCs tested in this work were provided by Maxwell Technologies, Switzerland, and had a nominal capacitance of 350 F (BCAP0350).

The constant load test set-up was designed for a maximum of 18 capacitors placed in a temperature chamber to ensure isothermal conditions. All capacitors were charged by only one 2-quadrant power supply (ET system electronic GmbH), which was switched to be successively connected to each of these capacitors. This type of arrangement allows testing of many capacitors at different voltages with one high quality power supply only, instead of using one power supply for each capacitor. A 2-quadrant power supply was chosen in order to be able to implement controled discharge steps into the test program.

Initially, the discharged capacitors were charged to the selectable maximum test voltage U_0 with a charge current of 1–5 A

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and held at this constant voltage for a defined time, typically 1 h after the first charge. Afterwards, the capacitors were switched to open circuit. A digital multimeter (Agilent 34970A with the respective relais and data-logger cards) checked the voltage of each capacitor in defined time intervals Δt of typically 30 min. When the voltage U had dropped by a defined value of ΔU_0 (typically between 10 and 50 mV) below the maximum test voltage ($U = U_0 - \Delta U_0$), the respective capacitor was recharged with a predefined constant recharge current I_{re} of typically 50–200 mA.

From the time t_2 needed for the recharge, it was possible to calculate the capacitance $C = I_{re}t_2/(U_0 - U)$ and the average leakage current $I_L = I_{re}t_2/n\Delta t$. From the potential jump dU associated with the switching of the recharge current I_{re}, the internal resistance $R = \mathrm{d}U/I_{re}$ was calculated. Due to the limited data acquisition rate of 1 s the determined resistance is neither comparable to the ESR usually determined at 1 kHz nor to the so-called DC resistance, but falls in between these two values. Similarly the limited data acquisition rate causes some scatter on the capacitance determined from the recharge time, which was in the order of minutes. As a consequence of the above test procedure the capacitors' test voltage is literally not constant, but is allowed to drop by 2% at maximum before the next recharge step. This 1% difference between average voltage and nominal test voltage is neglected.

In particular, three tests were performed with up to five capacitors each: performance at (i) nominal voltage and elevated temperatures up to 85 °C, (ii) room temperature (30 °C) and elevated voltages up to 3.5 V and (iii) both elevated temperature and voltage up to 3.0 V and 70 °C. The parameters recorded during the tests were capacitance, internal resistance and leakage current as functions of time. Electrochemical impedance spectra (EIS) were recorded before and after the aging experiments using an electrochemical workstation (Zahner IM6ex from Zahner-Elektrik, Germany) in the frequency range between 1 kHz and 10 mHz.

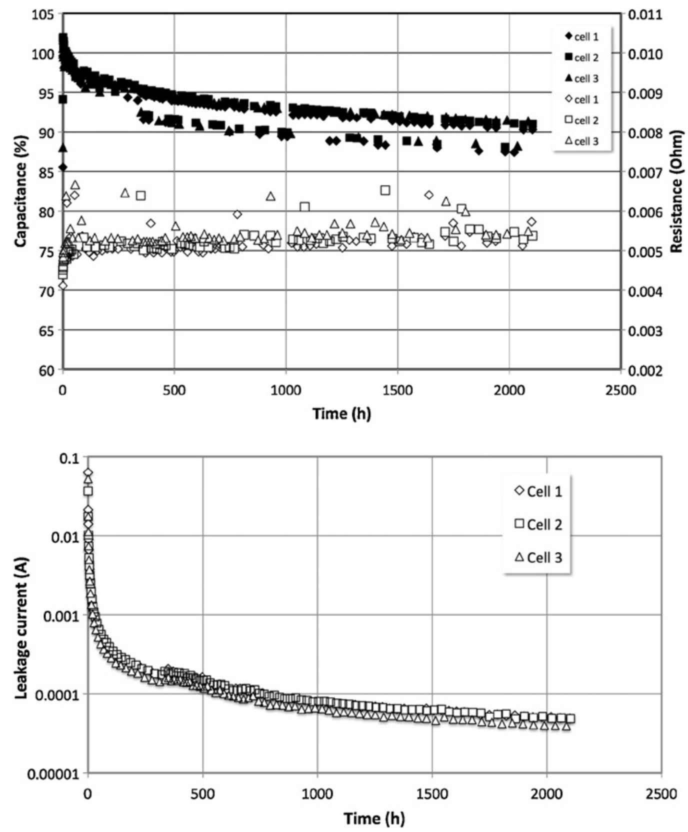

Fig. 1. Relative capacitance (filled symbols) and internal resistance (top) and leakage current (bottom) as a function of time. Load voltage 2.5 V, temperature 30 °C.

