Nafion membranes with a porous surface

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Literature on porous Nafion

474541 ALDRICH
Nafion® SAC-13
pore diameter >10 nm, pore volume >0.6 mL/g

1. Nafion-polyoxymetalate composite membrane

   leaching with alkaline solution →

2. Nafion-dibutylphthalate composite membrane

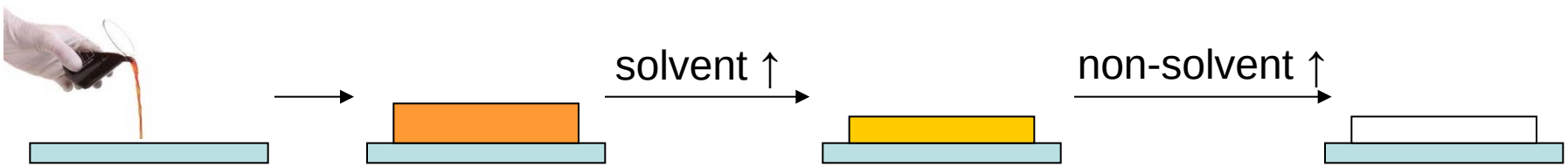
   leaching with ether/methanol →

3. Nafion membrane —propylene carbonate and water / 1 to 6 hours at 100 °C→ (PC degrades to CO_2, expanding the membrane)

4. Nafion membrane —supercritical CO_2 or liquid SO_2 / high pressure → low pressure→ (gas bubbles expand the membrane)

1. D.-J. Guo et al. , J. Mater. Chem., 2010, 20,10159.
2. M.-K. Song,, Electrochem. Solid-State Lett., 2004, 7, A127.
3. J. A. Hestekin, J. Membr. Sci., 2006, 281, 268.
4. Edward G. Howard and R. B. Lloyd (Du Pont), EP 1152830 B1, 2001.

Solution casting and solvent evaporation



pores are filled with non-solvent

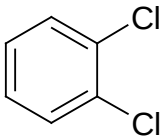
porous membrane

Casting solution:
- polymer
- solvent (high vapor pressure)
- non-solvent (low vapor pressure)

O. W. Reif, Adv. Biochem. Eng./Biotechnol., 2006, 98, 73.

Can we apply this process to Nafion dispersions?

- Commercial Nafion dispersion (consist of water and/or alcohols)
- non-solvent: ODB



	ODB	propanol	ethanol	water
vapor pressure at 20°C [mmHg]	1.2	14.9	44.6	17.5
boilling point [°C]	178 - 180	97	78	100
density [g/ml]	1.306	0.804	0.789	1

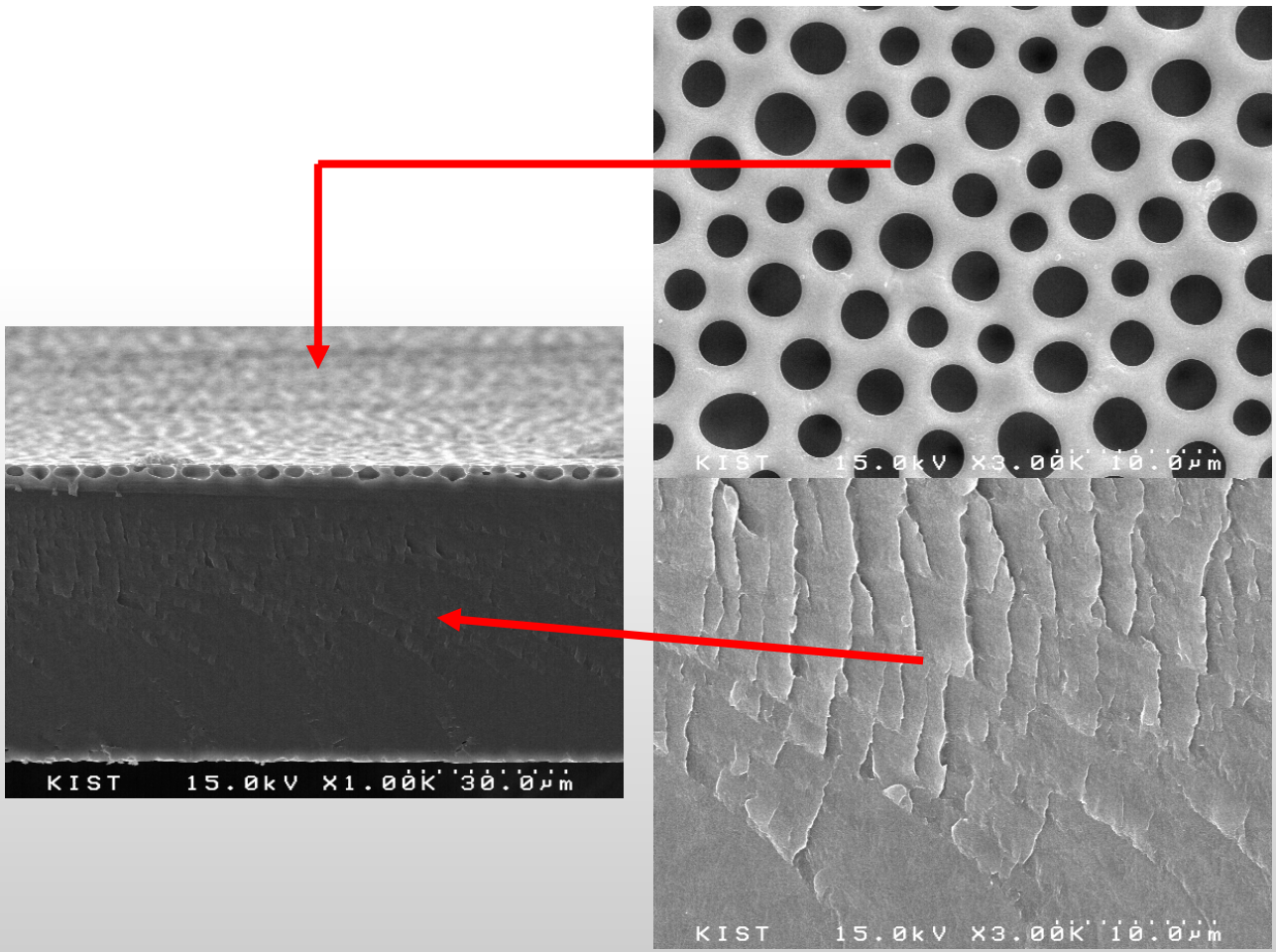
→ We get pores!

