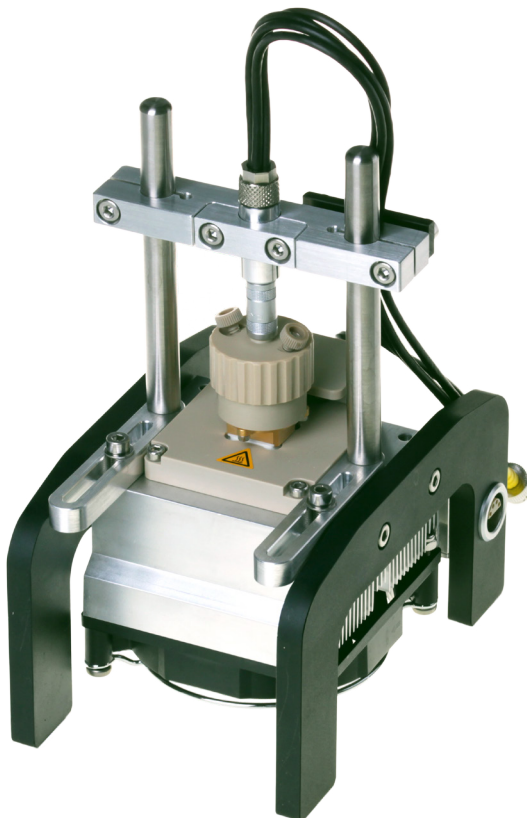


# Application note

## Electrochemical characterization of a porous carbon based electrochemical capacitor



# Introduction

Electrochemical capacitors are electrochemical storage devices storing energy in the electrochemical double layer at the electrode/electrolyte interface [1]. They are of great interest as they are capable of delivering the stored energy at high rates or currents, thus providing large power [2]. Electrochemical capacitors are also known e.g. as supercapacitors, ultracapacitors or other names being either trade marks or established colloquial names [1]. The term electrochemical capacitor was chosen here as it reveals the fact that besides storage in the electrochemical double layer there are in general additional contributions to the capacitance other than double layer effects [1]. Electrochemical capacitors bridge the gap between conventional capacitors such as electrolytic capacitors or metalized film capacitors and batteries in terms of specific energy and specific power as the latter energy storage devices are low power devices and the former ones suffer from low energy density [1]. As no to negligibly small chemical charge transfer reactions are involved during their charging and discharging, electrochemical capacitors are expected to have a much longer cycle life than batteries [1]. Additional advantages of electrochemical capacitors over other energy storage devices are a larger cycling capability, the possibility of fast recharging, a large operating temperature range, low self-discharge, few needs of maintenance and good environmental compatibility [1]. While other storage devices might be superior at one of these features, they also show distinct deficiencies at others, so that the combination of all these benefits is surely one great strength of electrochemical capacitors.

Although the concept of electrochemical ca-

[1] R. Kötz, M. Carlen, *Electrochim. Acta* **45** (2000) 2483–2498

[2] D. P. Dubai, Y. Wu and R. Holze, *Bunsen-Magazin* **17**, 6 (2015) 216–227

[3] M. D. Stoller and R. S. Ruoff, *Energy Environ. Sci.* **3** (2010) 1294–1301

pacitors is known since the middle of the last century, in the last years they draw greater attention in the context of hybrid vehicles to boost their battery or fuel cell to provide the necessary power for acceleration and allow for recuperation of brake energy [1]. However, today the largest part of the electrochemical capacitors sold is used in consumer electronic products mainly serving as backup source for e.g. memories, clocks or microcomputers [1].

In a capacitor of capacitance  $C$  electric energy  $E$  can be stored as electric charge  $Q$  at a voltage  $U$  [2]:

$$C = Q/U \quad \text{(Equation 1)}$$

$$E = 1/2 C \cdot U^2 \quad \text{(Equation 2)}$$

In electrochemical capacitors electric energy storage occurs at the electrochemical double layer or Helmholtz layer formed at the electrode/electrolyte interface due to accumulation of positive or negative ionic charges from the electrolyte at the surface of the solid electrode to compensate for the electronic charge at the electrode surface [1]. In concentrated aqueous electrolytes for instant the double layer capacitance is about 10 to 20  $\mu\text{F}/\text{cm}^2$  and can be calculated, assuming a relative dielectric constant  $\epsilon_r$  of 10 for water in the double layer and a typical thickness  $d$  of the double layer of 5 to 10 Å, according to the following equation [1]:

$$C/A = \epsilon_0 \epsilon_r / d \quad \text{(Equation 3)}$$

with  $A$  being the surface of the electrode and  $\epsilon_0$  as vacuum permittivity. Compared to conventional capacitors typically showing values in the range of pF and  $\mu\text{F}$  the capacitance and thus the energy density is rather high and can be additionally increased by using porous electrodes with an extremely large internal effective surface [1].

