Detailed analysis of the self-discharge of supercapacitors☆

Julia Kowal*, Esin Avaroglu, Fahmi Chamekh, Armands Šenfelds, Tjark Thien,
Dhanny Wijaya, Dirk Uwe Sauer

*Electrochemical Energy Conversion and Storage Systems Group, Institute for Power Electronics and Electrical Drives (ISEA), RWTH Aachen University,
Jaegerstr. 17-19, 52066 Aachen, Germany*

ARTICLE INFO

ABSTRACT

Self-discharge is an important performance factor when using supercapacitors. Voltage losses in the range of 5–60% occur over two weeks. Experiments show a dependency of the self-discharge rate on various parameters such as temperature, charge duration and short-term history. In this paper, self-discharge of three commercially available supercapacitors was measured under various conditions. Based on different measurements, the impact of the influence factors is identified. A simple model to explain parts of the voltage decay is presented.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Electrochemical double layer capacitors (EDLCs), often called supercapacitors or ultracapacitors, are currently discussed as a high-power storage device, beside others for automotive applications [1]. Though having poor volumetric and gravimetric energy density compared with batteries, they are an interesting option for applications where charging or discharging with high current rates is needed for only a few seconds. Moreover, EDLCs outperform nearly any battery technology in terms of cycle life and could potentially live as long as the applications they are used in [2,3]. On the other hand, self-discharge is much higher than that of batteries. Nevertheless, only few authors have investigated the self-discharge on laboratory supercap cells in detail [4–6]. Ricketts and Ton-That [5] came to the conclusion that self-discharge consists of a relatively fast diffusion process and a slower leakage current.

In this work, the self-discharge of three commercially available supercapacitors was measured under various conditions such as temperature, charge duration, state of charge, and short-term history. Based on these measurements, the impact of these factors is identified.

The dynamic electrical behaviour of a double layer capacitor can be described with the electric equivalent circuit in Fig. 1, which can be derived from impedance measurements. It consists of an inductance, a series resistance and the pore impedance $\underline{Z}_p$ [3,7–9].

The inductance L describes the inductive behaviour of the cell including the terminals and R_s is the ohmic series resistance of the double layer capacitor, which represents the ohmic losses in contacts, electrodes and bulk electrolyte [10].

The complex impedance $\underline{Z}_p$ with

$$\underline{Z}_p = \sqrt{\frac{R_p}{j\omega \cdot C_{dl}}} \cdot \coth\sqrt{j\omega \cdot R_p \cdot C_{dl}} \tag{1}$$

is the impedance of the porous electrodes [11,12]. C_{dl} is the capacitance of the double layer and R_p is the resistance of the electrolyte in the pores. $\underline{Z}_p$ can be approximated by an RC ladder network (Fig. 2) with an infinite number of elements according to [11,12].

Self-discharge can be described by adding a resistance R_{SD} in parallel to $\underline{Z}_p$ in Fig. 1. As a first simple approach, $\underline{Z}_p$ is replaced by a single capacitance when calculating R_{SD}.

2. Self-discharge measurements

The open circuit voltage of three types of commercially available carbon-based supercaps with acetonitrile electrolyte (Table 1) was measured under different conditions. Type C is much smaller than the two others and the structure of the electrode surface is different.

For charging, either voltage/current source HM 8413 by Hameg or a Digatron ME unit (10 A, 0–18 V) was used. Voltage was logged
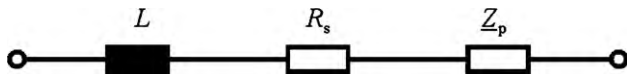
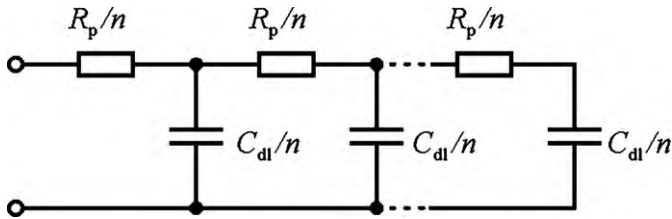Fig. 1. Equivalent electric circuit of a double layer capacitor [7].

Fig. 2. Equivalent circuit of the impedance of a porous electrode [11].

Table 1
Nominal capacitance and voltage of the measured supercaps.

	Capacitance	Nominal voltage
Supercap A	600 F	2.7 V
Supercap B	650 F	2.7 V
Supercap C	4 F	2.5 V

either with a data logger ICP 100 by Gartner Instruments or with the Digatron unit. The internal resistance of the data logger is about 1 MΩ and that of the Digatron unit is about 200 kΩ.

All measurements were done with the same procedure: the cells were charged from 0 V to a specific charge voltage, first with a constant current of 2 A and then with the constant charge voltage. In different measurements, parameters such as charge voltage, temperature, charge duration and charge or discharge history were varied to investigate their influence on self-discharge. Charge duration means the overall charging time, both constant current and constant voltage charging. The measurements were analyzed to identify time constants of voltage decay and self-discharge resistance.

