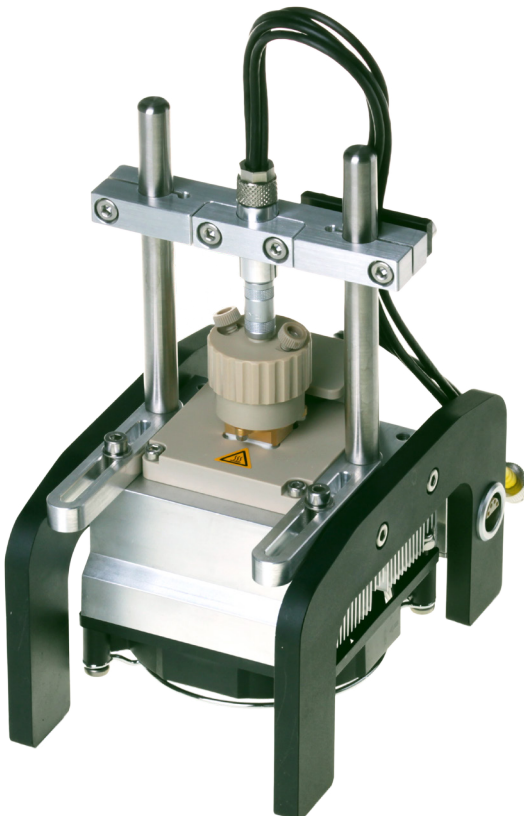


# Application note

## Temperature-dependent impedance measurements of separator materials

- » Conductivity determination
- » Variation of the dc-ion conductivity of the separator within a temperature ramp



# Introduction

In general, battery cells are composed of at least three components, namely two electrodes of opposite polarity, where the electrochemical reactions take place, and an electronically insulating electrolyte [1]. On the one hand it physically separates the electrodes and on the other hand guarantees sufficient ion transfer between both electrodes. In systems using liquid electrolytes, the electrolyte is soaked into so called separators, i.e. thin porous membranes, which avoid direct electronic contact between both electrodes and thus short circuiting of the whole cell, but are permeable to ionic flow [1]. The ionic resistivity of the separator should be low to avoid blocking of the ion transfer within the cell as good as possible. In consequence, information about the ion conductivity of the separator materials is an important value for characterization and rating of different separator materials.

Since typical applications of battery cells often operate in a wide temperature range, the temperature dependency of the conductivity of the separator/electrolyte system is of great interest. Especially at high temperatures, where partial melting of the separator structure might set in, sufficient conductivity should be still provided. At even higher temperatures, collapse of the porous structure is often desired as safety issue to prevent a thermal runaway of the cell by complete blocking of the ion movement between the electrodes (shut down). Typically, the resistivity of a microporous separator soaked with electrolyte is approximately 6-7 times that of a comparable electrolyte volume [1].

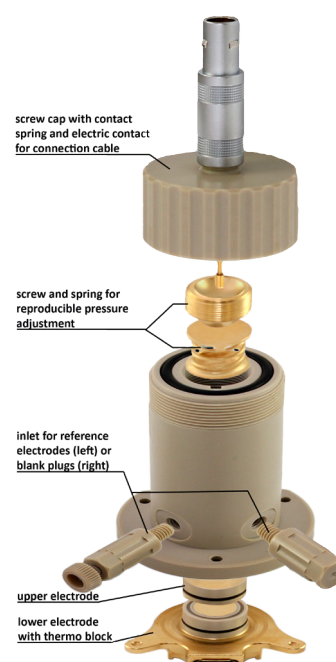
In this application note, an almost completely automated measurement routine for determination of the temperature-dependent dc-ion conductivity of electrolyte soaked separators is presented using electrochemical impedance spectroscopy. In the second step, the separa-

tor impedance at a selected frequency is recorded within a temperature ramp covering a wide temperature range from room temperature to 90 °C, i.e. a value easily reached during many battery applications, to directly investigate the impact of temperature on the dc-ion conductivity of the separator material.

