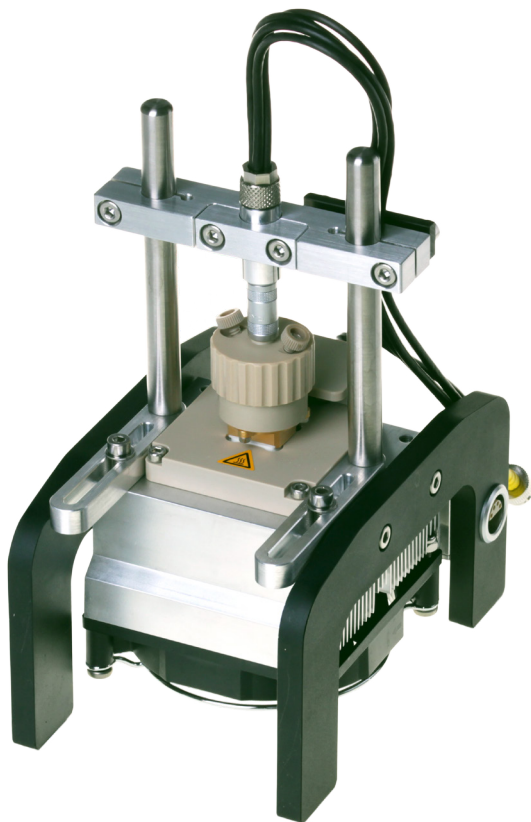# rhd instruments
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Application note

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

Introduction

Impedance spectroscopy measurements for temperatures ranging from 20 °C to 120 °C were performed to extract the dc-ion conductivity of the solid proton-conductor pentafluorophenylphosphonic acid.

The measuring setup is described in detail below as well as the measuring procedure. Finally, the results are presented as temperature-dependent Bode plots of the real part of the complex conductivity and as Arrhenius plot of the resulting dc-ion conductivity.

Experimental

a) *Chemicals*

The sample was kindly provided as dried powders by the Prof. Hoge group (University of Bielefeld) in a sealed flask which had been set under inert gas. After receipt of the material, it was stored inside a glove box under Ar atmosphere (MBraun, O_2 and $H_2O < 1$ ppm).

b) *Sample preparation & measuring setup*

From the sample material, pellets with a diameter of 12 mm were prepared applying a pressure of around 265 MPa for 30 min. Since the material was wax-like and sticky, the pellets were pressed between 2 gold-plated stainless steel discs, 12 mm in diameter.

For electrochemical characterization of the sample, a TSC battery measuring cell, see Figure 1, in combination with a modified Microcell HC setup has been used. This measuring cell enables e.g. the electrochemical investigation of planar, moisture-, air- or photosensitive substrates of variable shape under temperature control. The contact pressure was adjusted to 40.7 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. It enables adjusting sample temperatures ranging from -40 °C up to +100 °C (130 °C possible

@ RHD due to modification), depending on dew point and sample amount. For adjusting the sample temperature an rhd control unit was used. In combination with a Microcell HC setup the temperature accuracy is 0.1 °C in the thermo block.
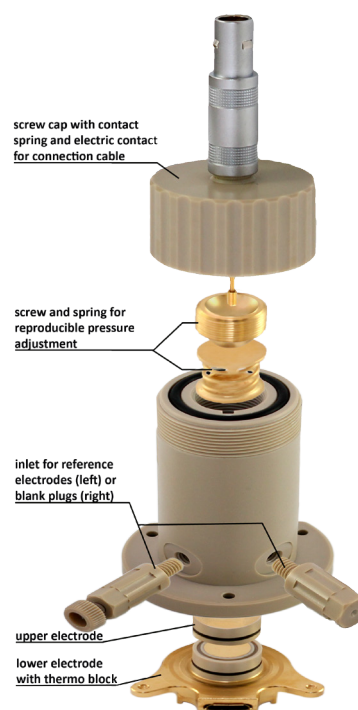
Figure 1: Exploded view of measuring cell TSC battery. The sample is placed between the upper and lower current collector.

A Metrohm Autolab PGSTAT204 equipped with a FRA32-module was used for the impedance measurements. For data acquisition, the NOVA 2.1 software (Metrohm Autolab B.V.) was used where the control of the sample's temperature is already integrated.

