First International Workshop

Durability and Degradation Issues in PEM Electrolysis Cells and its Components

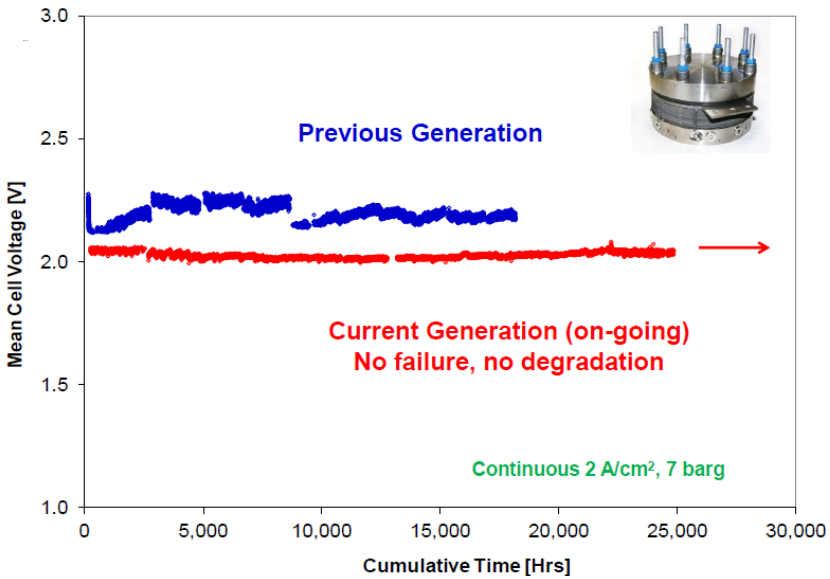
Degradation issues in NEXPEL and NOVEL

Magnus Thomassen, Luis Colmenares, SINTEF

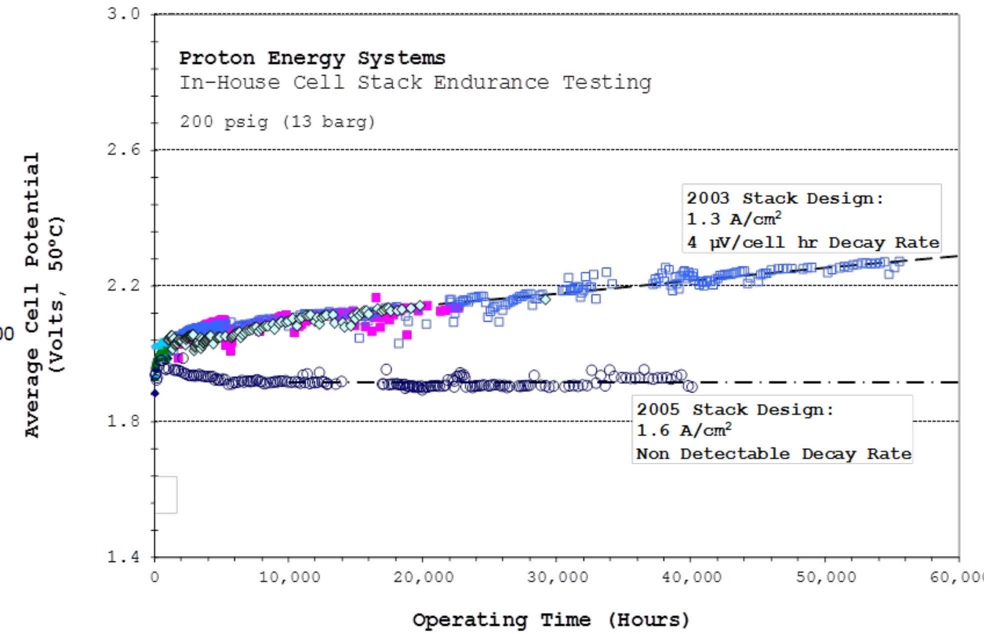
Outline

- Background
  - Why are we here?
- NEXPEL and NOVEL
  - A brief introduction to PEM degradation activities
- Degradation mechanisms in PEM electrolysers
  - Membranes
  - Catalysts
- First steps in developing AST protocols for PEM electrolysers
- Summary

Progress in efficiency and durability (PEM)



R. Schmid, in:, Symposium - Water Electrolysis and Hydrogen as a Part of the Future Renewable Energy System, 2012.



E. Anderson, in:, Symposium - Water Electrolysis and Hydrogen as a Part of the Future Renewable Energy System, 2012

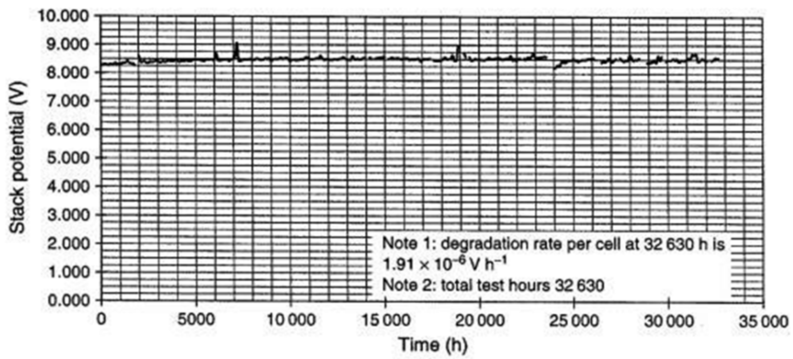


FIGURE 8. Life Test Data for Giner, Inc. Oxygen-Anode, Liquid Water Feed Electrolyzer (IRAD-014) (4-cell stack) (54°C; 6.9 MPa, H_2/Ambient O_2; Nafion 120, 300 μm thickness, 1200 EW; 4 mg Pt/cm^2-H_2 Side, 4 mg Pt-Ir/cm^2-O_2 Side) (27)

A.B. LaConti, L. Swette, in:, Handbook of Fuel Cells, John Wiley & Sons, Ltd, 2010

Challenges

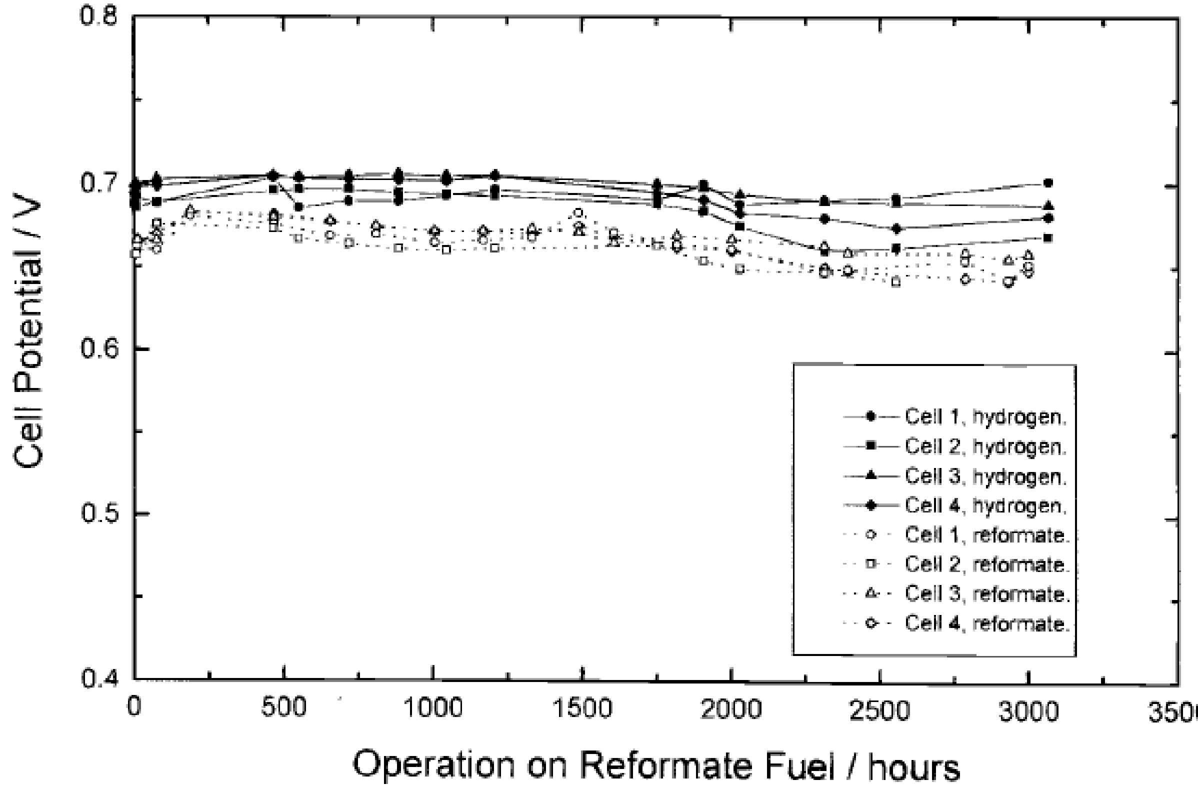
- Increased efficiency
  - Higher temperature
- Lower capital costs
  - Reduction of PGM loadings
  - Thinner membranes
  - Simpler systems (water purification, etc.)
- Intermittent operation
  - Temperature and pressure cycling
- High (differential) pressures

Risk of degradation increases significantly

15 years earlier:

