# Application note

## Temperature-dependent dc-ion conductivity of a solid proton-conductor


Dr. M. Drüschler, Dr. B. Huber

# Introduction

Impedance spectroscopy measurements for temperatures ranging from 20 °C to 150 °C were performed to extract the dc-ion conductivity of a novel solid proton-conductor.

Finally, the results are presented as temperature-dependent Bode plots of the real part of the impedance and as Arrhenius plot of the resulting dc-ion conductivity.

# Experimental

a) *Chemicals*

The sample was kindly provided as dried powder by Mohammad Zeyat (AG Lentz, Freie Universität Berlin) in a sealed flask under inert gas atmosphere.

b) *Sample preparation & measuring setup*

From the sample material, a pellet with a diameter of 10 mm was prepared by applying a pressure of around 891 MPa for 12 h. (force: 7 kN, area: 0.785 $cm^2$). A dimensionally stable pellets were obtained. The pellet was coated with a thin layer of graphite on both faces to improve the electrical contact to the current collectors.

For measurement of the sample, a TSC battery measuring cell, see Figure 1, in combination with a modified Microcell HC setup has been used. The used measuring cell enables e.g. the electrochemical characterization of planar, moisture-, air-, or photosensitive substrates of variable shape under temperature control. As current collectors, two planar gold-plated stainless steel disc electrodes with an effective, round-shaped contact of 8 mm in diameter were used. The contact pressure was adjusted to approximately 81 kPa using a gold-plated spring with a spring constant of 2.3 N/mm.

Regarding the Microcell HC setup, temperature is controlled via a Peltier element which allows adjusting the sample´s temperature from -40 °C up to +100 °C (150 °C possible via modification by RHD), depending on dew point and sample amount. For adjusting the sample temperature, an Eurotherm control unit was used. In combination with a Microcell HC setup the temperature accuracy is 0.1 °C.

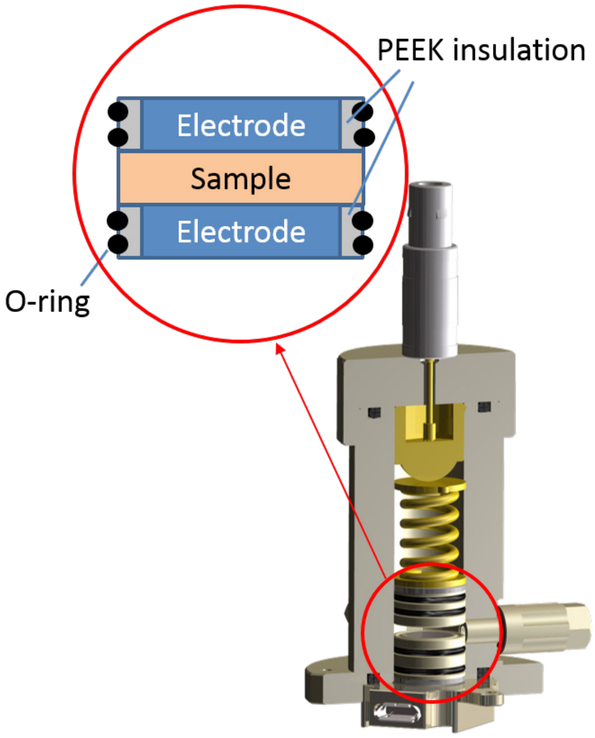


**Figure 1:**
Schematic drawing of measuring cell TSC battery. The sample is placed between the upper and lower electrode.

A Metrohm Autolab PGSTAT204 equipped with a FRA32-module was used for the impedance measurements. For data acquisition, the NOVA 2.1.4 software (Metrohm Autolab B.V.) was used. The control of the sample's temperature is integrated in NOVA.

The resulting impedance spectra were evaluated by equivalent circuit fitting using the impedance data analysis software RelaxIS® (rhd instruments GmbH & Co. KG).

c) *Measurement parameters*

The complex conductivity $\hat{\sigma}(\omega)$ can be deduced from the complex impedance $\hat{Z}(\omega)$ according to the following equation:

$$\hat{\sigma}(\omega) = C/\hat{Z}(\omega)$$

where $C$ is the cell constant of the measuring cell. For good to moderate ion conductors, the high-frequency response of the sample is governed by ion movement in the electrolyte bulk at a phase angle of 0°. Therefore, the sample´s impedance is purely resitive, and the Bode plots for the real part of the impedance $Z'(\omega)$ as well as for the real part of the complex conductivity $\sigma'(\omega)$ show a plateau. For ionic conductors with a relatively low conductivity, the plateau value is expected at intermediate to low frequencies. Since the ionic movement is thermally activated, the plateau shifts to higher frequencies with increasing temperature. Thus, the frequency range has to be selected in a way, that it covers the region where dc-ion conductivity is observable for the whole temperature range under investigation.

The frequencies used in this work ranged from 100 kHz down to 0.1 Hz. The ac voltage amplitude was set to 100 mV (rms). The systems´s linear response was veryfied using Lissajous-Plots.

