

## Work 5: Ion selective membrane conductivity determination

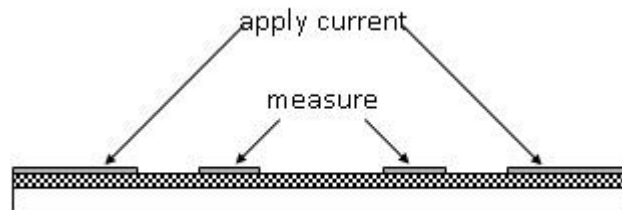
Conductivity of ion selective membrane represents crucial parameter of its application potential. Beside separation properties the high conductivity is required in the electromembrane separation processes (e.g. electrodialysis), industrial chemicals production (e.g. chlor-alkali industry) and power generation processes (e.g. PEM fuel cells). This is due to the fact that low ion conductivity causes high potential drop on membrane connected with higher energy consumption and low intensity of membrane process.

**Aim of work:** Measure ion conductivity of Nafion membrane in various ionic forms and at different temperatures.

**Theory:** Membrane conductivity can be measured in cross or longitudinal direction. With respect to experimental error longitudinal arrangement gives more reproducible results. The measurement is realized by electrochemical impedance spectroscopy (EIS) in a four-electrode arrangement, see Fig. 1. Membrane conductivity is calculated on the basis of its determined resistivity and sample dimensions using Eq. (1).

$$\sigma = \frac{l}{R \cdot A} \quad [\text{S/m}] \quad (1)$$

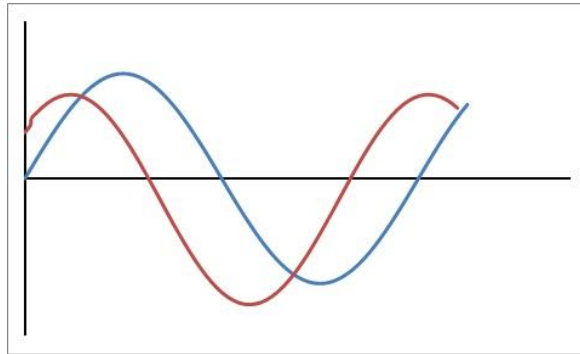
where  $\sigma$  stands for conductivity [ $\text{S m}^{-1}$ ],  $l$  represents the distance between sensing electrodes [m],  $R$  membrane resistance [ $\Omega$ ] and  $A$  the membrane cross-section area [ $\text{m}^2$ ].



**Fig. 1: Scheme of electrode connection to the membrane strip.**

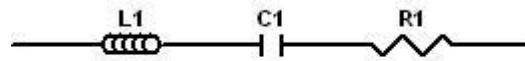
EIS represents highly sensitive experimental technique based on periodical perturbation signal, see Fig. 2. Three basic components describe respond of the system exposed to the alternating electrical field were defined. These are:

- Inductance (L)
- Capacitance (C)
- Ohmic resistance (R)



**Fig.2: Time dependence of the perturbation signal (blue line) and respond of the system (red line).**

LCR components represents model of equivalent circuit (Fig 3) in which every single component has a specific physical meaning.



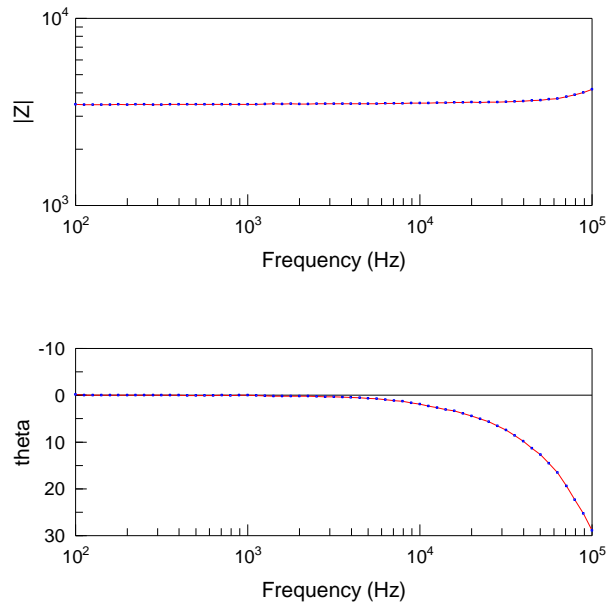
**Fig. 3: LCR equivalent circuit model.**

Component L represents inductor (inductance, L, henry). Its physical meaning is adsorption (at low frequencies) or interaction between wires (at high frequencies). Absolute impedance  $|Z|$  is in this case defined as  $|Z| = \omega \cdot L$ , where  $\omega$  represents frequency at which measured point was obtained and phase angle  $\theta$  is equal to  $90^\circ$ .

Component C represents capacitor (capacitance, C, farad). Its physical meaning is capacitance of the double layer. Absolute impedance  $|Z|$  is in this case defined as  $|Z| = 1/\omega \cdot C$  and phase angle  $\theta$  is equal to  $-90^\circ$ .