## Experimental

From the separator material discs of 12 mm in diameter were punched out and soaked in approx. 300 µl electrolyte for at least 24 h to guarantee sufficient wetting. As electrolyte 1 mol/l LiClO<sub>4</sub> in EC/DMC (1:1 w/w) was used.

For impedance measurements of the separator material, a TSC battery measuring cell, see Figure 1, in combination with a Micro-cell HC setup has been used. This measuring cell enables e.g. the electrochemical characterization of planar, moisture-, air- or photo-sensitive substrates of variable shape under temperature control. As electrodes, two plane stainless steel disc electrodes with an effective contact area of 8 mm in diameter were used. The contact area of the lower electrode was gold- or nickel-plated. Approximately 40 µl additional electrolyte was added to ensure complete filling of the spacing between both electrodes. The contact pressure was adjusted using a gold-plated spring with a spring constant of 2.3 N/mm to 4.6 N, i.e. 40.67 kPa related to the area.

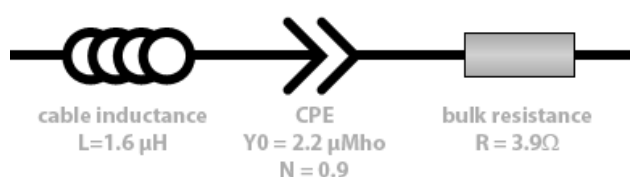


**Figure 1:** Exploded view of measuring cell TSC battery. The sample is placed between the upper and lower electrode.

[1] P. Arora, Z.J. Zhang, Chem. Rev. 2004, 104, 4419-4462

Besides the 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. 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. For sample tempering an Eurotherm control unit was used. It can be controlled either by the software from many measurement bridge manufacturers like Novocontrol, Biologic, Zahner or Solartron, as well as by a dll embedded into a NOVA specific procedure (hcDLL ACM). In combination with a Microcell HC setup the temperature accuracy is  $0.1\text{ }^{\circ}\text{C}$  in the thermo block.

For data acquisition, the NOVA 1.11 software (Metrohm Autolab B.V.) has been used. Determination of the dc-ion conductivity of samples with a well-known and relatively simple impedance spectrum can be performed fully-automated via a special procedure (hcDLL ACM, developed by rhd instruments GmbH & Co. KG) using the online-fit option of the NOVA software. For recording of single-frequency impedance data while performing a temperature ramp the software hc Studio (developed by rhd instruments GmbH & Co. KG) was used.



**Figure 2:** Equivalent circuit representing the impedance behaviour of the separator samples within the chosen frequency range.

In the present case, the equivalent circuit depicted in Figure 2 was used for fitting of the impedance spectra. Thereby,  $L$  symbols an inductor and represents the parasitic inductive artefacts at high frequencies due to e.g. connection cables.  $R$  is an ohmic resistor and typifies the resistance of the cables as well

as the resistance due to transport of the ions through the sample. The constant phase element CPE takes interface effects, i.e. charging of the electrochemical double layer at the interface electrode/sample, into account.

Starting at  $20\text{ }^{\circ}\text{C}$ , the sample was cooled down to  $0\text{ }^{\circ}\text{C}$ , reheated to  $20\text{ }^{\circ}\text{C}$ , again cooled down to  $0\text{ }^{\circ}\text{C}$  and finally heated to  $30\text{ }^{\circ}\text{C}$  in steps of  $5\text{ }^{\circ}\text{C}$ . At each temperature, an impedance spectrum was recorded for frequencies ranging from  $250\text{ kHz}$  down to  $100\text{ Hz}$  while applying an ac voltage amplitude of  $10\text{ mV}$  (rms) to the sample. To guarantee for reaching of the thermal equilibrium at each temperature, the respective value was held for  $120\text{ s}$  prior to start of the measurement. By recording four ascending and descending temperature ramps presence of the thermal equilibrium was verified. Reproducibility of the data was proven by analysis of at least two measurements for three samples. Using these, the mean dc-ion conductivity as well as the standard deviation was calculated for the respective temperatures.