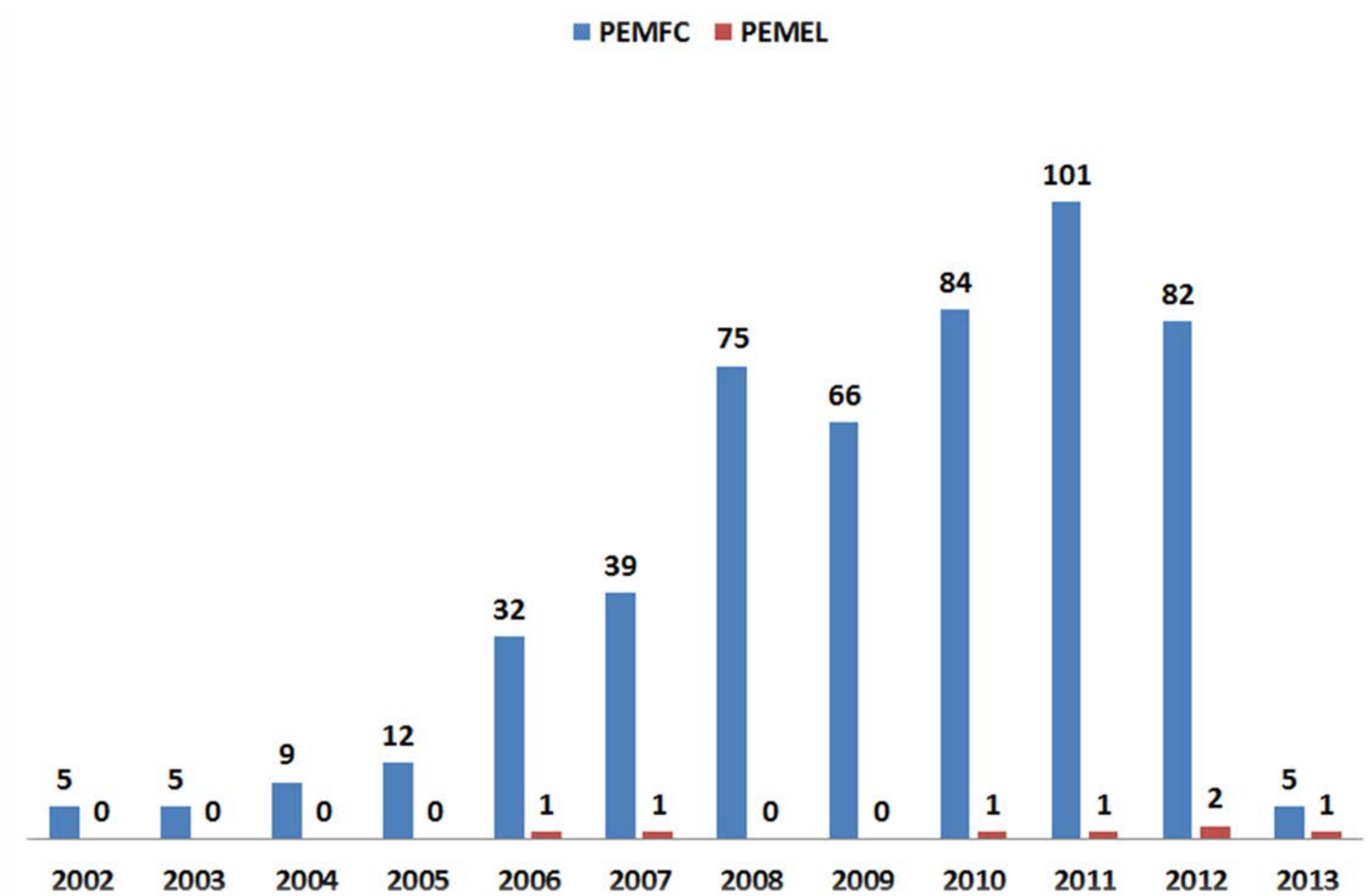
Minimal loss in performance after over 3000 h of stack operation

Fig. 17. The individual performance of the four cells in a Nafion 117 membrane based stack containing low platinum loading Type A cathodes (0.5 mg Pt/cm^2, 40 w/o Pt/XC72R) and Type B anodes (0.3 mg Pt/cm^2, 20 w/o Pt/10 w/o Ru/XC72R). The stack is operating at 538 mA/cm^2 on simulated reformate/air (with short interruptions to test the performance on H_2) at 5.4/5.4 atm and 1.3/1.8 stoichiometry with a 2% air bleed into the reformate.



D. P. Wilkinson, G. A. Hards *et al,* J. Electrochem. Soc. **144,** 11, (1997)

Background

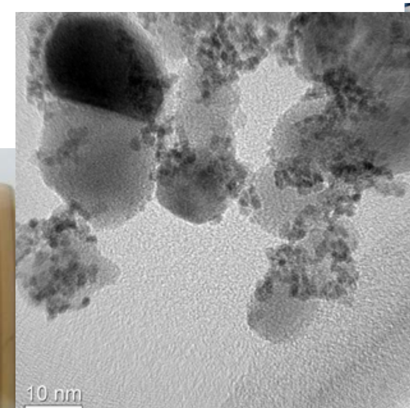


Number of hits in Web of Knowledge on the topics "PEM fuel cell degradation" or "degradation of PEM fuel cells" vs "PEM electrolys(z)er degradation" or "degradation of PEM electrolys(z)er" www.nexpel.eu

NEXPEL main objectives:

Develop and demonstrate a PEM water electrolyser integrated with Renewable Energy Sources (RES):

75% Efficiency (LHV), H_2 production cost ~ €5,000 / Nm^3h^{-1}, <u>target lifetime of 40,000 h</u>



NOVEL

www.novelhydrogen.eu

Goals of the Novel project:

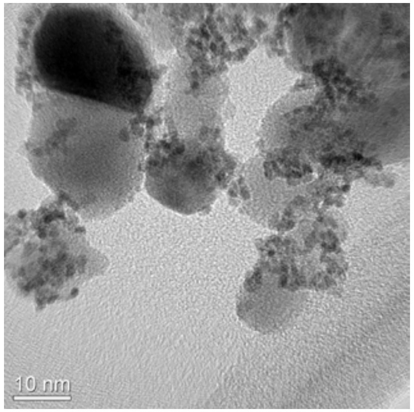
1. Reduce capital costs of main stack components
2. Increased electrolyser performance with;
   No impact on lifetime (> 40,000h operation)
3. Design of cost efficient systems with reduced impact on electrolyser lifetime
4. Improved understanding of degradation mechanisms in PEM electrolysers
5. Development of accelerated stress test protocols for lifetime evaluation and durability investigation of novel components.

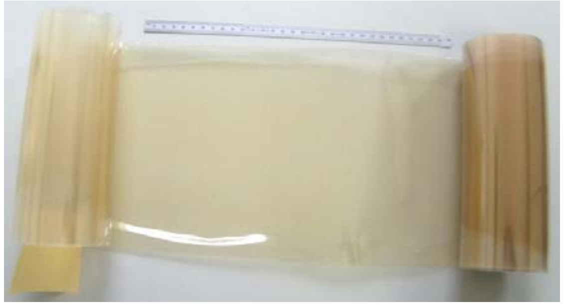
Todays topic

Degradation mechanisms and AST protocols for

Membranes

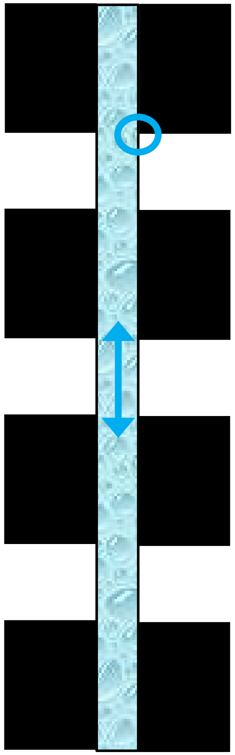
Catalysts





Membrane - Mechanical degradation

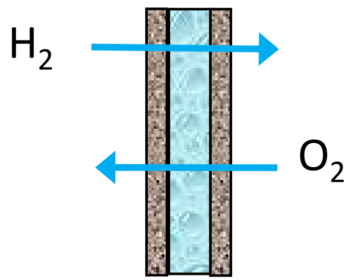
- Perforations, pinholes, cracks or tears
- Causes
  - In plane tension/compression due local drying/swelling
  - Inadequate heat or gas removal
  - Non-uniform compression / current density
  - membrane defects from manufacturing or improper MEA assembly
- Often leads to early life failure (catastrophic?)



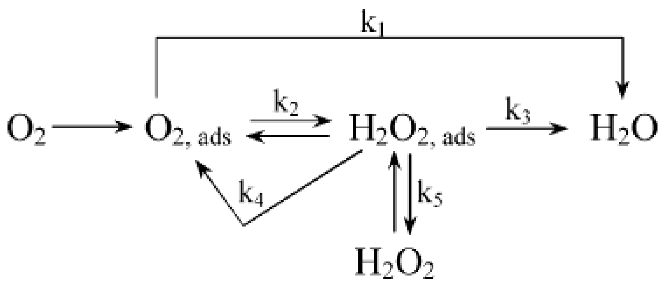
Fukuoka electrolyser accident

Membrane - Chemical Degradation

- Peroxide formation "fingerprint" for chemical degradation of ionomer



Gas crossover & chemical reaction



Oxygen reduction

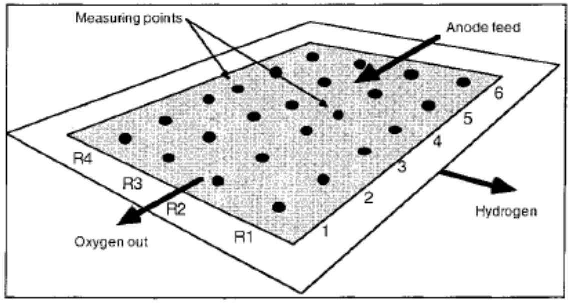
H_2O_2
$^{\bullet}OH$
$^{\bullet}OOH$

$$S + H_2O \rightleftharpoons S - OH_{ads} + H^+ + e^-$$
$$S - OH_{ads} \rightleftharpoons S - O + H^+ + e^-$$
$$2S - O \rightarrow 2S + O_{2(g)}$$

Oxygen evolution

$H_2O \rightarrow H_2O_2 + 2H^+ + 2e^-$ $E^{rev}=1.776$ V

Membrane chemical degradation- Earlier observations



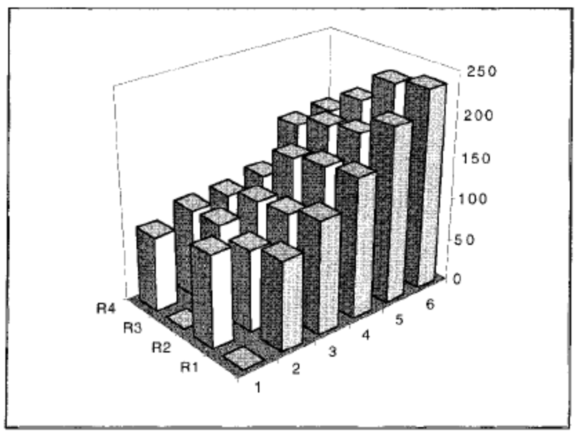


Fig. 6. (a) View on membrane as arranged for automatic measurement of the thickness distribution. Dots indicate measuring points on active area. Membrane is oriented such that anode face is up and cathode face is down. Direction of flows of water and products is indicated by arrows. (b) Local distribution of thickness for SWB-membrane no. 3. Column height represents the thickness recorded at the measuring dots. Membrane exhibits hot spots at the thin end (zero values).

