Probing membrane and interface properties by impedance spectroscopy

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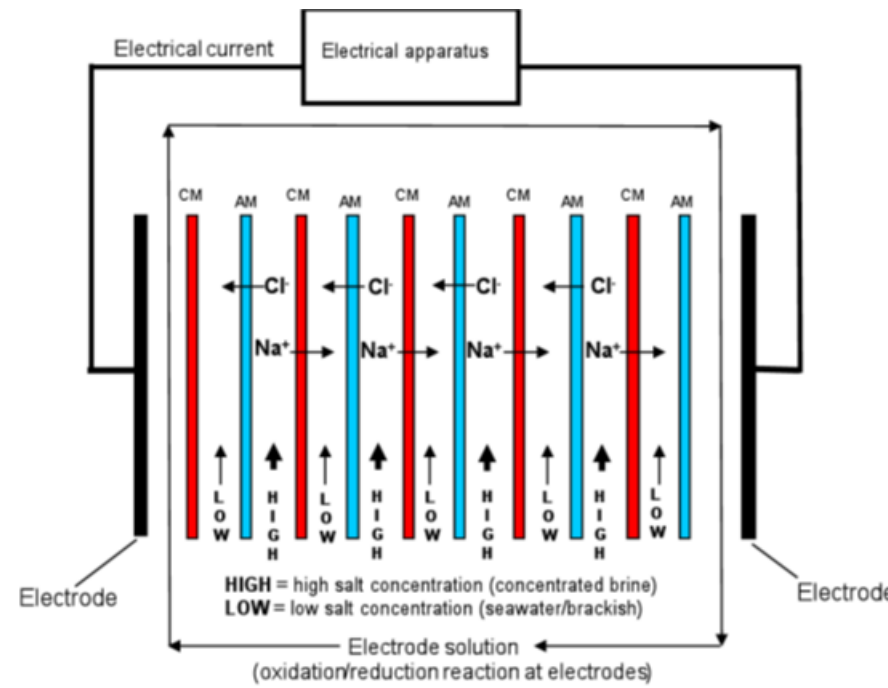[3]University of Calabria, Rende (CS), Italy

Reverse Electrodialysis Alternative Power production

REAPower

REAPOWER

www.reapower.eu

Project (n. 256736)

HIGH = high salt concentration (concentrated brine)
LOW = low salt concentration (seawater/brackish)

Electrode solution
(oxidation/reduction reaction at electrodes)

Nernst potential:

$$\Delta V^0{}_{theo} = \frac{RT}{zF} \ln\left(\frac{a_c}{a_d}\right)$$

The idea:

• **Capturing energy** from **Salinity Gradient Power (SGP) by Reverse Electrodialysis (RE)** using **brine** as concentrated solution, and **seawater** as diluted solution instead of seawater as concentrated and fresh water as diluted

• To avoid the use of freshwater

• Higher theoretical energy extractable

• Reduction of the internal electrical resistance of the stack
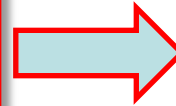
Reapower objectives:

Create/select and optimize **materials and components tailored to the requirements of the SGP-RE technology** operating with high salinity brine and seawater. These include the **membranes**, spacers, electrodes and electrolytes

→ New **Ion Exchange Membranes** (IEMs) for highly concentrated electrolyte solutions

Optimize the design of the SGP-RE cell pairs and stack using a computer modelling tool developed for that purpose

Low **electrical resistance**

Verify the model, and assess the developed materials, components and design through tests on laboratory stacks.

High **permselectivity**

Evaluate and improve the performance of the overall system through tests on a prototype fed with real brine from a salt pond

Chemical and mechanical **Stability**

Evaluate the results, analyze the economics and assess the perspectives of the technology

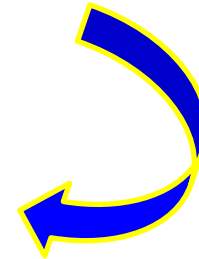# Membrane electrical resistance
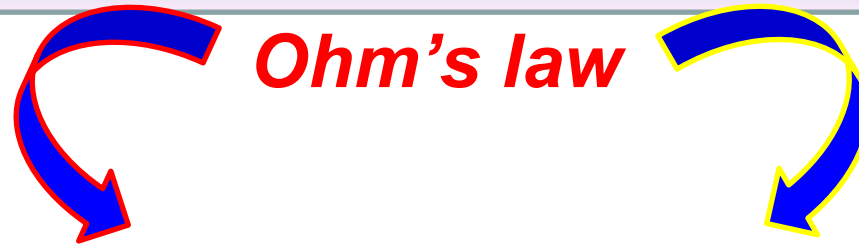
Ohm's law

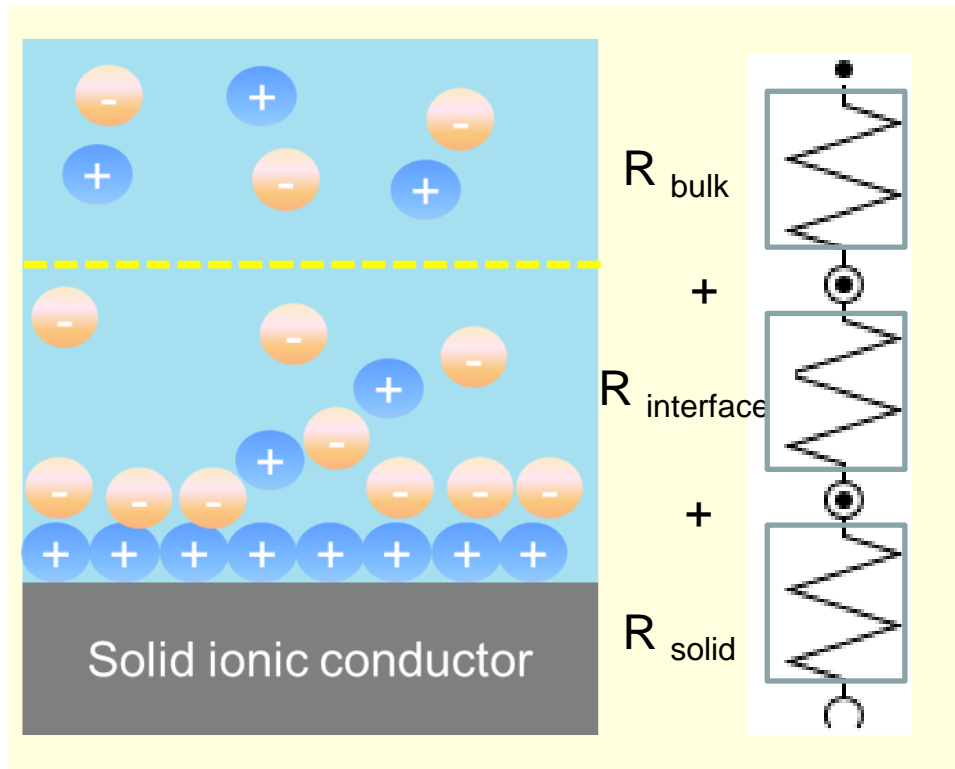**With DC: resistance (R)**

$$R = \frac{V}{I}$$

With AC: impedance (Z)

$$Z_{(\omega)} = \frac{U_{(\omega)}}{I_{(\omega)}} \qquad \omega = 2\pi\upsilon$$

Using an AC over a frequency range, it is possible to distinguish phenomena proceeding at different rates like polarization phenomena at the membrane interface

*At the **interface** between a solid ionic conductor (like an IEM) and a liquid electrolyte, physical and electrical properties change suddenly because of an **heterogeneous charge distribution** (polarization) which reduce the overall electrical conductivity of the system.*

