Membranes Development for Alkaline Water Electrolysis

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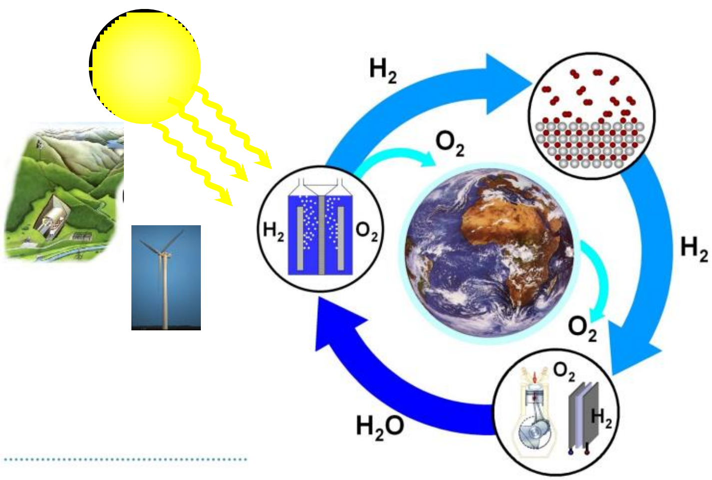
Materials Science & Technology

INDUSTRIE HAUTE TECHNOLOGIE

ELYGRID

Improvements to Integrate High Pressure Alkaline Electrolyzers for H_2 production from Renewable Energies to Balance the GRID

ELYGRID Project aims at contributing to the **reduction of the total cost** of hydrogen produced via electrolysis coupled to renewable energy sources (mainly wind turbines), and focusing on **mega watt size electrolyzers** (from 0,5 MW and up).



MAIN IDEAS:

- **Big size alkaline electrolyzers**
- **Reduction of Total Cost of Ownership (TCO)**
- **Prototyping and testing with intermittent feeding**
- **Industrialization and market oriented approach**

PROJECT: FUNDED BY: PARYNERS: COORDINATOR:

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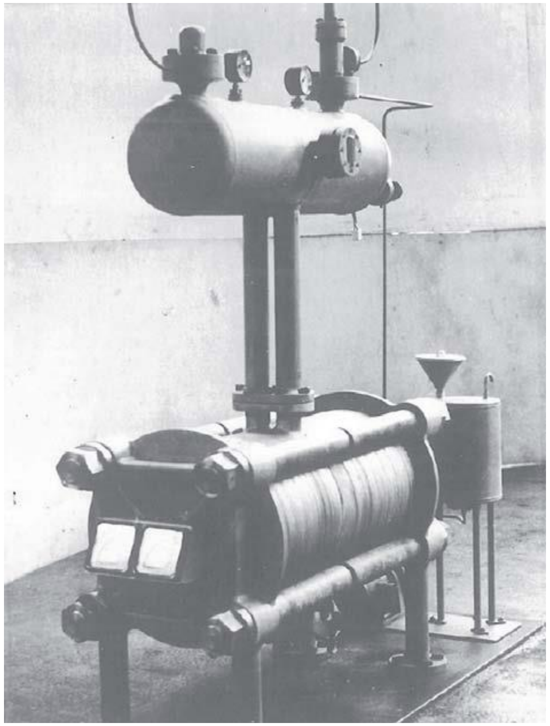
Hydrogen production via alkaline electrolysis



Left: Lurgi-Zdansky type alkaline electrolyser in 1949
Right: Electrolyser at Giovanola, Monthey

H_2 purity: 99.8 - 99.9 vol%
O_2 purity: 99.3 - 99.6 vol%

Working conditions: 32bar, 85°C, 25wt-% KOH
Production rate: 760 m³/h H_2 , equ. to 3.3 MW_{el}
Energy Consumption: 4,3 - 4,6 kWh/m³ H_2
Partial load: *25 tp 100 % of nominal capacity*

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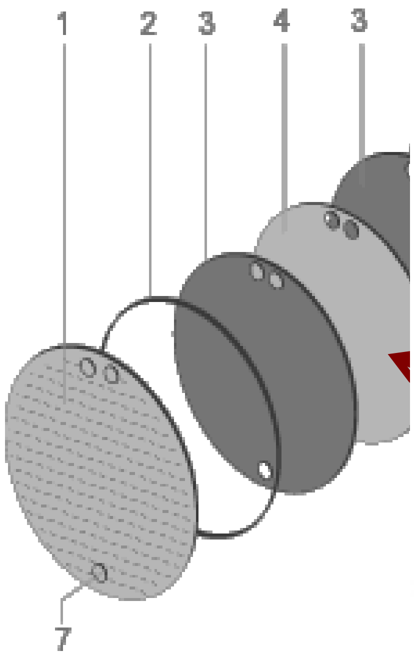
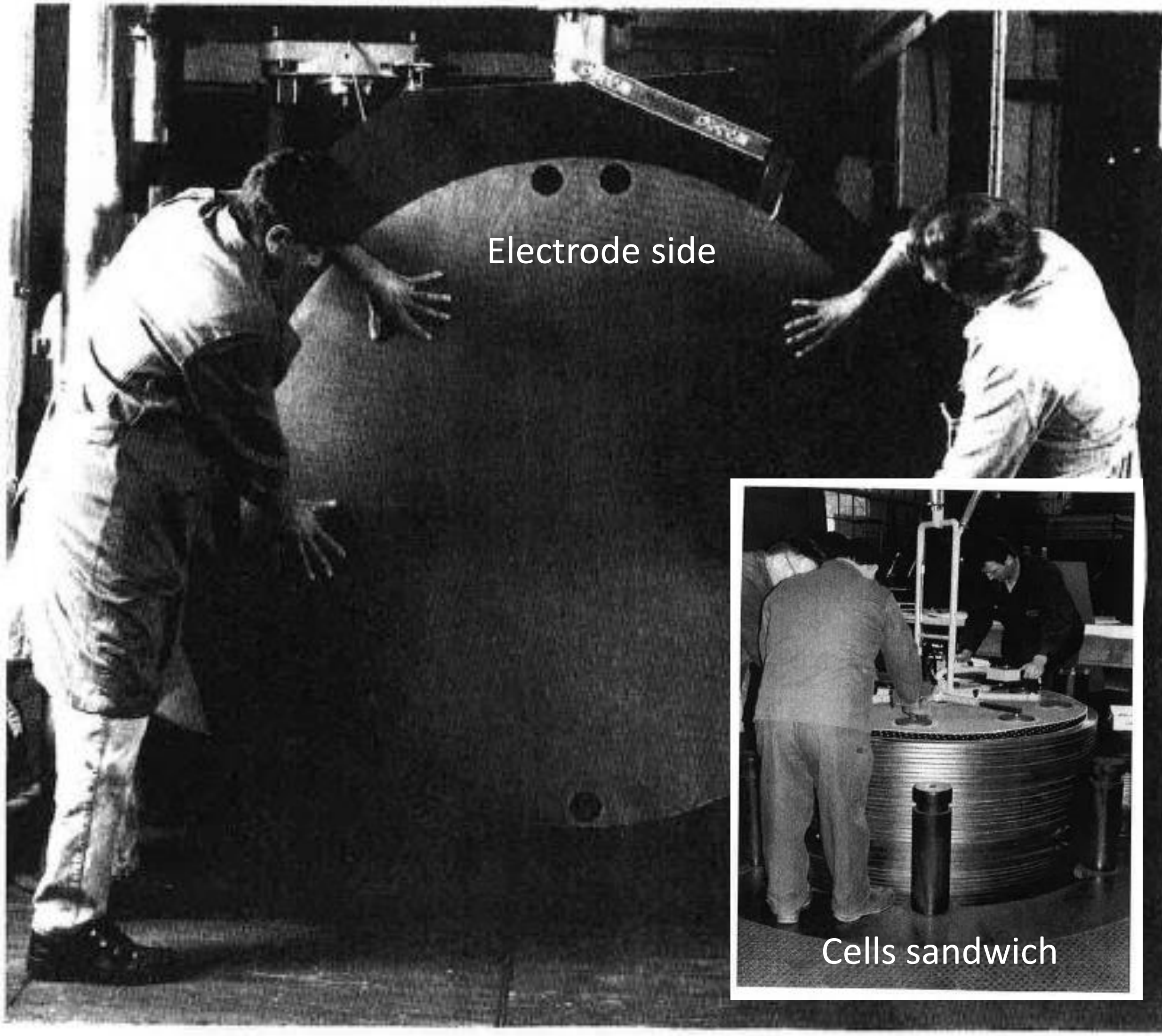
Stat

