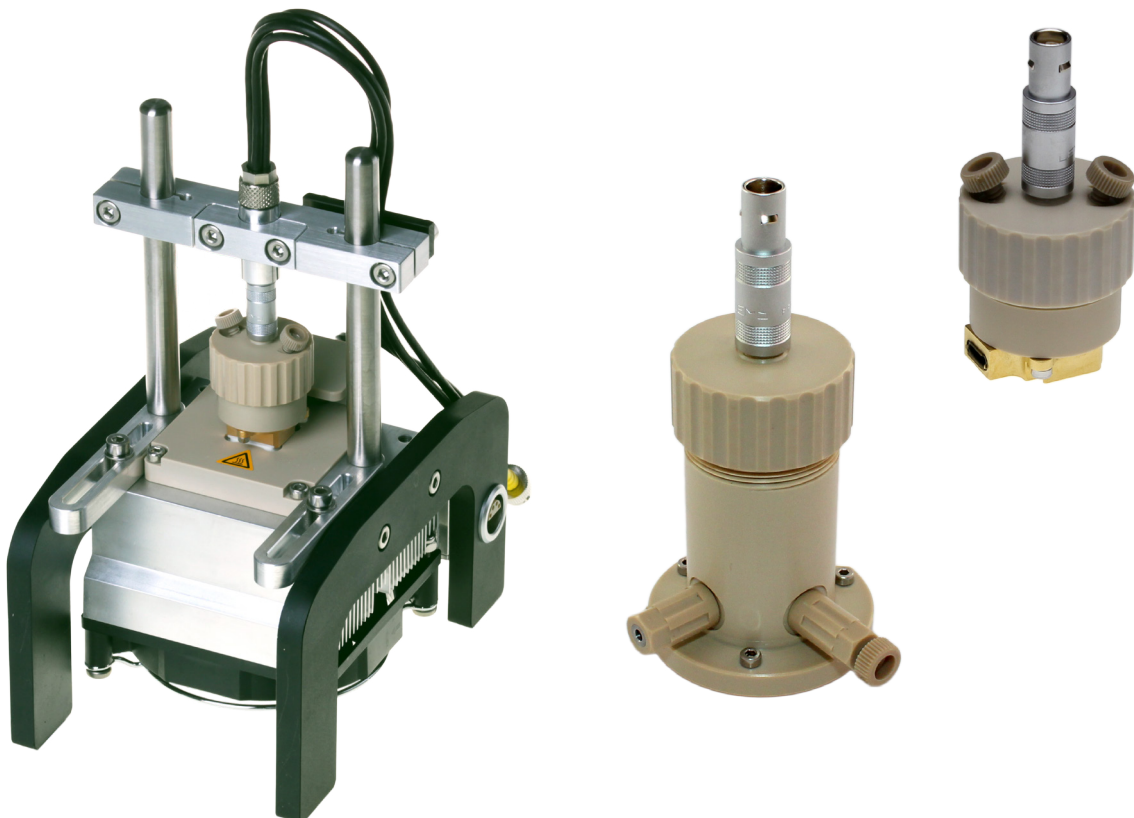


Application note

Determination of the MacMullin number

- » Important performance indicator for electrolyte soaked separators



Introduction

Battery cells are composed of at least three components, namely two electrodes of opposite polarity, being the location of the electrochemical reactions, and an electronically insulating electrolyte [4]. It not only serves as physical separator of the electrodes, but also guarantees sufficient ion transfer between them. 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 electrolyte soaked 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 these systems is an important value for characterization and rating of different separator materials.

An important figure for characterization of the blocking effect of the ionic flow of a certain separator/electrolyte combination is the so called MacMullin number N_M being defined as ratio of the resistivity of a separator soaked with electrolyte to that of the pure electrolyte occupying the same volume like the separator [2], [3]:

$$N_M = \frac{R_{\text{separator}}}{R_{\text{electrolyte}}} = \frac{\tau^n}{\varepsilon^m}$$

with τ as tortuosity and ε as porosity of the separator; n and m are empirical constants depending on the geometric model employed to describe the porous media [1], [3]. For example in the straight-capillary-tube model from Wyllie and Spangler n and m equal one [3]. The MacMullin number describes the relative contribution of a separator material to the cell resistance and thus can be used for

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

[2] R. B. MacMullin, G. A. Muccini, *A. I. Ch. E. J.* **1956**, 2, 393-403

[3] M. J. Martínez et al., *J. Electrochem. Soc.* **2009**, 156 1 B80-B85

prediction of its influence on the battery performance [1], [2]. It factors out the thickness of the material and is almost independent of the applied electrolyte [1]. Typically, the resistivity of a microporous separator soaked with electrolyte is approximately 6-7 times that of a comparable electrolyte volume [1]. Using the geometry dependent relationship between tortuosity and porosity, determination of the MacMullin number in addition delivers information about the microscopic structure of the separator material [3].

