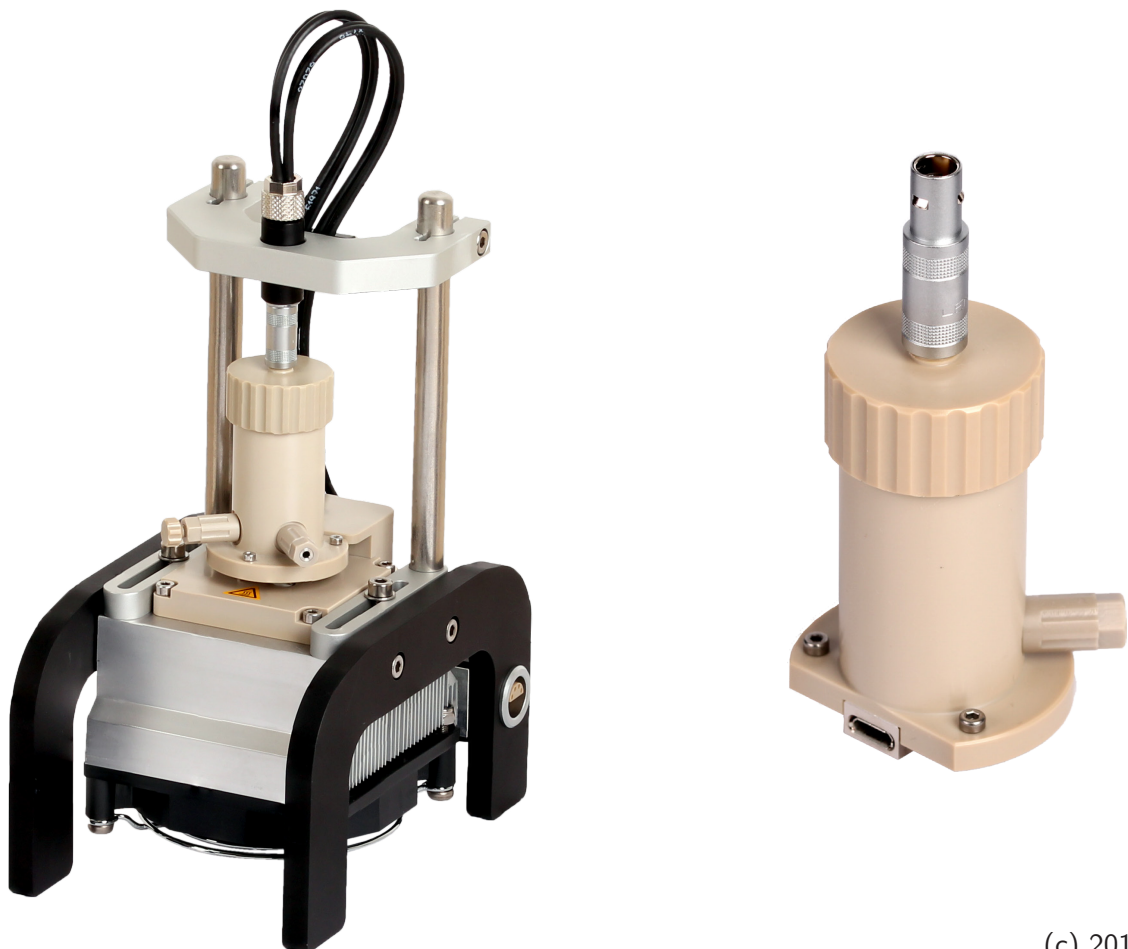# Application note

## Determination of the through-plane tortuosity of battery electrodes by EIS

# Introduction

Besides the transport parameters of the pure electrolyte like the conductivity $\sigma(T,c)$, the binary diffusion coefficient $D_{\pm}(T,c)$, the transference number $t_{+}(T,c)$, and the thermodynamic factor $f_{\pm}(T,c)$, the porosity $\varepsilon$ and (through-plane) tortuosity $\tau$ of the electrode material are key parameters which determine the electrode's suitability for high power applications [1].

In this application note, we demonstrate how to determine the through-plane tortuosity $\tau$ of a commercial lithium ion battery cathode material with known porosity and coating thickness based on the very elegant impedance spectroscopy (EIS) method presented e.g. by Landesfeind et al. [2].

# Experimental

## a) Chemicals

As electrolyte, two solutions of tetrabutylammonium hexafluorophosphate ($^{n}Bu_4NPF_6$) with different concentrations ($c_1 = 0.01$ mol/L and $c_2 = 0.10$ mol/L in an 1:1 (w:w) mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) were prepared. $^{n}Bu_4NPF_6$ was purchased in 98% purity at TCI Deutschland GmbH, EC and DMC ($\geq$99%, anhydrous) at Sigma-Aldrich Chemie GmbH. As separator, a Celgard 2340 monolayer polypropylene (PP) separator with 38 µm thickness (Celgard LLC) was chosen.