Self-discharge is typically represented by a resistance in parallel to the pore impedance in an electrical equivalent circuit model [4,6].[1] The measured self-discharge resistance is calculated as:

$$R_{SD} = -\frac{U(t)}{C \cdot ((dU(t))/dt)} \qquad (2)$$

where $U(t)$ is the open circuit voltage and C is the nominal capacitance of the supercap. More precisely, C probably also should be a function of time $C(t)$, but as a first approach, we only consider R_{SD} to be time variant.

To correct the resistance calculation, the internal resistance of the data logger R_{logger} needs to be considered, which is in parallel to the self-discharge resistance so that the real self-discharge resistance $R_{SD,real}$ is calculated as:

$$R_{SD,real} = \frac{R_{SD,meas} \cdot R_{logger}}{R_{SD,meas} - R_{logger}} \qquad (3)$$

2.1. Influence of initial voltage

The left-hand picture of Fig. 3 shows the decay of the open circuit voltage of supercaps type A, which had been charged for 24 h to

different voltages at 23 °C. For better comparison, the difference from the initial voltage is plotted. It can be seen that the open circuit voltage decreases faster when the cells had been charged to a higher initial voltage.

The right hand picture of Fig. 3 shows the corresponding self-discharge resistance calculated according to Eqs. (2) and (3). Although there are differences between the curves, no clear voltage dependency can be seen. After a steep linear rise in the beginning, the resistance increases more slowly after around 200 h.

2.2. Influence of temperature

Fig. 4 (left-hand picture) compares the open circuit voltage of supercaps type A at different temperatures that had been charged for 24 h to a voltage of 2.7 V. As expected, self-discharge is faster at higher temperatures.

The corresponding self-discharge resistance is illustrated in Fig. 4 (right hand picture). Similar to Fig. 3, the self-discharge resistance rises linearly at all temperatures before the slope becomes smaller. Self-discharge resistance decreases significantly with temperature.

2.3. Influence of charge duration

Fig. 5 shows the influence of charge duration on open circuit voltage decay for all three supercaps, when charging to 2.4 V at 25 °C. In all cases, the voltage remains much more stable after charging for one or five days, while it decreases dramatically in the first hours after charging for only 15 min. For types A and B, the curves of both charge durations show more or less the same slope after the first faster decay during the first 5–10 h. This suggests that there is a faster and a slower self-discharge mechanism of which the first one depends strongly on charge duration, while the second one is less dependent on charge duration. There are however two main differences between types A and B: the influence of charge duration is larger for supercap B and the slope of the curves is larger for supercap A. Those differences are probably caused by differences in materials and internal structure, but compared to type C, these differences are small so that it can be assumed that the structure of A and B is basically similar.

Type C shows a much more dramatical voltage drop, even after charging for five days. After charging for 15 min, the voltage decay even becomes linear within several hours, which became visible only after months for type A (Fig. 7). This can be explained by a different electrode structure leading to large shallow pores instead of small and deep pores.

2.4. Influence of short-term history

Fig. 6 shows voltage decay curves of supercaps A and B after charge and after discharge. For charge history, the supercaps were charged for 24 h to a voltage of 2.1 V and then charged again until they reached 2.4 V and left in open circuit. For discharge history, the cells were charged for 24 h to a voltage of 2.7 V and then discharged until they also reached a voltage of 2.4 V.

It can be seen that charge and discharge history cause a totally different behaviour. While after charging, the open circuit voltage drops immediately, it rises slightly after discharging. Only after a while, the curves become parallel to each other. This takes about 10 h for supercap A and more than 24 h for supercap B. Both after charging and after discharging, the voltage of supercap B drops faster than that of supercap A. When comparing to Fig. 5, the behaviour after charging is comparable to the behaviour after charge duration of 15 min, so the short-term history (charge or discharge) is – at least during the first hours – more important than the long charge before.