The complex conductivity  $\sigma(\omega)$  can be deduced from the complex impedance  $Z(\omega)$  according to the following equation:

$$\sigma(\omega) = C/Z(\omega)$$

where  $C$  is the cell constant of the measuring cell (see chapter „Data evaluation“). The high-frequency part of  $\sigma'(\omega)$ , the real part of  $\sigma(\omega)$ , is governed by ion movements in the bulk of the electrolyte. Thus, in Bode plots of  $\sigma'(\omega)$  the plateau value, being expected for good to moderate ionic conductors at high to intermediate frequencies, is given by the dc-ion conductivity.

To follow the development of the separator resistance within a temperature ramp, single-frequency impedance measurements were recorded. The frequency was selected so that it is located within the frequency region where dc-ion conductivity occurs. Here, the separator impedance equals its resistance, i.e. at a

phase angle of approx. zero degrees [1], where the Bode plots of the real part of the impedance as well as the real part of the complex conductivity show a plateau. This plateau shifts with increasing temperature to higher frequency values. Thus, for the single-frequency measurement the frequency was selected in a way that it is as close as possible to the high-frequency border of the plateau while the phase angle is nearly  $0^\circ$ . 100 kHz were selected for this purpose, see Figure 6. Thus even for investigation of a relatively broad temperature range this frequency still should be within the plateau. For this measurement, the temperature was raised from 20 to 90 °C by 3 °C/min. Approximately every 10 s a single-frequency impedance measurement was performed. To verify the reproducibility of the analysis three different samples were measured.

## Data evaluation

Using the well-defined geometry of the cell interior of TSC battery and the thickness of the separator material, the cell constant  $C$  was calculated to

$$C = d/A = 0.003979 \text{ cm}^{-1}$$

where  $A$  and  $d$  are the sample area and thickness, respectively. In the present study the thickness  $d$  of the separator was 20  $\mu\text{m}$  and the area was calculated to  $A = \Pi \cdot r^2 = \Pi \cdot (0.4 \text{ cm})^2$  using the radius  $r$  of the disc electrodes. Although the actual size of the separator is with a diameter of 1.2 mm larger, only the active area of the disc electrodes was used for calculation of the cell constant, since for species with a very low electronic conductivity, as it holds for the present sample, current flow almost completely takes place in the region between the electrode areas. Thus, the separator parts outside this region could be neglected.

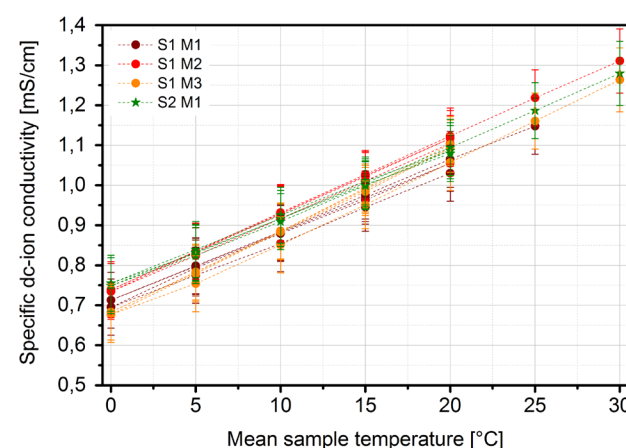
In case of unknown cell geometries the cell constant can be determined by means of a reference sample with a known dc-ion con-

ductivity and geometries comparable to the sample whose conductivity should be determined. Thus, by performance of an impedance measurement the cell constant can be calculated and subsequently used for analysis of the sample of interest.

By means of the cell constant together with the bulk resistance determined from fitting of the respective impedance spectra the temperature-dependent dc-ion conductivity was determined fully-automated by hcDLL ACM procedure. Results of the three separator samples, each measured at least twice, are exemplarily depicted in Figure 3, showing a linear increase of the conductivity with temperature. Averaging the measurements results in the mean dc-ion conductivities summarized in Table 1 for the respective temperatures together with the appendant standard deviations.