- Turbid membranes
- Thickness increases with ODB content

mg ODB per ml Nafion solution	Preparation method	Membrane appearance	Thickness [μm]
0	Casting	Transparent	23 ± 1.9
40	Casting	Transparent	Not obtained
80	Casting	Transparent	Not obtained
140	Casting	Turbid	26.5 ± 1.7 (SEM: 25)
160	Casting	Turbid	29.5 ± 2.4
180	Casting	Turbid	29.6 ± 1.6
200	Casting	Turbid	31.8 ± 2.8
220	Casting	Turbid	37.3 ± 2.7 (SEM: 36)
360	Casting	Irregular membrane	Not obtained
415	Turbid solution, not cast		

J. Mater. Chem., 2012, 22, 14602–14607.

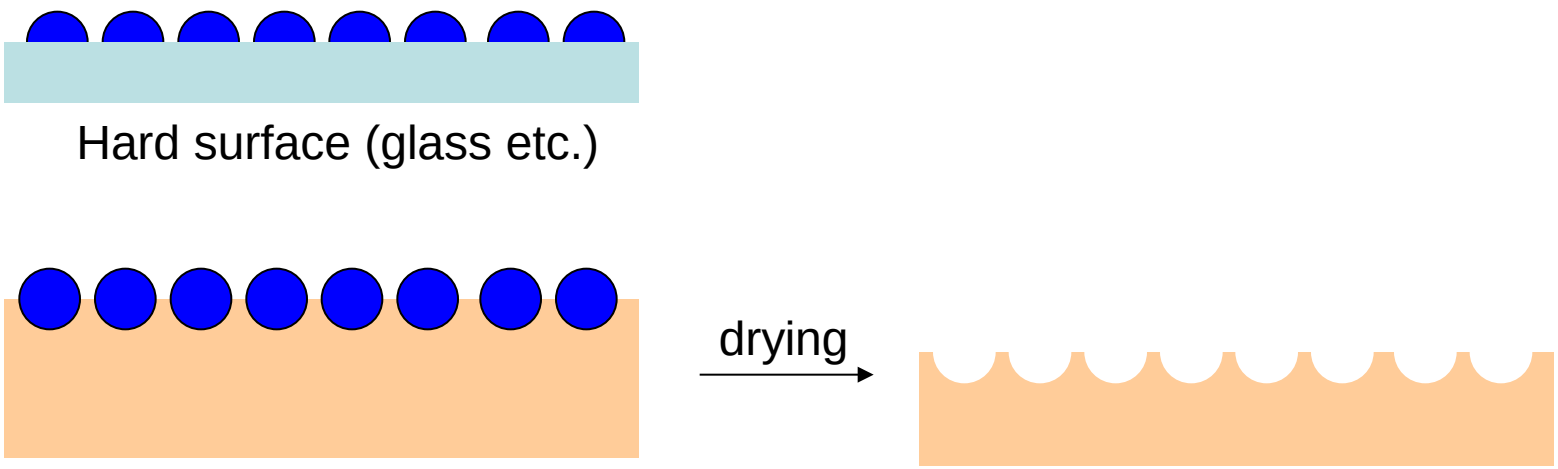
…but pores are only on the surface.



Similar to breath figures:

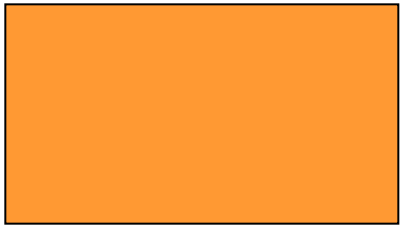
Polysulfone in chloroform → -6°C due to evaporation.

Water droplets are formed by condensation from atmosphere.

