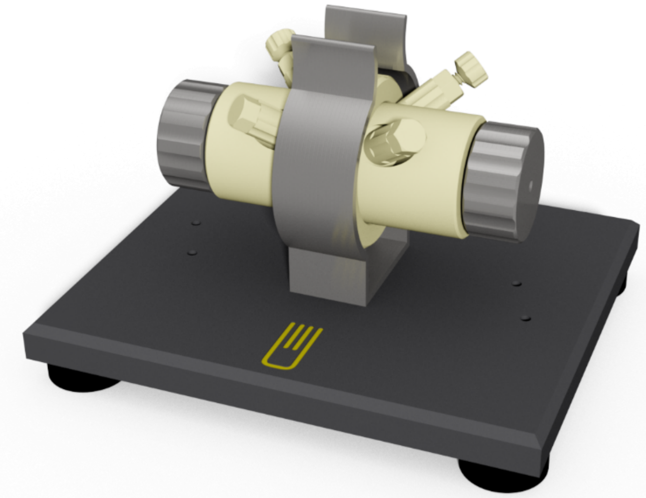
Application note

Determining the Ionic Conductivity of a Free-Standing Membrane



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rhd instruments GmbH & Co. KG

Introduction

Ion conducting membranes are used in a number of electrochemical applications such as fuel cells, redox flow batteries, sensors, electrolysers, and metal-air batteries [1]. A key property of such membranes is the ionic conductivity, which can be determined by impedance spectroscopy. This is a suitable method due to its ability to distinguish the influence from other conflating factors such as charge transfer resistance, electrode polarisation, etc [2].

In this application note, we describe the determination of the ionic conductivity of an ion conducting membrane at a temperature of 20 °C by measuring impedance spectra in a TCE Cell One test cell (rhd instruments GmbH & Co. KG) and fitting the resulting data to an equivalent circuit (RelaxIS 3 software, rhd instruments GmbH & Co. KG). In this cell setup, the membrane is not in direct contact with the electrodes, and it is hence ideal for measuring the properties of the freestanding membrane immersed in an electrolyte.

Experimental

Aqueous sulphuric acid was used as electrolyte. A circular specimen (18 mm Ø) of a membrane with a thickness of 35 µm was punched out and soaked in the electrolyte for 24 h prior to measurement.

The membrane was mounted in the TCE Cell One electrochemical test cell between two PEEK blocking disks. The blocking disks have a central hole with 2 mm diameter, and are 0.5 mm thick. Circular stainless-steel plate electrodes (6 mm Ø) were used in a two-electrode configuration (**Figure 1**). The inner cell diameter is 10 mm, the distance between the electrodes is 16 mm, and the electrolyte volume is 1.7 ml.

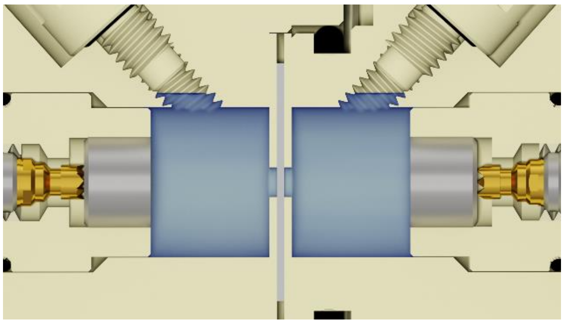

Figure 1. Schematic of the TCE Cell One electrochemical test cell, used for all measurements in this application note. The membrane can be seen in grey in the centre of the cell, between two blocking disks with central holes. The two electrodes to the left and right are contacted from either side, and on top the ports for electrolyte filling can be seen.

The cell was placed in a climate chamber, and after reaching the temperature set point of 20.0 °C, a waiting time of 40 min was chosen to ensure complete thermal equilibrium before starting the measurements.

A Metrohm Autolab PGSTAT204 equipped with an FRA32-module and controlled through the NOVA 2.1.5 software was used for all impedance measurements. The recorded impedance data were evaluated by equivalent circuit fitting using the impedance data analysis software RelaxIS 3 (rhd instruments GmbH & Co. KG).

Impedance measurements were performed in a frequency range of 1 MHz to 100 Hz with an amplitude of $V_{AC,rms} = 10.0$ mV. Impedance spectra were recorded with and without the membrane in place, and in each case the measurement was repeated five times to ensure the reproducibility.

Step	Action to be performed
1	Clean the test cell and polish the electrodes.
2	Place the blocking disks (with or without the membrane) in the test cell.
3	Fill the test cell with electrolyte and close it.
4	Place the test cell in a climate chamber and connect the impedance analyser in two-electrode configuration.
5	Set the temperature to 20.0 °C and wait for temperature equilibration (30 – 40 min).
6	Perform an impedance spectroscopy measurement.
7	Drain the electrolyte from the test cell and clean it.

