

Short communication

Temperature behavior and impedance fundamentals of supercapacitors

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Abstract

Electrochemical impedance spectroscopy (EIS) is one of the most important analytical tools for characterization of electrochemical double-layer capacitors (EDLC). As an example, we have characterized a commercial capacitor (BCAP0350 Maxwell Technologies) by EIS, and we will discuss the typical performance of an EDLC compared to an ideal capacitor.

EIS was used to determine internal resistance and capacitance of the same capacitor as a function of temperature and as a function of time during constant voltage tests. In addition, the effect of the electrolyte on the temperature behavior was investigated. While the capacitance is a very weak function of temperature, the ESR increases significantly with reduced temperature. Temperature effects are much more pronounced for propylene carbonate (PC) than for acetonitrile (AN)-based electrolytes. From the data obtained at various temperatures and voltages, we could determine acceleration factors for the degradation. On the basis of an Arrhenius plot of the leakage current measured during load life tests at capacitor voltages between 2.5 V and 3.0 V and temperatures between -40°C and $+70^{\circ}\text{C}$, we determined acceleration factors for capacitor degradation of about 2 for a temperature increase of 10°C and also a factor of about 2 for a potential increase of 0.1 V.

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1. Introduction

Electrochemical impedance spectroscopy (EIS) is one of the most frequently used analytical tools for the characterization of supercapacitors. The fundamentals of such EIS measurements have been described in several publications in general and also for electrochemical double-layer capacitors (EDLC) applications in particular [1–6]. In the first part of this paper, we will demonstrate which useful data can be obtained by an EIS analysis of a commercial 350 F capacitor based on organic electrolyte and activated carbon (AC).

EDLCs are well known for their good power performance and extreme stability in terms of cycle life [5]. However, similar to batteries, the rather limited temperature range for EDLC applications is considered to be disadvantageous from the consumer point of view. Today, manufacturers typically specify an operation temperature range from -40°C to $+70^{\circ}\text{C}$ for capacitors based on acetonitrile (AN) or propylene carbonate. While low-temperature performance of EDLC is rather good when using AN as electrolyte the high vapor pressure of AN at tem-

peratures above $+70^{\circ}\text{C}$ is a significant drawback [7]. Many applications require high temperatures and as a consequence, the utilization of EDLCs in such applications would require cooling means.

In addition, temperature aspects of supercapacitors play an important role for degradation and lifetime estimations and for the optimization of supercapacitor performance with respect to a specific application. The lifetime of EDLCs will be reduced at elevated temperatures, and it is important to provide data, which allow estimating the lifetime for conditions that deviate from the recommended specifications, i.e. nominal voltage and ambient temperature. Such data can be obtained from a procedure known, e.g., from aluminum electrolytic capacitors [8]. The procedure consists in measuring the leakage current under various temperature and voltage conditions and plotting the data in an Arrhenius-type plot. From such a plot, the activation energy of the electrochemical processes leading to the overall leakage current can be derived.

It is not the intention of the authors to compare different technologies, such as those of Maxwell Technologies SA with those of other suppliers. The device of Maxwell Technologies was taken as exemplary to demonstrate some fundamental aspects of EDLCs. Other devices may perform differently.

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2. Experimental

Impedance measurements were performed with an electrochemical workstation IM6 (Zahner-Elektrok, Germany), sometimes, in combination with a 40 A power potentiostat PP240. In order to eliminate any resistive contributions from contacts or leads, the four-point probe technique was employed.

Some measurements were performed with coin-type laboratory cells (0.8 cm² active area) with titanium current collectors and standard cell components: 150 μm thick activated carbon electrodes and a 60 μm thick paper separators. When using aprotic solvents, the cells were assembled inside a glove box (argon, < 10 ppm water). Battery grade electrolyte solutions (1 M Et₄NBF₄ in acetonitrile and in propylene carbonate, respectively) were provided by Honeywell Specialties Chemicals, Germany. Sulfuric acid (98%, analytical grade, Aldrich) and deionized water were used to prepare the aqueous electrolyte solution.