Cell mountening at IHT, Cell diameter 1.6 m





1.Cell partition
2.Gasket
3.Electrode mesh
4.Membrane (Asbestos)
5.Hydrogen duct
6.Oxygen duct
7.Electrolyte duct

(Ullmann's Encyclopedia, 2006)

Cathode	$H_2O + e^- \rightarrow \frac{1}{2}H_2 + OH^-$
Anode	$2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^-$
Overall	$H_2O \rightarrow H_2 + \frac{1}{2}O_2$

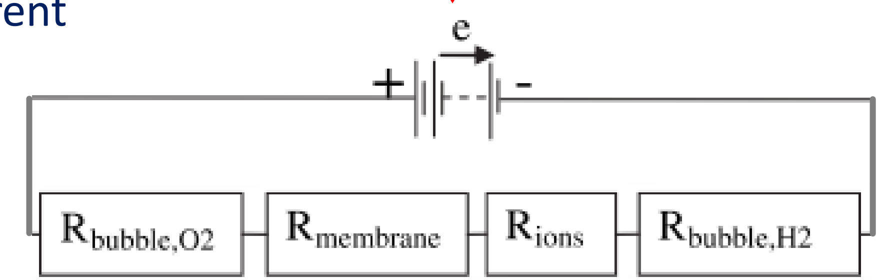
Electrolyzer cell potential:

$$E_{cell} = \boxed{E_0 + \eta_a + |\eta_c| + I} * \boxed{\boldsymbol{R}}$$

E_0: equilibrium cell potential

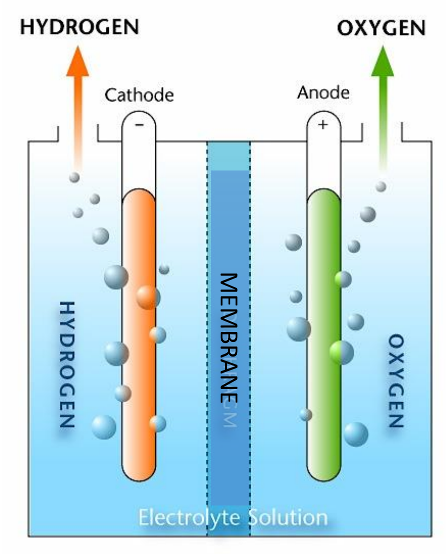
$\eta_{a,c}$: anodic, cathodic over potential

I: Applied current



Zeng *et al.*, *Progress in Energy and Combustion Science* **2010**, *36*, 307-326

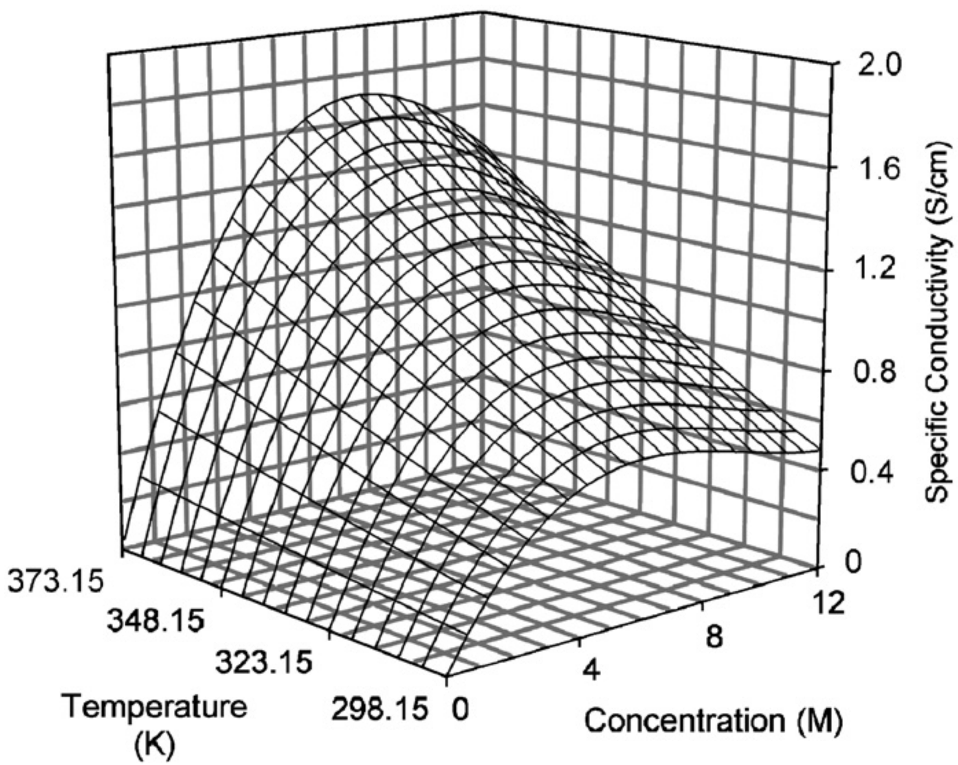
Principle of water electrolysis



Membrane requirements:

- ion-permeable
- gas-tight
- chemically stable
- electrically insulating
- mechanically robust

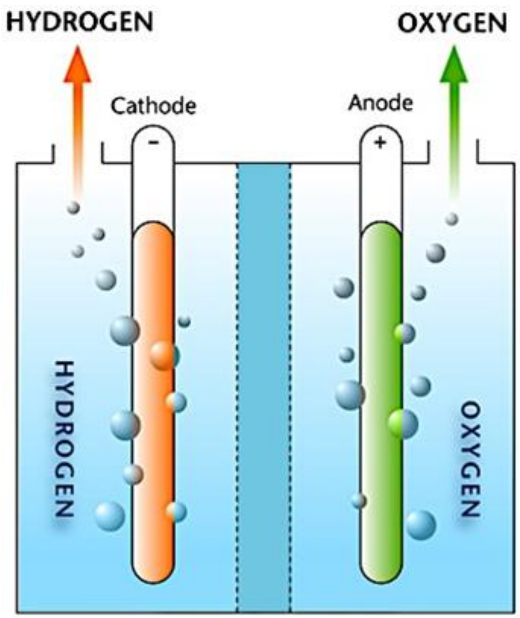
Specific conductivity of KOH



Specific conductivity of KOH (Giliam, R., et al. 2007)

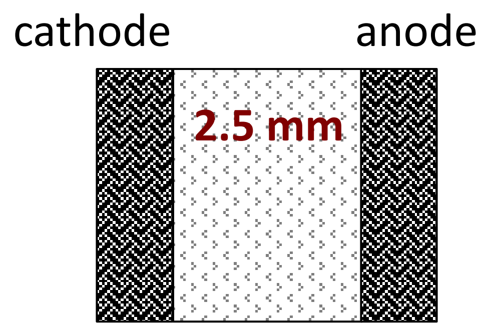
Main objectives for Developing a new type of membrane

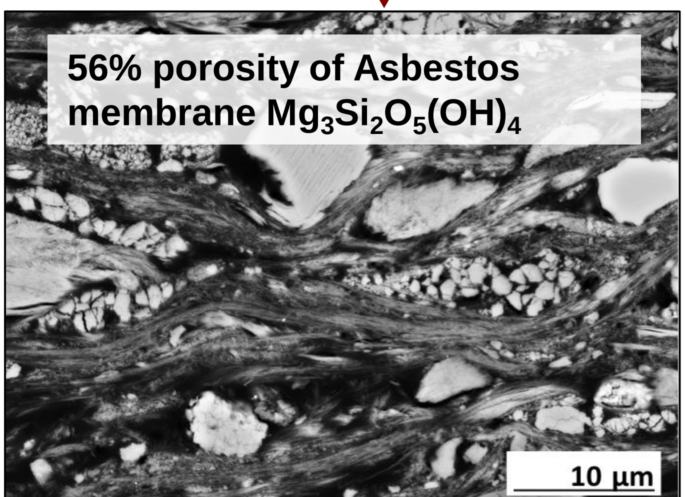
- stable at KOH temperatures up to 120 ° C
- for KOH concentration of 30wt%
- Reduction of cell voltage from 1.9 to 1.6 V
- Increase of current density by a factor 2: 200 → 400 mA/cm²
- Improve stack efficiency by 10 %
- Identification of the limiting factors for membrane functionality (aging, contaminations, …)

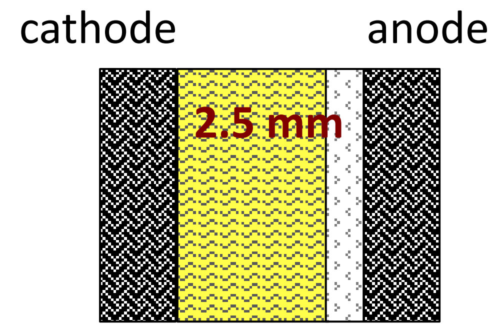


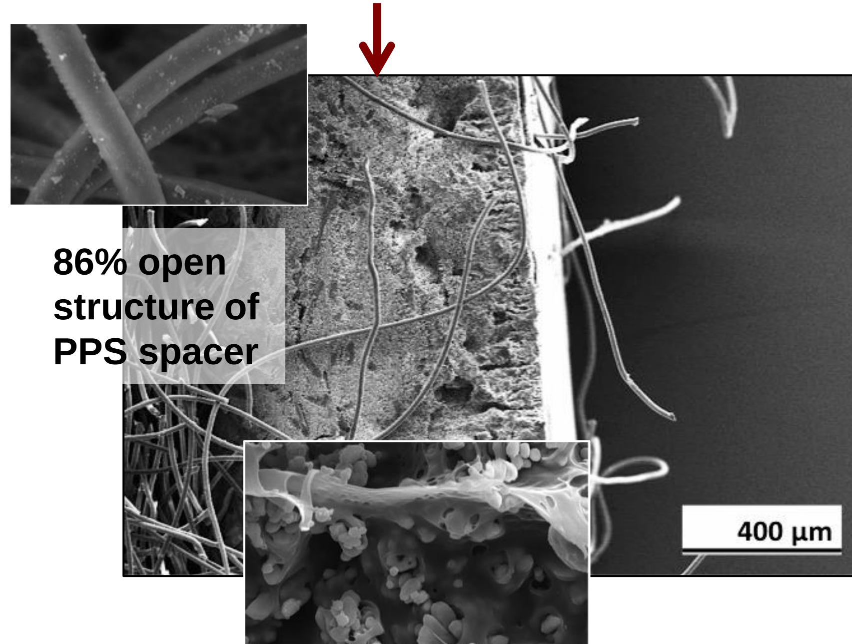
IHT Industrial alkaline electrolyzer

Concept of Asbestos replacement









Dense composite layer

Supporting Structurte

Polyphenylene Sulfide (*PPS*) felt:

T_m: 285°C T_g: 90°C

Chemically stable

- acids, bases, solvents

Porous (~85%)

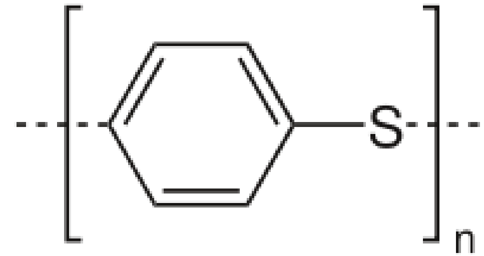
Flexible

BUT:

Hydrophobic surface

Porosity too high

→ gas bubbles break through



Repetitive unit of PPS

PPS felt 3,3mm BWF

Hydrophilic filler material selection

Mineral base fillers

$Mg_3Si_2O_5(OH)_4$ chrysotile Asbestos

$CaSiO_3$ wollastonite

$(Mg,Fe)_2SiO_4$ olivine

$BaSO_4$ barite 99% purity

Synthetic based fillers

$BaTiO_3$ 98% purity, perovskite str., electroceramics

ZrO_2 3YSZ (TOSOH), technical ceramics, SOFC

Chemical corrosion experiment

T = 85°C (120°C running)

KOH(25wt%) (35wt% running)

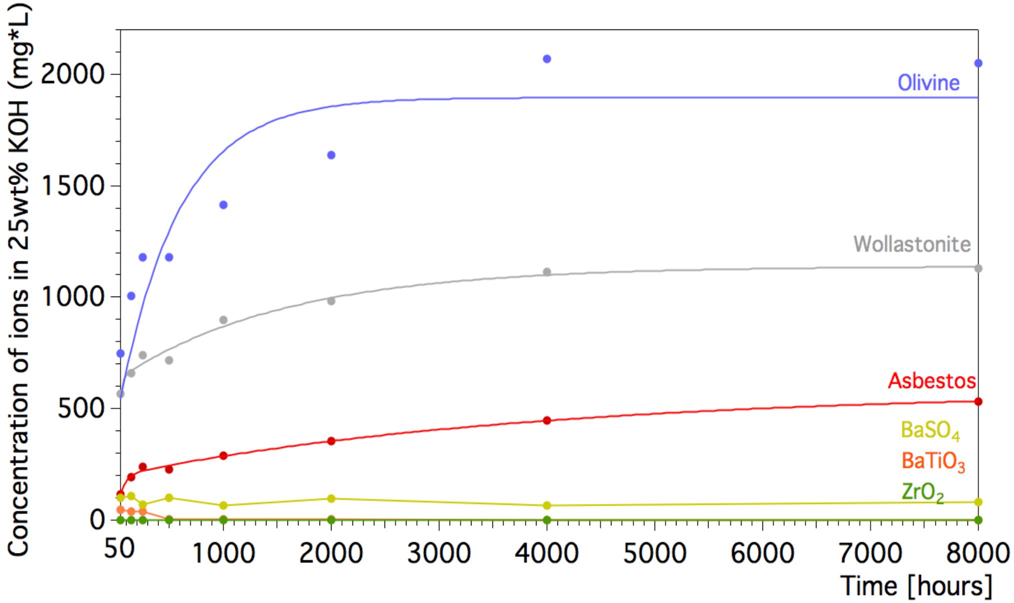
filler : KOH = 20 mM : 200 mM

t(h) = 50, 150, 255, 500; 1000; 2000; 4000; 8000

Method:
ICP-MS (Inductively coupled plasma mass spectroscopy)

www.webmineral.com

Corrosion Experiments, 85°C, 24 wt% KOH



Dissolution effect of individual materials shows the concentration of elements (mg/L) found by ICP-MS for each particular material versus time in hours

Time (hours)	Mass loss of the particular filler (%)					
	Asbestos (Mg,Si)	Wollastonite (Si,Ca)	Olivine (Mg,Si)	ZrO_2 (Zr)	$BaSO_4$ (Ba)	$BaTiO_3$ (Ba,Ti)
50	0.078	0.888	0.967	0.000	0.079	0.036
150	0.129	1.032	1.298	0.000	0.084	0.029
255	0.160	1.160	1.521	0.000	0.054	0.029
500	0.152	1.120	1.525	0.000	0.077	0.002
1000	0.194	1.405	1.827	0.000	0.050	0.002
2000	0.236	1.536	2.114	0.000	0.076	0.002
4000	0.300	1.740	2.674	0.000	0.050	0.001
8000	0.356	1.768	2.647	0.000	0.062	0.001

MEMBRANE PRODUCTION

Inorganic Filler

- Hydrophilic surfaces
- Chemical stability
  - Finally increase of operating Temp.

$BaSO_4$, $BaTiO_3$, ZrO_2
Chemical stability

Bariumsulfate ($BaSO_4$)
Wollastonite ($CaSiO_3$)
Olivine ($(Mg,Fe)_2[SiO_4]$):
Chemical similarity to asbestos
Price

Organic Binder PSF

- Fixation of powder to felt
- Chemical stability
- Solubility in organic solvents
  - Advanced production from solution

Polysulphone (PSF)
T_g: 187°C

N-methyl-2-pyrolidon (NMP)