Starting at 150 °C, the sample was cooled down to 30 °C in steps of 10 °C. For each temperature setp an impedance spectrum was recorded. To guarantee for thermal equilibrium the sample was held at the respective temperature for at least 1200 s after reaching the temperature set-point before measurement.

Using the graphite coated contact area and the thickness of the pellet (measured by means of a micrometer screw, COOLANT PROOF Micrometer IP65, Mitutoyo Corp.), the cell constant $C$ was calculated to be 0.0623 $cm^{-1}$

# Results

The internal cell resistance of the used TSC battery measuring cell was determined to be 0.59 Ω (= blank value). However, due to the moderate conductivity of the sample and thus high resistances, this value was neglected.

For fitting the impedance data a simple standard equivalent circuit shown in Figure 2 was used.

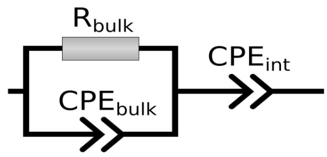


**Figure 2:** Equivalent circuit

The parallel $R_{bulk}$-$CPE_{bulk}$ unit describes the bulk response while the $CPE_{int}$ element holds for interfacial processes.

Using the cell constant as well as the bulk resistance $R_{bulk}$ determined by fitting the respective impedance spectra, the temperature-dependent dc-ion conductivity was obtained, see table 1

**Table 1:** $\sigma_{dc}$ as function of sample temperature.

| Temperature [°C] | $R_{bulk}$ [Ohm] | $\sigma_{dc}$ [S/cm] |
|---|---|---|
| 150 | 3,76E+04 | 1,66E-06 |
| 140 | 4,91E+04 | 1,27E-06 |
| 130 | 6,84E+04 | 9,12E-07 |
| 120 | 9,83E+04 | 6,35E-07 |
| 110 | 1,43E+05 | 4,37E-07 |
| 100 | 2,08E+05 | 3,00E-07 |
| 90 | 3,17E+05 | 1,97E-07 |
| 80 | 4,93E+05 | 1,26E-07 |
| 70 | 7,70E+05 | 8,11E-08 |
| 60 | 1,20E+06 | 5,20E-08 |
| 50 | 1,87E+06 | 3,33E-08 |
| 40 | 2,87E+06 | 2,17E-08 |
| 30 | 4,28E+06 | 1,46E-08 |

The Bode plots of the real part of the impedance for all temperatures are depicted in Figure 3.

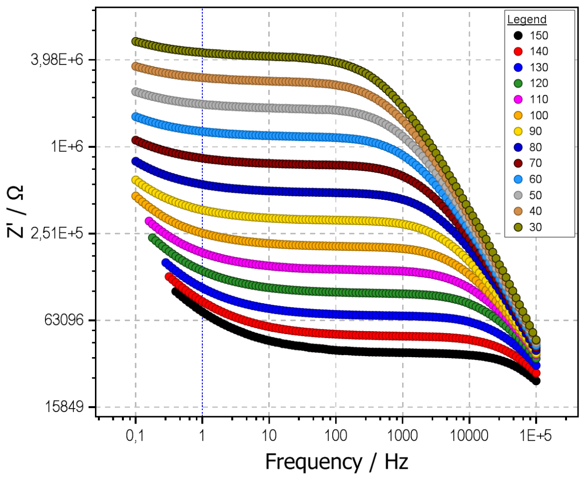


**Figure 3:** Bode plots of the real part of the impedance at different sample temperatures.

In Figure 4 an Arrhenius plot of the temperature-dependent dc-ion conductivity is depicted showing the expected increase in conductivity with increasing temperature *T*.

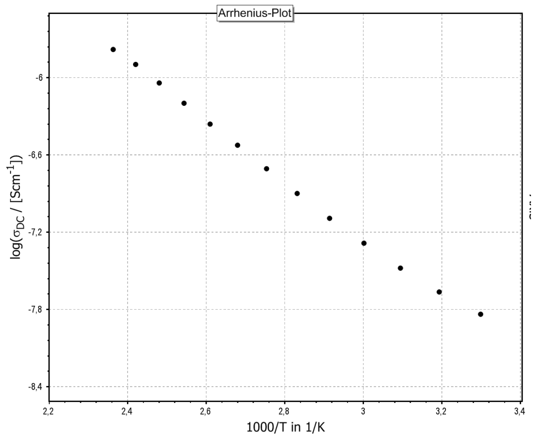


**Figure 4:** Arrhenius plot of the temperature-dependent dc-ion conductivity of the sample.

By fitting the determined conductivity data to the Arrhenius equation

$$\sigma_{DC} = \sigma_0 \exp(-E_A/(RT))$$

with $\sigma_0$ as the pre-exponential factor, $E_A$ as the activation energy and $R$ as the gas constant, the activation energy was determined to be 0.38 eV, which is in good accordance with typical activation energies for proton conductors reported in literature [1], [2].

[1] M. Bazaga-García et al., J. Am. Chem. Soc. 136 (2014) 5731-5739

[2] E.W. Stein et al., Solid State Ionics 83 (1996) 113-124

# Acknowledgement

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