3. Results

In the following, the degradation of the 350 F BCAP0350 capacitors is compared in terms of relative capacitance loss (%), internal resistance and leakage current. In addition, for some capacitors, EIS were recorded after the end of test. EIS characterization was always performed after the end of the test with the discharged capacitor at room temperature. Typically, the initial capacitance was between 100% and 115% of the nominal capacitance, which corresponds to up to 400 F for the fresh capacitor. The measured internal resistance R was neither comparable to the 1 kHz resistance nor to the DC resistance usually referred to in data sheets. As a consequence of the measurement procedure, R was found to lie between these two values, being closer to the DC value.

3.1. Reference

2.5 V, 30 °C: The performance of three capacitors was measured under nominal working conditions at 2.5 V cell voltage and 30 °C. Capacitance, internal resistance and leakage current are shown in Fig. 1 as a function of time. For the time period of 2 months, the capacitance dropped by about 10% and the internal resistance increased by about 4%. Two different time domains may be identified in terms of the rate of aging. The high initial rate for $t < 50$ h is followed by a significantly slower aging rate. The data scatter in capacitance data in Fig. 1a is mainly due to the digital resolution of the data acquisition unit.

During the test period of 2 months, the leakage current dropped from 80 mA to 70 μA. After 70 h, a value of 0.4 mA was observed, which is in good agreement with the value given in the data sheet. While the behavior of capacitance and internal resistance is well expected, the results for the leakage current are very encouraging. For applications in which the capacitor has a backup function and needs to be fully charged during a long time, the leakage current corresponding to the necessary trickle charge current becomes rather small. After 2 months, the current is only 70 μA which corresponds to 200 nA F^{-1}. In other words, self-discharge under constant voltage conditions decreases with time and eventually adopts very small values.

Fig. 2 shows the electrochemical impedance spectra (EIS) before (dashed lines) and after the constant voltage test for these nominal conditions. In agreement with the data recorded online, there are only small differences between the spectra. Noteworthy is the absence of a semi-circle in the EIS at high frequencies which indicates good contact between activated carbon and current collector and between carbon particles. The high frequency resistance of 0.35–0.4 mΩ is smaller than the value determined during the load test via current interruption. However, the low frequency value between 0.5 and 0.6 mΩ agrees quite well with the data obtained during the load test.

The deviation of the low frequency tail of the EIS from the ideal capacitive behavior characterized by a vertical line has been observed previously for EDLCs and other electrochemical systems, and is usually described by a constant phase element (CPE). The presence of a CPE may arise from surface roughness [3], non-uniformity of the double layer thickness [4], a distribution in microscopic charge transfer rates or adsorption processes [5]. Pajkossy [6] and Kerner [7] have shown experimentally that even surface roughness on an atomic scale can produce such CPE behavior.