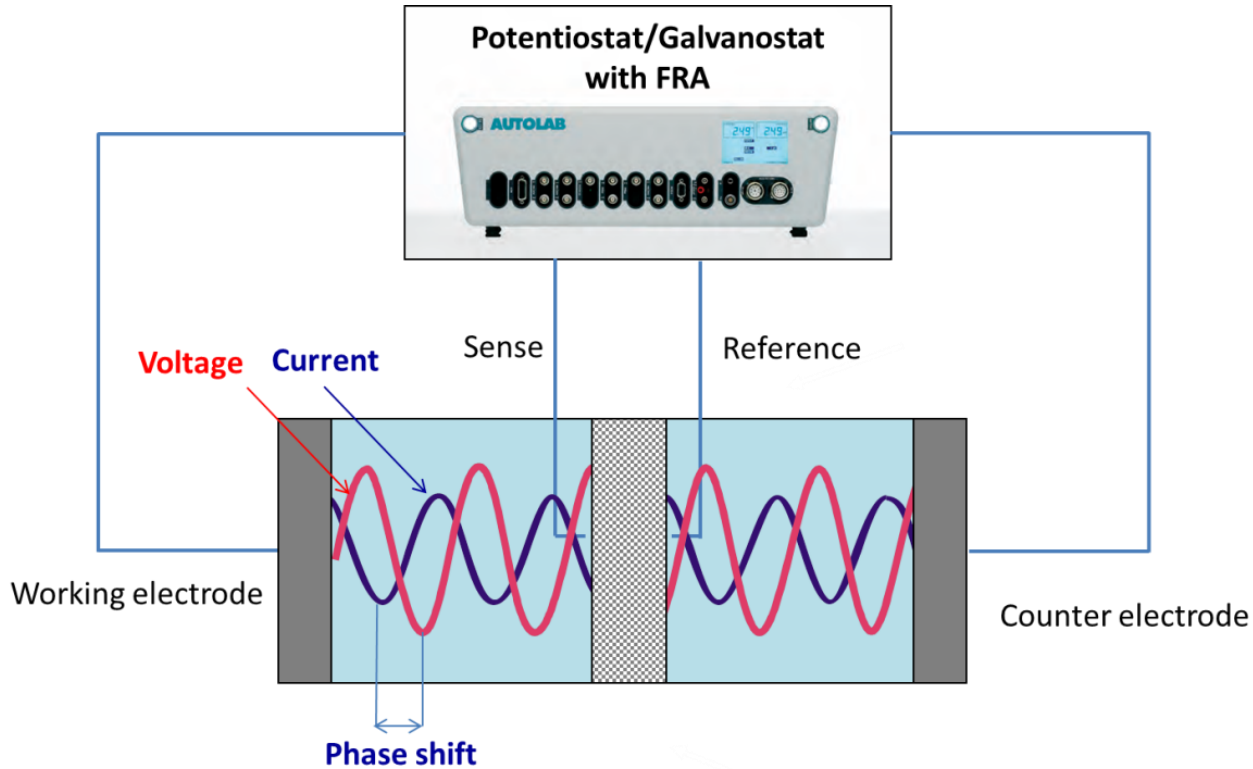**With DC: resitance (R)**

$$R = \frac{V}{I}$$

➢ *unable to distinguish the resistance of the ionic conductor from the interface resistance*

With AC: impedance ($Z_{(\omega)}$)

$$Z_{(\omega)} = \frac{U_{(\omega)}}{I_{(\omega)}} \qquad \omega = 2\pi\upsilon$$

✓ *it is possible to separate the contribution of the solid electrolyte from the contribution of its interface to the total resistance*

Electrochemical Impedance Spectroscopy (EIS)

$$U_{(\omega)} = U_o \sin \omega t$$

$$I_{(\omega)} = I_o \sin (\omega t + \varphi)$$

$$\omega = 2\pi\nu$$

$$Z_{(\omega)} = \frac{U_{(\omega)}}{I_{(\omega)}} = \frac{U_o e^{j\omega t}}{I_o e^{j(\omega t + \varphi)}} = |Z| e^{j\varphi} = |Z|\cos\varphi + j\,|Z|\sin\varphi$$

$$e^{j\varphi} = \cos\varphi + j\sin\varphi$$

$$j = \sqrt{-1}$$

Real part: resistance

Imaginary part: reactance

E. Barsoukov, J. R. Macdonald, Impedance Spectroscopy. Theory, Experiment, and. Applications, Second Edition. John Wiley & Sons, New Jersey, 2005.

The bipolar concentration polarization is time dependent and the concentration profiles undergo an inversion during each AC cycle

$$R_{tot} = R_{m+s} + R_{edl} + R_{dbl}$$

AC cycle

DL SL   SL DL

DBL   EDL   EDL   DBL

CEM

DL SL   SL DL

DBL   EDL   EDL   DBL

ITM
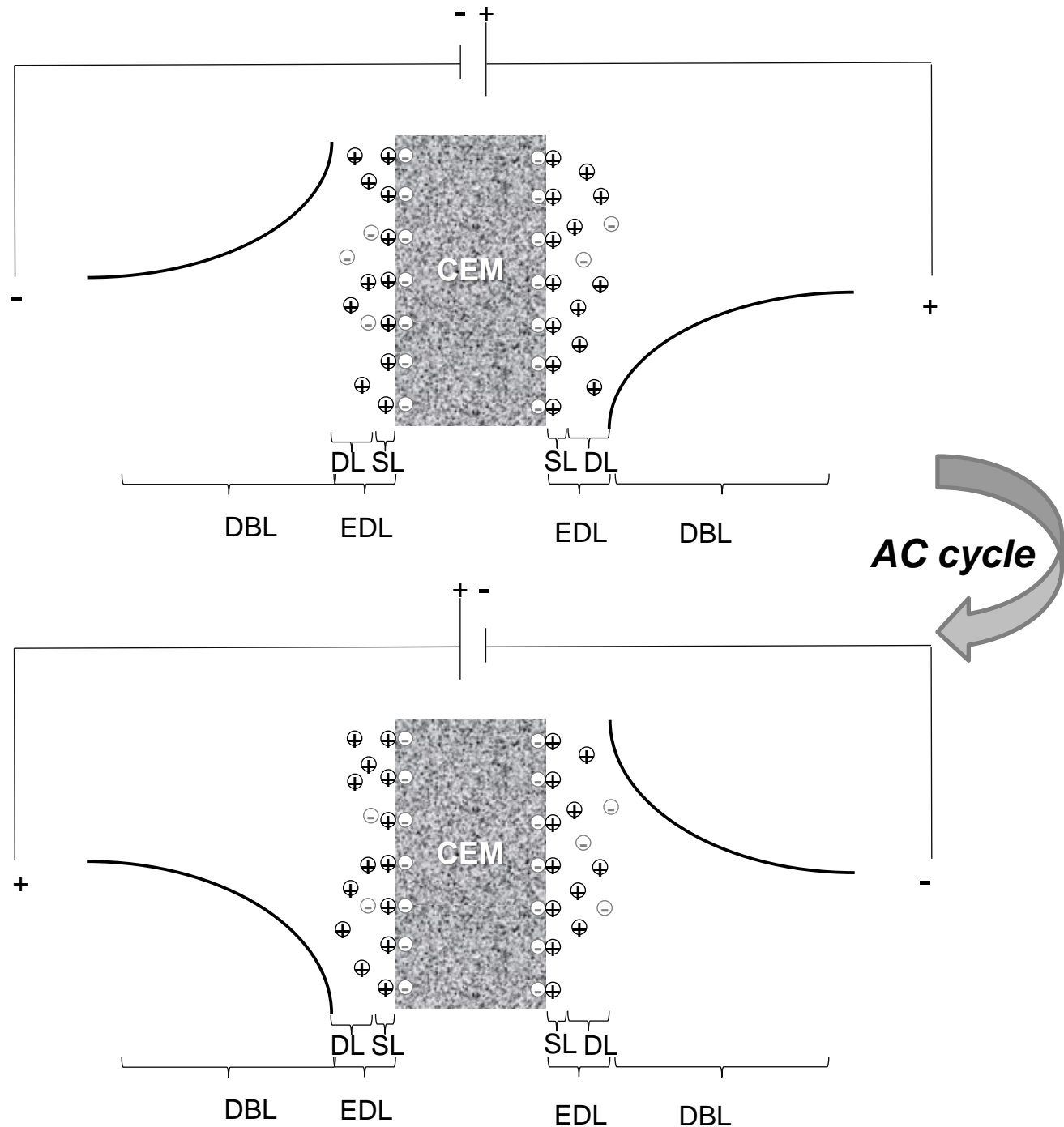
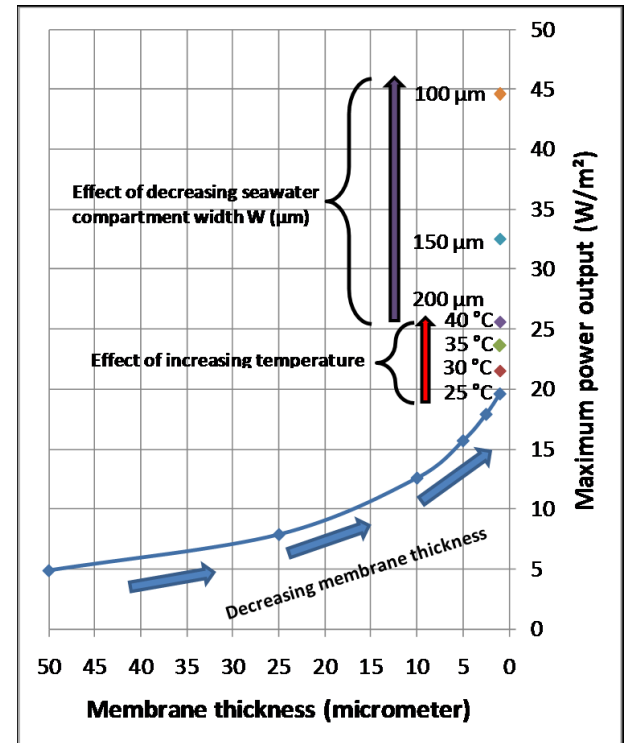# Homogeneous reinforced PEM developed by Fujifilm Manufacturing Europe BV for SGP-RE
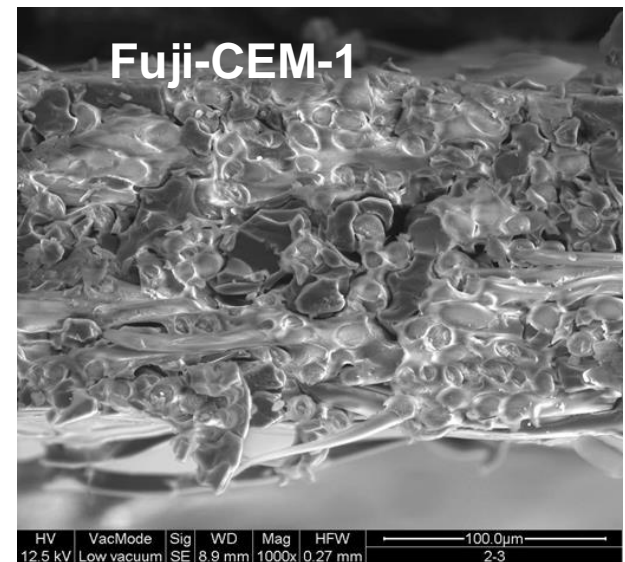
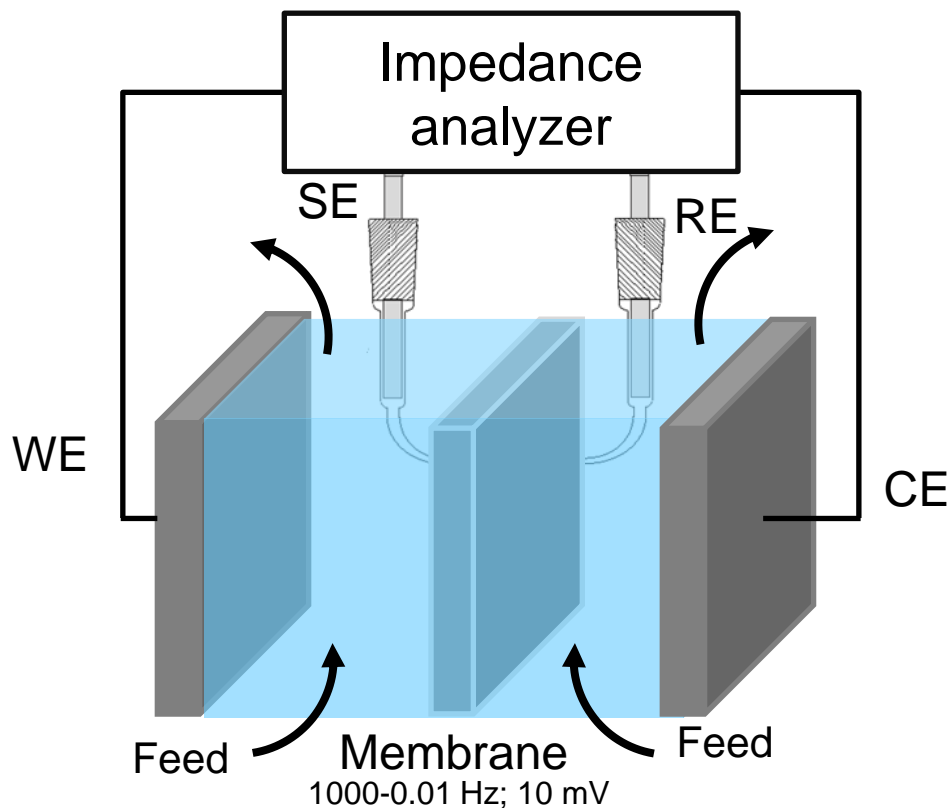| Membrane	Thickness (µm)*	Ion exchange capacity (mmol/g membrane)	Water uptake (%)*	Density of fixed charges (mol/L)*
Fuji-AEM-1	166±1	1.1±0.1	50.1±2	2.2±0.3
Fuji-AEM-2	129±2	1.4±0.1	36.7±0.04	3.8±0.2
Fuji-AEM-3	109±2	1.6±0.3	53.1±1.2	2.9±0.6
Fuji-CEM-1	170±1	1.6±0.1	47.3±0.8	3.4±0.2
Fuji-CEM-2	114±2	1.1±0.1	45.4±0.4	2.4±0.2
Fuji-CEM-3	113±2	1.0±0.3	55.3±0.2	1.8±0.5

