

# Advances in Science and Engineering for Brackish Water and Seawater Desalination II

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## Probing membranes and interfaces properties by impedance spectroscopy

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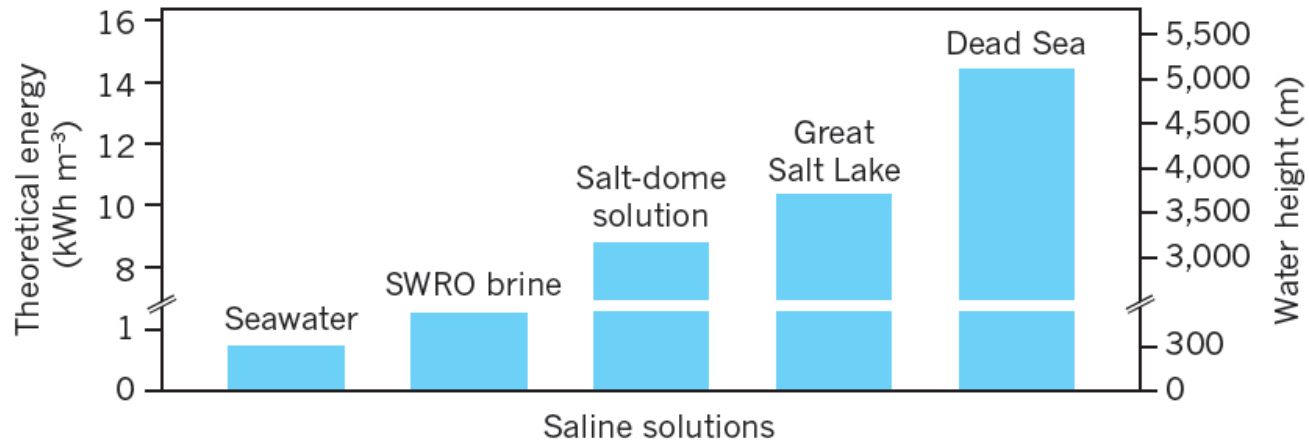
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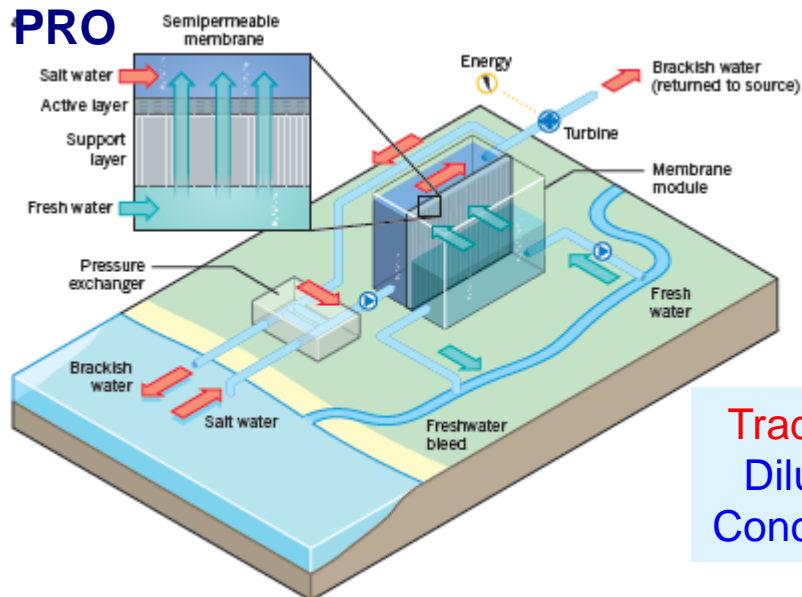
<sup>3</sup>University of Calabria, Rende (CS), Italy



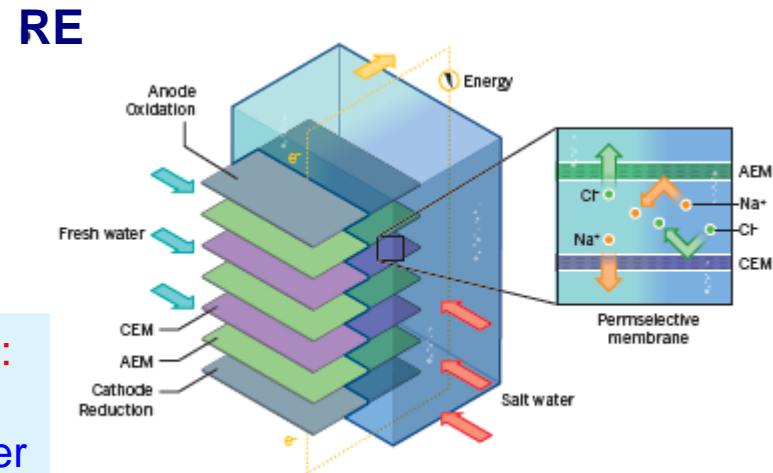
**Salinity Gradient Power (SGP)** is the energy available from the controlled mixing of two solutions with different salt concentrations.



**Pressure-retarded osmosis (PRO) and reverse electrodialysis (RE) are emerging as sustainable processes for capturing energy from saline solutions**



**Traditional approach:**  
 Diluate: fresh water  
 Concentrate: seawater



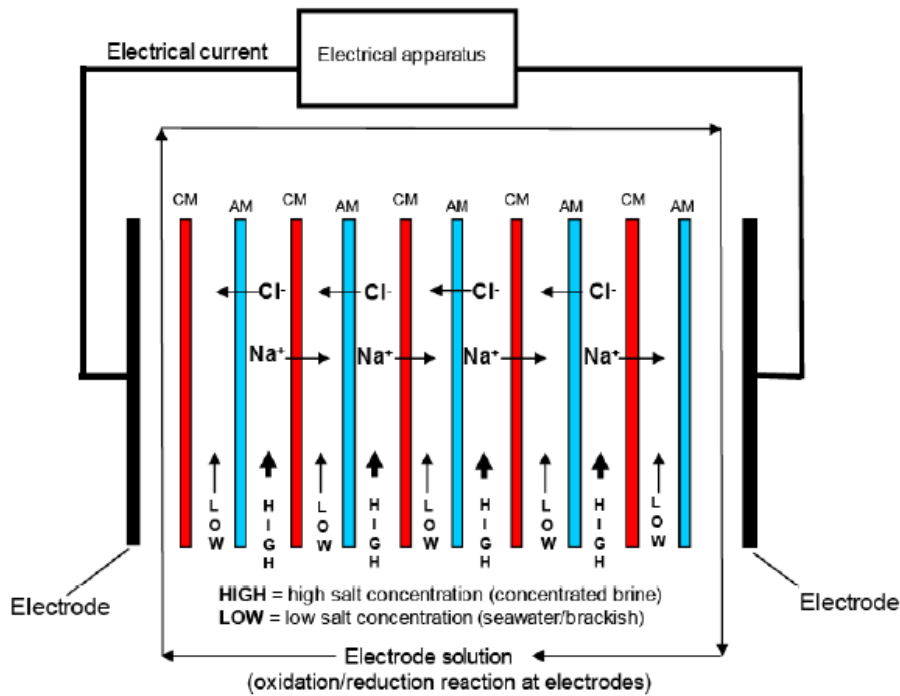
# Reverse Electrodialysis Alternative Power production



www.reapower.eu

## REAPOWER

Project (n. 256736)



**Nernst potential:**

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



## The idea:

- Power production through **Salinity Gradient Power-Reverse Electrodialysis (SGP-RE)** using **brine** as concentrated solution, and **seawater** as diluted solution.



- To avoid the use of freshwater
- Higher theoretical energy extractable
- Reduction of the internal electrical resistance of the stack

# Reapower objectives:

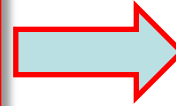
Create/select and optimise **materials and components tailored to the requirements of the SGP-RE technology** operating with high salinity brine and seawater. These include the **membranes**, spacers, electrodes and electrolytes

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

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

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

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



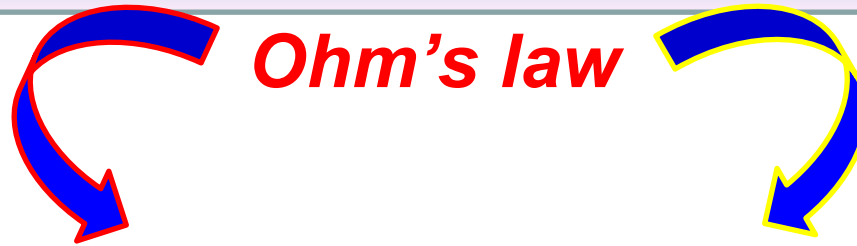
**New Ion Exchange Membranes** for highly concentrated solutions

