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Lorenz Gubler :: Paul Scherrer Institut

Membranes for Water Electrolysis -
Target-Oriented Choice and Design of Materials

Durability and Degradation Issues in PEM Electrolysis Cells and its Components
February 16, 2016 :: Fraunhofer ISE, Freiburg, Germany

Acknowledgement

NOVEL Novel materials and system designs for low cost, efficient and durable PEM electrolysers

New Energy World JTI
fuel cells & hydrogen for sustainability

SINTEF

SEVENTH FRAMEWORK PROGRAMME

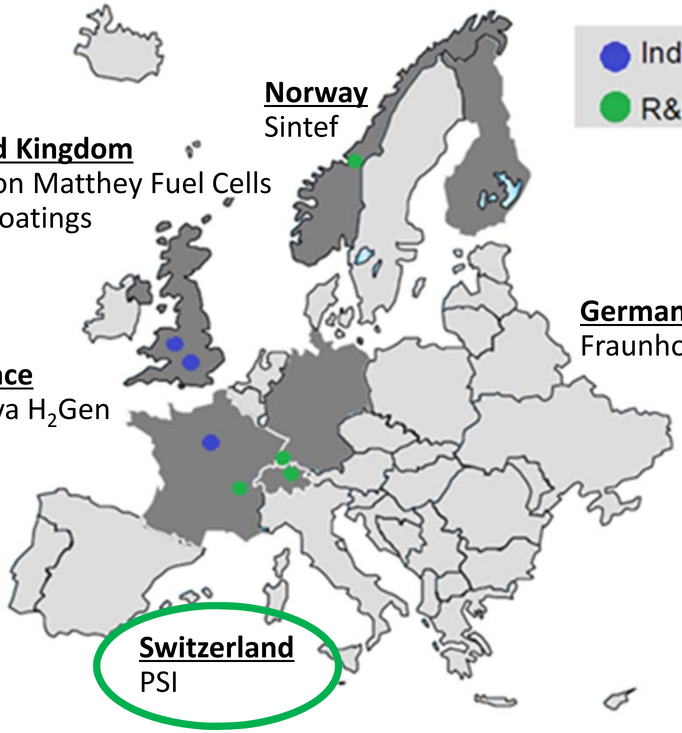
Johnson Matthey Fuel Cells
the power within

Innovation in Motion Miba

AREVA H_2Gen

cea

Fraunhofer ISE



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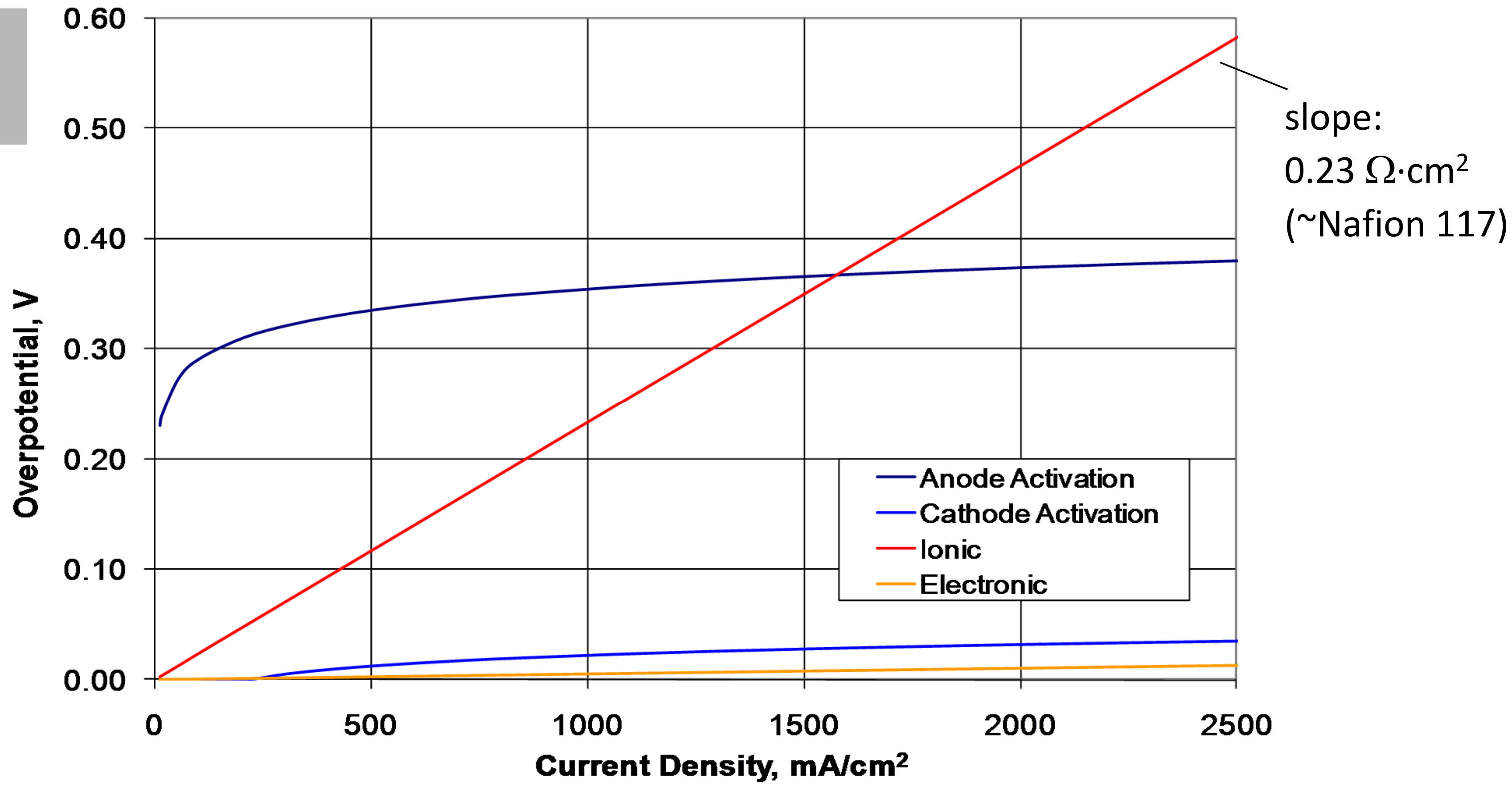
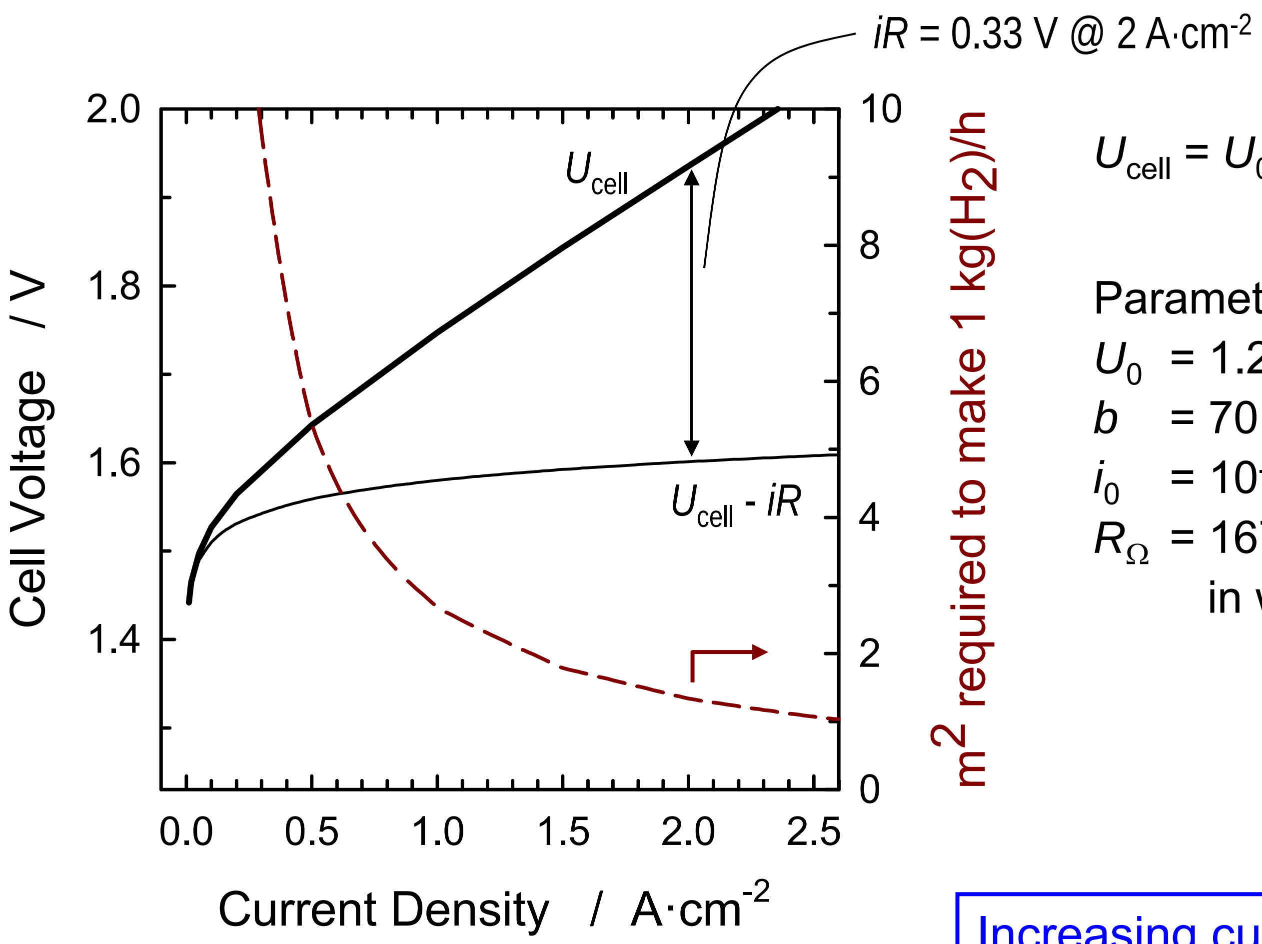
Loss Terms in PEM Electrolysis



