Aging effects of membranes during electro-chemical cycling

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FuMA-Tech GmbH

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Funktionelle Membranen und Anlagentechnologie

For You and Planet Blue. BWT BEST WATER TECHNOLOGY

- **Introduction of Fumatech as part of BWT**
- **Selection of membranes for water electrolysis: good and poor candidates**
- **Screening tools**
- **Conclusion**

Where we belong to

Brands

BWT
BEST WATER TECHNOLOGY

HOH
Best Water Technology

Cillit

CHRIST aqua

bestwater components

permo
TRAITEMENT DES EAUX

CPS Service

water + more

CENTRE PILOTE EAU DOUCE

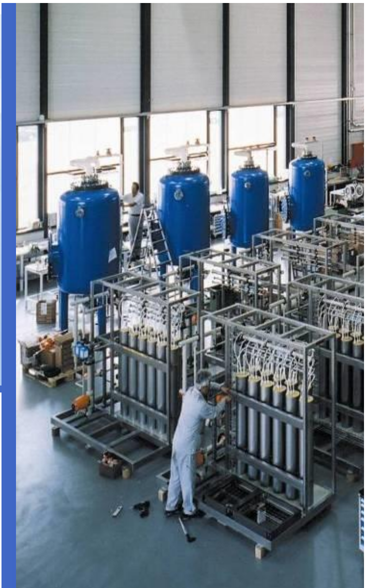
Anna®

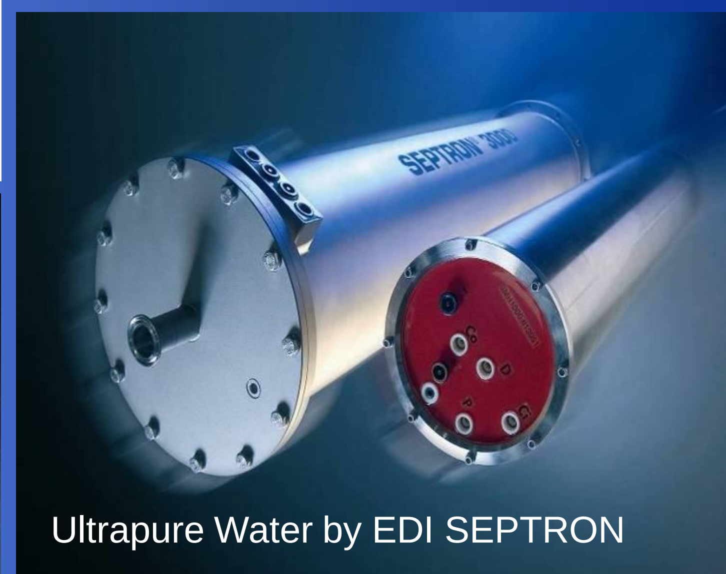
Brands

fumatech
Funktionelle Membranen und Anlagentechnologie

- fumion®
- fumapem®
- fumasep®
- fumados®
- fumatech®

BWT established products





Fuma-Water treatment modules

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- Aseptic membrane technology (RO, NF, UF)
  - Product water production for beverage industries
  - Product separation for food & life science industries
  - Sterile filtration
- Multi-chamber membrane electrolysis
- On-site generation of disinfection chemicals (HOCl)
- Electrodialysis
- Electrodialysis with bipolar membranes
- Acid dialysis

fumados®

- Dendrimer type polyacrylate based scale inhibitors

fumasep®

- Ion-exchange membranes
  - Micro-heterogeneus anion- and cation exchange membranes
  - IEx-membranes for electrodialysis and donnan dialysis
  - Bipolar membranes
  - Oxidation stable and chlorine tolerant anion-exchange membranes
  - Membranes for capacitive electrodeionisation
  - Membranes for RED energy production
  - Membranes for sea water desalination
- Perfluorinated membranes for electrolysis
- Membrane humidifiers
- Flat sheet membranes for ERV applications

Membranes for Energy applications

LTPEM (50-90 °C)
F-940-rfs
SPS-membranes

Redox-Flow-Batteries
FAP-membranes
F-930-rfd
Hybrid membranes

MTPEM (90-120 °C)
FS-720-rfs
Composit membranes
Humidification membrane

AEM (50-75 °C)
FAA-3

HTPEM (150-180 °C)
A-membrane

Alk. Water elektrolysis
FAAM-75-rf
FAAM-15

DMFC (50-80 °C)
F-1850
E-730

PEM-water electrolysis
Membranes: F-9100rf,
F-9120rf, F-9180rf
CCM: fumea EF-10

Membrane and CCM for PEMWE and measures for estimation of their durability

Requirements for PEMWE-Membrane

1) **Low resistance: what is optimal EW and thickness?**
2) **High mechanical durability: reinforcement yes or not?**
3) **High chemical durability: Addition of other substances than PFSA necessary?**
4) **Low Hydrogen permeation: Addition of Pt to Anode necessary?**
5) **Easy coatability and assembly into cell: a lot depending on CCM-production procedure and cell's design**
6) **Reasonable price: a limited CO2-footprint of PFSA material and Pt/Ir production is given = given price even for large volumes**
7) **Durability: what kind of protocol and what does it reflect?**

Measures for the investigation

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Ex-situ and in-situ charecterisation:

Conductivity, break-in period

Performance

Hydrogen permeation at various T, p

Estimation of F-ion release

Ex-situ and in-situ accelerated stress protocols:

Ex-situ: Pressure cycling (simulated by He/N2)

In-situ: Load cycling = how the profile should look like in order to observe membrane-related and catalyst-related impact?

Typical performance of WE membranes

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Membrane	Resistance / $mOhm.cm^2$	Thickness / µm	Dim. Swelling / %	U @ 2 A/cm2 @ 80 °C
F-1075-PK	90	70-75	< 1	1,74 V
F-10100-PK	125	95-100	< 2	1,80 V
F-10120-PK	155	115-120	< 2	1,85 V
F-10140-PF	190	135-140	< 3	1,90 V
F-10180-PTFE	240	170-175	< 5	2,05 V
FS-990PK	85	90-95	< 5	1,71 V

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A good example: Break-in Procedure SSC-PFSA