* in NaCl 0.5M at 20°C

$$IEC = \frac{mmoles\ H^+ or\ OH^- exchanged}{W_{dry}}$$

$$wu\% = \frac{W_{wet} - W_{dry}}{W_{dry}} \cdot 100 \qquad D_{fix} = \frac{IEC}{wu\%} \cdot 100$$

Fuji-CEM-1

E. Brauns Desalination 237 (2009) 378–391

Electrochemical Impedance Spectroscopy (EIS)

Impedance analyzer

SE

RE

WE

CE

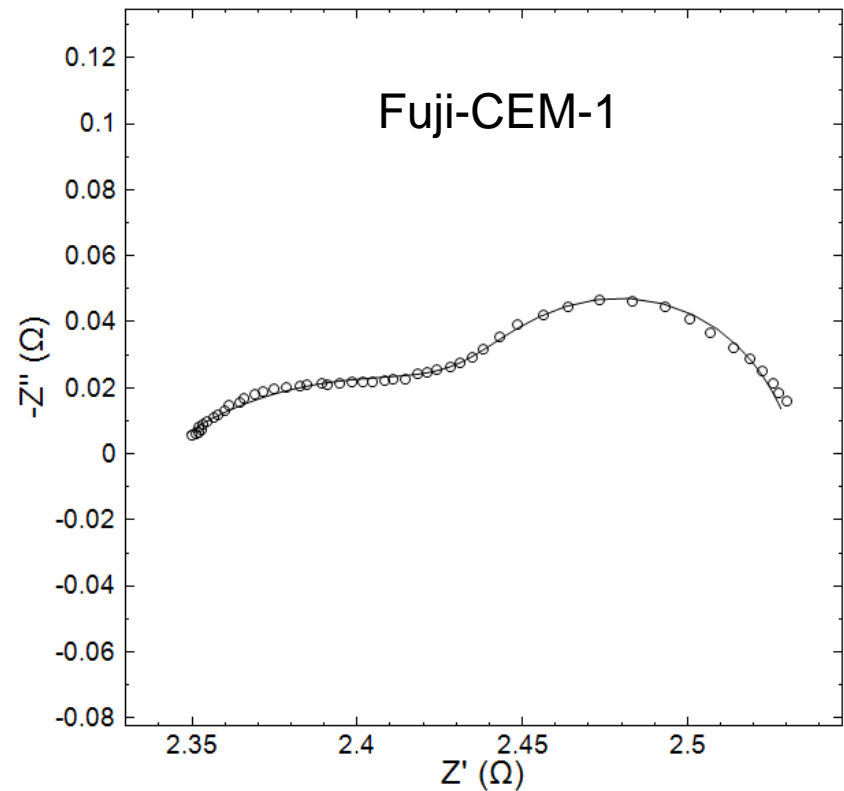Feed

Membrane
1000-0.01 Hz; 10 mV

Feed

- Solution velocity (1.5 – 4 cm s^{-1})

- Solution concentration (0.5 - 4 M)