High **permselectivity**

Chemical and mechanical **Stability**

Low **electrical resistance**

# Membrane electrical resistance



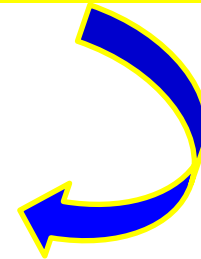
*Ohm's law*

**With DC: resistance (R)**

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

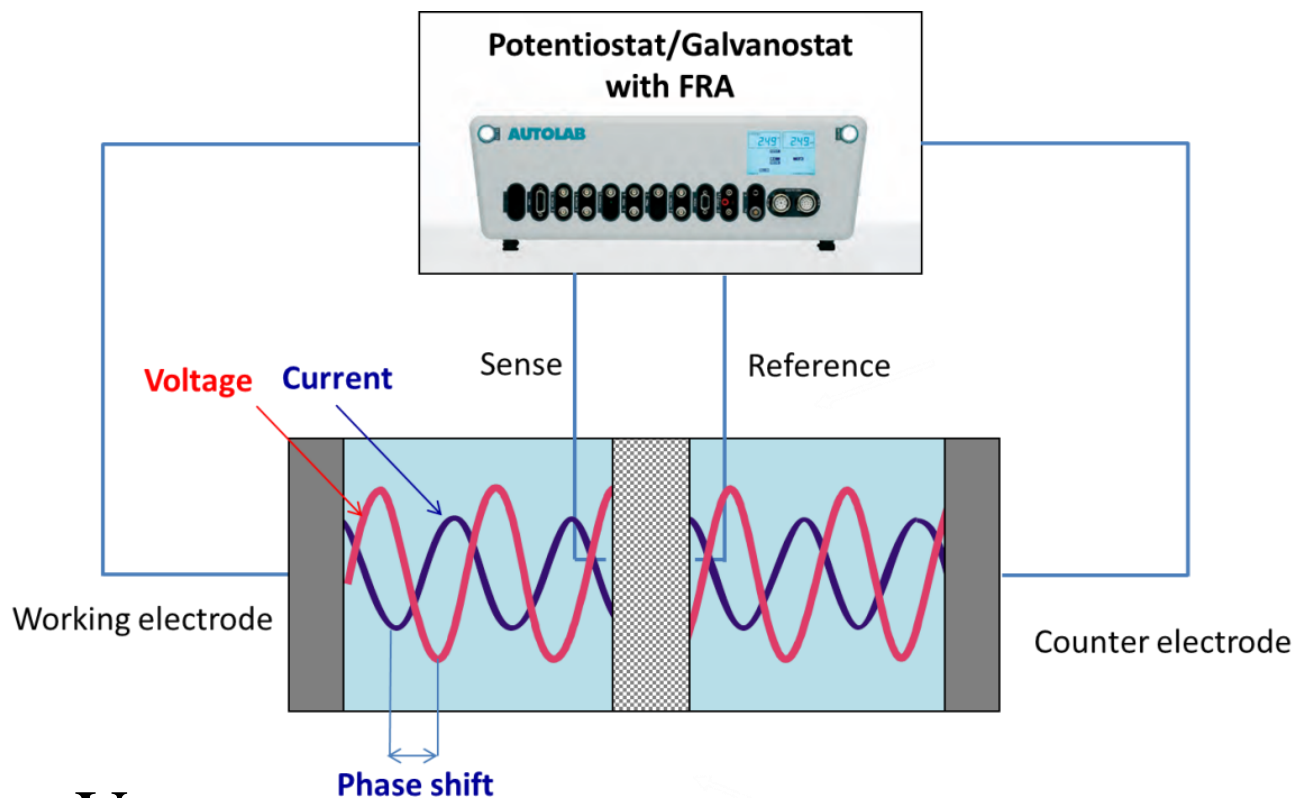
**With AC: impedance (Z)**

$$Z_{(\omega)} = \frac{V_{(\omega)}}{I_{(\omega)}} \quad \omega = 2\pi\nu$$



***Using an AC over a frequency range, it is possible to distinguish phenomena proceeding at different rates like bipolar concentration polarization***

# Electrochemical Impedance Spectroscopy (EIS)



$$Z_{(\omega)} = \frac{V_{(\omega)}}{I_{(\omega)}}$$

$$V_{(\omega)} = V_o \sin \omega t$$

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

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

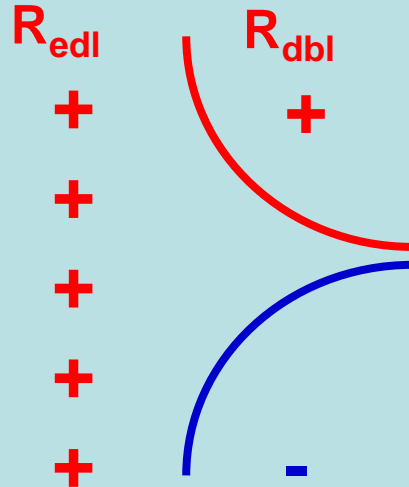
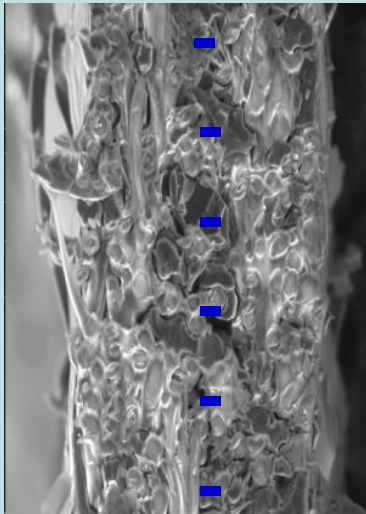
$$Z_{(\omega)} = |Z| \cos \varphi + j |Z| \sin \varphi$$

Real part:  
resistance

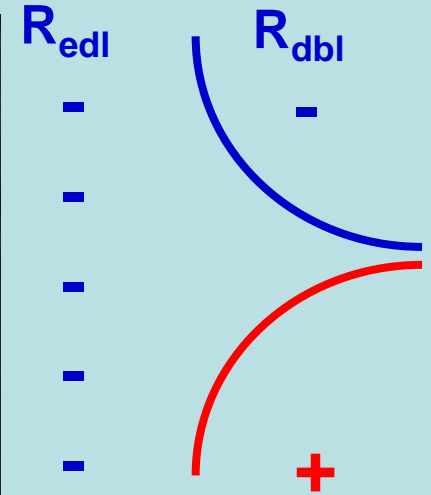
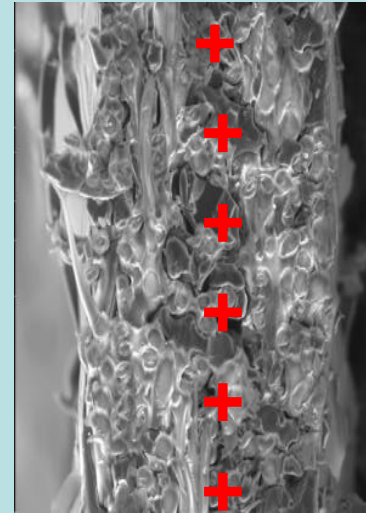
Imaginary part:  
reactance