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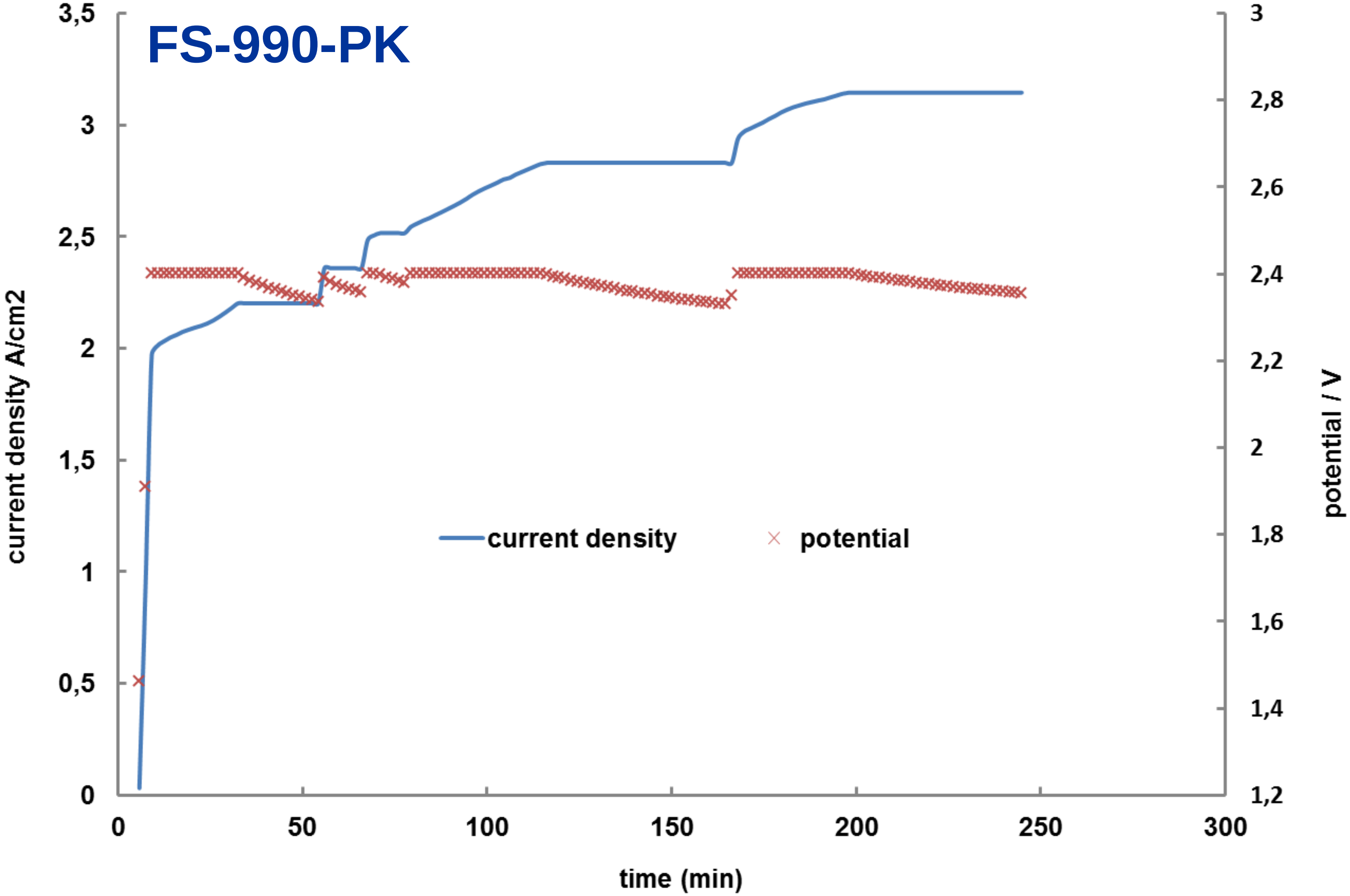
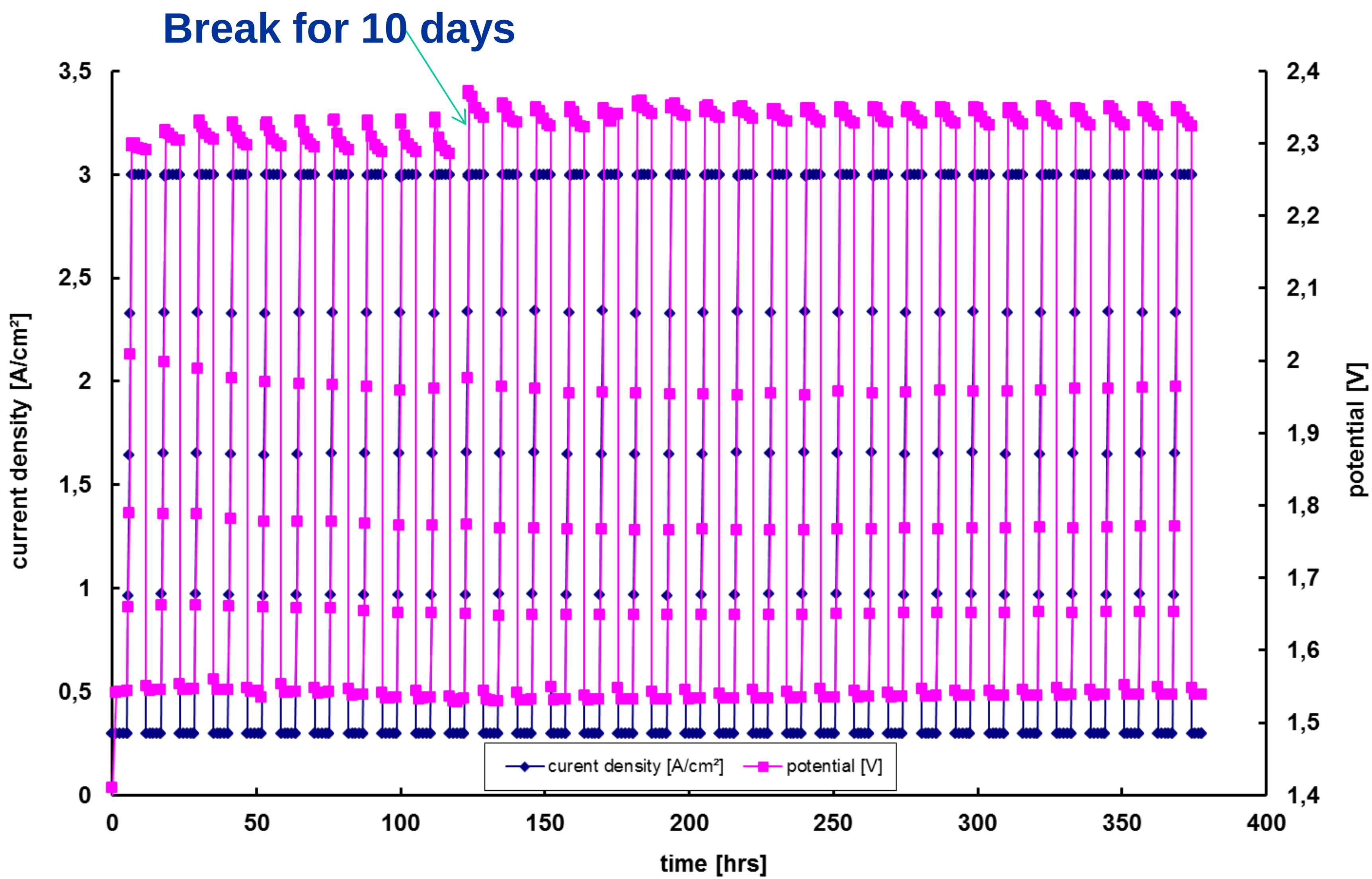


Break-in period: within 1 hr the CCM can be well operated, full activation within ca 4 hrs