---

[1] In the analysis of the measurements (Section 3) it turned out that most of the measured voltage decay rather is a redistribution process and not a leakage. Consequently, only the leakage part should be represented by a resistance, while the redistribution part is better modelled by a more complex circuit [13]. However, the equivalent time-dependent resistance including the redistribution effects is calculated and given exemplarily for three experiments in the following.
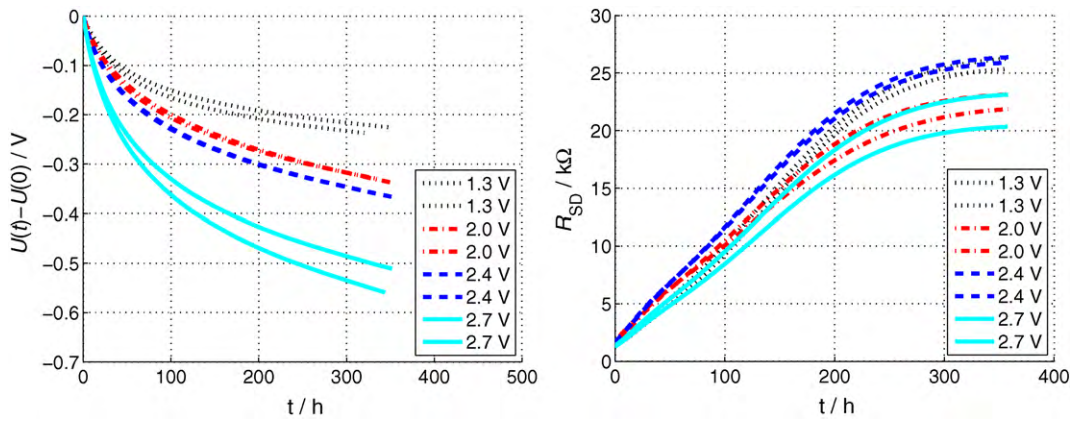
Fig. 3. Open circuit voltage (left) and self-discharge resistance (right) of supercap A for different initial voltages at 23 °C after charging for 24 h. Two different samples were measured under all conditions.
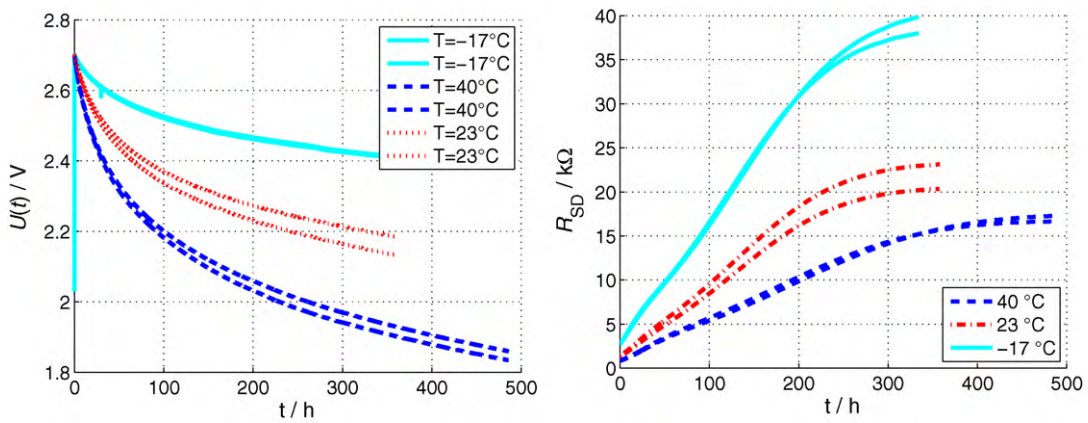

Fig. 4. Open circuit voltage (left) and self-discharge resistance (right) of supercap A for different ambient temperatures after charging for 24 h to 2.7 V. Two different samples were measured under all conditions.

2.5. Long-term test

For one supercap of type A, a long-term self-discharge test was performed (and is still ongoing). The cell was charged to 2.7 V for 24 h, and then open circuit voltage was logged for 14 days continuously. Afterwards, open circuit voltage was measured once a week manually. The supercap is at room temperature in an office room.

Fig. 7 (left) shows the voltage measurement. It becomes clear that to completely understand self-discharge it is not enough to only consider the first two weeks. After some 100 days, the voltage decay becomes linear (about 10 mV/week), while it was exponential before. After about 300 days, the cell was moved to another office room with lower and more constant temperature and from
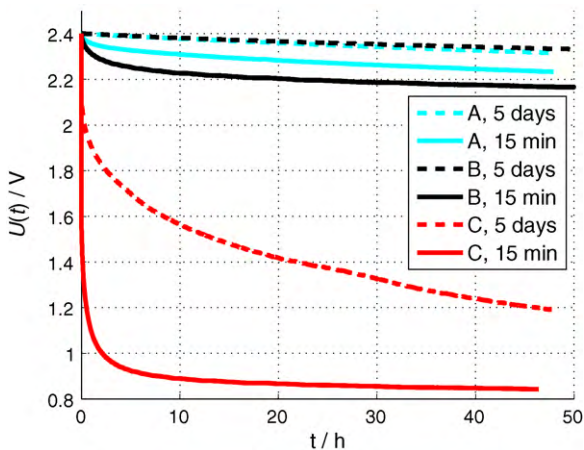

Fig. 5. Open circuit voltage of supercaps A, B and C for different charge durations at 25 °C, initial voltage 2.4 V (right hand figure: only A and B).
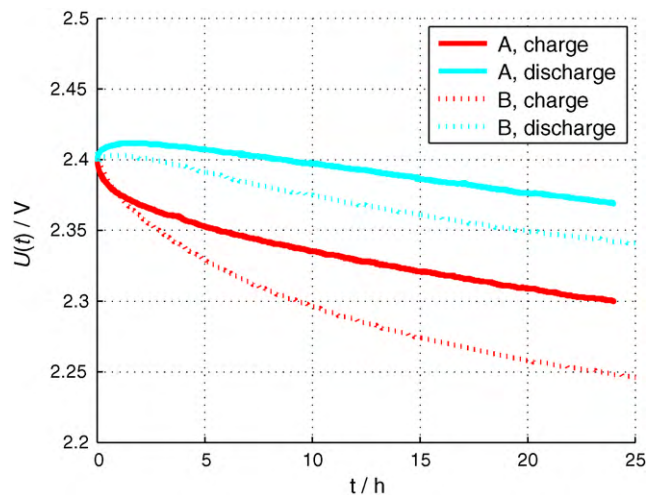