# Concentration polarization: electrical double layer (EDL) and diffusion boundary layer (DBL)

CEM



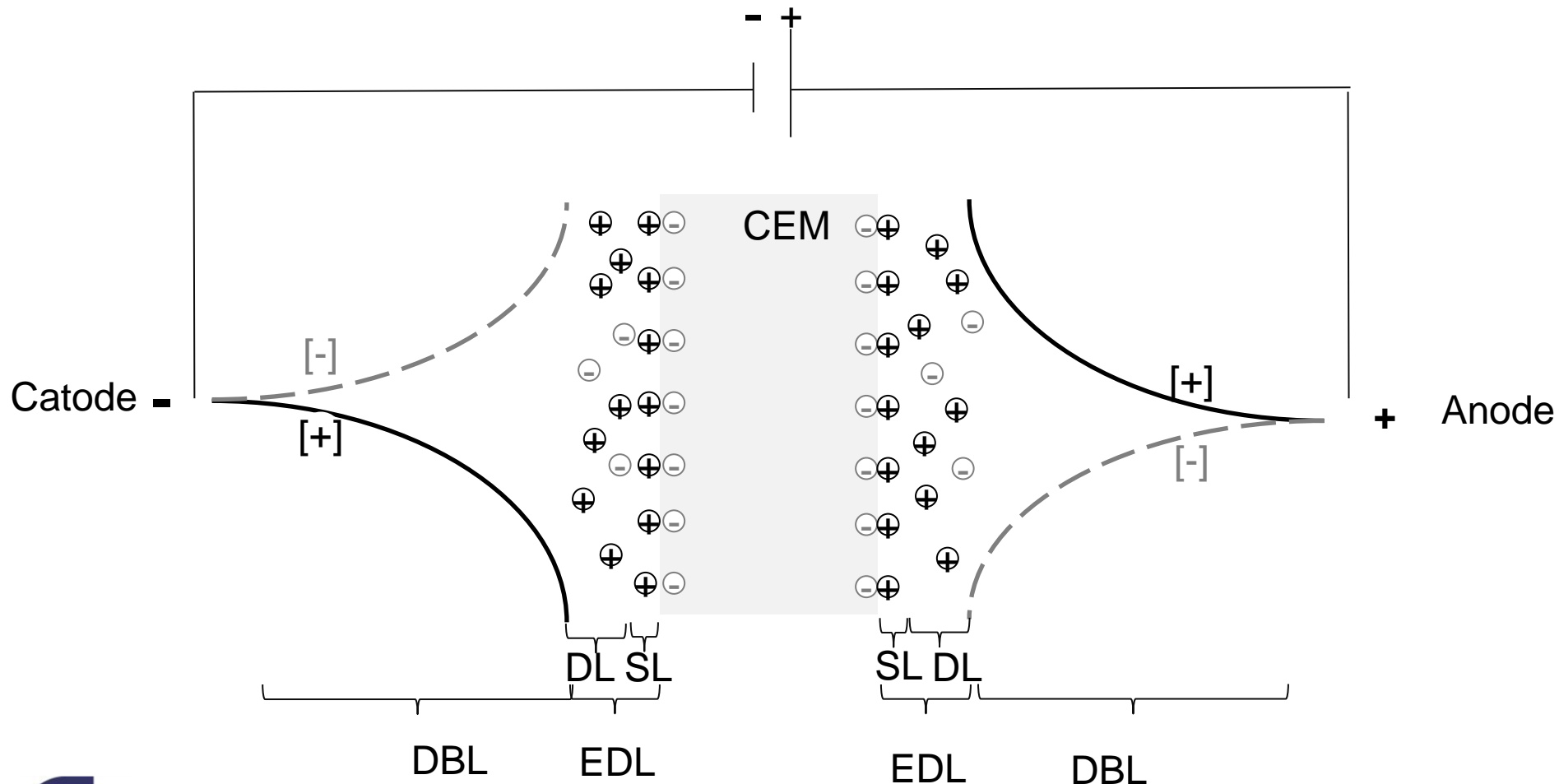
AEM



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

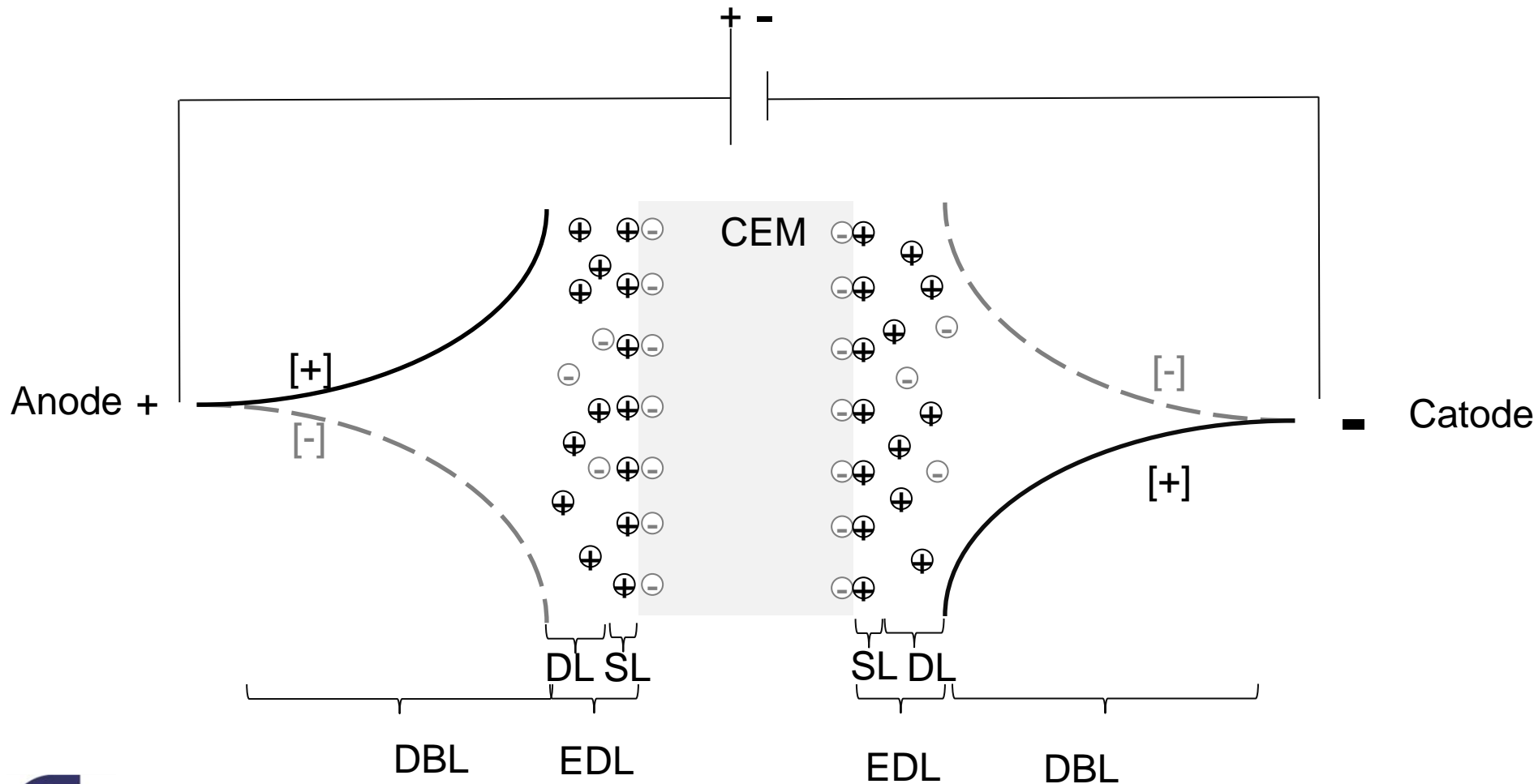
*At the interfaces between a solid ionic conductor and a liquid electrolyte, physical and electrical properties change suddenly because of an heterogeneous charges distribution (polarization) which reduce the overall electrical conductivity of the system.*

# The bipolar concentration polarization is time dependent and it undergoes an inversion during each AC cycle

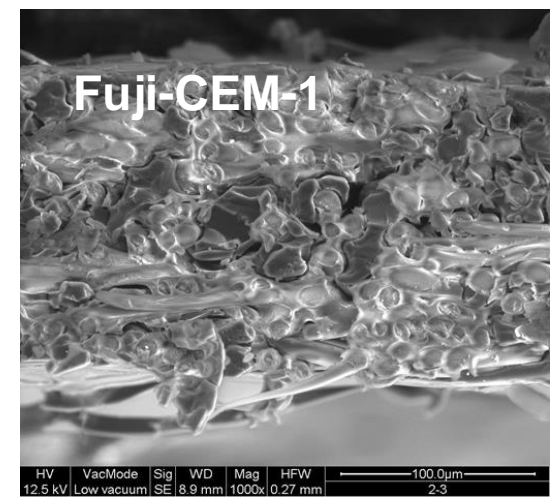




# The bipolar concentration polarization is time dependent and it undergoes an inversion during each AC cycle

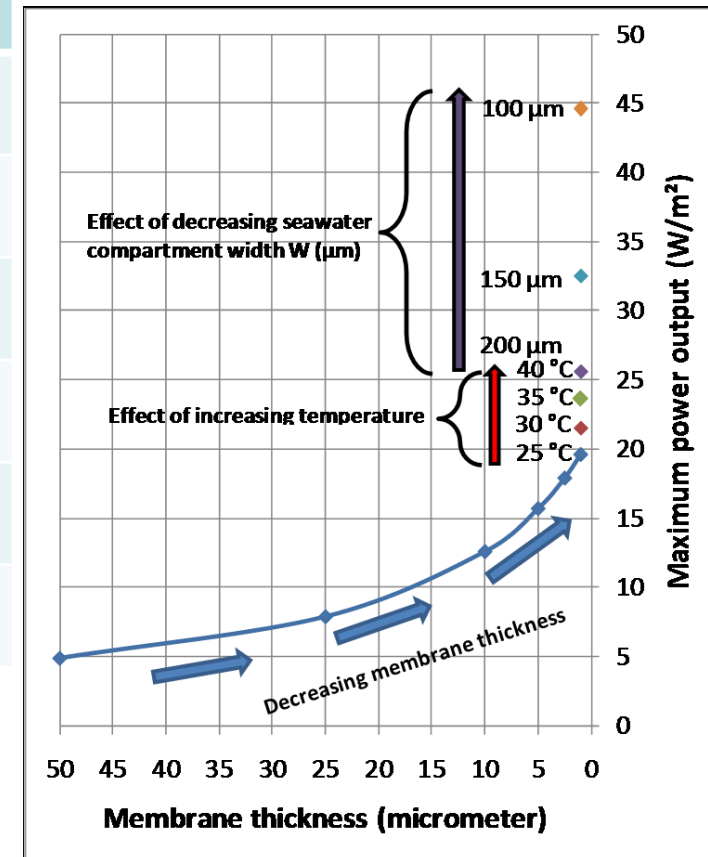


# Homogeneous reinforced IEM membrane developed by Fujifilm Manufacturing Europe BV for SGP-RE

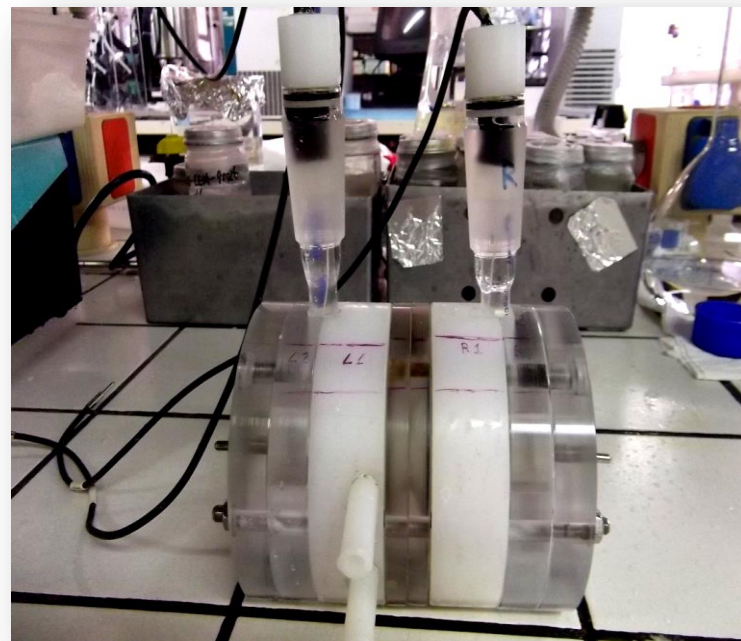
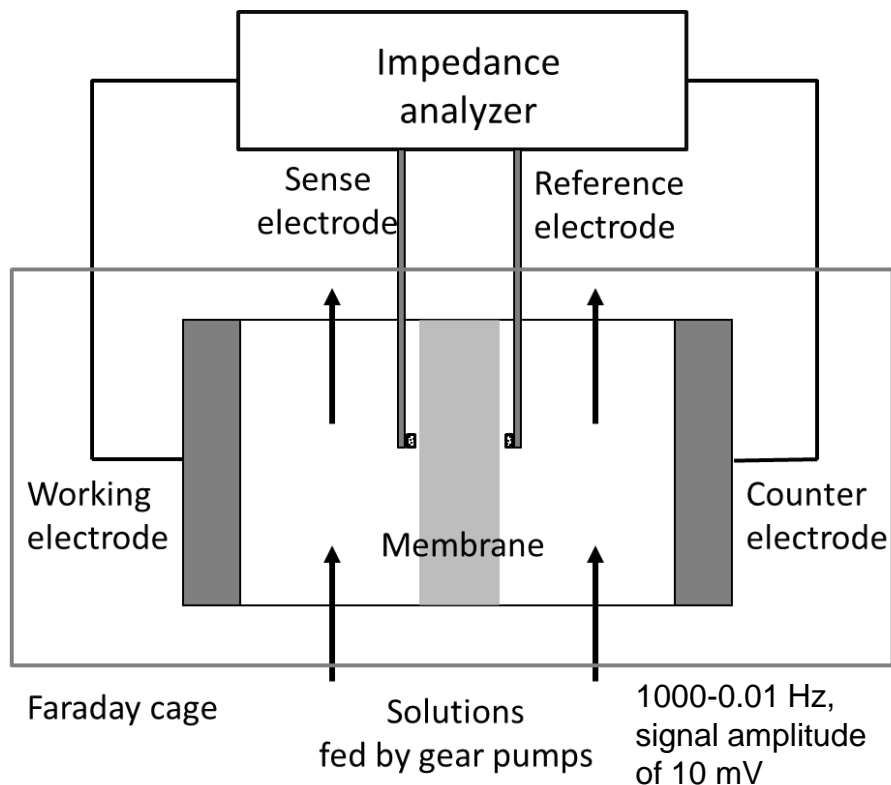


Membrane	Thickness (µm)*	Ion exchange capacity (mmol/g membrane)	Swelling (%)*	Density of fixed charges (mol/L)*
Fuji-AEM-1	166±1	1.1±0.1	50.1±2	2.2±0.3
Fuji-AEM-2	129±2	1.4±0.1	36.7±0.04	3.8±0.2
Fuji-AEM-3	109±2	1.6±0.3	53.1±1.2	2.9±0.6
Fuji-CEM-1	170±1	1.6±0.1	47.3±0.8	3.4±0.2
Fuji-CEM-2	114±2	1.1±0.1	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