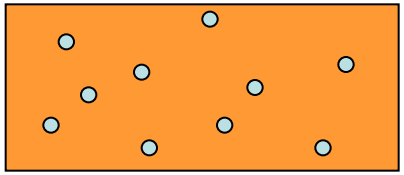


But:
Nafion dispersions are water based
→ other mechanism

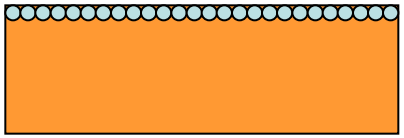
Proposed mechanism



Casting solution:
- Nafion
- Water
- Alcohols
- ODB



- Alcohol concentration ↓
- ODB droplets form
- Density of solution ↑

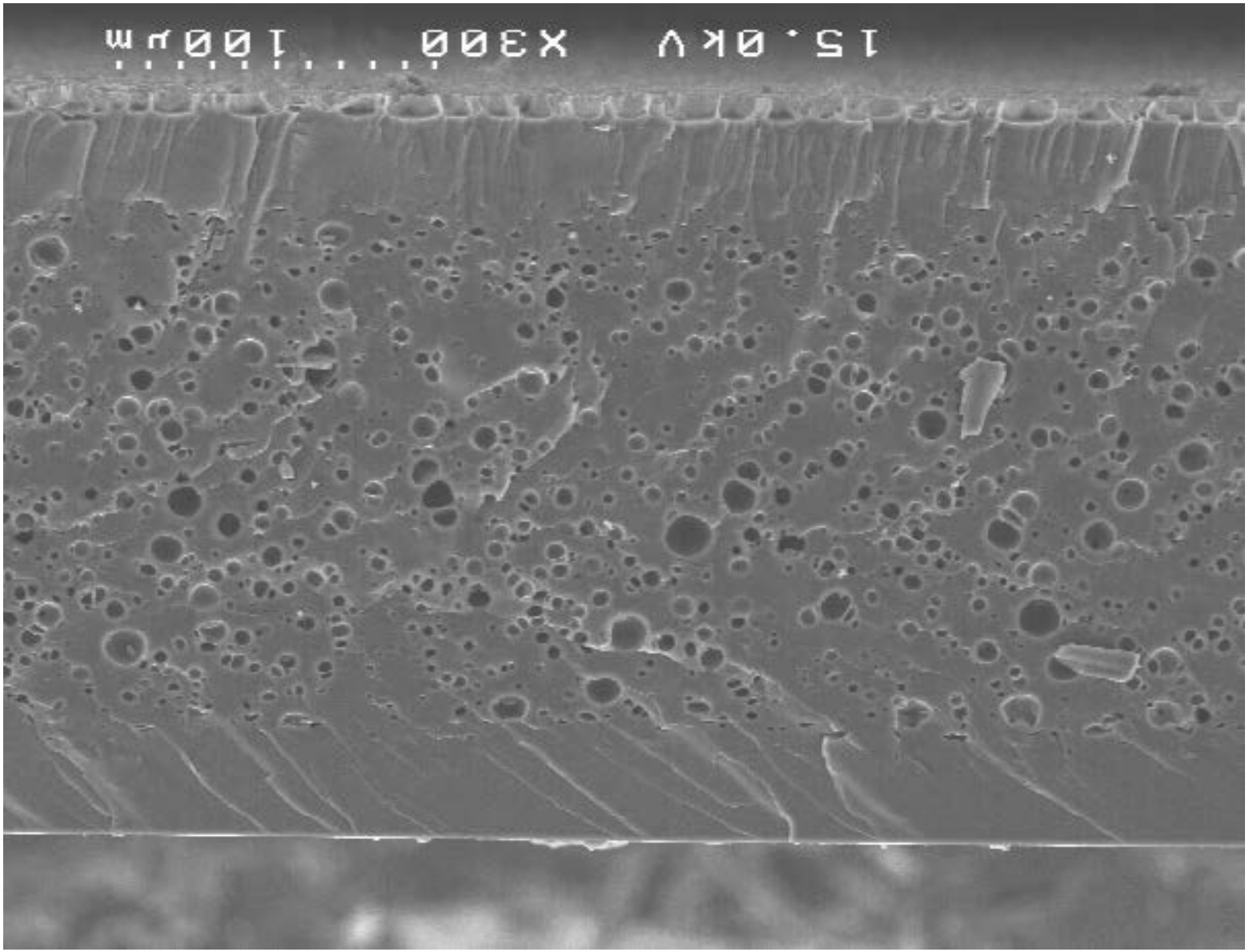


ODB droplets rise to surface

Calculated average density:
Around 40-50% Nafion: density >1.3

	ODB	propanol	ethanol	water	Nafion
vapor pressure at 20°C [mmHg]	1.2	14.9	44.6	17.5	-
boilling point [°C]	178 - 180	97	78	100	-
density [g/ml]	1.306	0.804	0.789	1	1.97

Preparation of very thick membranes (ca. 240 µm thick)



