DEPARTMENT OF INORGANIC TECHNOLOGY

HydrogenDays 2014

ICT PRAGUE

Alkaline water electrolysis with solid polymer electrolytes

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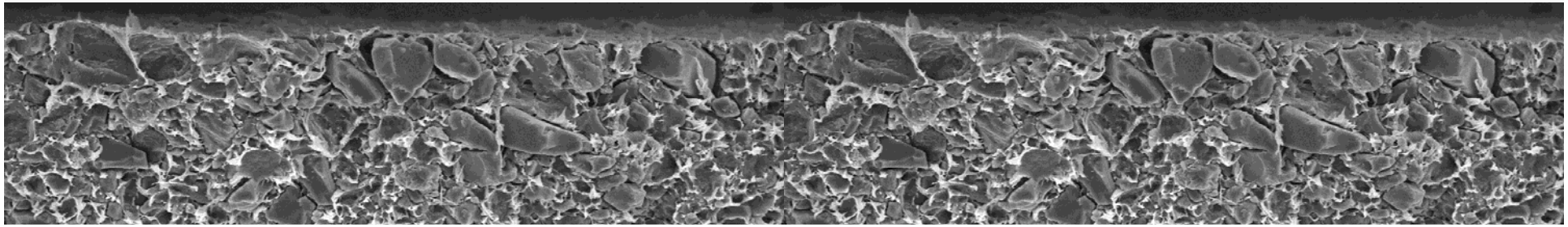
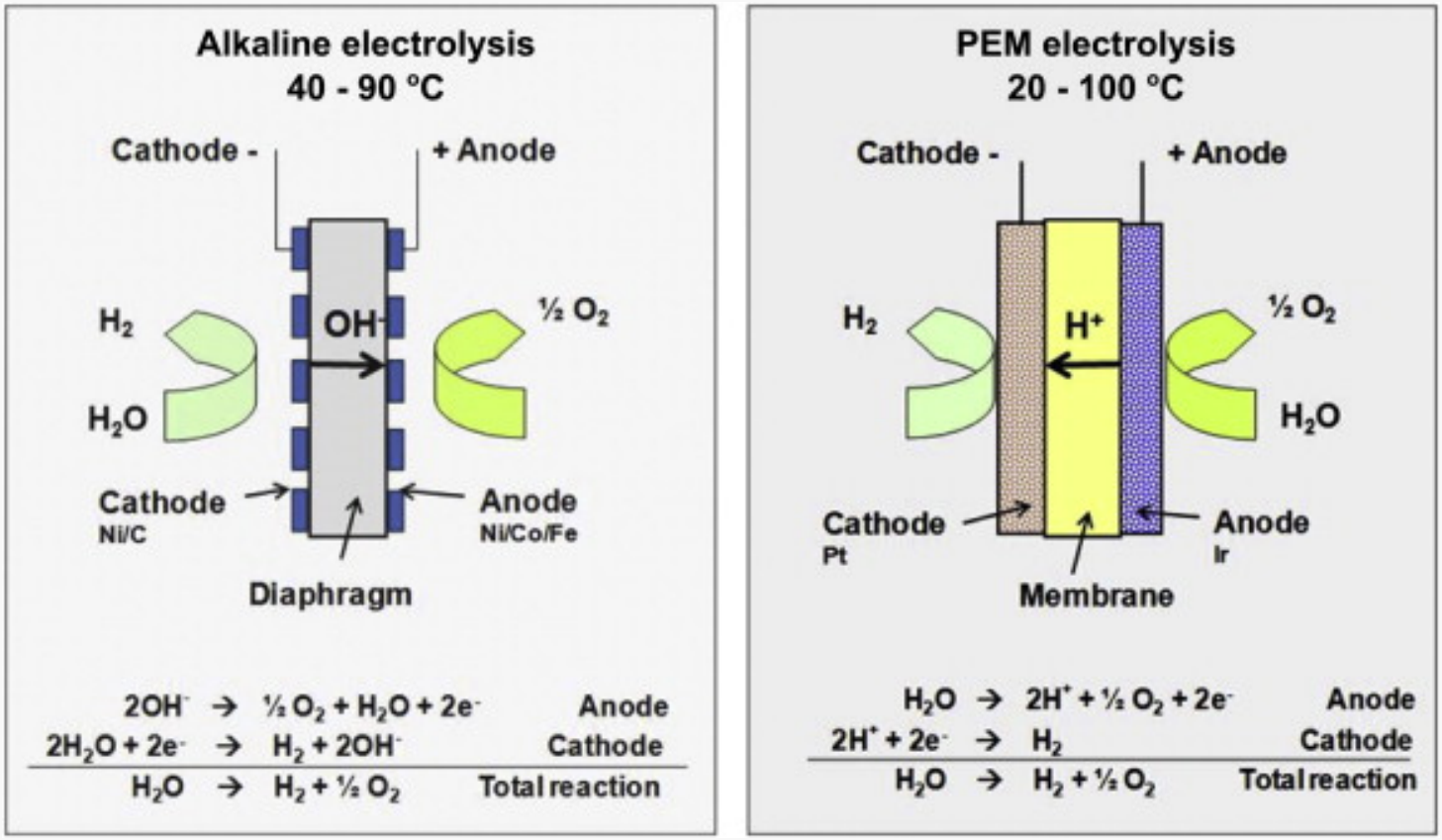


Alkaline vs. Proton Exchange Membrane water electrolysis



Carmo M, Fritz DL, Mergel J, Stolten D. A comprehensive review on PEM water electrolysis. International Journal of Hydrogen Energy. 2013;38:4901-34
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Alkaline water electrolysis

Advantages

- Well-established technology
- Robust and reliable
- No platinum metals needed
- Low investment cost