- Temperature (20 - 40°C)
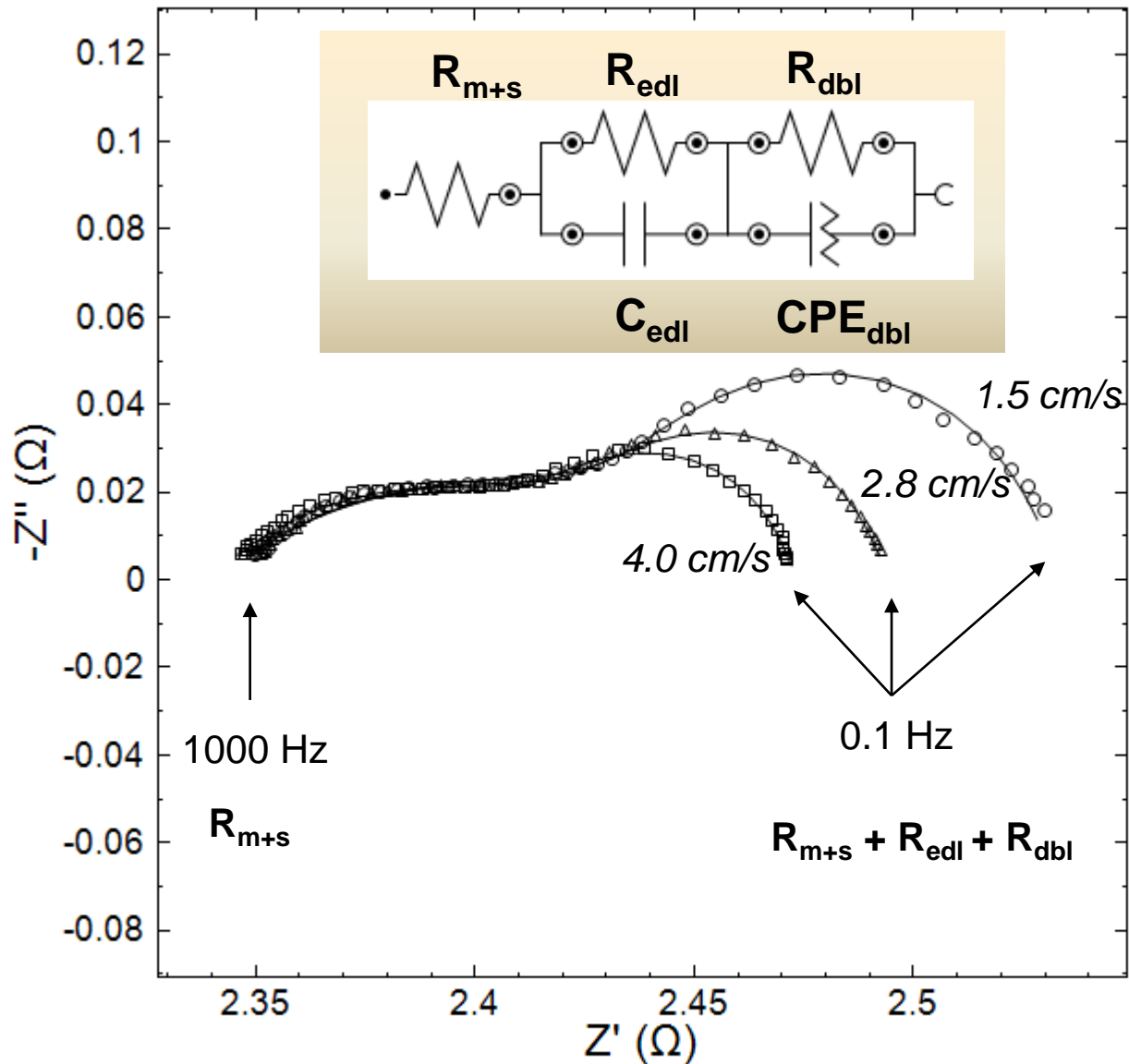
active membrane area: 3.14 cm^2

Equivalent circuit model used to fit EIS spectra
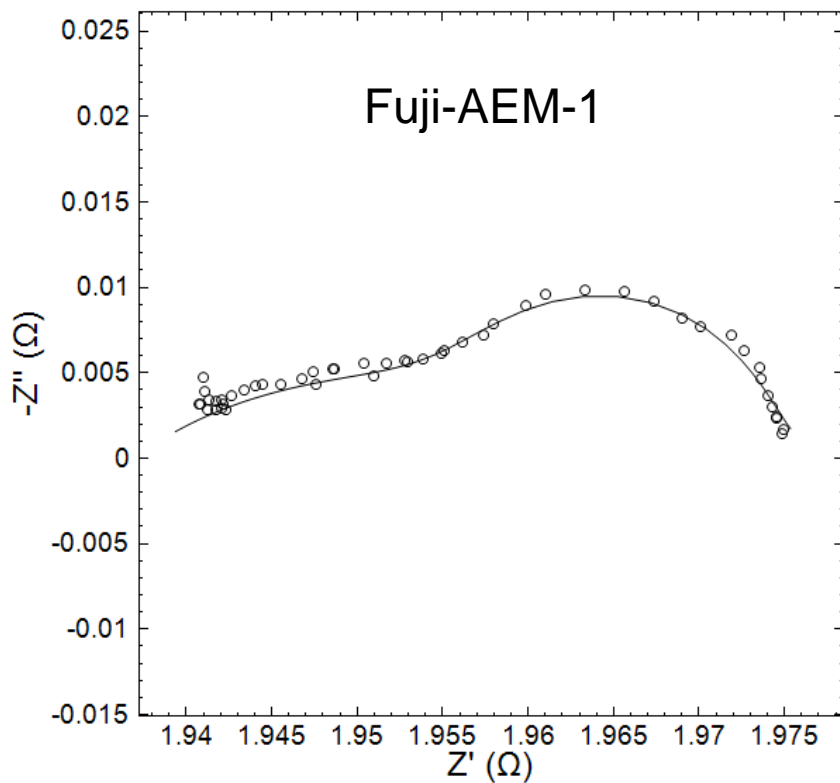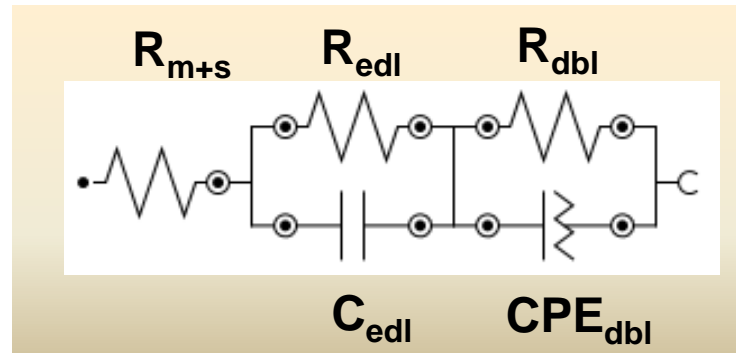
1000-0.01Hz, 0.5 M NaCl; 20°C; velocity 1.5 cm s^{-1}
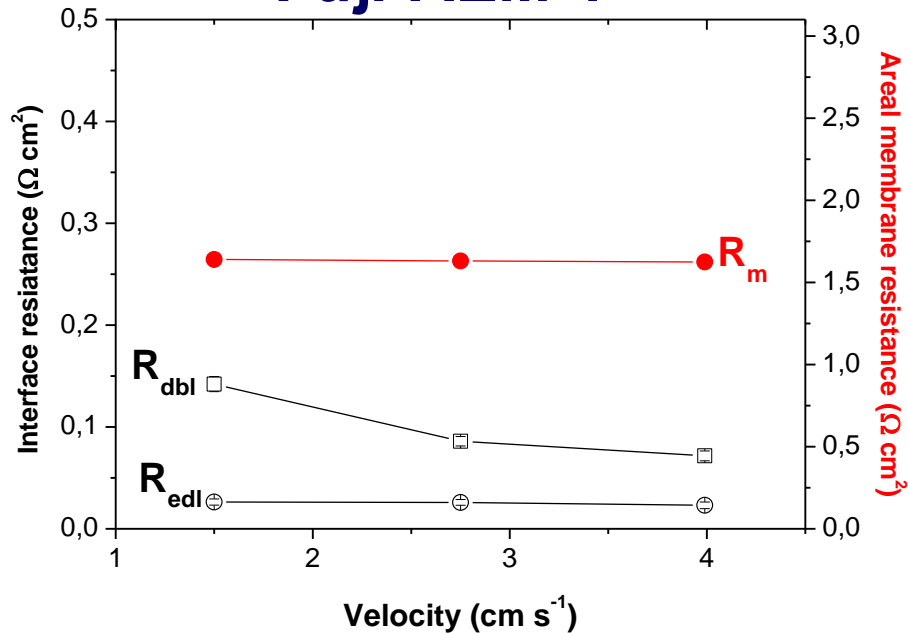
Effect of the solution velocity
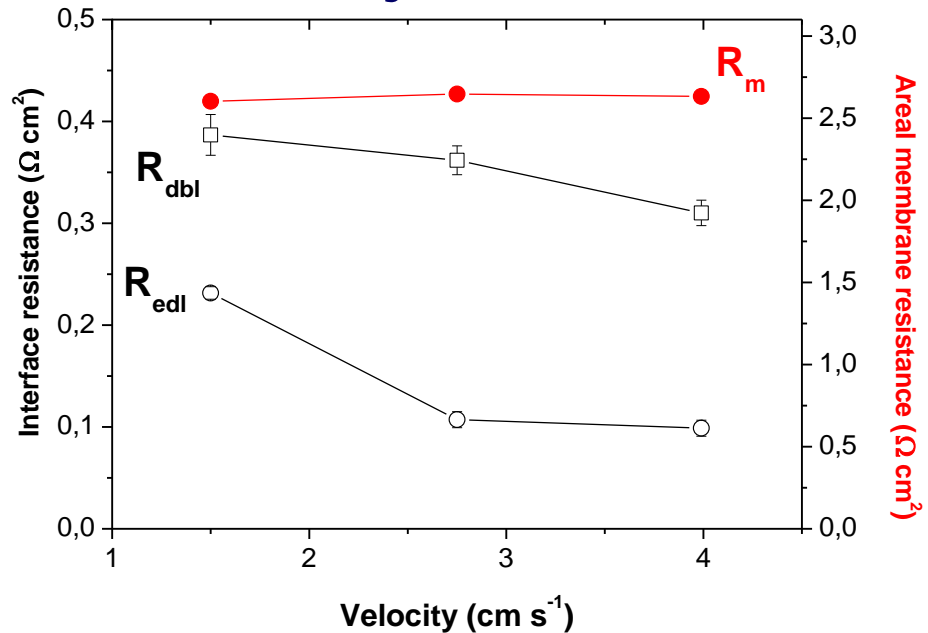