Fig. 6. Open circuit voltage of supercaps A and B after charging for 24 h to 2.1 V, then charging to 2.4 V (charge) or charging for 24 h to 2.7 V, then discharging to 2.4 V at 25 °C.
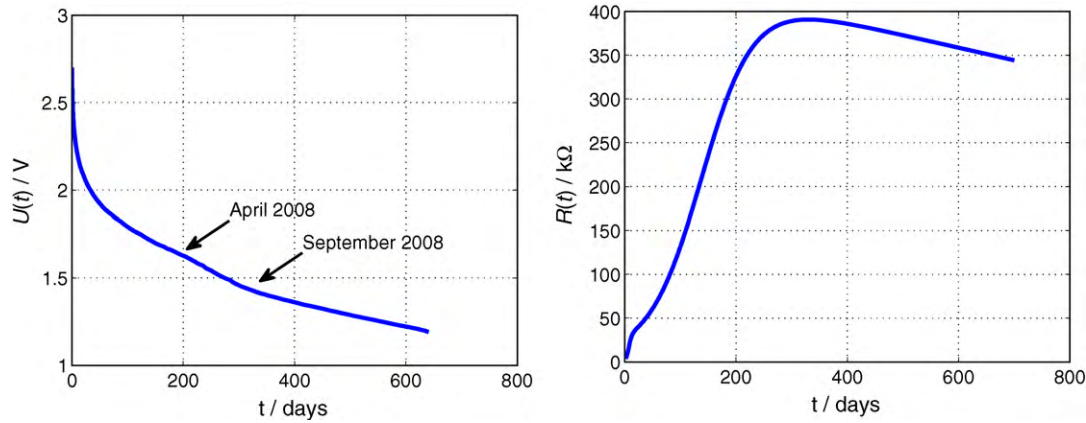
Fig. 7. Long-term open circuit measurement; supercap A was charged for 24 h to 2.7 V. Arrows indicate beginning and end of summer 2008. Afterwards, the cell was moved to an office with lower and more constant temperature. Left: open circuit voltage, right: calculated self-discharge resistance.

then until today the voltage decreases only by about 4 mV/week. It can be concluded that this part of the voltage decay is strongly dependent on temperature.

Looking at the corresponding self-discharge resistance (right hand picture of Fig. 7), the importance of the long-term test becomes even more obvious: in contrast to what could be assumed from the measurements presented above, the self-discharge resistance does not continue to rise, but reaches a maximum of 400 kΩ and then decreases linearly. This maximum coincides with the point in time, when voltage decay becomes linear.

3. Interpretation

In the following, only the measurements of supercap A are interpreted. An analytical function is fitted to the voltage decay measurements to obtain model parameters (Section 3.1) and a simple model to explain the ion distribution is introduced in Section 3.2.

3.1. Mathematical representation of voltage decay and self-discharge resistance

From most measurements it becomes clear that self-discharge consists of at least two mechanisms with two different time constants. It is not possible to fit the measured curves to a single exponential function, but good agreement can be obtained when using a function of the type

$$U(t) = a_1 \cdot \exp\left(-\frac{t}{\tau_1}\right) + a_2 \cdot \exp\left(-\frac{t}{\tau_2}\right) \tag{4}$$

For the long-term test (Section 2.5) it is not possible to fit this behaviour with exponential functions alone, it is necessary to also add a linear term $a_3 - a_4 t$ to Eq. (4). Even though the fit with two and three exponential functions looks quite well, the squared 2-norm of the residual $\Sigma(U_{\mathrm{meas}}(t) - U_{\mathrm{fit}}(t))^2$ is much better adding the linear term: for a fit with two exponential functions, the residual is 4.14, for three exponential functions it is 0.64 and for two exponential functions and a linear term it is 0.87. For three exponential functions and a linear term, the residual is only 0.050. Because of the two bends in the voltage decay curve, only the first 200 days were considered in the fit and the linear decay was fixed to 4 mV/week. Comparison with the complete curve shows a better agreement of both curves with linear term.

Thus, to completely describe the self-discharge behaviour, at least the linear term must be added to Eq. (4). Since the third exponential and the linear term are not visible in all measurements except the long-term measurement, it is not useful to add both

Table 2
Function parameters for long-term measurement of supercap A.

a_1	190 mV	τ_1	24.8 h
a_2	310 mV	τ_2	165 h
a_3	470 mV	τ_3	1730 h
a_4	1.73 V	a_5	23.8 μV h^{-1} = 4 mV/week

Table 3
Parameters of supercap A according to Eq. (5) as a function of initial voltage at 23 °C. The values are averaged over the two measured cells. Corresponding voltage decay curves are shown in Fig. 3.