A good example: F-10100PK



F- emission: randomly measured, always below detection limit

Durability of fumea® EF-10

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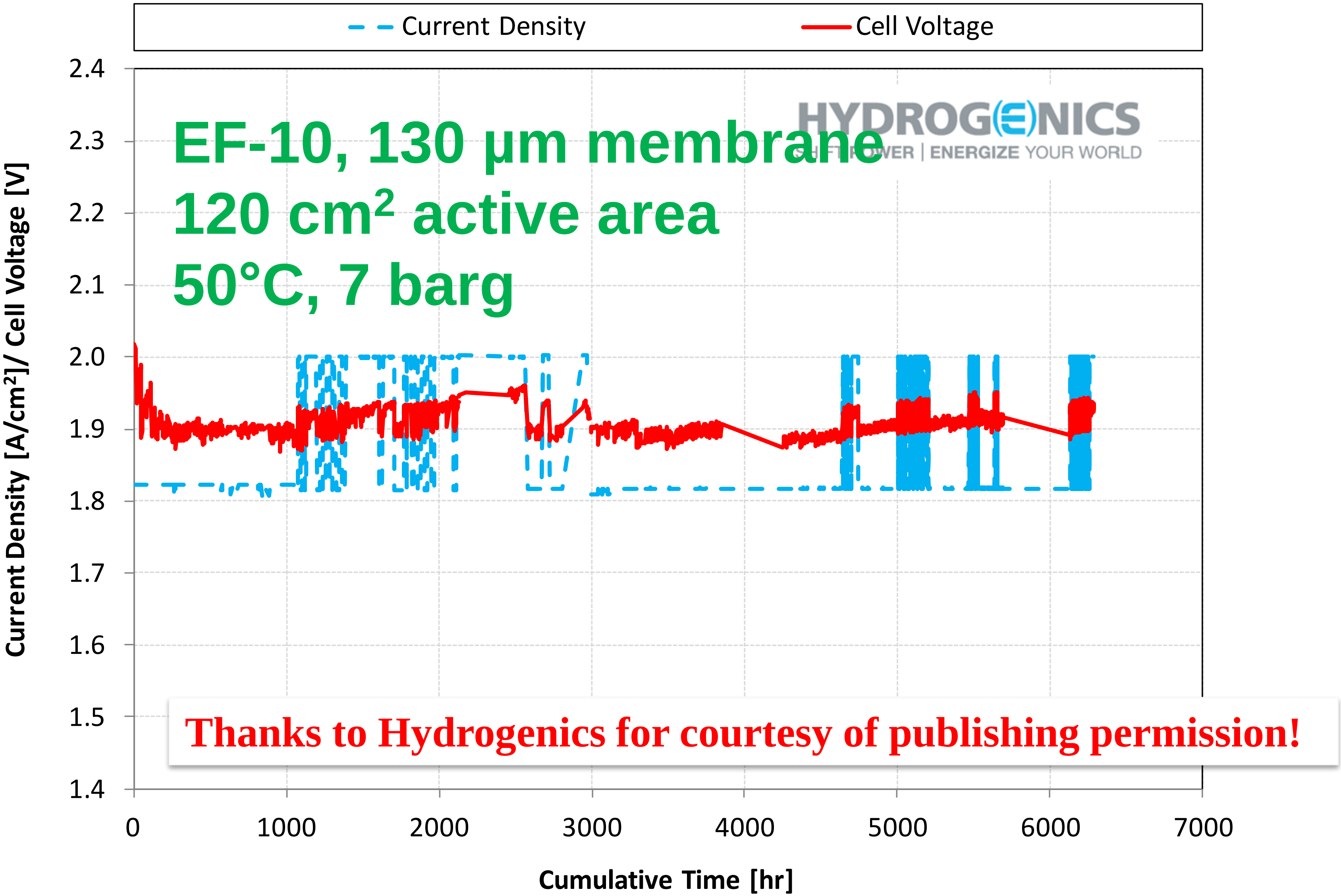

Our experiences say that

- If the membrane is „thick enough“ and without defects,
- If the catalyst coating is well homogeneous and symmetrical,
- If the assembly has been done well,
- If the Ti plate is fine and
- If no water contamination happens,

Then it is difficullt to find reason of some degradation and the least on the membrane

Troublesome candidates

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Membrane	Descrip.	Thickness (µm)	Resistance (mOhm.cm2)	Price	Gas purity	Critical point
FZP-990PK	Reinforced membrane with inorganic part ZrP	90-95	130 -> 350 (after 300 hrs)	OK	Perfect	ZrP not stable during load cycling at high potential
F-9240 PTFE	Thick reinforced membrane of low EW	230-245	220	Way too high	Depending on cell design	Swelling in Z-direction makes the cross-over cell-dependend
F-10130PK/rf	Double reinforc.	130-135	790 -> 180 (after about 700 hrs)	Material-wise OK, production-wise too high	Good	Extrem slow break-in, not clear durability of the interface

Case 1: ZrP-membrane

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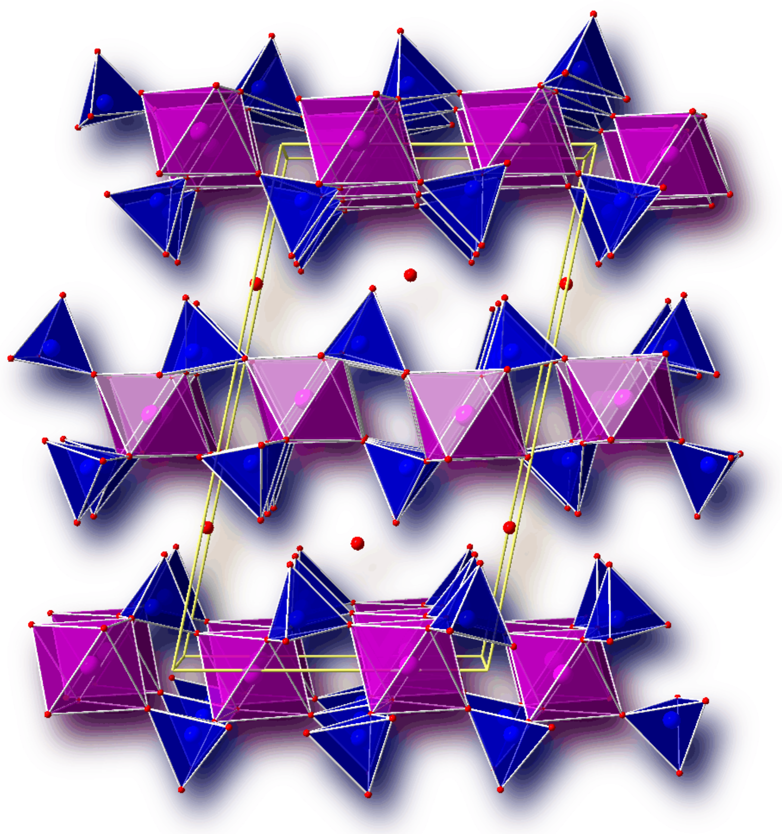
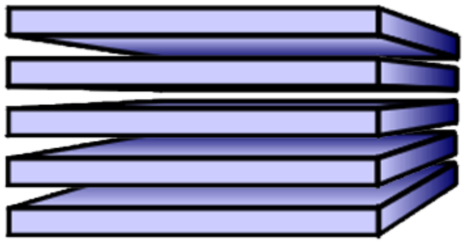
α-Zirconium phosphate $Zr(HPO_4)_2 \cdot H_2O$



