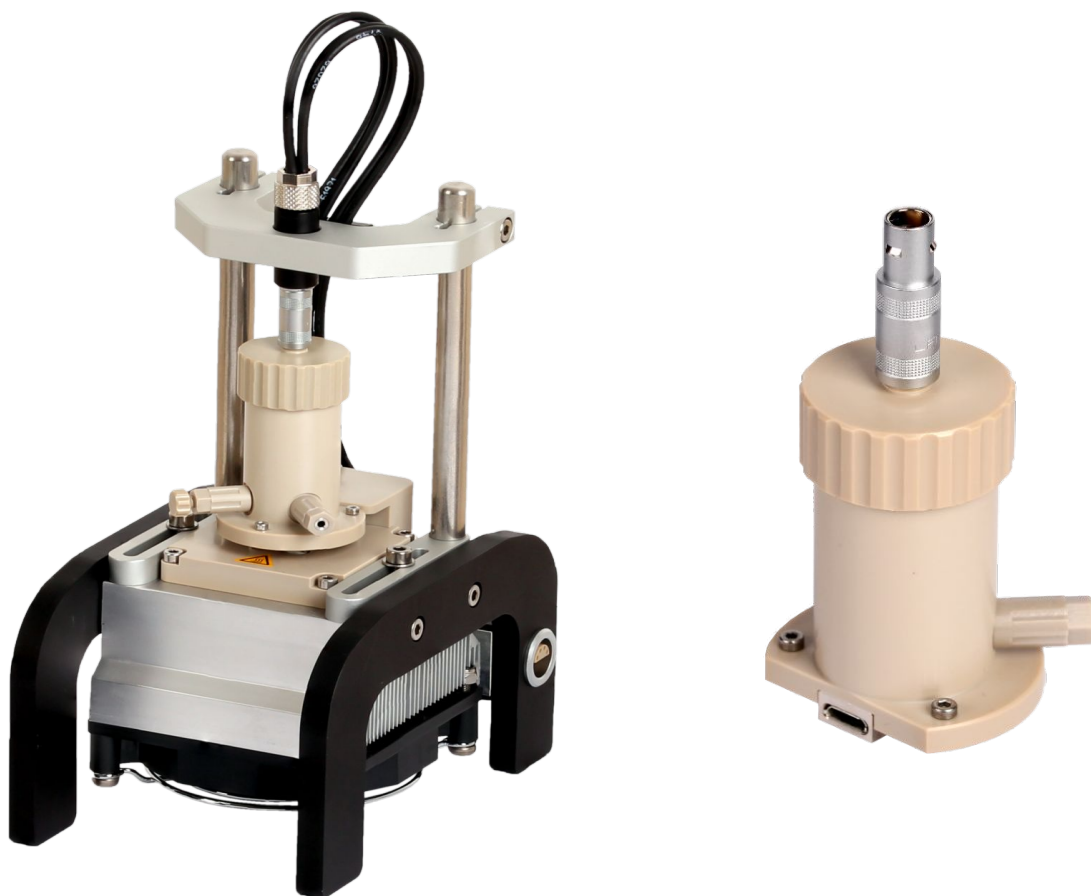


Application note

Determination of
MacMullin numbers:
The stacking-method



Introduction

One important component of lithium ion batteries is the separator foil – a thin electronically insulating, porous membrane that prevents the electrodes from being in direct contact with each other while being permeable for ionic current. To maintain a good lithium ion battery performance, the resistance to the ionic current of a separator foil filled with electrolyte should be low. Consequently, information about the effective ion conductivity of these systems is an important parameter for the performance of a separator material.

Usually, one does not focus on the effective ionic conductivity, but on another quantity: the so-called MacMullin number N_M [1]. The MacMullin number is the ratio of the ionic conductivity of the pure electrolyte $\sigma_{\text{electrolyte}}$ and ionic conductivity of the separator foil filled with electrolyte $\sigma_{\text{separator}}$.

$$N_M = \frac{\sigma_{\text{electrolyte}}}{\sigma_{\text{separator}}}$$

Therefore, the MacMullin number is a quantity for the decrease of the effective conductivity by the presence of a separator foil. For lithium ion battery separators, often a value between 4 and 20 is found [1]-[3]. Theoretically, the MacMullin number is linked to the separator foil's porosity ε and tortuosity τ [2]-[3].

In this application note, we want to focus on showing how to determine the MacMullin number following the so-called stacking-method approach introduced by Landesfeind *et al.* [3].

Experimental

a) Chemicals

As electrolyte a 1 mol/l LiPF₆ (lithium hexafluorophosphate) solution in a 1:1 (v:v) mixture of EC (ethylene carbonate) and DMC (dimethyl carbonate) (purchased from Sigma-Aldrich / Merck KGaA) was used without any further purification. After receiving, the electrolyte

has been stored and handled inside of an argon-filled glove box (M. Braun Inertgas-Systeme GmbH).