As active material, electrode sheets based on aluminium foil coated with lithium iron phosphate (LFP) were purchase from Customcells Itzehoe GmbH. The porosity $\varepsilon$ was given as 37% by the manufacturer and the film thickness as 114 µm.

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

## b) Sample preparation & measuring setup

For electrochemical measurements, a TSC battery standard measuring cell in combination with a Microcell HC setup (rhd instruments GmbH & Co. KG) was used. The design of the measuring cell is shown as schematic drawing in Figure 1.

As working and counter electrode, LFP was used.

The active electrode area was 1.13 cm$^2$, given by a diameter of 1.2 cm of the punched-out electrode specimens. The PP separator soaked with electrolyte solution was placed between the electrodes. To ensure good wettability, the separator was stored in the electrolyte solution for 48 h before assembling the measuring cell.

The sample temperature was conrolled by the Microcell HC Setup using Peltier technique. The temperature accuracy of this setup is 0.1 °C with regard to the sensor position in the measuring cell base unit. For the experiments presented here, the temperature was set to 20 °C.
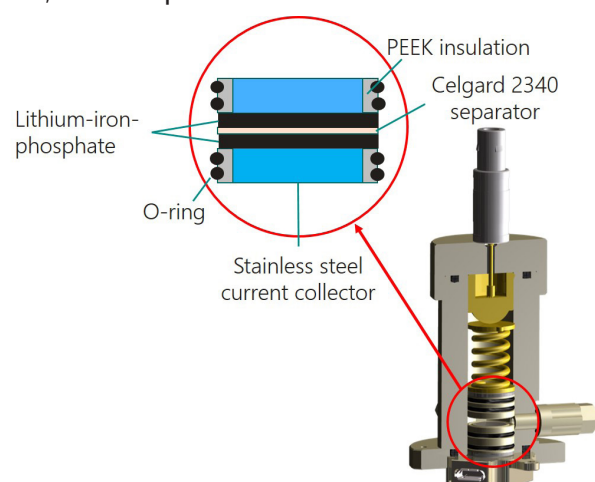


**Figure 1:** Schematic drawing of the TSC battery standard measuring cell. As working and counter electrode, LFP was used. A porous Celgard 2340 PP separator soaked with a solution of $^{n}Bu_4NPF_4$ in EC:DMC 1:1 (w:w) was placed between the electrodes.

A PGStat204 potentiostat/galvanostat equipped with a FRA32-module (Metrohm Autolab B.V.) was used for EIS experiments. For data acquisition, the NOVA 2.1.4 software was used. The control of the Microcell HC temperature unit is integrated in NOVA.

Impedance data was evaluated by means of the RelaxIS 3® software suite (rhd instruments GmbH & Co. KG).

## c) Measurement parameters

For the potentiostatic EIS measurement, the ac voltage amplitude was set to 1 mV (rms). Impedance data were collected for frequencies ranging from 100 kHz to 10 mHz with 20 measuring points per decade.

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# Results

In a first step, the dc-ion conductivity values $\sigma_{dc}$ of the pure electrolyte solutions were determined by using a TSC 1600 closed GC measuring cell at a sample temperature of 20 °C according to the standard procedure described in our previous application note 'Determination of the dc-ion conductivity of a mixture of ion liquids' [4]. The resulting $\sigma_{dc}$ values as a function of electrolyte concentration are listed in the following table.

| c [mol/L] | $\sigma_{dc}$ @ 20 °C [mS/cm] |
|-----------|-------------------------------|
| 0.01      | 0.4                           |
| 0.10      | 2.7                           |

In a second step, the EIS spectra of the LFP-electrolyte-soaked-separator-foil-LFP samples were measured. As an example, the impedance spectrum (Nyquist plot) for an electrolyte concentration of 0.01 mol/L is depicted in Figure 2.

