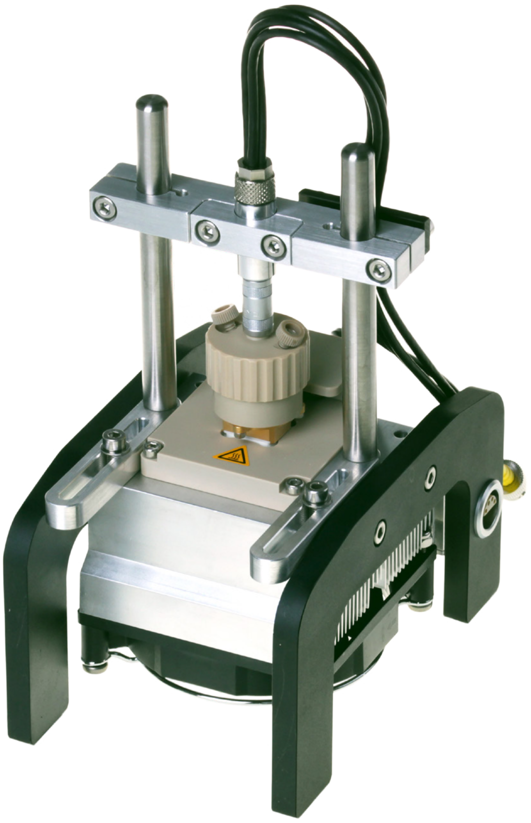
Application note

Determination of the dc-ion conductivity of glass ceramics partially coated with gold



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Introduction

We have carried out temperature-dependent impedance spectroscopy measurements to extract the dc-ion conductivity of glass ceramic test samples partially coated with gold.

The measuring setup is described in detail below as well as the measuring procedure. Finally, the results will be presented as Bode plots of the real part of the complex conductivity and as Bode plots of the complex permittivity.

Experimental

For impedance measurements of the samples, a TSC Sw closed measuring cell has been used in combination with a Microcell HC setup (provided by rhd instruments GmbH & Co. KG), see Figure 1.

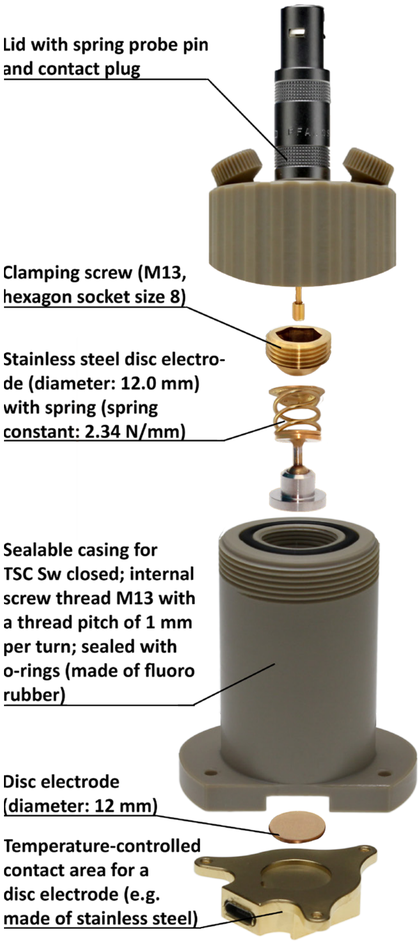

Figure 1: Exploded view of measuring cell TSC Sw closed for studies on solid and polymeric samples. To control the sample's temperature, the TSC Sw closed has to be used in combination with a Microcell HC setup.

The sample (glass ceramic disc, diameter 10 mm, thickness 1 mm) was placed in between two mirror-like polished stainless steel disc-electrodes. To ensure a good electric contact, a contact pressure of nearly 82 kPa was established. After preparing the measuring cell, the system was completed by fixing the measuring cell on top of the Microcell HC basis. The temperature was controlled by using a Peltier element which allows for adjusting sample temperatures ranging from -40 °C up to +100 °C. Although the measurements have not been carried out under non-condensing conditions and the power of the Peltier element is limited, it was possible to carry out measurements within a temperature range from -40 °C up to +100 °C by transferring the whole setup into a rhd cooling box. First, the sample was cooled down to -40 °C, then it was heated up to +100 °C in steps of 10 °C and after reaching the high temperature limit it was cooled down again to -40 °C in steps of 10 °C. After reaching a temperature, at which a measurement should be carried out, a waiting time of 10 min was inserted in the measuring program to guarantee for complete temperature equilibration.

