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Determining the Tortuosity and the Pore Resistance of Porous Lithium-Ion Electrodes using Electrochemical Impedance Spectroscopy via a Gamry Interface 5000E

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High performance lithium-ion batteries (LIBs) are needed to enable fast charging of electric vehicles. Therefore, it is necessary to increase the rate capability of LIBs, which can be achieved by tuning the electrodes, e.g. by using artificial graphite that has a more sphere-like structure. This variation in electrode design decreases the parameters tortuosity and pore resistance. A quick and reliable characterization method is needed to validate the expected change in parameters. Usually, rate tests are time consuming due to the test procedure itself and the formation prior to the tests.

In the following application note, it will be shown that electrochemical impedance spectroscopy (EIS) provides a powerful tool for electrode characterization since it is fast (measurement times are shorter than 5 minutes per coin cell under the presented conditions) and nondestructive.

EIS can be used to determine the pore resistance of electrodes independently of other impedances in the cell. The pore resistance results from the ion movement in the electrolyte and hence does not depend on the charge transfer reaction in the cell. Therefore, this measurement is conducted using only the polarization of the electrodes similar to a double layer capacitor.

1 Theory

In this section, a method for determining the pore resistance of a porous electrode based on EIS measurements is explained. Furthermore, it is shown how to calculate the tortuosity of a porous electrode once the pore resistance is quantified. For a general introduction into EIS, the application note [Basics of Electrochemical Impedance Spectroscopy](#) can be referenced.

1.1 Pore resistance

To determine the pore resistance by EIS, an equivalent circuit for the structure of a porous electrode is needed. A general equivalent circuit that can be adjusted to the purpose of this experiment has been reported by H. Göhr^[1]. The modified circuit, i.e. the transmission line model (TLM) in blocking conditions is depicted in Figure 1.

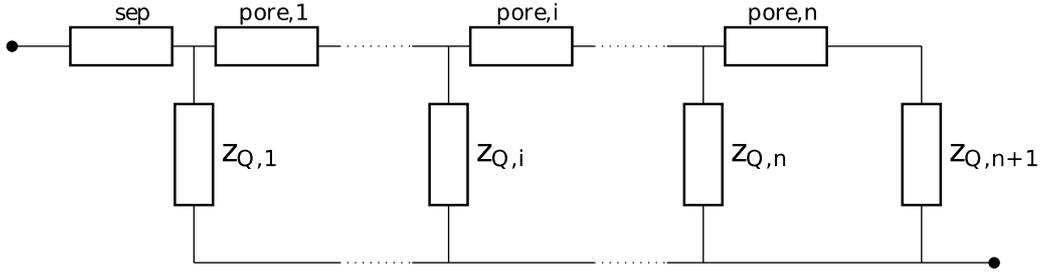


Figure 1: Adjusted equivalent circuit of the transmission line model (TLM) in blocking conditions adopted from Göhr et al.^[1]

R_{sep} represents a real impedance stemming from the ionic resistance in the separator. The upper chain of the TLM represents the infinitesimal pore resistances $r_{\text{pore},i}$, which sum up to the pore resistance R_{pore} of the electrode via

$$\sum_i^n r_{\text{pore},i} = R_{\text{pore}} \quad (1)$$

Since the electric conductivity of graphite $\sigma_{\text{el}} = (\mathcal{O}(10^2) - \mathcal{O}(10^4)) \text{ S/cm}^{[2]}$ is several orders of magnitude larger than the ionic conductivity of the electrolyte $\sigma_{\text{ion}} = \mathcal{O}(10^{-4}) \text{ S/cm}$, the electric resistance is negligible compared to the pore resistance. Hence, the lower chain, representing the electric pathway along the electrode, is shorted.

The vertical infinitesimal impedances $z_{Q,i}$ represent the mechanisms at the interface between electrolyte and surface area of the active material. This interface is modeled under blocking conditions (no charge transfer) via a constant phase element with the electrode's double layer capacitance Q , angular frequency ω , constant phase exponent α and the imaginary unit j . The infinitesimal impedances add up to

$$\left(\sum_i^n \frac{1}{z_{Q,i}} \right)^{-1} = Z_Q = \frac{1}{Q(j\omega)^\alpha} \quad (2)$$

The impedance of the TLM under blocking conditions is given by

$$Z_{\text{block}} = R_{\text{sep}} + \sqrt{\frac{R_{\text{pore}}}{Q(j\omega)^\alpha}} \coth \left(\sqrt{R_{\text{pore}} \cdot Q(j\omega)^\alpha} \right) \quad (3)$$

1.2 Tortuosity

The tortuosity τ of a porous electrode can be defined as the fraction of the measured resistance through the electrode and the theoretically calculated resistance.

$$\tau = \frac{R_{\text{pore}}}{R_{\text{theo}}} \quad (4)$$

The theoretical resistance of a porous electrode is given by

$$R_{\text{theo}} = \frac{d}{\varepsilon \sigma A_{\text{cross}}} \quad (5)$$

with an electrode that is soaked with an electrolyte of conductivity σ_{ion} and exhibits a thickness d , porosity ε and cross-sectional area A_{cross} . Thus, from Equations (4) and (5) for the tortuosity follows

$$\tau = \frac{\varepsilon \sigma A_{\text{cross}} R_{\text{pore}}}{d} \quad (6)$$

For a more detailed insight into the theory, the reader is referred to the work of Landesfeind et al.^[3].