Ohmic (mainly membrane) losses dominate at high current density

K. Ayers et al., *ECS Trans.* 33/1 (2010) 3

Simple Electrolysis Model



$U_{cell} = U_0 + b \cdot \log(i/i_0) + iR_\Omega$:

Parameters:

U_0 = 1.23 V

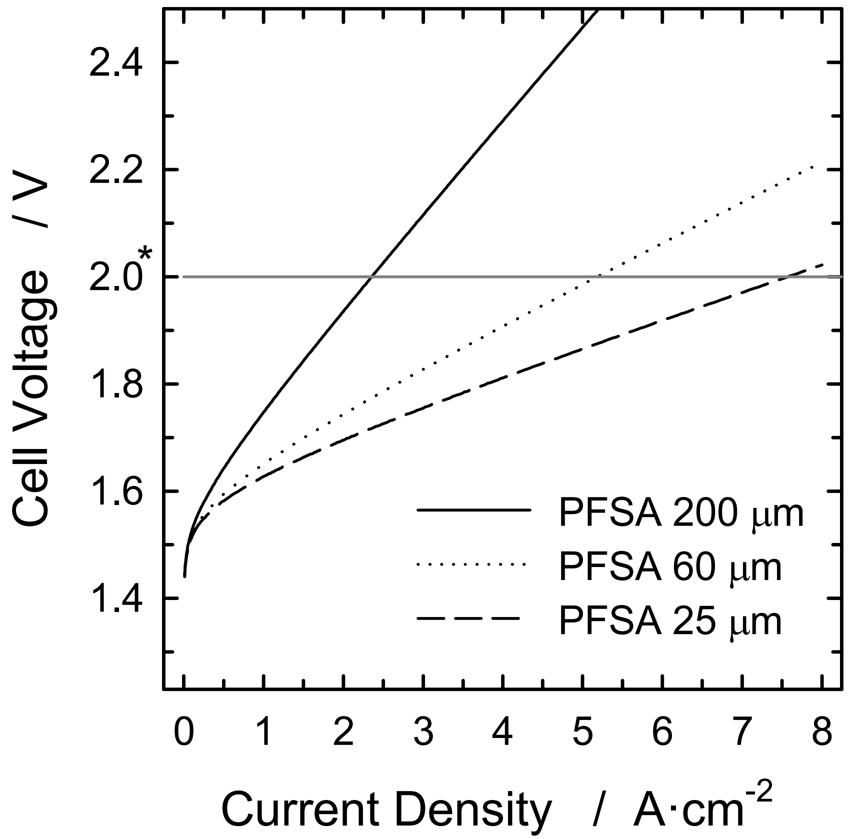
b = 70 mV/decade

i_0 = 10^{-5} A/cm$^2_{geom}$

R_Ω = 167 Ω·cm^2 (Nafion 117 in water @ 80°C)

Increasing current density can reduce size of electrolyzer

Reducing Membrane Thickness



*η = 74% (HHV)

$R_\Omega = R_0 + R_m$

non-membrane ohmic resistance:

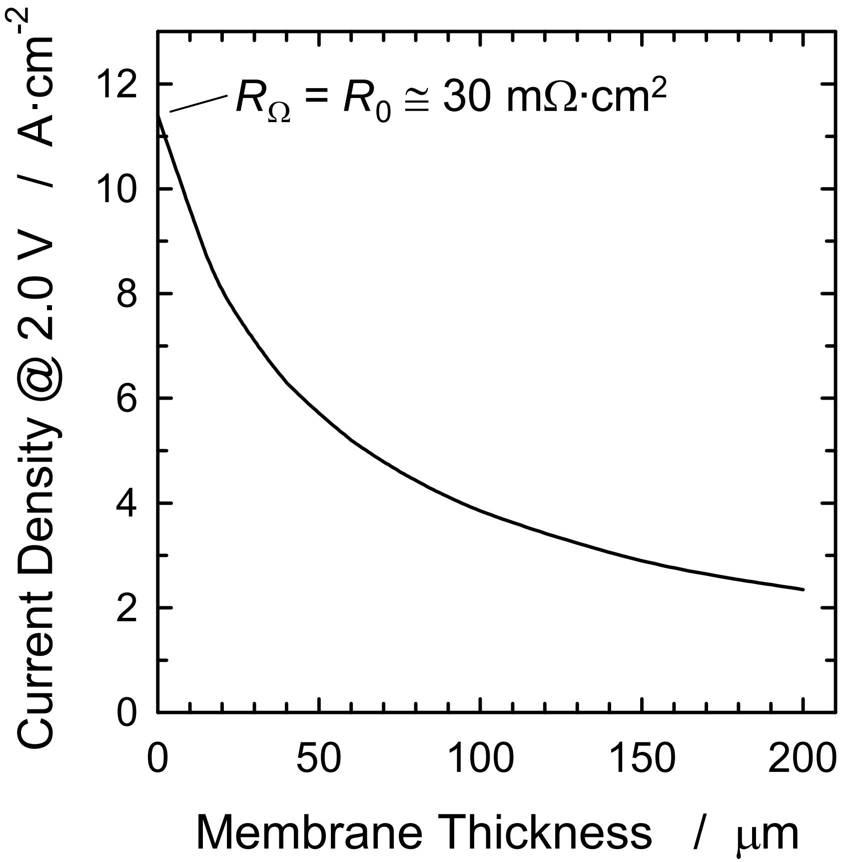
$R_0 \cong 30\ m\Omega \cdot cm^2$

$R_m = \delta / \sigma$ (σ: conductivity; δ: membrane thickness)

δ (μm)	R_Ω (mOhm·cm²)
200	167
60	71
25	47

Reducing membrane thickness allows much higher current density at given cell voltage (i.e., efficiency)