\* NaCl 0.5M at 20°C



# Electrochemical Impedance Spectroscopy (EIS)

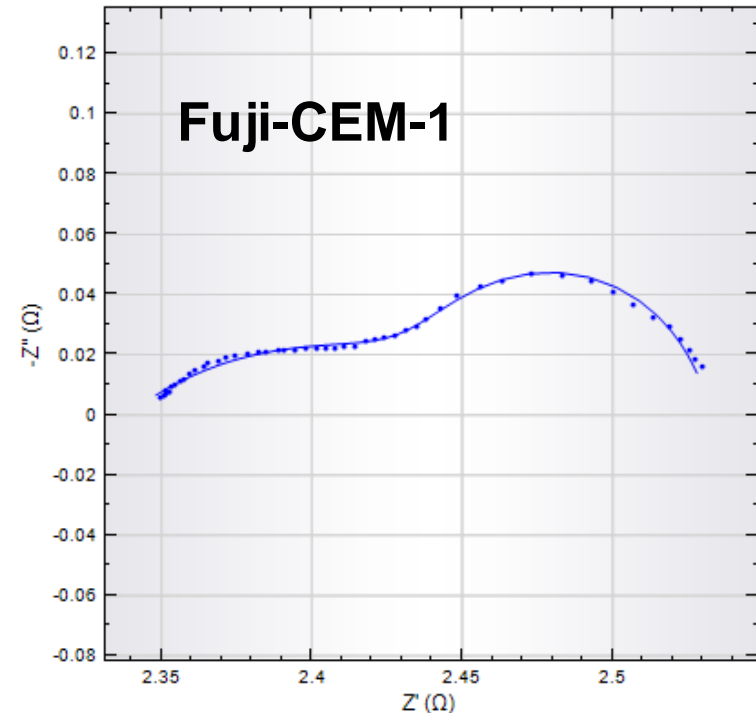
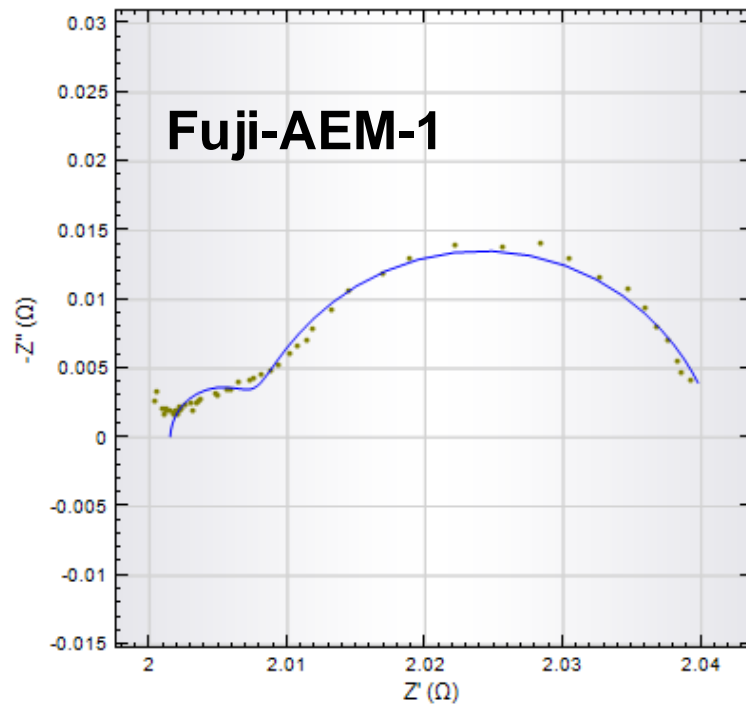
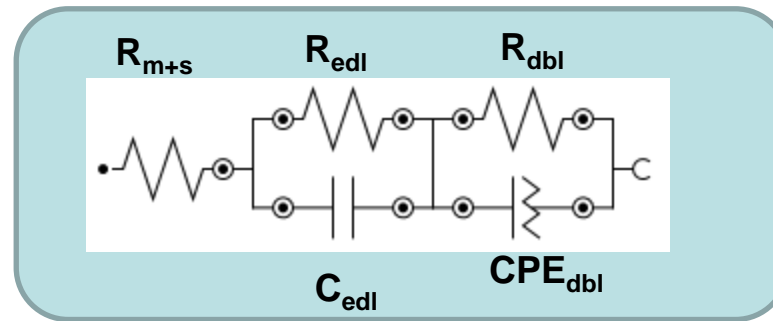


- Solution velocity ( $1.5-4 \text{ cm s}^{-1}$ )
- Solution concentration ( $0.5-4 \text{ M}$ )
- Temperature ( $20-40^\circ\text{C}$ )

*E. Fontananova et al. submitted*



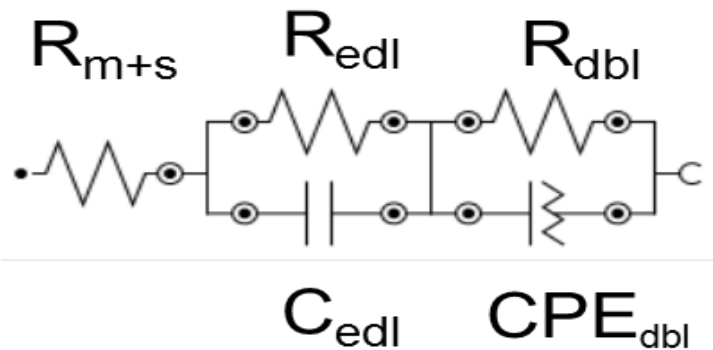
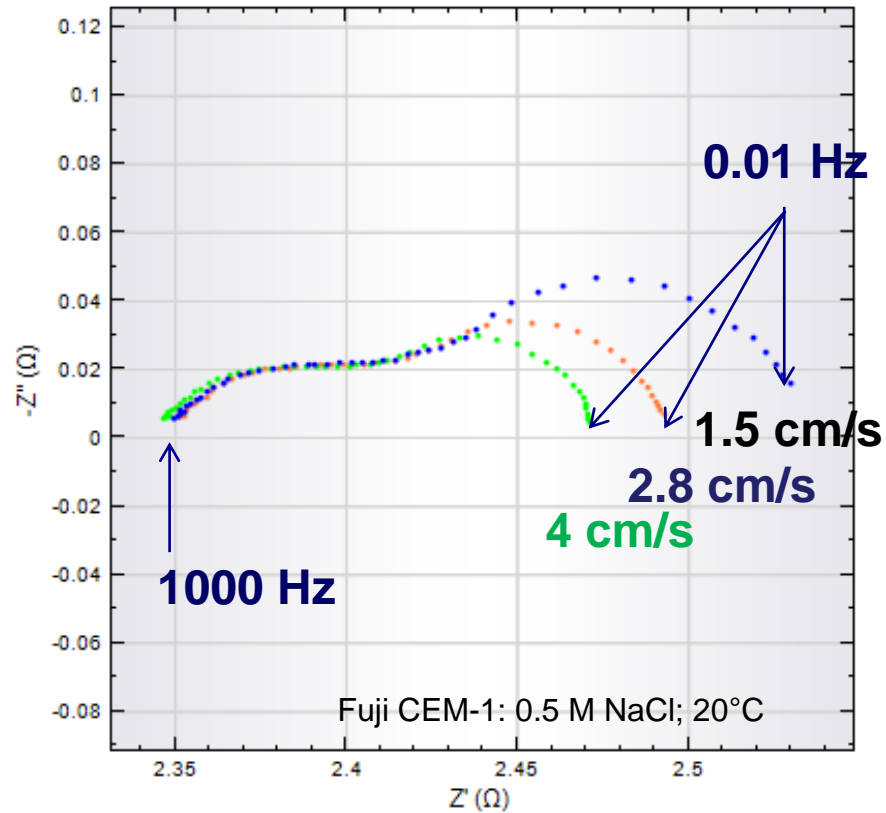
# Equivalent circuit model used to fit EIS spectra:



Conditions: 1000-0.01 Hz; 0.5 M NaCl; 20°C; velocity 1,5 cm s<sup>-1</sup>

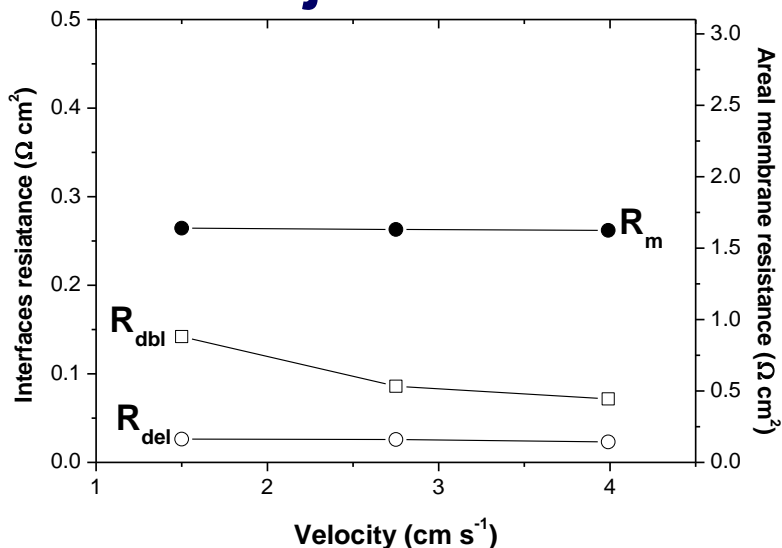
**Good convergence of the fitting model with the experimental data**

# Effect of the velocity on the resistances



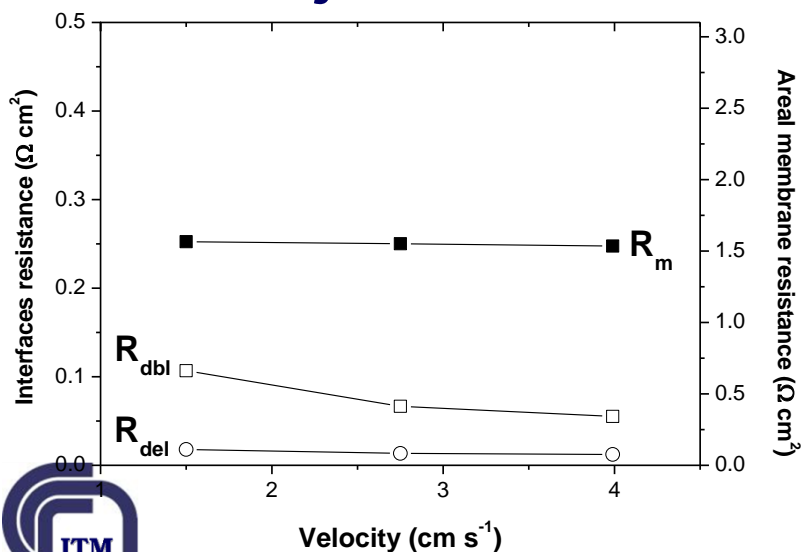
# Effect of the velocity on the resistances

