Application Area: Fundamental

Determination of the T-dependent conductivity of a solid proton conductor

Keywords

Electrochemical impedance spectroscopy (EIS), Conductivity Determination, Proton Conductor, Metrohm Autolab, Microcell HC

Introduction

The proton conductivity of membranes made of a proton conductive material like Nafion® is an essential quantity to be determined. It has to be taken into account when designing a well-performing Polymer Electrolyte Fuel Cell (PEFC) or a Redox Flow Battery based on aqueous electrolyte solutions. Since the conductivity of these materials significantly depend on the water content, it should be known for the specific sample and should be stable during the measurement. In this application note, we present the results of an exemplary study of $\sigma_{DC}(T)$ determined by impedance spectroscopy for a novel solid proton conductor in its dry state.

Experimental Setup

The combination of the measurement setup Autolab Microcell HC with a Metrohm Autolab potentiostat/galvanostat instrument with a FRA32M module, as shown in Figure 1, provides an automated temperature-controlled electrochemical measurement system for moisture-sensitive samples.

Figure 1 - The Autolab Microcell HC combined with the Metrohm Autolab PGSTAT204 with FRA32M module.

The proton conducting sample was kindly provided as dried powder by M. Zeyat (AG Lentz, Freie Universität Berlin) in a sealed flask under Argon. From the sample material, a pellet with a diameter of 10 mm was prepared applying a pressure of slightly less than 900 MPa for 12 h (force: 7 kN, area: 0.785 cm^2). A self-standing pellet was obtained. The pellet was coated on both faces with a thin layer of graphite to improve the electrical contact to the current collectors.

For the measurement, a TSC battery standard measuring cell, see Figure 2, in combination with a modified Autolab Microcell HC setup enabling higher sample temperatures of up to +150 °C has been used. As current collectors, two planar stainless-steel electrodes pressed-into PEEK were used, offering an effective, round-shaped contact area with a diameter of 8 mm. To improve the contact to the sample, the stainless-steel electrodes were electro-plated with gold beforehand. The contact pressure was adjusted to approximately 81 kPa using a gold-plated spring with a spring constant of 2.3 N/mm.

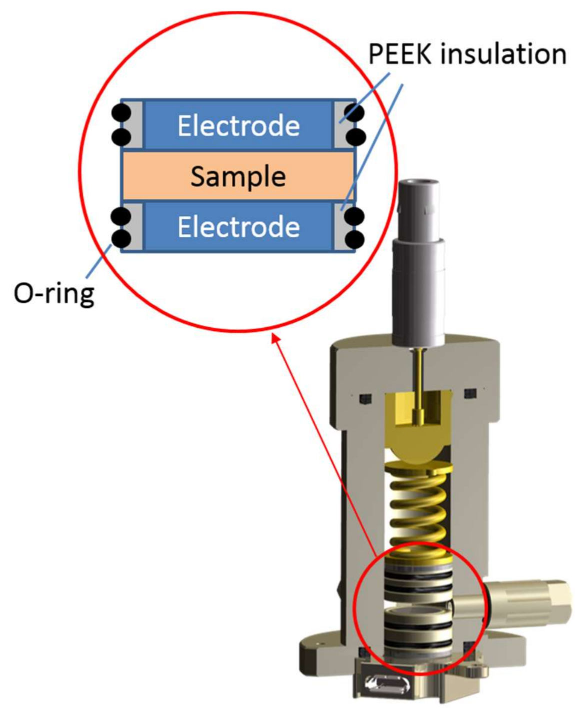

Figure 2 – Schematic drawing of measuring cell TSC battery. The sample is placed between lower and upper current collector.

Experimental parameters

The measuring frequencies ranged from 100 kHz down to 0.1 Hz. The AC voltage amplitude was set to 100 mV (RMS) while verifying that the system's response is still linear by evaluating the Lissajous-plots and checking the recorded data by means of the Kramers-Kronig relation.

Starting at +150 °C, the sample was cooled down to +30 °C in steps of 10 °C. At each temperature, an impedance spectrum was recorded. To guarantee for thermal equilibrium, the sample was held at the respective temperature value at least for 1200 s prior to start of each measurement.

Using the graphite coated contact area *A* and the thickness *d* of the pellet measured by means of a micrometer screw, the cell constant $K_{cell} = d/A$ was calculated to be 0.0623 cm^{-1}.