At every temperature, an impedance spectrum was taken for frequencies ranging from 1 MHz down to 0.1 Hz while applying an ac-voltage amplitude of 100 mV (rms) to the sample. All of the measurements have been performed by using a PGSTAT302N with FRA32M and ECD module (Metrohm Autolab B.V). For data acquisition, the NOVA 1.9 software has been used, but the measurements would have also run with NOVA 1.10. A dll was embedded into a NOVA specific procedure (hcDLL, developed by rhd instruments) to allow for controlling the sample's temperature with the Microcell HC setup. For measuring the dc conductivity of samples with a well-known (simple) impedance spectrum, e.g. for quality management, a special procedure is available which enables fully-automated measurements and uses the online-fit option of the NOVA software. However in the present case, the impedance spectrum of the sample was unknown and since the dc conductivity had to be probed within a relatively broad temperature range leading to a non-negligible shift of process-related time constants, the measurements were carried out without an online-fit and the recorded data were fitted to an adequate equivalent circuit afterwards.

The procedure described above has been carried out for two samples, one coated with gold on each face and another without gold-coating, labeled Glass_w/oAu and Glass_wAu, respectively.

Results and discussion

The complex conductivity $\hat{\sigma}(\omega)$ can be deduced from the complex impedance $\hat{Z}(\omega)$ according to Equation 1.

$$\hat{\sigma}(\omega)=\frac{d}{A}\cdot\frac{1}{\hat{Z}(\omega)} \qquad \textbf{(Equation 1)}$$

ω is the angular frequency (the relationship between this quantity and the measuring frequency ν is as follows: $\omega = 2\pi\nu$), *d* is the sample thickness and *A* represents the electrode area. The quotient of *d* and *A* is called the cell constant and is given as 0.127324 cm^{-1} in the present case. The results of the impedance measurements are depicted as Bode plots of the real part of $\hat{\sigma}(\omega)$, since the plateau value, which is expected for a good to moderate ion conductor at high to intermediate frequencies, is given by the dc-ion conductivity. $\hat{\sigma}(\omega)$ is given as

$$\hat{\sigma}(\omega)=\frac{d}{A}\cdot\left[\frac{Z'(\omega)}{(Z'(\omega))^2+(Z''(\omega))^2}+i\cdot\frac{Z''(\omega)}{(Z'(\omega))^2+(Z''(\omega))^2}\right]$$
$$=\sigma'(\omega)+i\cdot\sigma''(\omega) \qquad \textbf{(Equation 2)}$$

where $Z'(\omega)$ and $Z''(\omega)$ are the real and imaginary part of the complex impedance, and $\sigma'(\omega)$ and $\sigma''(\omega)$ are the real and imaginary part of the complex conductivity.

The complex permittivity $\hat{\varepsilon}(\omega)$ and $\varepsilon'(\omega)$ can be calculated from the complex conductivity (or the complex impedance, respectively,) as demonstrated in Equation 3.

$$\hat{\varepsilon}(\omega)=\frac{\hat{\sigma}(\omega)}{i\cdot\varepsilon_0\cdot\omega}=\frac{d}{A\cdot\varepsilon_0\cdot\omega}\cdot\left[\frac{Z''(\omega)}{(Z'(\omega))^2+(Z''(\omega))^2}-i\cdot\frac{Z'(\omega)}{(Z'(\omega))^2+(Z''(\omega))^2}\right]$$
$$=\varepsilon'(\omega)+i\cdot\varepsilon''(\omega)$$

(Equation 3)

a) *Glass_w/oAu*

In Figure 2, the Bode plots of $\sigma'(\omega)$ and of $\varepsilon'(\omega)$ are presented for the sample Glass_w/oAu which has not been coated with gold.

