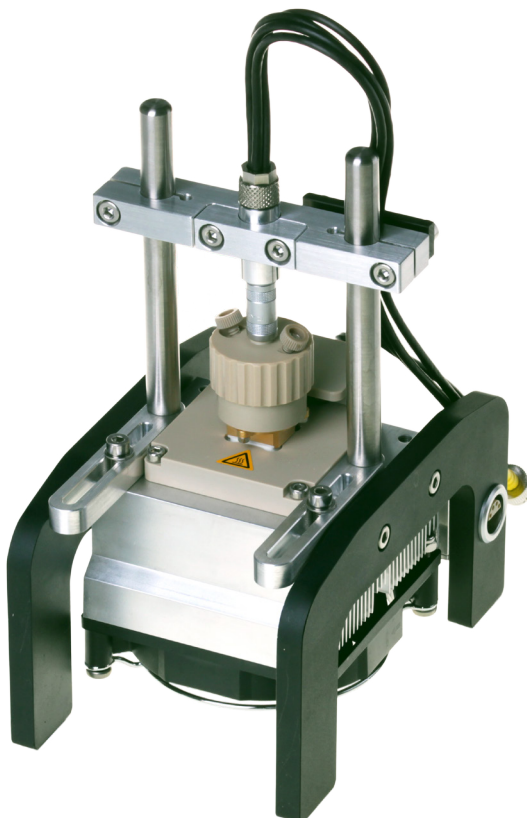


Application note

Test measurements of proton conducting electrolytes

- » 6 M aqueous solution of KOH
- » saturated solution of NH_4Cl in 1,2-propylene carbonate



Introduction

Impedance spectroscopy measurements for temperatures ranging from 10 °C to 60 °C were performed to extract the dc-ion conductivity of two test samples (6 M aqueous solution of KOH and a saturated solution of NH₄Cl in 1,2-propylene carbonate).

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

Experimental

For impedance measurements of the samples, a TSC 1600 closed measuring cell has been used in combination with a Microcell HC setup (provided by rhd instruments GmbH & Co. KG), see Figure 1.

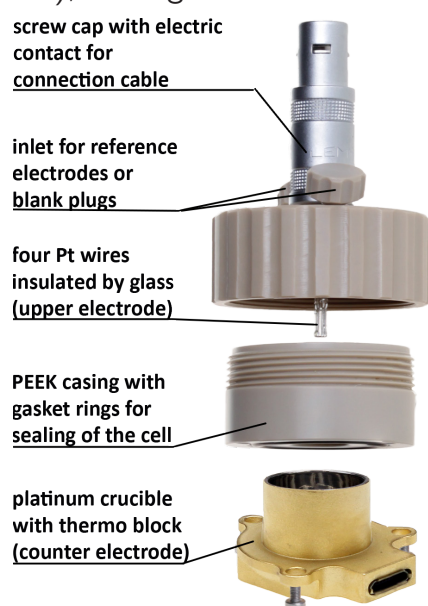


Figure 1: Exploded view of measuring cell TSC 1600 closed for studies of volatile and/or sensitive samples outside a glove box. The liquid sample is filled into the platinum crucible. To control the samples' temperature, the TSC 1600 closed has to be used in combination with a Microcell HC setup.

The two samples have been prepared by using standard laboratory chemicals which were not of highest purity. In fact, the dry 1,2-propylene carbonate has been used as received from the supplier and thus should have contained a non-negligible amount of residual water. Furthermore, NH₄Cl shows only low solubility in 1,2-propylene carbonate (even a 10 mM

solution seems not to be producible, see for instance I. S. Zaitseva, O. Yu. Sytnik, A. P. Krasnoperova, N. V. Bondarev, *Russian Journal of General Chemistry* **2005**, *75*, 25-30) and thus we used a saturated solution. However, since it is the goal of this study to demonstrate that the measuring system consisting of a Microcell HC setup and a TSC 1600 closed measuring cell can be used to measure the specific ion conductivity of a variety of liquid samples with conductivities diverging over several orders of magnitude, no additional care has been taken for these issues.

In each case, 1.2 mL of the sample was filled into the sample container of the TSC 1600 measuring cell which is made of platinum. By screwing the lid on top of the container, the measuring cell was closed. The lid contains an electrode plug consisting of four glass surrounded platinum wires with a diameter of 0.25 mm. Then the air-tight measuring cell was transferred to the measuring station which consists of a Metrohm PGSTAT204 equipped with a FRA32-module and a Microcell HC basis in combination with a temperature controller. The system was completed by fixing the measuring cell on top of the Microcell HC basis.