In a typical setup of an electrochemical capacitor single cell two electrodes with high surface area soaked with electrolyte are physically separated by a porous separator containing the same electrolyte like the active mate-

rial [1]. There are three different groups of electrode materials utilized in electrochemical capacitors, namely carbon based, polymeric and metal oxides [1]. Due to its high surface area, low costs and established electrode production technologies, carbon in various modifications like powders, woven cloths, felts or fibers is the most frequently employed one. As charge storage on carbon electrodes is predominantly capacitive in the electrochemical double layer, among the different material categories used in electrochemical capacitors they come closest to an actual electrochemical double layer capacitor, while for both the metal oxide and polymer based electrochemical capacitors redox reactions significantly contribute to the capacitance [1]. However, even carbon based electrochemical capacitors show some pseudocapacitance due to surface functional groups generally present on activated carbons [1]. Carbon based electrodes often contain besides the high surface carbon compound also conductive, low surface additives such as carbon black to improve the electrical conductivity and a binder to keep the particles together. These electrodes are attached to current collectors commonly made of metal foils to conduct the electrical current from each electrode [3]. Besides symmetrical capacitors constructed of two electrodes of the same material, also hybrid ones exist using a combination of a faradic battery-type electrode coupled with a capacitive one [3].

Both electrochemical capacitors based on aqueous or organic electrolytes exist. Advantages of the former ones are a higher conductance, lower costs and less stringent purification and drying procedures during fabrication. On the other hand the limiting cell voltage of an electrochemical capacitor single cell using aqueous electrolytes is restricted to typically 1 V, while for those based on organic electrolytes typically 2.3 to 2.5 V are achievable [1], [3]. As the maximum stored energy  $E$  is, see Equation 2, determined by the square of the single cell voltage  $U$ , the available energy

is significantly increased by using organic electrolytes in comparison to aqueous ones [1].

The most important metric for an electrode material is its specific capacitance  $C_{sp}$  in F/g, i.e. the capacitance per unit mass [3]. Often not only the mass of the active material in the electrode is used, but masses of binder and conducting additives are included, but almost never the weight of the current collectors [2]. Regarding the specification of an electrochemical capacitor, care has to be taken whether the values correspond to single electrode measurements or are calculated for a complete capacitor as the difference between these two situations is a factor of four: for a capacitor two electrodes are needed with doubled weight and half the total capacitance as according to Kirchhoff's laws the total capacitance  $C_{total}$  calculates from the capacitances of the single electrodes  $C_1$  and  $C_2$  to  $1/C_{total} = 1/C_1 + 1/C_2$  [1]. Assuming  $C_1 = C_2$  results in  $C_{total} = C_1/2$ , i.e. the total capacitance is half the value of the capacitance of a single electrode. Thus, for calculation of the specific capacitance for one electrode from the capacitance measured from the 2-electrode cell  $C_{total}$  (in F) the following equation with  $m$  as total mass of the active material in both electrodes holds [3]:

$$C_{sp, total} \text{ (F/g)} = 4 \cdot C_{total} / m \quad \text{(Equation 4)}$$

Another important point during characterization of electrochemical capacitors is the use of a reference electrode, i.e. a 3-electrode configuration, as the results gained with this setup differ from 2-electrode tests in several important aspects [3]. The 2-electrode configuration mimics closer the situation in packed capacitor modules commercial available consisting of multiple repeating single cells to achieve the desired voltage, while the 3-electrode setup is commonly employed in electrochemical research [3]. In a symmetrical 2-electrode cell the potential differences applied to each electrode are equal to each other and are half the value applied to the cell

which is plotted on e.g. the abscissa of a cyclic voltammogram (CV) chart [3]. Thus, for a given potential range the potential applied to the working electrode in a 3-electrode cell is twice the value applied to the electrodes in a 2-electrode cell, resulting in a doubled calculated capacitance for the former cell type [3].

To improve the electrochemical capacitor performance, besides optimization of electrolyte and electrode materials, control of the equivalent series resistance (ESR) within the cell is important as this parameter directly influences the achievable power  $P$  [1], [2], [3]:

$$P = U^2/ESR \quad (\text{Equation 5})$$

The ESR contains all Ohmic components inside a device between the external contacts, i.e. the resistances of wires, electrolyte solution, active masses, current collectors and separator, so that only a portion of the measured resistance can be attributed to the electrode material itself [2], [3]. As aqueous electrolytes show compared to organic ones a higher conductivity and thus a lower ESR their maximal usable power is higher, thus partly compensating the lower cell voltage achievable with aqueous based electrochemical capacitors [1].