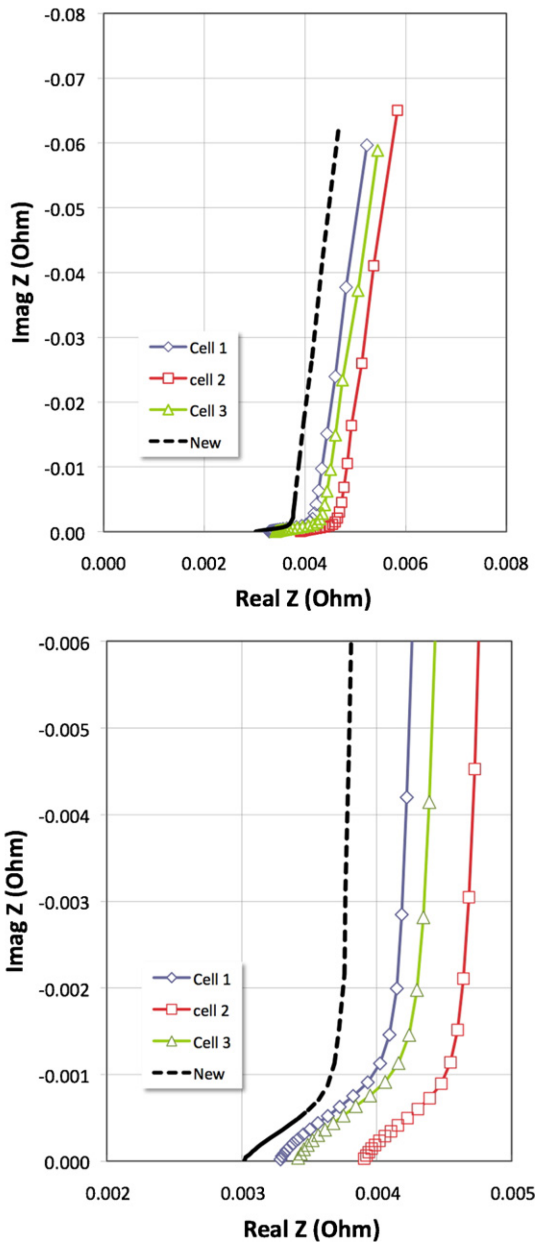

Fig. 2. Nyquist plots of the three cells of Fig. 1 after the end of test. The dashed line represents a new cell. The bottom figure shows an enlarged segment.

3.2. Effect of voltage

3.3 V at 30 °C: In order to establish the influence of increased capacitor voltage on the aging, five capacitors were tested at a voltage of 3.3 V at 30 °C. The end-of-life criterion for the capacitance of the five cells was reached after 100–200 h. The rate of capacitance loss varied among the cells, but the respective absolute capacitance remained within the 10% uncertainty given by the manufacturer. Similarly, the internal resistance increased from about 7–10 mΩ after 650 h, which is clearly below the end-of-life criterion. The respective leakage current decreased from 500 mA to about 1 mA. After 650 h, one of the five cells (cell 3) exhibited a drastically increasing leakage current. This event can be correlated to the opening of the cell at the safety valve (see below).

The waves in the leakage current measured at 30 °C reflect day time temperature variations exceeding 30 °C which could not be compensated by the oven (no cooling involved). The lack of data for times between 340 and 400 h in Fig. 3 is due to a failure of the data acquisition unit during a week end.

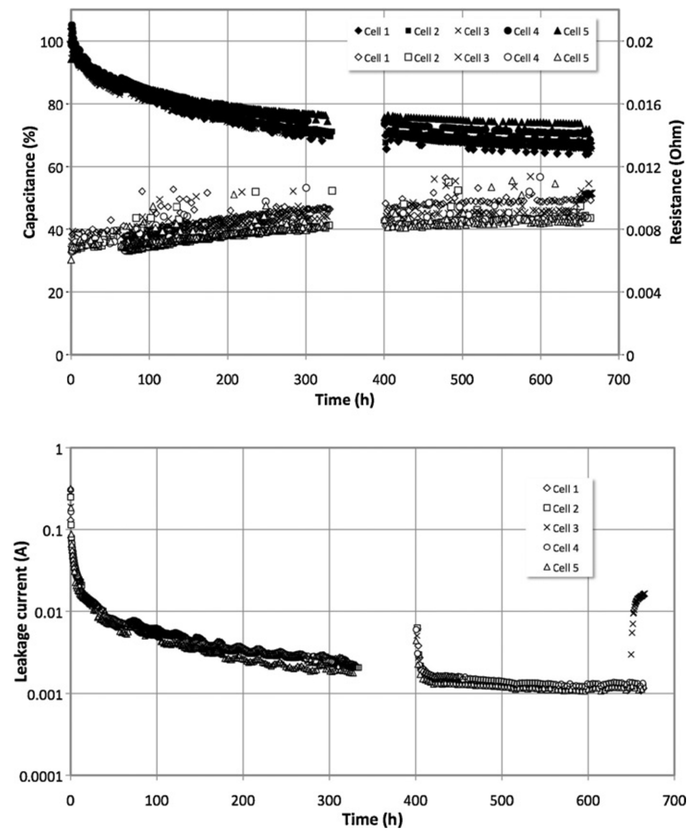

Fig. 3. Relative capacitance (filled symbols) and internal resistance (top) and leakage current (bottom) as a function of time for five capacitor cells. Load voltage 3.3 V, temperature 30 °C.