Fuji CEM-1: 0.5 M NaCl; 20°C

Effect of the solution velocity

Fuji-AEM-1 / Fuji-CEM-1 resistance plots

0.5 M NaCl; 20°C

- $R_m > R_{dbl} > R_{edl}$
- R_m is indipendent from the solution velocity
- R_{dbl} decreases with the increasing of the velocity
- R_{edl} is not influenced from the velocity for AEM, but in the case of the CEM a significant effect on the R_{edl} was observed

Membrane and interface resistances

Membrane	AMR (Ωcm^2)	R_{edl} (Ωcm^2)	R_{dbl} (Ωcm^2)	Thickness (μm)
Fuji-AEM-1	1.63±0.001	0.0259±0.003	0.0860±0.007	166±1
Fuji-AEM-2	1.55±0.001	0.0135±0.002	0.0667±0.003	129±2
Fuji-AEM-3	1.10±0.001	0.0184±0.003	0.0562±0.004	109±2
Fuji-CEM-1	2.65±0.001	0.107±0.006	0.362±0.020	170±1
Fuji-CEM-2	2.97±0.001	0.0759±0.006	0.299±0.010	114±2
Fuji-CEM-3	1.64±0.001	0.149±0.005	0.146±0.031	113±2

0.5M NaCl; 20°C; 2.8 cm s^{-1};

Membrane resistance is higher than interface resistances
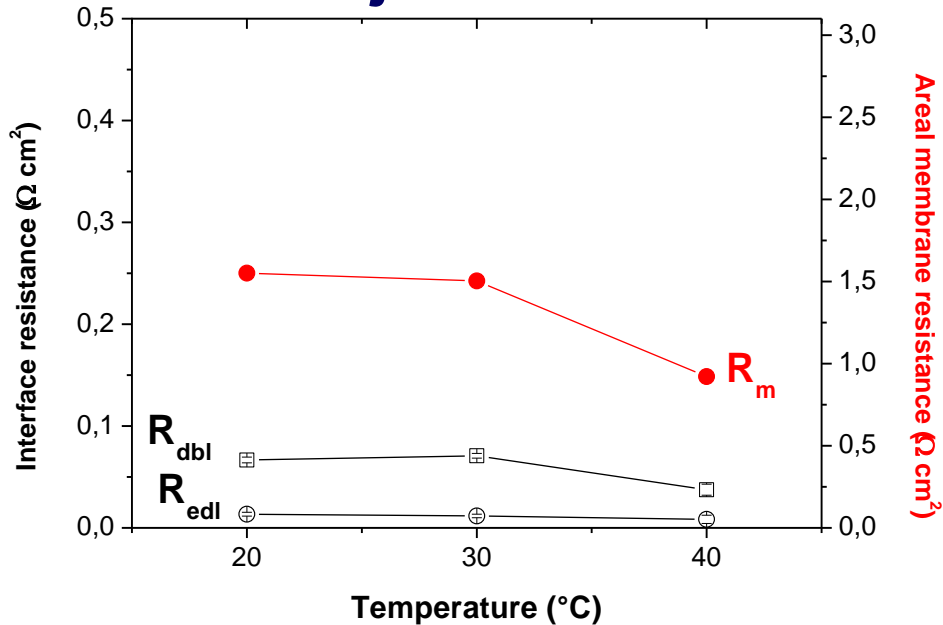
CEMs have higher resistances than AEMs

Ion	Mobility[a] (10^{-8} m^2 V^{-1} s^{-1})	Stokes radius[b] ($\mathring{A}$)
Cl$^-$	6.88	1.21
Na$^+$	4.98	1.84

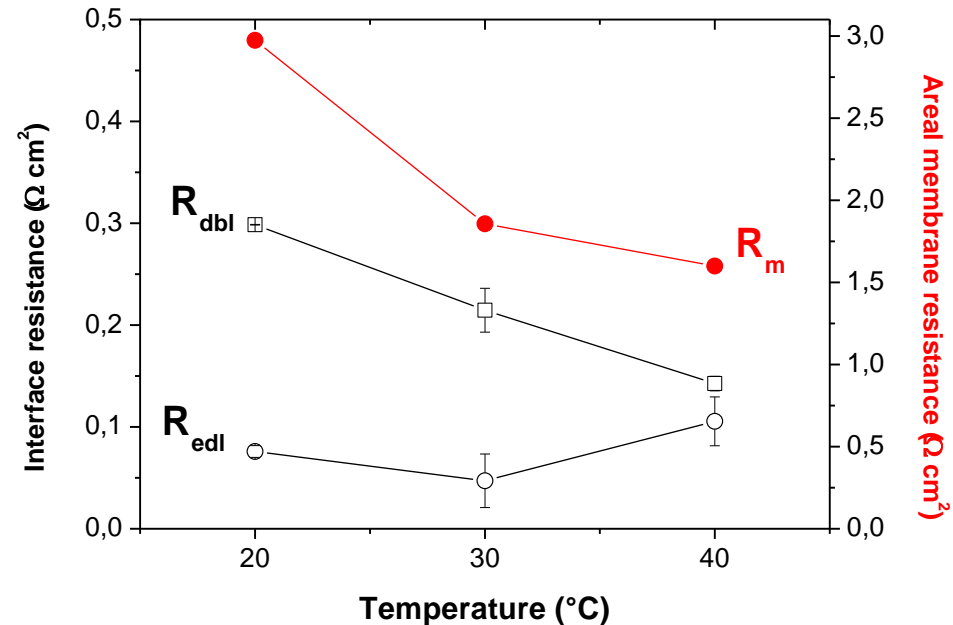[a]S. Koneshan et al. *J. Phys. Chem. B* 1998**,** *102,* 4193-4204
[b]P.C.F. Pau et al. *J. Phys. Chem.* 1990, *94,* 2671-2679