Results and Discussion

In case of the measuring cell TSC battery standard, an internal cell resistance of 0.6 Ω was determined (= blank value w/o sample). However, due to the moderate conductivity of the sample and thus high resistances, this value was neglected.

Bode plots of the real part of the recorded impedance are presented in Figure 3 for all sample temperatures.

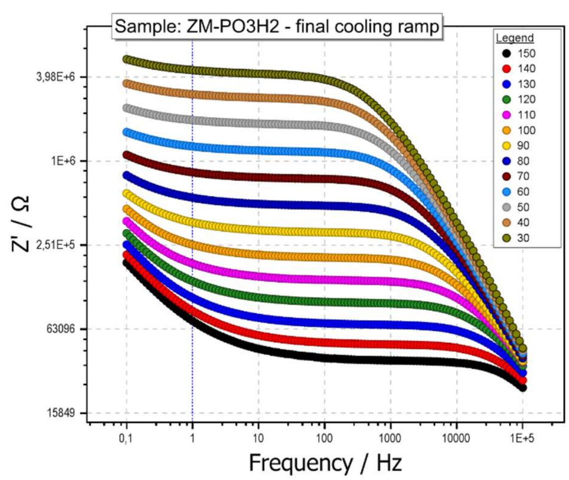

Figure 3 – Bode plots of the real part of the impedance at different sample temperatures.

The Bode-plots exhibit a clearly visible plateau region for frequencies at which the overall impedance behavior is dominated by the resistive contribution by bulk ion or proton transport. The plateau value is given by R_{bulk} and increases with decreasing sample temperature as expected for ion or proton conduction.

For fitting the impedance data a simple standard equivalent circuit shown in Figure 4 was used. The parallel R_{bulk}-CPE_{bulk} unit describes the bulk response while the CPE_{int} element holds for interfacial processes.

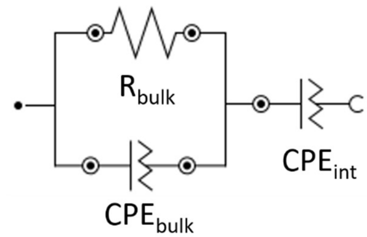

Figure 4 – Equivalent circuit.

Using the cell constants together with the bulk resistance R_{bulk} determined by fitting of the respective impedance spectrum, the temperature-dependent DC-ion conductivity was obtained, see Table 1.

Table 1 – σ_{DC} as function of sample temperature.

Temperature (°C)	R_{bulk} (Ω)	σ_{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

Further analysis can be done by creating an Arrhenius-plot of the σ_{DC} values, see Figure 5.

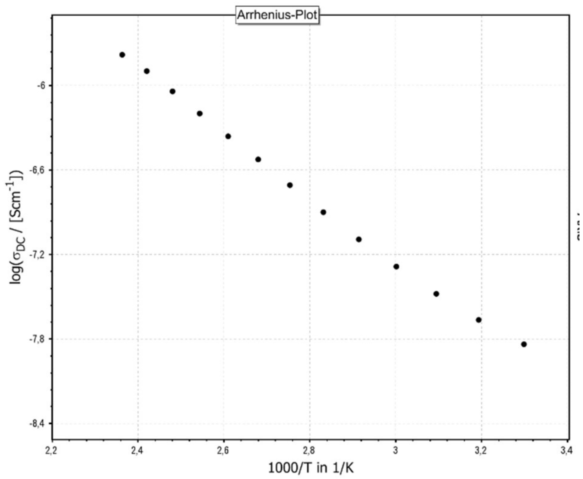

Figure 5 – Arrhenius-plot of σ_{DC}.

By fitting the determined conductivity data to the Arrhenius equation:

$$\sigma_{DC} = \sigma_0 \mathrm{e}^{-\frac{E_A}{RT}} \quad (1)$$

With σ_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.

Conclusions

The combination of the Autolab Microcell HC setup with the Metrohm Autolab potentiostat/galvanostat instruments fitted with the FRA32M module allows for an automatic determination of the temperature-dependent σ_{DC} values. This convenient combination offers the possibility to significantly reduce the time spent on performing measurements and analyzing the recorded data.

Furthermore, the measuring cell TSC battery standard allows for studying smallest sample amounts under exclusion of moisture and oxygen and thus broadens your experimental horizons and saves valuable laboratory time.

References

Metrohm Autolab Application Note AN-EC-010 "In-temperature Ionic Conductivity Measurements with the Autolab Microcell HC Setup".

Date

June 2019 AN-EC-023

For more information

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