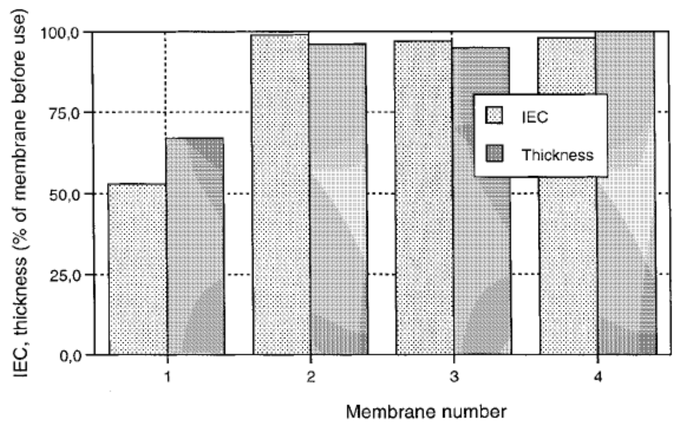


Fig. 8. Membrane thinning in a 30 cm^2 multimembrane laboratory cell: Membrane 1 was facing the cathode, membrane 4 was facing the anode. Ion exchange capacity and thickness of the membranes is given as a percentage of the corresponding values of membranes before use.

"PEM water electrolysers: evidence for membrane failure in 100kW demonstration plants" S. Stucki, G. G. Scherrer, *et al. J. Appl. Electrochem.* 28 (1998) 1041-1049

AST protocol for membrane chemical stability

- PEM Fuel cells: OCV hold
- PEM Electrolysers: ?

Table 3
MEA Chemical Stability and Metrics
Table revised December 10, 2009

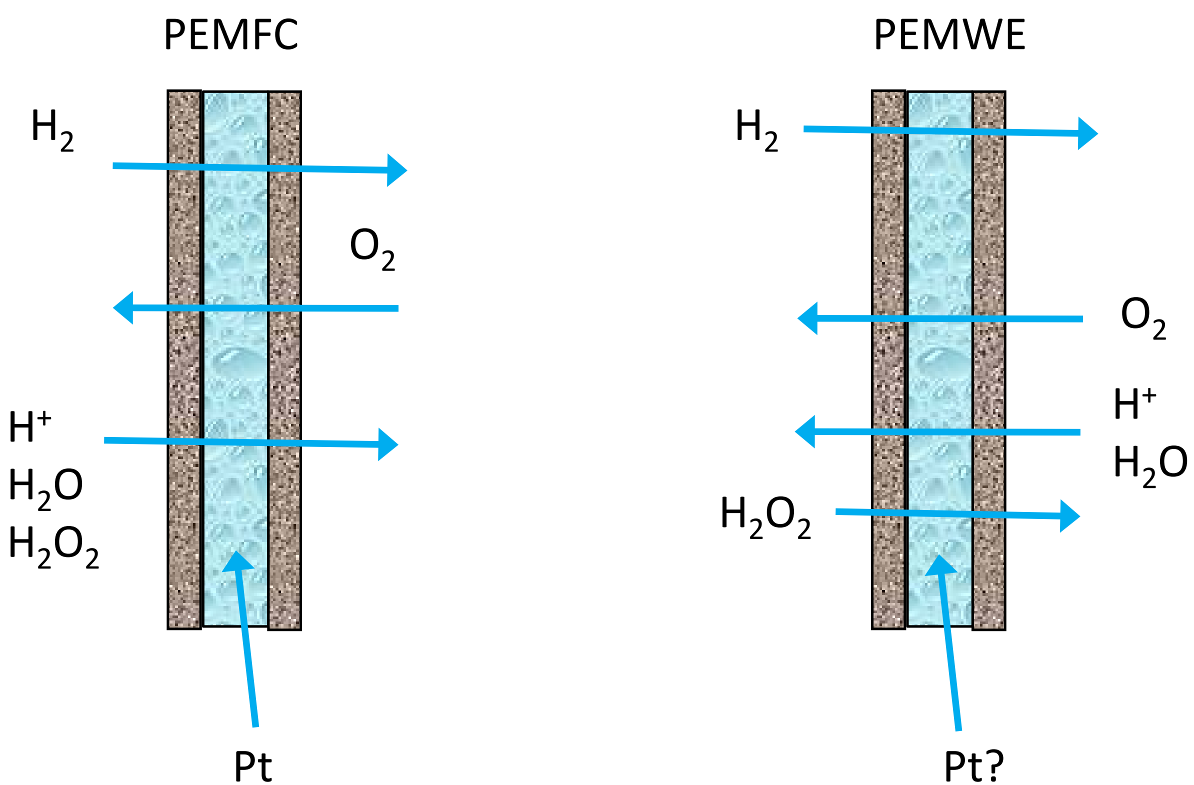
Test Condition	Steady state OCV, single cell 25-50 cm^2	
Total time	500 h	
Temperature	90°C	
Relative Humidity	Anode/Cathode 30/30%	
Fuel/Oxidant	Hydrogen/Air at stoics of 10/10 at 0.2 A/cm^2 equivalent flow	
Pressure, inlet kPa abs (bara)	Anode 150 (1.5), Cathode 150 (1.5)	
Metric	**Frequency**	**Target**
F^- release or equivalent for non-fluorine membranes	At least every 24 h	No target – for monitoring
Hydrogen Crossover (mA/cm^2)*	Every 24 h	$\leq$2 mA/cm^2
OCV	Continuous	$\leq$20% loss in OCV
High-frequency resistance	Every 24 h at 0.2 A/cm^2	No target – for monitoring
Shorting resistance**	Every 24 h	>1,000 ohm cm^2

* Crossover current per USFCC "Single Cell Test Protocol" Section A3-2, electrochemical hydrogen crossover method.

** Measured at 0.5V applied potential, 80°C and 100% RH N_2/N_2. Compression to 20% strain on the GDL.

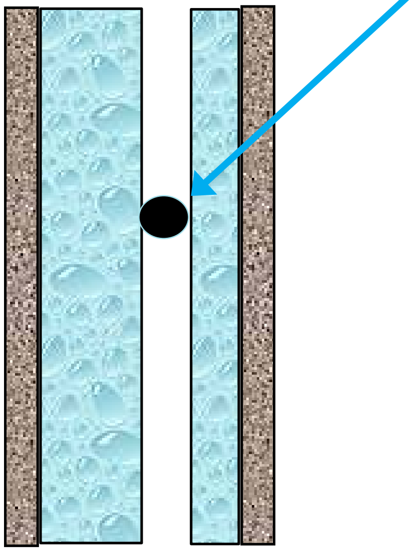
USCAR FUEL CELL TECH TEAM
CELL COMPONENT ACCELERATED STRESS TEST PROTOCOLS FOR PEM FUEL CELLS, 2010

PEM Fuel cells vs. PEM electrolysers

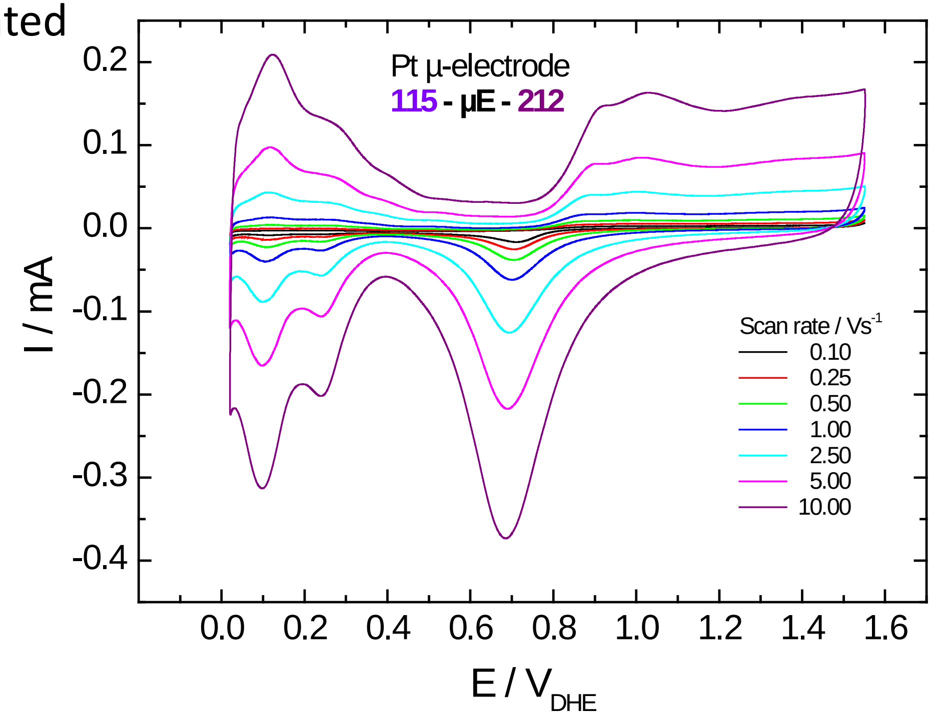


Peroxide detection using µ-electrodes.