3. Results and discussion

3.1. Impedance of EDLC

Electrochemical impedance is usually measured by applying an ac potential to an electrochemical cell and measuring the current through the cell. For a sinusoidal potential excitation, the response to this potential is an ac current signal, containing the excitation frequency and its harmonics. This current signal can be analyzed as a sum of sinusoidal functions. Electrochemical impedance is normally measured using a small excitation signal. This is done so that the cell's response is pseudo-linear. In a linear (or pseudo-linear) system, the response to a sinusoidal potential E will be a sinusoid current I at the same frequency but shifted in phase. The resulting impedance Z is a complex number:

$$Z = \frac{E}{I} = Z_0 \exp(j\phi) = Z_0(\cos\phi + j \sin\phi)$$

and is often represented in the so-called Nyquist plot, where the imaginary part of the impedance is plotted as a function of the real part. For an ideal capacitor, the Nyquist plot would show a vertical line only coinciding with the vertical axis with the real part of Z being 0. The respective impedance is $Z = 1/(j\omega C)$. For an ideal capacitor connected in series with a resistor (with resistance R), the vertical line in the Nyquist plot is shifted on the vertical axis by the amount of R .

In practice, EDLCs are often described by such an RC series connection. However, R and $C = 1/(\omega \text{Im} Z)$ now depend on frequency; therefore, the impedance's real part is referred to as equivalent series resistance (ESR).

Fig. 1 shows the measured impedance spectrum of a commercial 350 F capacitor (BCAP0350 Maxwell Technologies) recorded at room temperature (RT).

The ESR decreases towards higher frequencies and intersects the real axis ($\text{Im} Z = 0$) at about 0.75 mΩ. At such high frequencies, the EDLC behaves almost like a simple resistor (neglecting some minor inductive contributions). The region with 45° slope at intermediate frequencies (100–1 Hz) can be assigned to the

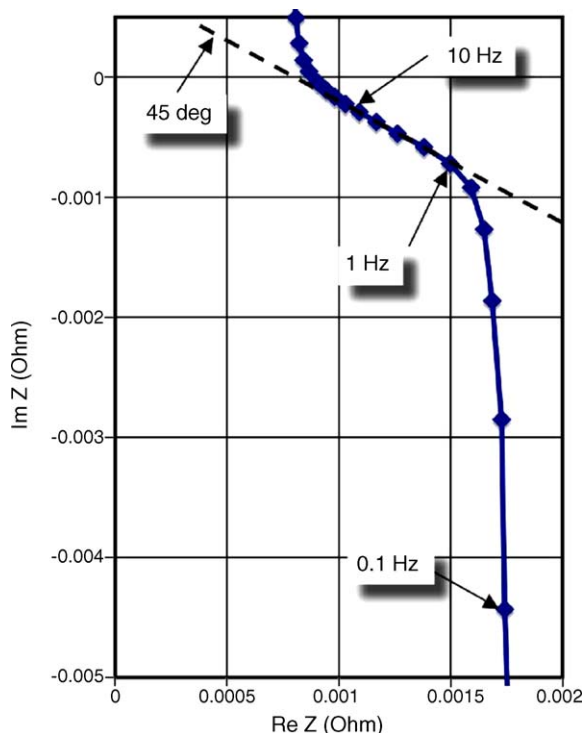


Fig. 1. Nyquist plot of the impedance of a BCAP0350 measured at 2.5 V. Measurement frequencies are indicated at the curve.

behavior of the porous structure and is often called the distributed resistance. Finally, for low frequencies (<1 Hz), the spectrum approaches a vertical line with a real part of the impedance of about 1.8 mΩ. In this 'dc-domain', the DLC behaves almost like an ideal RC series connection with R and C being no longer frequency-dependent. For convenience, the EDLC performance is often given by only three parameters: the high-frequency ESR, the low-frequency (dc) ESR and the (low-frequency) capacitance.

The deviation of the EDLC behavior from that of an ideal capacitor is visualized in Fig. 2, where the capacitance $C = 1/(\omega \text{Im} Z)$ and the ESR are plotted as a function of frequency.