Effect of the temperature
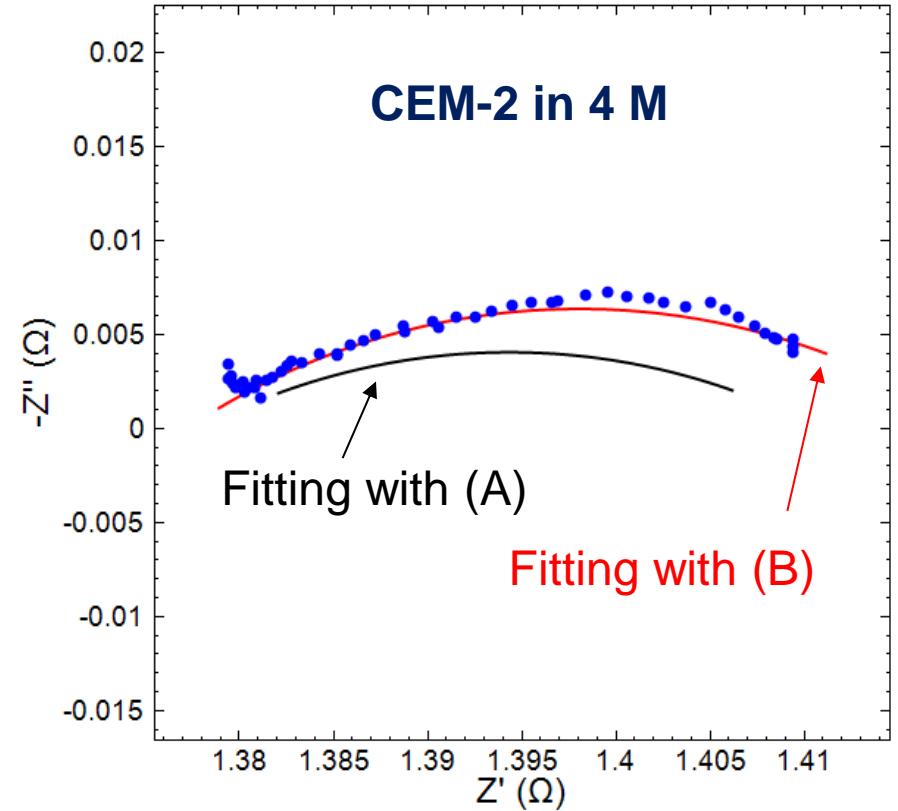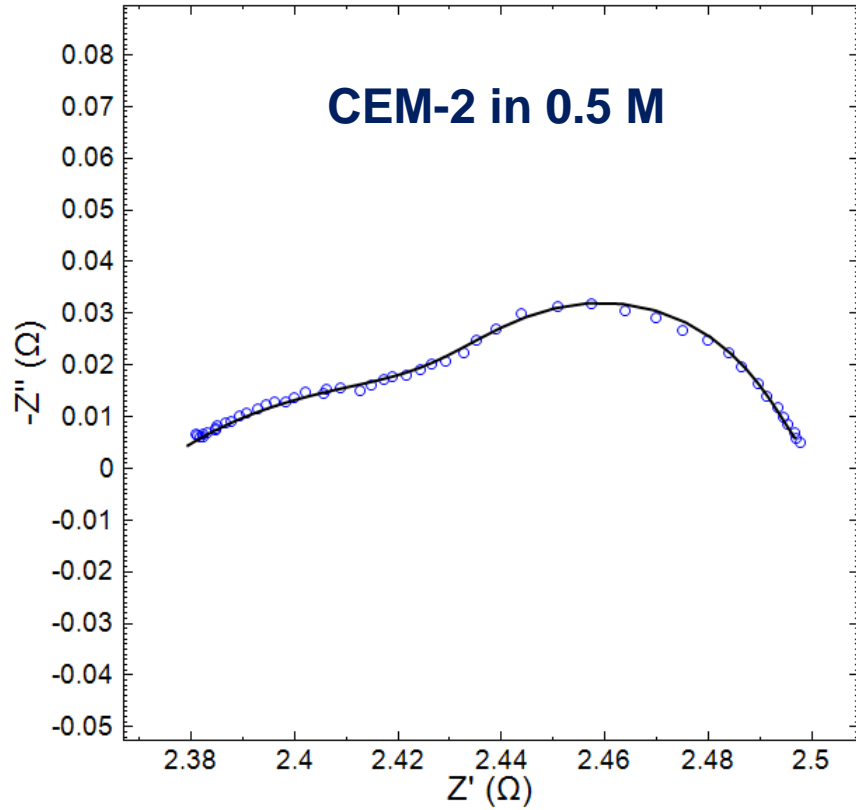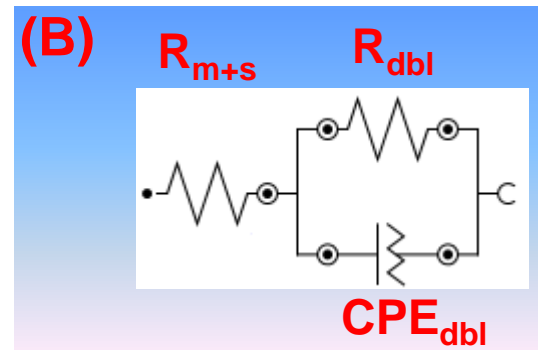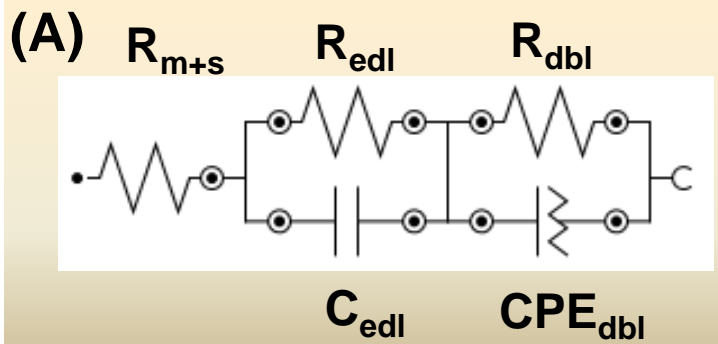
Fuji-AEM-2

Fuji-CEM-2

0.5 M NaCl; 2.8 cm s^{-1}

➢ The resistance of the ion transport through the membrane decreases with the temperature, because of the increasing ion mobility

# Use of concentrated electrolyte solution

20°C; 2.8 cm s^{-1}

For a symmetric monovalent electrolyte the **Debye length** (1/k), i.e. how far the net electrostatic effects of charge carriers in solution persist, **is reciprocally proportional to the square root of the concentration (C_0)**

$$1/k = \sqrt{\frac{\varepsilon_r \varepsilon_0 RT}{2F^2 C_0}}$$

1/k

Russel, W.B., Saville, D.A. and Schowalter, W. R. Colloidal Dispersions, Cambridge University Press, 1989.
K. Bohinc, V. Kralj-Iglic, A. Iglic, Electrochim. Acta 46 (2001) 3033-3040
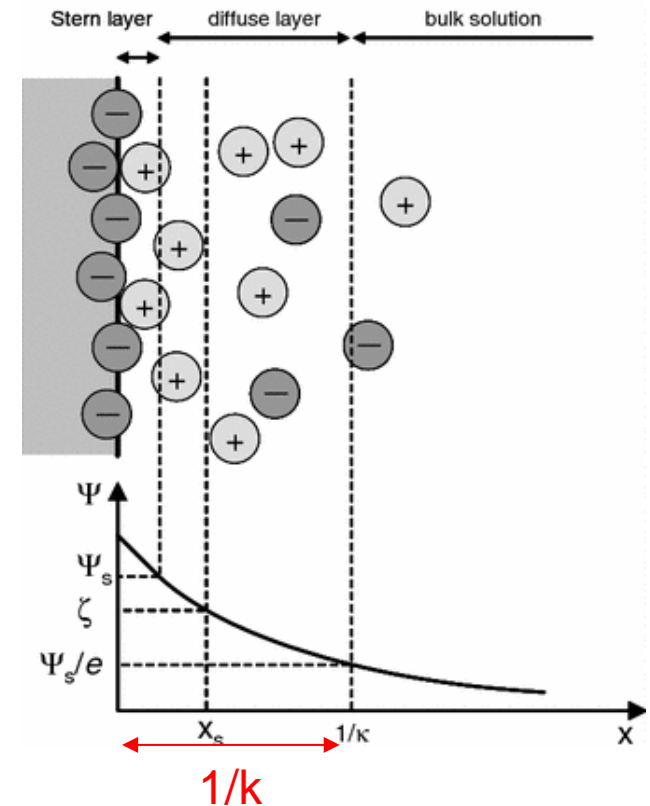
Schematic representations of EDL structures according to the Gouy–Chapman–Stern model (reproduced D. Handy et al. The ecotoxicology and chemistry of manufactured nanoparticles, in Ecotoxicology, Springer 2008)

The thickness of the EDL is approximately the Debye length and it **is expected to decrease with the solution concentration because an increasing shielding** of the attractive electrical interactions between the counter-ions and fixed charged groups of the membrane, increasing solution concentration (or ionic strength for multivalent electrolytes).
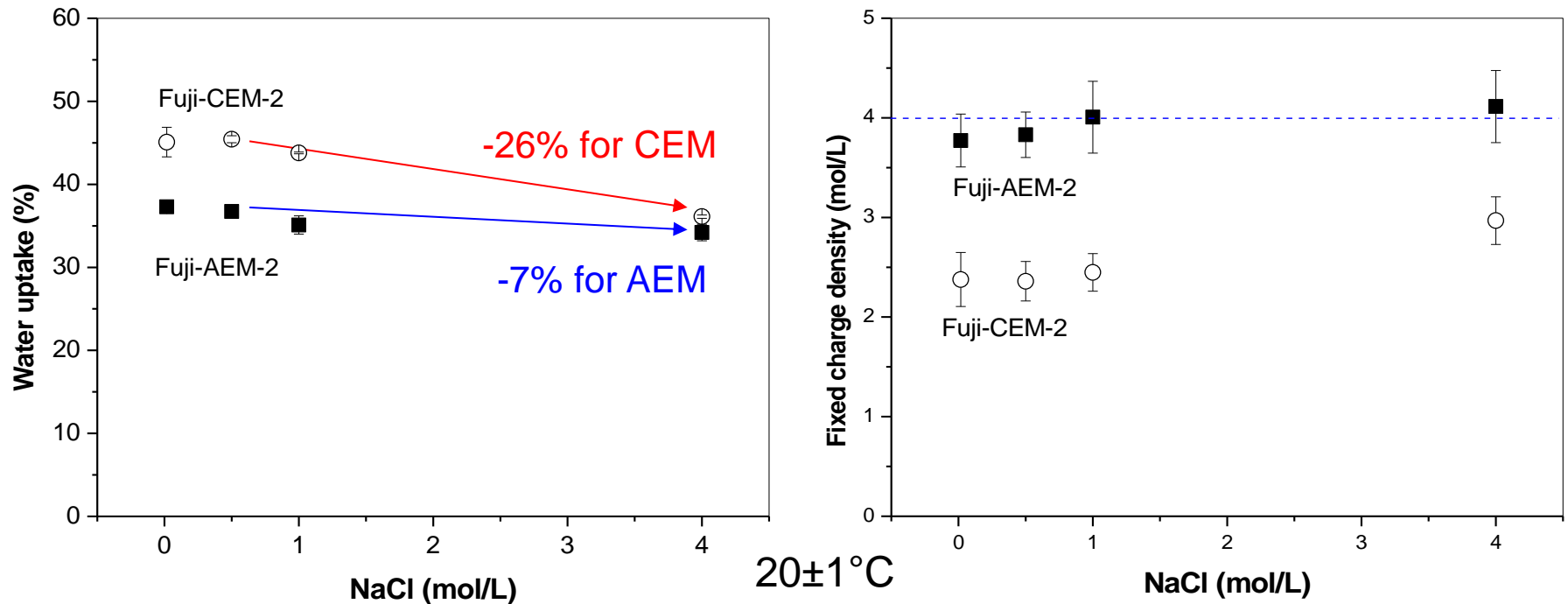
Effect of the solution concentration

Membrane	0.5 M			4.0 M		
	R_m (Ω cm^2)	R_{edl} (Ω cm^2)	R_{dbl} (Ω cm^2)	R_m (Ω cm^2)	R_{edl} (Ω cm^2)	R_{dbl} (Ω cm^2)
Fuji-AEM-2	1.551±0.001	0.013±0.002	0.067±0.003	1.436±0.001	-	0.167±0.014
Fuji-CEM-2	2.974±0.001	0.076±0.006	0.299±0.010	3.501±0.050	-	0.131±0.001

Conditions: 2.8 cm s^{-1}, 20±1°C

➢ With AEM-2 a small decrease of the R_m is observed from 0.5 to 4M solution (-7%).