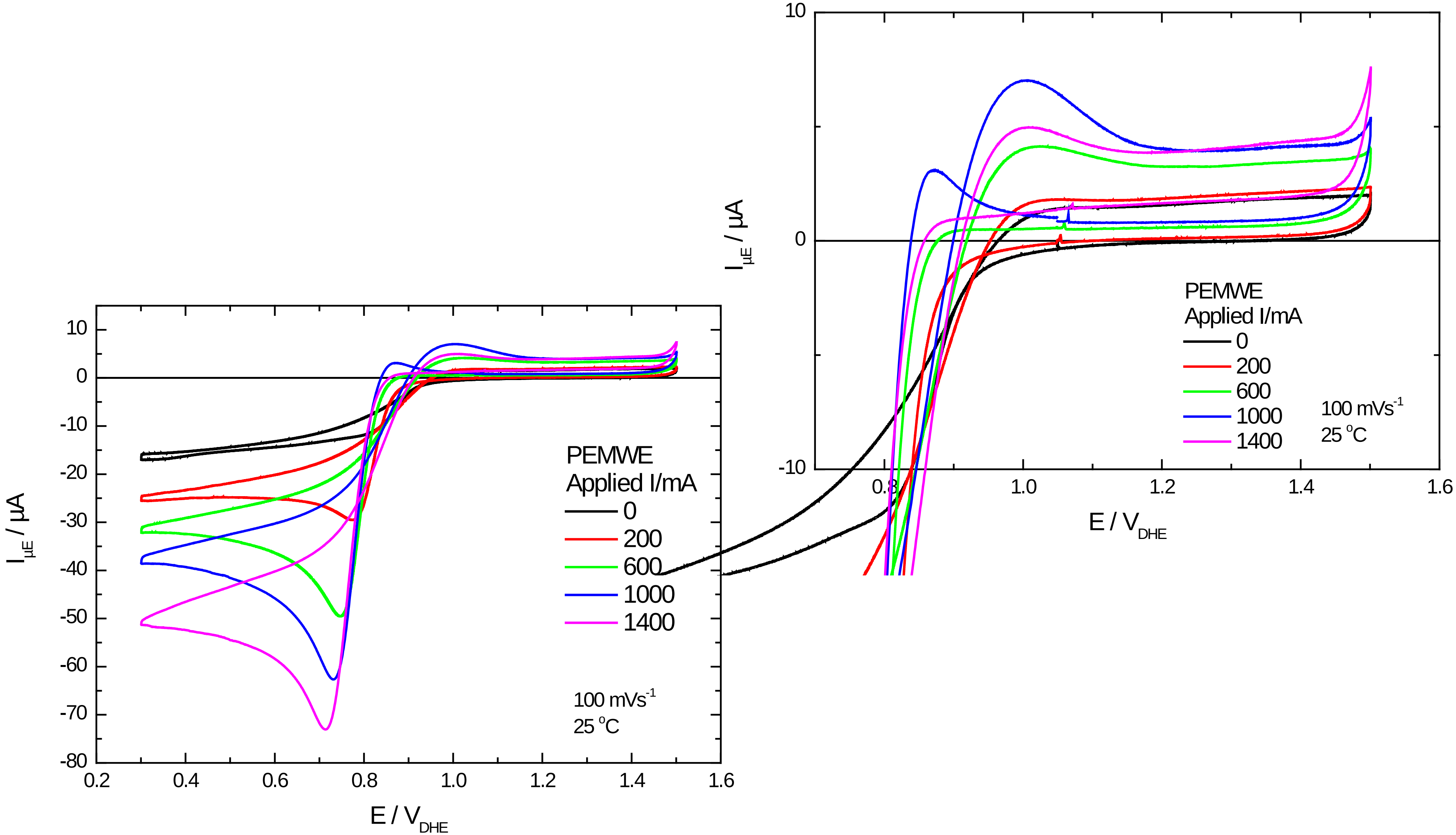
- Electrolyser operated at 25 °C, at current densities between 50 mA and 1.5 Acm^{-2}



Pt wire 50 µm
PTFE insulated

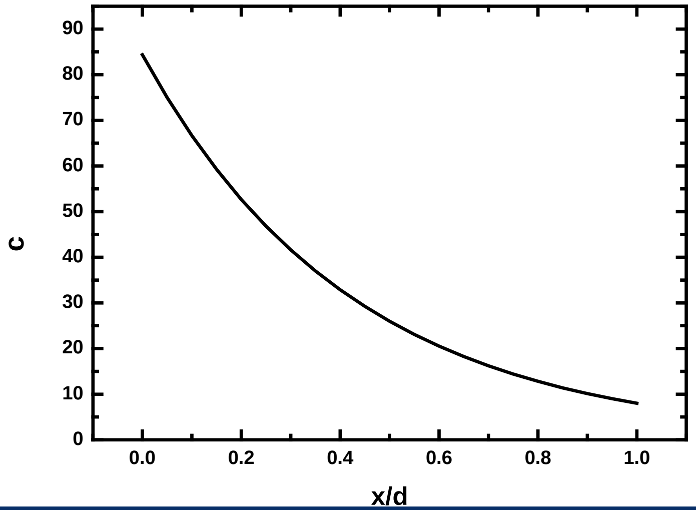


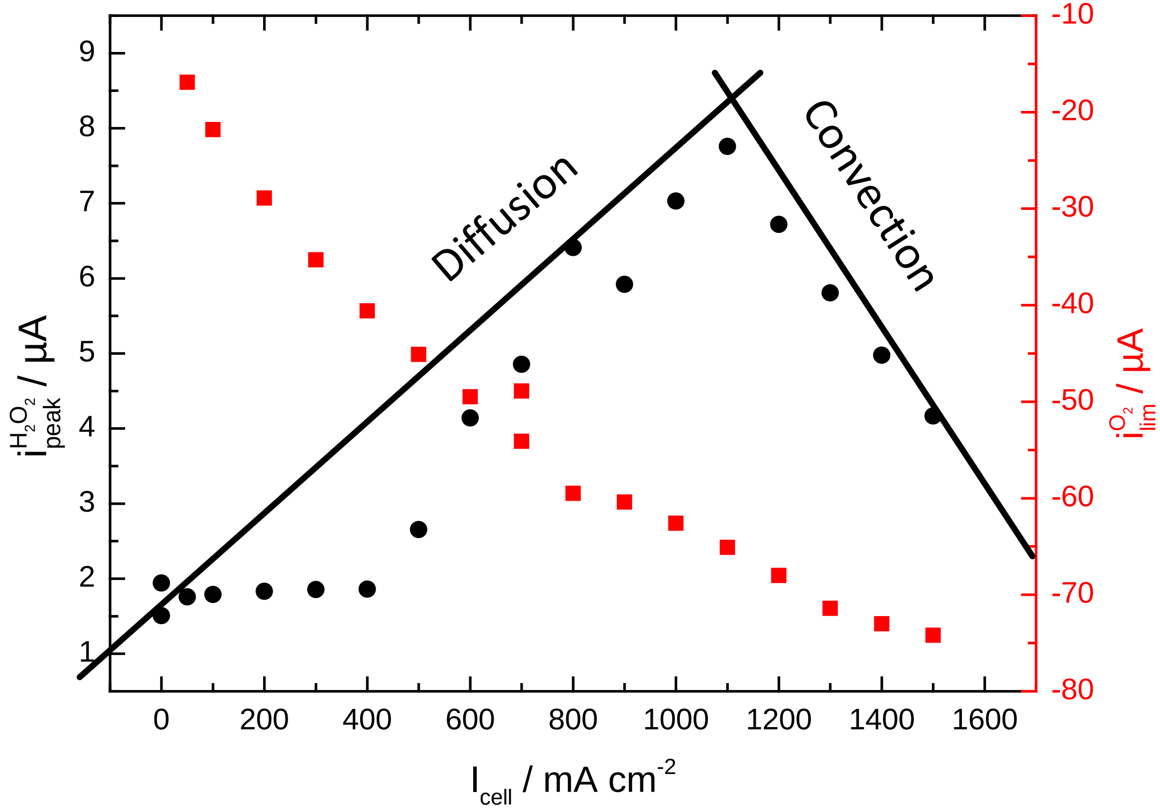
Peroxide detection using µ-electrodes.