The capacitance of an EDLC decreases with increasing frequency. The decrease occurs in Fig. 2 for the BCAP0350 at about 1 Hz. Simultaneously, the ESR increases with decreasing frequency. While at high frequencies, the ESR is lowest (0.8 mΩ at 1 kHz), it doubles towards low frequencies. At frequencies above 100 Hz, an EDLC behaves more like an ohmic resistor than like a capacitor.

Finally, it is well possible to calculate the Ragone plot from measured impedance data as was described in detail by Christen et al. [9]. As can be seen in Fig. 3, the BCAP0350 capacitor has a maximum energy of 5 Wh kg⁻¹ and can achieve a maximum power of about 20 kW kg⁻¹. The respective time constants are also plotted in Fig. 3. The typical working range of this capacitor falls around 1 s.

3.1.1. Temperature effects

As demonstrated above, EIS is a well-suited technique to characterize capacitor performance. We, therefore, measured

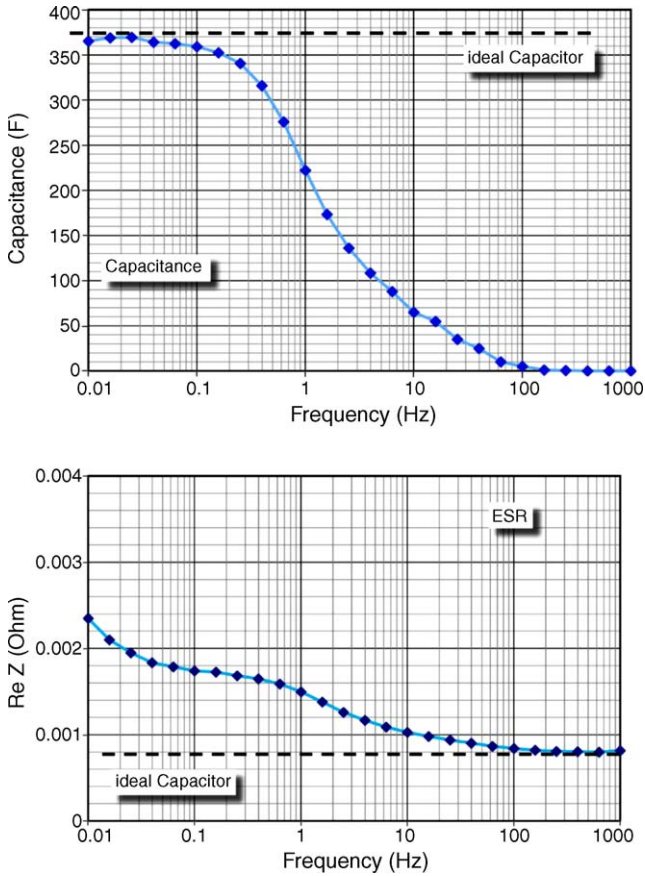


Fig. 2. Capacitance (top) and ESR (bottom) of a BCAP0350 as a function of frequency. The dashed line indicates the behavior of an ideal capacitor.

the EIS of a BCAP0350 at various temperatures in order to determine the dependence of the characteristic parameters on temperature. Fig. 4 shows the impedance plots between -40°C and $+70^{\circ}\text{C}$ for a BCAP0350.

From Fig. 4, it is obvious that decreased temperatures increase the ESR measured at high frequency and also the 45° region associated with the distributed resistance. The explicit results are plotted in Figs. 5 and 6 for the capacitance and the resistance, respectively.

While the dependence of the capacitance on temperature is rather weak (see Fig. 5), a significant increase of resistance with

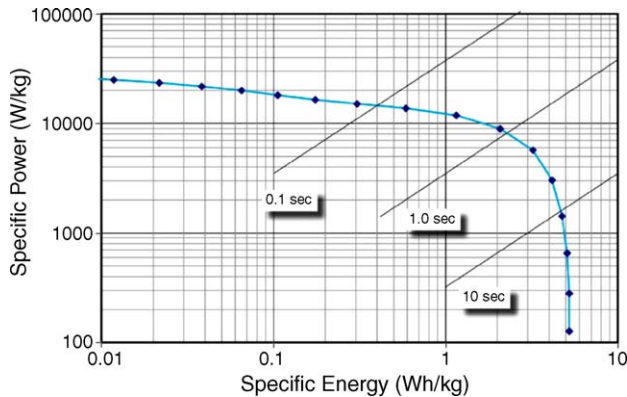


Fig. 3. Ragone plot calculated from the impedance data of Fig. 1.