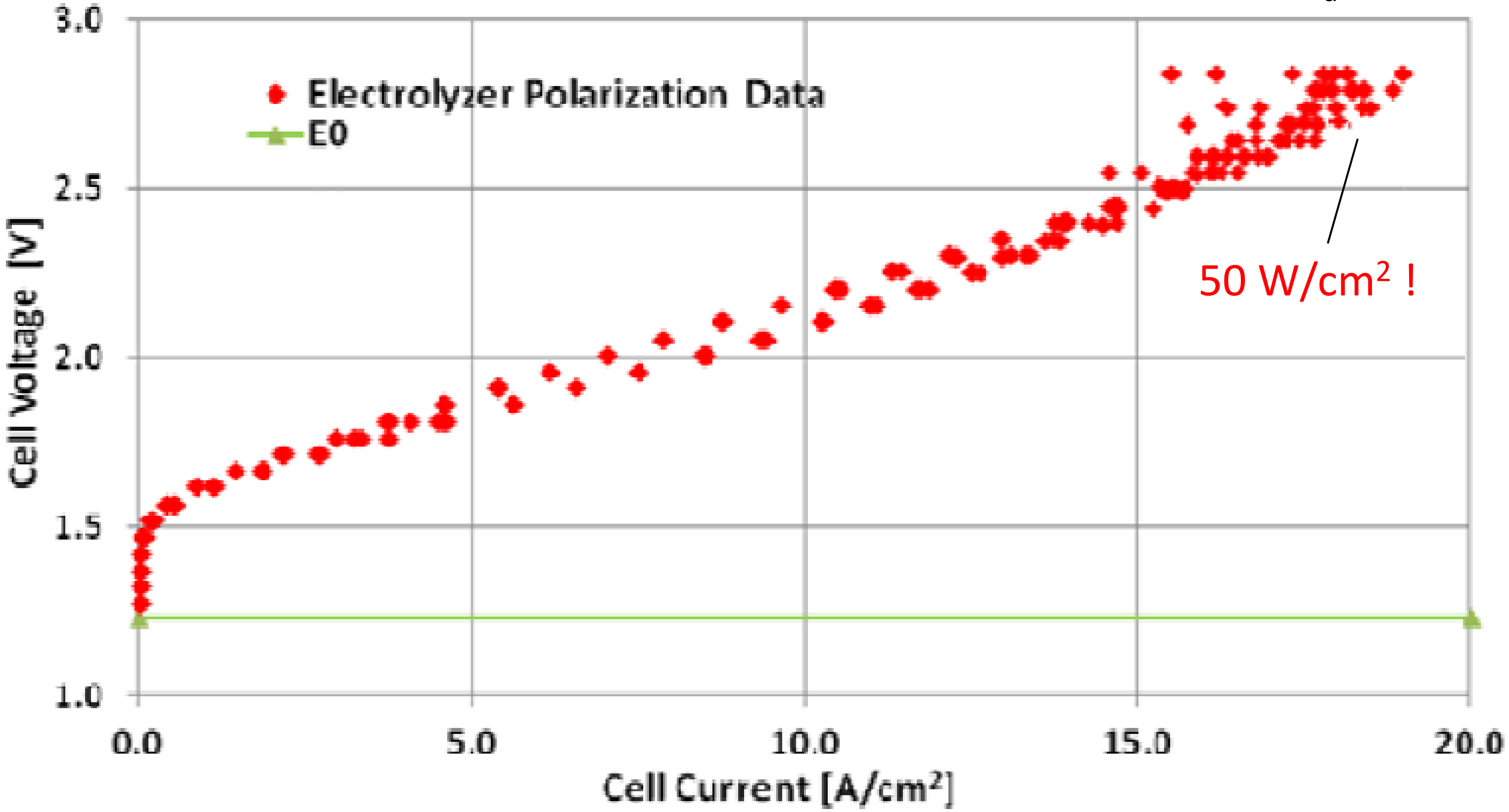
Reducing Membrane Thickness



Residual ohmic resistance R_0 may increase over time due to passivation of Ti current collector and bipolar plate

Performance reported by 3M

50 μm PFSA membrane (825 EW)*, NSTF catalyst, 80°C, 1 bar_a

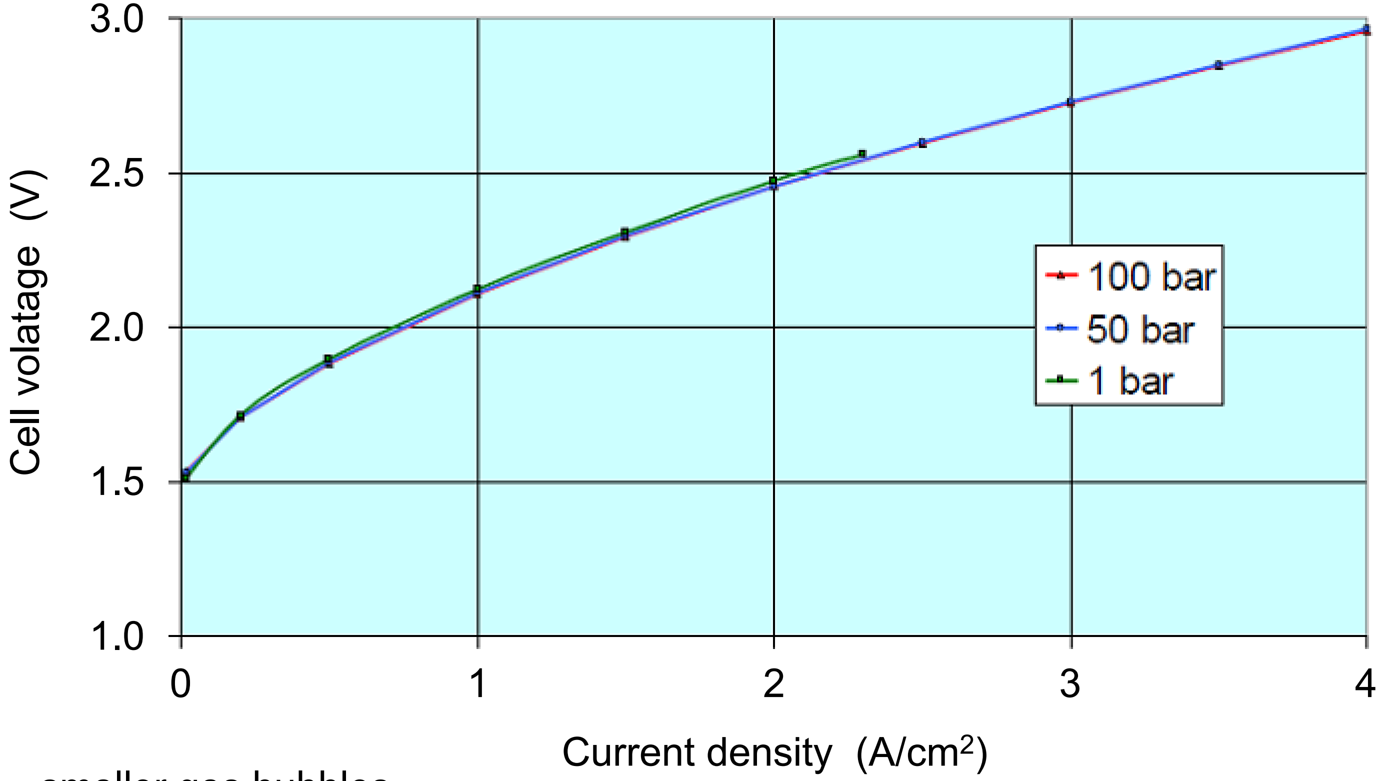


*σ ≅ 0.25 S/cm @ 80°C

Thermal management ?

Lewinski et al., *ECS Transactions* 69 (2015) 17, 893

High Pressure Operation: Lab Test Data

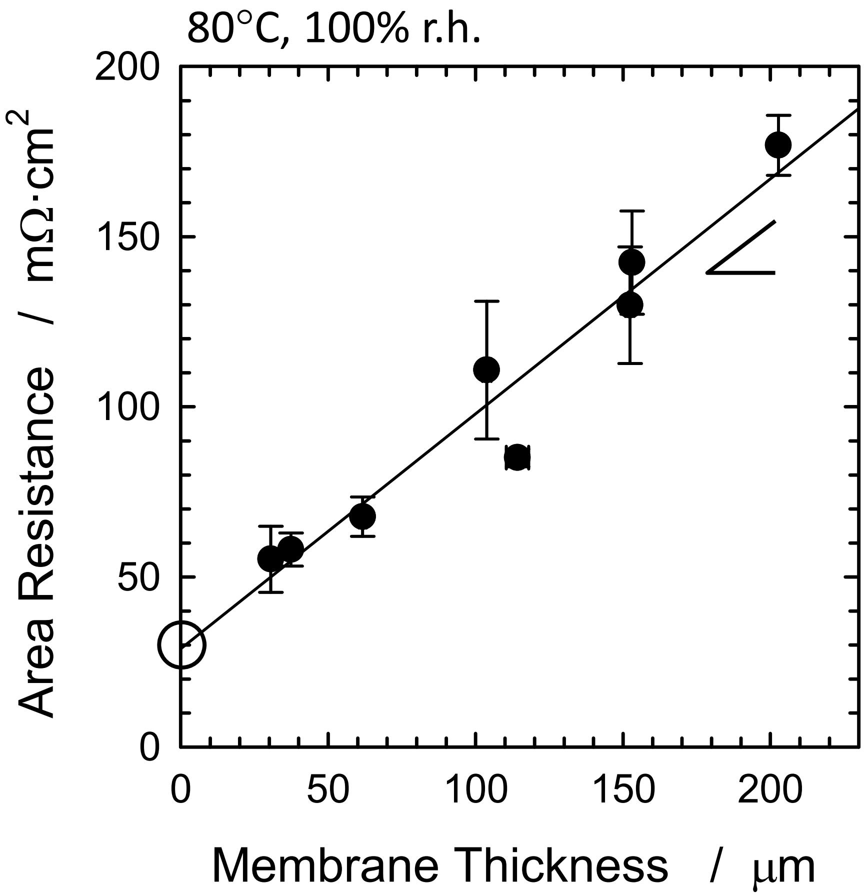


p↑ → smaller gas bubbles
→ lower mass transport losses

There is little influence of the pressure on the polarization behavior of the electrolysis cell