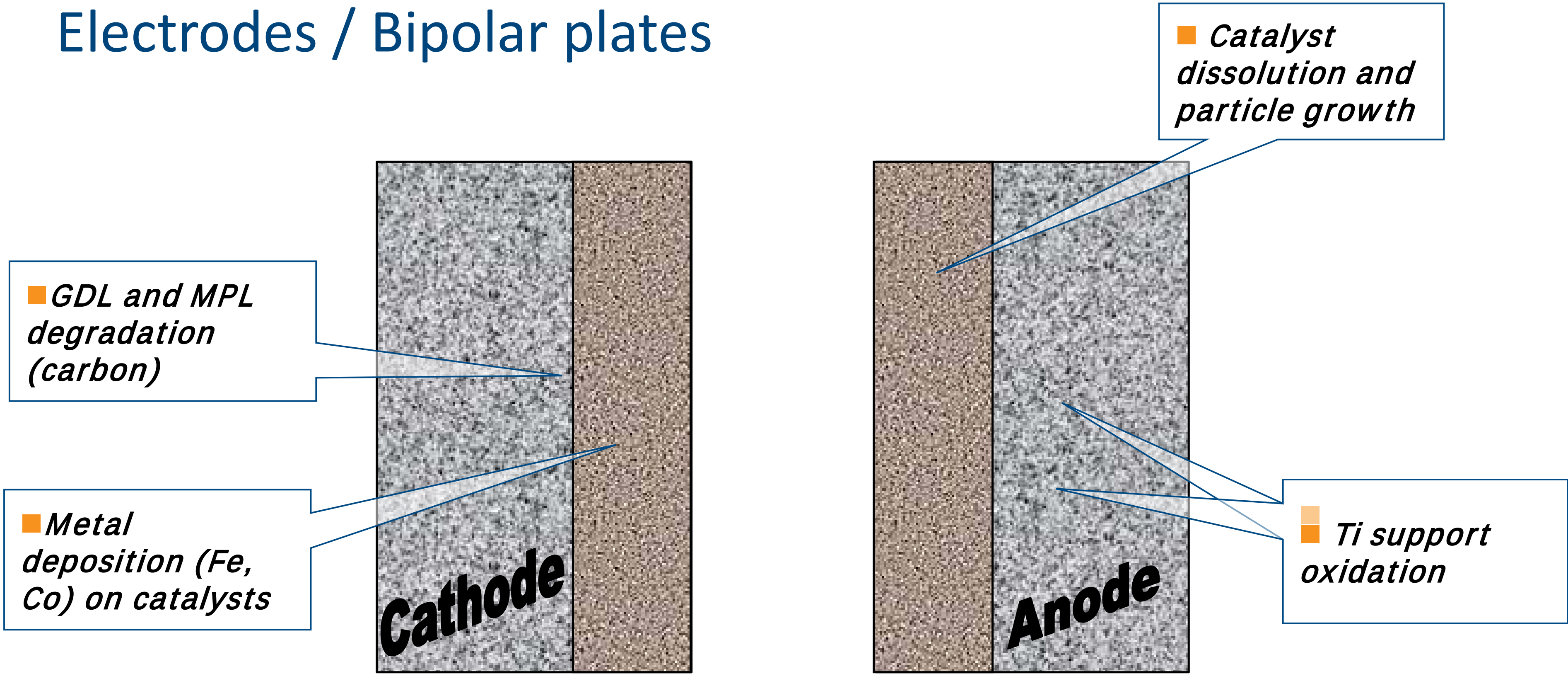
Peroxide detection using µ-electrodes.

- Convective flux seems to outweigh peroxide diffusion above 1.2 Acm^2
- Peroxide concentrations will be significant at positions close to the anode, even at high current densities.

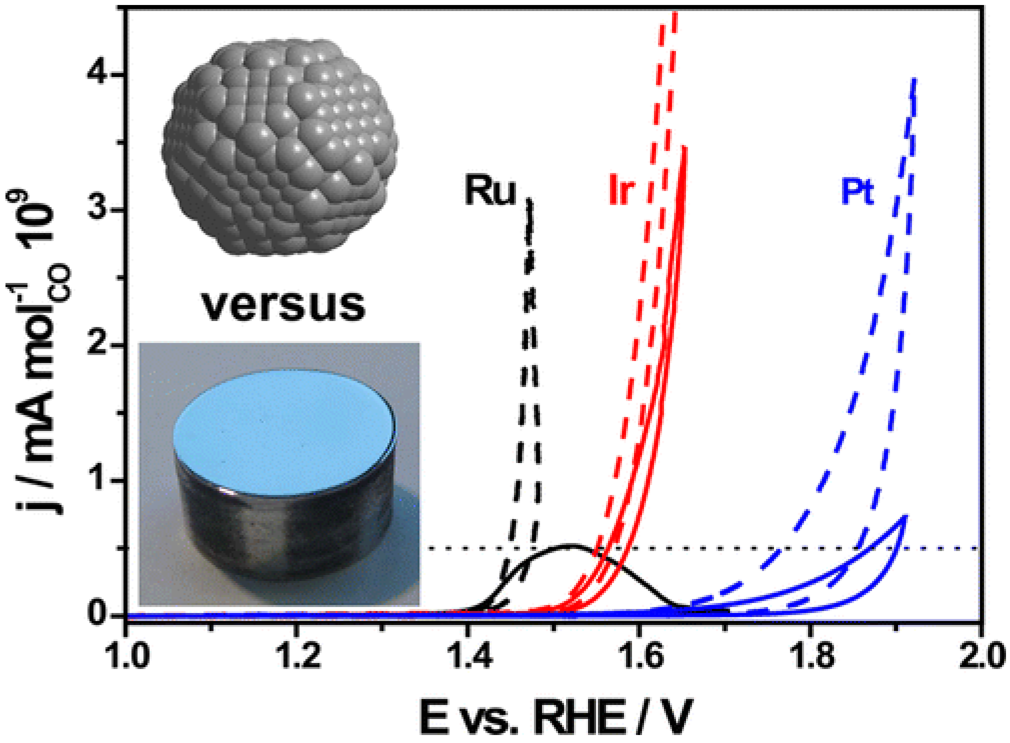




Electrodes / Bipolar plates

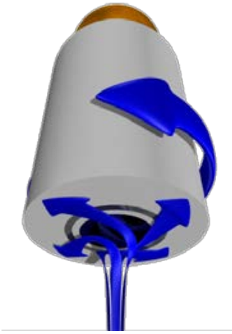


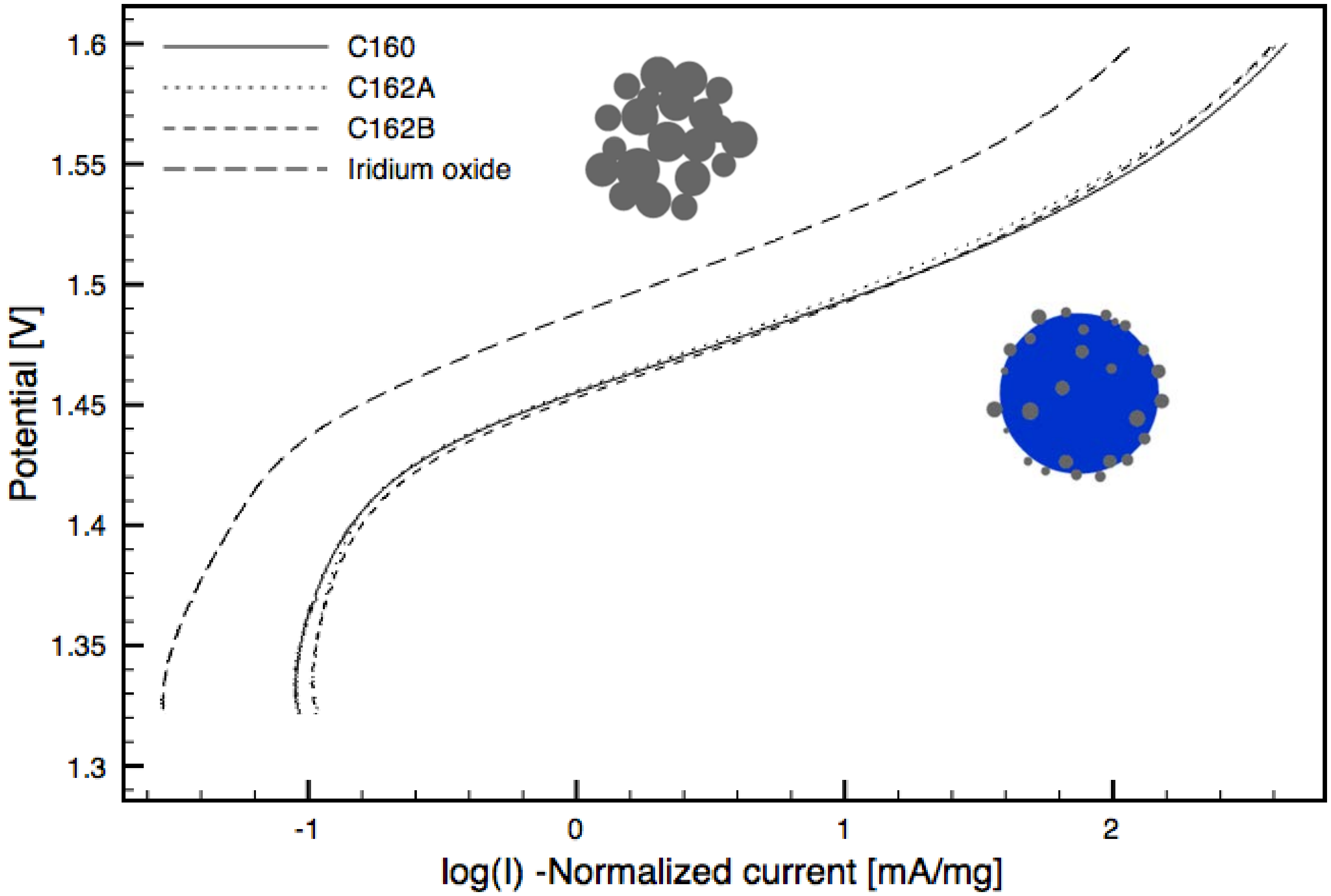
Nanostructuring of Ir and Ru



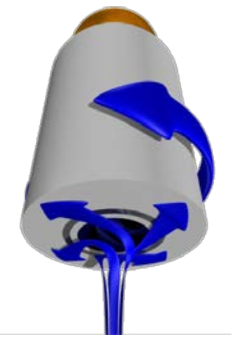
T. Reier, M. Oezaslan, P. Strasser *ACS Catal.*, **2012**, *2* (8), pp 1765–1772