Determination of both the ESR and the capacitance of an electrochemical capacitor is for example possible by electrochemical impedance spectroscopy (EIS). Here, differences between conventional and porous carbon based electrochemical capacitors are clearly visible. While an ideal capacitor exhibits in the Nyquist plot a vertical line intersecting the abscissa at its ESR, an electrochemical capacitor with same ESR also starts at the ESR but with a 45° impedance line and approaching an almost vertical line only at low frequencies. The non-vertical slope of the low frequency part is a typical feature of electrochemical charging processes and may be interpreted e.g. as distribution in macroscopic path length or microscopic charge transfer, as adsorption processes or surface roughness

[1]. In the equivalent circuit used for fitting of the impedance data it can be modeled by a constant phase element (CPE) instead of a capacitor [1]. Capacitance can be calculated from a CPE by using Brug's formula [4].

The Warburg region showing a 45° angle is caused by the distributed resistance/capacitance in a porous electrode. At higher frequencies only part of the active porous layer is accessible leading to a decrease of both the resistance and the capacitance of a porous electrode [1].

Using impedance spectroscopy the RC-time constant, another important number for characterization of electrochemical capacitors, can be determined. It is a measure of the time needed to (dis)charge a capacitor as the resistor determines the rate, i.e. the current, at which charge can be delivered for a given voltage according to Ohm's law [5]. As a rule of thumb the RC-time constant is defined as the low frequency capacitance, see e.g. Figure 4, times the resistance at 1 kHz [1]. However, usage of the ESR seems to be more reasonable as it sums all Ohmic contributions to the total cell resistance which all affect the (dis)charge rate. The RC-time is typically in the range of some tenth of seconds to few seconds [1]. Typically, an increased film thickness leads to a higher RC-time constant as both the capacitance at low frequencies as well as the resistance of the film increase with film thickness [1]. However, for applications requiring fast provision of charge a low RC-time constant is beneficial [5].

For determination of the capacitance of an electrochemical capacitor also galvanostatic, i.e. constant current (CC), cycling or cyclic voltammetry (CV) measurements can be used [3]. Constant current cycling is the most reliable method for determination of the cell capacitance also established in industry [3].

[4] G. J. Brug et al., J. Electroanal. Chem. 176 (1984) 275-295

[5] *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications*, B. E. Conway, 1999, Springer Science+Business Media, LLC

Galvanostatic cycling of electrochemical capacitors typically delivers triangular shaped curves if the cell voltage is plotted as function of time, see for example Figure 7. For capacitance calculation the current  $I$  applied to the cell under investigation is divided by the slope  $dU/dt$  of the CC curves [3]:

$$C = I/(dU/dt) \quad (\text{Equation 6})$$

In case the CC curves are no straight lines, as it often holds for pseudocapacitive materials, usage of the slope would be insufficient, but for capacitance determination integration of the area under the potential curve in the potential vs. time plot is needed with  $\Delta U$  as potential difference between anodic and cathodic potential limit  $U_a$  and  $U_c$ , respectively, and  $t_s$  and  $t_f$  as start and end time of the respective charge or discharge curve [2]\*:

$$C = \frac{2I \cdot \int_{t_s}^{t_f} U dt}{(\Delta U)^2} \quad (\text{Equation 7})$$

Although capacitance determination from CC curves is recommended, usage of cyclic voltammetry is also widely used. The general shape of the CV of an electrochemical capacitor is rectangular, but in case of pseudocapacitances from surface functional groups also peaks appear [1]. For capacitance calculation from CV data likewise Equation 6 can be used with  $dU/dt$  as scan rate and  $I$  as average current [3]. However, in case the current is not a horizontal line enabling simple determination of the average current, integration of the part of the CV recorded in positive or negative potential scanning direction is recommended [2]. The obtained area is divided by the potential difference  $\Delta U$  and the applied scan rate [2]:

$$C = \frac{\int_{U_c}^{U_a} I dU}{\Delta U \cdot \frac{dU}{dt}} \quad (\text{Equation 8})$$

Prior to data recording the cell should be cy-

\* The factor two results from the equation for stored energy  $W$  of a capacitor:  $W = 1/2CU^2 = P \cdot t$ ; inserting  $P = U^2/ESR = U \cdot I$  (Ohm's law) and rearranging results in  $2I \cdot t \cdot U/U^2$

clered for at least 20 cycles as in the beginning there are increased current levels thus resulting in overestimated capacitances [3]. For the same reason the potential range should be limited to the range between 0 V and the maximum voltage as cycling from negative to positive voltages likewise causes increased currents due to reversing the polarity of the cell [3]. In this regard special care has to be taken when using 3-electrode cells as here the potential across the counter electrode is not controlled or measured, so that reverse polarization of the working electrode may occur unless the point of zero charge location is experimentally determined and used as lower voltage limit [3].

Very low (dis)charge rates can lead to large errors especially in case of small electrode masses, as in this case currents from cell leakage, faradaic reactions and capacitances from other cell components largely contribute to the measured signal [3]. Thus, it is recommended to adjust the current in CC experiments to provide charge and discharge times of approximately 5 to 60 s; in CV experiments the voltage scan rate should be at least 20 to 40 mV/s resulting in (dis)charge times in the order of a minute to adequately reflect a material's performance [3].