As equivalent circuit, a serial connection of an Ohmic resistor representing all series resistances including the ion movement in the electrolyte soaked separator network, and a simplified transmission-line open element (TMLqo) with constant phase elements instead of ideal capacitors was chosen [2]. The TMLqo represents the movement of the ions inside of the branched network of the electrode material and the formation of the double layer at the active material particles while charge transfer is suppressed and intercalaction not possible for the selected electrolyte cations (= so-called non-Faradaic case).
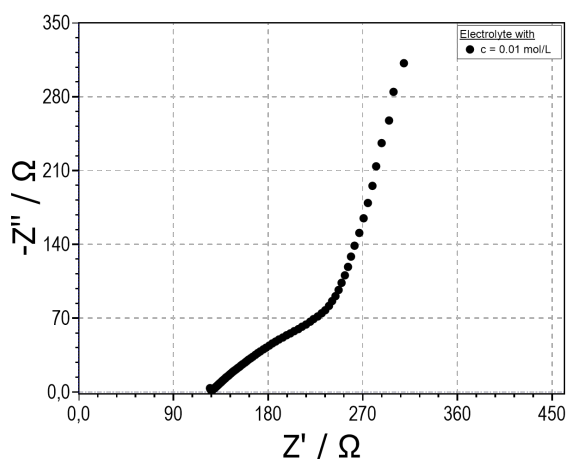


**Figure 2:** Impedance spectrum measured for the sample LFP-electrolyte soaked separator foil-LFP for a bulk electrolyte concentration of 0.01 mol/L. The

data points are shown for frequencies ranging from 100 kHz to 100 mHz.

If the electronic resistance of the active material film is negligible, see schematic drawing in Figure 3, which is a very important prerequisite for the validity of that approach since only in that case precise values for the effective ionic resistance of the electrolyte within the porous electrode network can be obtained [3], the impedance $Z(\omega)$ of the TMLqo element is given as follows [2]:

$$Z(\omega) = \sqrt{\frac{R_{ion}}{Q(i\omega)^\alpha}} \cdot coth\left(\sqrt{R_{ion}Q(i\omega)^\alpha}\right)$$

Here, Q and $\alpha$ are parameters related to the CPE element standing for the capacity of the porous film, i is the imaginary unit and $R_{ion}$ stands for the effective ionic resistance of the electrolyte within the pores of the active material.
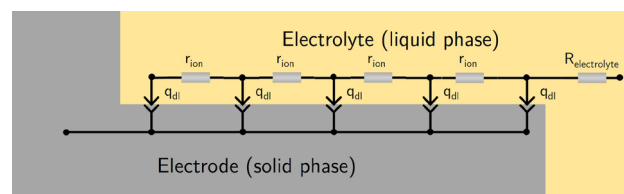


**Figure 3:** Schematic drawing of the (one-dimensional) simplified non-Faradaic transmission line element TMLqo representing the processes taking place inside of slit-like pore for the case that the electronic resistance of the electrode material is negligible.

The resulting fit parameters are listed in the following table.

| c [mol/L] | $R_{ion}$ [$\Omega$] | Q [Fs$^{(\alpha-1)}$] | $\alpha$ [1] |
|-----------|----------------------|------------------------|--------------|
| 0.01      | 367.4                | 0.0045                 | 0.84         |
| 0.10      | 42.7                 | 0.0072                 | 0.87         |

From the determined $R_{ion}$ values, the dc ion conductivities $\sigma_{dc}$, the geometric electrode area A, the film thickness d, and the film porosity $\varepsilon$, the through-plane tortuosity $\tau$ can be calculated as follows:

$$\tau = \frac{R_{ion}A\sigma_{dc}\varepsilon}{2d}$$

The determined through-plane tortuosity values using electrolyte solutions of two different concentrations are summarized in the following table.

| c [mol/L] | τ [1] |
|-----------|-------|
| 0.01 | 2.6 |
| 0.10 | 2.2 |

The determined values seem to be almost independent of the concentration of the electrolyte concentrations chosen for this study. That means that the product of electrolyte bulk conductivity times the apparent ionic resistance is almost independent of the bulk electrolyte conductivity, which is a proof for a negligible electronic resistance of the active material and thus for the validity of the chosen simplified transmission-line element [3]. In general, it is recommended to use a electrolyte solution of low conductivity to make sure that the electronic resistance of the electrode material is negligible [3].

The values determined here are similar to the values determined by Landesfeind et al. for a LFP coating [2].

## Summary

In this application note, we showed how to determine the through-plane tortuosity of a commercial lithium ion battery cathode material with negligible electronic resistance by means of impedance spectroscopy based on a simplified transmission line model.

## Acknowledgement

## Literature

[1] J. Landesfeind, A. Eldiven, H.A. Gasteiger, J. Electrochem. Soc. 165 (5) A1122-A1128 (2018).

[2] J. Landesfeind, J. Hattendorff, A. Ehrl, W.A. Wall, H.A. Gasteiger, J. Electrochem. Soc. 163 (7) A1373-A1387 (2016).

[3] J. Landesfeind, M. Ebner, A. Eldiven, V. Wood, H.A. Gasteiger, J. Electrochem. Soc. 165 (3) A469-A476 (2018).

[4] RHD application note 'Determination of the dc-ion conductivity of a mixture of ion liquids', M. Länger, downloadable via www.rhd-instruments.de/en/support/downloads

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