➢ On the contrary, R_m increases for the CEM-2 (+18%)

Of course, considering also the solution resistance the effect is a neat reduction of the total resistance in both cases (R_s for 0.5 M: 4.51 Ωcm^2 ; for 4 M: 0.83 Ωcm^2)
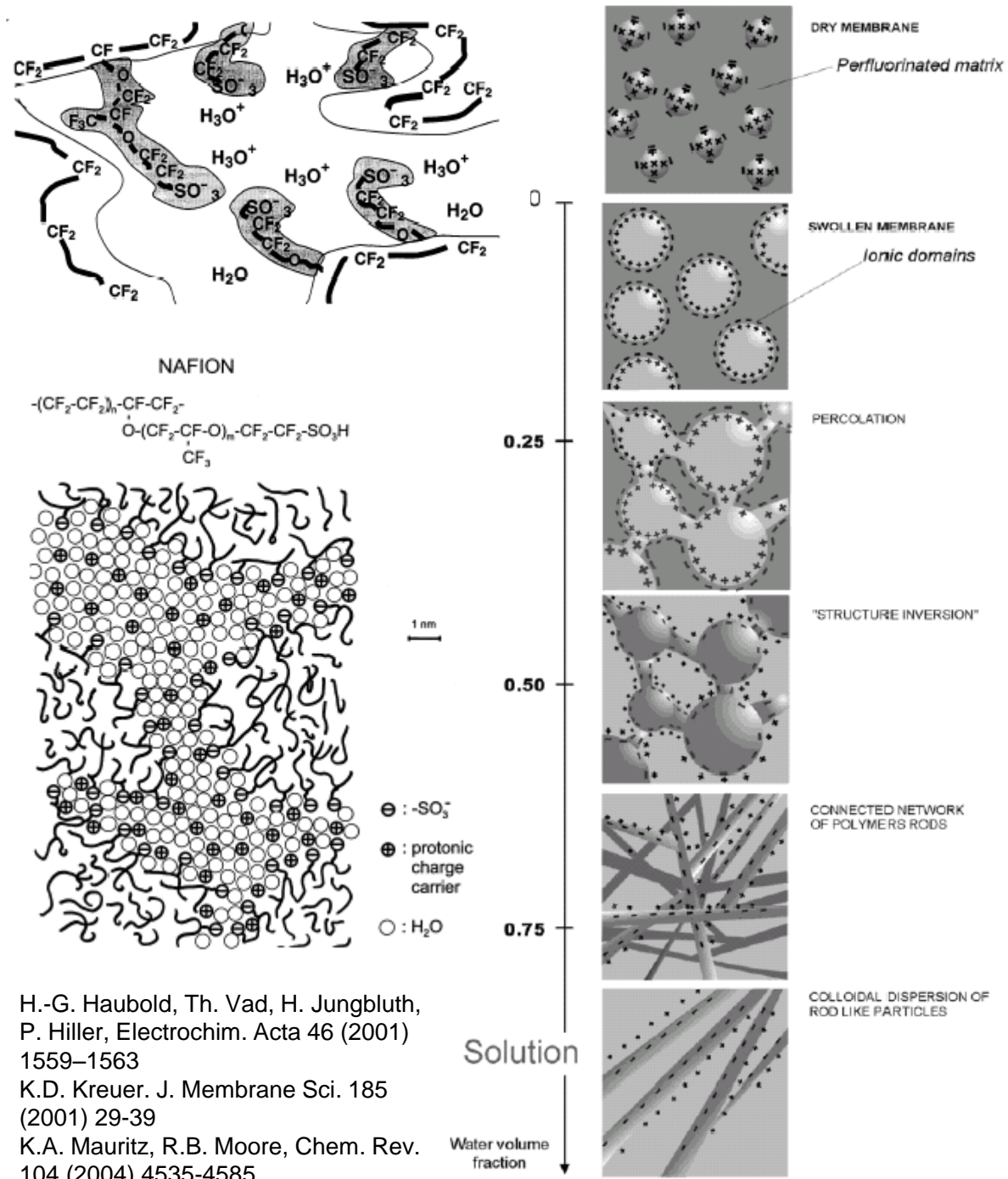
Effect of the external solution concentration on membrane water uptake

20±1°C

➤ Increasing the solution concentration the membrane water uptake decreases and the fixed charge density increases.

➤ The Fuji-CEM-2 is more sensitive to shrinking going from the 0.5 to the 4M solution than the Fuji-AEM-2 (-26% of mass swelling vs. -7%) because of its lower fixed charge density (=> higher osmotic pressure difference between the external solution and the membrane).

- ➤ Decreasing the membrane water uptake, the **hydrophilic channels of the IEMs** (pathway for ions and water transport) **become more narrow**

- ➤ Moreover, increasing the fixed charge density the **ion transport through the membrane is more difficult** because of the stronger interactions between the mobile ions and the fixed charged groups that can form **isolated ionic domains not well interconnected each other**

NAFION

$-(CF_2\text{-}CF_2)_n\text{-}CF\text{-}CF_2\text{-}$
$O\text{-}(CF_2\text{-}CF\text{-}O)_m\text{-}CF_2\text{-}CF_2\text{-}SO_3H$
CF_3

1 nm

⊖ : $-SO_3^-$
⊕ : protonic charge carrier
○ : H_2O

0
0.25
0.50
0.75

Solution

Water volume fraction

DRY MEMBRANE
— Perfluorinated matrix

SWOLLEN MEMBRANE
Ionic domains

PERCOLATION

"STRUCTURE INVERSION"

CONNECTED NETWORK OF POLYMERS RODS

COLLOIDAL DISPERSION OF ROD LIKE PARTICLES

H.-G. Haubold, Th. Vad, H. Jungbluth, P. Hiller, Electrochim. Acta 46 (2001) 1559–1563
K.D. Kreuer. J. Membrane Sci. 185 (2001) 29-39
K.A. Mauritz, R.B. Moore, Chem. Rev. 104 (2004) 4535-4585

ITM

Temperature evolution of the ¹H NMR spectra of the membranes swelled up to saturation in salt solutions

