![Metrohm Autolab logo]

Application Area: Batteries

Determination of the Through-Plane Tortuosity of Battery Electrodes by EIS in a symmetric Lithium-iron-phosphate cell

Keywords

Batteries, conductivity, tortuosity, electrochemical impedance spectroscopy, EIS

Introduction

Besides the transport parameters of the pure electrolyte (e.g., 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 ϵ and (through-plane) tortuosity τ of the electrode material are key parameters that determine the suitability of the electrode for high power applications[1].

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

The tortuosity of a path is defined by the ratio of the length of the path to the distance between its ends.

Experimental Setup

a) Chemicals

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

As an electrode, commercial lithium–iron–phosphate (LFP) coated on aluminum current collector were used. The LFP electrodes were purchased from Customcells Itzehoe GmbH. The porosity (ε) of electrodes was given as 37% by the manufacturer with the film thickness of 114 µm.

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

b) Sample preparation & measuring setup

For electrochemical measurements, a TSC battery measuring cell in combination with a Metrohm Autolab Microcell HC setup was used. The design of the measuring cell is shown as a schematic drawing in Figure 1.
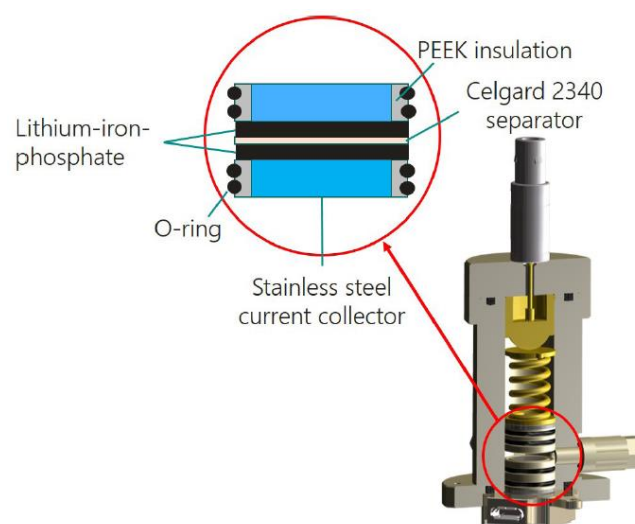

Figure 1 - Schematic drawing of the TSC battery measuring cell. LFP electrodes were used as a counter and working electrodes in this setup. A porous Celgard 2340 PP separator soaked with the electrolyte was placed between the electrodes.

LFP electrodes were used as the counter and working electrodes. The active electrode area was 1.13 cm², 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 controlled by the Metrohm Autolab 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.

A Metrohm Autolab PGSTAT204 potentiostat/galvanostat equipped with a FRA32M module was used for EIS experiments, Figure 2.

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Figure 2 – The Metrohm Autolab PGSTAT204, equipped with the FRA32M module.

For data acquisition, the NOVA software was used. The control of the Microcell HC temperature unit is integrated in NOVA.

EIS data were 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 root means square (RMS). Impedance data were collected for frequencies ranging from 100 kHz to 10 mHz with 20 measuring points per decade.

Results and Discussion

In a first step, the dc-ion conductivity value σ_{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 AN-EC-010 'In-temperature Ionic Conductivity Measurements with the Autolab Microcell HC Setup'[4]. The resulting σ_{dc} values as a function of electrolyte concentration are listed in the following table.

C [mol/L]	σ_{dc} at 20 °C [mS/cm]
0.01	0.4
0.10	2.7

In a second step, the EIS spectra of the symmetric LFP cell were measured. As an example, the impedance spectrum (Nyquist plot) for the electrolyte with the salt concentration of 0.01 mol/L is depicted in Figure 3.
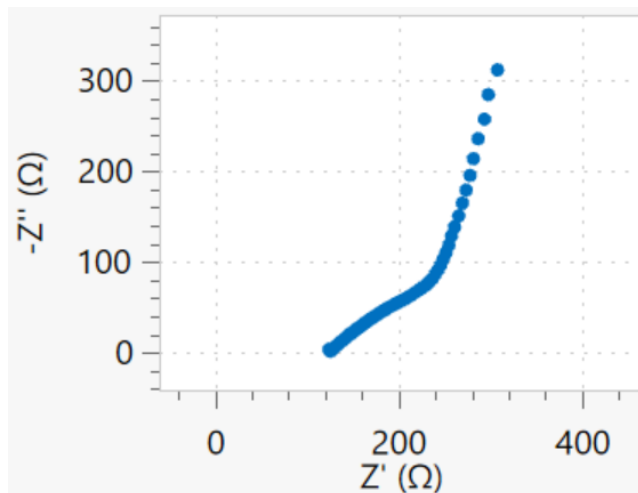

Figure 3 - Impedance spectrum measured for the symmetric LFP cell for the electrolyte with the salt concentration of 0.01 mol/L. The data points are shown for frequencies ranging from 100 kHz to 100 mHz.

To fit the impedance data, an equivalent circuit was used. For the 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, from the RelaxIS 3® software suite) 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. The charge transfer is suppressed and intercalation is not possible for the selected electrolyte ions (so-called «non-Faradaic» case).

A very important prerequisite for the validity of such an approach is that the electronic resistance of the active material film must be negligible. This is depicted in Figure 4.
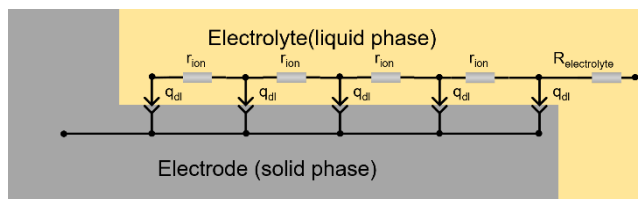

Figure 4 - Schematic drawing of the (one-dimensional) simplified non-Faradaic transmission line element TMLqo, representing the processes taking place inside of slit-like pore for the case that the electronic resistance of the electrode material is negligible.

In that case, precise values for the effective ionic resistance of the electrolyte within the porous electrode network can be obtained[3], and the impedance Z(ω) of the TMLqo element is given as follows[2]:

$$Z(\omega) = \sqrt{\frac{R_{ion}}{Q(i\omega)^\alpha}} \cdot \coth\left(\sqrt{R_{ion}Q(i\omega)^\alpha}\right) \qquad 1$$

Where R_{ion} (Ω) is the ionic resistance, Q $(F \cdot s^{\alpha-1})$ contains information on the impedance, $i = \sqrt{-1}$, ω (Hz) is the angular frequency and α is the exponent that takes into account the non-ideality.

The resulting fit parameters are listed in the following table.

C (mol/L)	R_{ion} (Ω)	Q $(F \cdot s^{\alpha-1})$	α
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 σ_{dc}, the geometric electrode area A, the film thickness d, and the film porosity ε, the through-plane tortuosity τ can be calculated as follows:

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

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

C [mol/L]	τ
0.01	2.6
0.10	2.2

The determined values seem to be almost independent of the concentration of the selected salt in the electrolyte. 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 an 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 electrode[2].

Conclusions

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

The development of this application note was based on recent works on battery electrode tortuosity done by Prof. Dr. Hubert Gasteiger group at Technical University of Munich.

References

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

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[4] AN-EC-010 'In-temperature Ionic Conductivity Measurements with the Autolab Microcell HC Setup https://www.metrohm.com/en/applications/AN-EC-010

Date

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For more information

Additional information about this application note and the associated NOVA software procedure is available from your local **Metrohm distributor**. Additional instrument specification information can be found at **www.metrohm.com/en/products/electrochemistry**.