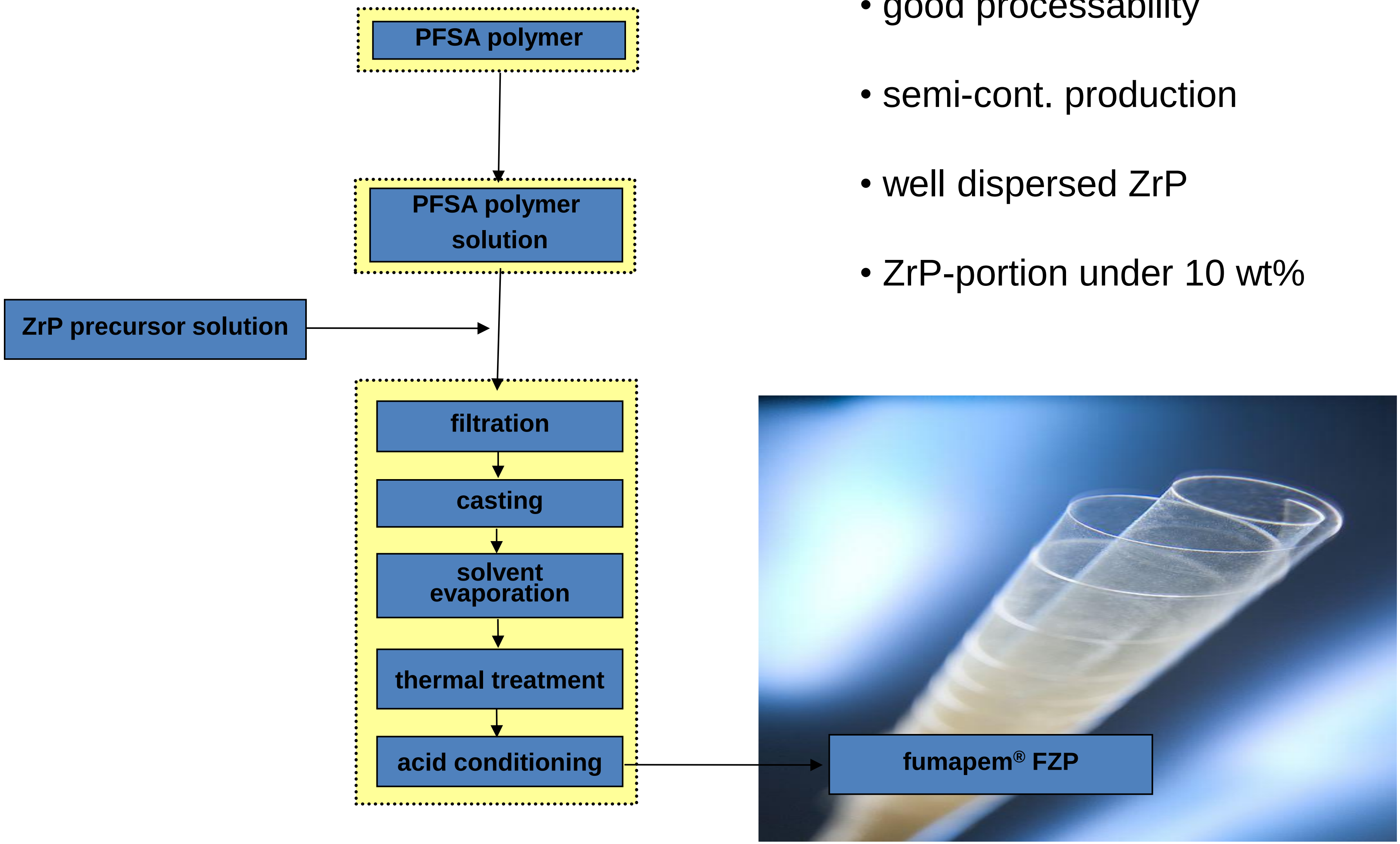
- insoluble in water
- acidic sites
- low conductivity
- layered structure



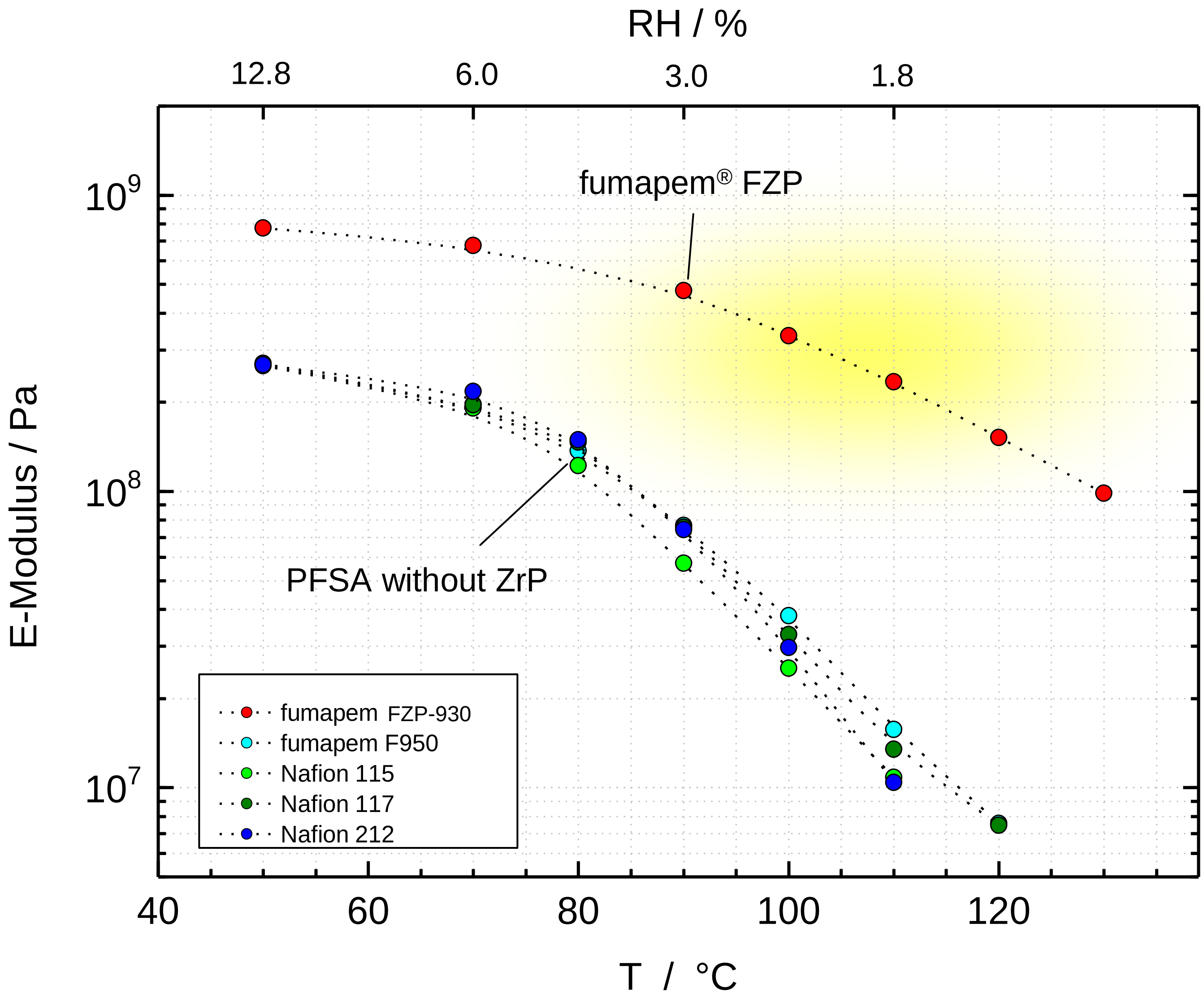
Prof. Alberti (University of Perugia)

Production of fumapem® FZP

- good processability
- semi-cont. production
- well dispersed ZrP
- ZrP-portion under 10 wt%



Mechanical properties vs. temperature



DMA measurement was carried out on a Tritec 2000 analyser (Triton) at a frequency = 1 Hz and a displacement = 0.02 mm.

