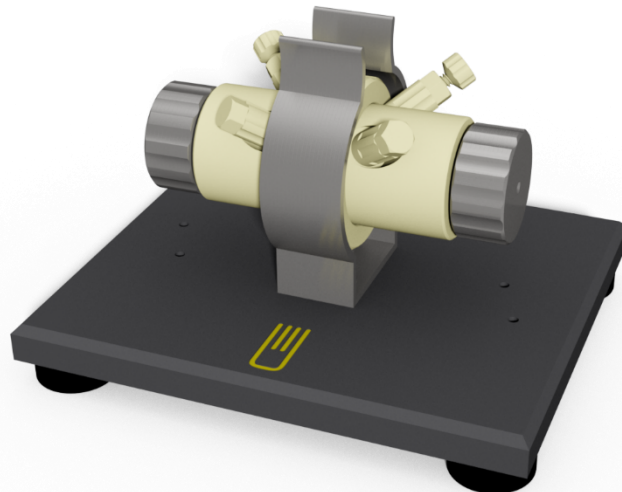




# Application note

## Determining Through-Plane Membrane Conductivity using Four-Electrode EIS

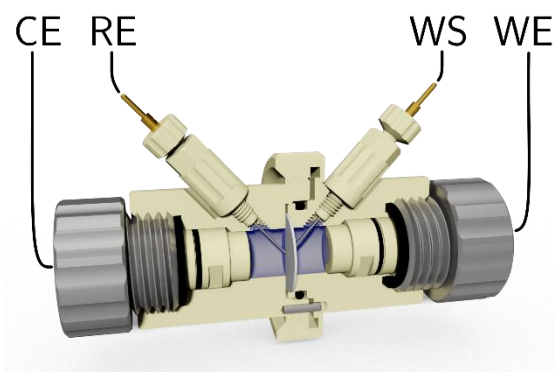


## Introduction

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

EIS can in principle be carried out in a two- or four-electrode configuration in order to measure membrane conductivity. In a four-electrode configuration, the current path (between the counter (CE) and working electrodes (WE)) is separated from the sense electrodes (working sense (WS) and reference electrodes (RE)), as shown in **Figure 1**. The RE and WS do not carry current, but merely sense the potential gradient created by the current flowing between the WE and CE. Thus, any contributions from the WE and CE interfaces, such as contact resistances, charge transfer reactions, or ion blocking behaviour, are removed from the EIS measurement [3]. Four-electrode EIS is however more experimentally challenging than two-electrode EIS, as the results are very dependent on the exact placement of the RE and WS electrodes. Moreover, the potentials of the WE and CE are not

controlled, which could lead to unwanted redox reactions occurring there.



**Figure 1.** The TCE Cell One electrochemical test cell in four-electrode configuration, used for all measurements in this application note. The outer electrodes are connected to the working and counter electrode terminals of the potentiostat, while the inner electrodes are connected to the (working) sense and reference electrode terminals. The membrane is placed in the centre of the cell, with the reference and sense electrodes on either side.

Four-electrode EIS is often used to determine the in-plane membrane conductivity since that requires a less complicated setup, despite usually being of less practical relevance than the through-plane conductivity. Measurements with the TCE Cell One, however, determines exclusively the through-plane conductivity due to the placement of the sense electrodes on either side of the membrane, as can be seen in **Figure 1**.

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 four-electrode impedance spectra in a TCE Cell One test cell (Figure 1, 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. If a simpler setup is desired, the TCE Cell One can also be used in two-electrode configuration to determine membrane conductivity [4].

## 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.

Circular stainless-steel plate electrodes (6 mm Ø) were used as WE and CE. Platinum wires (0.5 mm Ø) inserted into PEEK capillaries were used as pseudo RE and WS (Figure 1), where only the tip of the wires was exposed to the electrolyte, as the sides were insulated by PEEK. The RE and WS were placed in close proximity to the membrane on either side, without physical contact with the membrane. The inner cell diameter is 10 mm, the distance between the working and counter electrodes is 16 mm, and the electrolyte volume is 1.7 ml.

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.

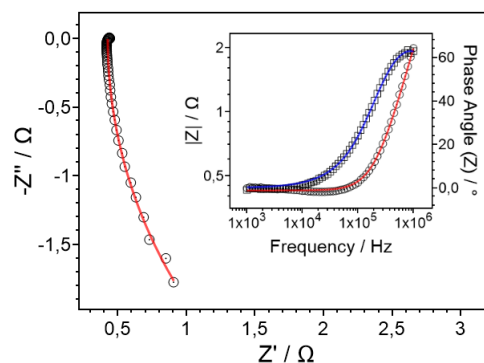
A Metrohm Autolab PGSTAT204 equipped with an FRA32-module and controlled through the NOVA 2.1.5 software was used for all impedance measurements. The recorded impedance data were evaluated by equivalent circuit fitting using the EIS data analysis software RelaxIS 3 (rhd instruments GmbH & Co. KG).