	1.3 V	2.0 V	2.4 V	2.7 V
a_1	34.1 mV	40.2 mV	46.2 mV	74.3 mV
τ_1	13.1 h	11.7 h	10.8 h	12.1 h
a_2	127 mV	162 mV	179 mV	275 mV
τ_2	61.1 h	69.1 h	63.7 h	63.9 h
a_4	1.11 V	1.81 V	2.16 V	2.42 V
a_5	212 μV h^{-1}	389 μV h^{-1}	408 μV h^{-1}	541 μV h^{-1}

Table 4
Time constants of supercap A at different temperatures; the values are averaged over eight measured cells. Corresponding voltage decay curves are shown in Fig. 4.

	−17 °C	23 °C	40 °C
τ_1	11.0 h	11.9 h	15.6 h
τ_2	62.3 h	64.4 h	92.1 h

terms.[2] Thus, for analysis of the other measurements, the following Eq. (5) was used and for the long-term measurement, another exponential term with factor a_3 and time constant τ_3.

$$U(t) = a_1 \exp\left(\frac{-t}{\tau_1}\right) + a_2 \exp\left(\frac{-t}{\tau_2}\right) + a_4 - a_5 t \tag{5}$$

Table 2 lists the resulting function parameters for the long-term test of supercap A.

In the following, all parameters are given for a fit with Eq. (5), although the tests were not long enough to see the linear term and thus the linear decay parameter a_4 is overestimated. For a more detailed analysis, longer measurements are necessary. Thus, we focus on qualitative interpretation here.

Tables 3–6 list function parameters for supercap A for the measurements described in Section 2. From these tables, it can be

---

[2] The linear term instead of the third exponential function was chosen because the residual is in the same range for the long-term test, but comparison showed that after a year, adding the linear term is more important than the third exponential function.

Table 5
Function parameters for different charge durations of supercap A, corresponding to Fig. 5.

	5 days	2 h	15 min
a_1		10.0 mV	44.8 mV
τ_1		1.47 h	0.61 h
a_2	28.9 mV	50.6 mV	51.2 mV
τ_2	26.7 h	13.1 h	11.9 h
a_4	2.37 V	2.34 V	2.30 V
a_5	1.3 mV h^{-1}	1.5 mV h^{-1}	1.5 mV h^{-1}

Table 6
Function parameters for charge and discharge history of supercap A, corresponding to Fig. 6.

	Charge	Discharge
a_1	18.9 mV	−13.9 mV
τ_1	1.00 h	1.33 h
a_2	86.5 mV	112 mV
τ_2	21.3 h	65.2 h
a_4	2.29 V	2.31 V
a_5	627 μV h^{-1}	652 μV h^{-1}

concluded that a_1 and a_2 as well as a_4 and a_5 rise with initial voltage (Table 3). a_1 further becomes smaller with increasing charge duration (Table 5) and even negative after discharge (Table 6). The corresponding time constant τ_1 increases significantly with charge duration and slightly with temperature (Table 4), while it is more or less independent from charge or discharge history. Hence, the first part of voltage decay, characterised by a_1 and τ_1 depends mainly on charge duration, which could also be seen in the voltage decay curves (Fig. 5). The parameters of the second phase, a_2 and τ_2, are less dependent on charge duration, but slightly more on charge/discharge history, which is displayed in the similar slope after some hours of open circuit (Fig. 5). The temperature dependence of τ_2 is similar to that of τ_1. Apart from a clear voltage dependency, the parameters of the linear term a_4 and a_5 do not depend on other influence factors. However, this must not be over interpreted, as the linear term cannot be seen in the measurements.

Modelling all these influences by a single variable resistance is possible, but the parameterisation of this resistance is complex, since all parameters depend on various influence factors such as initial voltage, temperature and short-term history. In the following, another modelling approach is presented, which will be developed further in a following paper [13].

3.2. Mechanisms of self-discharge

From the presented measurements it can be concluded that voltage decay during self-discharge can be described with two phases of exponential decay and a phase of linear decay, which only can be seen after some 100 days. If the supercap was charged long enough (in the range of days) or discharged shortly before the open circuit condition, the first phase is not visible or inverted respectively.