A. Reiner, Siemens

Area Resistance and Membrane Thickness

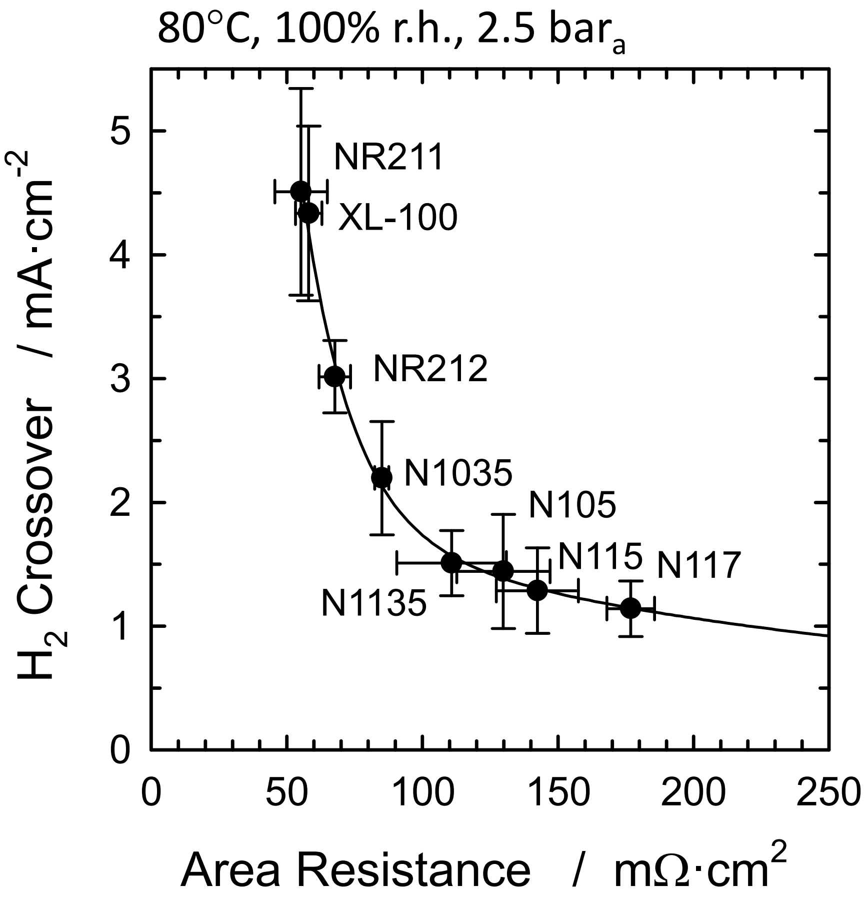


Area resistance R_Ω
(Nafion with EW 1'100):

$R_\Omega = R_0 + R_m$
$R_m = \delta / \sigma$

fitting parameters:
$R_0 = 30\ \Omega\cdot cm^2$
$\sigma = 146$ mS/cm

Resistance - Gas Crossover Tradeoff



fit H_2 crossover i_x:

$$i_X = 2F \frac{P(H_2)}{\color{blue}{\delta}} p$$

$\rightarrow$ $\boldsymbol{P(H_2)} = 4.5 \cdot 10^{-13} \frac{mol \cdot cm}{cm^2 \cdot s \cdot kPa}$

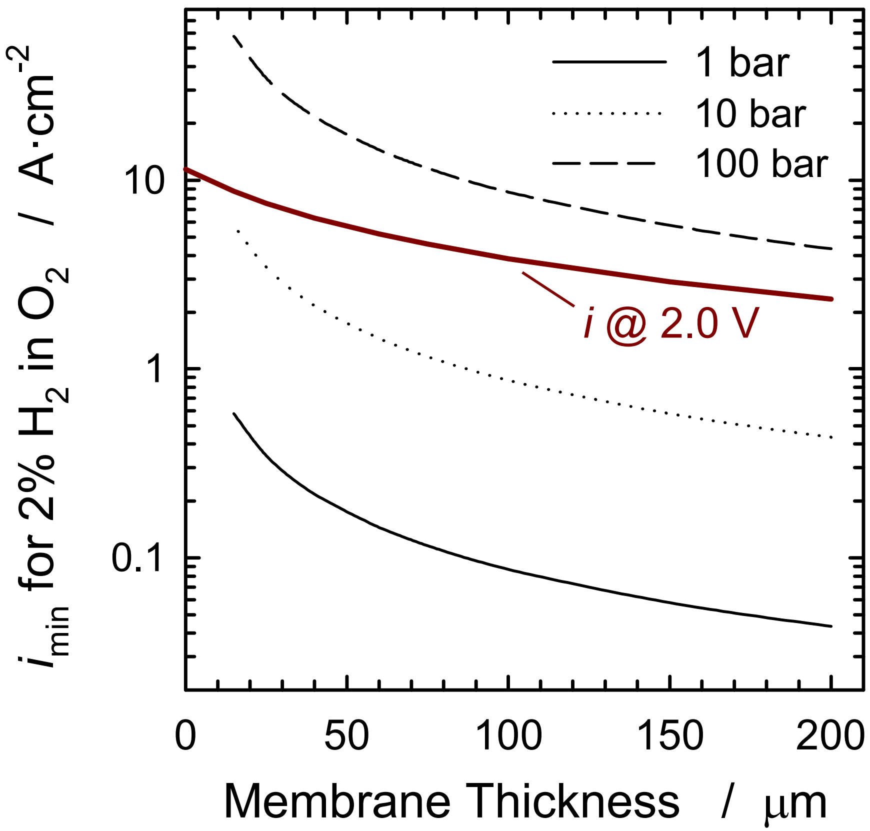
fit area resistance R_Ω (EW 1'100):

$R_\Omega = R_0 + \color{blue}{\delta} / \sigma$

$\rightarrow$ $\boldsymbol{R_0} = 30\ \Omega \cdot cm^2$, $\sigma = 146$ mS/cm

A. Albert, *ACS Appl. Mater. Interf.* 7 (2015) 22203

Gas Crossover - Minimum Current Density



Nafion gas permeabilities

$P(H_2)$ $\frac{\text{mol·cm}}{\text{cm}^2\text{·s·kPa}}$	$P(O_2)$ $\frac{\text{mol·cm}}{\text{cm}^2\text{·s·kPa}}$	Ref.
$5.32 \cdot 10^{-13}$	$2.52 \cdot 10^{-13}$	1
$5.10 \cdot 10^{-13}$	$2.70 \cdot 10^{-13}$	2
$1.8 \cdot 10^{-13}$	$8.0 \cdot 10^{-14}$	3
$4.50 \cdot 10^{-13}$	n/a	4

$P(H_2) \approx 2 \times P(O_2)$

$$c(O_2 \text{in } H_2) = p \cdot \frac{P(O_2)}{\delta} \cdot \frac{2F}{i}$$

$$c(H_2 \text{in } O_2) = p \cdot \frac{P(H_2)}{\delta} \cdot \frac{4F}{i} \approx 4 \times c(O_2 \text{in } H_2)$$

[1] M. Schalenbach et al., *J. Phys. Chem. C* 119 (2015) 25145
[2] T. Sakai et al., *J. Electrochem. Soc.* 132 (1985) 1328
[3] Z. Zhang et al., *J. Membr. Sci.* 472 (2014) 55
[4] fit of H_2 crossover data

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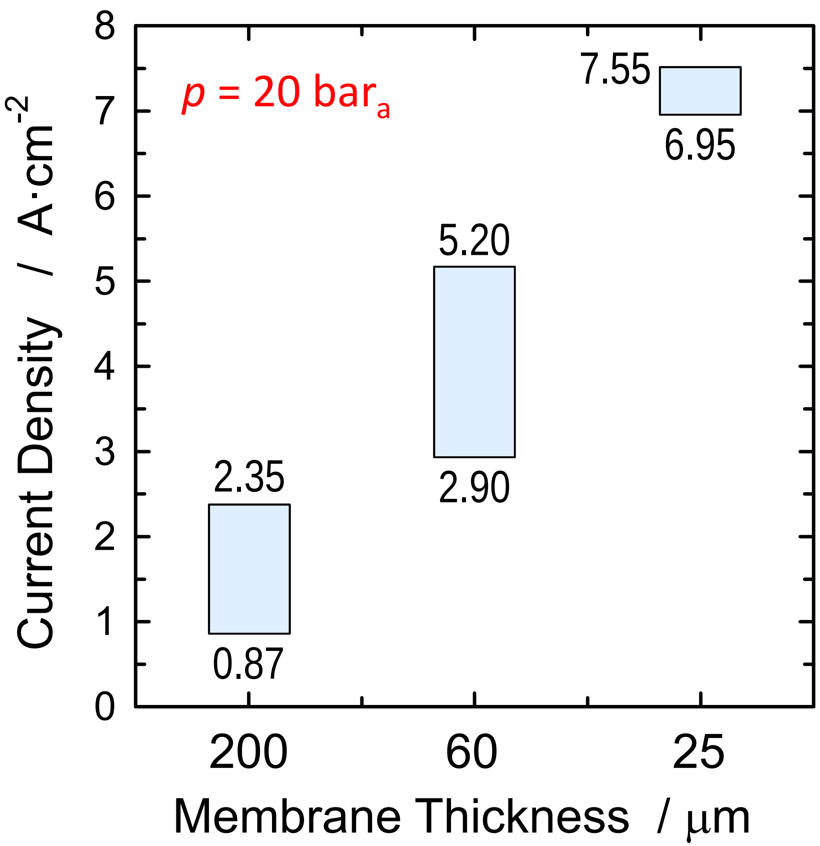
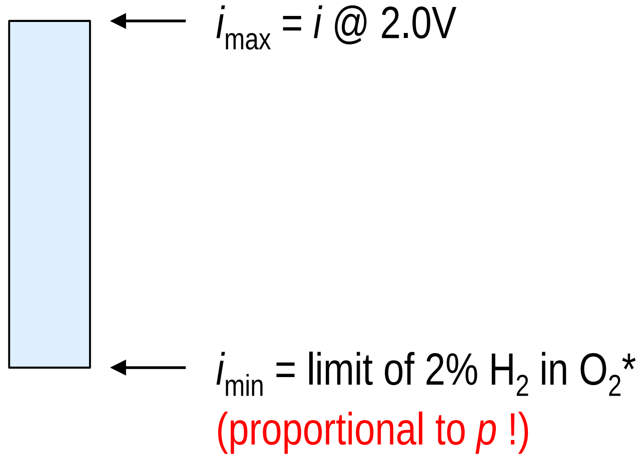
Operational Range (Turndown Ratio)