As with CC curves, capacitance determined from CV measurements depends on scan rate and voltage range [3]. The wider the voltage range, the higher is the resulting capacitance, but bears the risk of lifetime shortening and poor efficiencies due to non-reversible reactions within the cell [3]. While the capacitance of ideal capacitors exhibiting pure capacitive behaviour shows no dependency on scan rate, in case of electrochemical ones the capacitance increases with decreasing scan rate [5].

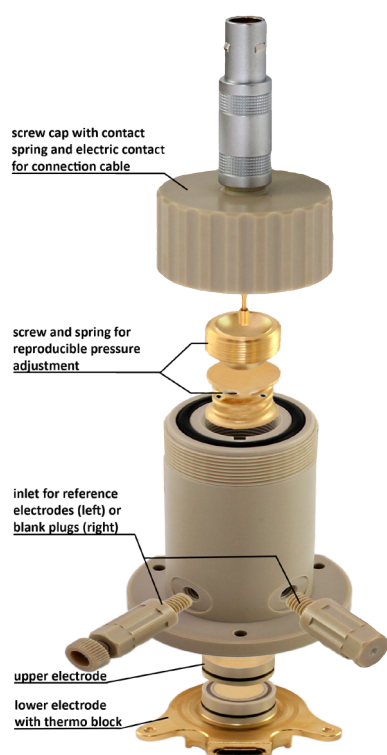
In this application note three different methods for determination of the capacitance of an electrochemical capacitor built of two porous carbon electrodes in an organic electrolyte, namely CV, EIS and CC cycling, are presented

and compared.

## Experimental

For all electrochemical studies a TSC battery measuring cell, see Figure 1, in combination with a Microcell HC setup has been used. This measuring cell enables e.g. the electrochemical characterization of planar, moisture-, air- or photosensitive substrates of variable shape under temperature control. The PEEK casing guarantees hermetic sealing of the cell interior from the outside.

As upper and lower current collector electrodes two plain disc electrodes with an effective contact area of 8 mm in diameter were used. While the upper current collector electrode was made of stainless steel, the lower one consisted of nickel-plated copper.



**Figure 1:** Exploded view of measuring cell TSC battery. The sample is placed between the upper and lower electrode. The two plugs laterally screwed into the casing enable the insertion of reference electrodes.

Besides measuring cell TSC battery mounted onto the Microcell HC setup, a Metrohm Autolab PGSTAT204 equipped with a FRA32-module was used for the

electrochemical analysis. For data acquisition, the NOVA 1.11 and 2.0 software (Metrohm Autolab B.V.) has been employed. In the Microcell HC setup, temperature is controlled via a Peltier element which enables adjusting sample temperatures ranging from  $-40\text{ }^{\circ}\text{C}$  up to  $+100\text{ }^{\circ}\text{C}$ , depending on dew point and

sample amount. In combination with a Microcell HC setup the temperature accuracy is  $0.1\text{ }^{\circ}\text{C}$  in the thermo block.

Porous carbon coated onto aluminum foil with an area density of approximately  $0.9\text{ mg/cm}^2$  (kindly provided by Fröba group, Hamburg University [6]), 11.8 mm in diameter, was employed as electrode material on both anode and cathode side of the test cell. All electrochemical studies were performed in a 2-electrode setup without reference electrode.

As separator two layers of borosilicate fiberglass filter by Whatman®, 12 mm in diameter, were used. As common in literature 1 mol/l tetraethylammonium tetrafluoroborate (Sigma-Aldrich,  $> 99.0\%$  purity) in acetonitrile (ROTIDRY®, min. 99.9 %, by Carl Roth) was employed as electrolyte [1]. Approximately 100  $\mu\text{l}$  of electrolyte were added to ensure complete wetting of both electrodes as well as the separators. All chemicals were used as received without further purification.

Cell preparation occurred in an argon filled glove box (MBRAUN,  $\text{H}_2\text{O}$  and  $\text{O}_2$  content  $< 0.1\text{ ppm}$ ). The contact pressure was adjusted using a gold-plated spring with a spring constant of 2.3 N/mm to 40.7 kPa.

Prior to electrochemical tests, the assembled cells were stored for approximately 20 h at room temperature to let the porous electrode materials soak with electrolyte. All measurements were performed at  $20\text{ }^{\circ}\text{C}$ .

In the testing procedure, firstly an impedance spectrum was recorded at open circuit potential (OCP), followed by approximately 60 cycles of cyclic voltammetry at different scan speeds starting and ending at OCP, partly interrupted for impedance measurements. Thereafter, constant current cycling was performed over 10 cycles, followed by cyclic voltammetry at different scan speeds starting and ending at OCP. At each different scan speed three to ten cycles were recorded. Part-

[6] R. Heimböckel et al., *Appl. Surf. Sci.* (2017), in press.

ly, after finishing measurements at one scan speed an impedance spectrum was recorded. Subsequently, long term constant current cycling over 1000 cycles followed by a final impedance measurement was performed.

