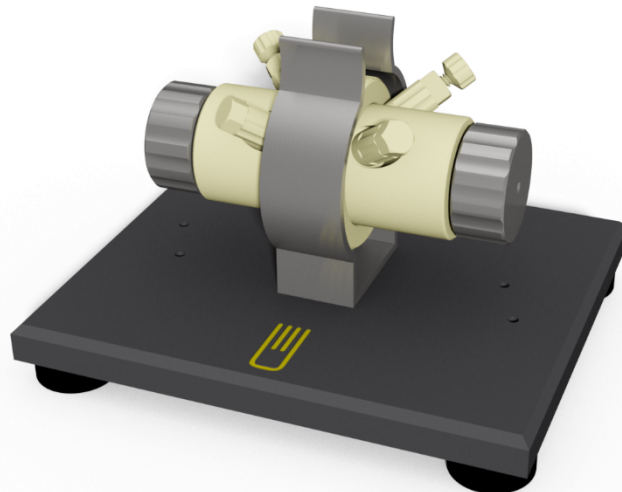




# Application note

## DC Method to Determine the MacMullin Number of Separators



## Introduction

Separators are used in battery cells to avoid electrical contact between the electrodes, while allowing fast ion transport. They typically constitute a porous network, the structure of which influences the ion movement. The extent to which the ion conduction is restricted, compared to the pure electrolyte, is indicated by the MacMullin number ( $N_M$ ):

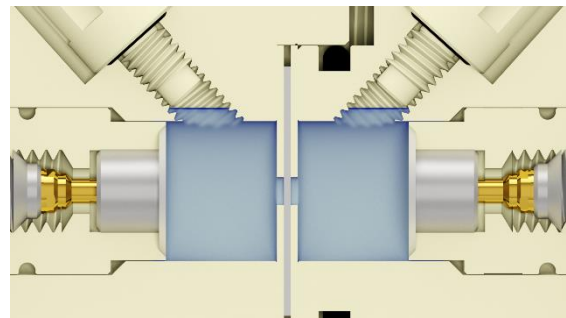
$$N_M = \frac{\sigma_{electrolyte}}{\sigma_{separator}}$$

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 order to determine  $N_M$ , the conductivity is often measured by alternating current (AC) methods such as electrochemical impedance spectroscopy (EIS) [4]. While EIS is quite powerful and precise, it requires expensive equipment, and the acquired data is not always straightforward to interpret. For these reasons, direct current (DC) methods are sometimes preferable as a means of measuring conductivity.

In this application note, we describe the determination of the MacMullin number of a commercially available lithium-ion battery separator by a simple DC method, namely linear (current) sweep voltammetry (LSV), in a TCE Cell One test cell.

## Experimental

A 1 mol/l solution of  $\text{LiPF}_6$  in ethylene carbonate : dimethyl carbonate (1:1 by volume) was used as electrolyte. Circular specimens (18 mm  $\varnothing$ ) of a commercially available ceramic coated tri-layer polyethylene (PE) / polypropylene (PP) / polyethylene (PE) separator with a thickness of 20  $\mu\text{m}$  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.



*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.*

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 approximately 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 controlled through the NOVA 2.1.5 software was used for all measurements. Linear sweep voltammograms were recorded with the NOVA "LSV staircase" command in galvanostatic mode. The procedure was as follows: After temperature equilibration (60 min), the open circuit potential (OCP) was measured, and 0 V vs OCP was applied for 60 min. EIS was then performed for comparison, although this step is not required if only the DC method is desired. More details about the AC method can be found in a previous application note [4]. The instrument was then switched to galvanostatic mode and 0 A applied for 10 min prior to the LSV measurement. The current was swept at a scan rate of 60 µA/s (15 µA current staircase steps) until a potential of 9.5 V was reached. The potential was measured in the last quarter of the current step ( $\alpha = 1$ ). The LSV measurements were recorded with and