Fig. 8 shows an approach based on ion distribution in a model pore to explain the first phase of voltage drop. Exemplarily a pore at the negative electrode is regarded. At the positive electrode, the same processes occur, but with the opposite sign of the charges. In the completely discharged condition (Fig. 8(a)) positive and negative ions are equally distributed. With beginning charge (Fig. 8(b)), electrons move to the electrode surface and attract the positive ions in the pore. The negative ions still present in the pore are repelled because of the excess of negative charges and move towards the pore opening. With continuing charge (Fig. 8(c)), also positive ions from the bulk electrolyte are attracted and negative ions from the pore move farther away from the pore. Positive ions from the bulk electrolyte accumulate at the opening of the pore (Fig. 8(d)).
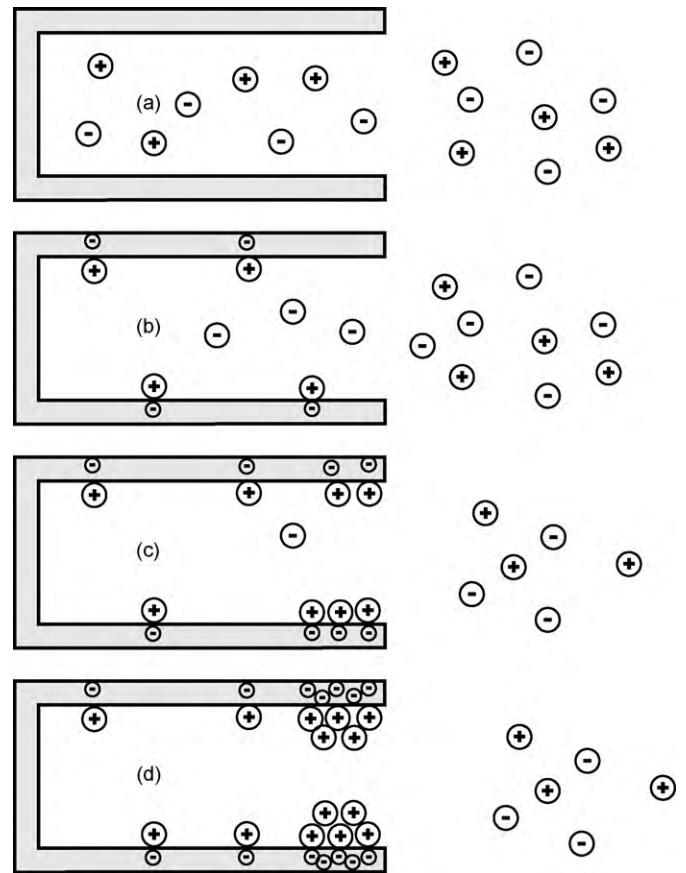

Fig. 8. Schematic ion distribution model during charging (a) discharged condition, (b)–(d) continuing charging.

Fig. 9 represents schematically the ion distribution for a long (left-hand pictures) and a short (right-hand pictures) charge duration as in the measurements presented in Section 2.3. Both start from the situation in Fig. 8(d). If charging continues while the voltage is kept constant (and the current decreases) as in the left-hand pictures, more charge enters the pore, indicated by the red charge carriers. At the same time, the charge carriers move further down the pore and the distribution becomes very uniform.

If charging is stopped before the ions are equally distributed along the depth of the pore as in the right-hand pictures, positive ions and electrons will also distribute equally after some time, but as the voltage is not kept constant during this charge flow, the redistribution causes a voltage drop. This process can also be explained considering Fig. 2 during charging, mainly the first capacitor at the pore opening is charged first and afterwards charge is balanced further down the ladder, either during continuing charging or during rest. If charging stops after short time, nearly only the first capacitor is charged and divides its charge further down the pore. Thus, the amount of charge Q of the first capacitor decreases and with $U = Q/C$ also its voltage. What is measured from outside is more or less the voltage of the first capacitor. If charging continues for a longer time, also the other capacitors of the ladder are charged and when charging stops, the first capacitor does not distribute much of its charge, so its voltage also stays more stable.