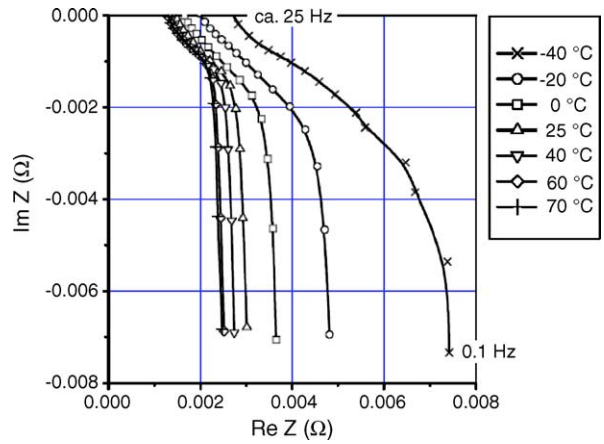


Fig. 4. Nyquist plots of the impedance data measured for a BCAP0350 as a function of temperature.

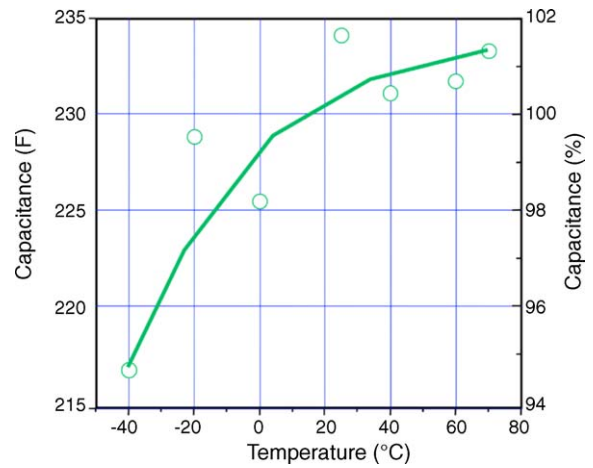


Fig. 5. Capacitance as function of temperature deduced from the data in Fig. 4. Capacitance was determined from impedance spectra at 0.1 Hz and at a cell voltage of $U=0.0\text{ V}$.

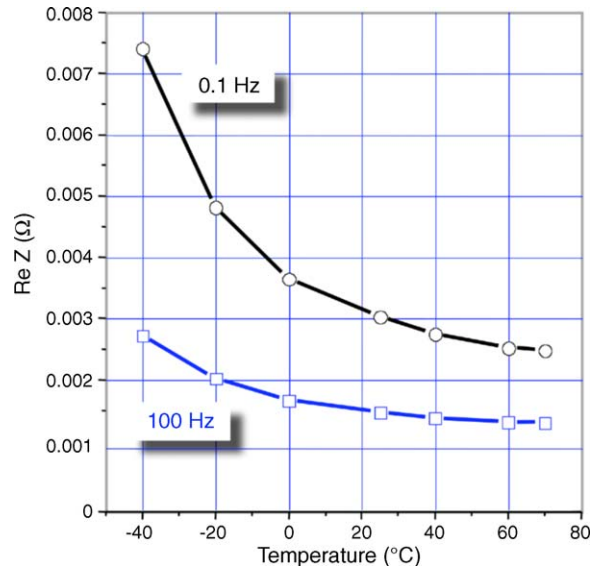


Fig. 6. ESR measured at two different frequencies (100 Hz and 0.1 Hz) as function of temperature. Cell voltage $U=0.0\text{ V}$.

decreasing temperature is observed in Fig. 6. The capacitance measured at 0.1 Hz varies by roughly 6% only within the temperature range from -40°C to $+70^{\circ}\text{C}$. It is possible that the measurement frequency of 0.1 Hz is still too high for very slow processes occurring at low temperatures and that the variation of the capacitance at lower frequency would be reduced further.