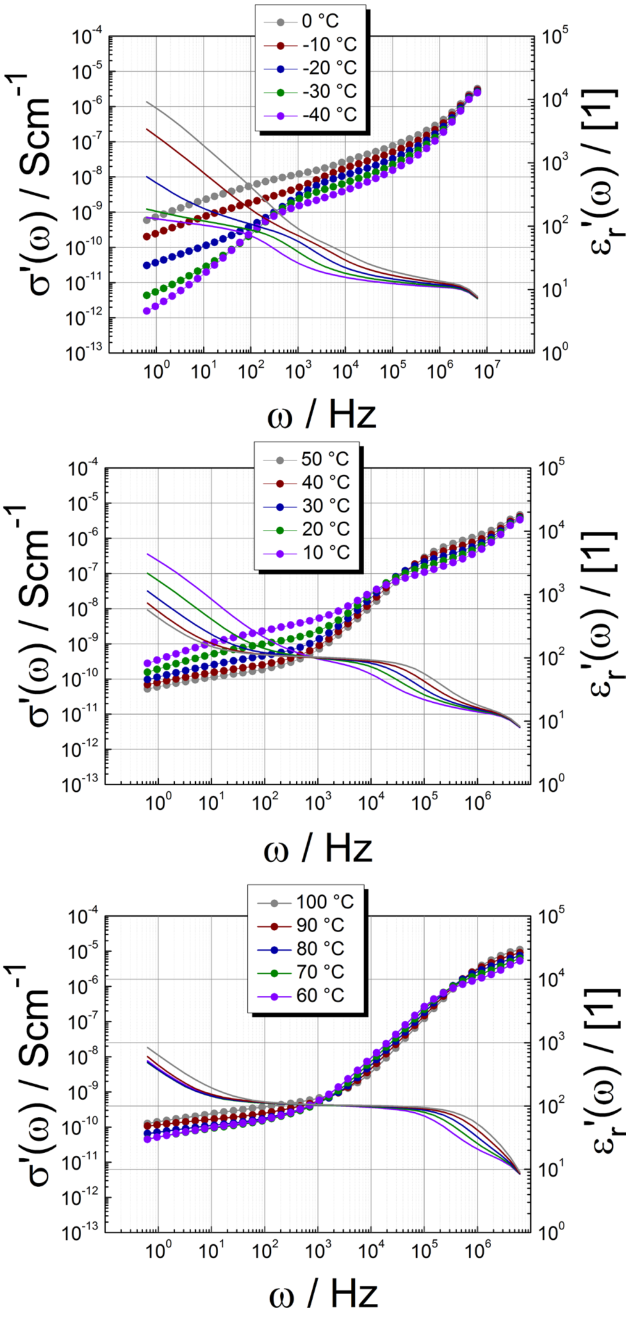

Figure 2: Bode plots of $\sigma'(\omega)$ and of $\varepsilon'(\omega)$ for temperatures ranging from -40 °C to 100 °C.

$\varepsilon'(\omega)$ shows two plateaus which can most likely be assigned to $\varepsilon_{r,\infty}$ and $\varepsilon_{r,0}$. Thus, this intermediate- and high-frequency parts of $\sigma'(\omega)$ and $\varepsilon'(\omega)$ are governed by ion movements in the bulk of the solid electrolyte. The low-frequency part showing a further increase of $\varepsilon'(\omega)$ is determined by electrode polarization effects. However, the σ'(ω) spectra show two "plateaus" and these plateaus show a relatively complex temperature behaviour. While the values of the high-frequency plateau increase with increasing temperature, the plateau visible at intermediate frequencies decreases for temperatures ranging from 10 °C to 50 °C.

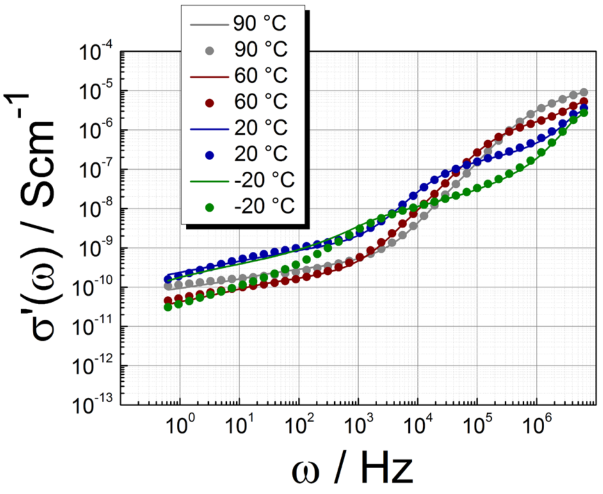

Figure 3: Bode plots of σ'(ω) and of ε'(ω) for the same temperatures during the heating and cooling stage.

To demonstrate that 10 min are enough to allow the system to thermally equilibrate, Bode plots of σ'(ω) and of ε'(ω) are depicted in Figure 3 for the same temperature recorded during the heating and the cooling stage, respectively.

To extract the dc conductivity σ_{DC}, we tried to fit the impedance spectra using an equivalent circuit consisting of at least two R-CPE-elements describing the bulk and interface and another resistor representing the cable and contact resistance, all connected in series (J. C. Dyre, P. Maass, B. Roling, D. L. Sidebottom, *Rep. Prog. Phys. 72* (**2009**) 046501 (15pp)).