As reliable capacitance values only can be gained after at least 20 cycles, in this application note only data recorded after the about 60 initial CV cycles are presented [3].

For both CV and CC cycling measurements, the potential range was set to 0.0 to 2.5 V. For CV measurements the scan speed was varied between 2 and 2500 mV/s. Constant current charging and discharging of the cell occurred at 8 mA, i.e. approximately 4 A/g referring to the mass of the electrodes. This results in a charge and discharge time around 20 s as recommended in literature [3].

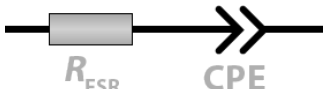
All impedance spectra were recorded for frequencies ranging from 500 kHz down to 10 mHz while applying an ac-voltage amplitude of 5 mV (rms) to the sample. For fitting of the impedance data the impedance analysis software RelaxIS® (distributed by rhd instruments GmbH & Co. KG) was used.

## Results and discussion

### a) Impedance spectroscopy

For fitting of the data measured by impedance spectroscopy the equivalent circuit presented in Figure 2 was used. Thereby,  $R_{ESR}$  symbols the combined resistance of the electrode materials, the electrolyte as well as the contact resistances in the cell and the CPE takes interface effects, i.e. charging of the electrochemical double layer at the interface electrode/sample, into account. Employment of a Warburg resistance was in this case not needed as noteworthy ion diffusion/transport in the electrolyte only occurs at lower temperatures or if even lower frequencies would be measured. For fitting the frequency range was limited to exclude inductive influences at higher frequencies.

For calculation of an estimated capacitance value from the values of the CPE element determined by impedance spectroscopy, Brug's formula, see Equation 9, was used [4]. Values of the fits together with the resulting capacitances and the respective errors are summarized in Table 1.

$$C = \left( \frac{Q}{R_{ESR}^{\alpha-1}} \right)^{1/\alpha} \quad (\text{Equation 9})$$


**Figure 2:** Equivalent circuit representing the impedance behaviour of the electrochemical capacitor sample within the chosen frequency range.

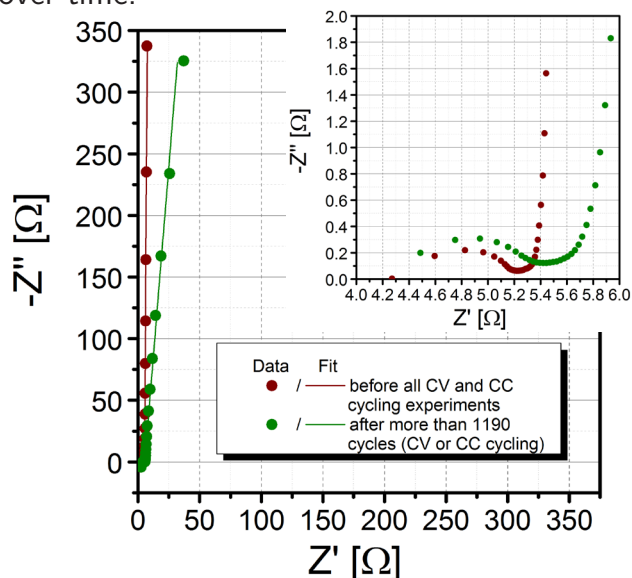
**Table 1:** Summary of the values determined by fitting of the impedance data to the equivalent circuit presented in Figure 2 together with the resulting capacitances calculated via Brug's formula and the respective errors. For all quantities determined by fit of the impedance data the fit error is given, while in case of the specific capacitance the error was calculated by error propagation assuming an inaccuracy of 0.0001 g for the balance used to determine the weight of the electrodes.

Equivalent circuit element	Before all CV and CC cycling experiments		After more than 1190 cycles (CV or CC)	
	Value	Error	Value	Error
$R_{ESR}$ ( $\Omega$ )	5.29	0.43 %	5.41	0.75 %
CPE Q ( $\text{mF} \cdot \text{s}^{\alpha-1}$ )	46.6	0.06 %	42.4	1.26 %
CPE $\alpha$	1.00	0.02 %	0.95	0.61 %
$C_{sp}$ (F/g)	84.3	9.18 %	71.1	11.41 %

The Nyquist plot of the impedance data given in Figure 3 shows more or less the features theoretically expected for an ideal electrochemical capacitor: in the high frequency region a small semicircle is visible, while at lower frequencies a vertical line is approached [1].