Step	Action to be performed
1	Clean the test cell and polish the electrodes.
2	Place the membrane in the test cell (skip this step to measure the electrolyte contribution without membrane).
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 four-electrode configuration (see Figure 1).
5	Set the temperature to 20.0 °C and wait for temperature equilibration (40 min).
6	Perform an EIS measurement.
7	Drain the electrolyte from the test cell and clean it.

Potentiostatic EIS measurements were performed in a frequency range of 1 MHz to 1 kHz with an amplitude of  $V_{AC,rms} = 100 \mu\text{V}$ . 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.

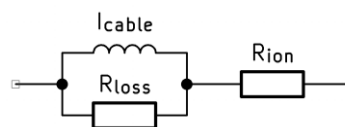
## Results

A typical four-electrode impedance spectrum of the TCE Cell One with the membrane can be seen in **Figure 2**. At high frequencies ( $>100 \text{ kHz}$ ), the inductance of the cables and connections dominate the spectrum ( $I_{cable}$ ). 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 is sometimes observed in low-impedance systems such as this, and can be modelled with a resistor ( $R_{loss}$ ) in parallel with the inductor. At low frequencies the impedance approaches the ionic resistance ( $R_{ion}$ ) of the system. No blocking behaviour occurs since the EIS measurements are carried out in four-electrode configuration. This can be observed in the Bode plot as a plateau in  $|Z|$  below 10 kHz.



**Figure 2.** Nyquist plot of the impedance spectrum of the TCE Cell One with the membrane. A Bode plot is depicted in the inset ( $|Z|$  is shown as red circles (left y-axis, logarithmic scale) 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 3**. 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 ( $R_{membrane}$ ). In order to determine  $R_{electrolyte}$ , impedance spectra were also recorded for cells without any membrane (only filled with the same electrolyte).



**Figure 3.** Equivalent circuit used for fitting the spectra.

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:  $R_{membrane} = 281 \pm 20 \text{ m}\Omega$ .

	$R_{ion} \text{ (m}\Omega\text{)}$	
	Electrolyte	Electrolyte + Membrane
Repetition 1	103.8	336.0
Repetition 2	69.6	351.9
Repetition 3	57.9	339.5
Repetition 4	59.3	371.0
Repetition 5	46.8	342.0
<i>Standard deviation</i>	19.6	12.6
<i>Mean</i>	67.5	348.1

The membrane conductivity  $\sigma$  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. Note that the relevant area in the equation above is only that which contributes to the ionic conductivity of the membrane (*i.e.* the inner cell cross-section area), not the whole membrane area which extends beyond the inner cell diameter as it is clamped in place. The ionic conductivity of the membrane was determined to be  $15.9 \pm 1.2 \text{ mS/cm}$ . This can be compared to the value

determined by two-electrode EIS for the same membrane ( $18.5 \pm 0.5 \text{ mS/cm}$ ) [4].

## Summary

In this application note we demonstrate how to determine the ionic conductivity of a membrane using four-electrode EIS. The TCE Cell One test cell presents an easy and reproducible way to specifically measure the through-plane conductivity for free-standing membranes in aqueous or organic electrolytes.

## Acknowledgements

The development of the test cell TCE Cell One used for this application is part of a sub-project related to the project LIMES funded by the Federal Ministry of Economic Affairs and Climate Action as part of the 7. Energieforschungsprogramm which is highly appreciated. LIMES is a joint research project with the two partners rhd instruments GmbH & Co. KG and Karlsruhe Institute of Technology (KIT). We thank our project partners Dr. Andreas Hofmann and Ingo Reuter from KIT for the fruitful collaboration as well as for the valuable and inspiring input.

Supported by:



on the basis of a decision  
by the German Bundestag

## 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.
- [3] G. Fafilek, "The use of voltage probes in impedance spectroscopy," *Solid State Ionics*, vol. 176, p. 2023, 2005.
- [4] "Application note: "Determining the Ionic Conductivity of a Free-Standing Membrane"," July 2022. [Online]. Available: [https://rhd-instruments.de/download/appnotes/application-note\\_TCE%20Cell%20One\\_Membrane\\_conductivity.pdf](https://rhd-instruments.de/download/appnotes/application-note_TCE%20Cell%20One_Membrane_conductivity.pdf).