As battery separator material, a trilayer separator based on polyethylene/polypropylene with a thickness of 21.5 μm was used.

b) Sample preparation & measuring setup

Round-shaped specimens with a diameter of 12 mm were punched out from the separator foil, using the [OAB cutter tool](#) (rhd instruments GmbH & Co. KG). To ensure an optimal wetting, the specimens were stored for at least 24 h in the electrolyte solution.

For the electrochemical measurements, a [TSC battery standard cell](#), see **Figure 1**, in combination with a [Microcell HC setup](#) (rhd instruments GmbH & Co. KG) was used. As current collectors, two planar stainless steel disc electrodes (\varnothing 8 mm) press-fitted into a PEEK sleeve were used. For calculating the cell constant, the area of the stainless steel electrodes and the separator thickness were considered, resulting in a value of 0.0043 cm^{-1} . The contact pressure applied onto electrolyte-soaked separator foil stack inside of the TSC battery cell was adjusted to approximately 100 kPa using a gold-plated spring with a spring constant of 2.43 N mm^{-1} . At this contact pressure, no significant compression of the separator foil was found.

In the Microcell HC setup, the temperature is adjusted via a Peltier element. The accessible temperature range is -40 °C to +100 °C. For measuring the temperature, a Pt100 temperature sensor is embedded in the base unit of the TSC battery cell, at a position very close to the sample. The accuracy of the temperature is 0.1 °C with regard to the sensor position inside of the base unit. For the determination of the MacMullin number, the temperature was adjusted to 20.0 °C.

Because the TSC battery measuring cell is completely airtight, the experiments took place on the Microcell system outside of the glove box.

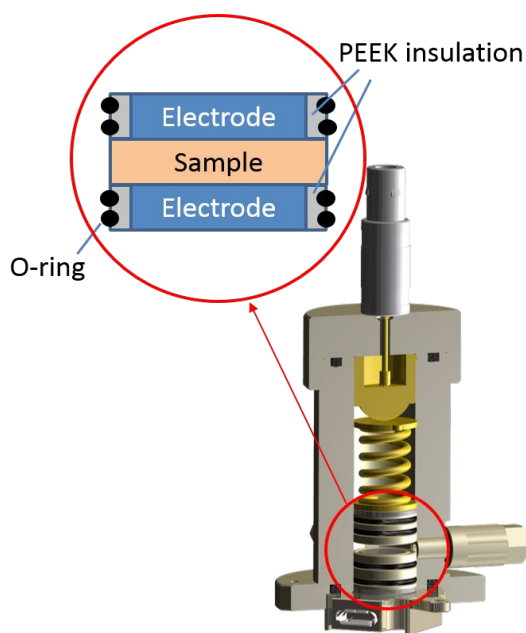


Figure 1: Schematic drawing of the measuring cell TSC battery standard. The separator foils filled with electrolyte were placed between the upper and lower electrode.

For the impedance measurements, a Metrohm Autolab PGSTAT204 equipped with a FRA32-module was used. The communication with the temperature controller is integrated in the NOVA 2.1.5 software enabling automated measuring routines.

The recorded impedance data were evaluated by equivalent circuit fitting using the impedance data analysis software RelaxIS 3 (rhd instruments GmbH & Co. KG).

c) Measurement parameters

The impedance measurements were performed at a frequency range of 1 MHz to 100 Hz with an amplitude of $V_{AC,rms} = 10.0$ mV.

After reaching the temperature set point of 20.0 °C, a waiting time of 300 s was chosen to ensure for complete thermal equilibrium.

Step	Action to be performed
1	Transferring the cell into the glove box and loading the cell with one specimen of the electrolyte-filled separator foil.
2	Taking the prepared cell out of the glove box and connecting it to the Microcell HC cell stand.
3	Connecting the measuring device (2-electrode configuration).
4	Setting the temperature to 20.0 °C and waiting for 300 s.
5	Performing an impedance spectroscopy measurement.
6	After finishing step 5, repeating steps 1-5 by adding further specimens of the electrolyte-filled separator foil (one per loop) until a stack of five specimens is created.

Results

The resulting impedance spectra for different stack thicknesses are shown in **Figure 2**.

At high frequencies, the impedance behavior is dominated by inductive effects caused by the connection cables. The intersection at the Z' -axis is close to the bulk resistance value for bulk ion transport inside of the porous separator network. In absence of the inductive behavior at high frequencies, they would be identical. The increase at lower frequencies is then caused by electrode polarization.