The resulting impedance spectra were evaluated by equivalent circuit fit using the impedance data analysis software RelaxIS® (developed by rhd instruments).

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 part of $\sigma'(\omega)$, the real part of $\hat{\sigma}(\omega)$, is governed by ion movements in the bulk of the electrolyte, i.e. by the dc-ion conductivity. Here, the sample impedance equals its resistance, at a phase angle of approximately zero degrees, where the

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Bode plots of the real part of the impedance as well as of the real part of the complex conductivity show a plateau. For ionic conductors showing a relatively low conductivity, the plateau value is expected at intermediate to low frequencies. This plateau shifts with increasing temperature to higher frequency values. 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 measuring frequencies ranged from 1 MHz down to 0.1 Hz and the ac voltage amplitude was set to 10 mV (rms).

Starting at 20 °C, the sample was heated up in steps of 10 °C to 120 °C, and then cooled down to 20 °C again also using a step width of 10 °C.

At each temperature, an impedance spectrum was recorded. To guarantee for reaching the thermal equilibrium, the sample was held at the respective temperature value for 1800 s prior to start of the measurement.

Using the diameter as well as the thickness of the pellet (measured by means of a micrometer screw, Coolant Proof Micrometer IP65, Mitutoyo Corp.), the cell constant C was calculated, resulting in a value of 0.032 cm^{-1}.

Results

In case of the TSC battery, an internal cell resistance of 0.43 Ω was determined but was not taken into account due to the low conductivity and thus high resistance of the sample. Usually, the internal cell resistance had to be subtracted from the resistance resulting from the fit of the impedance data recorded for a sample. Using the cell constant together with the bulk resistance determined by fitting of the impedance spectra, the temperature-dependent dc-ion conductivity was obtained.

The impedance spectra could be fitted by a serial connection of a bulk impedance and an interfacial impedance. The bulk impedance consists of a parallel connection of one CPE element standing for the bulk capacitance and a resistor whereby the resistor describes the bulk resistance governed by bulk proton conductivity. The interfacial impedance is represented by a parallel connection of a CPE element and a resistor. The CPE element stands for the (differential) interfacial capacitance and the resistor for an unknown interfacial process (e.g. charge transfer). Depending on the measuring temperature, some circuit elements have to be left out or the frequency range for evaluating the data has to be adapted. This is because the time constants of the underlying processes show a significant temperature dependence leading to a shift of the related features visible in the spectra along the frequency axis. For example the bulk CPE element related with the bulk capacitance is not required for fitting the data at high temperatures. The equivalent circuit is depicted in the lower row of Figure 2.

Table 1: σ_{dc} as function of sample temperature.

Temperature [°C]	R_{bulk} [Ohm]	σ_{dc} [S/cm]
20	2.62E+5	1.24E-7
30	1.02E+5	3.17E-7
40	4.35E+4	7.45E-7
50	2.01E+4	1.61E-6
60	1.00E+4	3.23E-6
70	5.30E+3	6.11E-6
80	2.96E+3	1.09E-5
90	1.79E+3	1.81E-5
100	1.11E+3	2.91E-5
110	6.87E+2	4.71E-5
120	4.39E+2	7.38E-5
110	7.06E+2	4.59E-5
100	1.12E+3	2.88E-5
90	1.83E+3	1.77E-5
80	3.05E+3	1.06E-5
70	5.22E+3	6.20E-6
60	9.30E+3	3.48E-6
50	1.73E+4	1.87E-6
40	3.45E+4	9.37E-7
30	7.44E+4	4.35E-7
20	1.74E+5	1.86E-7

The Bode plots of the real part of the impedance at the diverse measurement temper-