## Fuji-AEM-1

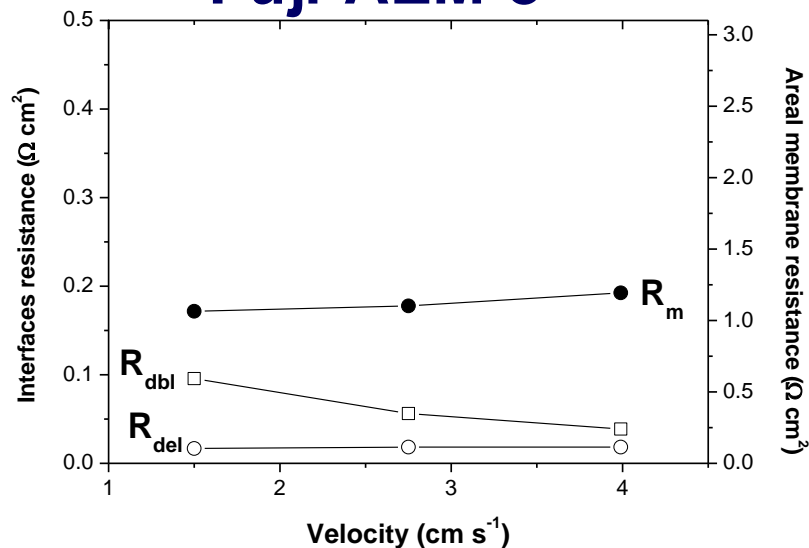


- $R_m > R_{dbl} > R_{edl}$
- $R_{dbl}$  decreases with the increasing of flow rate
- $R_m$  and  $R_{edl}$  are not significantly influenced from the flow rate

## Fuji-AEM-2



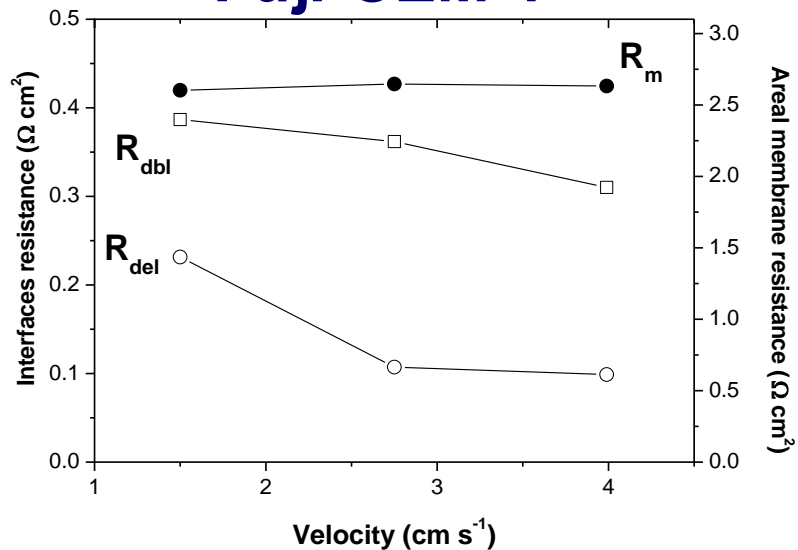
## Fuji-AEM-3



Conditions 0.5 M NaCl; 20°C

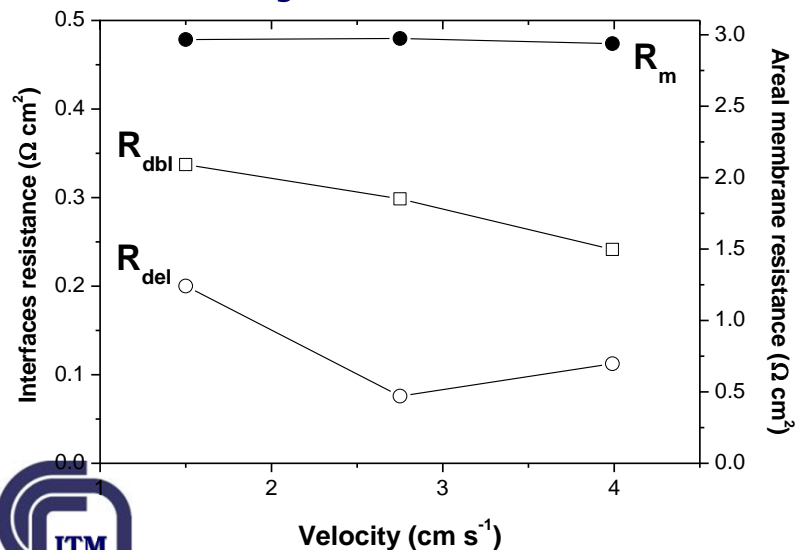
# Effect of the velocity on the resistances

## Fuji-CEM-1

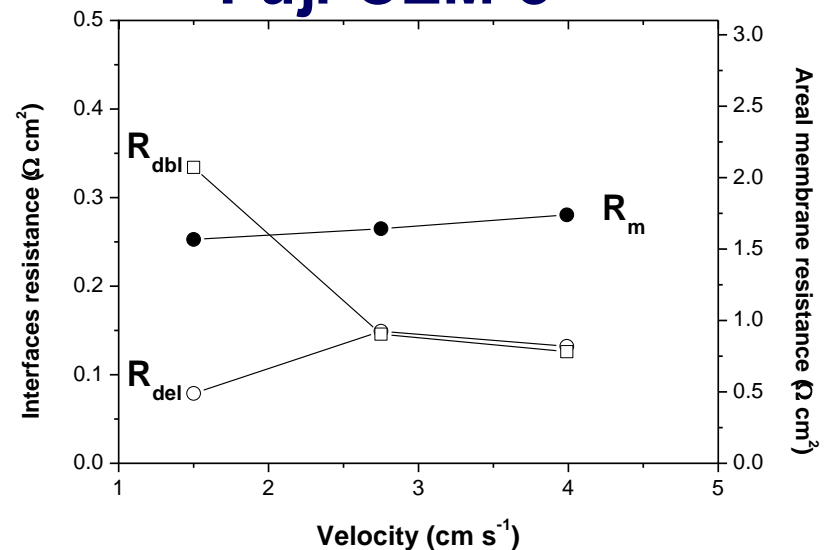


- $R_m > R_{dbl} > R_{edl}$
- $R_{dbl}$  decreases with the increasing of flow rate, but also the  $R_{edl}$  is influenced
- $R_m$  is not significantly influenced from the flow rate

## Fuji-CEM-2



## Fuji-CEM-3



Membrane	AMR ( $\Omega\text{cm}^2$ )	$R_{\text{edl}}$ ( $\Omega\text{cm}^2$ )	$R_{\text{dbl}}$ ( $\Omega\text{cm}^2$ )
Fuji-AEM-1	1.63	0.0259	0.0860
Fuji-AEM-2	1.55	0.0135	0.0667
Fuji-AEM-3	1.12	0.0184	0.0562
Fuji-CEM-1	2.63	0.107	0.362
Fuji-CEM-2	2.96	0.0759	0.299
Fuji-CEM-3	1.65	0.149	0.146

NaCl 0.5M; 20°C; 2.75 cm s<sup>-1</sup>

**AEMs have lower resistances than CEMs**

Ion	Mobility $u$ ( $10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ )
Na <sup>+</sup>	4.98 ± 0.19
Cl <sup>-</sup>	6.88 ± 0.31