3.5 V at 30 °C: Of the five cells tested at 3.5 V and 30 °C, cells 1 and 3 opened at the safety valve after about 150 h and the respective leakage current increased significantly (Fig. 4). The capacitance loss of 20% was achieved after 50–150 h, depending on the cell number and initial capacitance. During the time of the experiment (500 h), the internal resistance increased from 9 to 16 mΩ, which is still less than the end-of-life criterion.

3.3. Effect of temperature

2.5 V at 70 °C: Aging of capacitor cells was also affected by the operation temperature, which is given in the data sheets to fall between −40 and +65 °C. The constant load test performed at the nominal voltage of 2.5 V and an elevated temperature of 70 °C showed no abrupt or catastrophic failure of the capacitors. After 1600 h, the capacitance was still above the 80% end-of-life limit and was decreasing slowly. Similarly, the internal resistance increased only by about 50%. The leakage current dropped to 400 μA for all cells with the exception of cell 3 which had twice this leakage current.

After 1440 h, the decrease in leakage current observed in Fig. 5 is due to a decreased operation temperature, which was reduced to room temperature at this time.

2.5 V at 85 °C: The same experiment was performed at 85 °C. The capacitors aged similarly to the tests at 70 °C, with a capacitance loss of 20% achieved between 250 and 500 h. The leakage current also decreased smoothly to about 1.5 mA after 500 h. The increase in resistance was in the order of 90%.

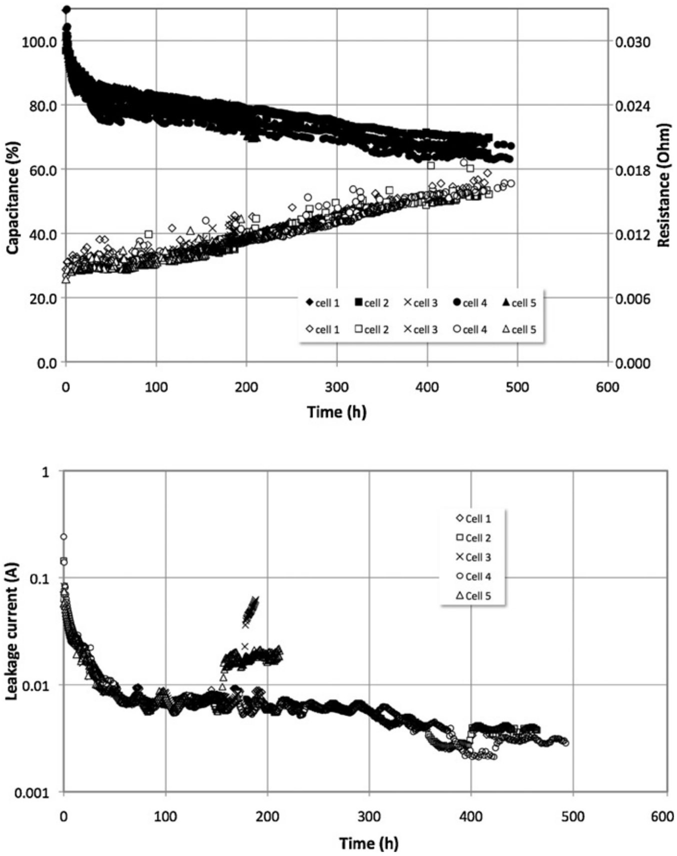

Fig. 4. Relative capacitance (filled symbols) and internal resistance (top) and leakage current (bottom) as a function of time for five capacitor cells. Load voltage 3.5 V, temperature 30 °C.