Fuji-AEM-2

Lower water content in the membranes swelled with concentrated solution
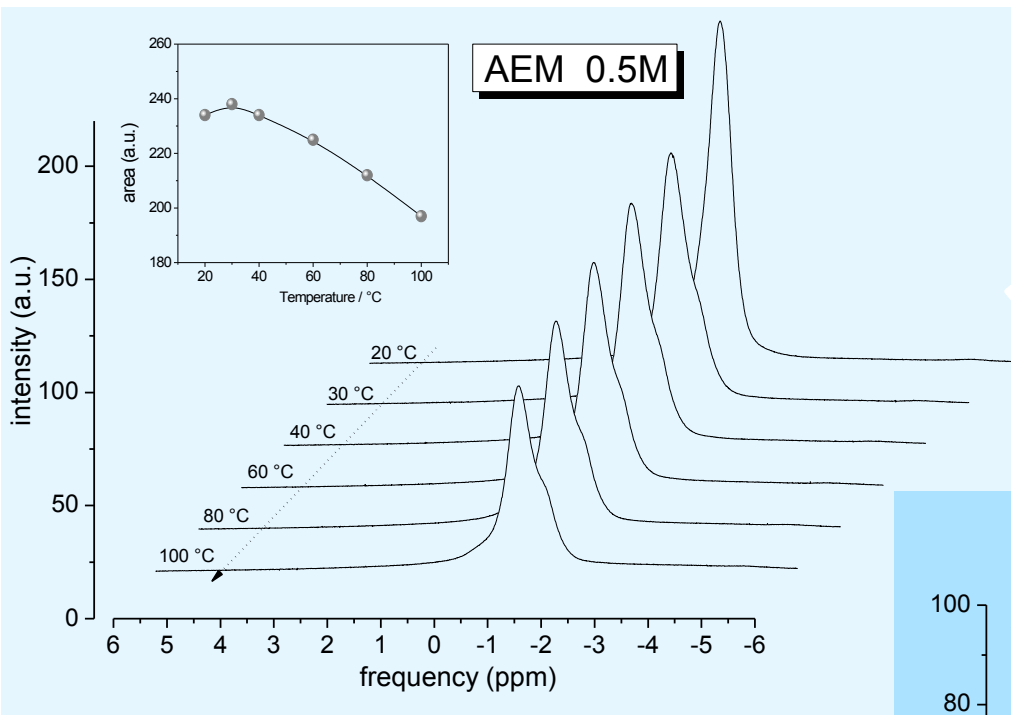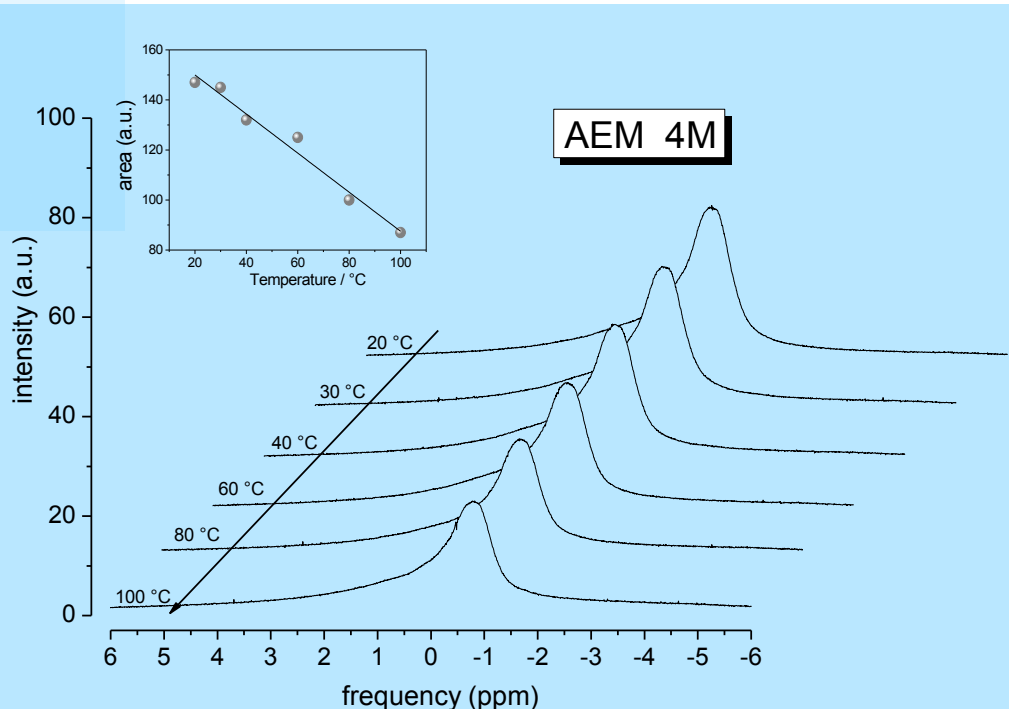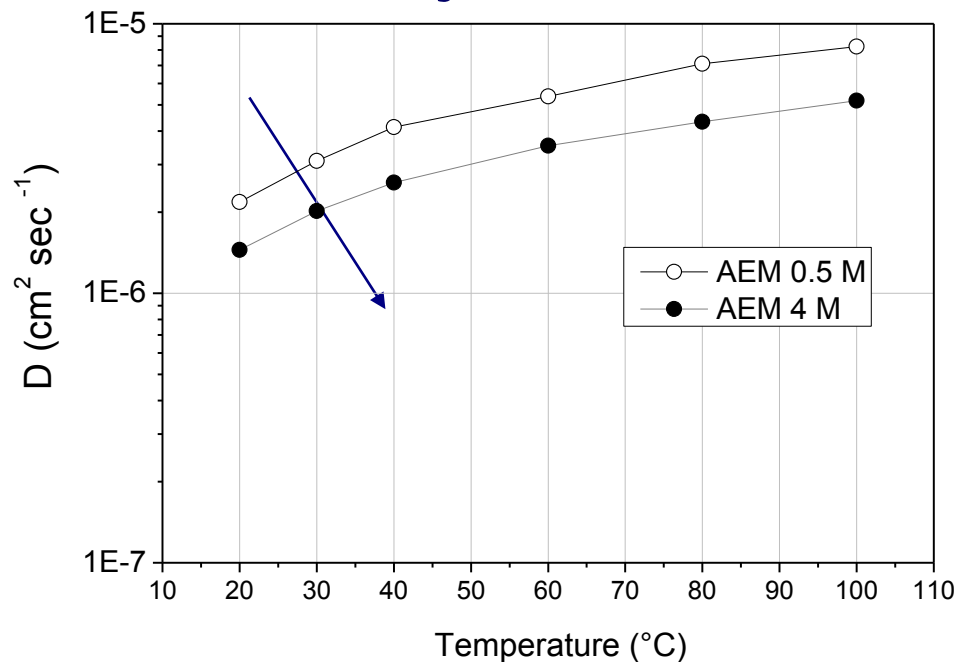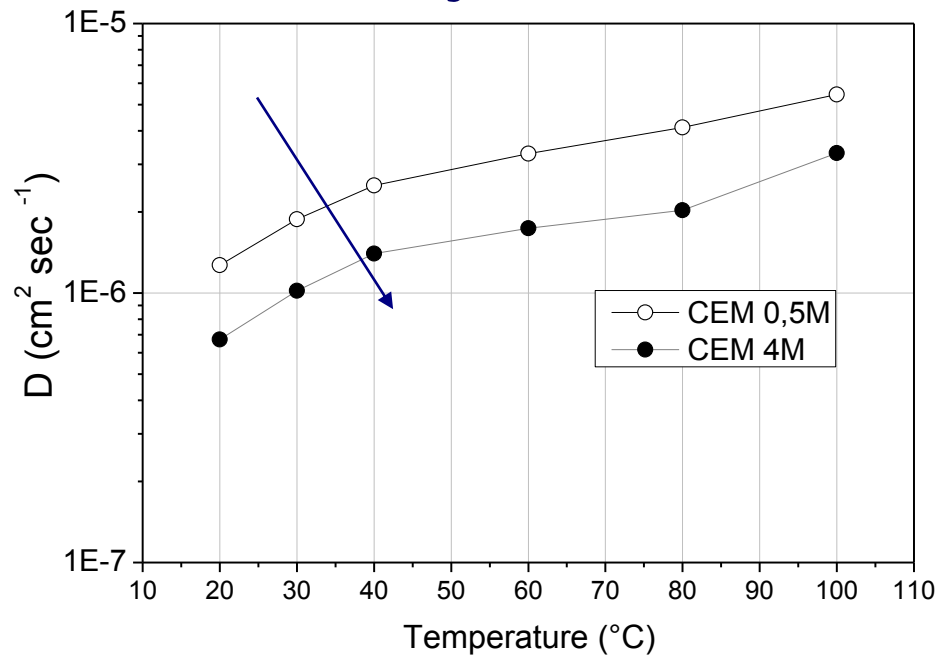
Self-diffusion coefficients (D) of water confined in the IEMs swelled up to saturation in salt solutions calculated by pulsed gradient spin echo (PGSE)-NMR technique

O. Stejskal and J. E. Tanner *The Journal of Chemical Physics* **1965**, *42*, 288

The water diffusion coefficient decreases with the electrolyte concentration => change in membrane microstructure

CONCLUSIONS

➤ The EIS is a powerful, non-invasive and non-destructive, technique to characterize the ion transport resistance through membranes and interfacial layers (electrical double layer and diffusion boundary layer).

➤ The areal membrane resistance was higher than interface resistances in the whole range of solution concentration, temperature and velocity investigated (0.5-4 M; 20-40°C; 1.5-4.0 cm s^{-1}) and it did not depend significantly from the solution velocity.

➤ On the contrary, the interface resistances can be reduced increasing the solution velocity.

➤ The CEMs were characterized by an higher electrical resistance in comparison with the AEMs.

➤ Membrane and interface resistances decreased with the temperature

➤ Increasing the solution concentration from 0.5 to 4 M the membrane resistance decreased for the Fuji-AEM-2 (charge density 4.1±0.4 mol/L in 4M) but increased for the Fuji-CEM-2 (charge density 3.0±0.2 mol/L in 4 M).

➤ The increased electrical resistance was due to changes of the membrane microstructure in concentered electrolyte solution, as confirmed by NMR analyses.

➤ *As a consequence, it was evident the necessity to use membranes with a fixed charge density higher, or at least similar, to the external solution in the case of electromembrane processes operating with concentrated solutions*

Acknowledgments

Thank You!