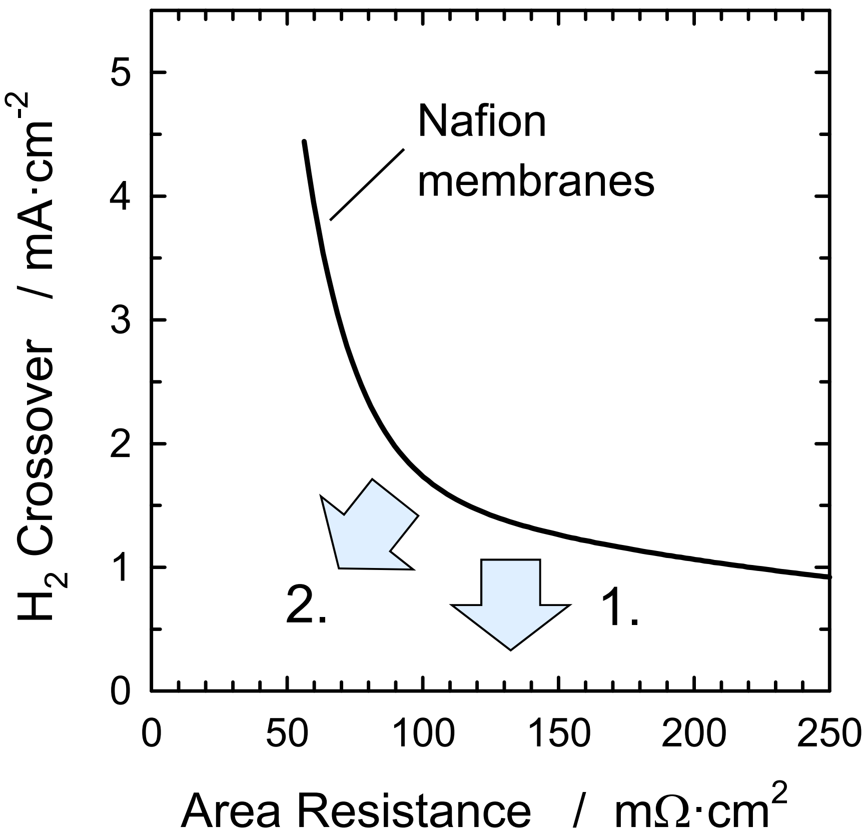
* ~equivalent to 0.5% O_2 in H_2

Operational range with thin membranes is limited due to crossover issue

→ Need to increase gas barrier properties of membrane

Membrane Development Strategies

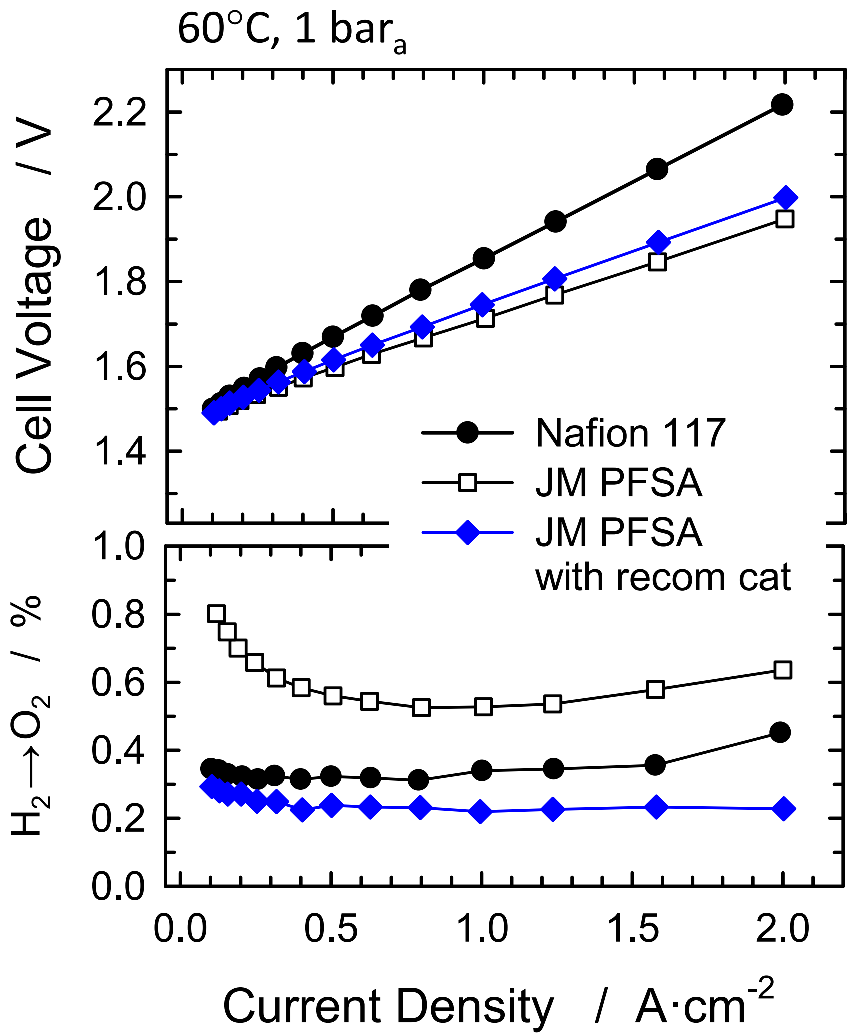
80°C, 100% r.h., 2.5 bar_a



1. **PFSA membranes**
   improve gas barrier properties

2. **Alternative membranes**
   choose materials with intrinsically better combination of resistance and gas permeability

Reinforced PFSA Membranes with Recombination Catalyst



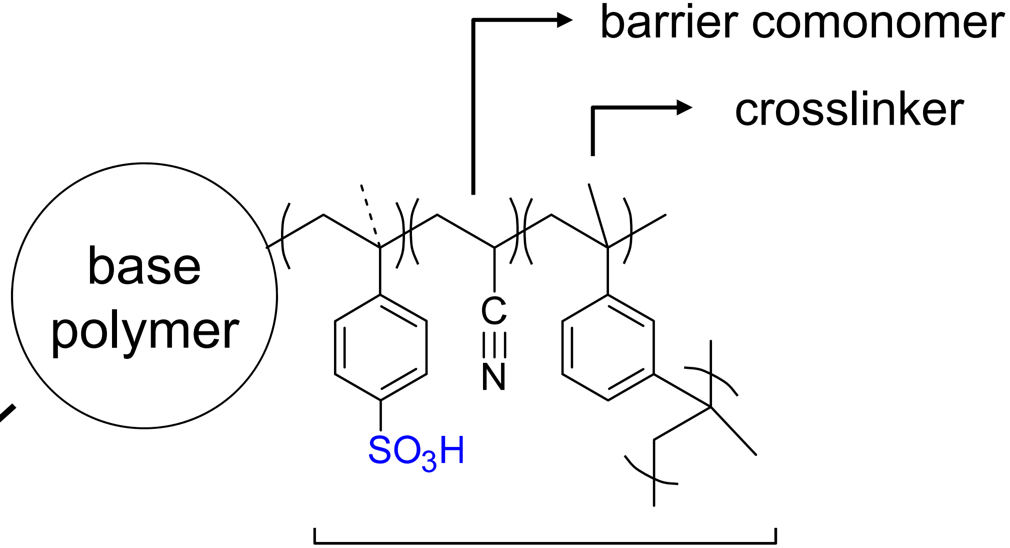
Johnson Matthey Fuel Cells
the power within

JM PFSA membrane:
(adapted automotive membrane)

- thickness ~60 μm
- reinforced
- containing PGM-type H_2-O_2 **recombination catalyst**