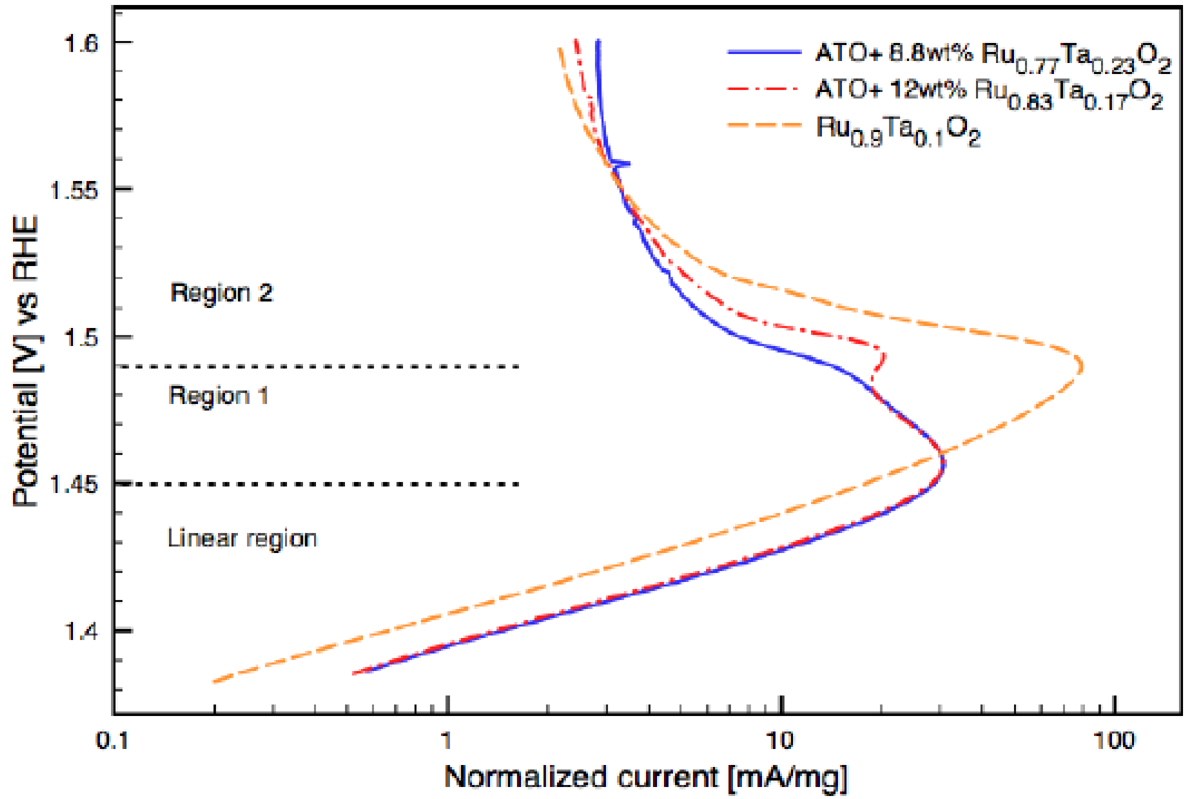
Supported vs. unsupported Ir



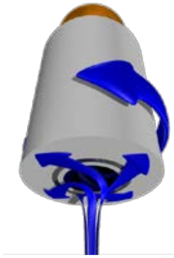


Supported vs. unsupported Ru

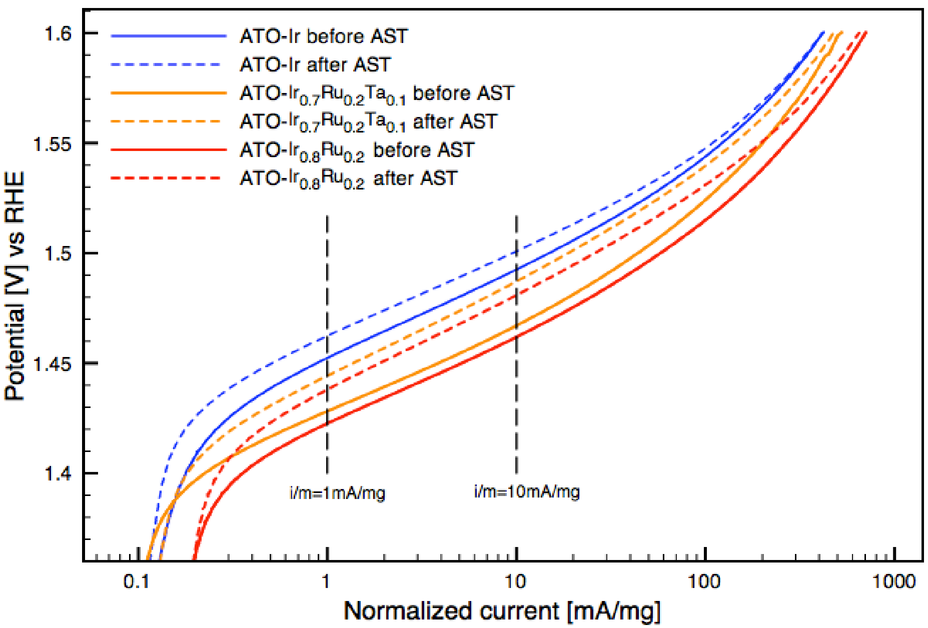




AST – Potential hold vs. voltage cycling

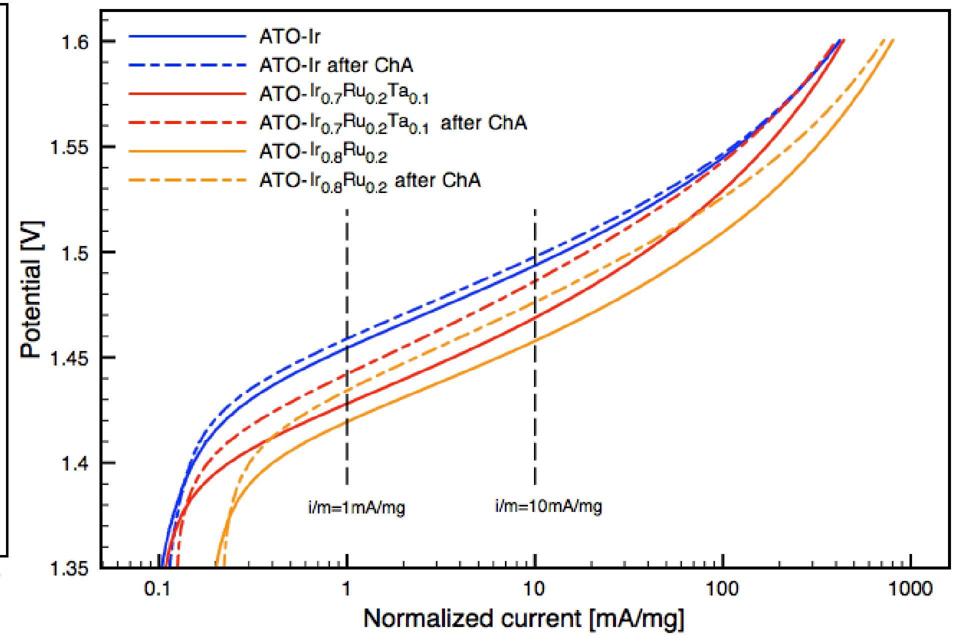


1.55 V 5h



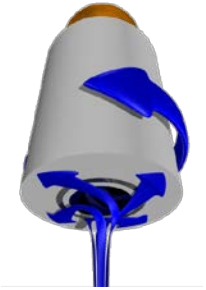
Catalyst	ΔE @ 1 mAmg^{-1}	ΔE @ 10 mA mg^{-1}
Ir	8	8
$Ir_{0.7}Ru_{0.2}Ta_{0.1}$	16	20
$Ir_{0.8}Ru_{0.2}$	15	19