Data from S. Koneshan et al. *J. Phys. Chem. B* 1998, 102, 4193-4204

**Apparent Permselectivity (PS)  
between 0.05M/0.5 M NaCl\*:  
> 90% for all samples**

**PS between concentrated solution  
(0.5M/4M NaCl) is above the  
threshold of 60% for\*:**

**Fuji-AEM-2: 65%**

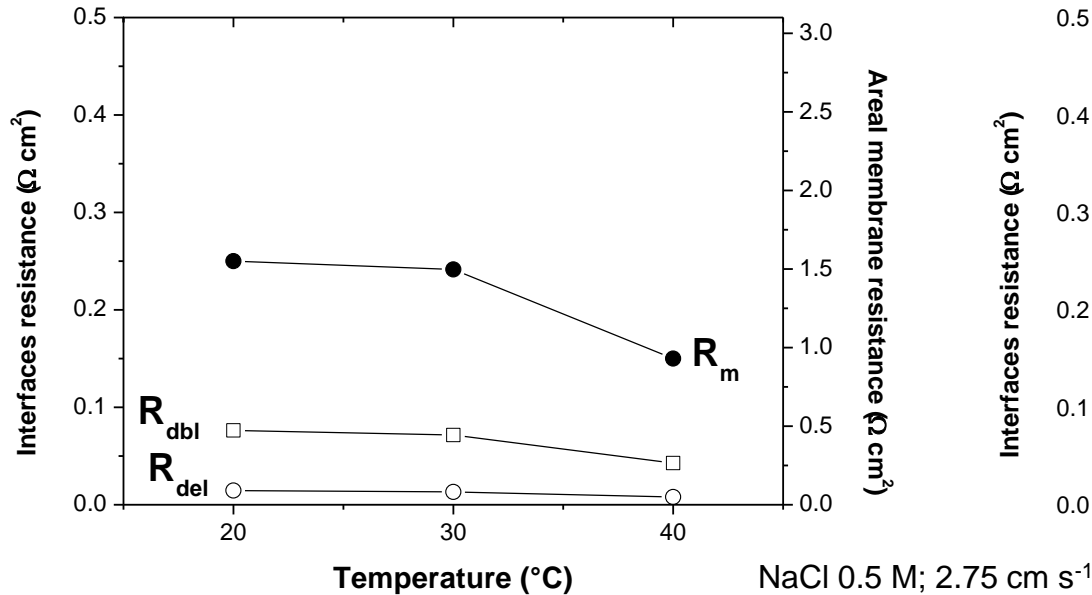
**Fuji-CEM-2: 84%**



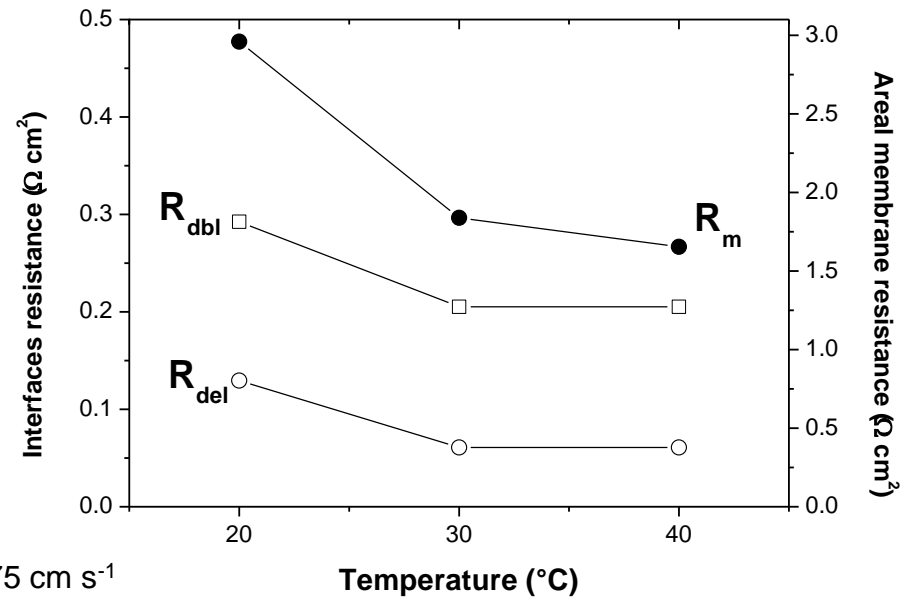


# Effect of the temperature on the resistances

## Fuji-AEM-2

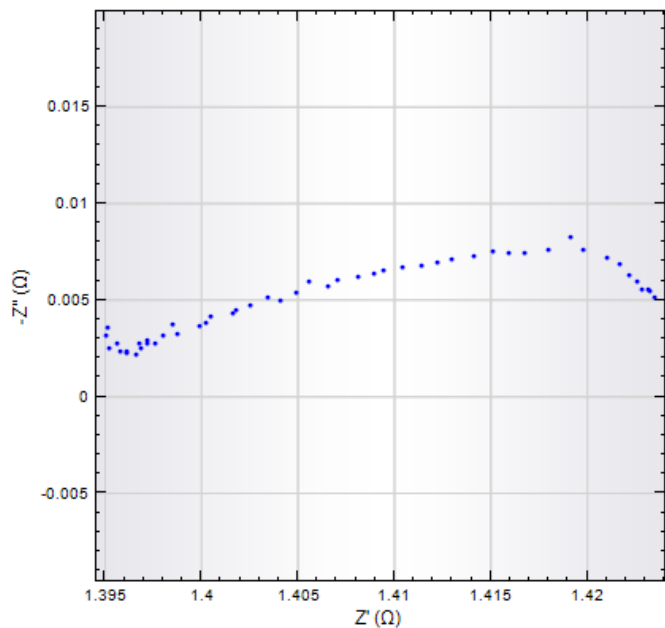


## Fuji-CEM-2

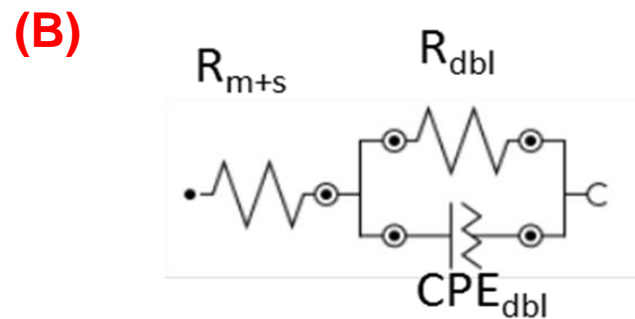
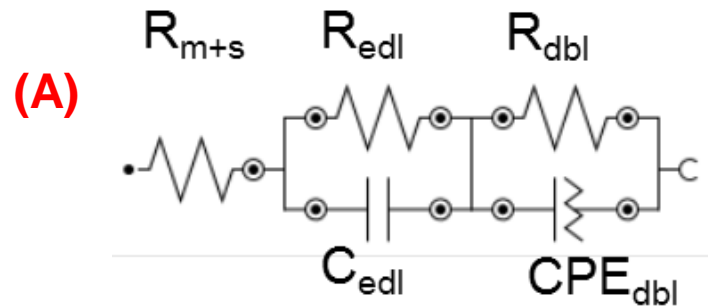


- The resistance of the ion transport through the membrane, as well as through the interfaces, decreases with the temperature, because of the increasing ion mobility

# Effect of the increasing solution concentration: test with 4 M NaCl



Fuji-CEM-2; NaCl 4 M; 20°C; 1.5 cm s<sup>-1</sup>



In the case of the EIS experiments with **4 M NaCl** solution, **the fitting with the equivalent circuit (A) does not converge** for most of the experiments.

Only in few cases, the model converges but it gives a  $R_{edl}$  values very low ( $\mu\Omega$ ) or negative, and the estimated error for  $R_{edl}$  is high ( $> 100\%$ ).

The data are successfully fitted with the **equivalent circuit (B)** reaching the convergence and a low estimated error ( $< 10\%$ )

**Increasing the solution ionic strength, the thickness of the electrical double layer decreases (the Debye radius decreases).**

**Increasing screening of the attractive electrical interactions between the counter-ions and fixed charged groups of the membrane, increasing the number of ions in solution.**

K. Bohinc et al, *Electrochimica acta* 46 (2001) 3033-3040; S. Sang et al *Colloids and Surfaces A: Physiochem. Eng Aspects* 315 (2008) 98-102; S. Sang et al *Colloids and Surfaces A: Physiochem. Eng Aspects* 320 (2008) 43-48

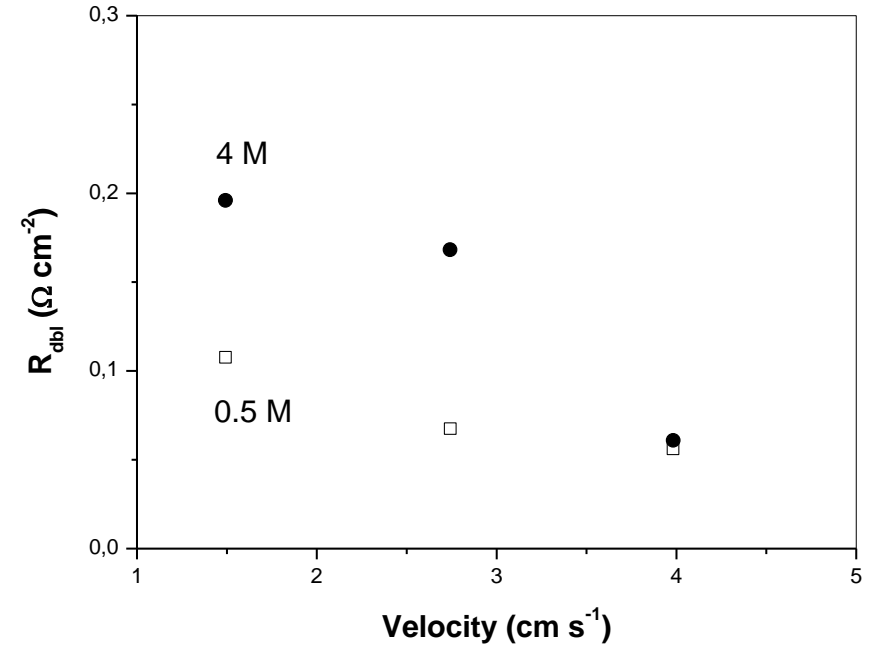
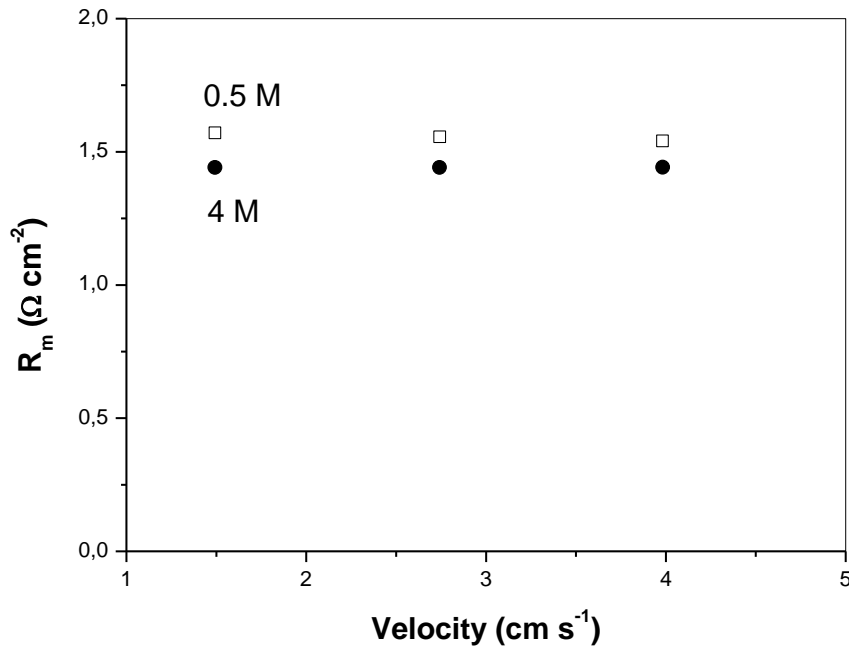