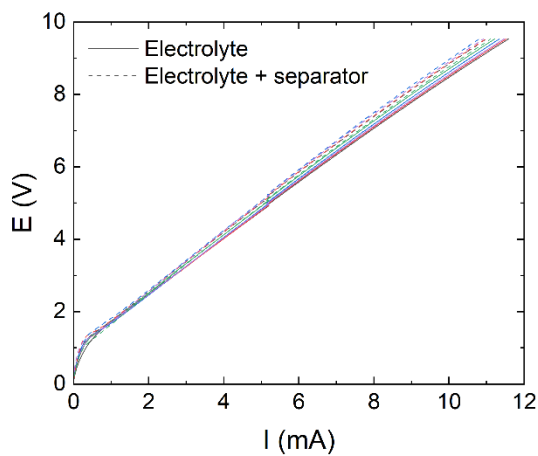
without the separator in place, and in each case the measurement was repeated ten times to ensure the reproducibility.

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 galvanostat 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 a linear current sweep voltammetry measurement.
11	Drain the electrolyte from the test cell and clean it. <b>N.B. Dispose of the lithium metal in a safe manner!</b>

## Results

Linear current sweep voltammograms with and without separator can be seen in Figure 2. At low currents (<1 mA), an initial non-linear stage is observed, where

interfacial processes occur, such as establishing an electrochemical double layer and solid electrolyte interface. At increasing currents, the potential increased linearly, although with a slightly lower slope at the end of the sweep. There was also a discontinuity at 5.2 mA, when the galvanostat switched current range. The slope was slightly higher when the separator was mounted in the cell, as compared to measurements without the separator.



**Figure 2.** Linear current sweep voltammograms for the TCE Cell One with Li metal electrodes, a lithium-ion battery electrolyte, and with (solid lines) or without (dashed lines) the separator under test.

The slope in the E/I curves in the linear region corresponds to the ionic resistance of the cell according to Ohm's law:

$$R_{ion} = \frac{dE}{dI}$$

$R_{ion}$  was thus evaluated as the E/I slope in the range 2 – 5 mA. In this range, all curves were linear with  $r^2 > 0.9999$ .  $R_{ion}$  values for the ten repetitions with and without the separator are shown in the table below. The

separator resistance could then be calculated as the difference between the mean values [5]:  $R_{separator} = 30.7 \pm 8.2 \Omega$  (95% confidence interval).

	$R_{ion} (\Omega)$	
	Electrolyte	Electrolyte + Separator
Repetition 1	763.0	813.1
Repetition 2	774.1	815.2
Repetition 3	794.5	820.8
Repetition 4	796.9	811.6
Repetition 5	782.5	826.3
Repetition 6	779.4	805.3
Repetition 7	778.9	807.9
Repetition 8	768.0	815.3
Repetition 9	780.1	798.6
Repetition 10	789.0	799.2
<b>Mean</b>	<b>780.6</b>	<b>811.3</b>
<b>Standard deviation of the mean</b>	<b>3.2</b>	<b>2.7</b>

The separator conductivity ( $\sigma$ ) can be calculated as

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

where  $d$  and  $A$  is the separator thickness and blocking disk hole area [5], respectively. In this way, the membrane conductivity was determined to be  $2.07 \pm 0.55 \text{ mS/cm}$  (95% confidence interval). This is close to the value determined by EIS ( $1.73 \pm 0.32 \text{ mS/cm}$ ) [4].

The conductivity of the electrolyte was measured as 9.89 mS/cm, according to a previously published method [6], and the MacMullin number can be calculated as the ratio of the ionic conductivity of the bulk electrolyte and the separator, respectively (see Introduction): Thus, a value of  $N_M = 4.8 \pm 1.3$  (95% confidence interval) was determined for this lithium ion battery separator. This value falls within the range of values previously measured for the same separator material, namely  $5.7 \pm 1.1$  as determined by EIS in the TCE Cell One [4], and  $4.6 \pm 1.0$ , which was measured using the so-called "stacking method" [7]. Moreover, the uncertainty was only slightly higher than for those AC methods.

## Summary

In this application note we demonstrate how to determine the MacMullin number of a lithium-ion battery separator in the TCE Cell One test cell using linear current sweep voltammetry, rather than a more commonly applied EIS method. This DC method is simpler and cheaper than EIS, while resulting in similar values of conductivity and MacMullin number for the separator material characterized here, as previously determined through AC methods. Moreover, in the TCE Cell One 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

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