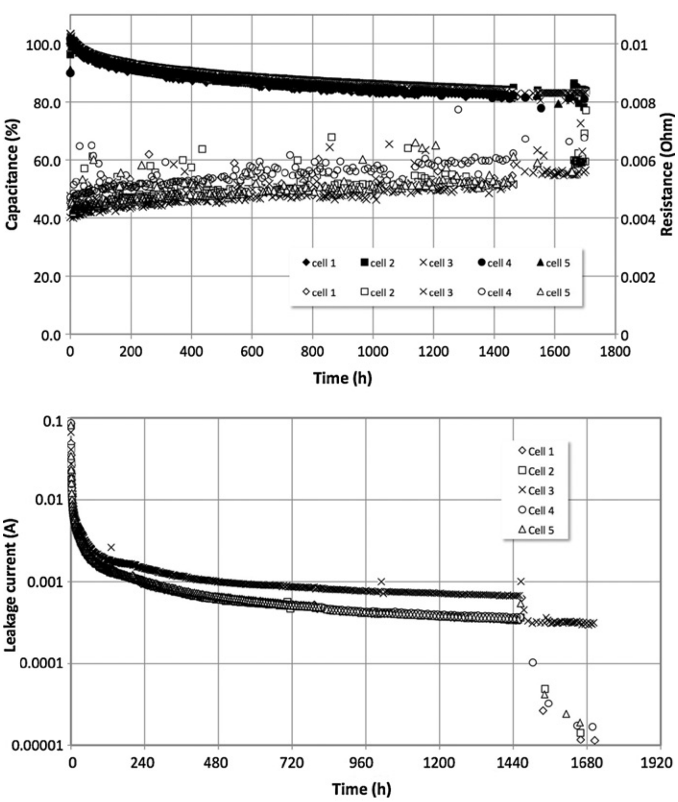

Fig. 5. Relative capacitance (filled symbols) and internal resistance (top) and leakage current (bottom) as a function of load time for five capacitor cells. Load voltage 2.5 V, temperature 70 °C.

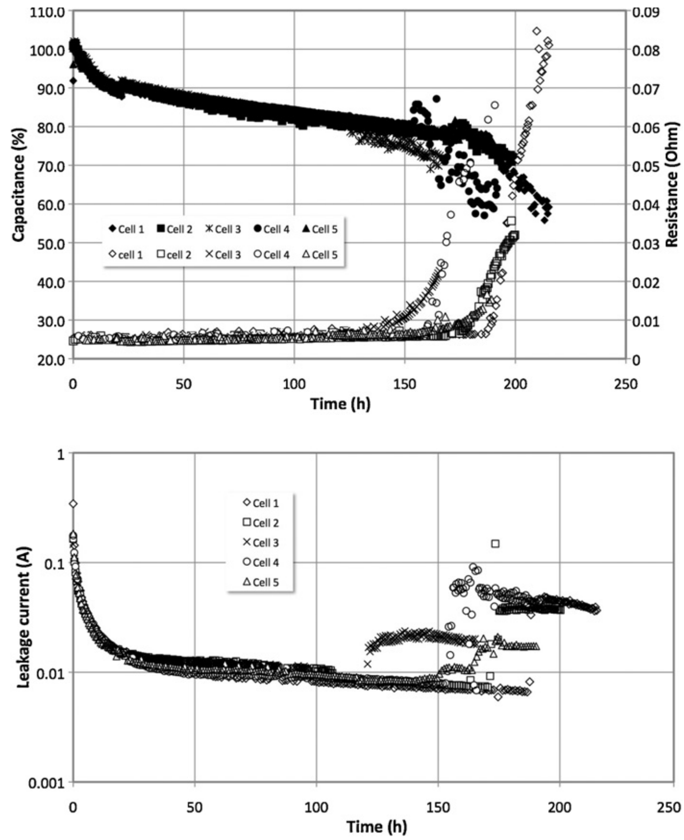

Fig. 6. Relative capacitance (filled symbols) and internal resistance (top) and leakage current (bottom) as a function of time for five capacitor cells. Load voltage 3.0 V, temperature 70 °C.

3.4. Combined effect of temperature and voltage

3.0 V at 70 °C: In one experimental series, both the voltage and the temperature were set above the respective nominal values. All of the five capacitors failed abruptly after different times by overpressure leading to an opening of the safety valve. The first event occurred after 120 h (cell 4) while the last capacitor opened after 185 h (cell 1). Simultaneously to the opening of the valve, both the rate of capacitance loss and the internal resistance increased notably. In agreement with the observations made above, opening of the safety valve causes a rapid increase of the leakage current by up to one order of magnitude (Fig. 6).

