

MEMBRANE AND INTERFACE INVESTIGATION BY IMPEDANCE SPECTROSCOPY

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This study deals with the membrane and interface (electrical double layer and diffusion boundary layer) investigation by electrochemical impedance spectroscopy (EIS). The EIS is a powerful technique for characterizing electrical behavior of systems in which electrical processes occur at different rates.¹ During an EIS experiment a small sine-wave voltage or current excitation is applied to a sample, while the amplitude and phase shift of the corresponding current or voltage signal is monitored, over a frequency range. A systematic study on the effect of solution concentration, temperature and velocity, on the electrical resistance of several anion- and cation- exchange membranes and their interface, was carried out. At the best of our knowledge, for the first time concentrations up to 4 M (NaCl in water) were used in this type of investigation.²

The interest towards concentrated solutions lies in the high salinity-gradient power (SGP) that can be extracted by membrane-based energy conversion processes, like pressure-retarded osmosis (PRO) and reverse electrodialysis (RE).³ Concentrated solutions are produced in numerous industrial activities such as salt works and salt mines. Moreover, brine solutions can be produced by reverse osmosis and/or membrane distillation of seawater. These solutions can be used as concentrated stream in SGP-RE stack employing as diluted stream sea or brackish water. This idea is at the basis of the European FP7 Project REAPower (Reverse Electro dialysis Alternative Power production; www.reapower.eu), and it can offer a huge potential for the improvement of the performance of the SGP-RE systems, which usually focus on the combination of fresh water, as the diluted solution, and seawater, as the concentrated. The use of more concentrated solution allows to reduce the electrical resistance within the low concentration compartment of the SGP-RE stack, boosting the power that can be extracted. However, is necessary to consider the effect of concentrated electrolyte solutions on membrane properties, including electrical resistance and permselectivity.

The experimental data showed that membrane electrical resistance was higher than the interfaces resistance in the whole range of concentration, temperature and velocity investigated (0.5-4 M; 20-40°C; 0-4.0 cm s⁻¹) and it did not depend significantly from the solution velocity. On the contrary, the interface resistances were reduced increasing the velocity (Figure 1).

With the increasing of the temperature, the membrane and interface resistances decreased. Increasing the solution concentration the resistance of the electrical double layer was reduced, and its contribution to the total resistance became negligible at 4M. This effect was due to the increasing screening of the attractive electrical interactions between the counter-ions and

fixed charged groups of the membrane, increasing the concentration of the external solution. A non-unique dependence of the membrane electrical resistance from the solution concentration, was observed.

The increasing of the solution concentration induced a moderate reduction of the membrane electrical resistance until the ions concentration in the membrane, was greater than in the external electrolyte solution. When the external solution had an ions concentration considerably higher than the membrane, the electrical resistance increased. This behavior was rationalized considering the unfavorable changes of the membrane microstructure in concentrated electrolyte solution (membrane shrinking).

Pulsed Gradient Spin Echo Nuclear Magnetic Resonance (PGSE-NMR) technique was used to measure the water self-diffusion coefficients in swelled membrane as a function of the solution concentration and temperature. These measurements gave additional important insights about the effect of the electrolyte solution concentration and membranes fixed charges density, on membrane microstructure and its mass and electrical transport properties.

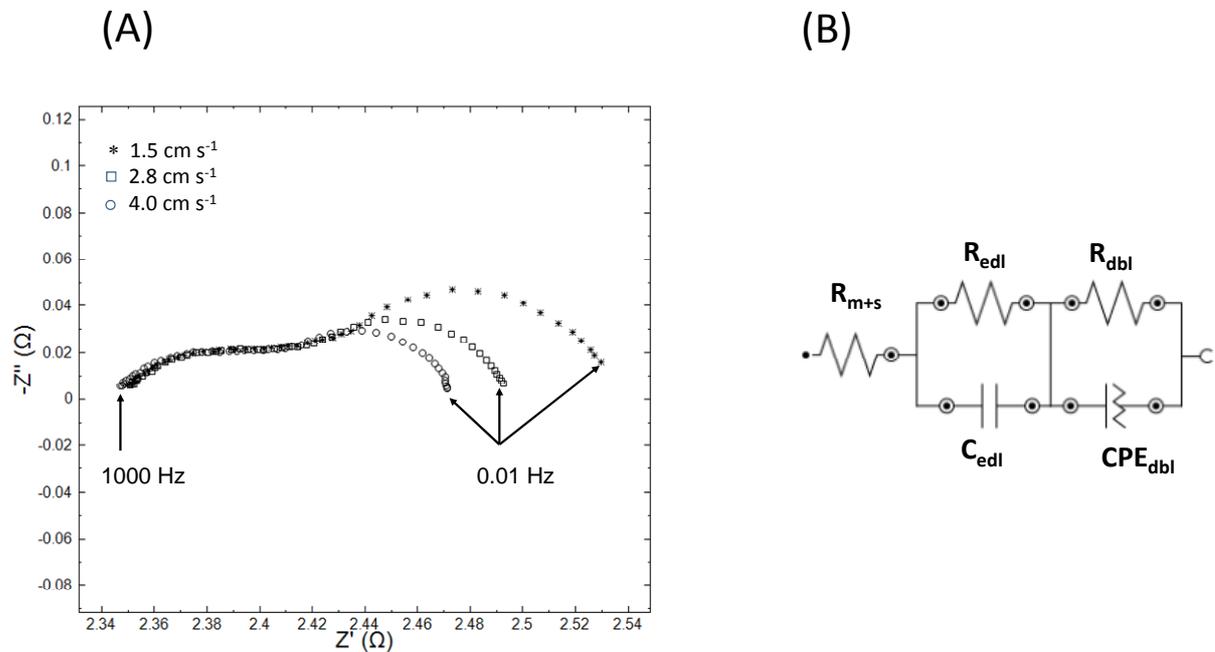


Figure 1. Nyquist plot of a cation exchange membrane measured in 0.5M NaCl solution at $20\pm 1^\circ\text{C}$ and three different velocities (A) and the equivalent circuit model used to fit the experimental data (B). In the model the resistor is indicated as: R; the capacitor as: C; the constant phase element (a non-ideal capacitor) as: CPE. The subscript “m+s” is referring to membrane plus solution; “edl” to the electrical double layer; “dbl” to the diffusion boundary layer

References

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