Aging profile FZP-990 PK

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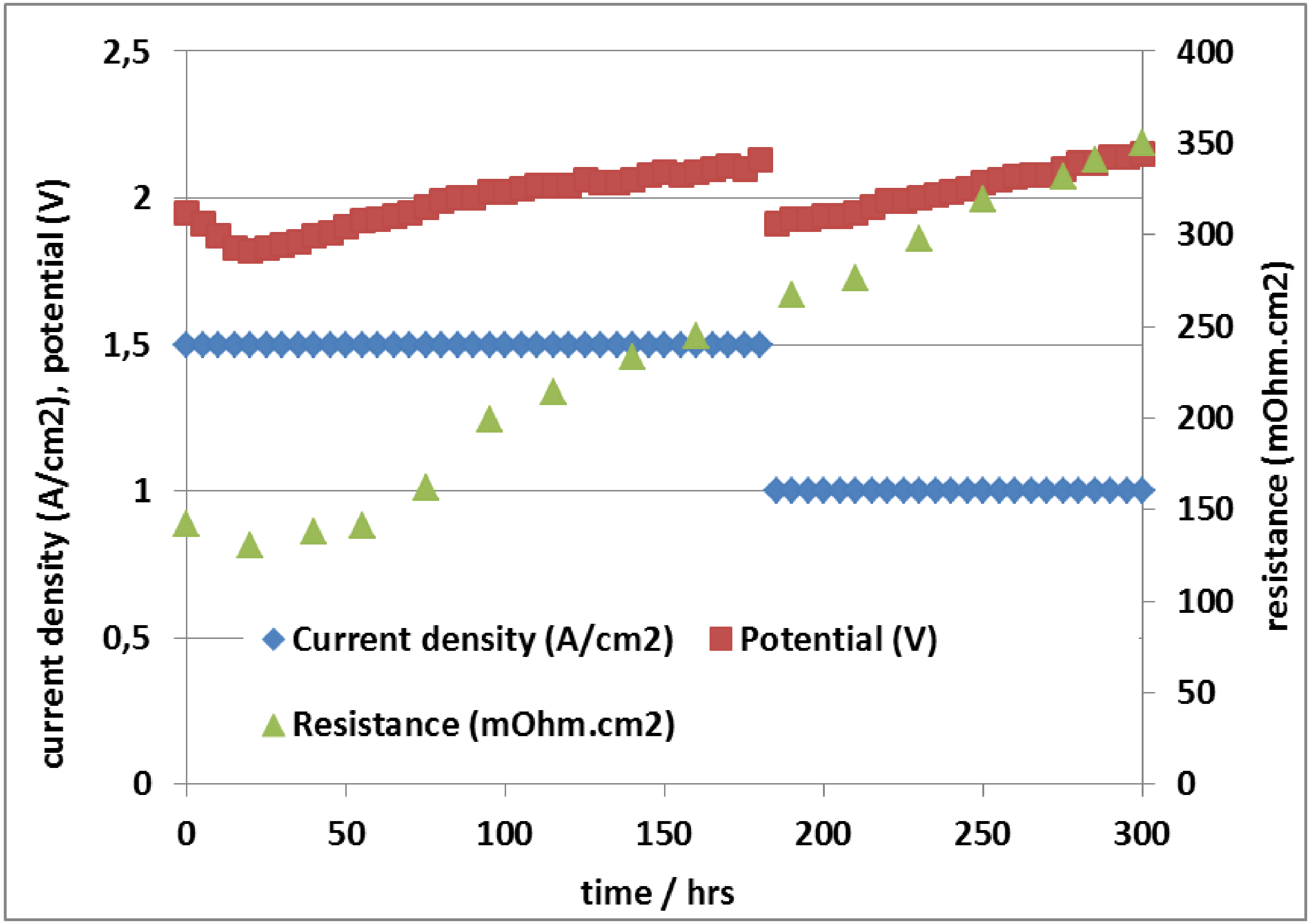

Why the resistance does grow and does it have something to do with ZrP phase?