3.5. Impedance measurements

The impedance spectra of the capacitors tested at 3.3 V and 30 °C are reproduced in Fig. 7 after 650 h and a capacitance loss of 30%. The effect of aging at increased voltage is visualized by the increased equivalent series resistance (ESR) from 3 to about 5 mΩ. In addition, a clear decrease of the slope in the low frequency branch is observed, which could be interpreted in terms of a parasitic side/parallel reaction (beginning of a semi-circle) or as a decreased CPE, indicating inhomogeneities. The data obtained for all five capacitors are very similar.

The effect of temperature on aging is also shown in Fig. 7, using the impedance spectra of the capacitors tested at 2.5 V and 70 °C recorded after 1700 h and a capacitance loss of 20%. Again, an increase of the ESR is observed, from 3 to 4 mΩ. Also, the slope of the low frequency part has decreased, albeit to a lesser extent than for the spectra of capacitors aged at elevated voltage. For aging at both elevated voltage and temperature, the 45° region

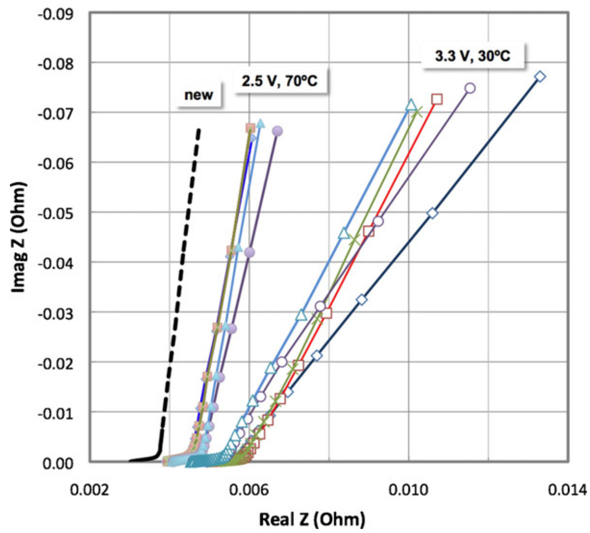

Fig. 7. Nyquist plots of the 5 capacitors after the load test at 3.3 V and 30 °C and after the load test at 2.5 V and 70 °C. The dashed curve represents a new capacitor.

of the Nyquist plot, representing the distributed resistance within the porous electrodes is extended compared to the new capacitor.

The impedance spectra of the capacitors after opening of the safety valve at 3.0 V and 70 °C look significantly different (Fig. 8). Obviously, failure by can opening has irreproducible effects on the EIS spectra which may depend on the time the capacitors were used after opening or on the magnitude of the leakage current which was not the same for the different capacitors (see Fig. 6). All capacitors show increased ESR between 25 and 700 mΩ. The two capacitors with the highest increase in ESR show clear semi-circles at higher frequencies, which could be due to an increased contact resistance between electrode and current collector, possibly due to current collector oxidation.

4. Discussion

For any demanding application of electrochemical double layer capacitors the mode of capacitor failure is of utmost importance to guarantee the safety of the circuit. The failure of the passive element should be predictable, not dramatic and it should occur during a finite time – not abruptly. For the design of a practical application, it is important to note that most of the capacitors

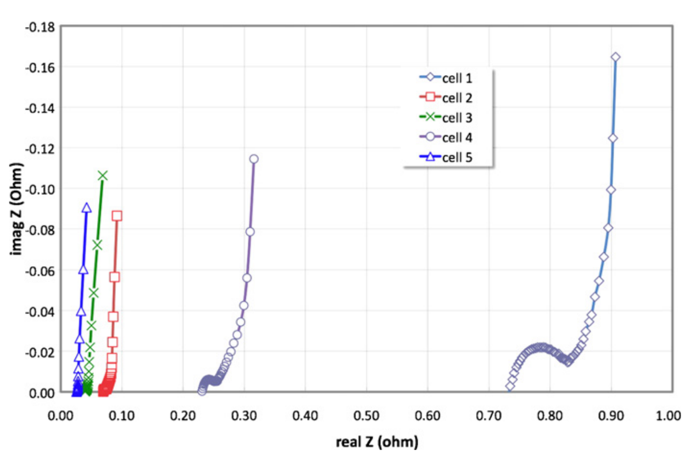

Fig. 8. Nyquist plots of the 5 capacitors after the load test at 3.0 V and 70 °C.