Fig. 10 represents schematically the ion distribution after charge and discharge corresponding to the measurements in Section 2.4: in both cases, a sufficiently long constant voltage charging to the respective voltage levels was performed, so that the ion distribution is uniform. Short discharging (right hand set of pictures) removes ions from the pore opening because they are easiest to move away. This causes redistribution in the following relaxation period, where
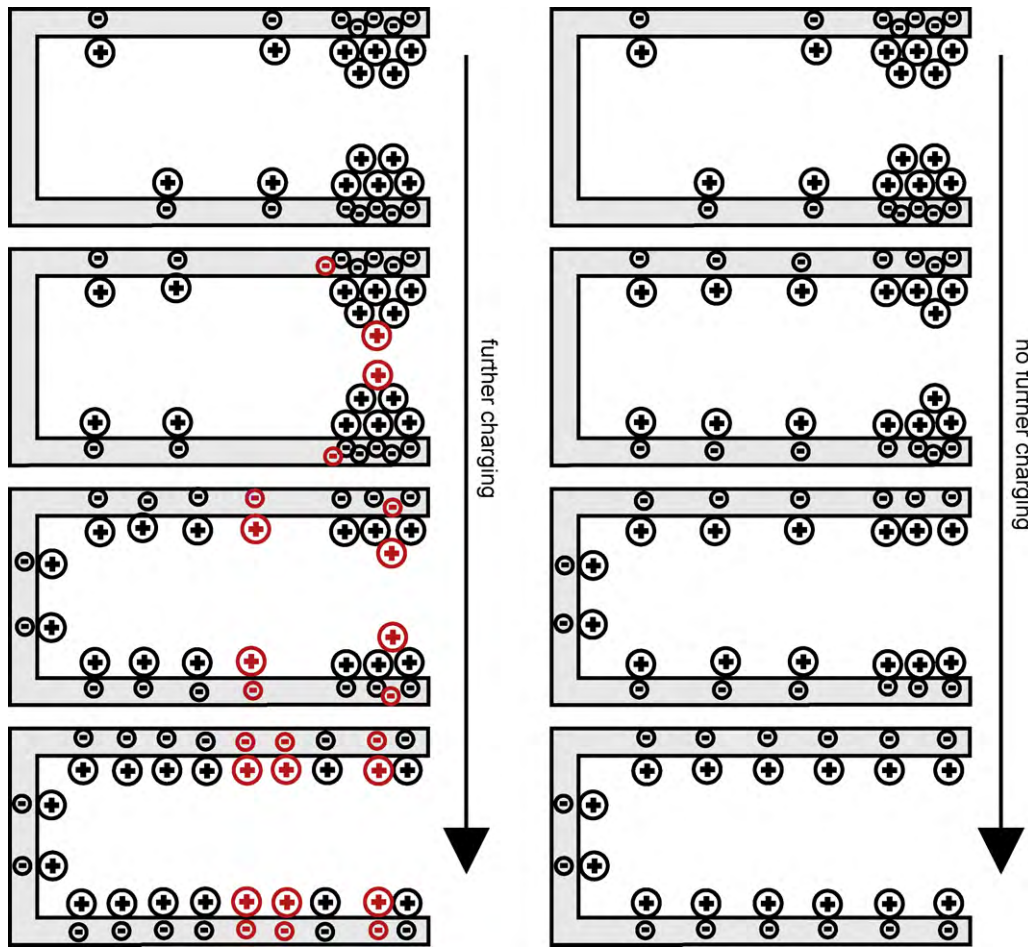
Fig. 9. Schematic ion redistribution model for different charge durations (corresponding measurements in Fig. 5) left: constant voltage charging with decreasing current rate but increasing amount of charge in the pore, right: redistribution after charging at a high current rate has stopped (constant amount of charge).
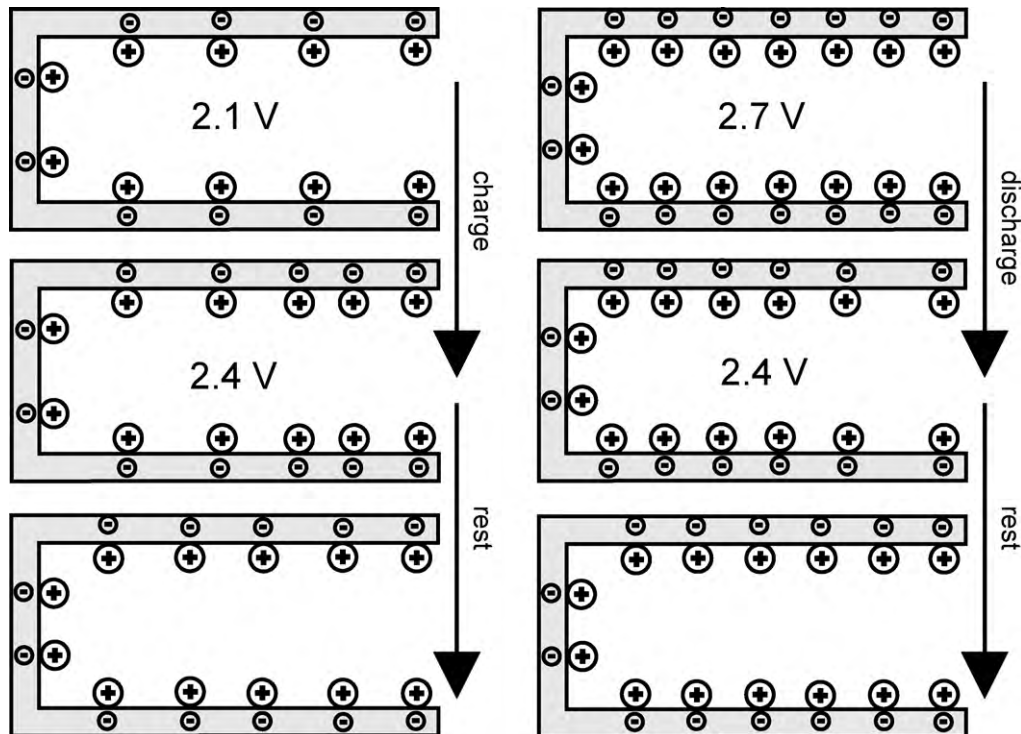

Fig. 10. Schematic ion redistribution model after short charging (left) and short discharging (right) starting from a long constant voltage charging with uniform ion distribution, corresponding measurements in Fig. 6.

ions are moved from the pore depth to the opening – or in the ladder network model to the first capacitor – which causes a voltage rise. Short charging (left-hand set of pictures) adds ions to the pore opening and thus the following relaxation period results in a voltage drop.