To use of advantages

Drawbacks

- Liquid electrolyte
  (up to 30 wt.% KOH)
- Inorganic diaphragm

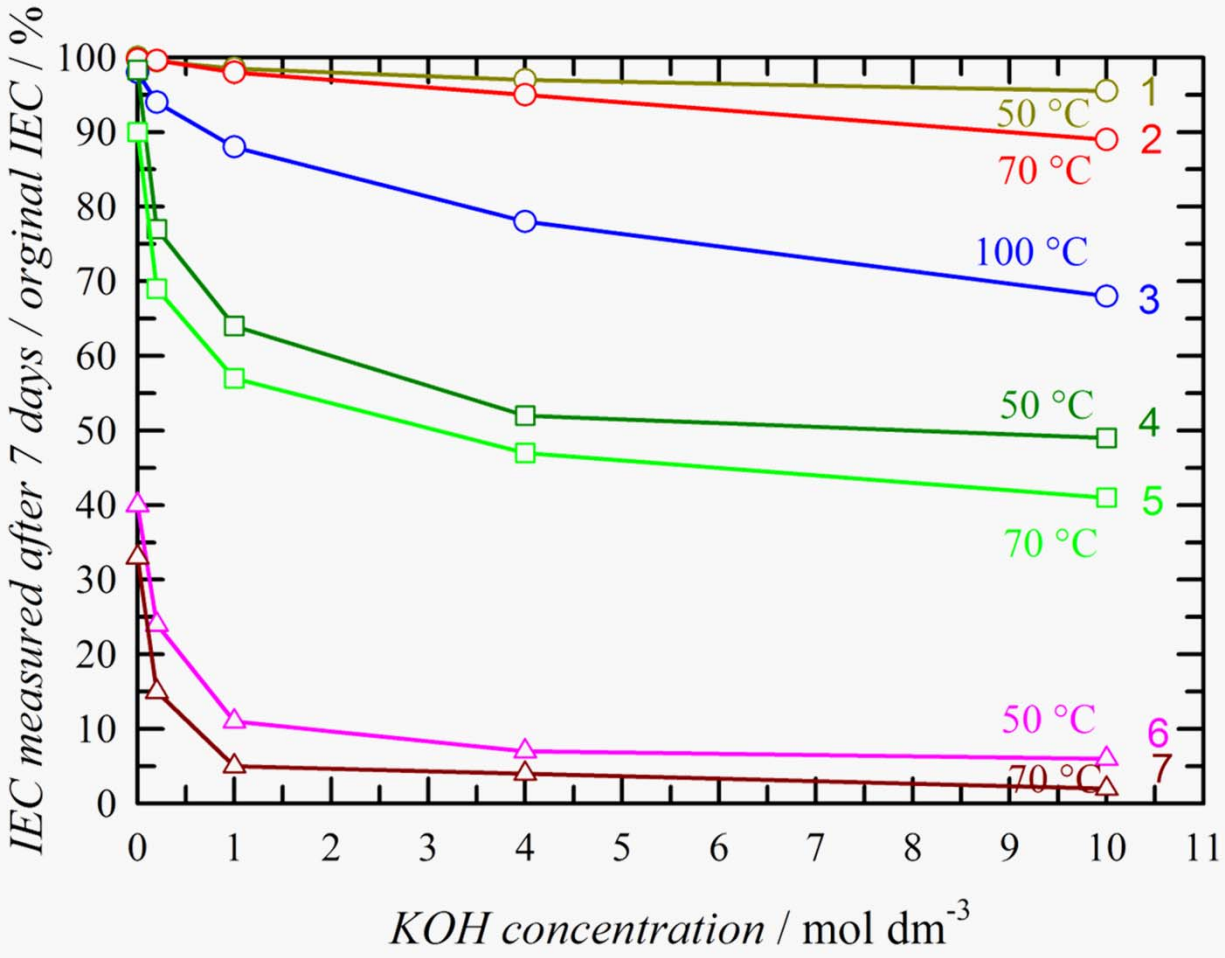
To overcome the drawbacks

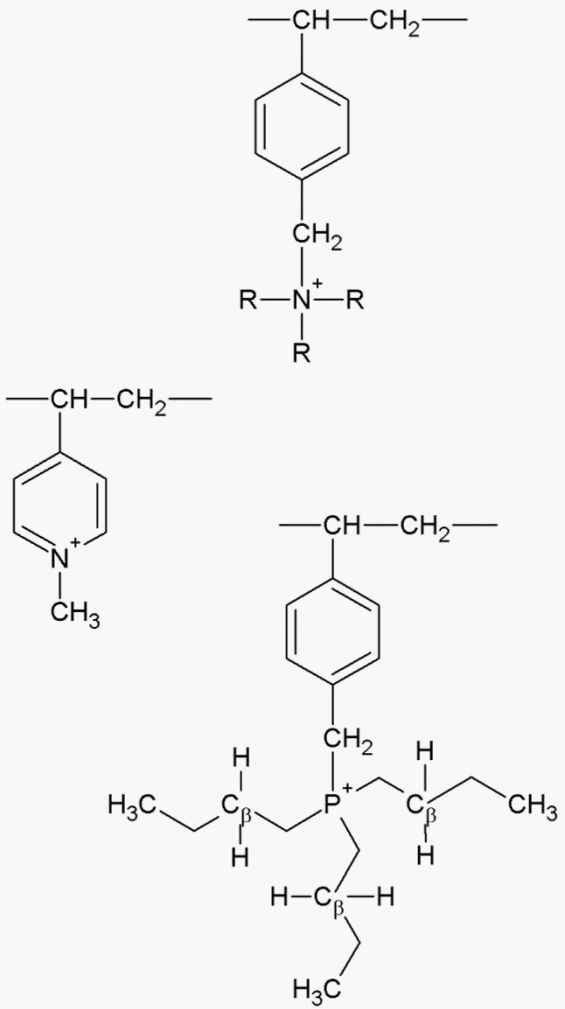
Alkaline polymer electrolyte

is desired to develop

Company	KOH conc. [wt. %]	Temperature [°C]	Pressure [bar]	Voltage [V]	Current density [A cm^{-2}]
Norsk Hydro	25	80	Atmospheric	1.75	0.175
IHT	-	85	32	1.95	0.200
De Nora	29	80	Atmospheric	1.85 – 1.95	0.150

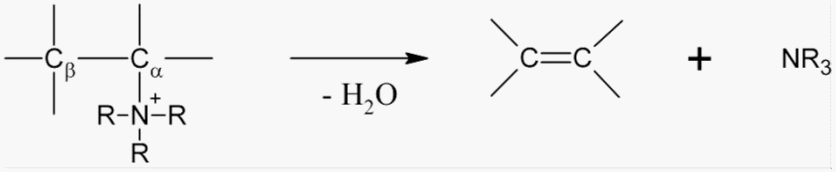
Stability of functional groups



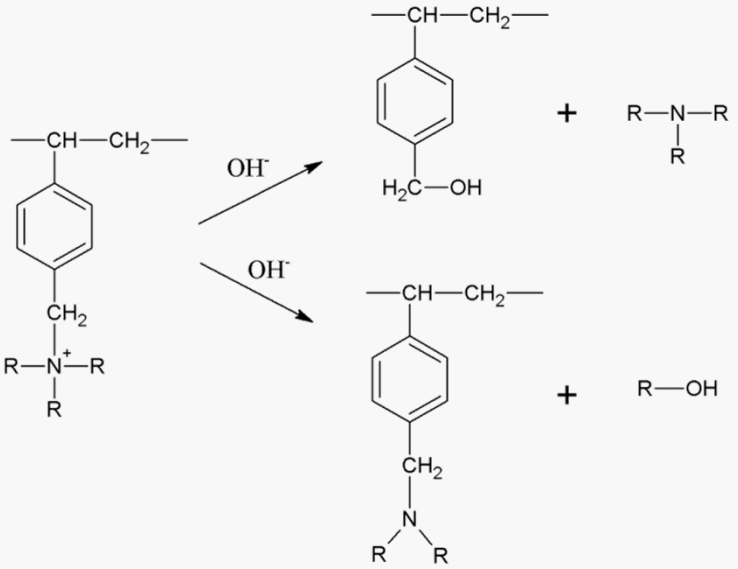


1 – 3: Functional group trimethylbenzylamonium
4 – 5: Functional group methylpiridinium
6 – 7: Functional group trimethylbenzylfosfonium