- Improved performance
- lower gas crossover

Ion Conducting Graft Copolymer Membranes



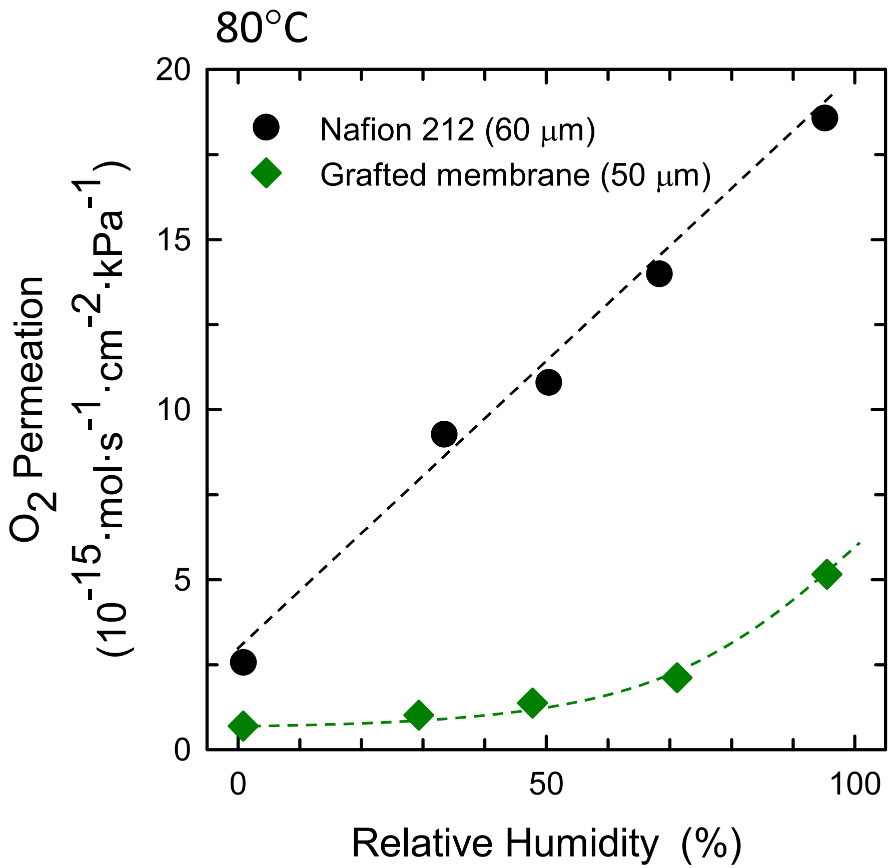
- partially fluorinated film (ETFE, ECTFE)
- chemically stable
- mechanically robust

polyelectrolyte grafts

- ion exchange groups
- additional functionalities (e.g. crosslinker, barrier groups)

L. Gubler, *Adv. Energy Mater.* 4 (2014) 1300827

Gas Permeation Properties



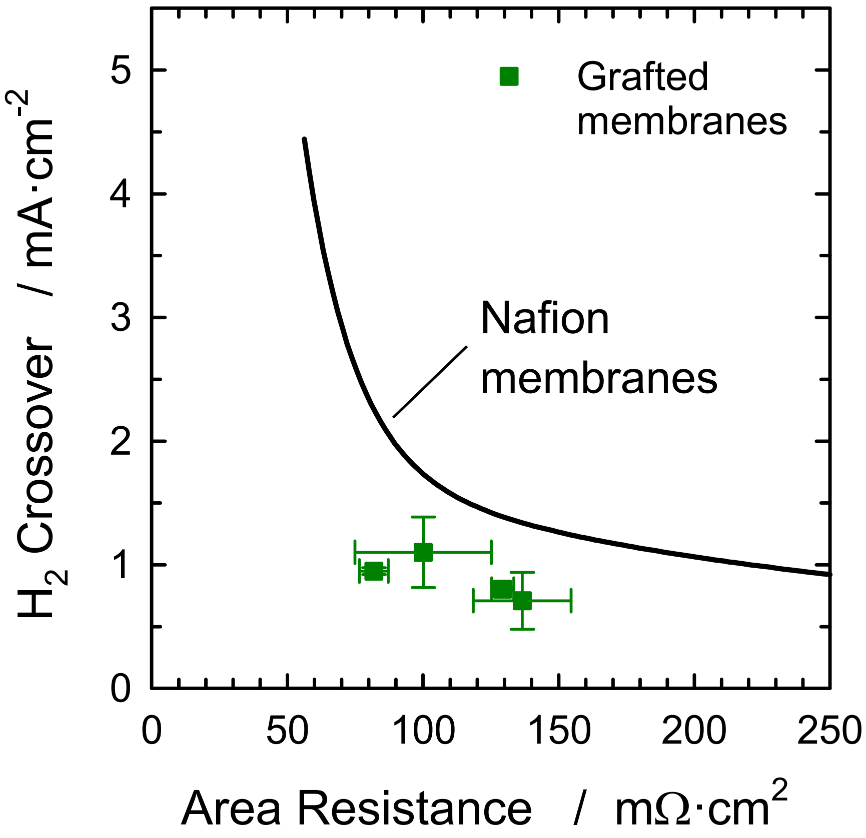
Gas permeation measured by mass spectrometry method*

Grafted membrane shows much lower gas crossover

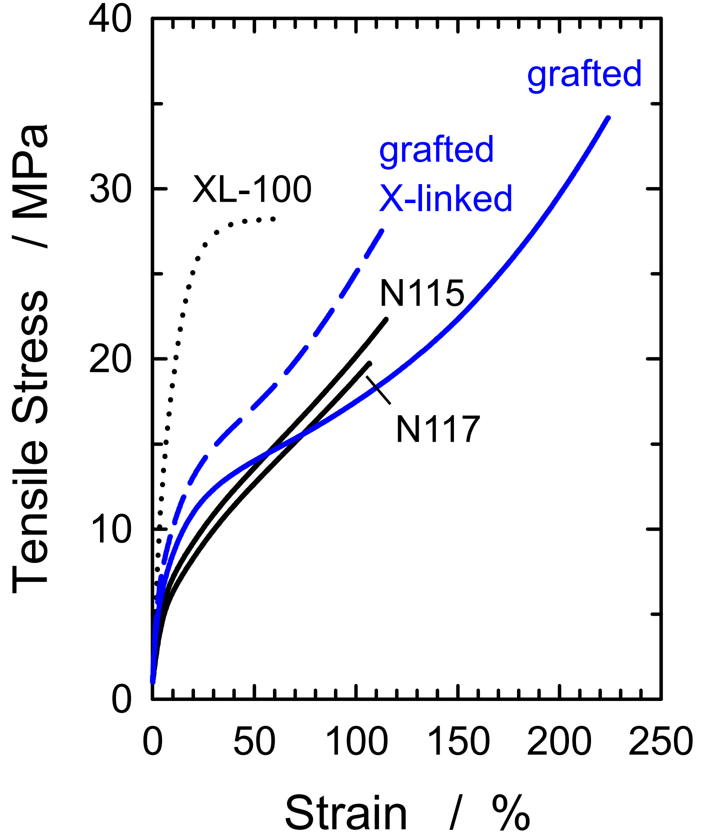
* Z. Zhang et al., *J. Membr. Sci.* 472 (2014) 55