In general when using a Microcell HC setup, the temperature is controlled by using a Peltier element which, in principle, allows for adjusting sample temperatures ranging from -40 °C up to +100 °C. However, the reachable low temperature limit depends on the measuring conditions (especially if you work under condensing conditions), on the chosen type of measuring cell and on the sample amount.

For enabling the usage of an online circuit fit analysis during the impedance measurement, we had to check whether the same equivalent circuit could be used to describe the recorded data for every temperature within the chosen range since varying the temperature generally leads to a non-negligible shift of process-related time constants.

Regarding the temperature program, the sample was cooled down to 10 °C first. Then, the temperature was raised in steps of 10 °C up to 60 °C. In every case after reaching a temperature, at which a measurement should be carried out, a waiting time of 7 min was inserted in the measuring program to guarantee for complete temperature equilibration.

At each temperature, an impedance spectrum was taken after reaching the thermal equilibrium for frequencies ranging from 500 kHz down to 10 kHz (in case of 6 M KOH solution) or from 500 kHz down to 10 Hz (in case of saturated NH₄Cl solution) while applying an ac-voltage amplitude of 10 mV (rms; KOH solution) or 50 mV (rms; NH₄Cl solution) to the sample. All of the measurements have been performed by using a PGSTAT204 equipped with a FRA32M, as has been mentioned before (Metrohm Autolab B.V.).

For data acquisition, the NOVA 1.10 software (Metrohm Autolab B.V.) has been used. A .dll file was embedded into a NOVA specific procedure (hcDLL, developed by rhd instruments GmbH & Co. KG) to allow for controlling the samples' temperature with the Microcell HC setup. For measuring the dc-ion conductivity of samples with a well-known (relatively 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. In case of the KOH solution, a serial connection of an inductor (representing the cable inductance), an ohmic resistor (describing the ion transport through the bulk) and a constant phase element (standing for the interfacial capacitance) has been used as equivalent circuit, see Figure 2a.



Figure 2a: Equivalent circuit representing the impedance behaviour of the KOH solution in contact with two platinum electrodes within the chosen frequency range.

In case of the NH₄Cl solution, the inductor was removed and an additional constant phase element (representing the bulk capacitance) was inserted in parallel to the bulk resistor, see Figure 2b.

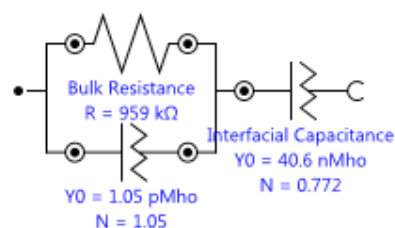


Figure 2b: Equivalent circuit representing the impedance behaviour of the NH₄Cl solution in contact with two platinum electrodes within the chosen frequency range.

Results

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

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

d is the sample thickness and A represents the electrode area. The quotient of d and A is called the cell constant. When using a measuring cell with a well-defined geometry (e.g. a sandwich-like concept), the quotient can easily be calculated. In case of other geometries, the measuring cell has to be calibrated by using a reference electrolyte with a known dc-ion conductivity. For the present measuring cell, the cell constant has been found to be $15.7 \pm 0.7 \text{ cm}^{-1}$ by using a reference standard (HI7035, from Hanna Instruments, $\sigma_{\text{DC}} = 111.8 \text{ mS/cm @ } 25 \text{ }^\circ\text{C}$). In case of the NH₄Cl solution, we confirmed this value by using another reference standard with significantly lower conductivity (HI70031, from Hanna Instruments, $\sigma_{\text{DC}} = 1.413 \text{ mS/cm @ } 25 \text{ }^\circ\text{C}$).

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

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

$$= \sigma'(\omega) + i \cdot \sigma''(\omega) \quad (\text{Equation 2})$$

where ω is the angular frequency (the relationship between this quantity and the measuring frequency ν is as follows: $\omega = 2\pi\nu$), $Z'(\omega)$ 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.

In Figure 3a and Figure 3b, Bode plots of $\sigma'(\omega)$ at different temperatures are presented for the aqueous 6 M KOH solution and for the saturated NH_4Cl solution in 1,2-propylene carbonate.