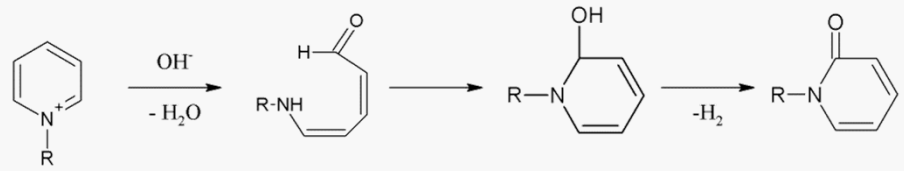
Degradation mechanisms



- Hofmann elimination



- S_N2 substitution



- Benzene ring opening

Anion exchange membranes

Heterogeneous membranes

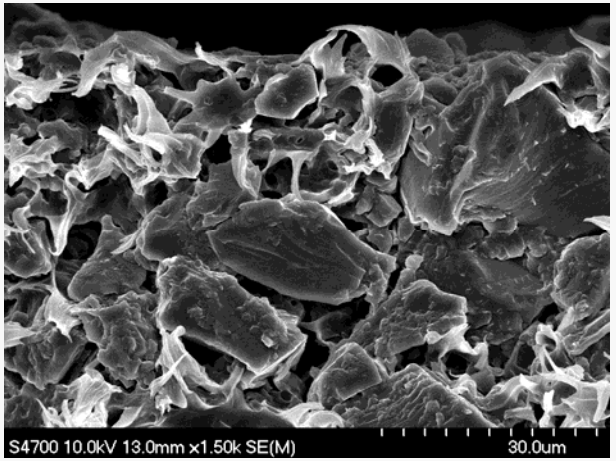
- Formed by anion exchange particles blended with a polymer binder
- Worse electrochemical properties
- Better stability

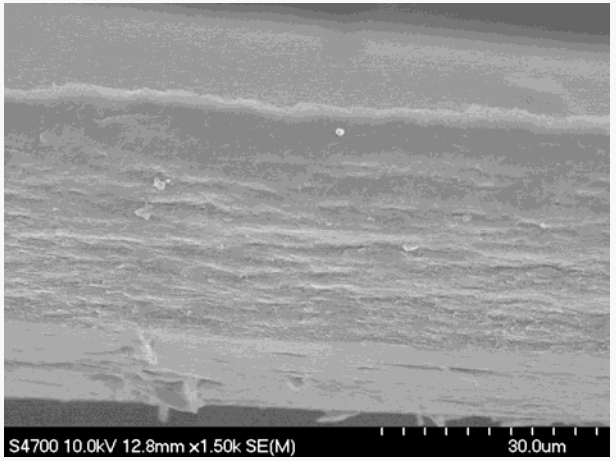
Homogeneous membranes

- Formed by one polymer/co-polymer
- Good electrochemical properties
- Lower stability

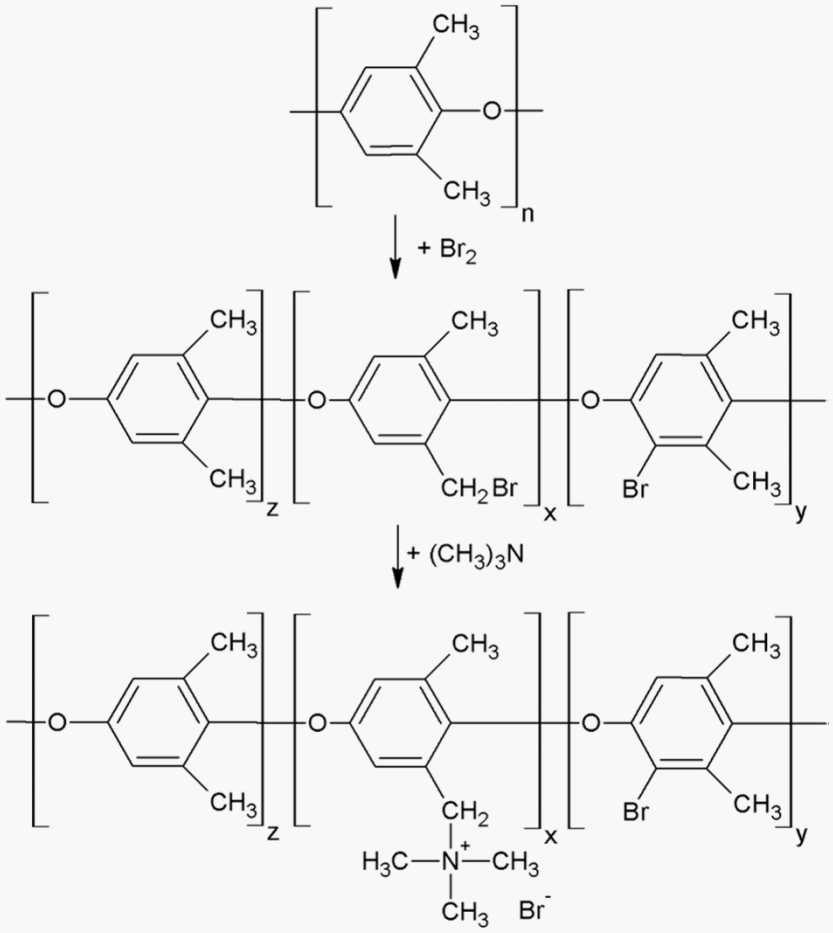
Preparation conditions

- Anion selective particles (66 wt.%) blended with polymer binder (34 wt.%) at 150 °C
- Press-moulding of the blend at 150 °C and 10 MPa
- Typical thickness 0.3 mm





Homogeneous membrane preparation



Bromation

- Bromine solution in chlorobenzene mixed with poly(phenylene oxide) (PPO)

Quaternization

- Brominated PPO immersed in trimethylamine
- Washing in HCl and water

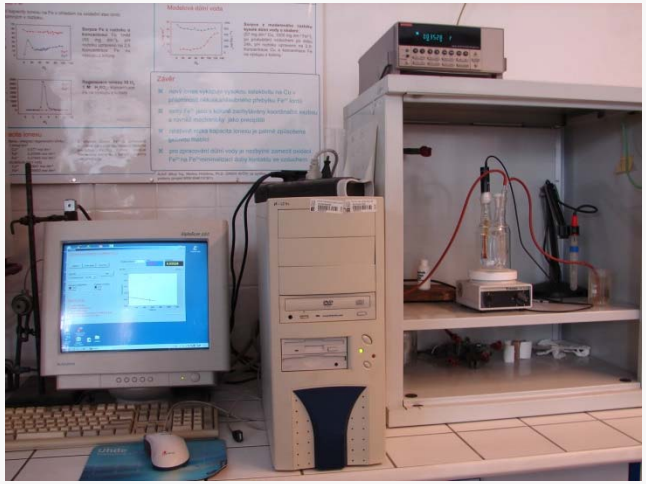
Preparation

- Casted on poly(tetrafluoroethylene) plate

Experimental methods

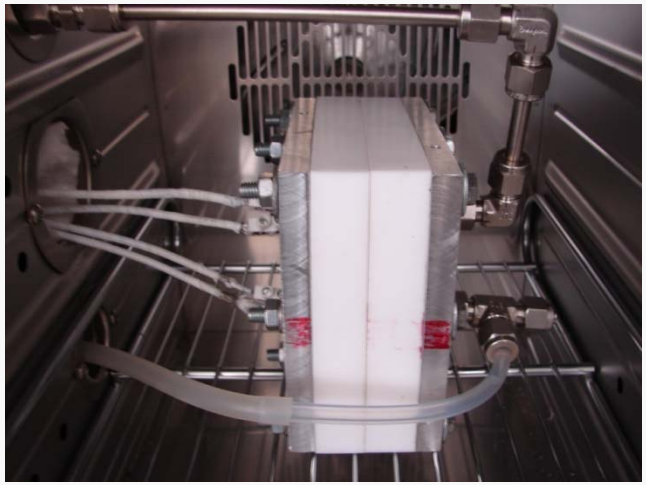
Ion Exchange Capacity

- Evaluated by potentiometry using pH glass electrode
- Digital electrometr Keithly
- pH Ross electrode
- Argon inert atmosphere
- Evaluated from OH^- ions change