Comparison of the impedance spectra recorded prior to and after all cycling experiments, i.e. more than 1190 cycles, shows a slight increase in the semicircle, i.e. an increased resistance and a bit less steep line in the low frequency range, thus pointing to slight degradation of the capacitor with time. However, this fading is acceptable and cycling over more than 1190 cycles with still sufficient capacitance is possible. Even after this prolonged cycling the ESR

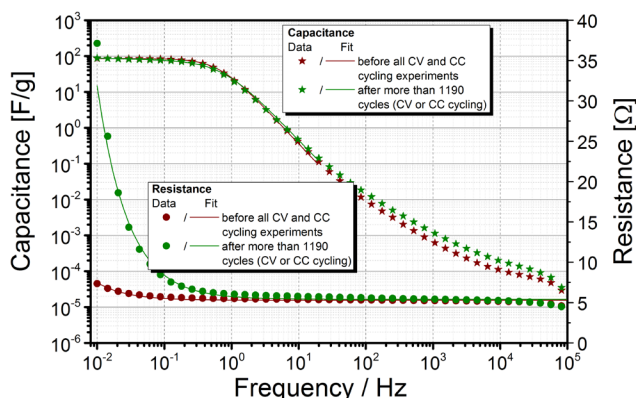
remains almost constant also pointing to only small fading of the electrochemical capacitor over time.



**Figure 3:** Nyquist plots showing the real part  $Z'$  and the imaginary part  $Z''$  of the impedance of an electrochemical capacitor test cell comparing the impedance measurements performed prior to and after all cycling experiments. The inset shows a magnification of the high frequency range to enlarge the region of the semicircle and the intersection with the abscissa, i.e. the ESR.

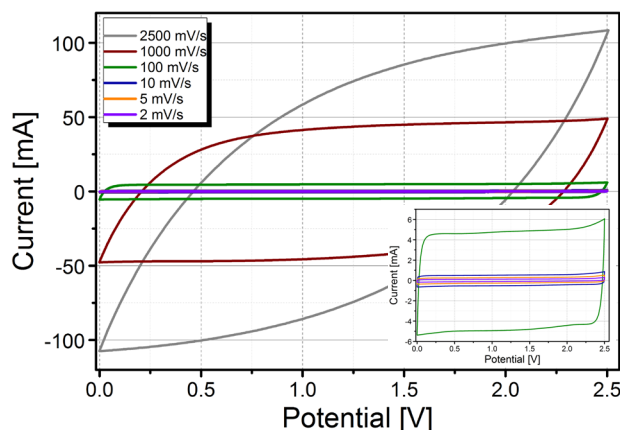
By plotting the capacitance vs. frequency, see Figure 4, the capacitance reaches an almost constant value at low frequency values, while it decreases noticeably at higher ones. The RC-time constant of the single electrode capacitor is roughly related to this cut-off frequency: the lower the RC-time constant the higher is this frequency above which the capacitance of the electrochemical capacitor decreases distinctly [1]. Calculation of the RC-time constant from the low frequency capacitance and the resistance at 1 kHz delivers a value of 0.24 s and 0.21 s for the impedance measurement performed prior to and after all cycling experiments, respectively, also showing only marginal degradation over time. Usage of the ESR instead of the resistance at 1 kHz for calculation of the RC-time constant results with 0.25 and 0.21 s for the impedance measurement performed prior to and after all cycling experiments, respectively, in nearly identical results. Thus, for the electrochemical capacitor presented in this applica-

tion note both methods can be employed.



**Figure 4:** Plot of the specific capacitance and resistance versus frequency of an electrochemical capacitor test cell comparing the impedance measurement performed prior to and after all cycling experiments.

In Figure 5 and Figure 6 cyclic voltammograms recorded at different scan speeds are summarized plotting the current and the specific capacitance, respectively, on the ordinate. For better overview, for each different scan speed only one representative cycle is presented. All curves show the rectangular shape typical for electrochemical capacitors. However, for the fastest scan speed the horizontal regions are hardly visible. As expected, with increasing scan speed the current increases, while the specific capacitance decreases.

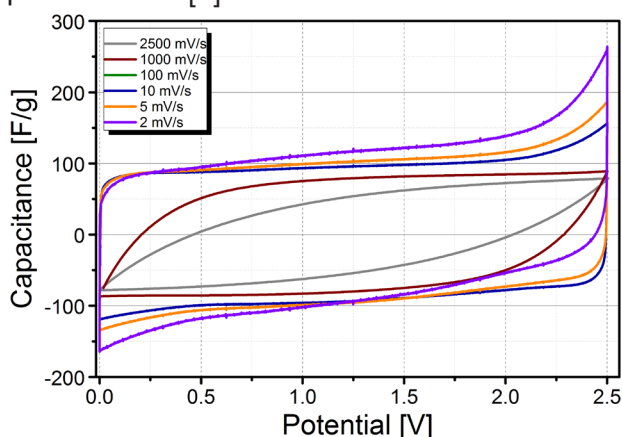


**Figure 5:** Cyclic voltammograms of an electrochemical capacitor test cell recorded at different scan speeds plotting the current on the ordinate. For better overview for each different scan speed only one representative cycle is presented. The inset magnifies the current responses of the smaller scan speeds. Prior to recording these cycles the cell was cycled for over 60 initializing CV cycles.