Property Map

80°C, 100% r.h., 2.5 bar_a

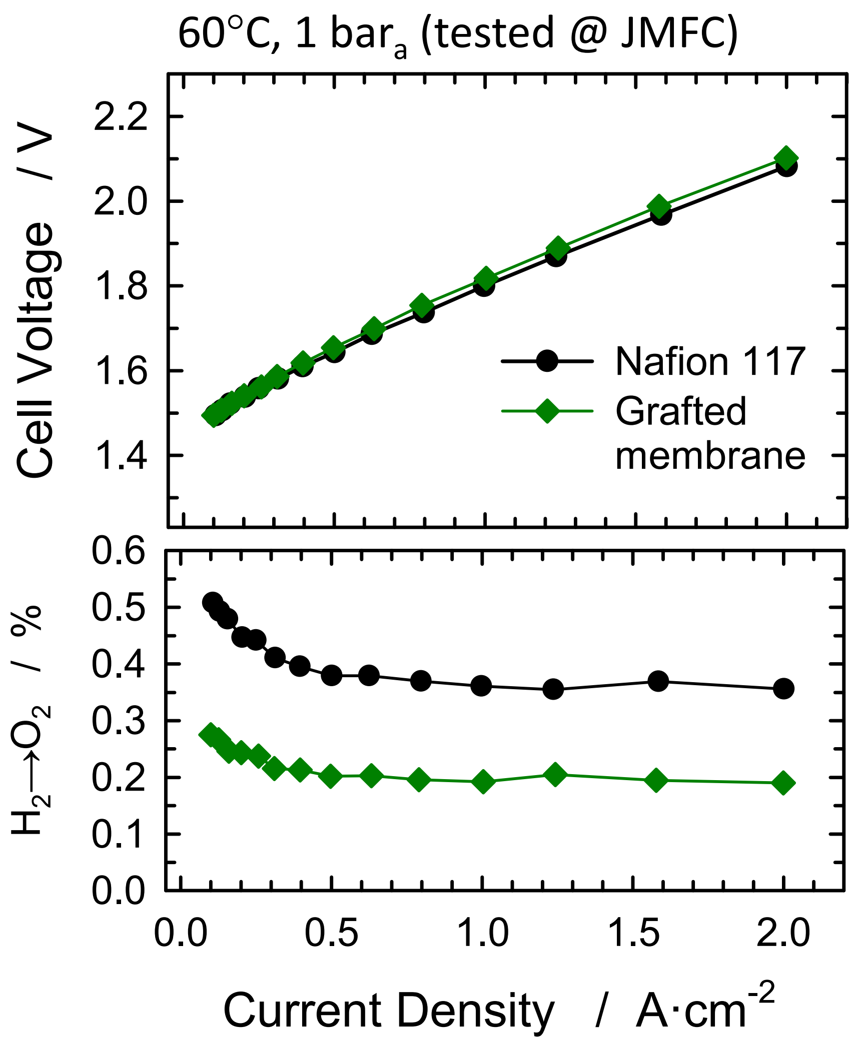


wet state, machining direction



A. Albert et al., *ACS Appl. Mater. Interf.* 7 (2015) 22203

Cell Performance with Grafted Membrane

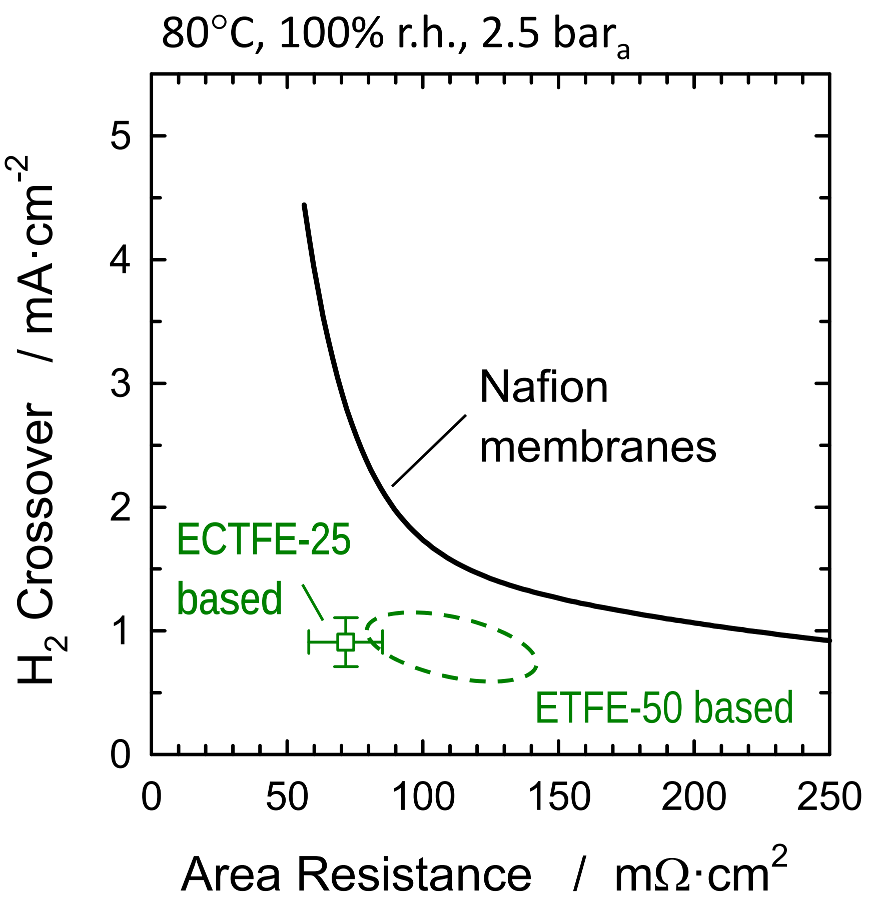


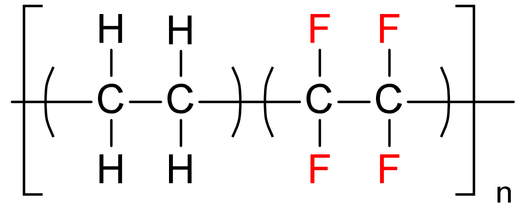
Grafted membrane vs. Nafion 117

- similar performance
- lower gas crossover (factor × ~2)

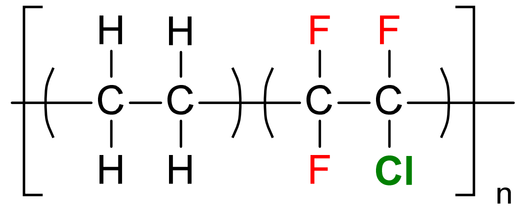
Further MEA (CCM) development required

Can We Do Better Than That ?





ETFE (50 μm)



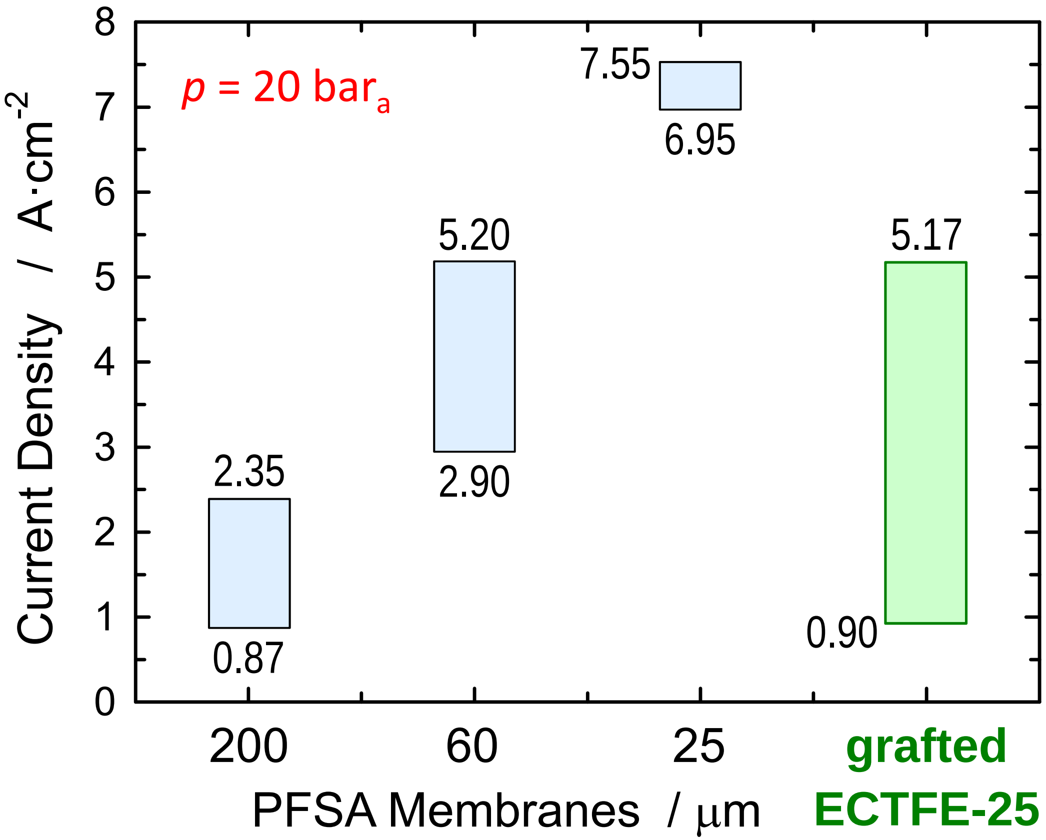
ECTFE (25 μm)

R_{Ω} = 70 mΩ·cm^2 ~ Nafion 212

i_x = 0.9 mA·cm^{-2} < Nafion 117

Thin membrane based on ECTFE-25 shows promising properties

Operational Range (Turndown Ratio)



