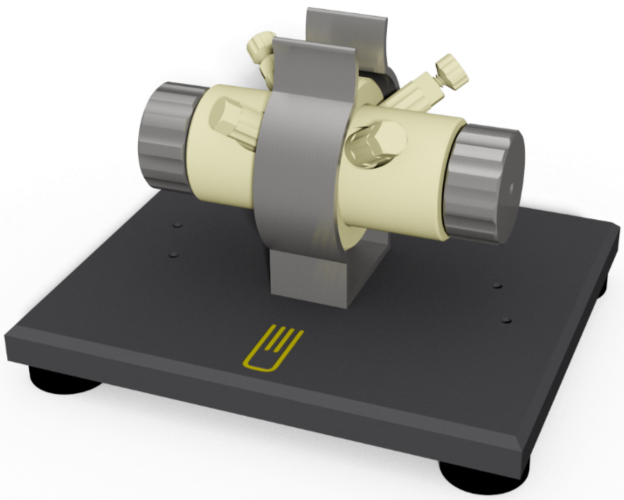
Application note

MacMullin Number Determination for Lithium-ion Battery Separators by EIS – an Alternative Approach



01/2023
rhd instruments GmbH & Co. KG

Introduction

Separators are used in battery cells to avoid electrical contact between the electrodes, while also allowing fast ion transport. The MacMullin number N_M describes how much the ionic conductivity through a separator is limited compared to the pure electrolyte:

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

The MacMullin number is related to the porosity and tortuosity of the separator, and is in the range 4 – 20 for common lithium ion battery separator materials [1, 2, 3]. Clearly this is an important property, since decreasing N_M can lead to a significantly lower internal cell resistance.

In this application note, we describe the determination of the MacMullin number of a commercially available separator by measuring impedance spectra in a TCE Cell One test cell (rhd instruments GmbH & Co. KG) and fitting the resulting data to an equivalent circuit (RelaxIS 3 software, rhd instruments GmbH & Co. KG). Lithium metal is used on the electrodes in order to also use the cell for subsequent direct current measurements (will be published in a separate application note), and would not be necessary for the EIS measurement itself.

Experimental

A 1 mol/l solution of $LiPF_6$ in ethylene carbonate : dimethyl carbonate = 1:1 by volume was used as electrolyte. Circular specimens (18 mm Ø) of a commercially available ceramic-coated tri-layer polyethylene (PE) / polypropylene (PP) / polyethylene (PE) separator with a thickness of 20 µm were punched out using an OAB Cutter tool (rhd instruments GmbH & Co. KG) and soaked in the electrolyte in a glove box for 24 h prior to measurement.

The separator was mounted in the TCE Cell One test cell between two PEEK blocking disks. The blocking disks have a central hole with 2 mm diameter, and are 0.5 mm thick. The inner cell diameter is 10 mm, the distance between the electrodes is 16 mm, and the electrolyte volume is 1.7 ml. The surface of a lithium ribbon (0.75 mm thickness) was brushed on both sides with a scalpel inside a glove box, to reveal a shiny metallic surface. Two circular stainless-steel plate electrodes with a punching edge were used to punch out lithium directly onto the electrodes (10 mm Ø). These lithium electrodes were mounted in the test cell in a two-electrode configuration (**Figure 1**). The cell was filled with electrolyte inside the glove box before sealing the ports. All measurements were performed outside the glove box in a climate chamber at 20.0 °C.

A Metrohm Autolab PGSTAT302N equipped with an FRA32-module and controlled through the NOVA 2.1.5 software was used for all impedance measurements. The recorded impedance data were evaluated by equivalent circuit fitting using the impedance data analysis software RelaxIS 3 (rhd instruments GmbH & Co. KG).

Step	Action to be performed
1	Soak the separator in electrolyte for 24 h.
2	Ensure that all cell components are clean and dry.
3	Punch out lithium on the two electrodes, and mount them in the test cell.
4	Place the blocking disks (with or without the separator) in the test cell.
5	Fill the test cell with electrolyte and close it.
6	Place the test cell in a climate chamber and connect the impedance analyser in two-electrode configuration.
7	Set the temperature to 20.0 °C and wait for temperature equilibration (60 min).
8	Measure the OCP of the test cell.
9	Apply 0 V *vs* OCP for 60 min.
10	Perform an impedance spectroscopy measurement.
11	Drain the electrolyte from the test cell and clean it. ***N.B.*** **Dispose of the lithium metal in a safe manner!**

After temperature equilibration, the open circuit potential (OCP) was measured, and subsequently 0 V *vs* OCP was applied for 60 min to ensure stable conditions at the start of the measurements. Impedance spectroscopy was then performed in a frequency range of 100 kHz to 1 Hz with an amplitude of $V_{AC,rms} = 10.0$ mV. This procedure was repeated ten times, both with and without the separator in place, to ensure reproducibility. Between each repetition, the cell was cleaned and dried, and a new separator inserted for each measurement.