As expected, increasing the stack thickness by adding further specimens of the electrolyte-soaked separator foil leads to a shift to higher values for the intersection point due to the higher bulk resistance value.

The spectra were fitted with the equivalent circuit shown in **Figure 3**. The inductance L_{cable} takes the high frequency contributions by the connection cables and further connecting parts into account, the resistor R_{ion} represents the ion migration in the porous separator network, and the constant phase element CPE_{pol} describes the electrode polarization at low frequencies.

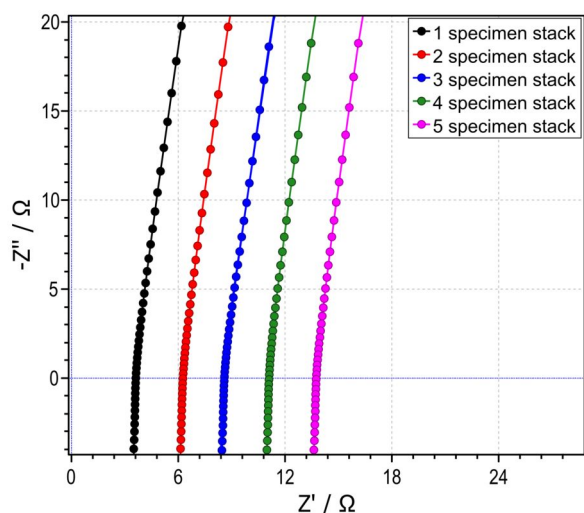


Figure 2: Impedance spectra of the soaked separator foils for different stack thicknesses. For a better visibility of the shift along the Z' -axis, the spectra were cut at 3 kHz. The points are the measured values and the lines represent the fit.

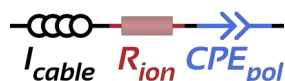


Figure 3: Equivalent circuit for fitting the impedance spectra.

The resulting stack-thickness dependent values for R_{ion} are given in the following table. The fit error of R_{ion} was lower than 0,4% in all cases:

$N_{specimen}$	R_{ion} / Ω
1	3.38
2	5.98
3	8.34
4	10.78
5	13.43

A plot of these values shows a linear relationship, where the slope gives a value of 2.49 Ω for the ionic resistance change per added specimen $\Delta R_{ion} / \Delta N_{specimen}$ (Figure 4).

Taking into account the separator thickness d , the active area A of the stainless steel electrode and the resistance per added specimen $\Delta R_{ion} / \Delta N_{specimen}$, the corresponding ionic conductivity of the electrolyte-soaked separator

$\sigma_{separator}$ can be calculated as shown in the following.

$$\sigma_{separator} = \frac{1}{\Delta R_{ion} / \Delta N_{specimen}} \cdot \frac{d}{A}$$

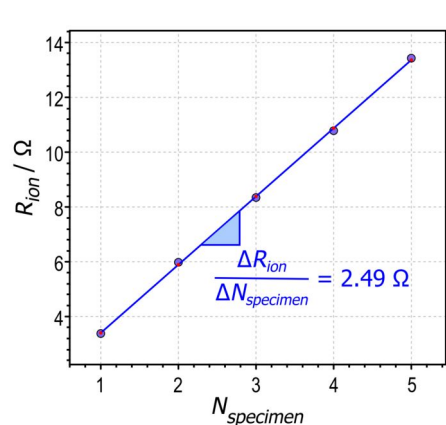


Figure 4: Plot of total ionic resistance value R_{ion} in dependence of the number of separator specimens $N_{specimen}$.

Here, a value of $\sigma_{separator} = 1.7 \text{ mS cm}^{-1}$ was determined at a temperature of 20 °C. Based on the method described in one of our previous application notes [4], the conductivity of the pure electrolyte solution at 20.0 °C was determined to $\sigma_{electrolyte} = 9.9 \text{ mS cm}^{-1}$.

Thus, we end up with a **MacMullin number** $N_M = 5.8$ which lies within the typical range for such separators [3].

It has to be mentioned, that Raccichini *et al.* found that the MacMullin number can be slightly dependent on the chosen electrolyte solution [5], although Landesfeind *et al.* showed that there was no dependence of the MacMullin number on the electrolyte salt, solvent composition and salt concentration for the samples chosen by them [3]. Therefore, further research has to be performed to shed more light on the influence of the electrolyte properties on the determined MacMullin number values for separator foil. Ideally, the MacMullin number should be determined by using the electrolyte that is used for the final application.

Summary

In this application note, we demonstrated how to determine the MacMullin number of separator foils by applying the so-called stacking method. We used a Microcell HC setup combined with a TSC battery standard cell for that purpose and selected a typical lithium-ion battery electrolyte as well as a typical separator material.

Acknowledgement

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