However, it was impossible to fit the whole impedance spectrum using such an equivalent circuit. Therefore, we decided to fit only the high frequency part and to extract the value for the high frequency plateau in σ'(ω), which is called σ_{hf} hereafter, by multiplying the reciprocal related resistance with the cell constant. The fit results are summarized in Table 1.

Table 1: σ_{hf} as a function of sample temperature (Glass_w/oAu).

Temperature [°C]	R_{hf} [Ω]	Error R_{hf} [Ω]	σ_{hf} [mS/cm]	Error σ_{fh} [mS/cm]
-40 °C	3.9054E7	3.5307E6	3.26E-09	2.95E-10
-30 °C	1.4877E7	9.7182E5	8.56E-09	5.59E-10
-20 °C	7.5628E6	2.7695E5	1.68E-08	6.17E-10
-10 °C	2.1475E6	1.1217E5	5.93E-08	3.10E-09
0 °C	1.9918E6	1.786E5	6.39E-08	5.73E-09
10 °C	8.1051E5	57392	1.57E-07	1.11E-08
20 °C	4.9406E5	18657	2.58E-07	9.73E-09
30 °C	2.6537E5	6618.3	4.80E-07	1.20E-08
40 °C	1.6496E5	3321	7.72E-07	1.55E-08
50 °C	99457	1769.2	1.28E-06	2.28E-08
60 °C	60622	1224.9	2.10E-06	4.24E-08
70 °C	37524	961.01	3.39E-06	8.69E-08
80 °C	23597	832.69	5.40E-06	1.90E-07
90 °C	15664	853.79	8.13E-06	4.43E-07
100 °C	10365	948.17	1.23E-05	1.12E-06

Finally, the Arrhenius plot is shown for sample Glass_w/oAu in Figure 4.

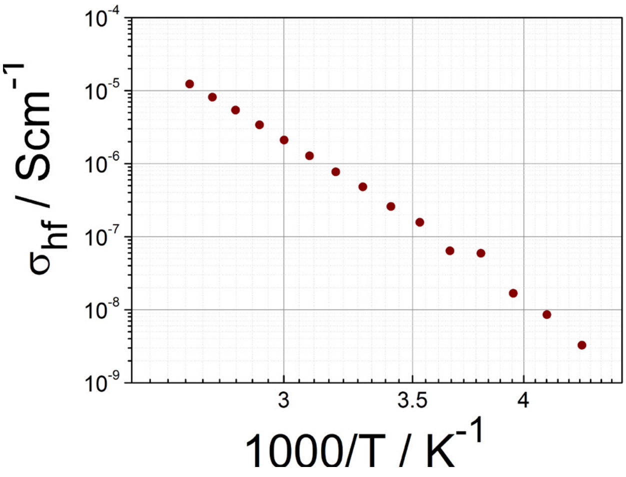

Figure 4: Arrhenius plot of σ_{hf} for sample Glass_w/oAu.

b) *Glass_wAu*

Please note:
The sample, which we have received for the measurements, had been asymmetrically coated with gold: one face was completely covered with a thin gold film while a small diffuse spot had been coated on the other face. Since our standard setup only allows for a sandwich-like contacting of the sample, there was one heterogeneous contact between the stainless steel electrode and the sample.

In figure 5, the Bode-plots of σ’(ω) and of ε’(ω) are presented for the sample Glass_wAu which has been coated with gold on both faces.