By usage of different cell geometries or volumes care has to be taken, as not just the absolute resistances e.g. determined by impedance spectroscopy of the electrolyte soaked separator and the pure electrolyte can be set in relation to each other, but the different cell constants C of the cells employed for electrochemical analysis of the separator, $C_{\text{separator}}$, and the electrolyte, $C_{\text{electrolyte}}$, respectively, have to be taken into account. This scaling factor is defined as

$$C = \frac{d}{A} \text{ [cm}^{-1}\text{]}$$

for a simple plate-plate geometry, where A [cm²] and d [cm] are the sample area and thickness, respectively. In consequence, for calculation of N_M also the ratio of the conductivities σ_i [S/cm] of the electrolyte soaked separator and the pure electrolyte can be employed:

$$N_M = \frac{\sigma_{\text{electrolyte}}}{\sigma_{\text{separator}}} = \frac{C_{\text{electrolyte}}}{R_{\text{electrolyte}}} \cdot \frac{R_{\text{separator}}}{C_{\text{separator}}}$$

Thereby, R [Ω] is the resistance of the sample. In case of unknown cell geometries the cell constant can be determined by means of a reference sample with a known dc-ion conductivity and geometries comparable to the sample whose conductivity should be determined. Thus, by performing an impedance measurement the cell constant can be calculated and subsequently used for analysis of the sample of interest. In case of liquid

samples for example KCl conductivity standards with conductivity values tabulated over a wide temperature range can be applied [4].

In this application note, an exemplarily measurement and evaluation routine for determination of the MacMullin number of a separator material is presented using an almost completely automated measurement routine for determination of the temperature-dependent dc-ion conductivity by means of the electrochemical impedance spectroscopy.

Experimental

a) Measurement equipment

From the separator material discs of 12 mm in diameter were punched out and soaked in approximately 300 μl electrolyte for at least 24 h to guarantee sufficient wetting. As electrolyte 1 mol/l LiClO_4 in EC/DMC (1:1 w/w) was used.

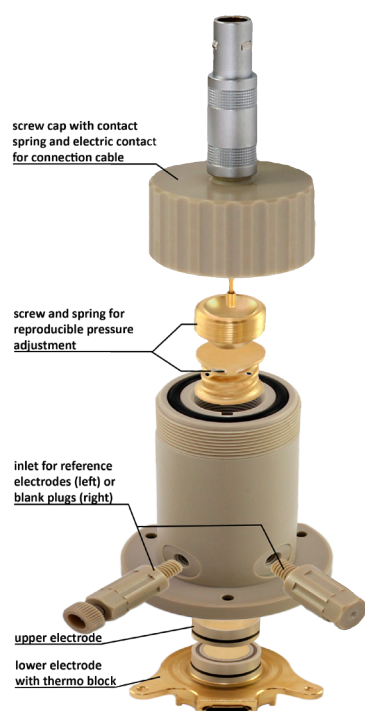


Figure 1: Exploded view of measuring cell TSC battery. The sample is placed between the upper and lower electrode.

For impedance measurements of the separator material, 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. 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 40.7 kPa.

The dc-ion conductivity of the pure electrolyte was determined using a TSC 1600 closed measuring cell as depicted in Figure 2, likewise mounted onto the Microcell HC setup. This measuring cell is designed for electrochemical investigation of liquid moisture-, air- or photosensitive samples under temperature control using low amounts of approximately 1.0 ml. The platinum crucible serves as counter electrode, while one of the four platinum wires separated by glass mounted in the screw cap and pointing downwards into the crucible is employed as working electrode. The PEEK casing guarantees hermetic sealing of the cell interior from the outside. The used electrolyte is volatile and evaporation during impedance measurement would affect its concentration and in turn its conductivity even if this sealed measuring cell is employed, due to the small dead volume just above the crucible. To minimize this effect, the cell interior was completely filled with electrolyte. Thus, 1.3 ml were used.



Figure 2: Exploded view of measuring cell TSC 1600 closed. The liquid sample is filled into the platinum crucible.

Besides the measuring cells TSC battery and TSC 1600 closed mounted onto the Microcell HC setup, a Metrohm Autolab

[4] R. H. Shreiner, K. W. Pratt, NIST Special Publication 260-142, 2004 Ed., „Standard Reference Materials: Primary Standards and Standard Reference Materials for Electrolytic Conductivity“

PGSTAT204 equipped with a FRA32-module was used for the electrochemical analysis. For data acquisition, the NOVA 1.11 software (Metrohm Autolab B.V.) has been used. 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 adjusting the sample temperature 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, developed by rhd instruments GmbH & Co. KG). It enables fully-automated determination of the dc-ion conductivity of samples with a well-known and relatively simple impedance spectrum using the online-fit option of the NOVA software. In combination with a Microcell HC setup the temperature accuracy is $0.1\text{ }^{\circ}\text{C}$ in the thermo block.