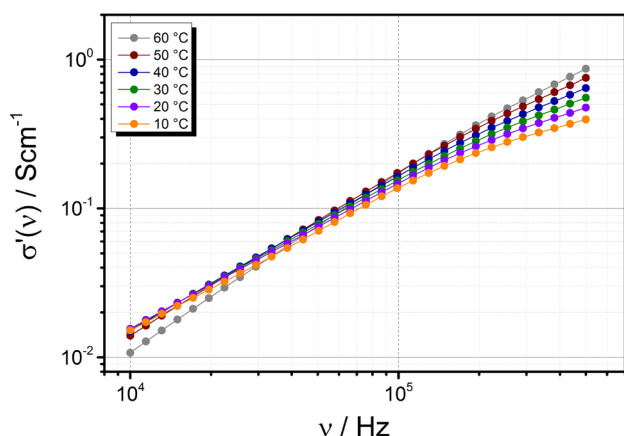


Figure 3a: Bode plot of $\sigma'(\nu)$ for temperatures ranging from 10 °C to 60 °C (6 M KOH solution).

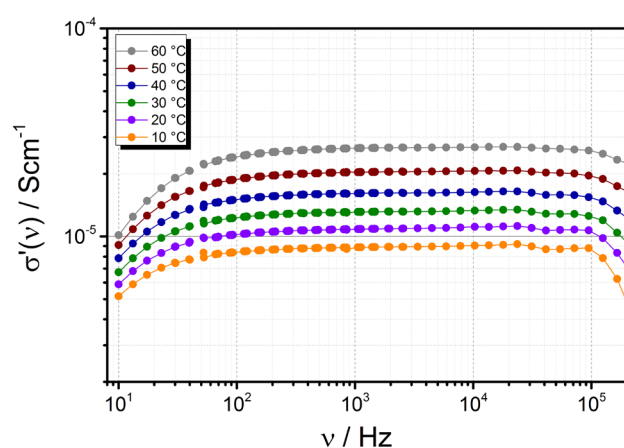


Figure 3b: Bode plot of $\sigma'(\nu)$ for temperatures ranging from 10 °C to 60 °C (saturated solution of NH_4Cl in 1,2-propylene carbonate). The data point at 50 Hz is missing as this is the frequency of the mains.

The high-frequency parts of $\sigma'(\omega)$ are gov-

erned by ion movements in the bulk of the electrolyte. The low-frequency parts showing a decrease of $\sigma'(\omega)$ are determined by electrode polarization effects. In case of 6 M KOH, the conductivity is relatively high and thus the expected dc-ion conductivity plateau is not fully reached at the high frequency limit of the chosen frequency range. However using an adequate equivalent circuit, the bulk resistances and hence the related conductivity values can conveniently be obtained by performing a fit of the recorded data. Besides, this is a well-suited example for demonstrating that single frequency measurements for determining conductivity values (which are carried out quite often) would lead to incorrect results due to the onset of electrode polarization at lower frequencies (in this case at frequencies lower than 1 MHz). In case of the saturated NH_4Cl solution, a broad dc-ion conductivity plateau is observable for frequencies ranging from a few hundred Hz to at least 1 MHz. Due to the low conductivity, the onset of electrode polarization becomes visible at frequencies lower than 100 Hz (in general, the onset frequency is governed by the inverse of the time constant for electrochemical double layer formation which is given as $\omega_{onset} = (2\pi \cdot \tau)^{-1} = (2\pi \cdot R_{bulk} \cdot C_{DL})^{-1}$).

To demonstrate that 7 min are enough to allow the system for thermally equilibrate, Bode plots of $\sigma'(\omega)$ could have been compared for the same temperature recorded during a heating and a subsequent cooling stage. However, this was beyond the scope of this study but should be a standard procedure when determining temperature dependent dc-ion conductivity values, especially in case of highly-viscous samples or when choosing large temperature steps.

To extract the dc-ion conductivity σ_{DC} , we fit the impedance spectra using the equivalent circuits depicted above (Figure 2a and Figure 2b): the reciprocal bulk resistance values were multiplied with the cell constant. The fit re-

sults are summarized in Table 1 and Table 2.

Table 1: σ_{DC} as a function of sample temperature for 6 M KOH in water.

Temperature [°C]	R_{bulk} [Ω]	Error R_{bulk} [Ω]	σ_{DC} [mS/cm]	Error σ_{DC} [mS/cm]
10	33.45	0.26	469.36	24.57
20	27.33	0.25	574.46	30.87
30	23.27	0.29	674.69	38.49
40	20.10	0.30	781.09	46.48
50	17.66	0.31	889.01	55.24
60	15.76	0.33	996.19	65.28

Table 2: σ_{DC} as a function of sample temperature for 10 mM NH_4Cl in 1,2-propylene carbonate.