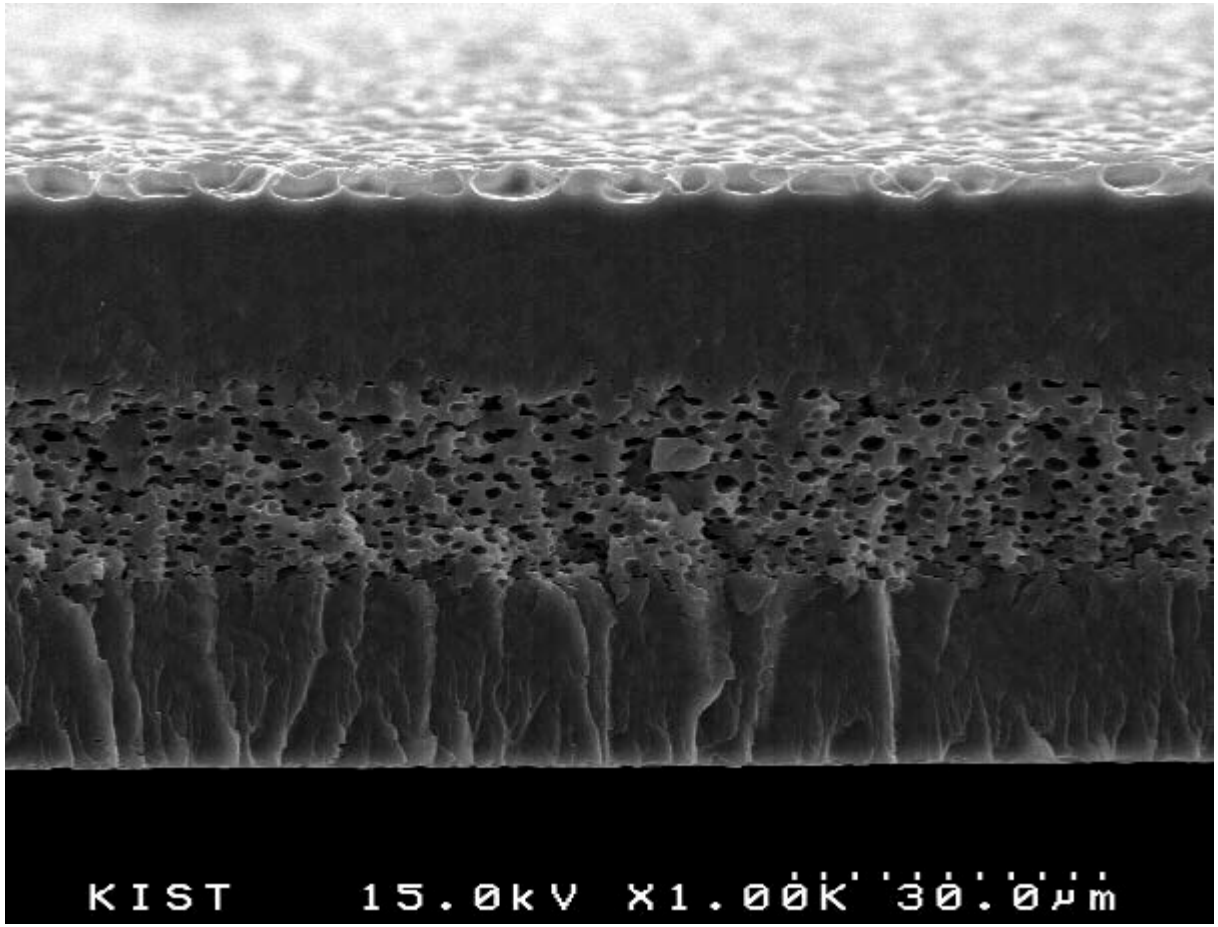
pores

dense

trapped bubbles

dense

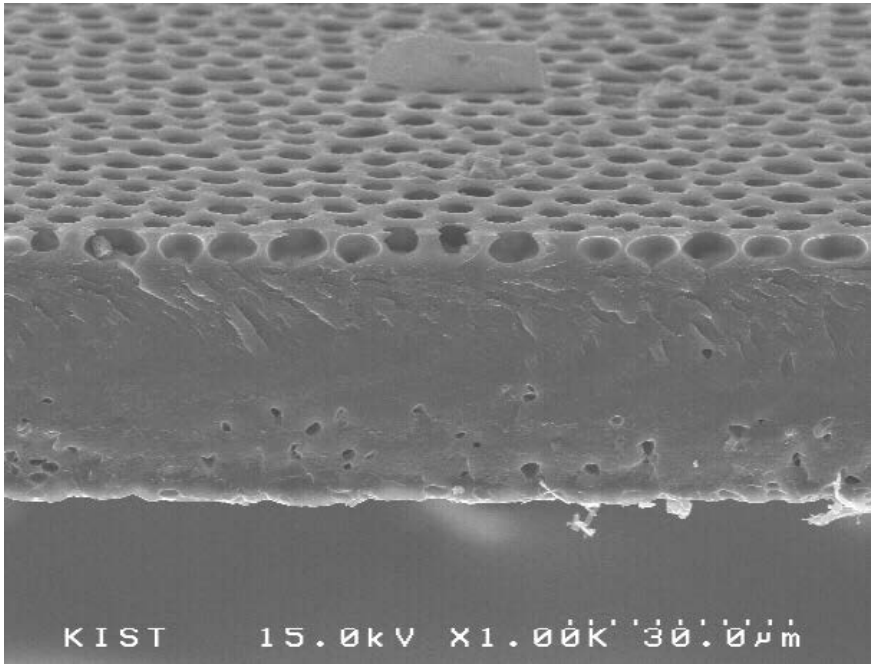
60 μm thick membrane

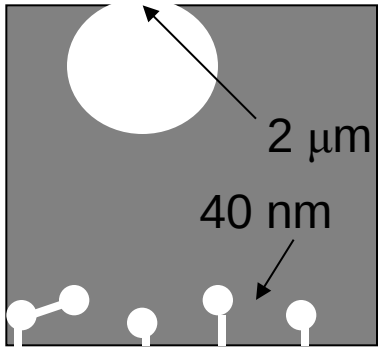


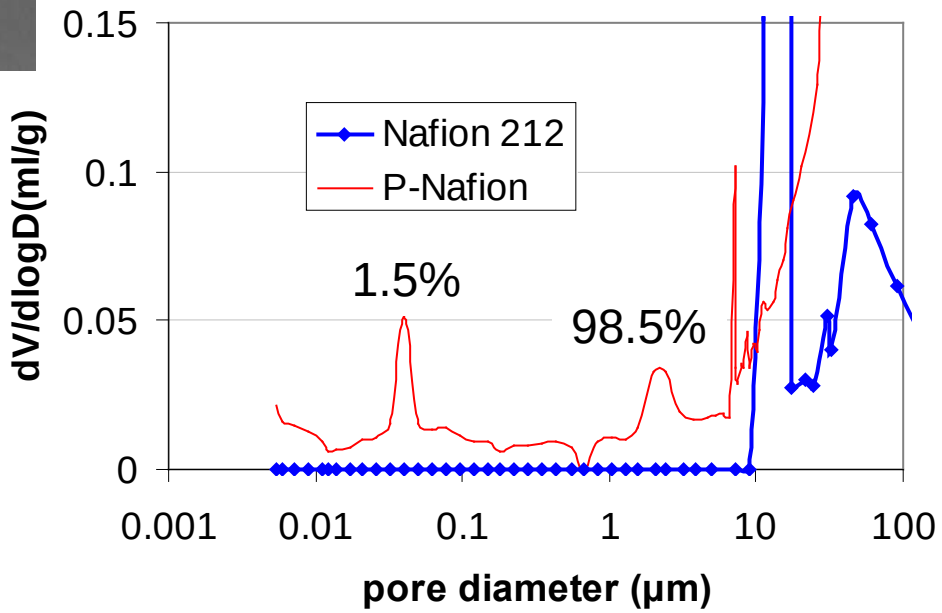
→Membrane formation probably depends on

- temperature
- rh

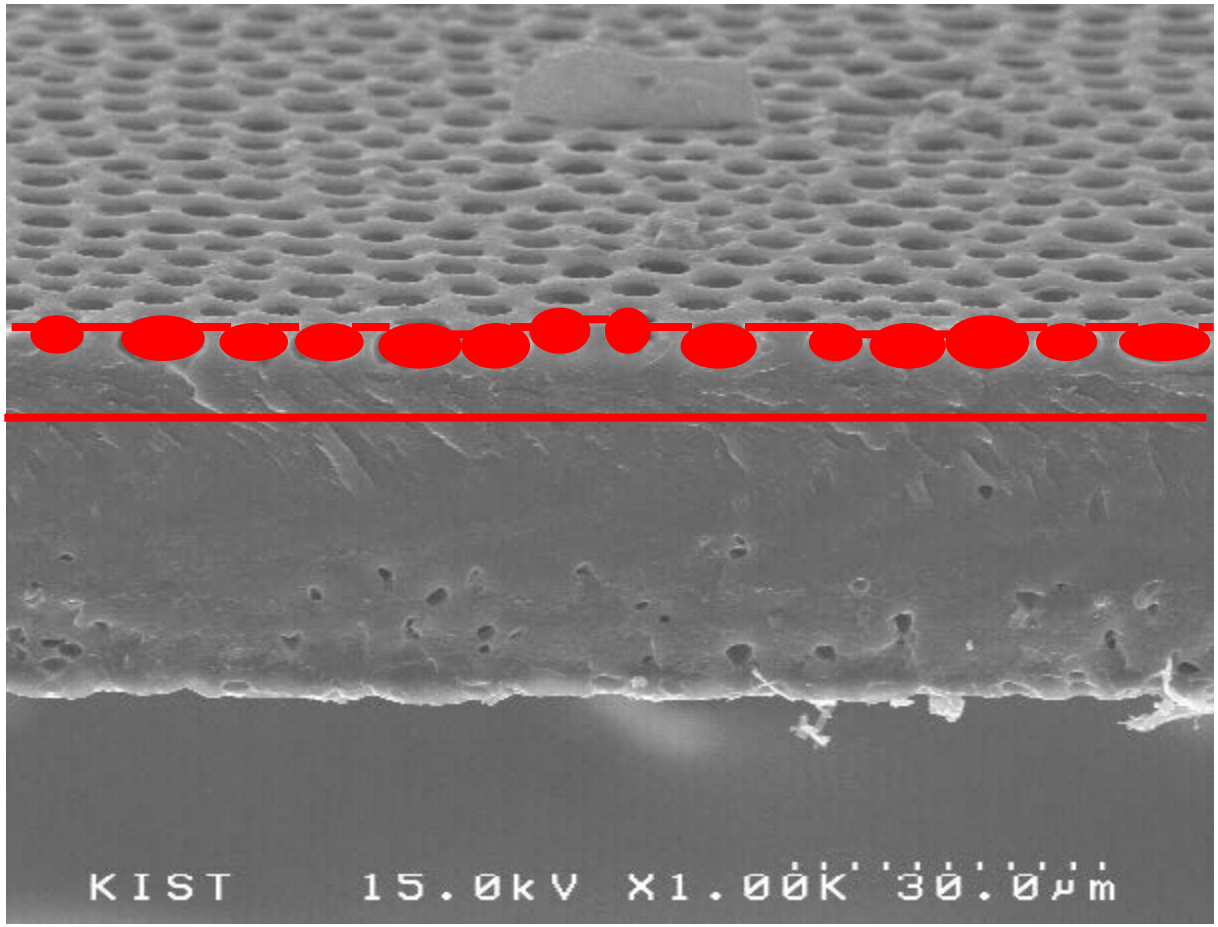