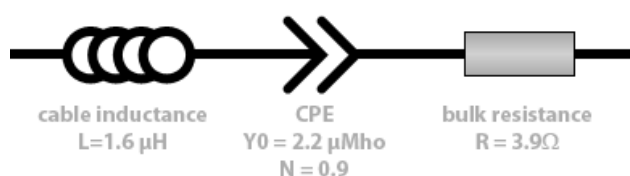


Figure 3: Equivalent circuit representing the impedance behaviour of the separator samples within the chosen frequency range.

In the present case, the equivalent circuit depicted in Figure 3 was used for fitting of the impedance spectra. Thereby, L symbolizes 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.

Partially, fit of the impedance data was performed for error minimization in the admittance instead of the commonly employed im-

pedance domain. In the former domain values at low frequencies are greater and thus have a higher weighting during minimization of the deviation in the fit routine. For this purpose, the impedance analysis software RelaxIS[®] distributed by rhd instruments GmbH & Co. KG was used.

b) Measurement parameters: separators

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 „Introduction“). The high-frequency part of $\sigma'(\omega)$, the real part of $\sigma(\omega)$, is governed by ion movements in the bulk of the electrolyte, i.e. by the dc-ion conductivity. Here, the sample impedance equals its resistance, i.e. at a phase angle of approximately zero degrees [1], where the Bode plot of the real part of the impedance as well as of the real part of the complex conductivity shows a plateau. For good to moderate ionic conductors the plateau value is expected at high to intermediate frequencies. This plateau shifts with increasing temperature to higher frequency values. Thus, the frequency range has to be selected in a way, that it covers the region where dc-ion conductivity occurs for the whole temperature range under investigation.

In consequence, for the electrolyte soaked separator samples a frequency range from 250 kHz down to 100 Hz was employed for all temperatures. Starting at $20\text{ }^{\circ}\text{C}$, the separator 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 while applying an ac voltage amplitude of 10 mV (rms) to the sample. To guarantee for reaching of the thermal equilibrium at each temperature, the respective value was held for 120 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 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

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

In the present study the thickness d of the separator was 20 μm 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 cm 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.

c) Measurement parameters: electrolyte

In case of the pure electrolyte, prior to sample measurement the cell constant was determined using the KCl conductivity standard 1413 by Hanna Instruments.

For identification of the required waiting time at each temperature to reach thermal equilibrium, firstly an impedance spectrum at 20 °C was recorded followed by a jump to 15 °C. At this temperature 15 impedance spectra were recorded directly one after another to monitor changes in the impedance of the sample due to temperature changes until these differences diminish thus showing the reaching of thermal equilibrium. This check reveals 720 s as required waiting time.

Using a fresh filling, afterwards impedance measurements for determination of the temperature-dependent dc-ion conductivity were performed over a frequency range from 500 kHz - 500 Hz with an ac voltage ampli-

tude of 10 mV (rms). Like for the electrolyte soaked separator samples, for the pure electrolyte presence of thermal equilibrium was verified by recording of ascending and descending temperature ramps: Starting at 20 °C, the sample was firstly cooled down to 0 °C, than reheated to 30 °C and finally cooled down to 20 °C in steps of 5 °C.

Data evaluation

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 for the electrolyte soaked separator. In case of the pure electrolyte evaluation of the impedance data occurred by means of the impedance analysis software RelaxIS® because fitting was performed in the admittance domain. Averaging of the measurements at the respective temperatures results in the mean dc-ion conductivities summarized in Table 1 for both samples together with the appendant standard deviations.

Table 1: Mean σ_{dc} as function of sample temperature and its standard deviation (SD) of the electrolyte soaked separator as well as of the pure electrolyte LiClO_4 .

Temperature [°C]	Separator		Electrolyte	
	σ_{dc} [S/cm]	SD [S/cm]	σ_{dc} [S/cm]	SD [S/cm]
0	0.66E-3	0.07E-3	5.08E-3	-
5	0.75E-3	0.07E-3	5.69E-3	0.02E-4
10	0.84E-3	0.07E-3	6.31E-3	0.01E-4
15	0.94E-3	0.06E-3	6.94E-3	0.01E-4
20	1.03E-3	0.07E-3	7.57E-3	0.10E-4
25	1.13E-3	0.07E-3	8.19E-3	0.01E-4
30	1.22E-3	0.08E-3	8.81E-3	-

Results of the electrolyte soaked separator as well as of the pure electrolyte are depicted in Figure 4 and Figure 5, respectively, each showing a steady increase of the conductivity with temperature. For better comparison of the different temperature ramps of a single sample only the four ramps of one selected

separator sample are exemplarily presented. In most cases, the conductivity values of the four temperature ramps show only negligible divergence of less than 3.3 % at the respective temperatures, thus confirming the presence of thermal equilibrium. In case of the pure electrolyte the divergence was with less than 0.3 % even lower.