Ionic Conductivity

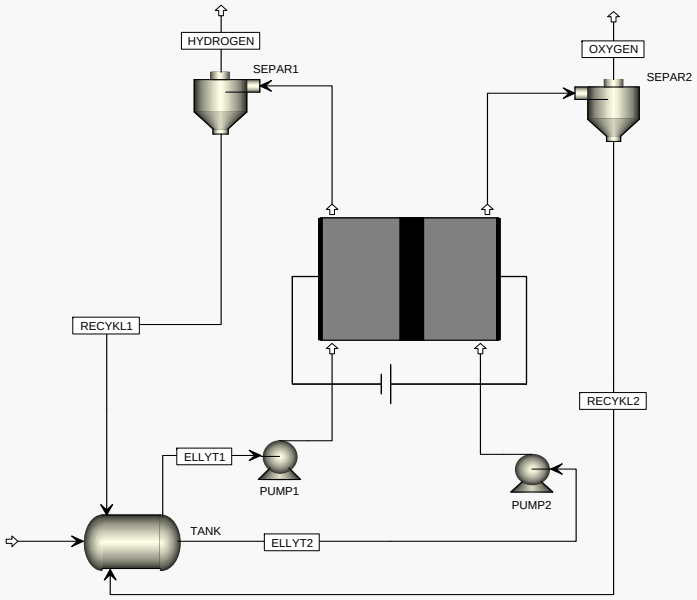
- 4-electrode arrangement
- Measured in OH^- form
- Perturbation signal amplitude: 5 mV
- Frequency range: 65 kHz – 100 Hz
- 0 V vs. OCP
- Deionized water environment

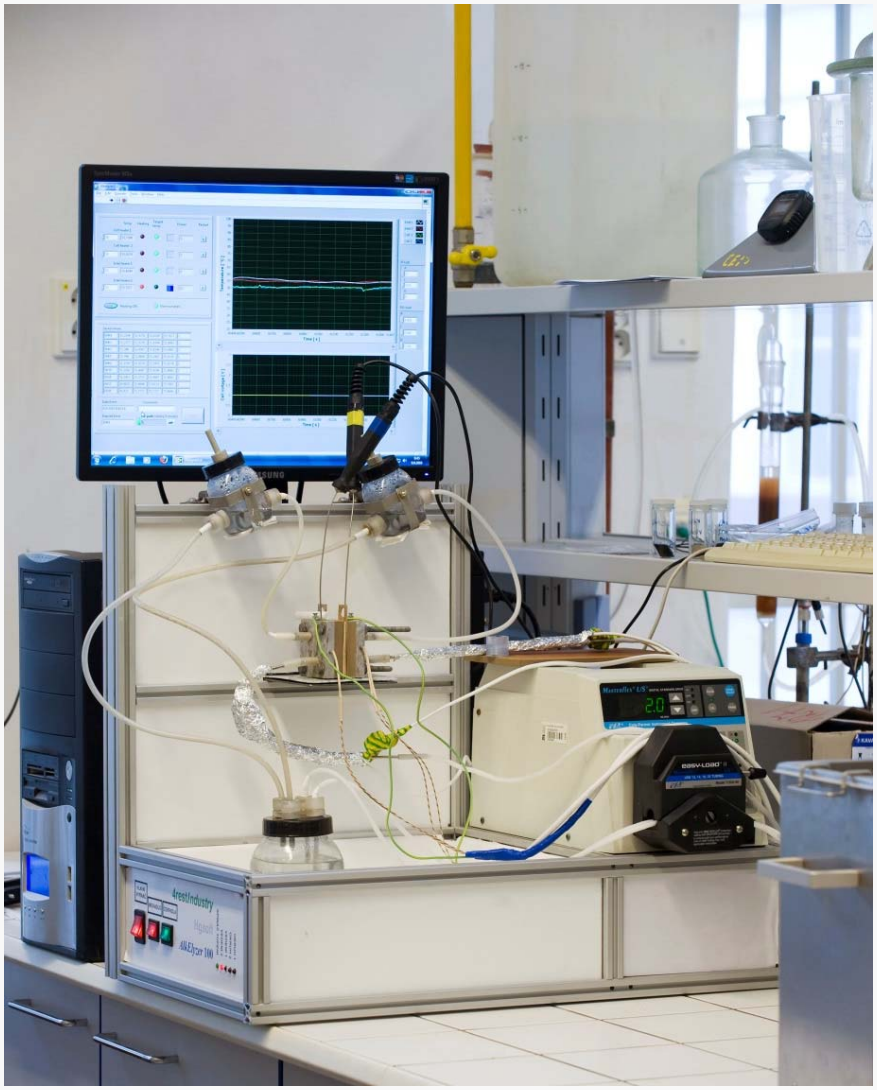


Experimental methods

Alkaline water electrolysis

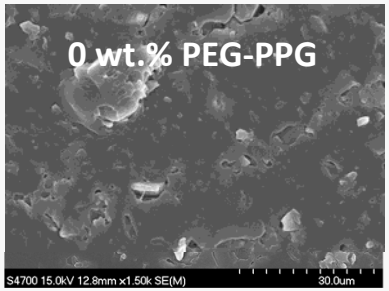
- 2-electrodes arrangement
- KOH solutions
- Flow rate: 5 ml min^{-1}
- Polymer electrolyte:
  anion selective membrane

