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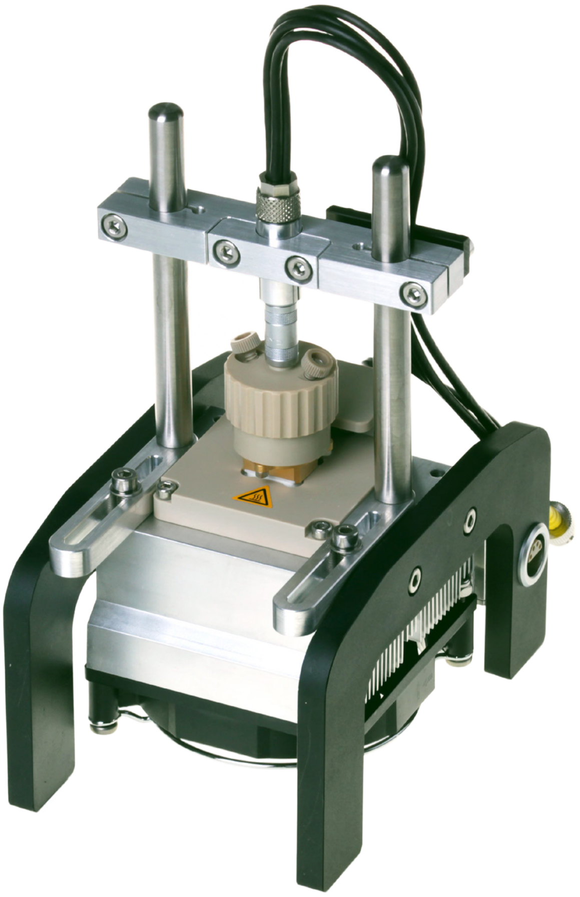
Application note

Determination of the dc-ion conductivity of a mixture of ionic liquids



Mareike Falk

Introduction

We have carried out impedance spectroscopy measurements for temperatures ranging from -35 °C to +100 °C to extract the dc-ion conductivity of a mixture of the two ionic liquids 1-methyl-1-propylpiperidinium bis(fluorosulfonyl)imide and N-propyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide.

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

Experimental

For impedance measurements of the sample, 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.

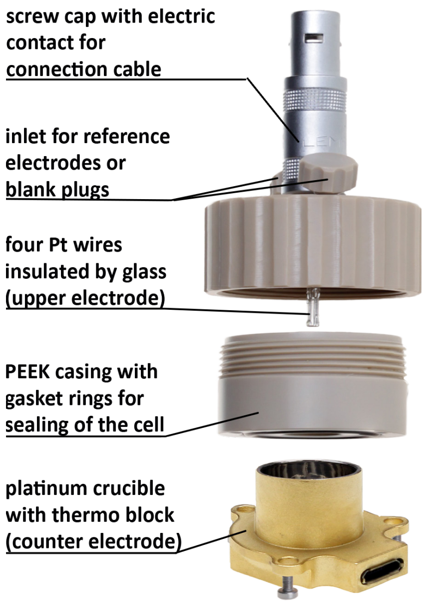


Figure 1: Exploded view of measuring cell TSC 1600 closed for studies of volatile and/or sensitive samples outside a glove box. To control the samples' temperature, the TSC 1600 closed has to be used in combination with a Microcell HC setup.

The sealed sample was unpacked and stored inside a glove box (MBRAUN, UNIlab MB-20-G, H_2O and O_2 content $<$ 0.1 ppm). 1.2 mL of the sample (mixture of two ionic liquids) was filled into the sample container of the TSC 1600 closed 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 each. Then the air-tight measuring cell was transferred to the measuring station outside the glove box. The station consists of a Metrohm PGSTAT204 equipped with a FRA32-module, a Microcell HC basis in combination with a temperature controller and, finally, a rhd Cooling Box. The rhd Cooling Box is needed to allow for cooling down samples to temperatures well below the dew-point under condensing conditions. 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, on the chosen type of measuring cell and on the sample amount. Although the present 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 -35 °C (absolute limit for this configuration: -39 °C) up to +100 °C when performing the experiment inside a rhd Cooling Box.