The ESR measured at 100 Hz, on the other hand, increases at the lowest temperature by 70% from $1.5\text{ m}\Omega$ to $2.6\text{ m}\Omega$. However, the resistance measured at 0.1 Hz increases by 200% from $2.5\text{ m}\Omega$ to $7.5\text{ m}\Omega$. As described before, the low-frequency resistance is mainly dominated by the distributed part (45° region) and thus, it can be concluded that the lower temperature significantly alters the current flow in the porous structure. Similar results for the temperature dependent capacitance and resistance were obtained by Schwake [10].

3.1.2. Acetonitrile versus propylene carbonate

With respect to safety aspects propylene carbonate (PC) may have some advantages as solvent in EDLCs as compared to acetonitrile. Therefore, we investigated the temperature behavior of these two electrolytes in laboratory capacitor cells. The comparison of both electrolytes is plotted in Figs. 7 and 8 in terms of the cell capacitance and the cell resistance. Note that the employed electrode material was different from that used in the BCAP0350 device.

It is obvious that the use of PC in an EDLC introduces some loss in performance [10]. A significant increase of the cell resistance measured at 0.01 Hz with decreasing temperature is observed for PC. Such an increased resistance will have significant impact on the power capability of the EDLC at low temperatures. In addition, a significant decrease of capacitance is observed in PC, which is almost absent for AN. It cannot be excluded that similar to the results presented in Fig. 5, the temperature dependence of the capacitance will be reduced at lower measurement frequencies. The

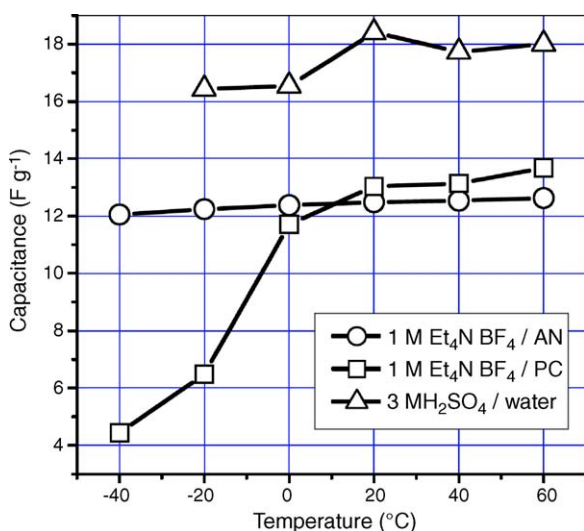


Fig. 7. Capacitance as a function of temperature measured at 0.1 Hz and $U=0.0\text{ V}$. Measurements performed in coin-type laboratory cell. Electrolytes: $3\text{ mol l}^{-1}\text{ H}_2\text{SO}_4$ (triangles); $1\text{ mol l}^{-1}\text{ Et}_4\text{NBF}_4$ in AN (circles); $1\text{ mol l}^{-1}\text{ Et}_4\text{NBF}_4$ in PC (squares).

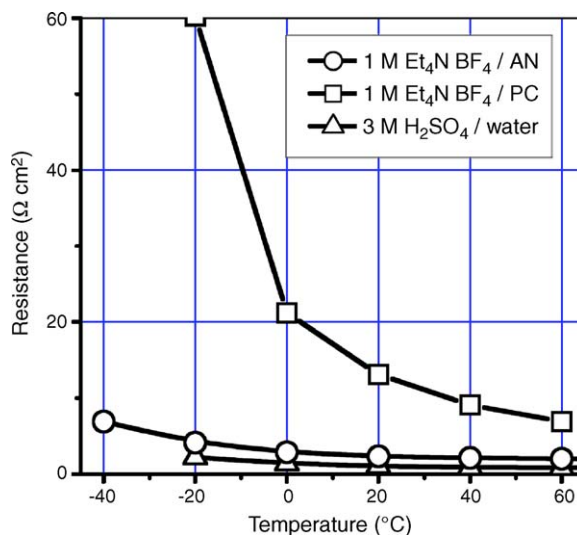


Fig. 8. ESR measured at 0.01 Hz and $U=0.0\text{ V}$ as a function of temperature in different electrolyte solutions: $3\text{ mol l}^{-1}\text{ H}_2\text{SO}_4$ (triangles); $1\text{ mol l}^{-1}\text{ Et}_4\text{NBF}_4$ in AN (circles); $1\text{ mol l}^{-1}\text{ Et}_4\text{NBF}_4$ in PC (squares). Measurements performed in coin-type laboratory cell.

capacitance measured in AN and H_2SO_4 shows only a minor temperature effect. The highest capacitance was observed in H_2SO_4 and results from the possible contribution of surface functional groups on the carbon introducing some additional pseudo-capacitance.