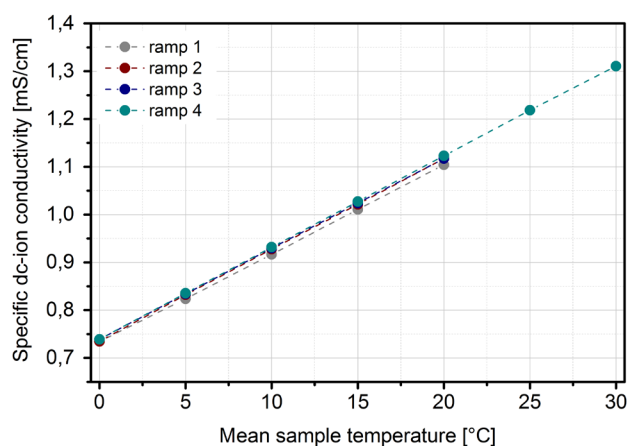
**Table 1:** Mean  $\sigma_{\text{dc}}$  as function of sample temperature as well as its standard deviation. For data evaluation results of three different samples were taken into account.

Temperature [°C]	$\sigma_{\text{dc}}$ [S/cm]	Standard deviation [S/cm]
0	0.66E-3	0.07E-3
5	0.75E-3	0.07E-3
10	0.84E-3	0.07E-3
15	0.94E-3	0.06E-3
20	1.03E-3	0.07E-3
25	1.13E-3	0.07E-3
30	1.22E-3	0.08E-3

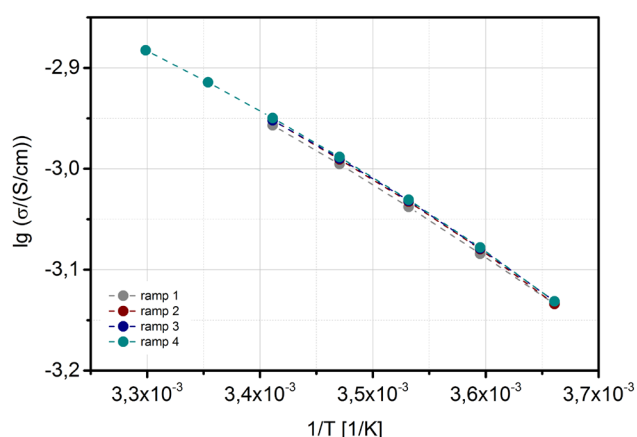


**Figure 3:** Temperature-dependent dc-ion conductivity of the separator samples together with the respective standard deviations. „S“ labels the sample number, while „M“ designates the different measurements of one sample.

For better comparison of the different temperature ramps of a single sample the four ramps are exemplarily presented in Figure 4. The software also calculates values for an Arrhenius type representation of the data, i.e. the inverse temperature and the natural logarithm of the conductivity, see Figure 5. Nearly linear sloping in this representation indicates almost Arrhenius type temperature behaviour, while a nonlinear sloping points to Vogel-Fulcher-Tammann behaviour [2]. As can be seen from both representations, the conductivity values of the four temperature ramps show only negligible divergence of less than 2 % at the respective temperatures, thus confirming the presence of thermal equilibrium.



**Figure 4:** Comparison of the four temperature ramps measured for determination of the temperature-dependent dc-ion conductivity of one separator material to check the presence of thermal equilibrium.

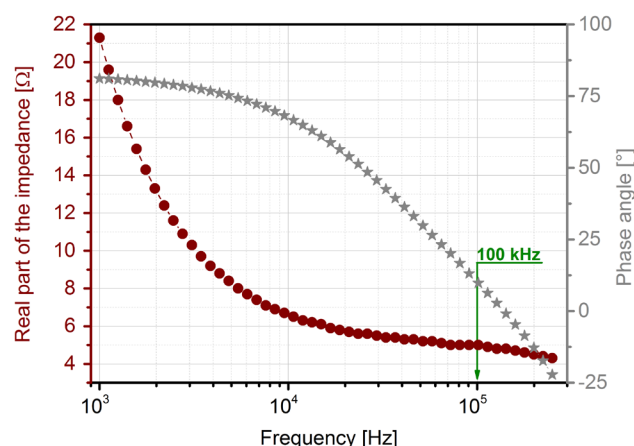


**Figure 5:** Arrhenius type representation of the temperature-dependent impedance measurement of the separator

[2] Volkmar M. Schmidt, „Elektrochemische Verfahrenstechnik: Grundlagen, Reaktionstechnik, Prozessoptimierung“, John Wiley & Sons, 2012

material.