For enabling the usage of an online circuit fit analysis during the impedance measurement, the experiment has been split into two parts since the dc-ion conductivity had to be probed within a relatively broad temperature range leading to a non-negligible shift of process-related time constants. First, the temperature was raised from +20 °C to +100 °C in steps of 10 °C. After reaching the high temperature limit, the sample was cooled down again to 0 °C which was the low temperature limit of this first experiment. Finally, the sample was heated up to +20 °C again. Second, the temperature was lowered from +10 °C to -40 °C and then, after passing this low temperature limit, raised again to +10 °C. In every case 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.

During the first experiment, an impedance spectrum was taken at every temperature for frequencies ranging from 150 kHz down to 5 kHz while applying an ac-voltage amplitude of 10 mV (rms) to the sample. For the second experiment, the spectra were recorded for frequencies ranging from 25 kHz to 500 Hz. 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 was embedded into a NOVA specific procedure (hcDLL, developed by rhd instruments GmbH & Co. KG) to allow for controlling the sample's 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 the present case, this procedure could be used although the equivalent circuit had to be modified to account for cable inductance and parasitic high frequency capacitance, see Figure 2.

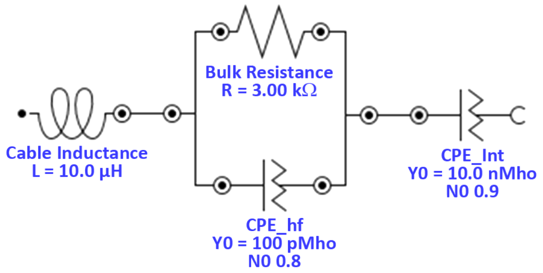


Figure 2: Equivalent circuit representing the impedance behaviour of the system under study within the chosen frequency range.

For temperatures lower than 0 °C (second experiment), the equivalent circuit shown in Figure 2 is further simplified by leaving out the two elements representing the cable inductance and the parasitic high frequency capacitance (CPE_hf).

Results

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

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

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. 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 ± 0.7 cm^{-1} by using a reference standard (HI70031, from Hanna Instruments, σ_{DC} = 1.413 mS/cm @ 25 °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

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

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.

In Figure 3, Bode plots of $\sigma'(\omega)$ at different temperatures are presented for the ionic liquid sample.

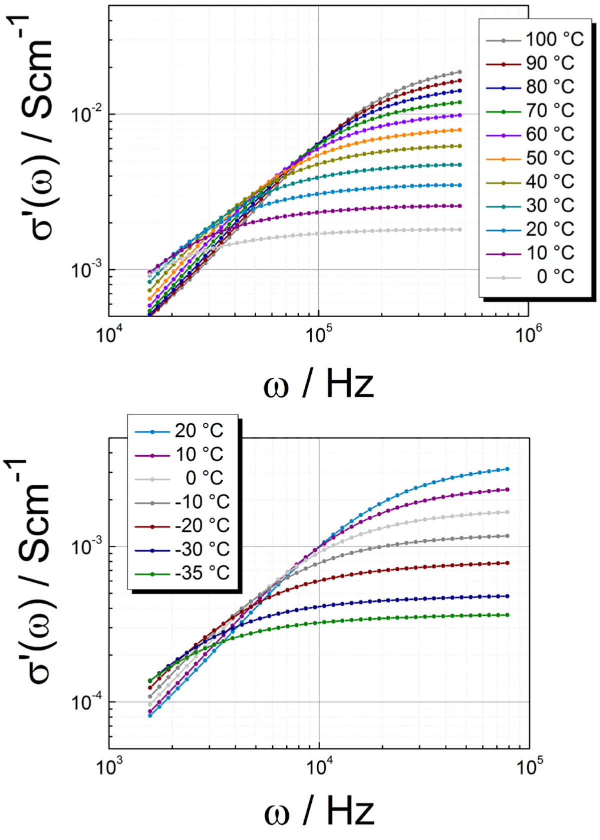


Figure 3: Bode plots of σ'(ω) for temperatures ranging from -35 °C to 100 °C.

The high-frequency parts of σ'(ω) are governed by ion movements in the bulk of the electrolyte. The low-frequency parts showing a decrease of σ'(ω) are determined by electrode polarization effects.