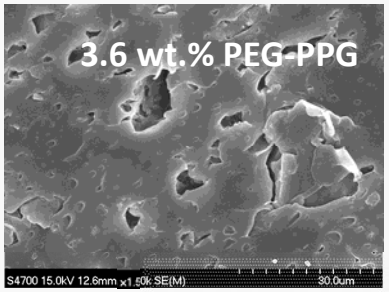


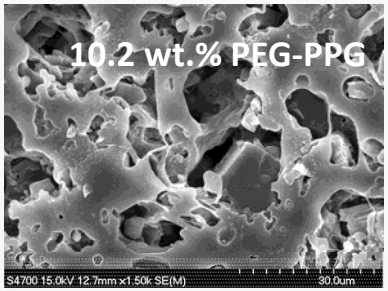


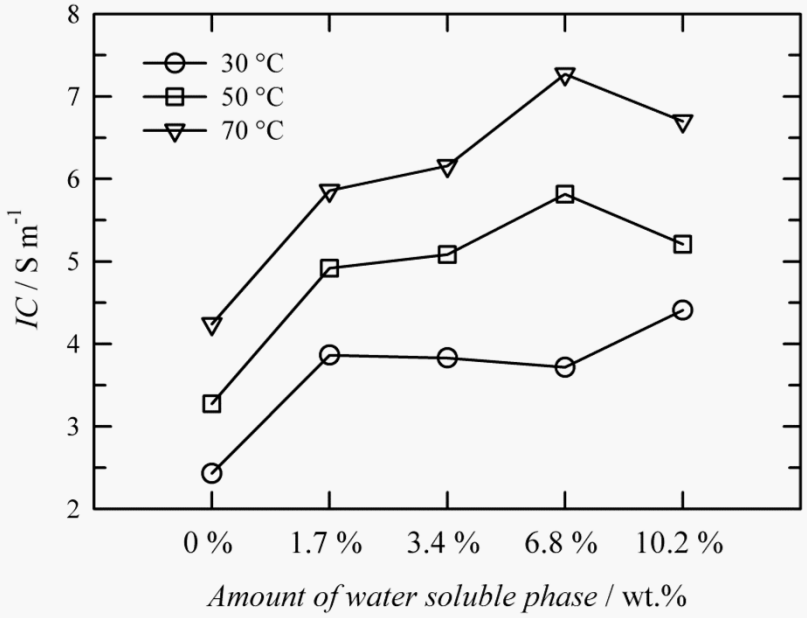
Heterogeneous membranes

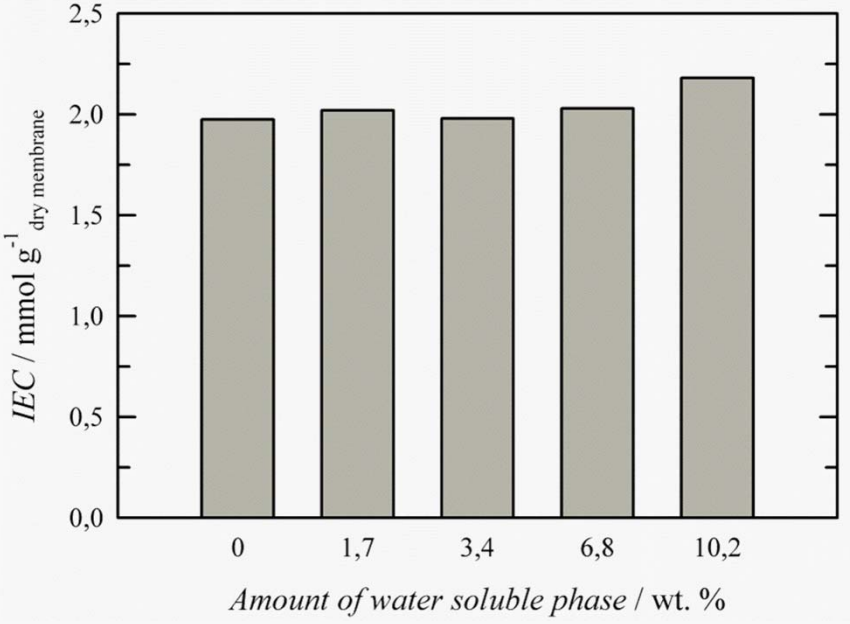
- Inert phase: Low density polyethylene (23.6 - 34 wt.%)
- Anion selective phase: Dowex Marathon A (66 wt.%)
- Water soluble phase: poly(ethylene-*ran*-propylene glycol) (0 – 10.4 wt.%)