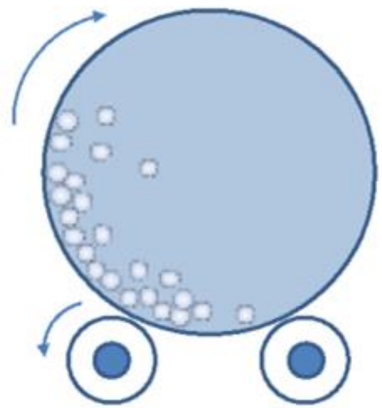
MEMBRANE PRODUCTION

Inorganic powder

Organic solvent

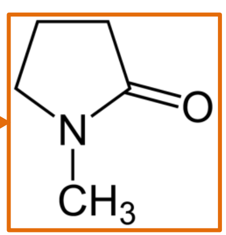
Organic binder

Milling and mixing

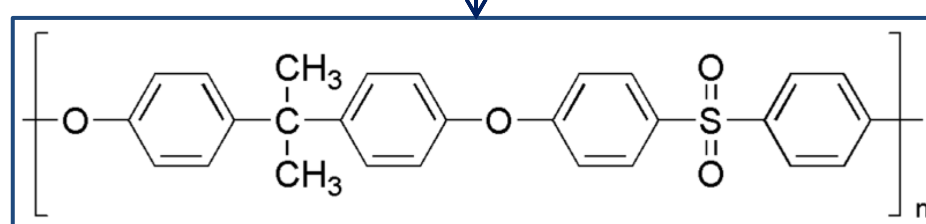


Milling media: 2-3mm YZO spheres
Velocity: ca. 0.67m*s-1
Time: 24 hours

Slurry



NMP

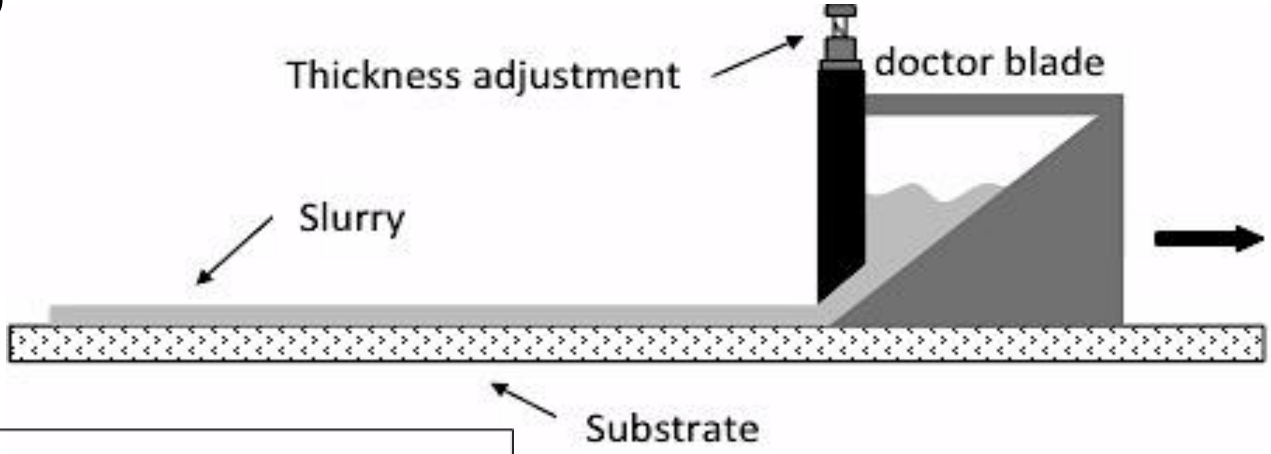


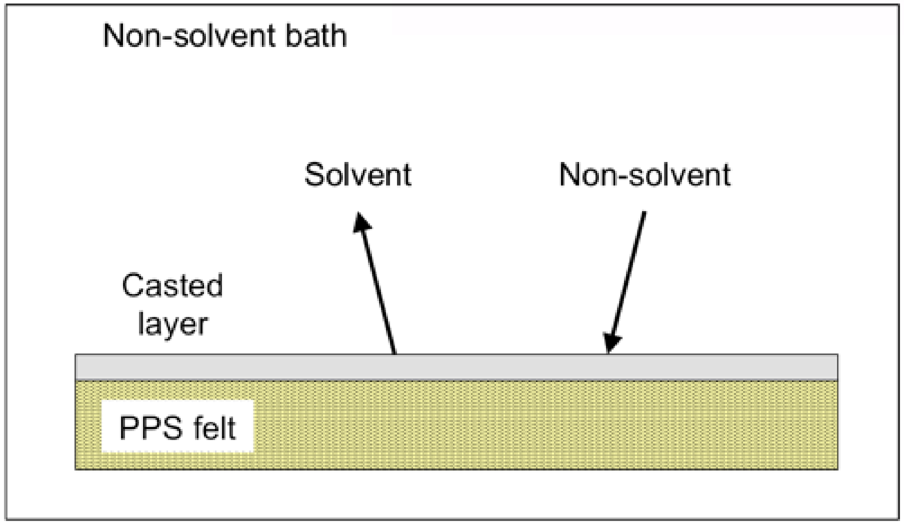
PSF

patent on membrane manufacturing filed in May 2013

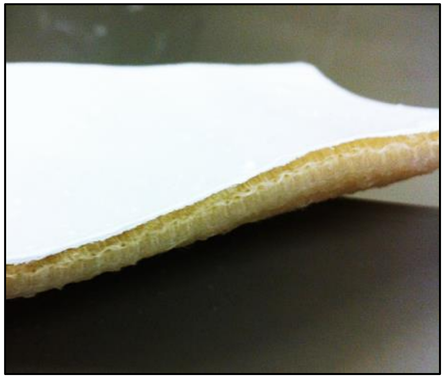
Example for layer tape casting on PPS felt/net