**The  $R_{edl}$  contribution to the total resistance becomes negligible at 4M NaCl.**

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

# Effect of the concentration on the resistances

## Fuji-AEM-2

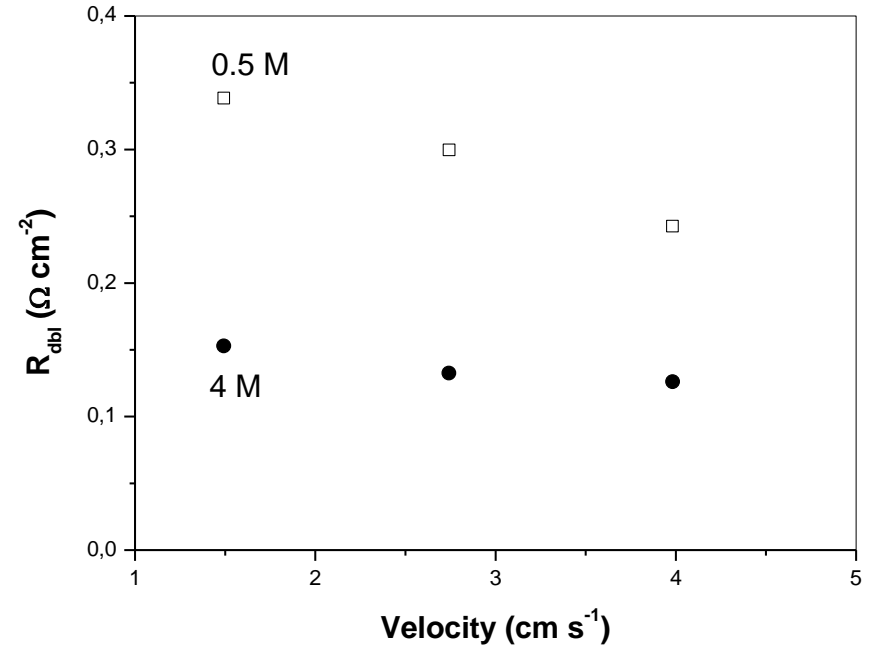
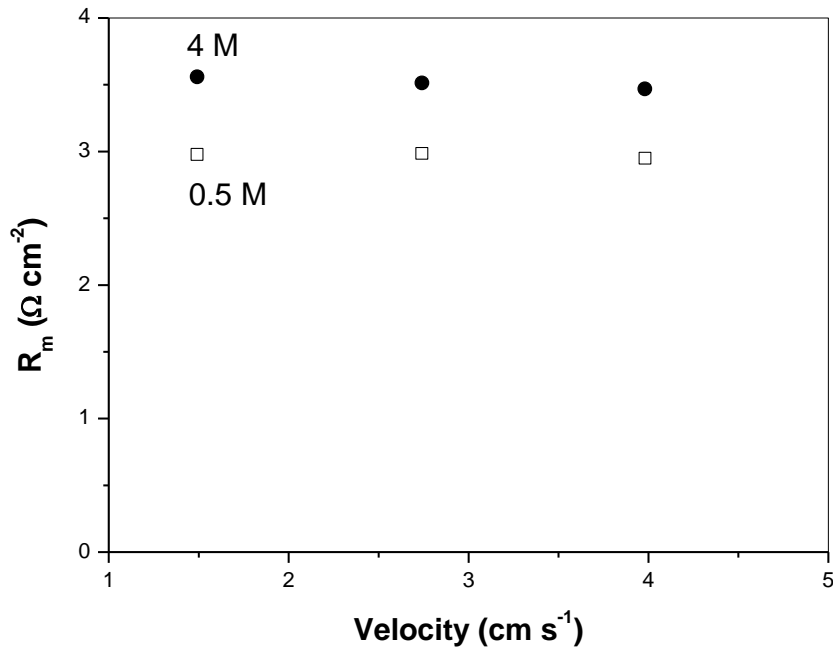


20°C; 2.75 cm s<sup>-1</sup>

- A small decrease of the  $R_m$  is observed from the 0.5 to 4M solution
- The increase of the concentration tends to increase the  $R_{dbl}$
- The contribution of  $R_{edl}$  is negligible

# Effect of the concentration on the resistances

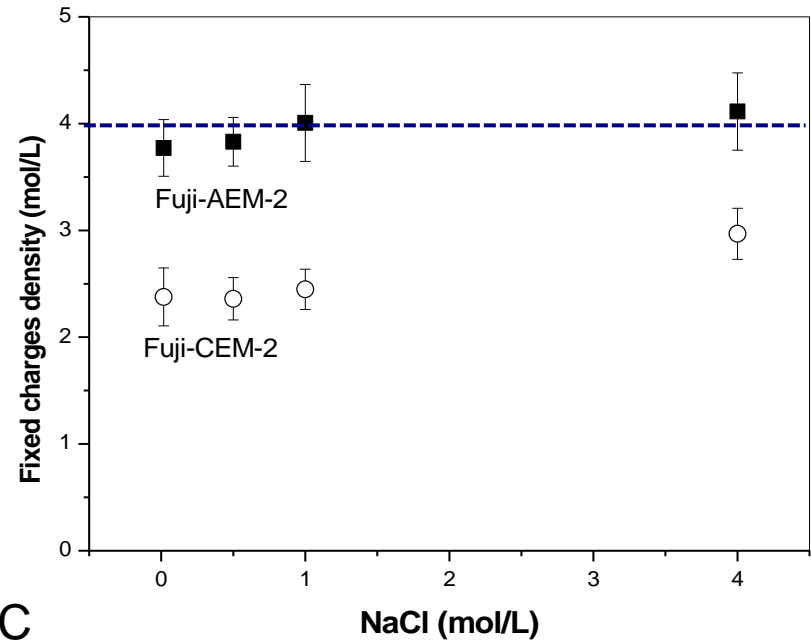
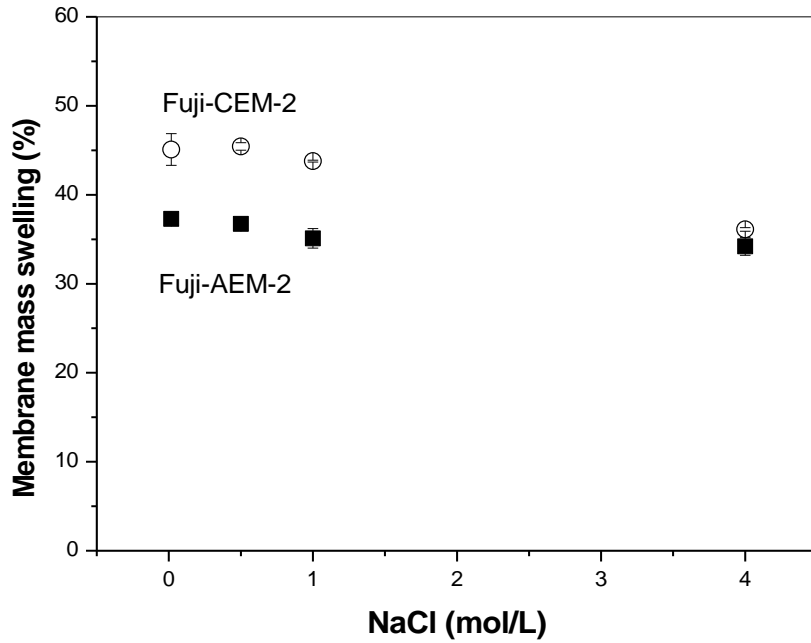
## Fuji-CEM-2



20°C; 2.75  $\text{cm s}^{-1}$

- An increase of the  $R_m$  is observed from the 0.5 to the 4M solution
- The increase of the concentration tends to decrease the  $R_{dbl}$

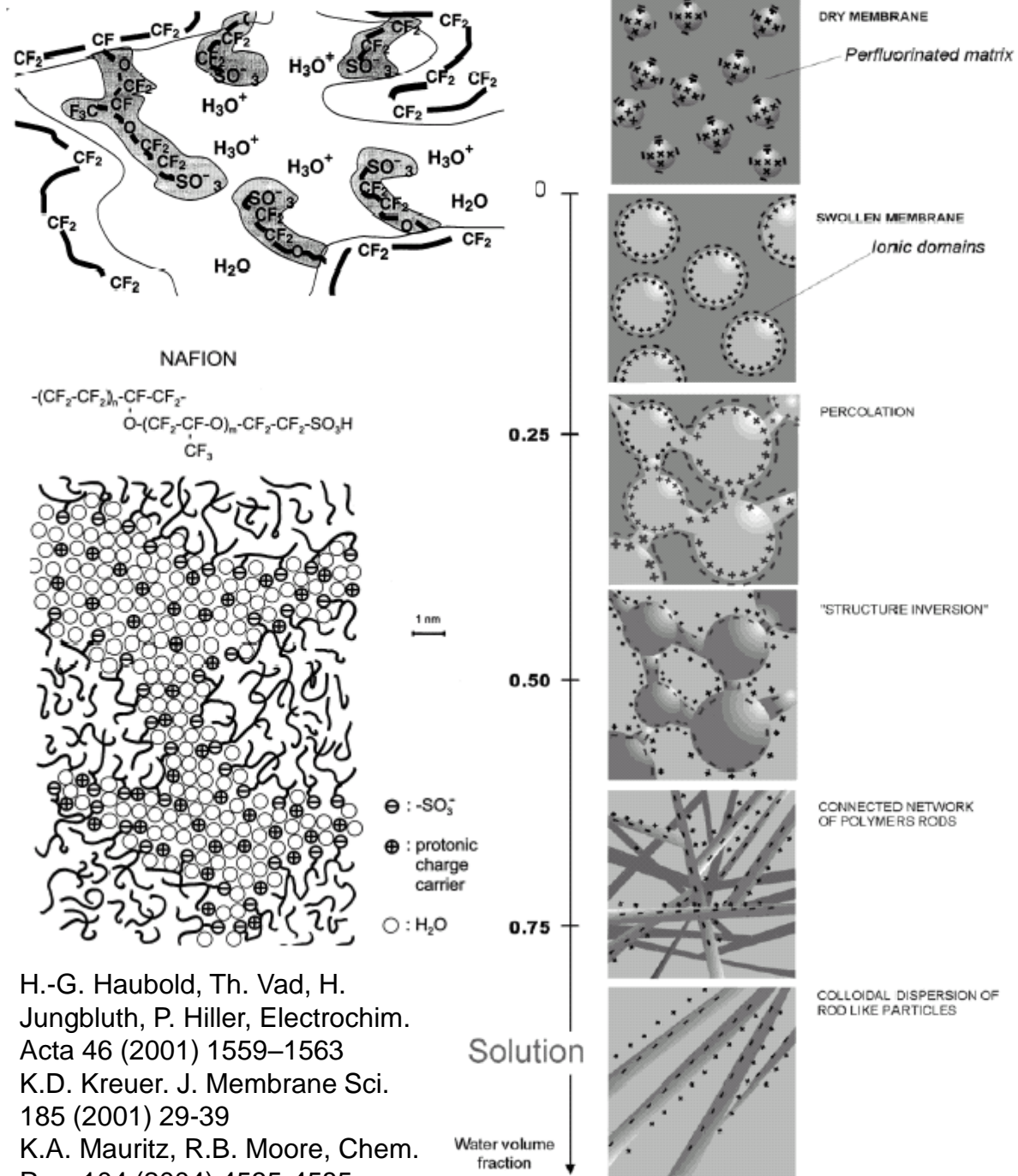
# Effect of the external solution concentration on swelling



- 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 (-21% of mass swelling vs. -7%) because of its lower fixed charge density (=> higher osmotic pressure difference between the solution and the membrane).