To demonstrate that 10 min are enough to allow the system to thermally equilibrate, Bode plots of σ'(ω) are depicted in Figure 4 for the same temperature recorded during the heating and the cooling stage, respectively.

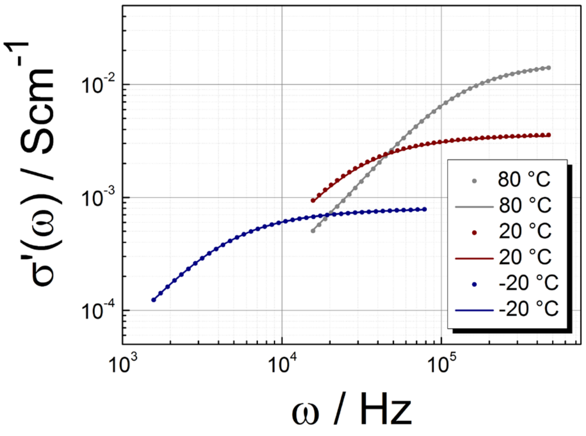


Figure 4: Bode plots of σ'(ω) for the same temperatures during the heating and cooling stage.

To extract the dc-ion conductivity σ_{DC}, we fit the impedance spectra using the equivalent circuit depicted above (Figure 2): the reciprocal bulk resistance values were multiplied with the cell constant. The fit results are summarized in Table 1.

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

Temperature [°C]	R_{bulk} [Ω]	Error R_{bulk} [Ω]	σ_{DC} [S/cm]	Error σ_{DC} [S/cm]
-35 °C	43,681.0	144.2	3.6E-4	1.7E-5
-30 °C	33,072.0	102.5	4.7E-4	2.3E-5
-20 °C	20,186.0	64.6	7.8E-4	3.7E-5
-10 °C	13.330,0	33.3	1.2E-3	5.6E-5
0 °C	9,230.7	23.1	1.7E-3	8.0E-5
10 °C	6,488.5	107.7	2.4E-3	1.5E-4
20 °C	4,757.3	85.2	3.3E-3	2.1E-4
30 °C	3,533.8	35.7	4.4E-3	2.4E-4
40 °C	2,658.3	21.5	5.9E-3	3.1E-4
50 °C	1,978.7	7.3	7.9E-3	3.8E-4
60 °C	1,549.7	6.7	1.0E-2	5.0E-4
70 °C	1,236.0	6.2	1.3E-2	6.3E-4
80 °C	1,012.2	6.5	1.6E-2	7.9E-4
90 °C	843.8	7.6	1.9E-2	1.0E-3
100 °C	714.8	8.3	2.2E-2	1.2E-3

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

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

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

Finally in Figure 5, the Arrhenius plot is shown for the present sample.

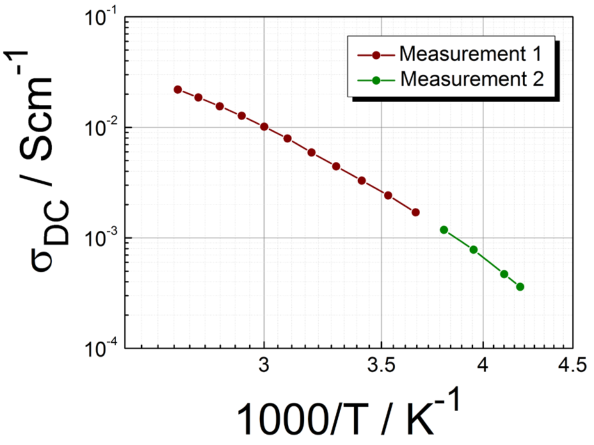


Figure 5: Arrhenius plot of σ_{DC} for the ionic liquid mixture.

Discussion

With regard to the two ionic liquids 1-methyl-1-propylpiperidinium bis(fluorosulfonyl)imide ($Pi_{13}FSI$) and N-propyl-N-methylpyrrolidinium bis(fluorosulfonyl)-imide ($Pyr_{13}FSI$), only a few publications exist which report physical-chemical properties.