- low Ohmic resistance
- low crossover

- wider range of operating current density
- suitable for **dynamic operation**

i_{min} = limit of 2% H_2 in O_2

Cell tests to be done

Durability

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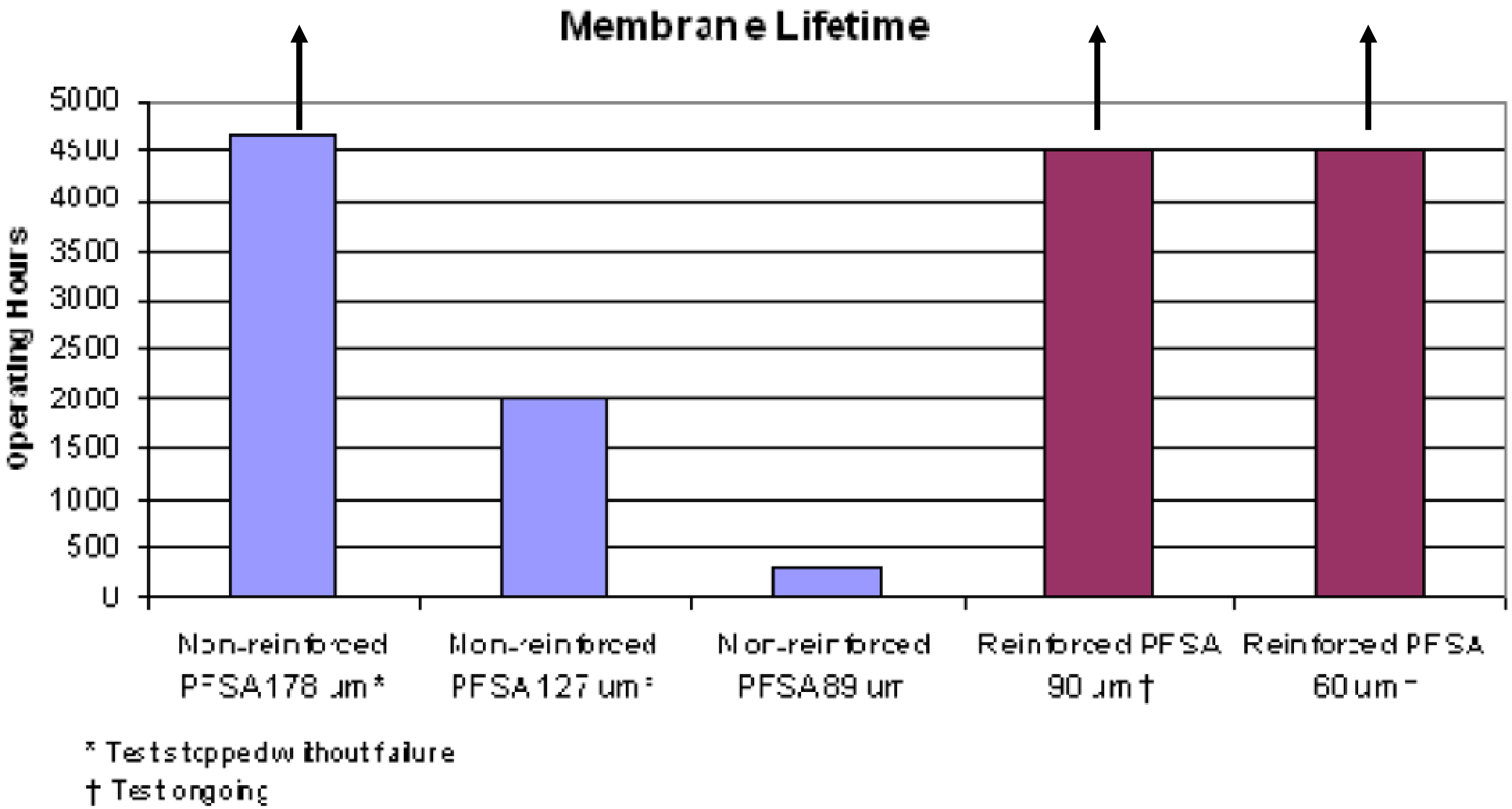
Membrane Degradation Mechanisms

- **Metal ion contamination** (reversible)
  - Water supply issue
  - Corrosion of bipolar plates
  - Core shell / alloy catalysts

- **Loss of mechanical integrity:**
  - Mechanical stress, creep
  - Overall membrane thinning
  - Local thinning

- **Chemical degradation:**
  - H_2, O_2 crossover
  - H_2O_2 and radical formation
  - Fluoride release

Membrane Degradation Mechanisms

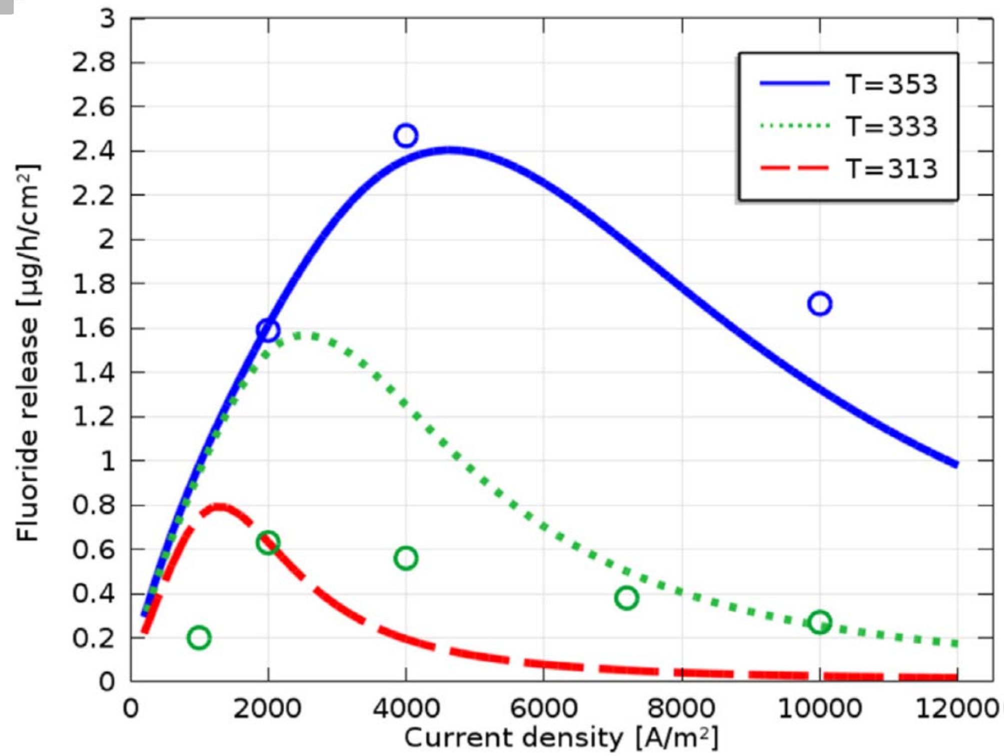


Need accelerated stress tests

K. Ayers et al., *ECS Trans.* 33/1 (2010) 3

Contributions within NOVEL

Investigation of chemical degradation by measuring fluoride emission rate (FER) coupled to a degradation model



FER in the fuel cell*:

FC under load: 0.01 - 0.1 $\mu g \cdot cm^{-2} \cdot h^{-1}$

FC under OCV: 1 - 10 $\mu g \cdot cm^{-2} \cdot h^{-1}$

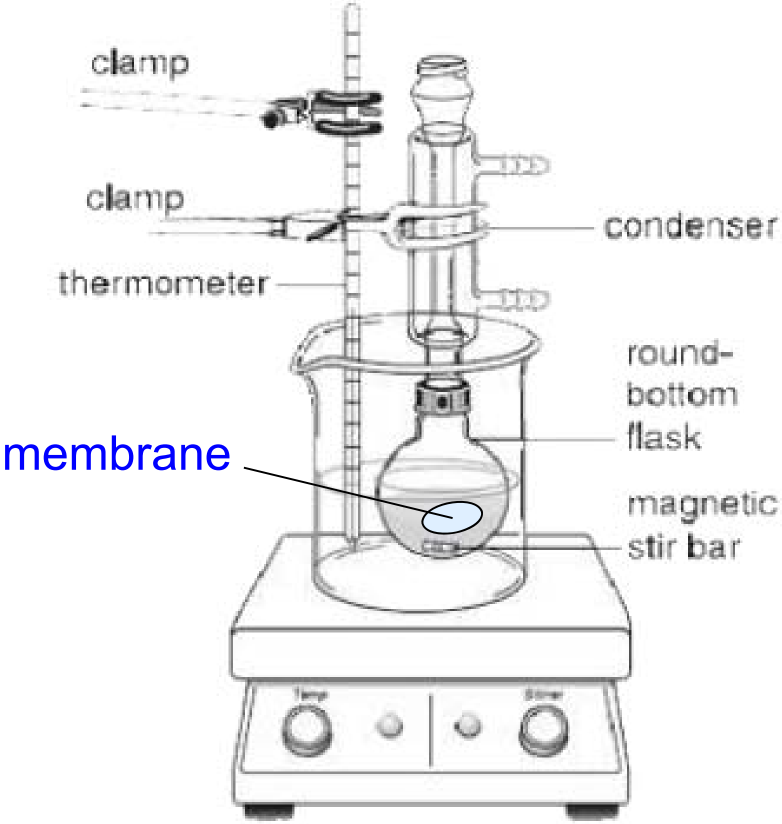
Shape of curve with maximum at intermediate current density well-reproduced by model

M. Chandesris et al., *Int. J. Hydrogen Energy* 40 (2015) 1353

* FER compilation in L. Gubler et al., *J. Electrochem. Soc.* 158 (2011) B755

Contributions within NOVEL

Thermal Stress Test (TST): exposure of membrane to 90°C for 5 days



post-test analysis of

membrane

- FTIR
- IEC
- SEM/EDX

solution

- UV-Vis
- Ion chromato-graphy

Membrane	IEC loss (%)
grafted, initial design	44.2 ± 0.8
down-selected grafted	4.2 ± 0.5
Nafion 117	< 1

A. Albert et al., in preparation

Conclusions

- Operation over large current density range desired
- Resistance - crossover tradeoff for a given ionomer type
- Strategies for improved membranes in NOVEL
  - Modified PFSA membranes (reinforced, with recombination catalyst)
  - Other ionomer classes with superior combination of resistance and gas barrier properties
- Durability aspects tackled within NOVEL
  - Radical induced degradation: model and experiment
  - Thermal stress test at 90°C in water

Thank You