Mercury porosimetry







Effect on Surface Area:

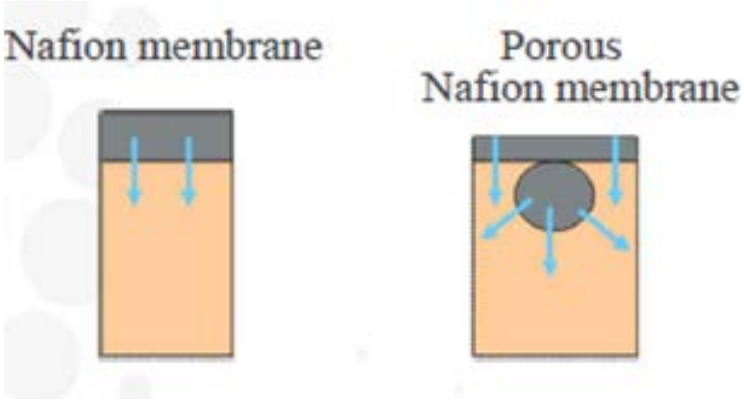


50 cm
16 cm

Assuming that 80% of the ellipsoids circumference is wall:
50x50 / 16x16 ≈ <u>10 times larger</u> surface area

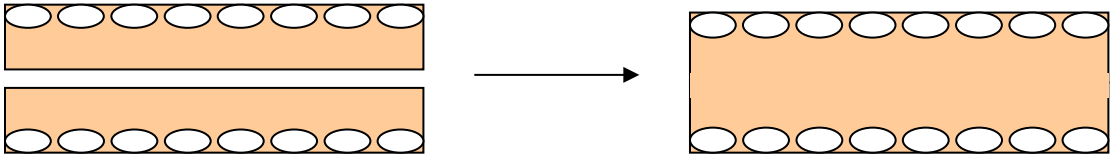
How can we use these materials?

1: Direct use in the fuel cell.