Charge and discharge capacitances were calculated by integration of the respective part



of the CV curve according to Equation 8 being summarized in Table 2. As can be seen from this table, the discharge capacitance is only for the two highest scan rates as high as the respective charge capacitance, but for lower values the charge capacitance is higher. With decreasing speed this difference increases, thus pointing to small side oxidation reactions becoming more relevant at lower scan speeds as here the current coming from the actual capacitance storage process reduces [3]. These additional currents from for example cell leakage or faradaic reactions are also obvious from the deviation from the rectangular shape close to the points of voltage reversal. For scan rates of 10 mV/s and below\* the discharge capacitance levels off around 90.5 F/g as in this speed range the capacitance plateau in the capacitance vs. frequency plot, see Figure 4 is reached, while the higher scan rates fall in the region showing reduced capacitance with increasing frequency values. Thus, the ideal scan speed range delivering high discharge capacity with high efficiency, i.e. high ratio of discharge to charge capacity, lies in the range between 10 and 100 mV/s, also being the scan speed range recommended in literature to adequately reflect a material's performance [3].



**Figure 6:** Cyclic voltammograms of an electrochemical capacitor test cell recorded at different scan speeds plotting the specific capacitance on the ordinate. For better overview for each different scan speed only one repre-

\* As the potential was varied between 0 and 2.5 V a scan speed of 2500 mV/s corresponds to a frequency of 1 Hz:  $2500 \text{ mV/s} / (2.5 \text{ V} - 0.0 \text{ V}) = 1/\text{s} = 1 \text{ Hz}$ ; thus a scan speed of 10 mV/s corresponds to 4 mHz.

sentative cycle is presented. Prior to recording these cycles the cell was cycled for over 60 initializing CV cycles.

**Table 2:** Summary of the charge and discharge capacitances determined from CV experiments by integration of the respective part of the CV curve according to Equation 8. For error calculation an inaccuracy of 0.0001 g for the balance used to determine the weight of the electrodes was assumed.

Scan rate [mV/s]	Charge capacitance		Discharge capacitance	
	Value [F/g]	Error [%]	Value [F/g]	Error [%]
2500	38.1	9.09	38.1	9.09
1000	63.2	9.09	63.2	9.09
100	86.4	9.09	85.0	9.09
10	99.1	9.09	90.4	9.09
5	106.9	9.09	91.7	9.09
2	111.5	9.09	90.1	9.09

One reason for the slightly reduced discharge capacitance determined for the lowest scan rate of 2 mV/s in comparison to the one achieved at 5 mV/s is the time for data recording of the potentiostat. Most potentiostats cannot provide a truly linear change of the potential with time during CV measurements, but vary the potential in a staircase type way. In this case, as it also holds for the potentiostat used for all measurements of the present application note, it is important, at which point of the voltage step the actual data recording occurs. If it is performed directly after the potential change, capacitive currents will dominate the measured current, while at the end of the step, shortly before the next potential raise will occur, mainly faradaic currents are measured as the capacitive ones have a shorter decay time: while capacitive currents decay exponentially, faradaic ones show at short times  $t$  approximately a  $1/t^{1/2}$  behaviour [7]. Although care was taken to set the recording time to the value recommended by the potentiostat manufacturer to mimic the truly linear voltage change best, this still might cause small deviation from the ideal situation resulting in slightly reduced measured capacitances [8], [9]. This problem

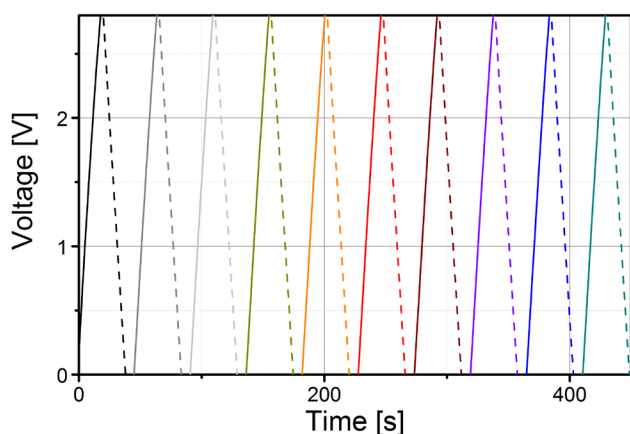
[7] D. G. Swartzfager, *Anal. Chem.* **48**, 14 (1976) 2189-2191

[8] M. Saralhan, R. A. Osteryoung, *J. Electroanal. Chem.* **222**, (1987) 69-100

[9] *Different approaches for capacitance measurements*, Autolab Application Note EC12 (2014)

is the most fatal for the lowest scan speeds as here the difference between the decay time of the capacitive currents and the step time of the voltage scan is greatest. The step size employed for the scan speeds of 100 mV/s and below was 1 mV, so that in case of the 2 mV/s measurement one voltage step took 0.5 s leading to a decay approximately twice as high as in case of a scan rate of 5 mV/s.