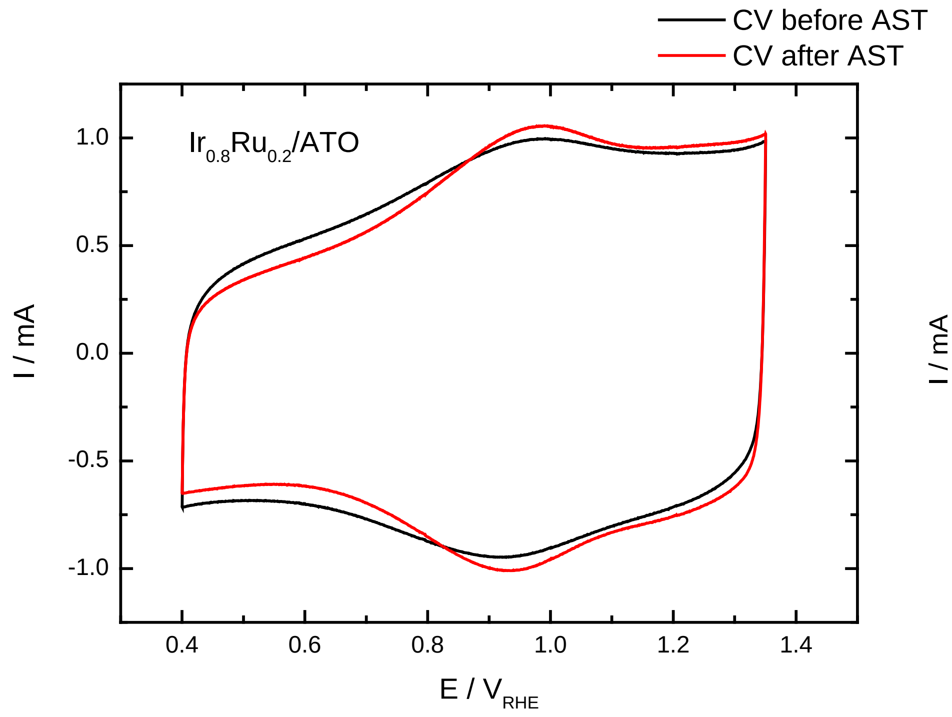
1.35-1.55 V, 10000 cycles, 1h

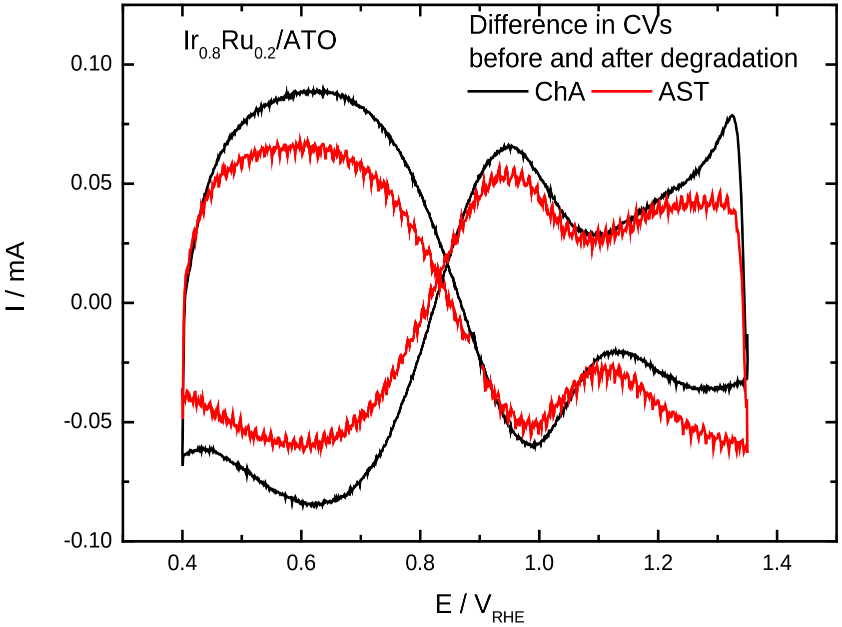


Catalyst	ΔE @ 1 mAmg^{-1}	ΔE @ 10 mA mg^{-1}
Ir	5	5
$Ir_{0.7}Ru_{0.2}Ta_{0.1}$	14	17
$Ir_{0.8}Ru_{0.2}$	15	18