Temperature [°C]	R_{bulk} [k Ω]	Error R_{bulk} [k Ω]	σ_{DC} [μ S/cm]	Error σ_{DC} [μ S/cm]
10	1,749.0	16.4	8.98	0.48
20	1,428.5	11.2	10.99	0.58
30	1,179.5	7.6	14.04	0.68
40	959.1	5.0	16.37	0.82
50	758.7	3.2	20.69	1.01
60	583.1	2.2	26.93	1.30

The error in σ_{DC} can be estimated using the law of error propagation, see (Equation 3).

$$\Delta\sigma = \left| \frac{\partial\sigma}{\partial R_{bulk}} \right|_{C_{cell}} \cdot \Delta R_{bulk} + \left| \frac{\partial\sigma}{\partial C_{cell}} \right|_{R_{bulk}} \cdot \Delta C_{cell} \quad (\text{Equation 3})$$

$$\Delta\sigma = \frac{1}{R_{bulk}^2} \cdot \Delta C_{cell} \cdot \Delta R_{bulk} + \frac{1}{R_{bulk}} \cdot \Delta C_{cell}$$

Finally in Figure 4, the Arrhenius plots are shown for both samples.

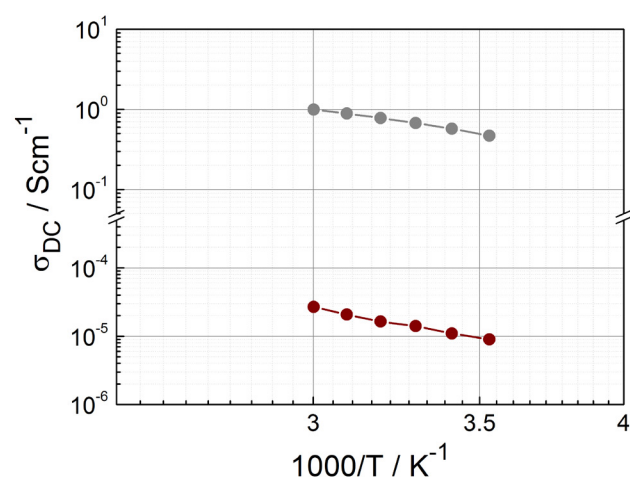


Figure 4: Arrhenius plots of σ_{DC} for both samples. Thereby, the black dots symbol the measurement of 6 M KOH in water, whereas the red ones show that of 10 mM NH_4Cl in 1,2-propylene carbonate.

Discussion

With regard to the aqueous KOH solution, one recent publication can be found which provides many temperature- and concentration-dependent data for the specific conductivity (R. J. Gilliam, J. W. Graydon, D. K. Kirk, S. J. Thorpe, *International Journal of Hydrogen Energy* **2007**, *32*, 359-364). Thus, the data obtained by us can readily be compared to the literature data, see table 3.

Table 3: σ_{DC} as a function of temperature for 6 M KOH, aqueous solution. Comparison of literature data with data obtained by the current study.

Temperature [°C]	σ_{DC} (Lit.) [mS/cm]	σ_{DC} (Meas.) [mS/cm]
10	461.8	469.36 \pm 24.57
20	569.7	574.46 \pm 30.87
30	685.3	674.69 \pm 38.49
40	807.7	781.09 \pm 46.48
50	936.0	889.01 \pm 55.24
60	1.069.6	996.19 \pm 65.28

The comparison results in a good agreement. However for temperatures higher than 30 °C, our data are lower than the literature values. There are several possible explanations for this trend: (i) most likely, the waiting time of 7 minutes between the temperature step and the measurement was too short to allow the system to fully equilibrate, (ii) the results of the data analysis and especially the fit could be further improved, (iii) the chemicals we had used to prepare the solution had not been of the same purity like these which have been used for preparing the solution for the literature study.

Regarding the solution of NH_4Cl in 1,2-propylene carbonate, we have only found one publication (E. M. Hanna, K. Al-Sudani, *Journal of Solution Chemistry* **1987**, *16*, 155-162). In this paper, Hanna and Al-Sudani report about concentration-dependent conductivity values of different salt solutions in propylene carbonate at 25 °C. E.g. the conductance of a 4.6 mM solution of NH_4I was found to be 28.484 (Scm²)/mol which can be converted

to a specific conductivity of 0.13 mS/cm being about one order of magnitude higher than the value we found for the saturated NH_4Cl solution at this temperature. The reason for this might be that the real concentration of the solution used by us for the measurements is unknown (the concentration dependence of most electrolytes exhibits a pronounced maximum) or that NH_4Cl solutions might generally show a somewhat lower conductivity than NH_4I solutions in 1,2-propylene carbonate.

Finally, it should be noticed that the measurement setup provided by us in combination with a TSC 1600 measuring cell is well suited to study the temperature dependence of the dc-ion conductivity of your samples.