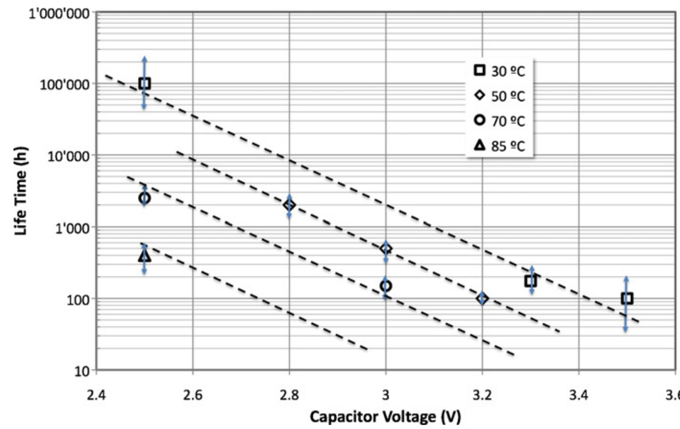

Fig. 9. Life time of tested capacitors (20% loss of capacitance) as a function of load voltage for different temperatures. The arrows at each data point indicate the variation of the 5 capacitors tested. The dashed lines are guidelines only.

have initial capacitances well above (typically 10%) the nominal capacitance of 350 F. Therefore, all capacitance values are given on a relative scale with the initial capacitance as the 100% starting value.

None of the forced temperature and voltage conditions caused a sudden end of capacitor life by short circuit or open circuit. As expected, forced load conditions made the capacitors age faster with a factor of about 2 for 100 mV above nominal voltage or a factor of 2 for 10 °C increase in temperature. This is reflected in Fig. 9, where the time to 20% capacitance loss based on real (not nominal) capacitance is plotted for the performed experiments at various voltages and temperatures. The data point at 2.5 V and 30 °C was extrapolated on a logarithmic time scale. These results are in good agreement with previous measurements based on leakage current [8,9]. However, as is evident from Fig. 5b, the amount of leakage current is not necessarily a good measure for the capacitance degradation. In Fig. 5b the leakage current of cell 3 is higher than that of the other cells although the rate of aging is identical for all cells. While the reduction of the temperature to 30 °C at the end of the test causes a significant reduction of the leakage current of most of the cells by more than an order of magnitude, the leakage current of cell 3 is only reduced by a factor of two.

For the experiment performed at 3.0 V and 70 °C the end-of-life by 20% capacitance loss was reached before the capacitors opened at the safety valve. However, opening of the safety valve does not result in an immediate failure of the respective capacitor. The main observation is an abrupt increase in leakage current, an accelerated increase in internal resistance and an accelerated decrease of capacitance. Therefore, it can be expected that the respective circuit with the failing capacitor can function for a certain time even after can opening. Our results show that there is no way to predict the opening of the gas discharge safety valve.

The event can only be detected immediately by the increased leakage current. It should not be neglected that the electrolyte which leaks out of the capacitor is harmful, but unwanted contact with operators can be prevented by a reasonable housing of the capacitor module. It should be kept in mind that can opening always occurs significantly later than the end-of-life criterion concerning capacitance has been met.

The reason for increased leakage current upon safety valve opening is most probably due to contact with humidity and oxygen from environmental air. Both components will result in parasitic side reactions on the anode and/or cathode. Simultaneously, the capacitance decreases slightly due to electrolyte loss/evaporation through the opening. However, there will be enough electrolyte

Fig. 10. A BCAP0350 capacitor (cell 2) tested at 3.0 V and 70 °C after safety valve opening after 200 h.

soaked in the active material and in the separator within the electrode coil to continue functioning of the capacitor within the electric circuit. Indeed, the electrolyte loss can be monitored by the weight loss of the capacitor. For the tests at 70 °C and 3.0 V the electrolyte loss after the test was determined to be in the order of 13 g for a total weight of about 56 g for the pristine capacitor. A picture of the opened capacitor is shown in Fig. 10.