Zhou et al. [Q. Zhou, W. A. Henderson, G. B. Appetecchi, M. Montanino, S. Passerini, *J. Phys. Chem. B* **2008**, *112*, 13577) have extensively characterized the ionic liquid $Pyr_{13}FSI$. In contrast to previously reported values for the dc-ionic conductivity, they found a significantly lower value for a temperature of 25 °C (6.4 mS/cm instead of 8.2 mS/cm). They attributed this discrepancy to different purity levels and different amounts of water. They also present an Arrhenius-plot of the measured dc-ion conductivity for temperatures ranging from 100 °C to -40 °C, but they unfortunately do not list the single values. Using a pixel analysis program, the following data can be extracted (Table 2).

For temperatures lower than -9 °C, $Pyr_{13}FSI$ exhibits a phase transition (crystallization) which leads to a dramatic decrease of the dc-ion conductivity.

Table 2: σ_{DC} as a function of temperature for $Pyr_{13}FSI$.

Temperature [°C]	σ_{DC} [mS/cm]
101	24.5
85	19.6
72	15.9
61	13.6
50	11.2
40	9.2
30	7.6
21	5.7
13	4.5
5	3.4
-2	2.6

In 2012, Makino et al. (T. Makino, M. Kanakubo, T. Umecky, A. Suzuki, T. Nishida, J. Takano, *J. Chem. Eng. Data* **2012**, *57*, 751) published a detailed report on the properties of $Pyr_{14}FSA$. Although Zhou et al. (see above) have shown that this ionic liquid should have a significantly lower dc-ion conductivity than $Pyr_{13}FSI$, the values reported in this report (Table 3) are higher than those for $Pyr_{13}FSI$ for temperatures higher than 30 °C. The reason for this discrepancy remains unclear. However, it is also not clear why the authors performed potentiostatic and galvanostatic measurements to obtain the bulk resistance and which equivalent circuit they used to fit the data ("by fitting the measured impedances to the best-fit form of an arbitrary electric circuit").

Table 3: σ_{DC} as a function of temperature for $Pyr_{14}FSI$.

Temperature [°C]	σ_{DC} [mS/cm]
80	22.3
70	18.6
60	15.3
50	12.3
40	9.6
30	7.2
20	5.3
10	3.6
0	2.4

Unfortunately, we were not able to find reliable data for the temperature dependent dc-ion conductivity of $Pi_{13}FSI$. The data sheet provided by solvionic SA reports a value of 3.7 mS/cm for this ionic liquid at 25 °C. Thus at 20 °C, the value for a mixture of $Pyr_{13}FSI$ and $Pi_{13}FSI$ should lie between 3 mS/cm and 5.5 mS/cm. We obtained a value of 3.3 mS/cm which seems reasonable.

In the literature, two interesting publications can be found which deal with the characteristics of a 1:1 mixture of the two ionic liquids $Pyr_{14}FSI$ and $Pi_{14}FSI$ (Lin et al.: R. Lin, P.-L. Taberna, S. Fantini, V. Presser, C. R. Pérez, F. Malbosc, N. L. Rupesinghe, K. B. K. Teo, Y. Gogotsi, P. Simon, *J. Phys. Chem. Lett.* **2011**, *2*, 2396; Lecoeur et al.: C. Lecoeur, B. Daffos, R. Lin, L. Divay, P Le Barny, M. Pham Thi, P.-L. Taberna, P. Simon, *Mater. Renew. Sustain. Energy* **2013**, *2*, 13). Lin et al. demonstrated that the 1:1 mixture shows an eutectic behaviour and thus offers an extended temperature range (down to at least -80 °C) with good ionic conductivity. For the dc ion-conductivity, the authors report a value of 4.9 mS/cm at 20 °C and of 28.9 mS/cm at 100 °C. However, compared to the values of pure Pyr_{14}FSI, which is the constituent with the higher dc ion-conductivity, both of these values are higher (see Zhou et al. (4.8 mS/cm @ 20 °C) and Makino et al).

In our case, the mixture of Pyr_{13}FSI and Pi_{14}-FSI also shows an eutectic behaviour since the results of the conductivity measurements and especially the Arrhenius plot do not give any hints for crystallization for temperatures ranging down to -35 °C. The pure ionic liquids melt at -9 °C (Pyr_{14}FSI, Zhou et al.) and 6 °C (Pi_{13}FSI, Lin et al.).