This simple pore model can only explain the first exponential voltage drop and not the appearance of several relaxation phases in the voltage decay curve. However, in reality the surface of supercap electrodes does not consist of uniformly shaped pores with constant diameter, but of branched pores with different and non-constant diameter. The different relaxation phases could be attributed to different pore sizes. A more sophisticated mathematical pore model has been developed recently at our institute [13]. Different time constants are represented by different pore sizes, but the principles of charge redistribution remain the same. Equal time constants are interpreted as equal pore size distribution. Types A and B show rather similar time constants compared to type C. Hence, the pore size distribution in types A and B can be assumed to be closer together than that of type C.

The mechanism described here is no physical self-discharge because the charge is still there and can be accessed in a very slow discharge. It does not cover the linear voltage decay during the long-term test. There must be another mechanism e.g. a leakage current through the electrolyte or a charge transfer from the carbon electrodes to the electrolyte resulting in physical charge loss. The temperature dependence observed in the long-term test (Fig. 7) indicates a rate process. If reversible charge transfer reactions are excluded as the origin for this leakage current, such a leakage current could be a kind of ageing, such as electrolyte decomposition. Further investigation on ageing is necessary to confirm a leakage current as the origin of the linear voltage decay.

4. Conclusion

Voltage decay of three types of commercially available supercaps was measured. It turned out that self-discharge depends strongly on short-term history, such as charge duration and charge or discharge before open circuit condition. Also, self-discharge depends on temperature, but only very little on charge voltage.

Voltage decay curves can be divided into three phases, two of which can be described by exponential functions and the third with a linear decrease. The first exponential function has a time constant in the range of hours and disappears after sufficiently long charging or after a short discharge. In contrast, the second exponential function could be found in all measurements and has a time constant in the range of days. After very long time (several months), voltage decay becomes linear with a slope of some mV per week.

Voltage decay measurements can give information about the internal structure of the electrodes, such as pore size distribution. The different behaviour of type C on the one hand and types A and B on the other hand can be explained with differences in the internal structure. For more precise correlation of voltage decay and internal structure, more measurements with different surface structures and different materials are needed.

We propose an explanation of self-discharge mechanism that is based on ion distribution within the pores. This approach fits well with all measurements described in this paper, but needs to be investigated further and extended. A mathematical model for these processes has been presented recently [13] and has been submitted for publication.

Based on our results, it should be considered to use the term "self-discharge" more precisely. In battery technology "self-discharge" is always a process that leads to a loss of charge, thus less Ah can be discharged from the batteries. Charged active material is converted to discharged active material during self-discharge. For supercaps, such a process only represents a very small part. The almost linear decay in the voltage curve which can be observed after long rest periods could be attributed to such a process. Our measurements indicate that the majority of the voltage decay in supercaps is just a redistribution of charge carriers or in other words the relaxation of an overvoltage due to concentration gradients of charge carriers. The charge carriers are not lost but just deeper inside the pores. During a very slow discharge the charge carriers can be extracted from the supercaps again. Therefore, this is strictly speaking no self-discharge process in the sense of battery technology.

Acknowledgement

References

[1] C. Ashtiani, R. Wright, G. Hunt, J. Power Sources 154 (2) (2006) 561–566.
[2] A. Burke, M. Miller, Z. McCaffrey, Proceedings of the International Electric Vehicle Symposium (EVS) 22, Yokohama, Japan, 2006, pp. 1385–1400.
[3] B.E. Conway, Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications, Kluwer Academic/Plenum Publishers, New York, 1999, ISBN: 0-306-45736-9.
[4] B.E. Conway, W.G. Pell, T.-C. Liu, J. Power Sources 65 (1997) 53–59.
[5] B.W. Ricketts, C. Ton-That, J. Power Sources 89 (2000) 64–69.
[6] J. Niu, B.E. Conway, W.G. Pell, J. Power Sources 135 (2004) 332–343.
[7] S. Buller, E. Karden, D. Kok, R.W. De Doncker, Modeling the dynamic behavior of supercapacitors using impedance spectroscopy, IEEE Trans. Ind. Appl. 38 (2002) 1622–1626.
[8] S. Buller, Impedance-Based Simulation Models for Energy Storage Devices in Advanced Automotive Applications, Ph.D. Dissertation, RWTH Aachen, Aachen, Germany, 2003.
[9] E. Karden, Using low-frequency impedance spectroscopy for characterization, monitoring, and modeling of industrial batteries, Ph.D. Dissertation, RWTH Aachen, Aachen, Germany, 2001.
[10] R. Kötz, M. Carlen, Principles and applications of electrochemical capacitors, Electrochim. Acta 45 (2000) 2483–2498.
[11] R. De Levie, Electrochemical response of porous and rough electrodes, in: Advances in Electrochemistry and Electrochemical Engineering, vol. 6, Wiley Interscience, 1967, pp. 329–397.
[12] J.R. Macdonald (Ed.), Impedance Spectroscopy, Emphasizing Solid Materials and Systems, John Wiley and Sons, 1987.
[13] Maximilian Kaus, Julia Kowal, Dirk Uwe Sauer, submitted to Electrochimica Acta, presented at ISEE Cap 09, June 29–July 2, Nantes, France.