The impedance spectra recorded after the load tests confirm the direct results of the online determination of capacitance loss and resistance increase. There is a slight difference between the EIS spectra recorded for the capacitors tested at 3.3 V and 30 °C (effect of voltage, Fig. 7) and those tested at 2.5 V and 70 °C (effect of temperature, Fig. 7). While the increase in high frequency ESR from 3 to 4.5 mΩ for the test at 3.3 V and to 4 mΩ for the test at 70 °C are comparable, the slope of the low frequency capacitive part is very different. There is almost no change in slope of the low frequency line for the test performed at nominal voltage of 2.5 V and a temperature of 70 °C, while for the test at nominal temperature of 30 °C and a voltage of 3.3 V the slope decreases from 89.3 to 84.3. Such a decrease may be interpreted as an increasing CPE contribution due to increase in inhomogeneity at the electrode/electrolyte interface [3–7].

After can opening, the EIS typically show a high frequency semi-circle (Fig. 8) which can be assigned to a contact resistance. It is likely that rupture of the safety valve leads to the accumulation of humidity and oxygen in the capacitor, which may result in passivation of the current collector. If some aluminum oxide is formed on the current collector, a semi-circle will be visible in EIS [10,11]. Similarly, during the accelerated aging test, the active electrode part may be delaminated from the current collector [12] giving rise to a semi-circle in the EIS. Unfortunately, it is not clear whether the appearance of a semi-circle in the EIS is a consequence of the can opening or is only due to the aging before can opening.

5. Conclusions

Commercial electrochemical double layer capacitors based on activated carbon and an acetonitrile based organic electrolyte were tested under constant voltage conditions at various temperatures and cell voltages. The main observations are summarized as follows.

All capacitors showed an initial capacitance significantly larger than the nominal capacitance (up to 400 F compared to 350 F) which falls within the 20% limit stated in the data sheet.

The leakage current during the constant voltage load test decreased steadily with time, reaching values in the range of nA F^{-1} which is significantly lower than the data given after e.g. 72 h in some data sheets. This is of significant consequence for EDLC applications where the capacitor has to be trickle charged over a long time.

The leakage current is not necessarily a measure for the rate of degradation as was observed for the test at 2.5 V and 70 °C (Fig. 5).

The 80% capacitance loss end-of-life criterion is always reached faster than the criterion for the doubling of the internal resistance.

The failure of all capacitors occurred via can opening at the pre-designed safety valve as a consequence of increased internal pressure. Can opening was always preceded by the capacitor end-of-life in terms of 20% capacitance loss.

The capacitors can be operated at 70 °C and nominal voltage for about 1600 h before the capacitance drops to 80% of the initial value.

As a thumb rule, a factor of 2 can be assumed for the increase in aging rate for an increase in voltage of 0.1 V or an increase in temperature by 10 °C. It seems that the voltage increase leads to a more significant pressure build-up than an increased temperature.

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References

[1] R. Kötz, J.-C. Sauter, P. Ruch, P. Dietrich, F.N. Büchi, P.A. Magne, P. Varenne, J. Power Sources 174 (2007) 264–271.
[2] FreedomCAR Ultracapacitor Test Manual, DOE/NE-ID-11173, Revision 0, September 21, 2004.
[3] R. de Levie, Electrochim. Acta 10 (2) (1965) 113–130.
[4] M.F. Mathias, O. Haas, J. Phys. Chem. 97 (36) (1993) 9217–9225.
[5] B.E. Conway, Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications, Kluwer Academic/Plenum Publishers, New York, 1999, ISBN 0-306-45736-9.
[6] T. Pajkossy, Solid State Ionics 176 (25–28) (2005) 1997–2003.
[7] Z. Kerner, T. Pajkossy, Electrochim. Acta 46 (2/3) (2000) 207–211.
[8] R. Kötz, M. Hahn, R. Gallay, J. Power Sources 154 (2006) 550–555.
[9] J.R. Miller, S. Butler, in: V. Gupta (Ed.), Recent Advances in Supercapacitors, Transworld Research Network, India, 2006, pp. 1–16.
[10] C.-W. Huang, H. Teng, J. Electrochem. Soc. 155 (10) (2008) A739–A744.
[11] M. Gaberscek, J. Moskon, B. Erjavec, R. Dominko, J. Jamnik, Electrochem. Solid-State Lett. 11 (10) (2008) A170–A174.
[12] S. Ishimoto, Y. Asakawa, M. Shinya, K. Naoi, J. Electrochem. Soc. 156 (7) (2009) A563–A571.