3.2. Lifetime (Arrhenius)

The effect of temperature on the degradation of electrochemical devices is a major issue in various applications. For the design of cells and modules, the knowledge about the effect of temperature on performance and lifetime is vital for a successful utilization of the respective device. Lifetime tests are rather time consuming when lifetimes of 10 or more years or cycle life of more than 500,000 cycles have to be guaranteed. Therefore, accelerated life tests have to be performed and factors for the effect of temperature and potential are needed. We have applied constant potential load tests at various temperatures and potentials. Similar to the established methods developed for electrolytic capacitors, we measured the decay of leakage current for the BCAP0350 at potentials between 2.5 V and 3.0 V and for temperatures between -40°C and $+70^{\circ}\text{C}$. All measurements were performed on one and the same cell. After equilibrating the cell at the respective potential, the leakage current was measured 10 h after a temperature step. The logarithm of the leakage current is plotted in Fig. 9 versus the reciprocal of the temperature in K. From this type of Arrhenius plot, one could determine the activation energy of the degradation processes, provided the plots result in straight lines.

As can be seen in Fig. 9, the plots do not exhibit straight lines, and we are only able to give reasonable estimations for the activation energies and acceleration factors. For the temperature range between 0°C and 60°C , an average activation energy of -0.57 eV (54 kJ mol^{-1}) was determined, while in the temperature range 0°C and -40°C , the effective activation

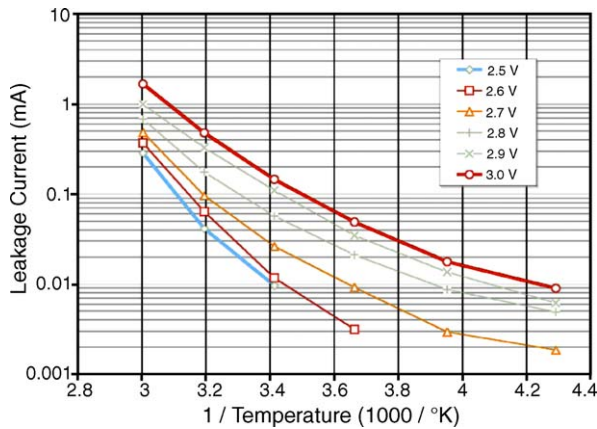


Fig. 9. Arrhenius plot of the leakage currents at various capacitor voltages and temperatures measured after 10h of constant conditions. At each voltage, the temperature of the EDLC was first held 100 h at 60 °C before the temperature was decreased in steps of 20 °C down to –40 °C.

energy was only -0.22 eV (21 kJ mol^{-1}). These activation energies are lower than the 0.8 eV usually assigned for Aluminum electrolytic capacitors.

It is not clear whether the changing activation energy is a result of two different processes with different activation energies or a result of the delicate experimental procedure. Due to the fact that the capacitor was allowed to equilibrate first for 100 h at 60 °C at each potential and subsequently for at least 10 h before each measurement after a temperature step of 20 °C, it cannot be excluded that the results are also affected by the capacitor's measurement history.

If the leakage current is considered to be proportional to the rate of aging processes, the acceleration factors for aging with temperature and maximum capacitor voltage can be derived. Aging of the capacitor is accelerated by a factor of 1.5–2 for an increase of the maximal cell voltage by 0.1 V. Similarly, an increase of the temperature of 10 °C will result in an accelerated aging factor between 1.7 and 2.5.

In Fig. 10, the result of the constant load test in terms of capacitance and ESR of a BCAP0350 at 25 °C and 2.5 V is plotted for the measurement period of about 4 months.