Figure 7 plots the first ten cycles of CC cycling showing the triangular shape expected for electrochemical capacitors. Charge and discharge capacitances calculated by integration of the respective portion of the CC curves according to Equation 7 are summarized in Table 3.



**Figure 7:** CC cycling of an electrochemical capacitor test cell recorded at a current of approximately 4 A/g. Prior to recording these cycles the cell was cycled for over 60 initializing cycles.

**Table 3:** Summary of the charge and discharge capacitances determined from CC cycling experiments recorded at a current of approximately 4 A/g. For error calculation an inaccuracy of 0.0001 g for the balance used to determine the weight of the electrodes was assumed.

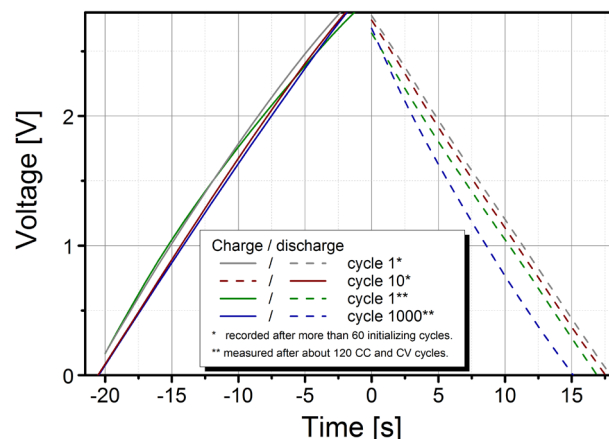
\* These are the first and last cycles depicted in Figure 7. Prior to recording these cycles the cell was cycled for over 60 initializing CV cycles.

\*\* Recording of these 1000 CC cycles occurred after about 120 CC and CV cycles.

Cycle no.	Charge capacitance		Discharge capacitance	
	Value [F/g]	Error [%]	Value [F/g]	Error [%]
1*	107.0	9.09	93.1	9.09
10*	101.0	9.09	91.8	9.09
1**	114.3	9.09	91.7	9.09
1000**	98.4	9.09	77.9	9.09

Even after more than 1190 cycles the trian-

gular shape of the charge-discharge curves is almost preserved as can be seen from Figure 8 and still over 84 % of the initial discharge capacitance are gained thus showing rather satisfactory long-term stability of the electrochemical capacitor.



**Figure 8:** CC cycling of an electrochemical capacitor test cell recorded at a current of approximately 4 A/g comparing the first and 10th CC cycle recorded after more than 60 initializing CV cycles as well as the first and 1000th CC cycle measured after about 120 CC and CV cycles. For better comparison of the discharge capacitances the curves were shifted along the abscissa to align the starting points of the respective discharge curves.

As the capacitance depends on the cycling rate, for comparison of the values determined from different electrochemical measurement methods, capacitances recorded during CV measurements at a scan rate of 100 mV/s were used as it is comparable to the rate used during CC cycling: a typical charge or discharge time is 17 s over a voltage range of 2.5 V resulting in a rate of  $2500 \text{ mV}/17 \text{ s} = 147 \text{ mV/s}$ . The discharge capacitances determined from the present porous carbon material using either CC cycling, CV measurements or impedance spectroscopy are summarized in Table 4.

**Table 4:** Comparison of the capacitances determined from different electrochemical measurement methods. In case of the CV experiments values measured at a scan rate of 100 mV/s were used as it is comparable to the rate used during CC cycling.

Electrochemical method	Discharge capacitance [F/g]
Cyclic voltammetry	85.0
CC cycling	91.8
Impedance spectroscopy	84.3

While the discharge capacitances determined from CV measurements and impedance spectroscopy of 85.0 and 84.3 F/g, respectively, are in good accordance the value determined from CC cycling is with 91.8 F/g 8 - 9 % higher. Thus, although CC cycling is the recommended method also applied in industry for capacitance determination of electrochemical capacitors both CV measurements and impedance spectroscopy also deliver reliable values that remain within the error tolerances [3]. Reasons for this discrepancy could be that calculation of the capacitance from a CPE element via Brug's formula is only a rough estimation thus causing slightly erroneous capacitance values determined from impedance spectroscopy. In case of CV measurements the not truly linear, but only staircase type sloping of the voltage change with time leading to slight decay of the capacitive currents at the point of the actual data recording thus resulting in slightly reduced measured capacitances is surely one error source.

Finally, based on our results a recommended procedure for testing electrochemical capacitors is, after the cell is run over at least 20 initializing cycles, to firstly perform CV measurements over a range of scan speeds to identify the ideal scan speed delivering both high discharge capacity and high efficiency. By using this value the optimal rate for CC cycling is calculated and used for extended charge-discharge test of the electrochemical capacitor test cell, as this electrochemical method should deliver the most reliable capacitance values.

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