PPS felt (Polyphenylensulfid)
technical textile





schematic description of the inversion process



coated PPS felt
thickness of coating:
0.2 – 1.5 mm

Kyoung-Yong Chun et al. Journal of Membrane Science, Volume 169, Issue 2, 2000

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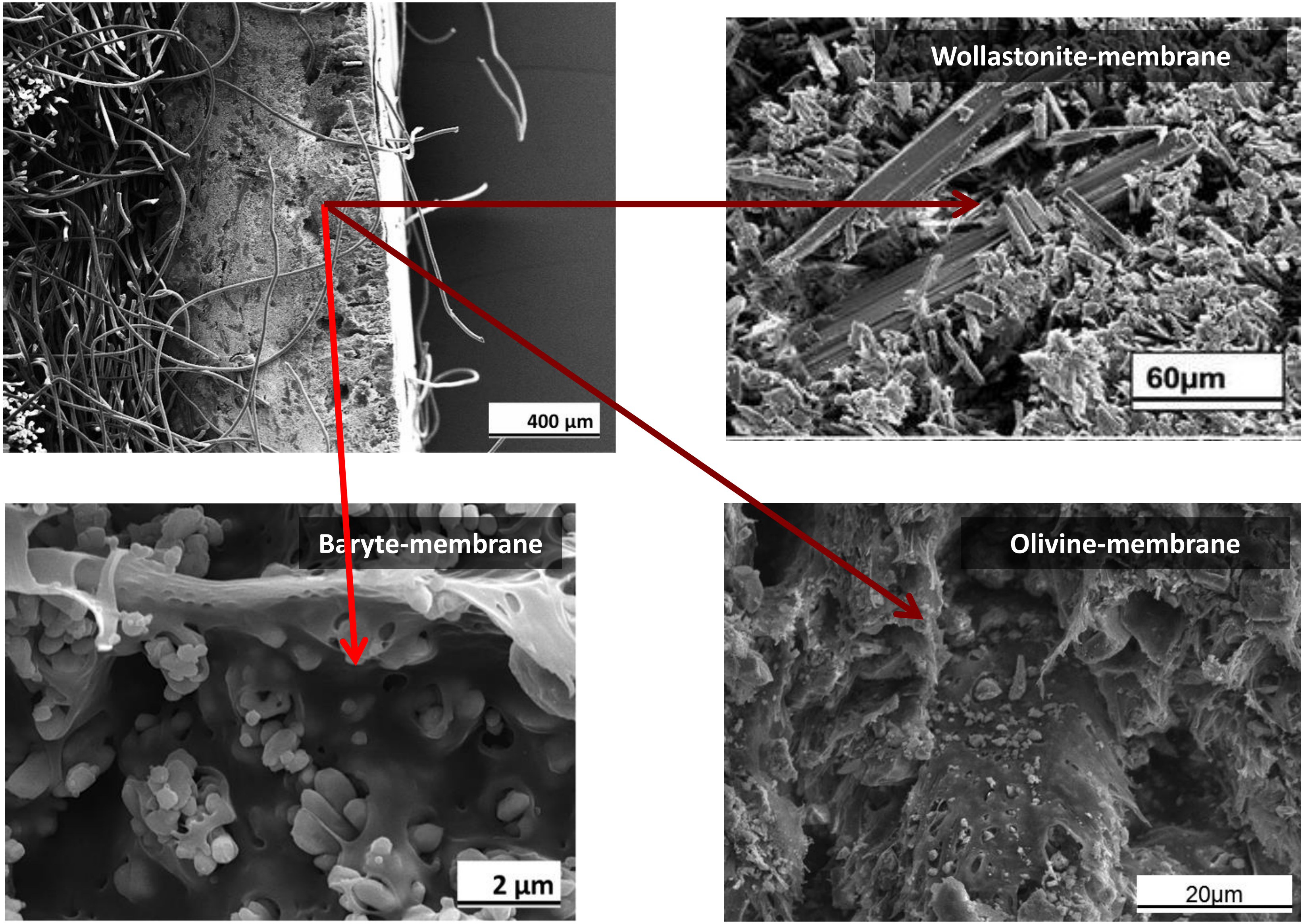
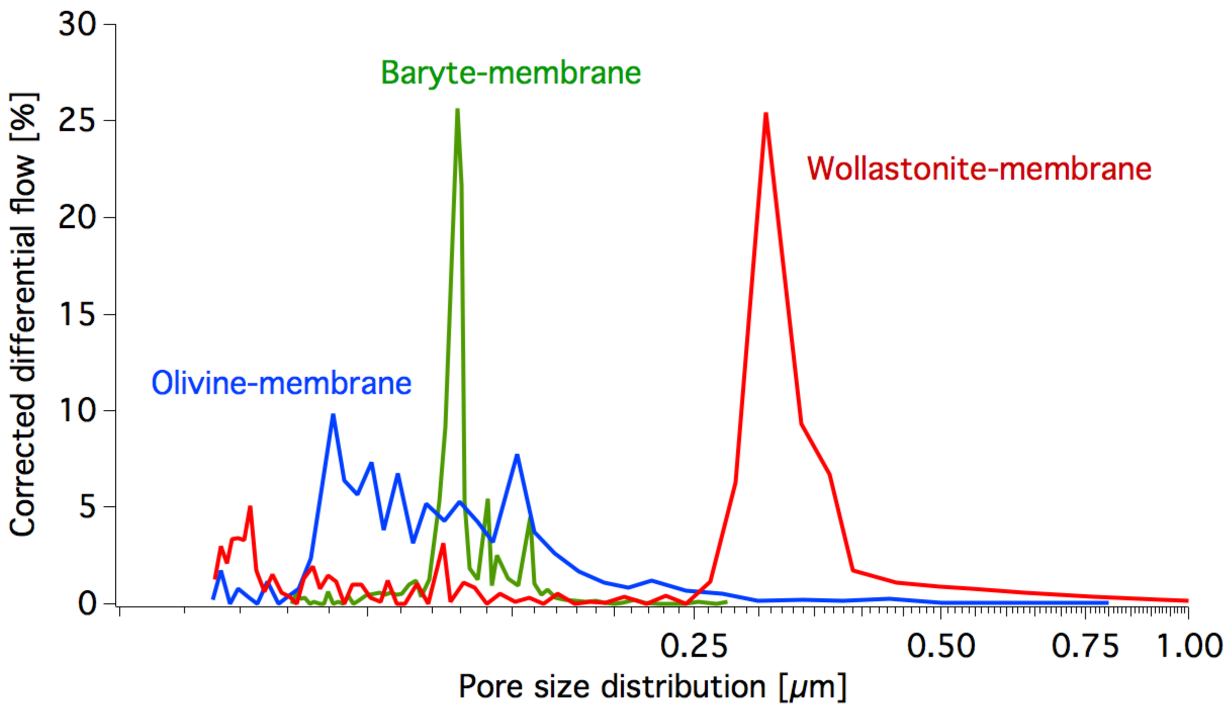
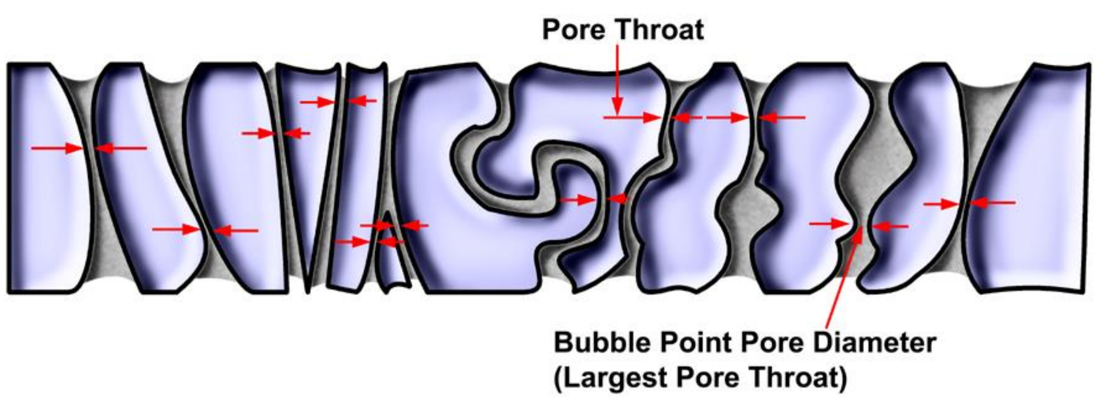
SEM pictures of membranes