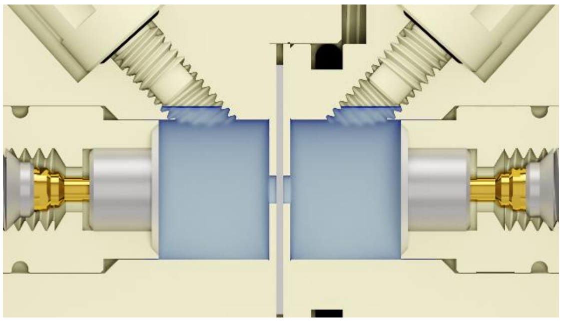


Figure 1. Schematic of the TCE Cell One electrochemical test cell, used for all measurements in this application note. The separator can be seen in grey in the centre of the cell, between two blocking disks with central holes. The two lithium electrodes to the left and right are contacted from either side, and on top the ports for electrolyte filling can be seen.

Results

A typical impedance spectrum of the TCE Cell One with the separator can be seen in **Figure 2**. Spectra without the separator show the same features (not shown). Below 500 Hz, the Nyquist plot consists of a semicircle corresponding to the charge transfer on the lithium metal/electrolyte interface. The charge transfer resistance shows a large variation between measurements (5 – 30 kΩ) reflecting the difficulty in obtaining a reproducible solid electrolyte interface (SEI) on the lithium metal. At intermediate frequencies (0.5 – 50 kHz), a smaller semicircle is evident as a shoulder (200 – 700 Ω), possibly originating from the SEI ionic resistance.

The intercept with the Z' axis is often taken as the ionic resistance (R_{ion}) of the system, but this is only true in the absence of inductive effects. If the inductance of the system is significant, the Z' intercept will differ from the actual value of R_{ion}. At high frequencies (>50 kHz), the inductance of the cables and connections dominate the impedance spectrum (l_{cable}).

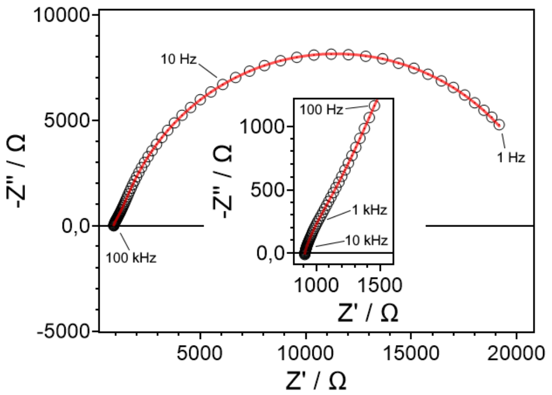


Figure 2. Nyquist plot of the impedance spectrum of the TCE Cell One with the separator. The high frequency region is magnified in the inset. The red line shows a fit to the equivalent circuit in Figure 3.

Based on the spectrum features described above, the impedance data were fitted to the equivalent circuit shown in **Figure 3**. Two Z_{arc} elements were used to fit the two semicircles [4].

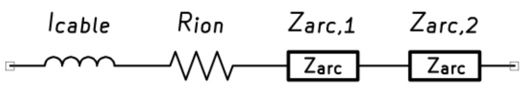


Figure 3. Equivalent circuit used for fitting the spectra.

R_{ion} values for the ten repetitions with and without the separator are shown in the table below. The separator resistance was calculated as the difference between the mean values [5]: $R_{separator} = 36.7 \pm 6.9\ \Omega$ (95% confidence interval).

	R_{ion} (Ω)	
	Electrolyte	Electrolyte + Separator
Repetition 1	845.2	893.1
Repetition 2	850.0	895.3
Repetition 3	863.9	905.0
Repetition 4	871.8	885.8
Repetition 5	855.6	897.0
Repetition 6	852.9	885.1
Repetition 7	840.9	886.7
Repetition 8	845.8	890.8
Repetition 9	856.4	880.4
Repetition 10	857.8	888.5
Mean	*854.0*	*890.8*
Standard deviation of the mean	*2.8*	*2.1*

The separator conductivity σ can be calculated as

$$\sigma = \frac{1}{R_{separator}} \cdot \frac{d}{A}$$

where d and A is the separator thickness and cross-section area, respectively. In the present cell configuration, A corresponds to the hole diameter of the blocking disks (**Figure 1**). This geometry increases the relative contribution of the separator resistance, increasing the measurement accuracy [5]. Using the above equation, the membrane conductivity was determined to be 1.73 ± 0.32 mS/cm (95% confidence interval).

The conductivity of the electrolyte was measured as 9.89 mS/cm, according to a previously published method [6]. The MacMullin number can then be calculated as the ratio of the ionic conductivity of the bulk electrolyte and the separator, respectively (see Introduction). Thus, a value of $N_M = 5.7 \pm 1.1$ (95% confidence interval) was determined for this lithium ion battery separator material.

Summary

In this application note we demonstrate how to determine the MacMullin number of a separator using the TCE Cell One by means of electrochemical impedance spectroscopy and equivalent circuit fitting. In this cell, the separator is completely free-standing in the electrolyte, without any influence of pressure exerted by electrodes, or of any chemical reactions occurring with the electrode material.

Acknowledgements

The development of the test cell TCE Cell One used for this application is part of a sub-project related to the project LiMES funded by the Federal Ministry of Economic Affairs and Climate Action as part of the 7. Energieforschungsprogramm which is highly appreciated. LiMES is a joint research project with the two partners rhd instruments GmbH & Co. KG and Karlsruhe Institute of Technology (KIT). We thank our project partners Dr. Andreas Hofmann and Ingo Reuter from KIT for the fruitful collaboration as well as for the valuable and inspiring input.

Supported by:

Federal Ministry for Economic Affairs and Climate Action

on the basis of a decision by the German Bundestag

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