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atures are depicted in Figure 2. The values measured for the heating ramp coincide well with those for the cooling ramp. However, for temperatures lower than 50 °C, the conductivity values obtained for the cooling ramp are slightly higher. This might either be related to a change of the material itself due to the thermal treatment or to an improved contact between the electrodes and current collectors.
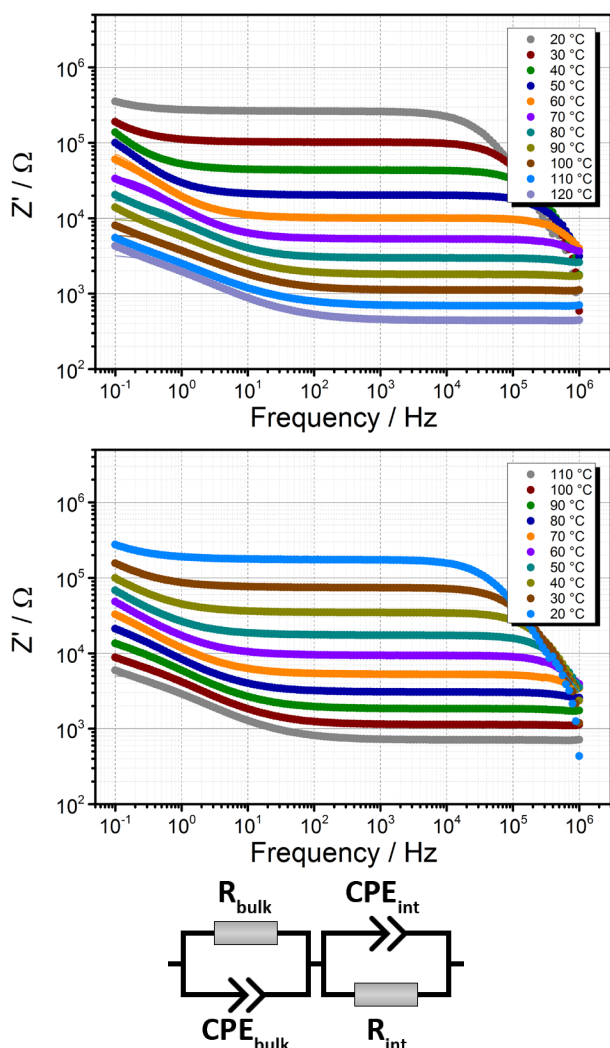
Figure 2: Bode plots of the real part of the impedance at the diverse measurement temperatures of the pentaflourophenylphosphonic acid sample. In the upper row the ascending and in the middle one the descending temperature ramp is depicted. In both graphs, the circles represent the measurement data, while the line symbols the fit to the equivalent circuit depicted in the lower row.

In Figure 3 an Arrhenius plot of the temperature-dependent dc-ion conductivity is depicted showing the expected increase in conductivity with increasing temperature T. In this representation the coincidence of the heating and cooling ramp for temperatures higher than 50 °C is even better visible revealing a complete thermal equilibration at the respective temperature. For possible reasons for the deviation between the ascending and descending temperature ramp at lower temperatures see the last paragraph. It is recommended to perform more than one heating and cooling cycle to verify that the material does not alter during this treatment.
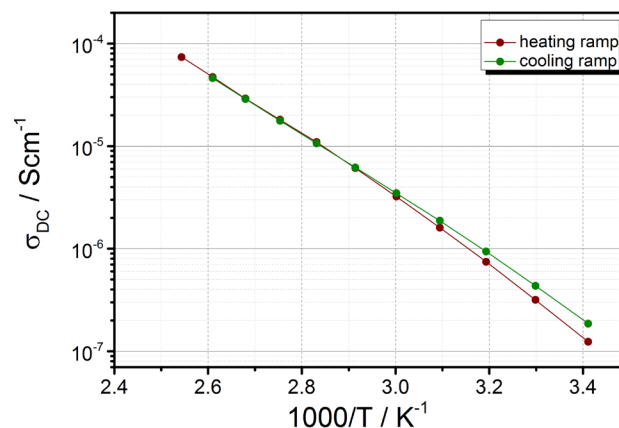
Figure 3: Arrhenius plot of the temperature-dependent dc-ion conductivity of the pentaflourophenylphosphonic acid sample.

By fitting both temperature ramps to the Vogel-Fulcher-Tamman (VFT) equation

$$\sigma = \sigma_0 \exp\left(-B/(T-T_0)\right)$$

with σ_0, B and T_0 as empirical constants, the activation energy E_A of proton conduction can be estimated. For this purpose, constant B is multiplied with the Boltzman constant k_B = 8.617 eV/K resulting in a value of 0.26 eV and 0.33 eV for heating and cooling ramp, respectively, which is in good accordance with typical activation energies for proton conductors reported in literature [1], [2].

Acknowledgement

[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

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