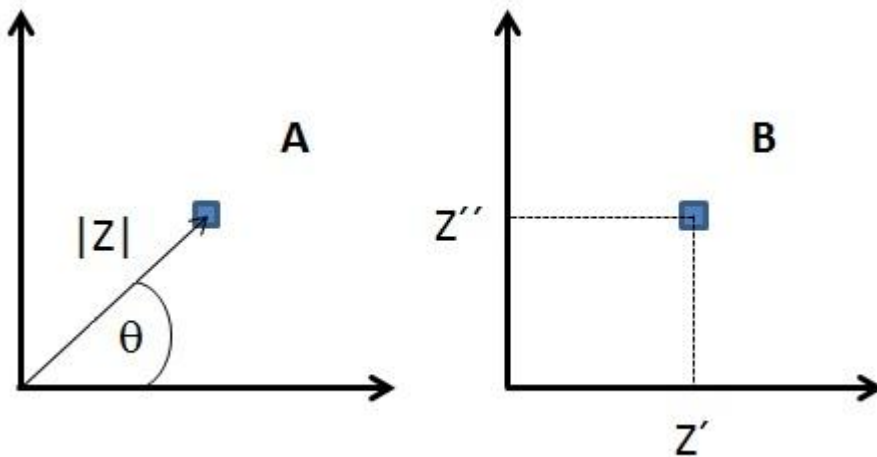
Component R represents resistor (resistance, R, ohm). Its physical meaning is either the resistance of conducting electrolyte or polarization resistance. Absolute impedance  $|Z|$  is in this case defined as  $|Z| = \text{constant}$  and phase angle  $\theta$  is equal to  $0^\circ$ .

Two types of the EIS data presentation are possible. The first of them are Bode plots, showing absolute impedance  $|Z|$  and phase angle  $\theta$  as dependence of the frequency, see Fig 4.



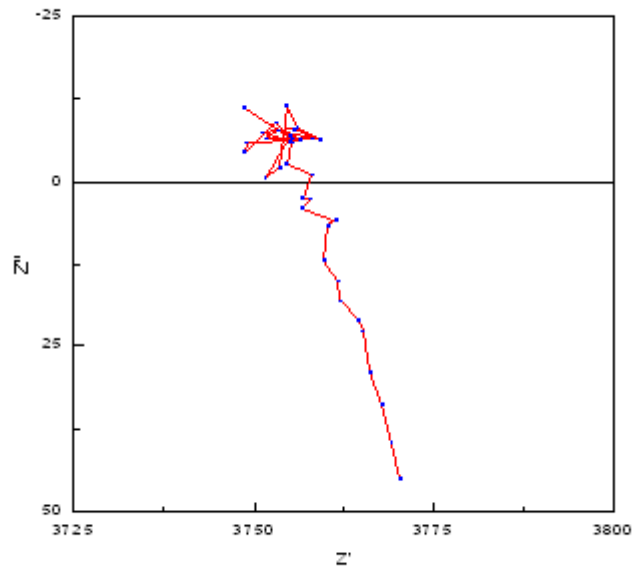
**Fig. 4: Sample of Bode plots impedance spectra.**

Two parameters specify a point in the plane. It is possible to use Polar coordinates ( $|Z|$  and  $\theta$ ) or Cartesian coordinates ( $X, Y$ ), as it is possible to see in Fig. 5A.



**Fig. 5: Two ways of specify of the point in the plane. A – Polar coordinates; B – Cartesian coordinates.**

It is clear from Fig 4 and Fig. 5A, that Bode plots use polar coordinates to specify a point in plane. Nyquist plot (Fig. 6), usage Cartesian coordinates represents an alternative.



**Fig. 6: Sample of Nyquist plot impedance spectra.**

Advantage of the Nyquist plot is in the simplicity of evaluation of the membrane resistance, because it is equal to the  $Z'$  value. However, frequencies are not shown in Nyquist plot. Nevertheless, transformation equations (2) and (3) between Bode and Nyquist plots result from Fig 5.

$$|Z| = \sqrt{(Z')^2 + (Z'')^2} \quad (2)$$

$$\text{tg } \Theta = \frac{Z''}{Z'} \quad (3)$$

**Safety Precautions:** Wear safety glasses and laboratory coat at all times in the laboratory. For work with acids wear rubber gloves.

**Apparatus:**

- 1) LCR bridge for electrochemical impedance measurement
- 2) Peristaltic pump
- 3) Tempered box
- 4) Conductivity measurement cell

**Tasks:**

- 1) *Assembly apparatus:*

Cut 3 strips of Nafion membrane in approximate dimensions of 1x5 cm. Put the strip to the conditioning solutions of  $0.5 \text{ mol dm}^{-3} \text{ NaCl}$ ,  $0.5 \text{ mol dm}^{-3} \text{ HCl}$  and  $0.5 \text{ mol dm}^{-3} \text{ CaCl}_2$  for 1 hour. After the conversion to the desired ionic form rinse the membrane strips by distilled water. Clamp the strip into the conductivity cell and connect to the LCR bridge.

2) *Experiments and results*

Measurements of the samples conditioned in  $0.5 \text{ mol dm}^{-3}$  NaCl and  $\text{CaCl}_2$  solutions are taken at laboratory temperature. Measurement of the sample conditioned in  $0.5 \text{ mol dm}^{-3}$  HCl is taken at laboratory and  $90^\circ\text{C}$  temperature. Measure the impedance spectra with amplitude of the perturbation signal equal to 50 mV. Measure absolute impedance  $|Z|$  and phase angle  $\theta$  for 10 frequencies in the range 10 kHz – 10 Hz. Create impedance spectra in the form of Bode and Nyquist plots. Analyze the spectra and calculate membrane conductivity. Compare conductivity of membrane in various ionic forms and at different temperatures.

3) Summarize your results and discuss it in laboratory protocol.