Results

A typical impedance spectrum of the TCE Cell One with the membrane can be seen in **Figure 2**. At high frequencies (>100 kHz), the inductance of the cables and connections dominate the impedance spectrum (l_{cable}). The inductance behaviour is however not ideal (*i.e.* parallel with the *Z''* axis), but curved in the Nyquist plot, indicating that there are some energy losses in the electromagnetic field created by the inductor. This can be seen in low-impedance systems where relatively high currents are passed through the cables, and can be modelled with a resistor (R_{loss}) in parallel with the inductor. The intercept with the *Z'* axis is often taken as the ionic resistance (R_{ion}) of the system, but this is only true in the absence of inductive effects. If the inductance of the system is significant, the *Z'* intercept will differ from the actual value of R_{ion}. At decreasing frequency, the impedance increases due to polarization (CPE_{pol}).

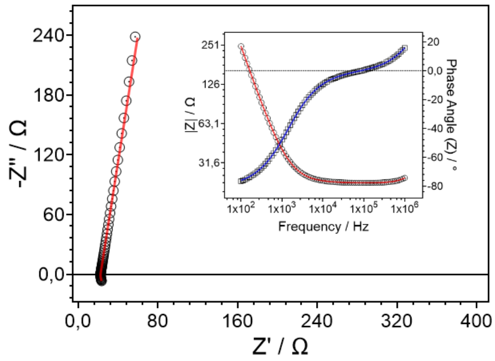

Figure 2. Nyquist plot of the impedance spectrum of the TCE Cell One with the membrane. A Bode plot is depicted in the inset where |Z| is shown as red circles (left y-axis) and the phase angle as blue squares (right y-axis). Lines indicate fits to the equivalent circuit shown in **Figure 3**.

Based on the spectrum features described above, the impedance data were fitted to the equivalent circuit shown in **Figure 3a**. In the TCE Cell One, the membrane is not in direct contact with the electrodes, and R_{ion} thus comprises the combined resistance of the bulk electrolyte ($R_{electrolyte}$) and the membrane ($R_{membrane}$) as shown in **Figure 3b**. Therefore, impedance spectra were also recorded for cells without any membrane (only filled with the same electrolyte), in order to determine $R_{electrolyte}$.

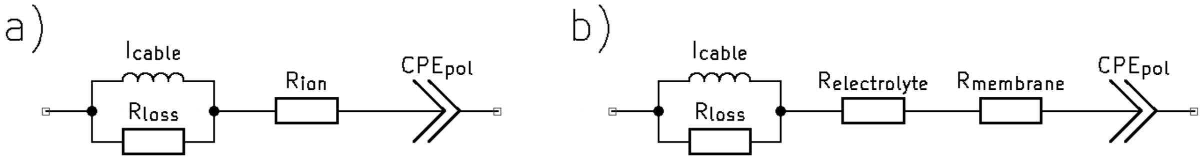

Figure 3. a) Equivalent circuit used for fitting the spectra. b) Alternative equivalent circuit showing the individual contributions of the bulk electrolyte and the membrane to the ionic resistance.

The fitted values of R_{ion} for the five repetitions with and without the membrane are shown in the table below, together with the mean R_{ion} value and the standard deviation of each measurement series. The membrane resistance could then be calculated as the difference between the mean values: $R_{membrane} = 6.04 \pm 0.16\ \Omega$ (95% confidence interval).

	R_{ion} (Ω)	
	Electrolyte	Electrolyte + Membrane
Repetition 1	15.95	22.12
Repetition 2	16.03	22.24
Repetition 3	16.11	22.19
Repetition 4	16.39	22.31
Repetition 5	16.30	22.11
Standard deviation	*0.16*	*0.08*
Mean	*16.16*	*22.20*

The membrane conductivity σ can be calculated as

$$\sigma = \frac{1}{R_{membrane}} \cdot \frac{d}{A}$$

where *d* and *A* is the membrane thickness and cross-section area, respectively. In this way, the membrane conductivity was determined to be 18.5 ± 0.5 mS/cm (95% confidence interval).

Note that the relevant area in the equation above is only that which contributes to the ionic conductivity of the membrane, determined here by the hole area of the blocking disks. By employing the blocking disks, the resistance contribution from the membrane is increased by this geometric restriction, leading to higher accuracy in determining the conductivity. In this case, therefore, *A* is the area of the blocking disk hole, not the total membrane area.

Summary

In this application note we demonstrate how to determine the conductivity of a membrane in a TCE Cell One test cell using impedance spectroscopy and fitting the data to a simple equivalent circuit. The accuracy was improved by the use of blocking disks, which limits the current path through the membrane to a smaller area, thus increasing the resistance contribution from the membrane itself.

Acknowledgements

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Literature

[1] K.-D. Kreuer, “Ion Conducting Membranes for Fuel Cells and other Electrochemical Devices,” Chem. Mater., vol. 26, p. 361, 2014.

[2] Z. Tang, Q.-A. Huang, Y.-J. Wang, F. Zhang, W. Li, A. Li, L. Zhang and J. Zhang, “Recent progress in the use of electrochemical impedance spectroscopy for the measurement, monitoring, diagnosis and optimization of proton exchange membrane fuel cell performance,” J. Pow. Sources, vol. 468, p. 228361, 2020.