Load cycling profile of FZP-990PK

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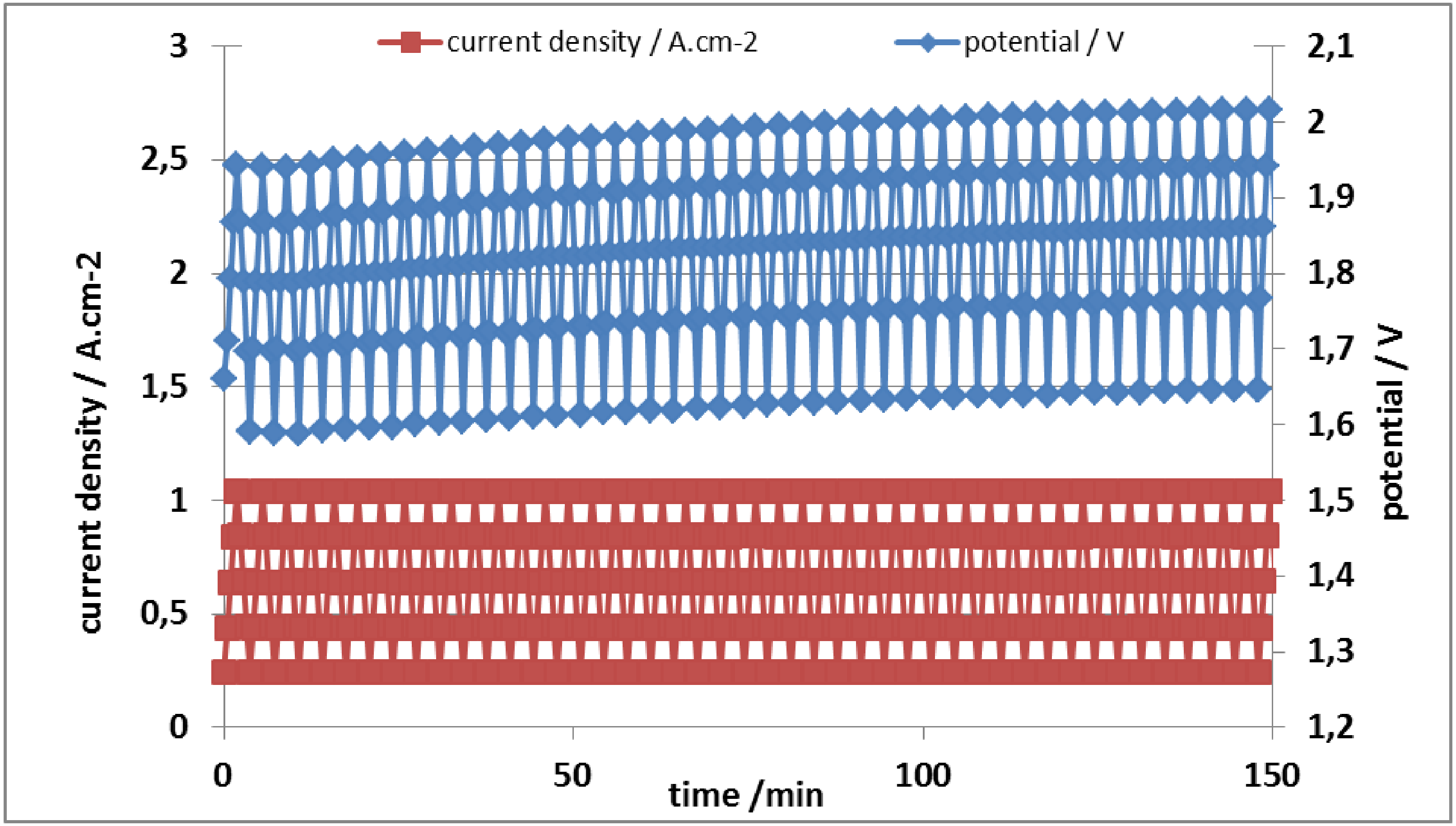
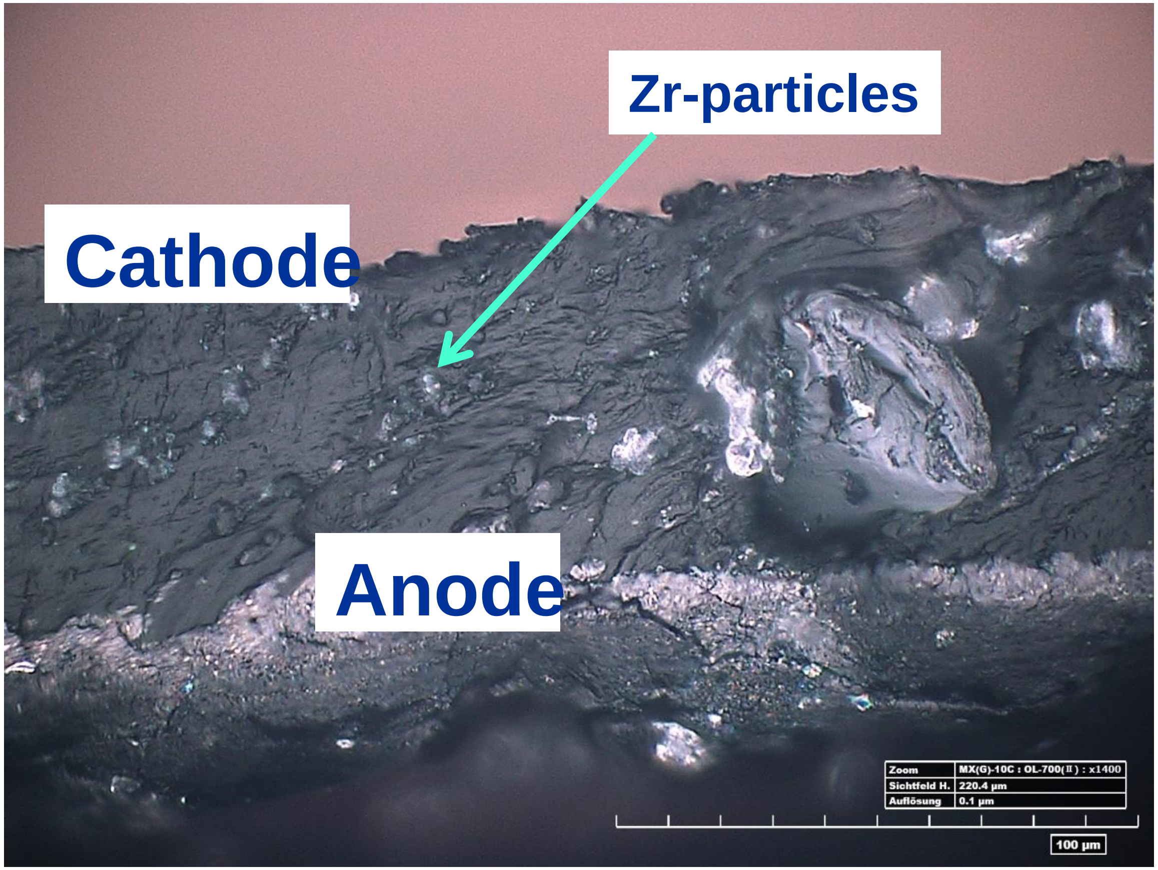
80 °C, atm. pressure



Constant shift of potential at all current densities: a similar picture has been received within 2,5 hrs as constand load over ca 25 hrs

SEM-EDX analysis: Phase separation, migration and precipitation of ZrO2



Cross-section measured by 3-D microscope

Case 2: F-9240PTFE

Facts:

Thick reinforced membranes, LSC-PFSA, EW 900

Not successful membrane at two customers and in one EU-project (NEXPEL)

Very much welcomed membrane at three customers, long-term field durability data at one of them quite OK

One of the most difficult riddles for WE-team of Fumatech until the time of Ekolyser project (national German project)