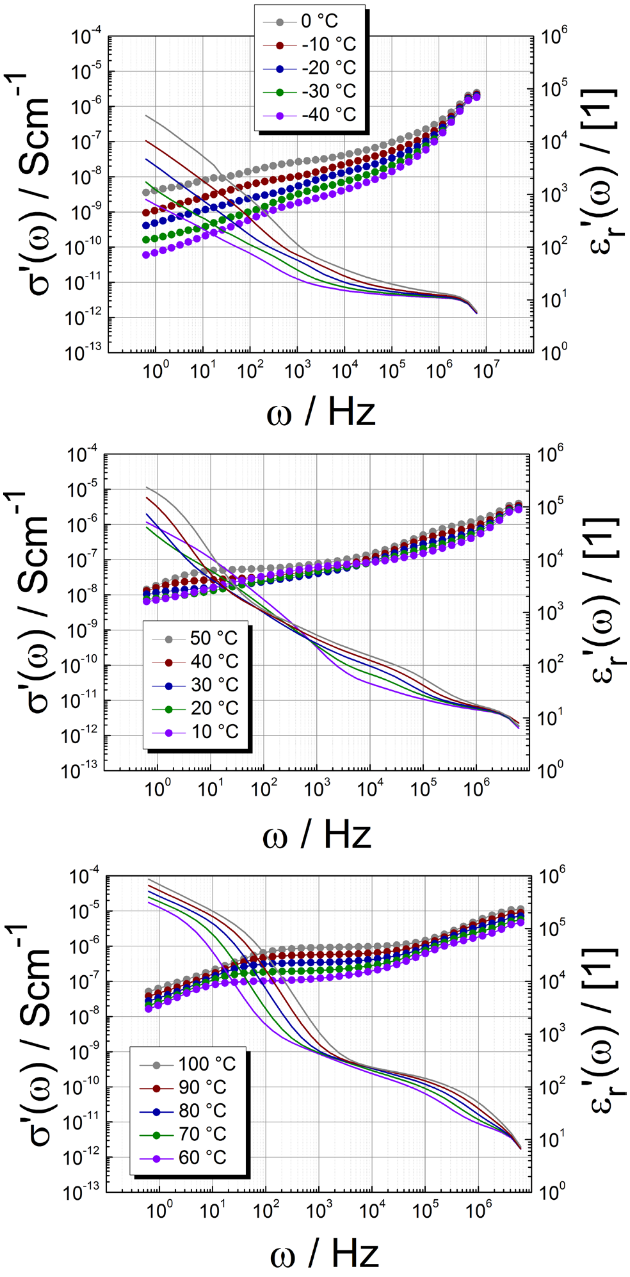

Figure 5: Bode plots of σ’(ω) and of ε’(ω) for temperatures ranging from -40 °C to 100 °C.

Again, there are two plateaus visible in the Bode plot of σ’(ω) and of ε’(ω) pointing to bulk processes. With regard to the plateau of σ’(ω) at intermediate frequencies, another temperature dependence was observed in comparison to sample Glass_w/oAu. However, a detailed discussion of the underlying processes is beyond the scope of this study.

For obtaining σ_{hf}, the same method has been used as the one described above. The fit results are listed in Table 2.

Table 2: σ_{hf} as a function of sample temperature (Glass_wAu).

Temperature [°C]	R_{hf} [Ω]	Error R_{hf} [Ω]	σ_{hf} [mS/cm]	Error σ_{fh} [mS/cm]
-40 °C	1.6021E7	1.0183E6	7.95E-09	5.05E-10
-30 °C	5.6486E6	6.2025E5	2.25E-08	2.48E-09
-20 °C	2.2063E6	3.2843E5	5.77E-08	8.59E-09
-10 °C	2.0921E6	1.4829E5	6.09E-08	4.31E-09
0 °C	5.0594E5	73839	2.52E-07	3.67E-08
10 °C	3.0897E5	27700	4.12E-07	3.69E-08
20 °C	3.8771E5	13326	3.28E-07	1.13E-08
30 °C	2.8534E5	3968	4.46E-07	6.21E-09
40 °C	1.773E5	3589.7	7.18E-07	1.45E-08
50 °C	1.1721E5	4072.3	1.09E-06	3.77E-08
60 °C	77628	4194	1.64E-06	8.86E-08
70 °C	56071	4722.7	2.27E-06	1.91E-07
80 °C	30265	3775	4.21E-06	5.25E-07
90 °C	17521	6972	7.27E-06	2.89E-06
100 °C	13291	4616	9.58E-06	3.33E-06

In Figure 6, the σ_{hf} values obtained for the samples Glass_w/oAu and Glass_wAu are both depicted in form of an Arrhenius plot.

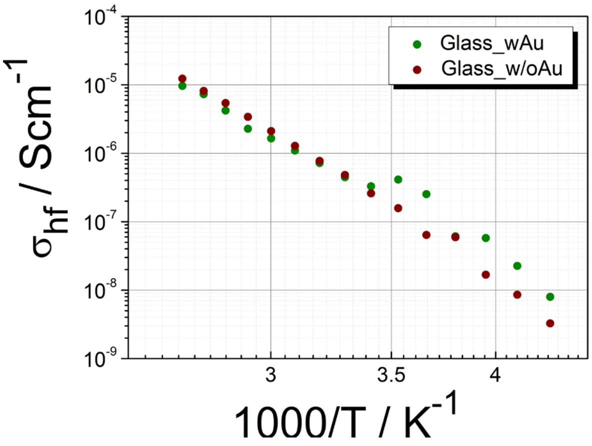

Figure 6: Arrhenius plots of σ_{hf} for samples Glass_w/oAu and Glass_wAu.