2 Experiment

The determination of the pore resistance requires the measurement of the electrochemical impedance of an electrode. Therefore, coin cells (CR2032) were built using typical lithium-ion anodes in a symmetric setup (c.f. Figure 2). Two layers of fiberglass separator were placed between the electrodes. To avoid intercalation and its contribution to the recorded impedance spectra, non-intercalating electrolyte (0,01 M TBAClO₄ in EC:EMC; 3:7; vol./vol.) with a conductivity of 287 $\mu\text{S}/\text{cm}$ at a temperature of 20 °C was used.

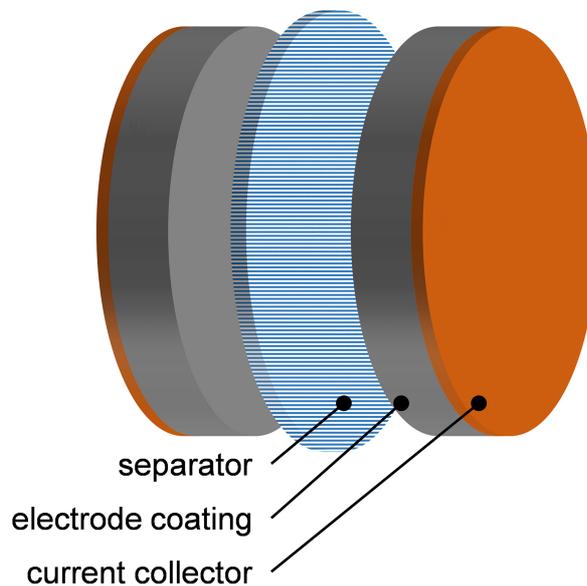


Figure 2: Schematic setup of a symmetric cell for pore resistance analysis. Separator and electrodes are soaked with electrolyte. The electrodes face each other.

After 3 hours of resting time for wetting, the electrochemical impedance spectra of the symmetric cells (five cells in total) were measured at a temperature of 20 °C using Gamry Instruments Interface™ 5000E potentiostat. The impedance was measured for frequencies ranging from 1 MHz to 0.1 Hz with an amplitude of 10 mV (rms).

3 Results

In figure 3 the resulting Nyquist plot as well as the model fit for one symmetric cell is shown. Since two identical electrodes are present in the system, the impedance values in the resulting spectrum are twice the impedance values of a single electrode. Therefore, the impedance of the equivalent circuit (c.f. Equation 3) must be multiplied by a factor of 2 to represent the measured spectrum.

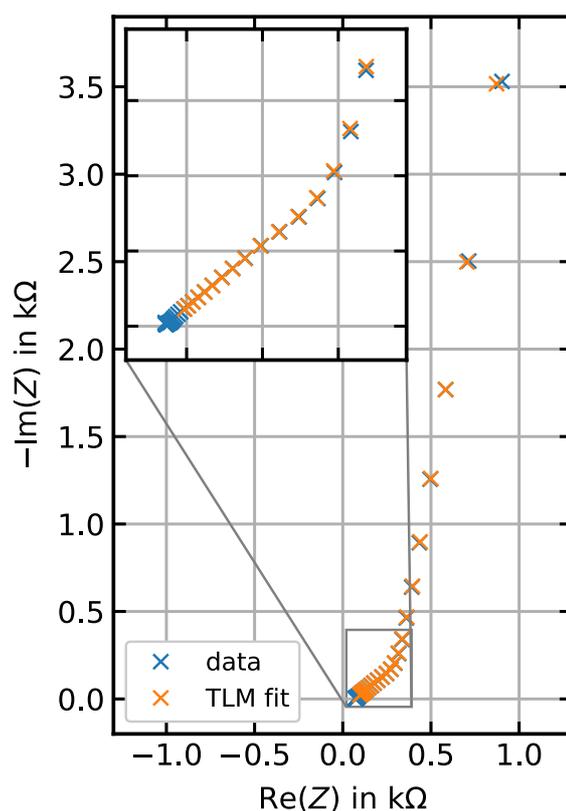


Figure 3: Measured impedance of one symmetric cell (blue) and TLM fit in Nyquist plot (orange).

For fitting, the implemented Nelder-Mead method of python's library scipy was used. Since there are high frequency artefacts that do not follow the model, only frequencies smaller than 3000 rad/s were considered for the optimization. Within this frequency range, the model shows good coincidence with the measured data. For the pore resistance R_{pore} a value of $(350 \pm 17) \Omega$ was observed leading to a tortuosity of $7,8 \pm 0,4$.

4 Conclusion

This application note presents a quick and reliable method to determine the pore resistance and the tortuosity of an electrode. The measurement times are small compared to conventional testing methods, such as rate tests. Within 5 identical cells the standard deviation of the ionic resistance and the tortuosity is less than 5%.

5 Literature

- [1] H. Göhr. „Impedance Modelling of Porous Electrodes“. In: *Advances in electrochemical applications of impedance spectroscopy* 1 (1997), pp. 2-3
- [2] Masaki Yoshio, Ralph J. Brodd, and Akiya Kozawa. *Lithium-Ion Batteries*. New York, NY: Springer New York, 2009. isbn: 978-0-387-34444-7. doi: 10.1007/978-0-387-34445-4
- [3] Johannes Landesfeind et al. „Tortuosity Determination of Battery Electrodes and Separators by Impedance Spectroscopy“. In: *Journal of The Electrochemical Society* 163.7 (2016), A1373-A1387. issn: 00134651. doi: 10.1149/2.1141607jes