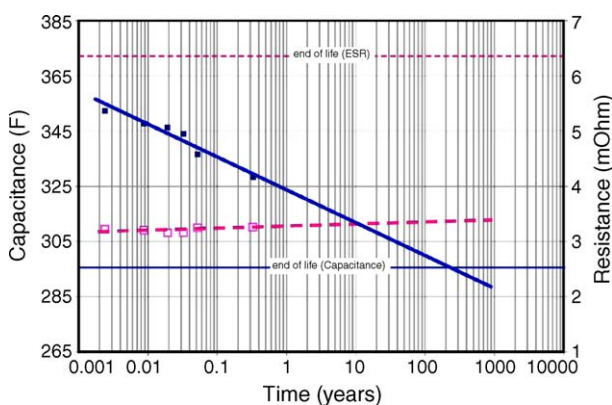


Fig. 10. Capacitance and ESR vs. log time (lifetime) for a capacitor held at 2.5 V at room temperature for up to 4000 h. The horizontal lines indicate the end of life criteria for C and ESR.

From Fig. 10, it becomes obvious that the lifetime of the capacitor is limited by the capacitance fading rather than by the increase in ESR. A linear extrapolation of the capacitance data results on a lifetime of more than 300 years until the capacitance decreases from 350 F by 20% to 280 F. Simultaneously, the increase in ESR is not significant.

Based on this measurement and on the acceleration factors determined before, one could expect a lifetime of about 20 years for a capacitor at 3.0 V and 25 °C and a lifetime of about 10 years for a capacitor at 65 °C and 2.5 V. Obviously, EDLCs can be used with a nominal voltage of 3.0 V, while maintaining a lifetime expectation of 10 and more years. However, it may well be possible that during this extrapolated time span other degradation processes become important which were not relevant during the relatively short period of the accelerated test.

4. Conclusions

Electrochemical impedance spectroscopy is an extremely useful tool for characterization of EDLC. With this technique, capacitance and various contributions to the ESR can be determined and separated. Application of this technique for the characterization of the temperature dependence of EDLC performance reveals a rather weak dependence of the capacitance on temperature for AN-based electrolytes. If PC is used as solvent, the capacitance decreases significantly with decreasing temperature.

The ESR increases with decreasing temperature independent of the electrolyte. The increase, however, is much smaller for AN-based electrolytes than for PC-based electrolytes.

On the bases of constant potential load tests, a hypothetical lifetime of more than 100 years could be extrapolated for a capacitor at room temperature and 2.5 V. Acceleration factors for the capacitor degradation were determined to be about 2 for a temperature increase of 10 °C and also about 2 for a voltage increase of 0.1 V.

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References

- [1] J.R. Macdonald (Ed.), *Impedance Spectroscopy*, Wiley, New York, 1987.
- [2] C. Gabrielli (Ed.), *Proceedings of the First International Symposium on Electrochemical Impedance Spectroscopy*, *Electrochim. Acta* 35 (2), 1990.
- [3] C. Gabrielli, Identification of electrochemical processes by frequency response analysis, Solartron Analytical, Technical Report Number 004/83, March 1998.
- [4] R. De Levie, in: P. Delahay (Ed.), *Advances in Electrochemistry and Electrochemical Engineering*, vol. 6, Interscience Publishers, 1967, p. 329.

- [5] R. Kötz, M. Carlen, *Electrochim. Acta* 45 (2000) 2483.
- [6] P. Kurzweil, H.-J. Fischle, *J. Power Sources* 127 (2004) 331.
- [7] M. Ue, K. Ida, S. Mori, *J. Electrochem. Soc.* 141 (1994) 2989.
- [8] C.R. Feger, T.F. Strange, *Passive Compon. Ind.* (November/December) (2002) 22.
- [9] T. Christen, M. Carlen, C. Ohler, in: *9th Seminar on Double Layer Capacitors and Similar Energy Storage Devices*, Deerfield Beach, FL, 1999.
- [10] A. Schwake, *13th Seminar on Double Layer Capacitors and Similar Energy Storage Devices*, Deerfield Beach, FL, 2003, pp. 36–46.