AST – Potential hold vs. voltage cycling

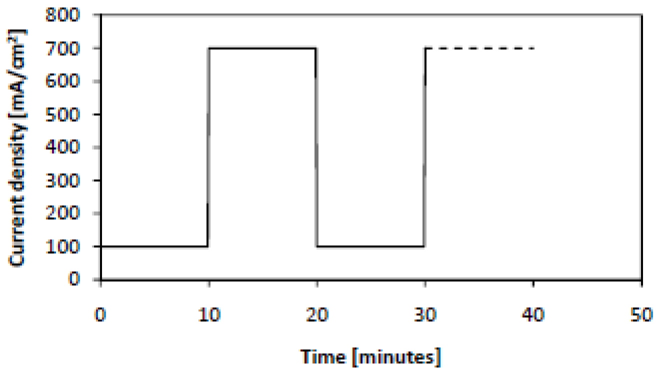


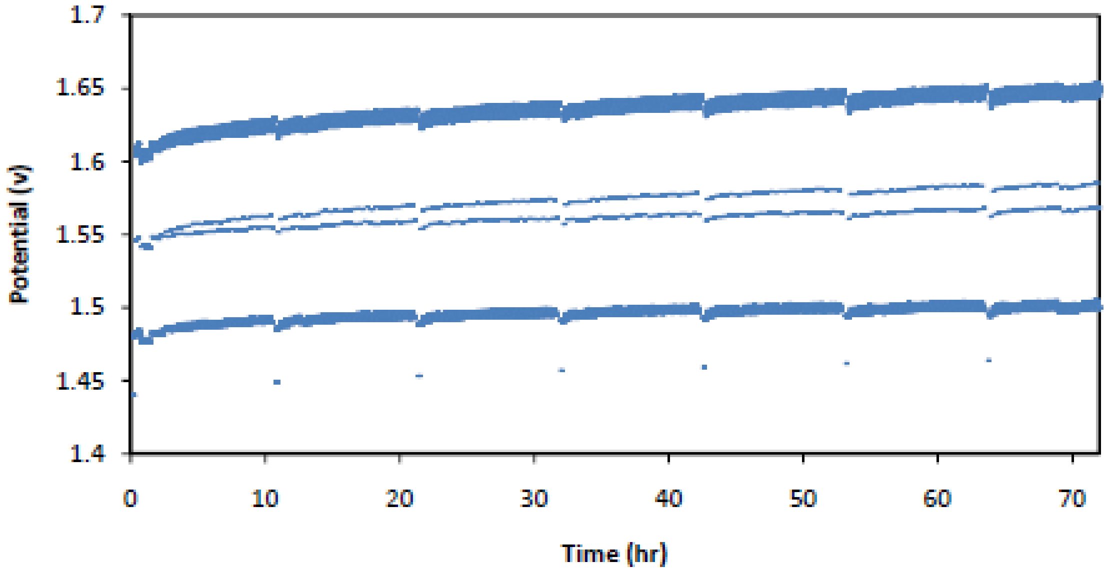




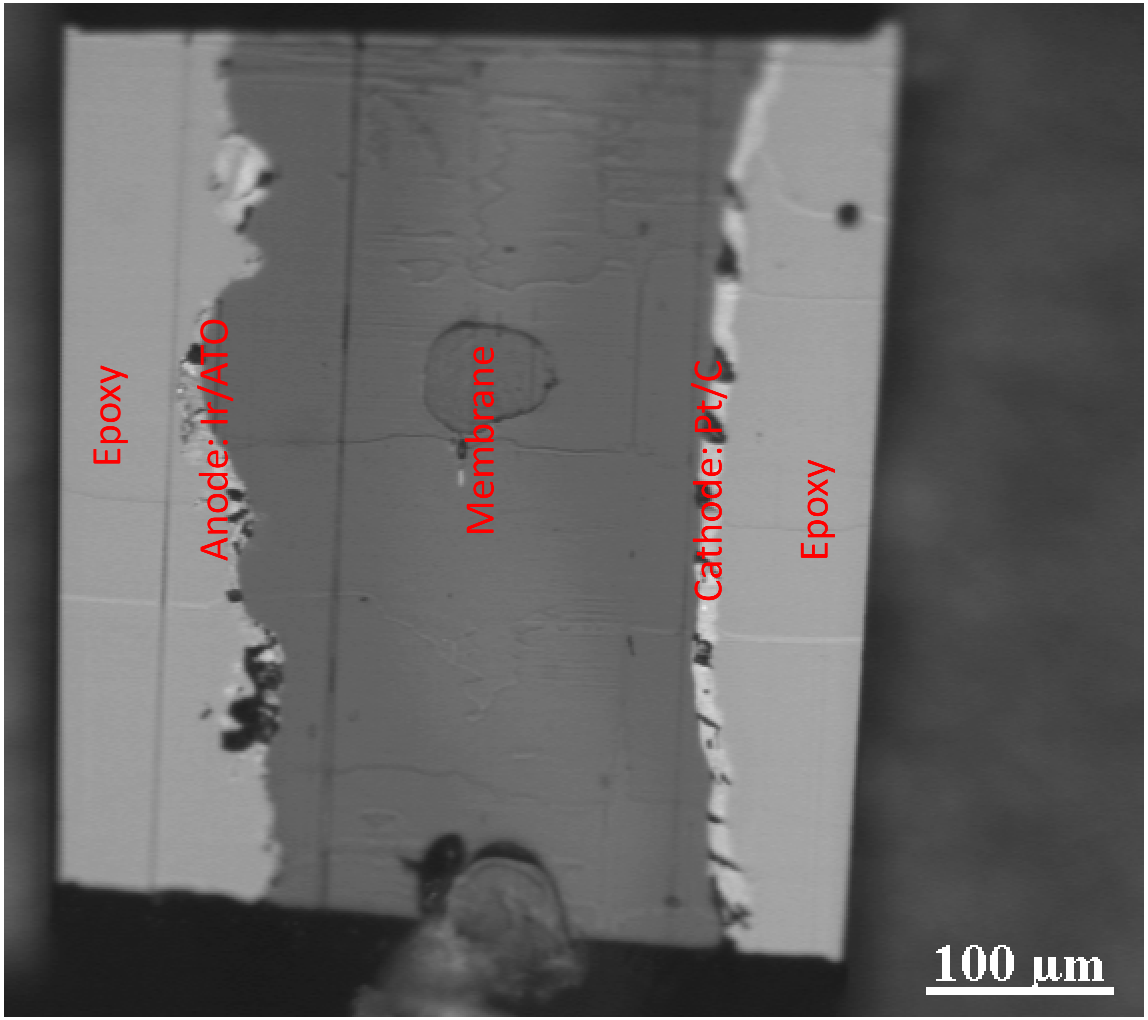
In situ degradation protocols

- Current cycling at 80 °C
- Polarisation curve every 10 h

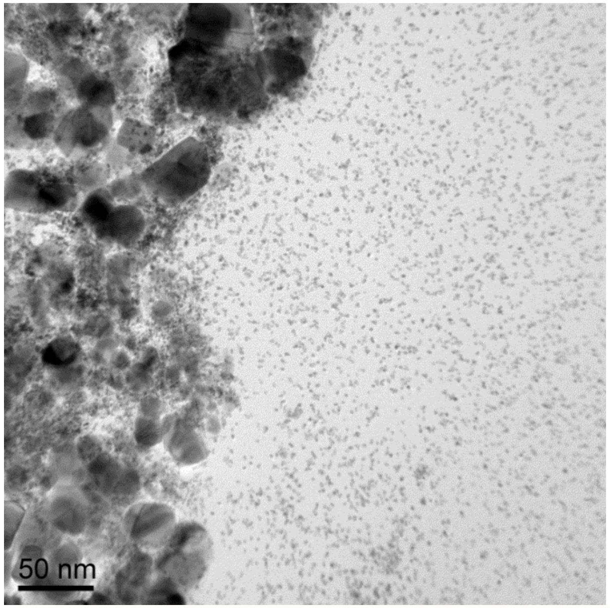


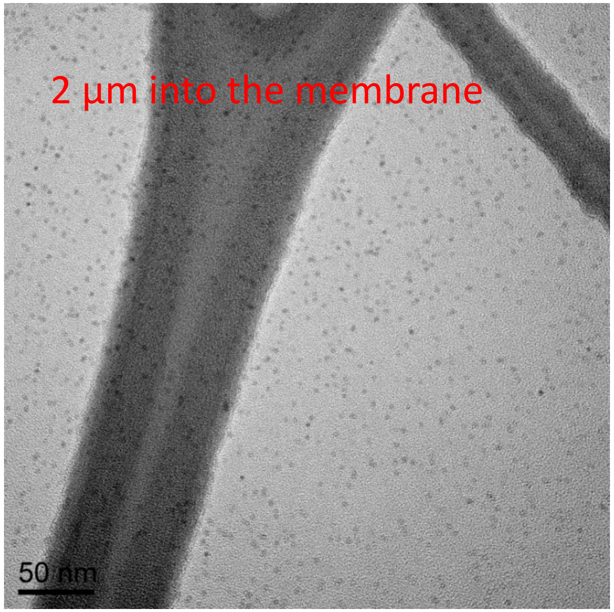


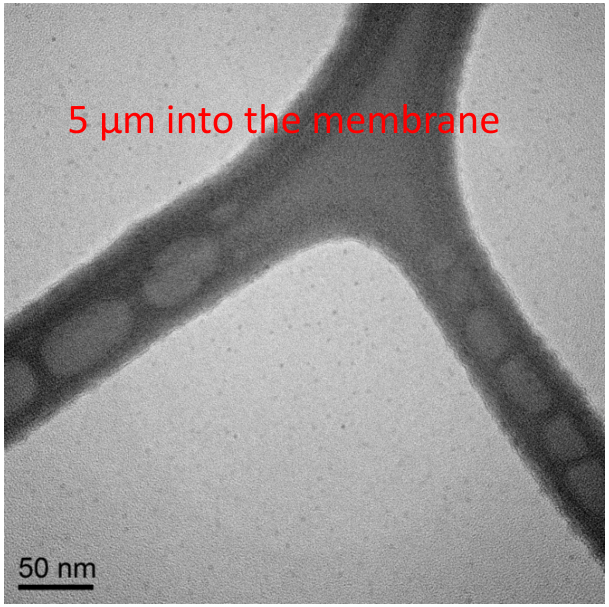
Long term test – TEM cross section analysis

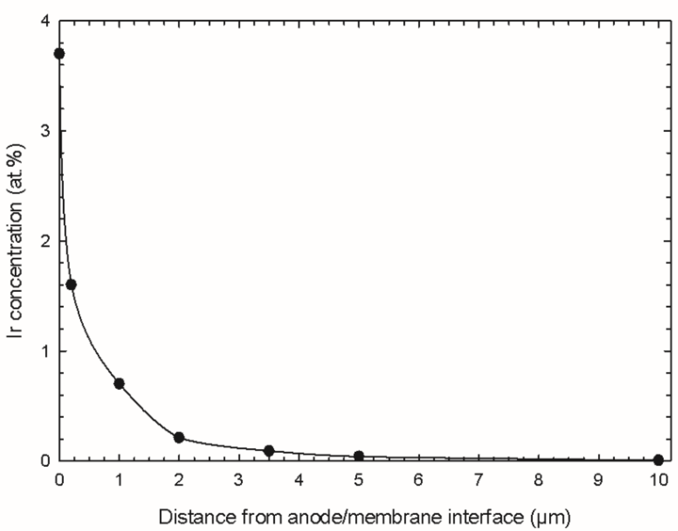


Ir/ATO - Anode



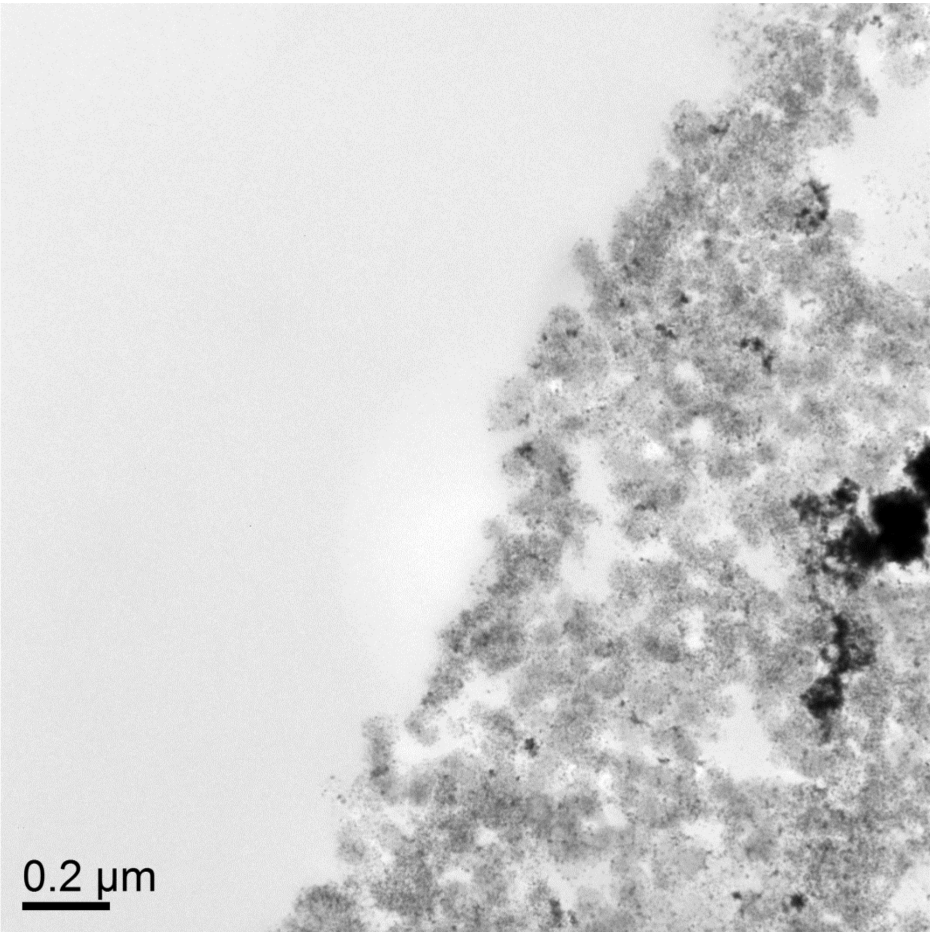


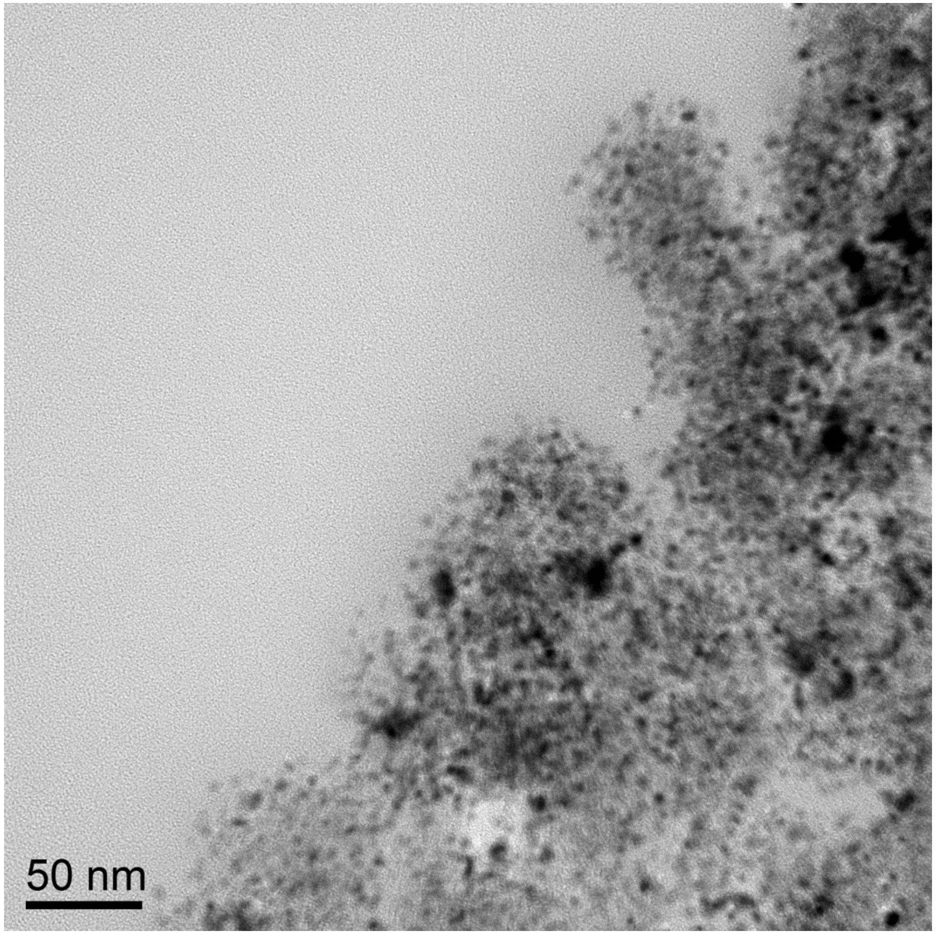




- A significant part of the Ir catalyst particles has diffused into the membrane
- No diffusion of ATO support into the membrane

Pt/C - Cathode





The interface between the membrane and the Pt/C cathode layer is sharp without any diffusion of particles into the membrane.

Summary

- The move towards cost reduction and efficiency improvements of PEM electrolyser will probably lead to increased degradation
- A lot can be learned / transferred from PEM fuel cells
  - Methodology
  - Diagnostic tools
- However, some degradation mechanisms are different
- Common accelerated stress test protocols (AST) for PEM electrolyser components is needed

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    Amin Zavieh

Partners

Nicolas Guillet, CEA

Tomas Klicpera, Fumatech

New Energy World JU

fuel cells & hydrogen for sustainability

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