Durability of fumea® EF-40 – stack data

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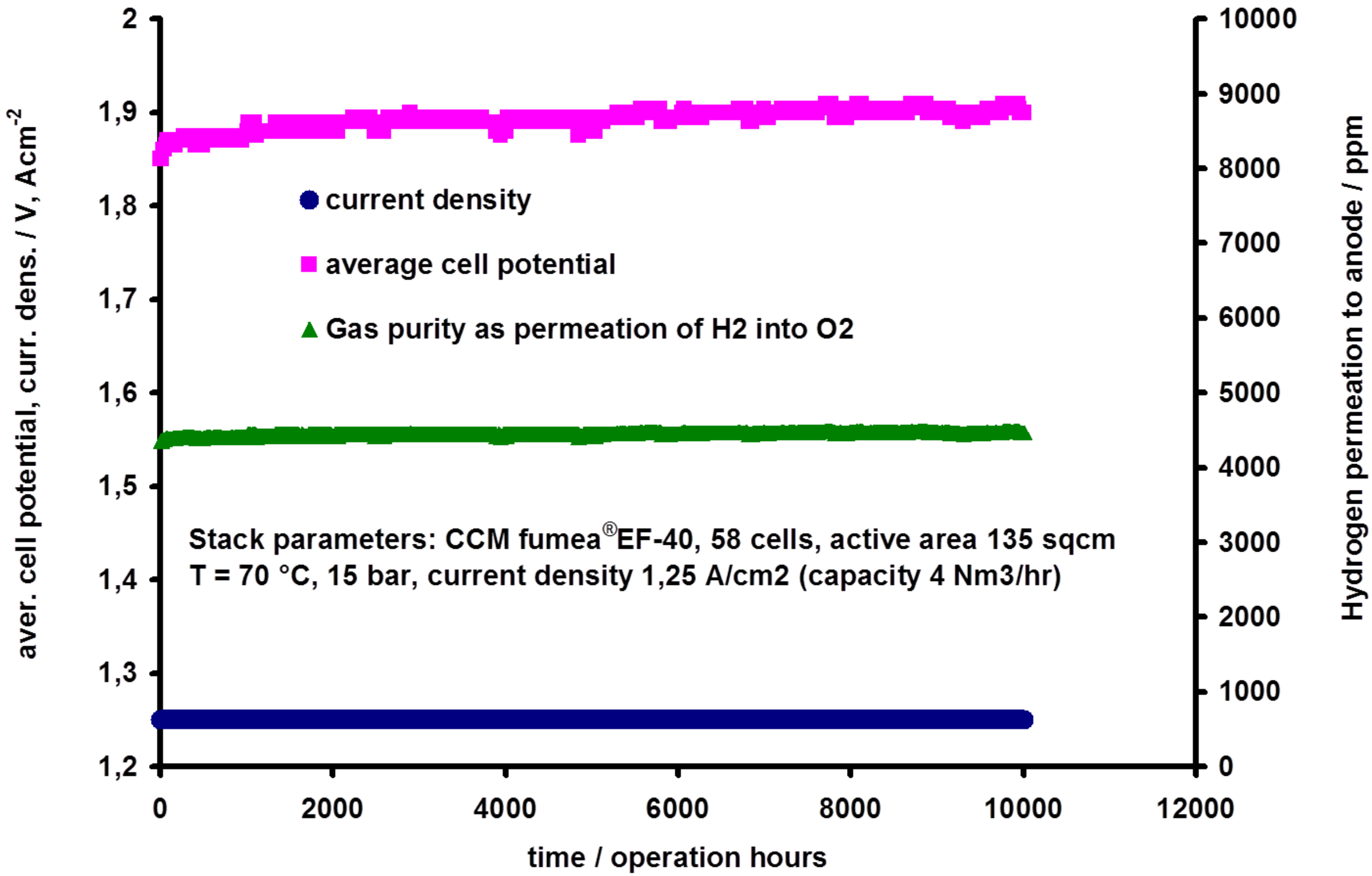
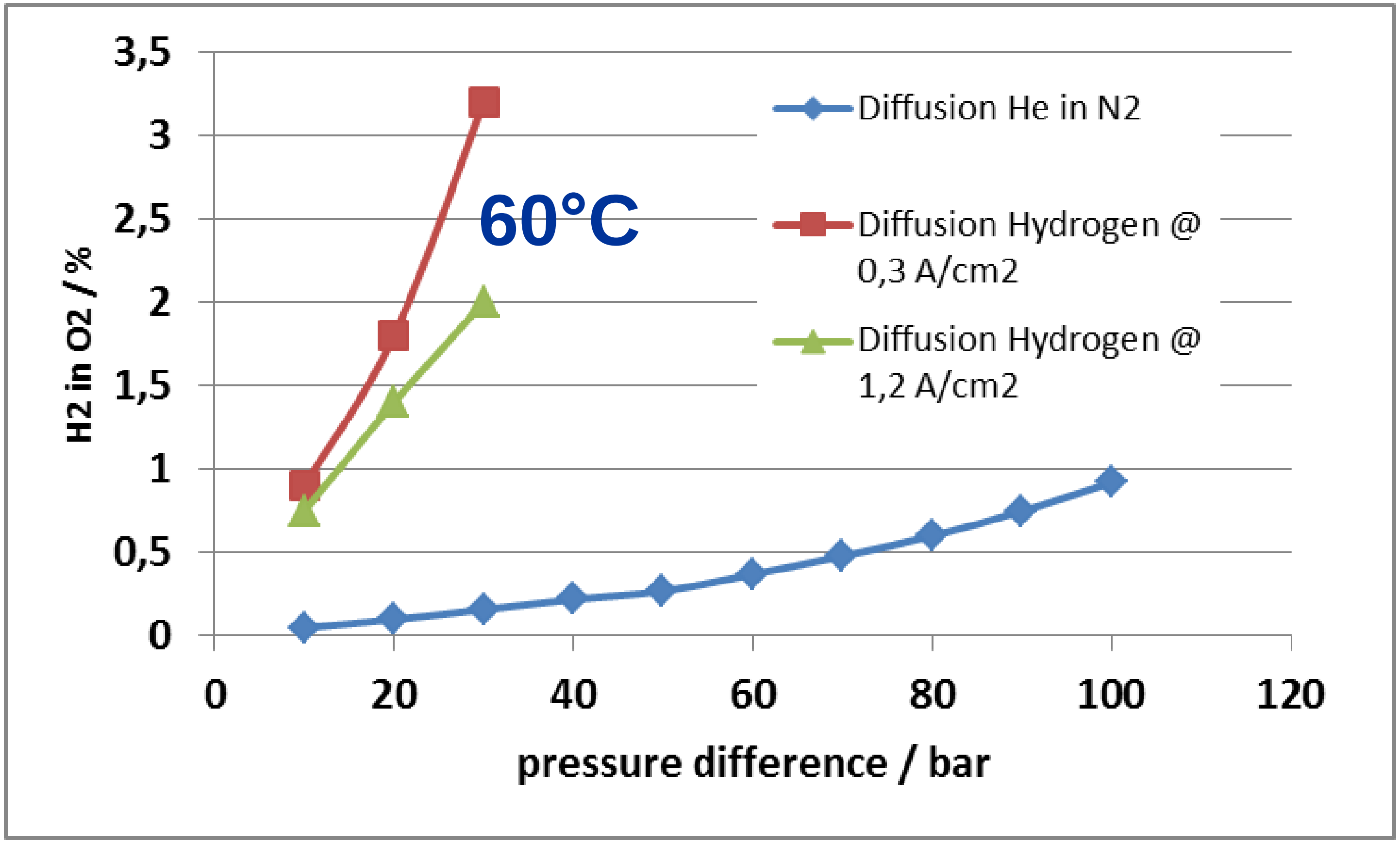


Membrane F-9240-PTFE (fumea© EF-40), idle filtered Electrolyser 20 kW class (170 A @ 120 V)

Diffusion properties in case of F-9240PTFE



Hint received within Ekolyser project:
***J. Phys. Chem. C*, 2015, 119 (45), pp 25145–25155**

Geometric projection: The diffusivity depends on channel opening => higher swelling contributes to gas diffusion yet faster than high IEC increases of the ionic conductivity…?

Load cycling of F-9240PTFE

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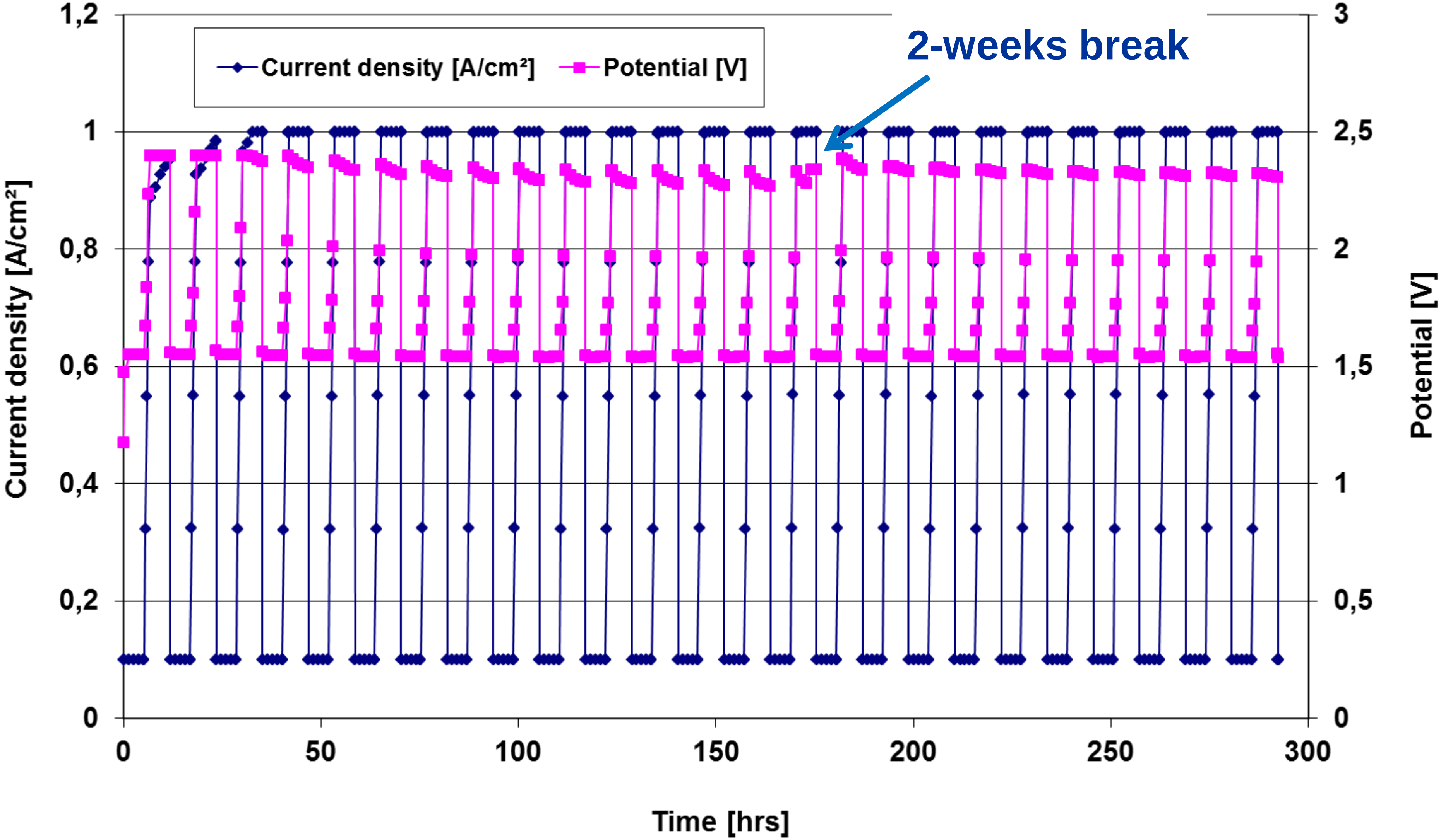