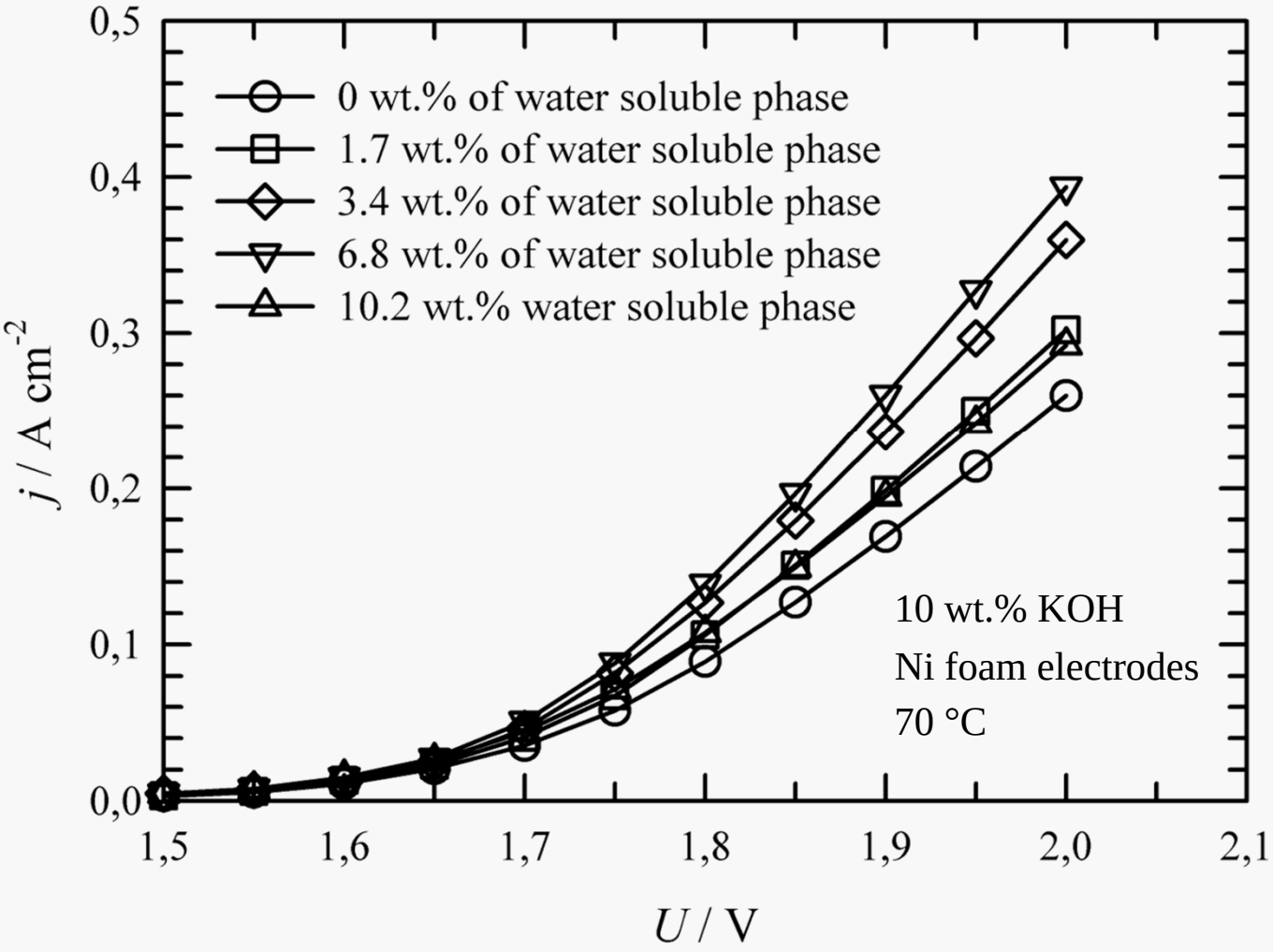




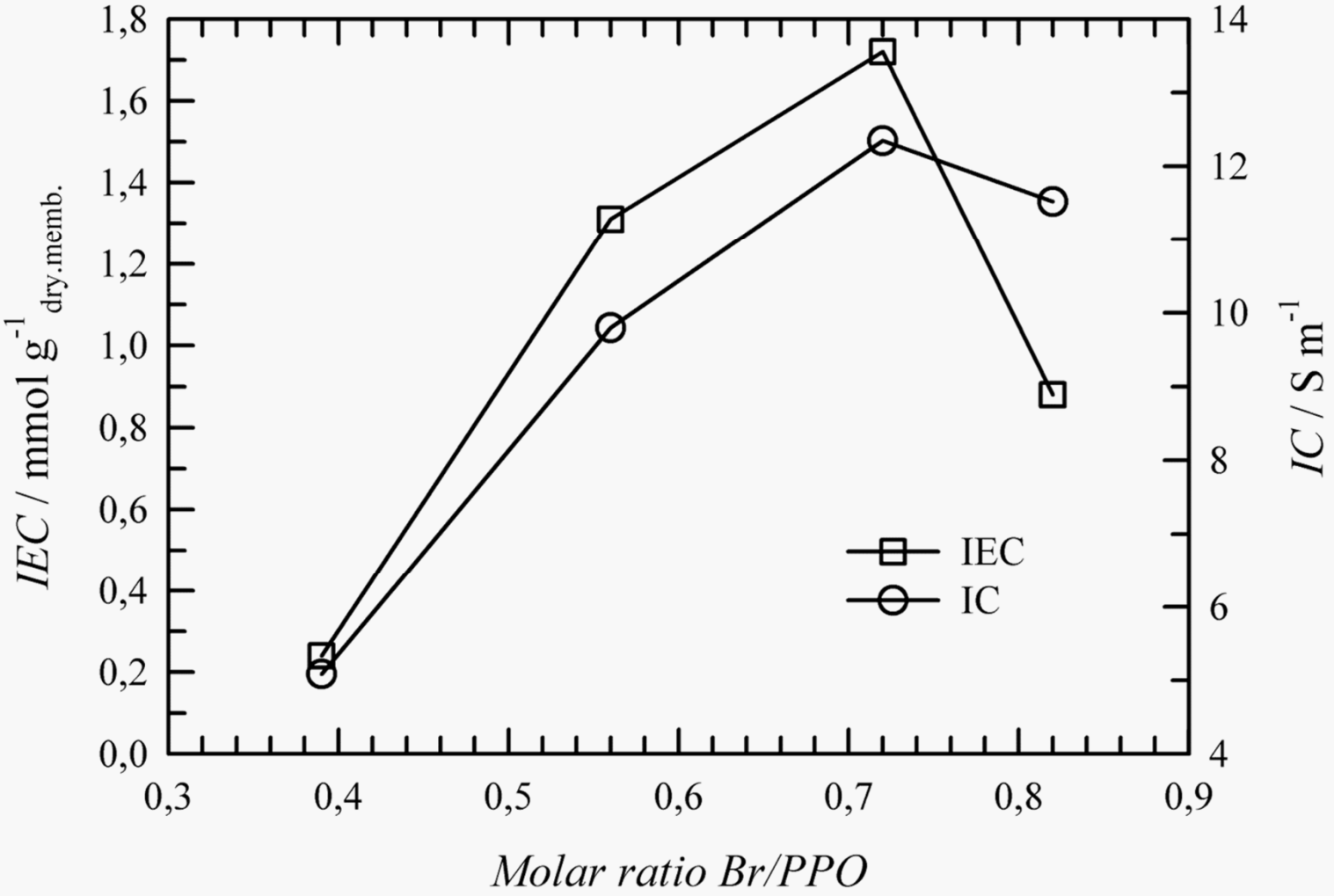




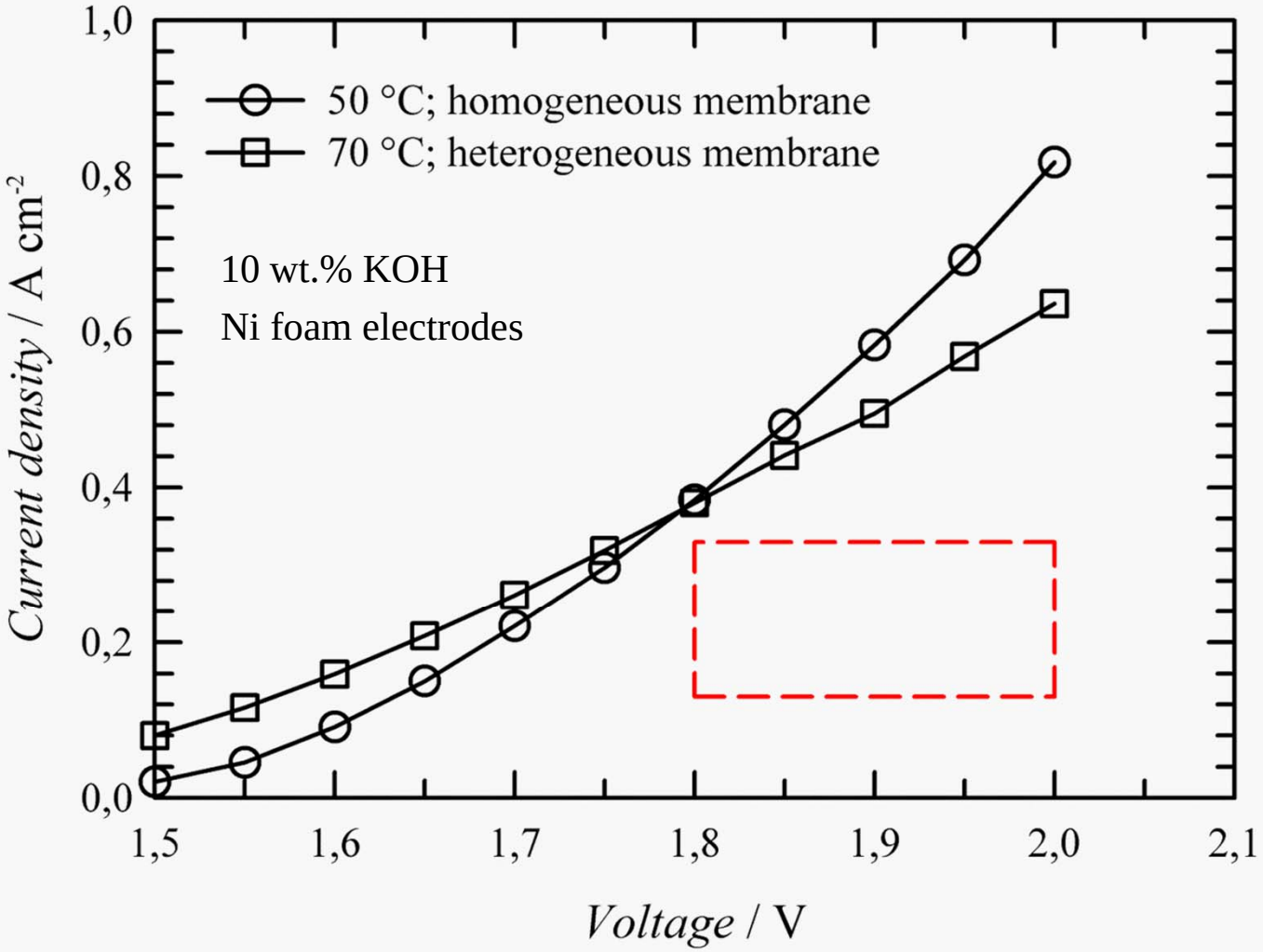
Alkaline water electrolysis



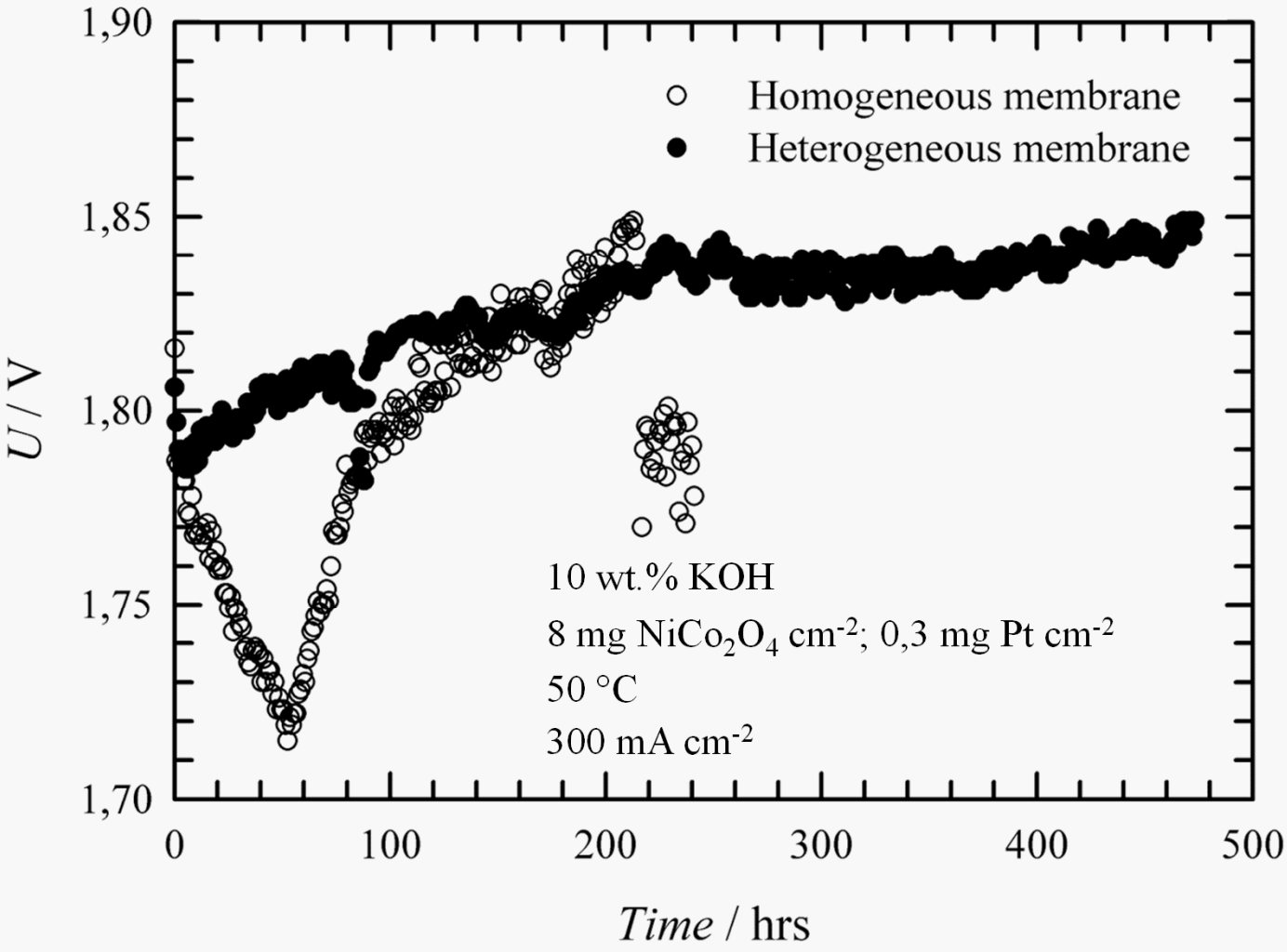
Homogeneous membrane



Alkaline water electrolysis - comparison



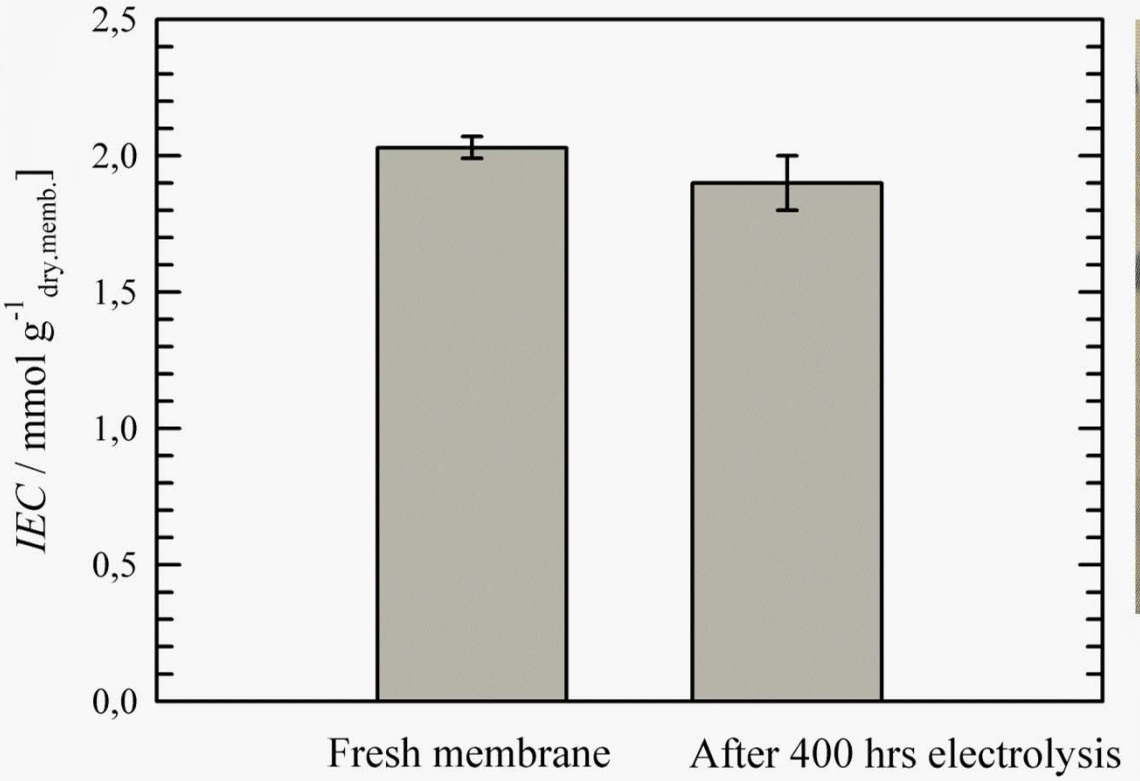
Long-term stability



Long term stability

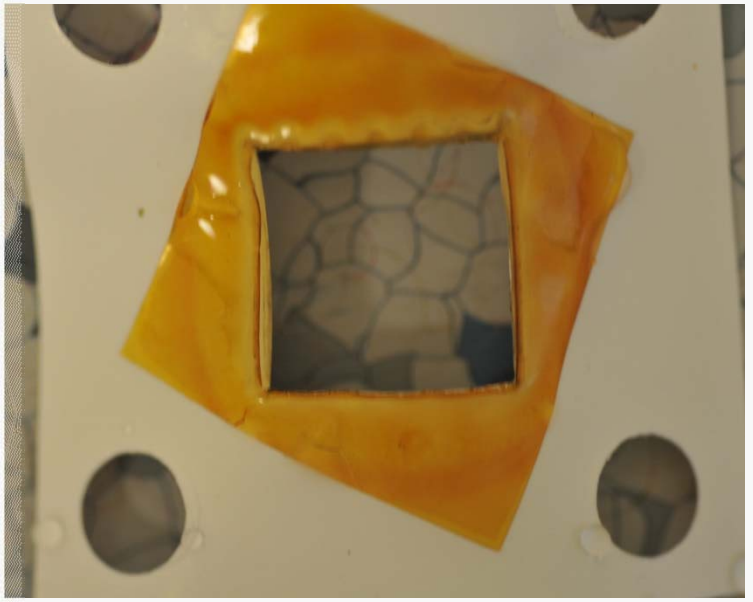
Heterogeneous membrane

- Difference of 0.02 mmol $g^{-1}_{dry\ memb.}$
- Insignificant from statistical point of view



Homogeneous membrane