After recording of complete impedance spectra in a rather narrow temperature range, the impedance of the separator was measured at a certain frequency within a temperature ramp covering a relatively broad range to directly evaluate the evolution of the dc-ion conductivity with temperature. For selection of a proper frequency, in Bode plots a value from the plateau in the real part of the impedance, for which the phase angle is close to zero, was chosen, see Figure 6, thus selecting 100 kHz. At higher frequency values the phase angle would be even closer to zero degrees. However, there, the impedance starts to decrease further due to inductive effects. In consequence, selection of a frequency value adjacent to this region would bear the risk of leaving the plateau and thus the zone of dc-ion conductivity.

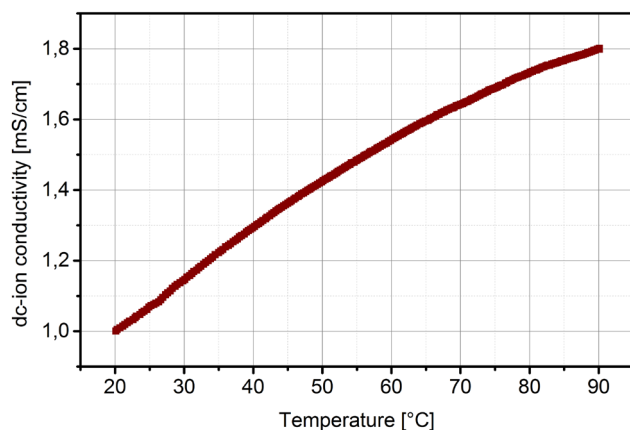


**Figure 6:** Bode plot of the real part of the impedance of the separator as well as the corresponding phase angle. The measurement was performed at 20 °C. 100 kHz, the frequency chosen for single-frequency impedance measurements, is marked by an arrow. This value was chosen, because the plateau shifts with increasing temperature to higher values. Thus, the frequency was selected in a way that it is as close as possible to the high-frequency border of the plateau while the phase angle is nearly 0°.

Results of the single-frequency impedance measurement are presented in Figure 7. The separator conductivity steadily increases with increasing temperature. Thereby, the enhancement of this value is distinctly larger in the beginning for lower temperature values, while it nearly levels off close to 90 °C.

However, comparison with Figure 3 shows a certain deviation to lower conductivity values. This discrepancy is mainly caused by two aspects: Firstly, as for recording of the data represented in Figure 7 only single-frequency impedance measurements were performed, no fitting of the data occurred. Thus, impact of other ohmic and inductive effects might result that otherwise would be identified and excluded by fitting, as it holds for the data presented in Figure 3. Secondly, due to performance of impedance measurements within a temperature ramp, no thermal equilibrium exists and the actual sample temperature should be lower. Impact of this factor is higher, the steeper the temperature ramp. In contrast to this, temperature is held for 120 s prior to impedance measurement for the data presented in Figure 3. Due to the small sample volume, in this case, reaching of the thermal equilibrium is expected. As the conductivity of the separator/electrolyte system increases with higher temperature, the shift to lower conductivity values for the measurement performed within the temperature ramp without thermal equilibration in comparison to those, where thermal equilibrium could establish, seems to be reasonable. In conclusion, single-frequency impedance measurements deliver only qualitative progresses and in turn qualitative information about the temperature-dependent behaviour of the sample. Nevertheless, it is a fast method for characterization of an electrolyte soaked separator.

100 kHz of the separator material within a temperature ramp of 3 °C/min from 20 to 90 °C.



**Figure 7:** Single-frequency impedance measurement at