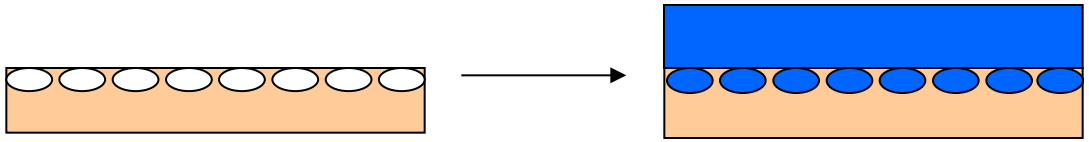


- Enhanced water back diffusion?
- Decreased interfacial resistance?
- low risk of delamination?

2: Pores on both sides by lamination



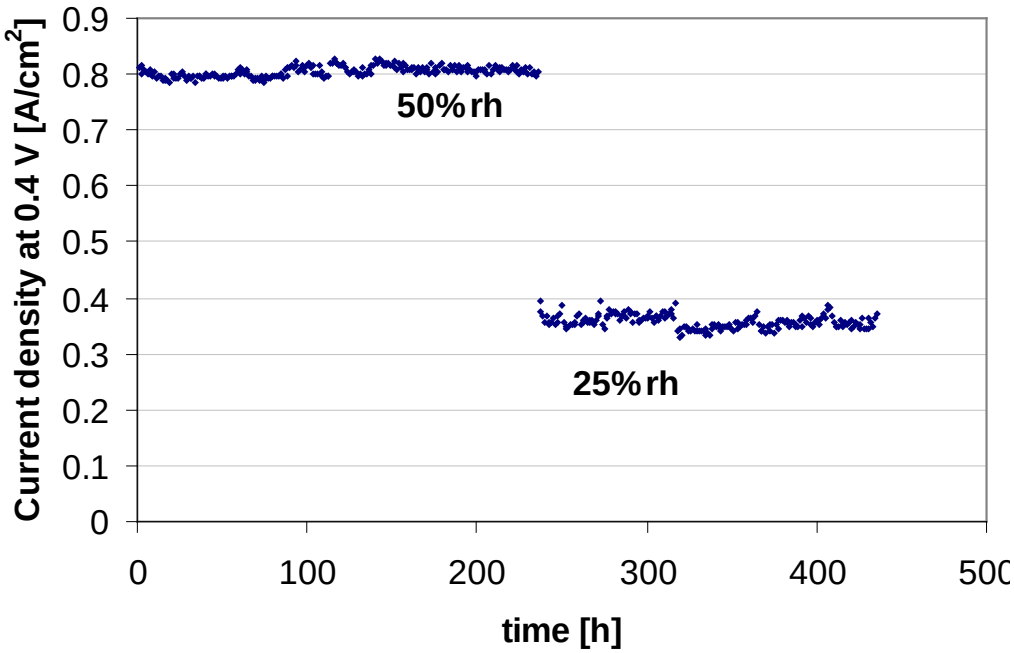
3: Bilayer membranes (e.g. Nafion / SPEEK)



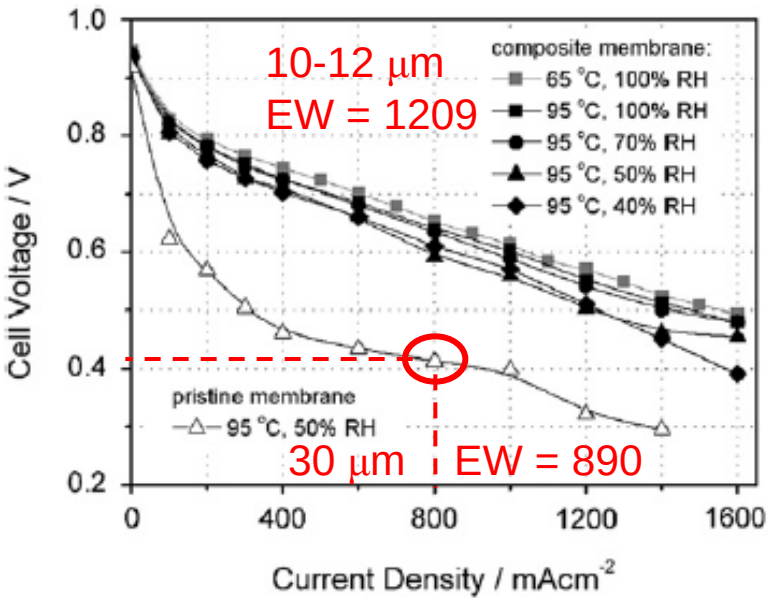
- low gas crossover?
- good catalyst / membrane interface?

SPEEK/SPEEK bilayers of different IEC:
Marrony, Rozière, Jones, Lindheimer, *Fuel Cells* **2005,** 5, 412 - 418.