F- emission: no traces detected, the conductivity stayed below 3 µS/cm

Cut-off section of FAC-240 load cycling

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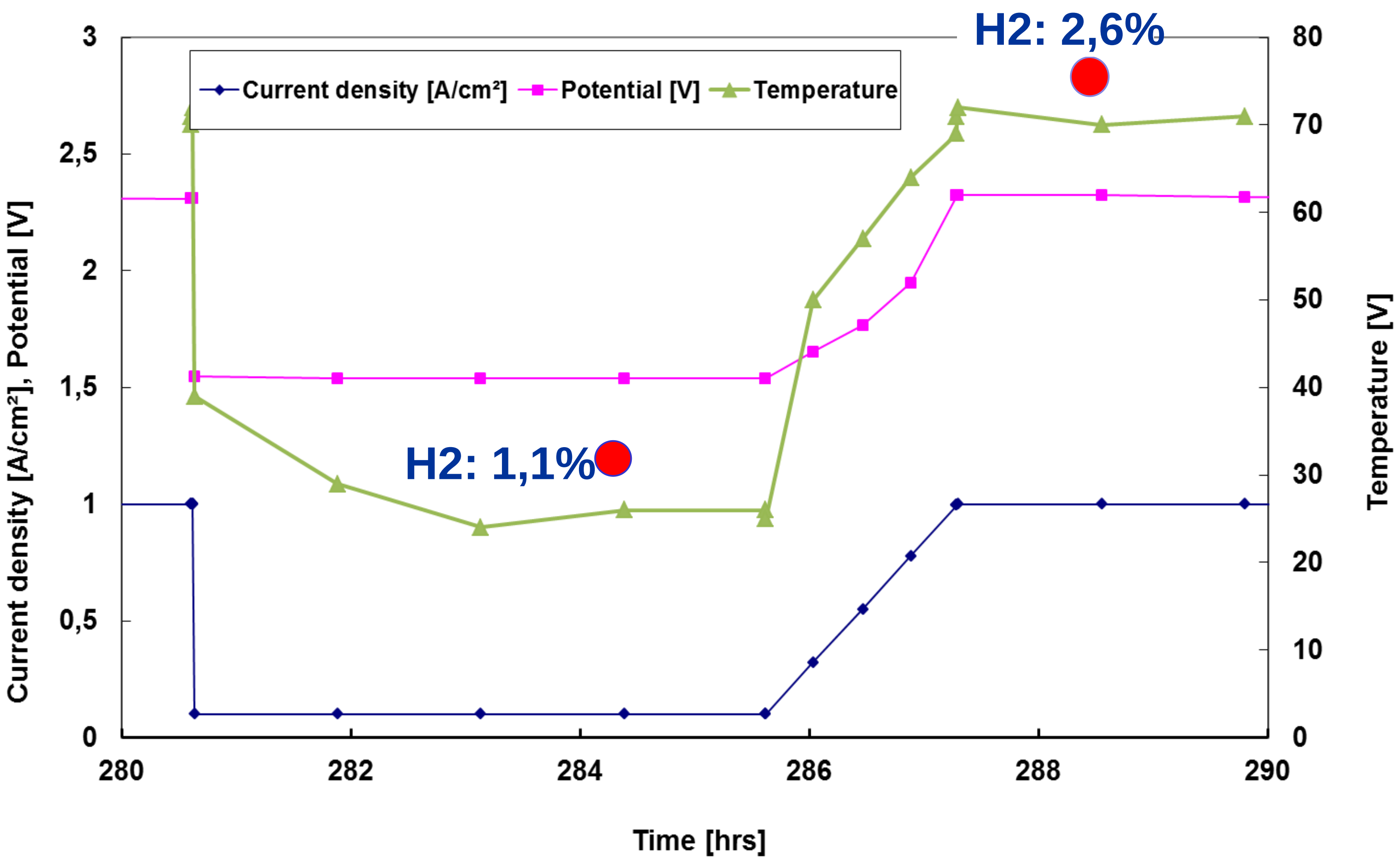


Confirmed: Effect of Temperature on H2 permeation in case of F-9240PTFE dominant. At low c.d the permeation should be theoretically higher, but it is not as the temperature is lower, too.

Lessons learned

FZP membranes good for other applications (Hydrogen pump, DMFC e.g.) but not for PEMWE

F-9240rf membrane good for various applications (water treatment, e.g.) but tricky for PEMWE

F-10120PK/rf maybe good for other applications where price and break-in „does not matter“, but less practical for PEMWE

„Good“ membranes: not much is seen in membrane’s structure over short to middle-term of investigation!

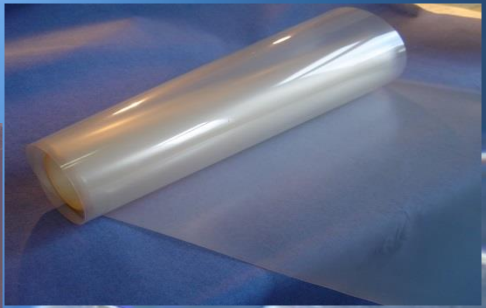
Too many ingrediences does not make the product better – woven-web reinforced membrane is arguably the best choice

The key is both chemistry of membrane and production technology

•*Polymer*

•*Dispersion*

•*Membrane*



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fumion®	ionomer resin as granular polymer, in solution form or in dispersion
fumion® FF	granular perfluorosulfonyl fluoride resin for extrusion
fumapem® F	perfluorosulfonic acid membranes for PEMFC
fumapem® S	hydrocarbon membranes for DMFC and PEMFC
fumapem® FZP	hybrid membranes for medium temperature PEMFC
fumapem® AM	membranes for high temperature PEMFC
fumasep® FAA	anion-exchange membrane for alkaline DEFC
fumasep® FAP	anion-exchange membrane for redox flow batteries
fumasep® FBM	bipolar membrane
fumasep®	ion-exchange membranes for humidifers, electrodialysis and electrolysis
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