Pore size distribution determined by Bubble point measurementt (BPM)





	POROLUX™ 1000
Measuring principle	Pressure Step
Max pressure	35 bar
Min pore (1)	18 nm
Max pore (2)	500 µm
Max flow	200 l/min
Sample holders	13-25-47 mm
Pressure sensors	2-50 bar
Flow sensors	10-200 l/min
FBP regulator	5-30 ml/min

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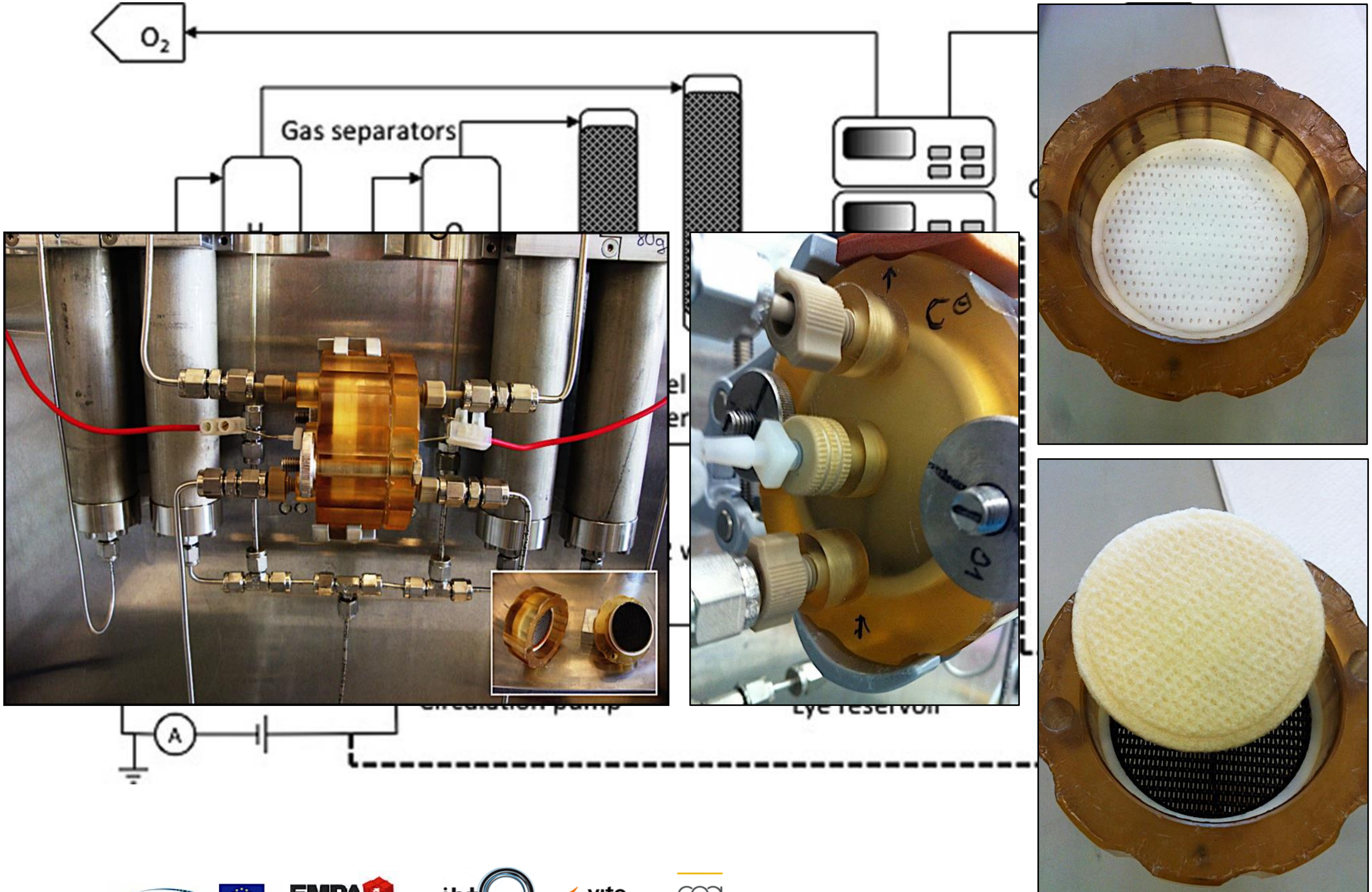
lab-electrolyzer system for membrane characterization @ ambient conditions