- Dissolved



Conclusions

Trimethylbenzyl ammonium functional groups showed the highest chemical stability

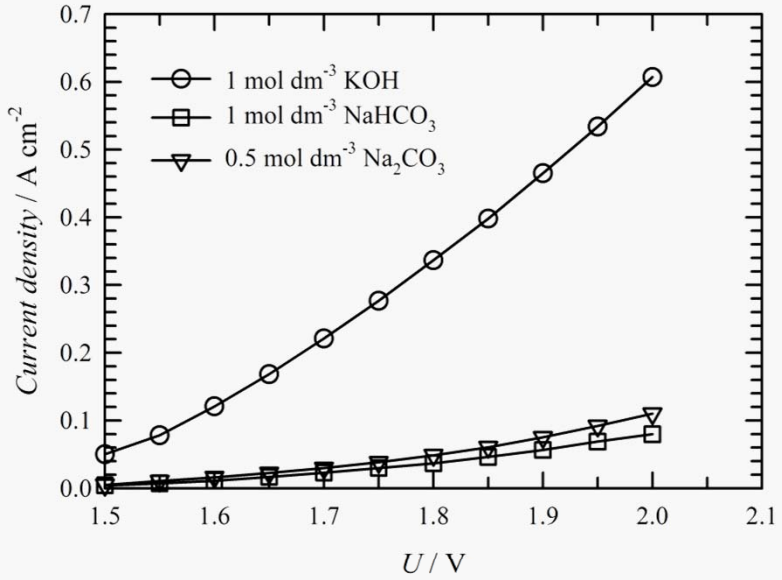
Addition of water soluble component resulted in increase of the porosity of the skin layer

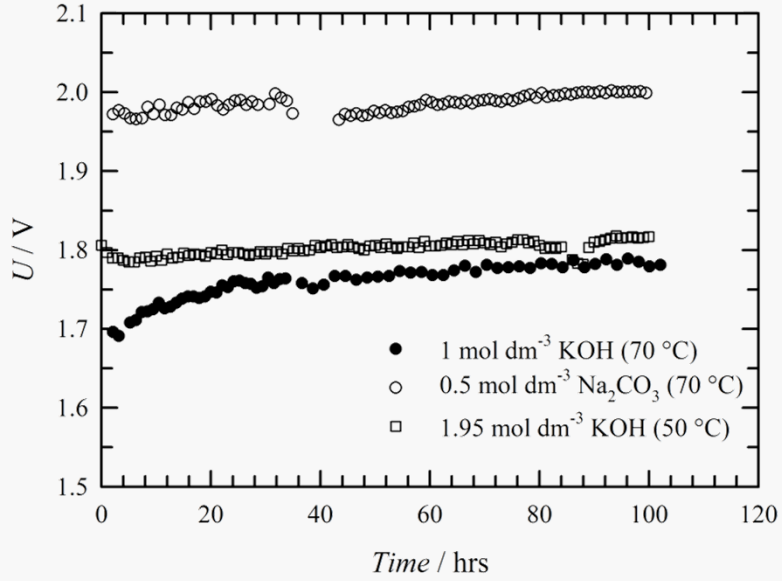
Positive influence of the increased porosity on electrochemical properties observed until 6.8 wt.% of water soluble component

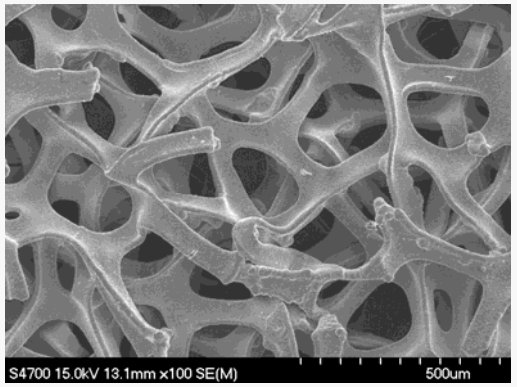
Homogeneous membrane showed better electrochemical stability

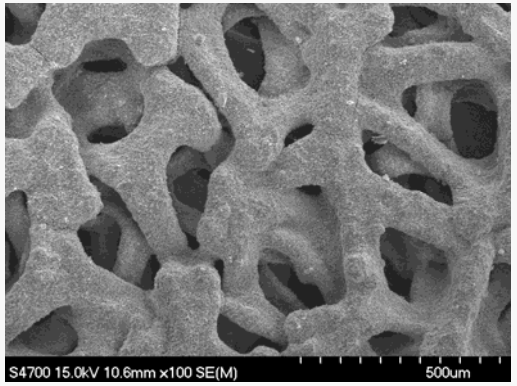