Stability of P-Nafion in a H_2/air fuel cell at 95°C



46 – 68 µm EW = 1000 g/mol



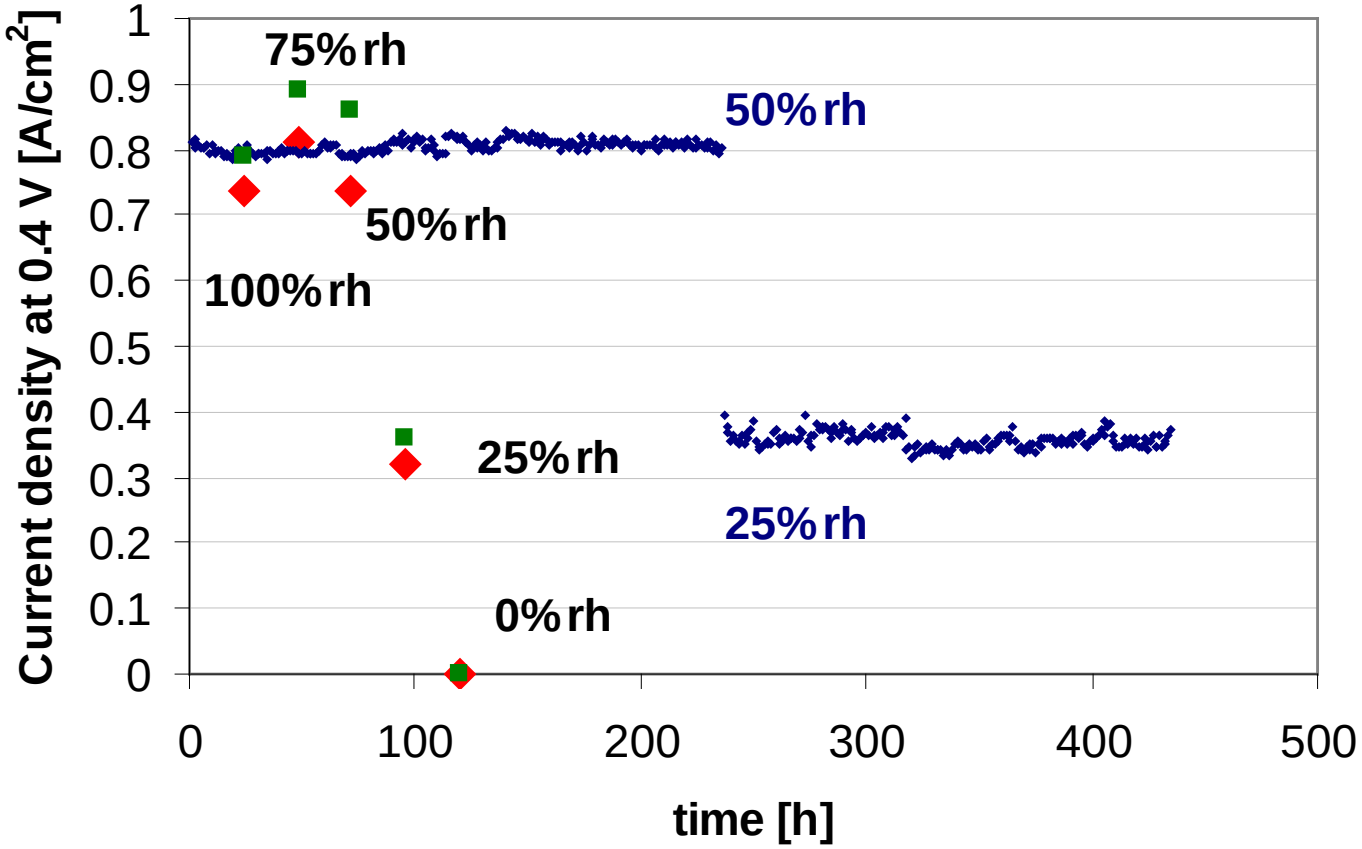
J. Pow. Sour. (2013) 277.