Membrane diameter: 50 mm

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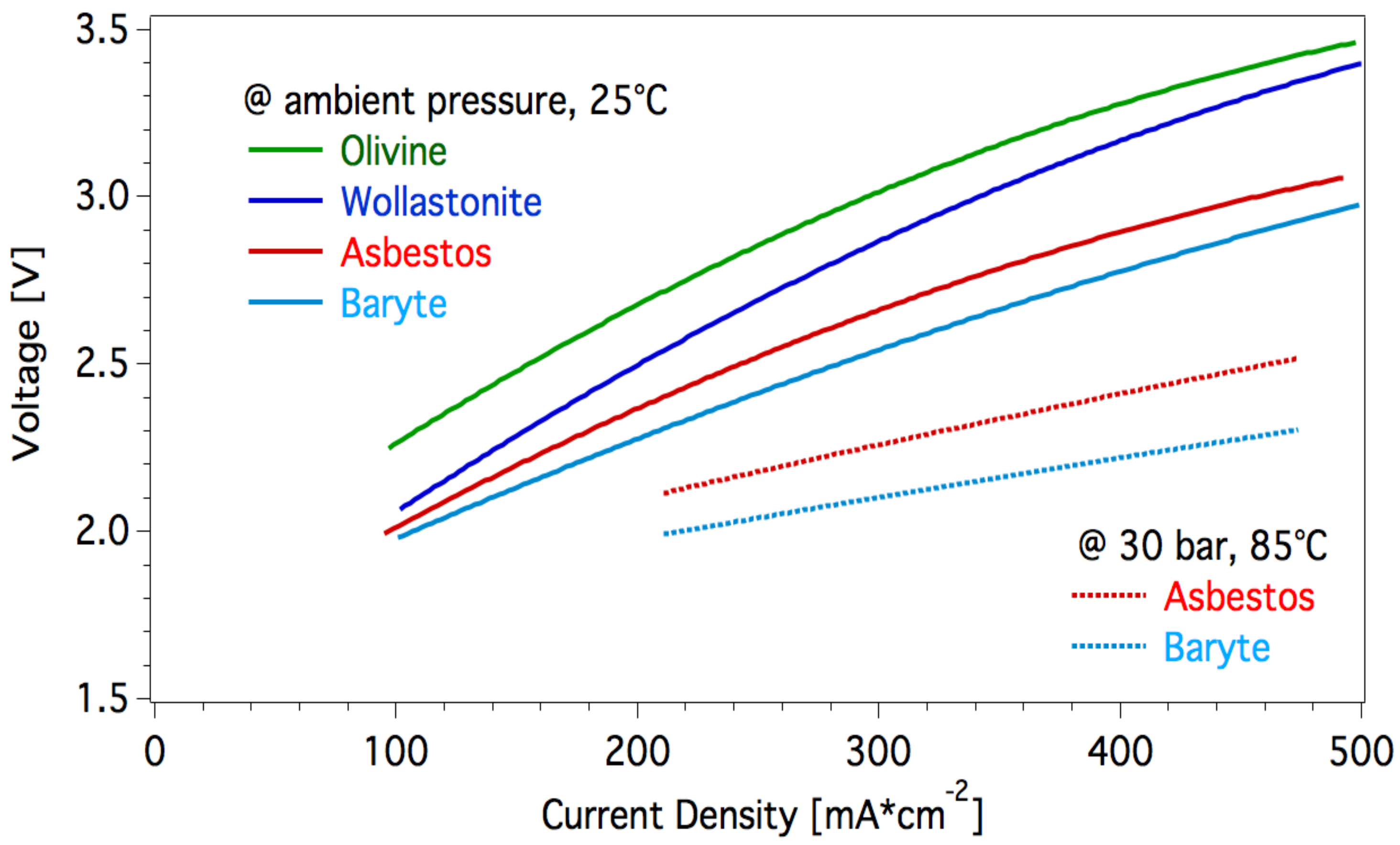
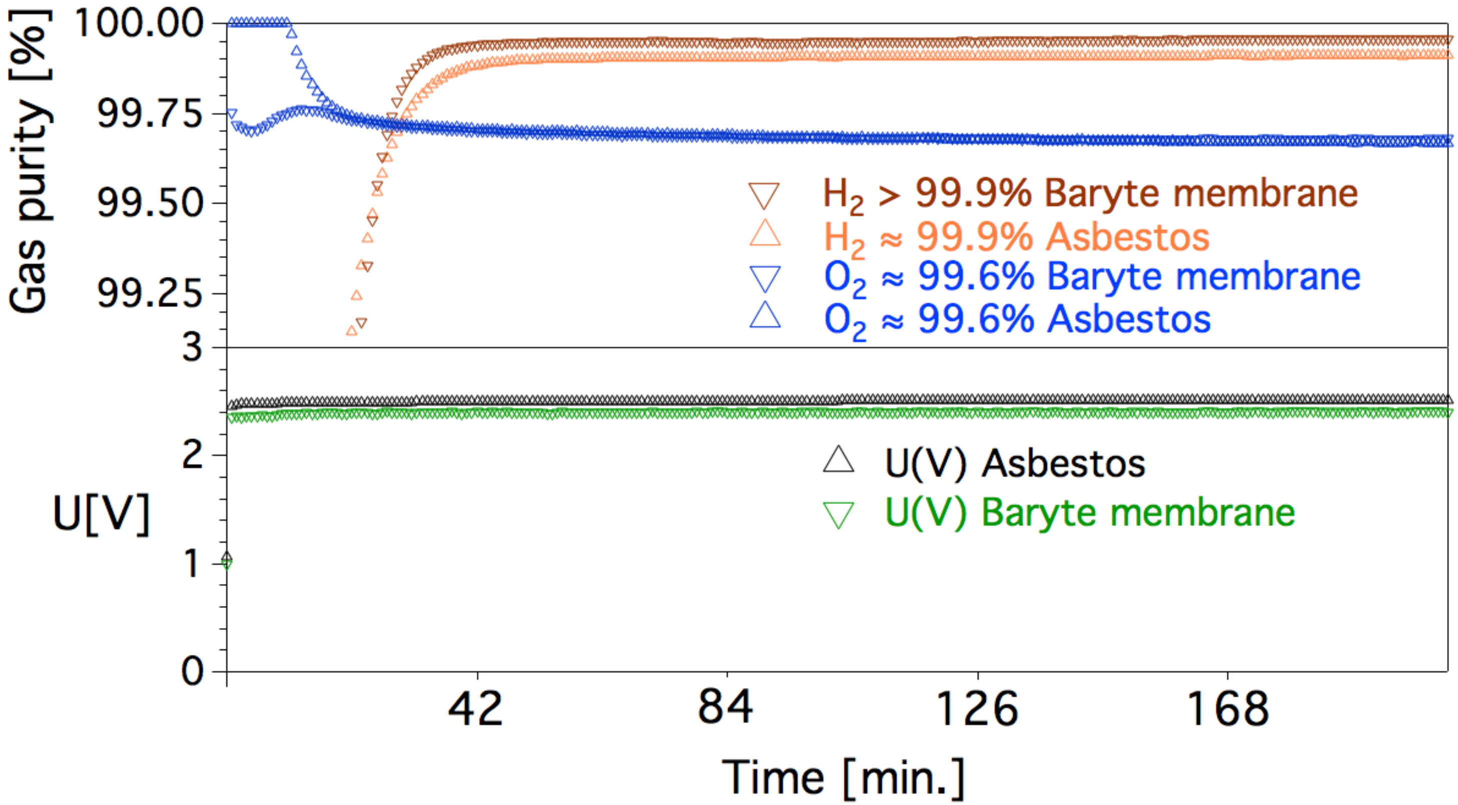
U/I characteristics of new membranes



Resistance measurement

Linear increase of current density 0-500 mA/cm² [250 mA/min]

Gas purity measurements @ ambient conditions



<u>*Long term measurement*</u>

200 mA/cm² (ca. 3,5 hours)

25°C, ambient pressure

Pump speed: 10ml/min

Recording of:

H_2 gas purity (≥ 99.9%)

O_2 gas purity (≥ 99.6%)

Voltage [V]: 2.3 - 2.4

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Conclusions

- New composite membranes have been developed
- Processing by tape casting or screen printing on PPS felts or meshes
- Electrolysis performance better than that of asbestos
- High purity of hydrogen/oxygen gases
- Upscaling of membrane manufacturing to 1.6 m diameter in preparation

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Thank you very much for your attention!

Acknowledgement

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