During long term operation only heterogeneous membrane showed sufficient chemical stability

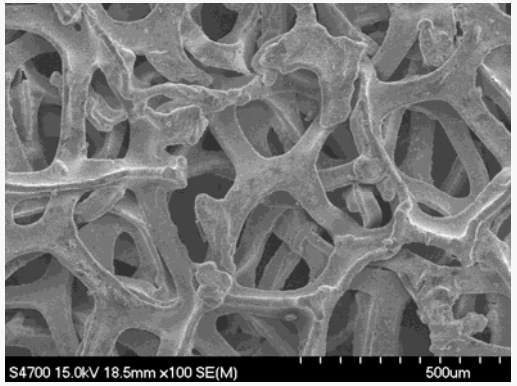
It is possible to reduce liquid electrolyte concentration due to utilization of solid polymer electrolyte


Current density / A cm-2
U / V
1 mol dm-3 KOH
1 mol dm-3 NaHCO3
0.5 mol dm-3 Na2CO3


U / V
Time / hrs
1 mol dm-3 KOH (70 °C)
0.5 mol dm-3 Na2CO3 (70 °C)
1.95 mol dm-3 KOH (50 °C)


S4700 15.0kV 13.1mm x100 SE(M)
500um


S4700 15.0kV 10.6mm x100 SE(M)
500um


S4700 15.0kV 18.5mm x100 SE(M)
500um