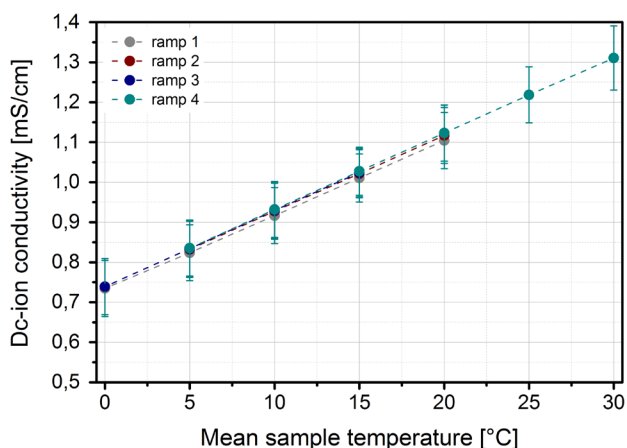


Figure 4: Comparison of the four temperature ramps measured for determination of the temperature-dependent dc-ion conductivity of one separator sample soaked with LiClO_4 to check the presence of thermal equilibrium. The respective standard deviations are also presented.

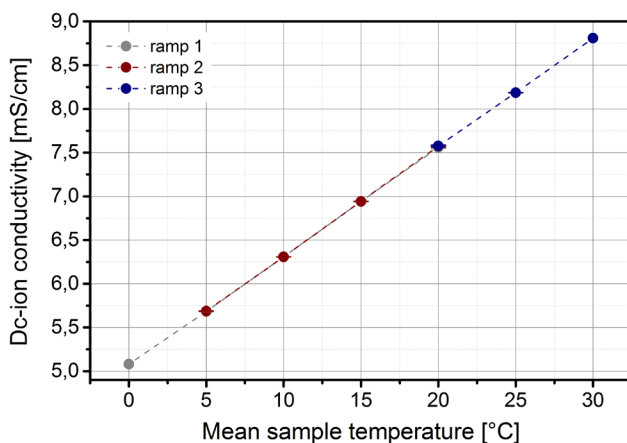


Figure 5: Comparison of the three temperature ramps measured for determination of the temperature-dependent dc-ion conductivity of the pure LiClO_4 electrolyte to check the presence of thermal equilibrium. The respective standard deviations are also presented.

In Table 2 the mean MacMullin numbers calculated for the respective temperatures taking into account the different temperature ramps are presented using the mean conductivity values determined by including results of all separator samples.

The corresponding plot is shown in Figure 6. Averaged over all temperatures and ramps a MacMullin number of 7.43 with a standard deviation of 0.14 resulted, thus fitting to the range reported in literature [1].

Table 2: Mean MacMullin numbers in dependence of the temperature. Values of different temperature ramps were averaged at the respective temperature.

Temperature [°C]	MacMullin number
0	7.69
5	7.58
10	7.50
15	7.41
20	7.33
25	7.28
30	7.23

However, as obvious from Figure 6, the MacMullin number decreases with increasing temperature. This might show a higher permeability of the separator material with increasing temperature due to e.g. softening and widening of the porous membrane structure, thus reducing its blocking effect on the ion movement.

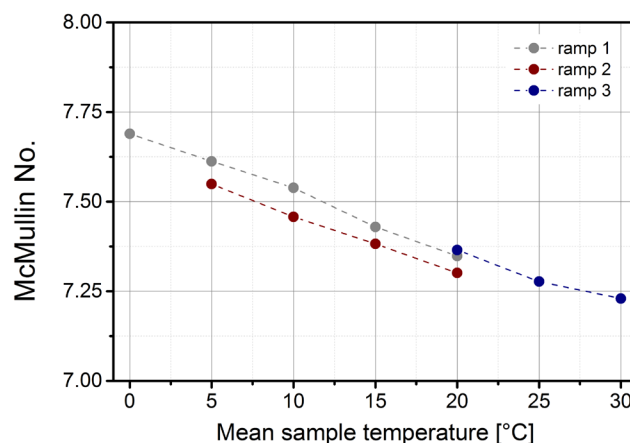


Figure 6: MacMullin numbers as function of the temperature for the different temperature ramps.