EW = 890 g/mol

SSC PFSA

- after measuring the iV curve at non-humidified conditions
- GDL: Sigracet 34BC

Comparison dense and porous SE20092 membranes

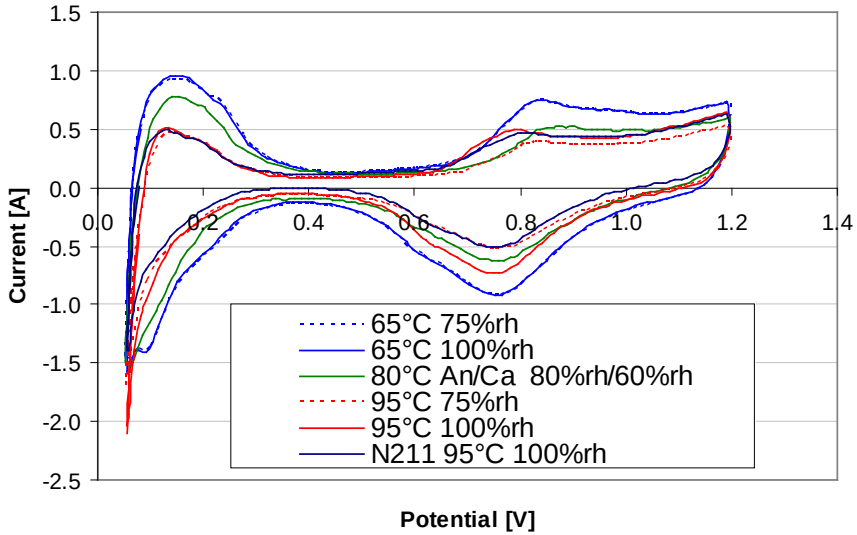


46 – 68 µm, P-Nafion 30-35 µm, P-Nafion

30 - 35 µm, dense membrane

Electrochemical Active Surface Area

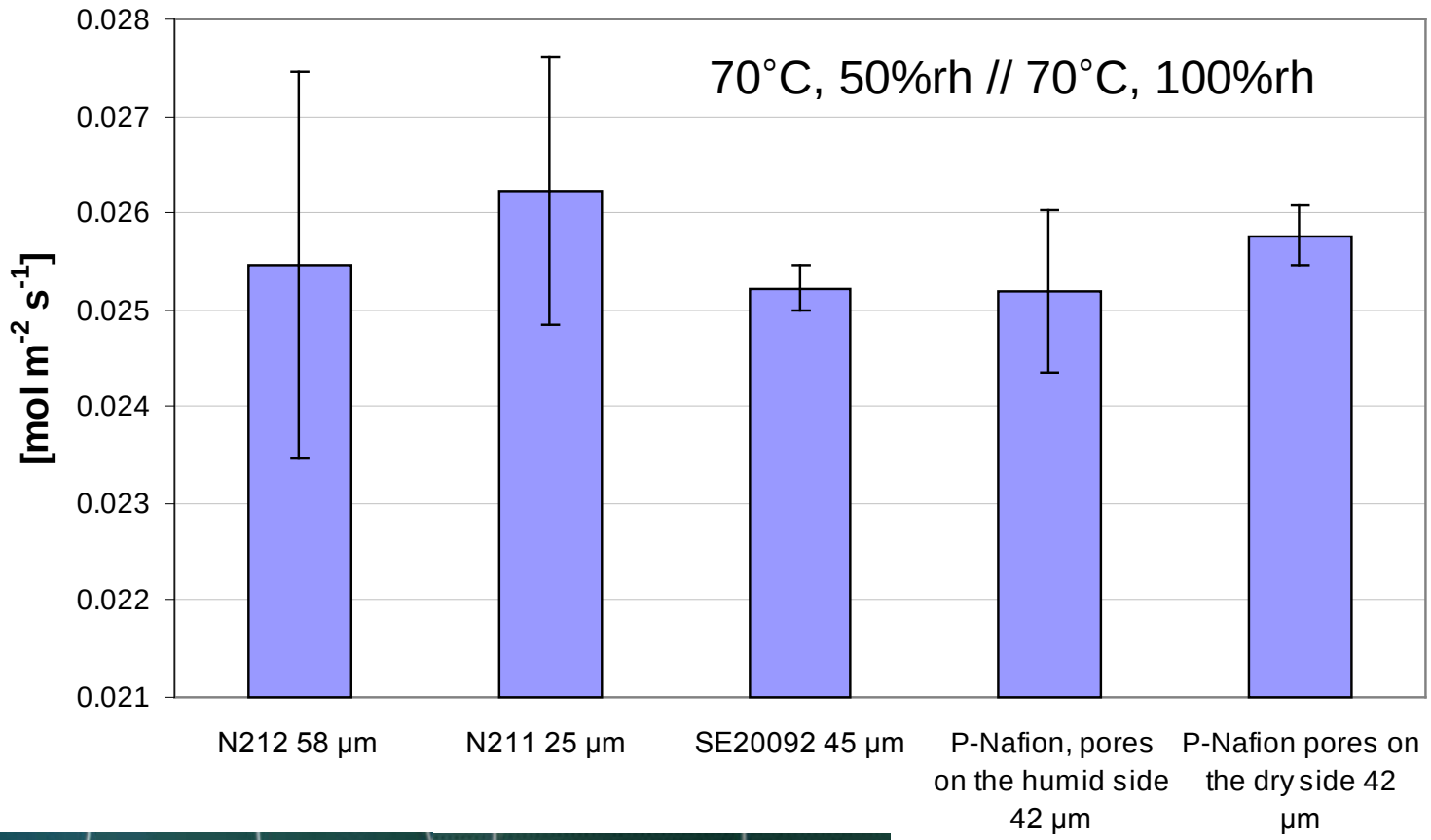
Membrane type	MEA batch	temperature [°C]	rh an./ca. [%]	ECSA (m^2/gPt)	Pt Utilization (%)
N212	1	65	75	**50**	17
N212, additive in catalyst ink	2	65	75	**57**	19
P-Nafion	3	65	75	**134**	44
P-Nafion	3	65	100	141	46
Nafion 211	4	95	100	**46**	15
P-Nafion (other MEA)	5	95	100	**64**	21
P-Nafion	3	95	100	**52**	17
P-Nafion	3	95	75	52	17

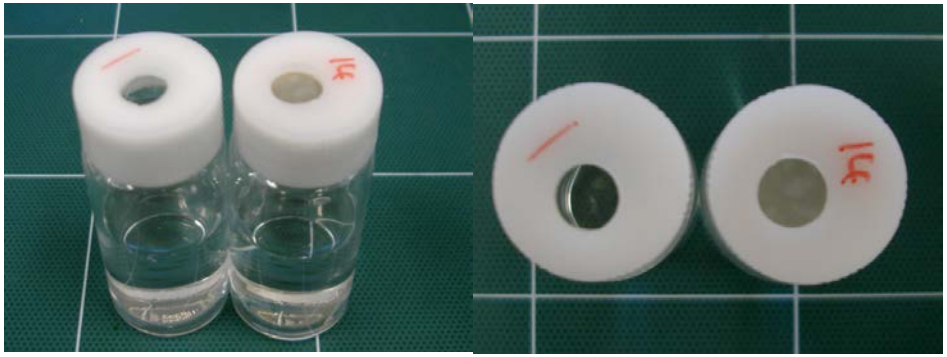


Nafion → P-Nafion
65°C: 135% - 168% increase
95°C: 13% - 39% increase

Conditions: 95°C, fully humidified

Water permeation through P-Nafion and Nafion





→ In a membrane humidifier, dry gas should pass the porous side.

→ Under fuel cell conditions, the humidity gradient would be even larger.

Membrane-electrode delamination: preliminary ex-situ test

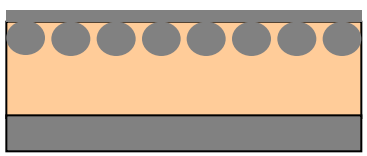
Nafion 212 CCM

water
15 min ultrasound

22wt% of electrode lost

11wt% per side?

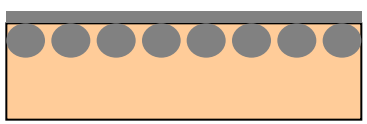
P-Nafion CCM



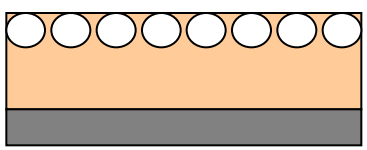
12wt% of electrode lost

11wt% smooth side?

1% porous side?



8wt% of electrode lost



22wt% of electrode lost

→P-Nafion is 3-10 times more stable.
But: more data needed on membrane/electrode interface (SEM, fuel cell)

Thank you for your attention.

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