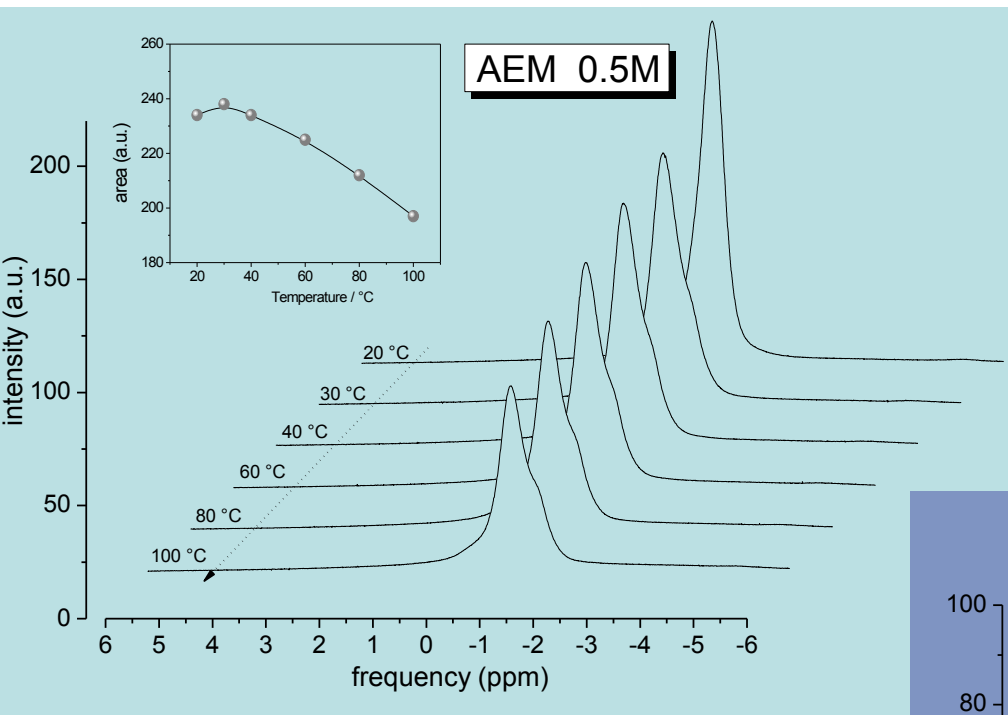
➤ Decreasing the membrane water uptake, the **hydrophilic channels of the IEMs** (pathway for the ions and water transport) **become more narrow**

➤ Moreover, increasing the fixed charges density the **ion migration through the membrane is more difficult** because of the stronger interactions with the fixed charged groups that can form **isolated ionic domains not well interconnected each other**

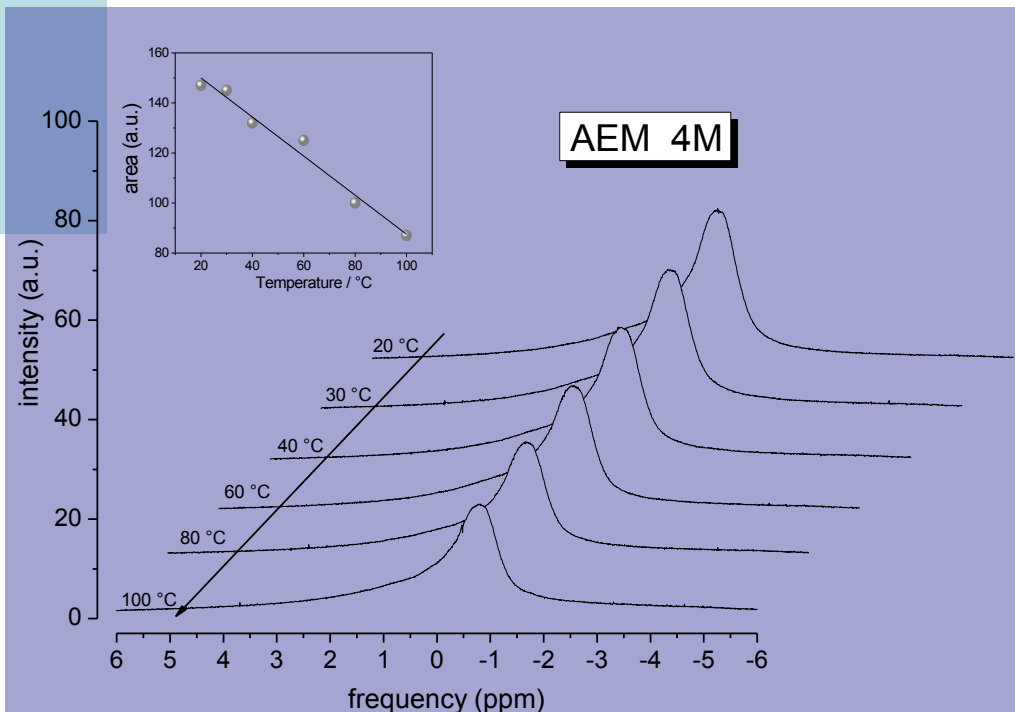


H.-G. Haubold, Th. Vad, H. Jungbluth, P. Hiller, *Electrochim. Acta* 46 (2001) 1559–1563  
 K.D. Kreuer, *J. Membrane Sci.* 185 (2001) 29-39  
 K.A. Mauritz, R.B. Moore, *Chem. Rev.* 104 (2004) 4535-4585

# Temperature evolution of the $^1\text{H}$ NMR spectra of Fuji-AEM-2 swelled in 0.5 and 4 M solution



*Lower water content in the membrane swelled with concentrated solutions*





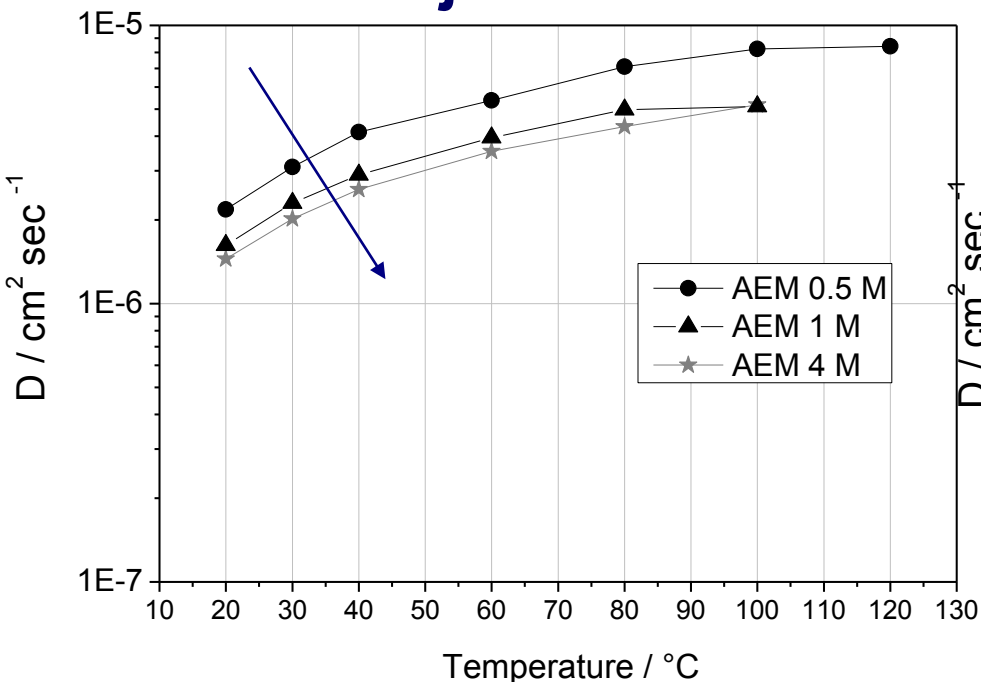
# Self-diffusion coefficients (D) of water confined in the IEMs swelled up to saturation in salt solutions calculated by pulsed gradient spin echo (PGSE)-NMR technique

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

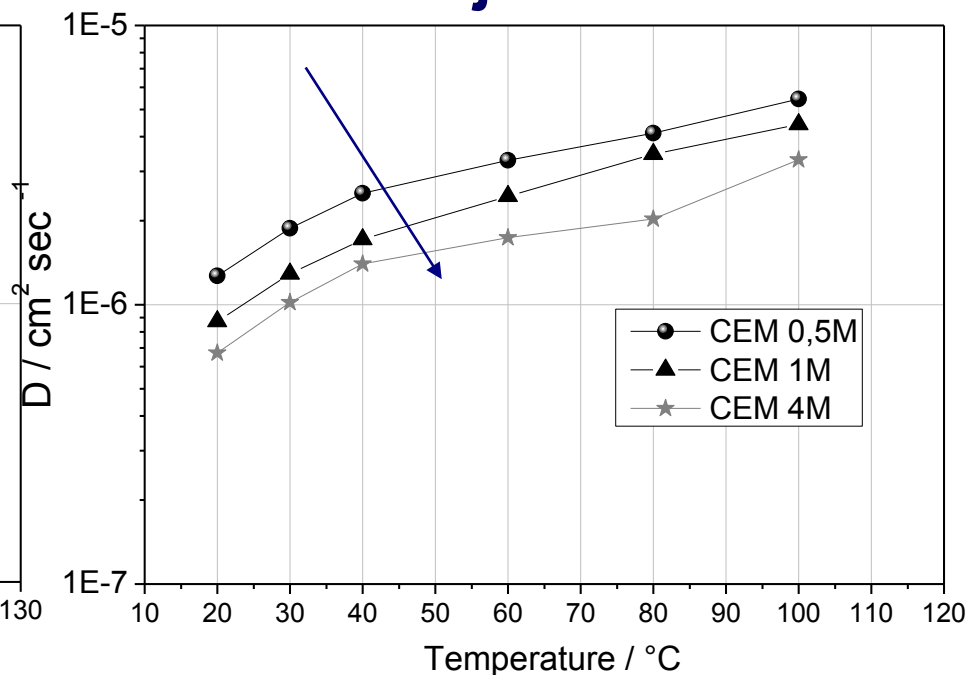
Coppola, L.; Muzzalupo, R.; Ranieri, G. A. *Journal de Physique II* **1996**, 6, 657

Gottwald, A.; Creamer, L. K.; Hubbard, P. L.; Callaghan, P. T. *The Journal of chemical physics* **2005**, 122, 34506

## Fuji-AEM-2



## Fuji-CEM-2



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

## CONCLUSIONS

- The EIS is a powerful, non-invasive and non-destructive, technique to characterize membranes and interfaces
- The areal membrane resistance is the dominant resistance in the whole range of solution concentration, temperature and velocity investigated (0.5-4 M; 20-40°C; 1.5-4.0 cm s<sup>-1</sup>) and it does not depend significantly from the velocity.
- On the contrary, the interfaces resistances can be reduced increasing the solution velocity.
- Membrane and interfaces resistance decreases with the temperature
- The resistances of the AEMs are in general lower than those of the CEMs
- Increasing the solution concentration from 0.5 to 4 M the membrane resistance decreases for the Fuji-AEM-2 (charge density 4 mol/L) but increased for the Fuji-CEM-2 (charge density 3 mol/L).
- The increased electrical resistance is due to changes in the membrane microstructure in concentrated solution, as confirmed by NMR analyses.

## **Acknowledgments**

This work was partially funded in the framework of the REAPower (Reverse Electro dialysis Alternative Power production) project, EU-FP7 programme (Project Number: 256736)

# **Thank YOU!**

