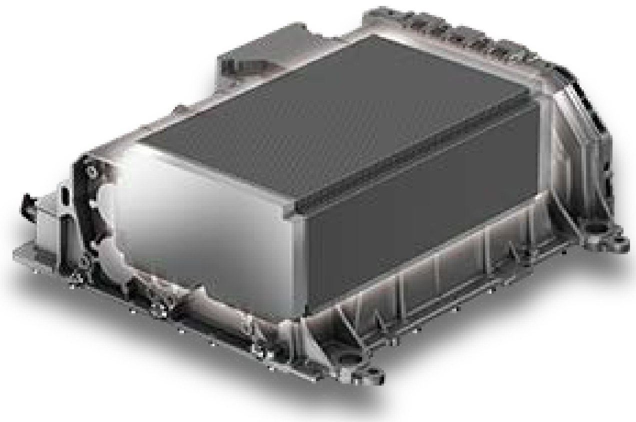
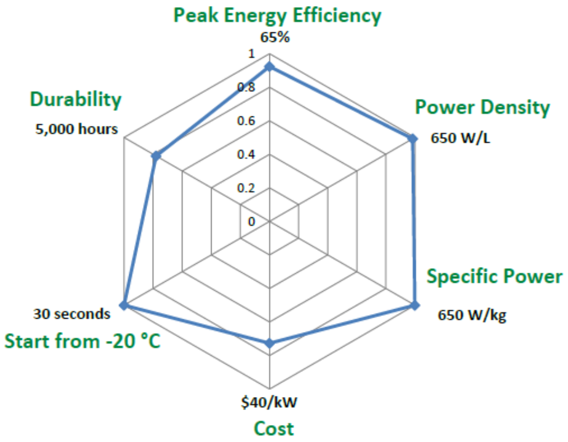
MATERIAL CHALLENGES FOR PEM FUEL CELLS AND ELECTROLYSERS

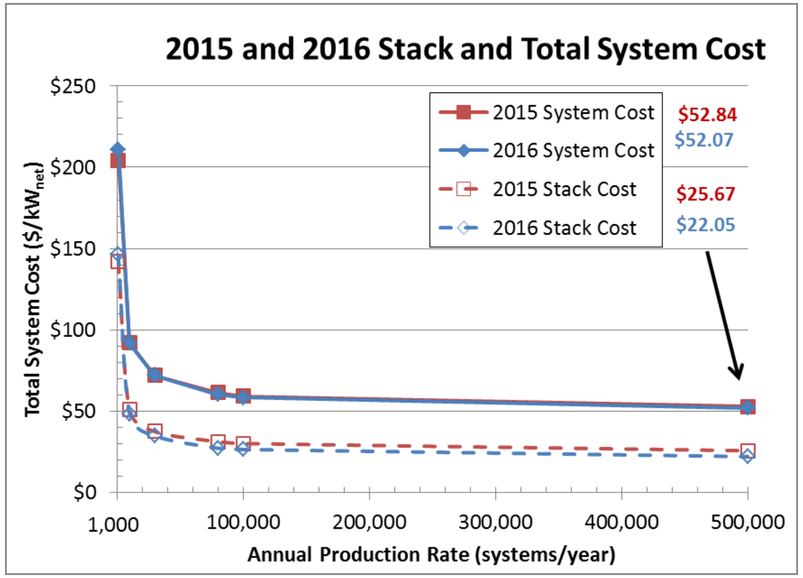
Degradation mitigation and cost reduction

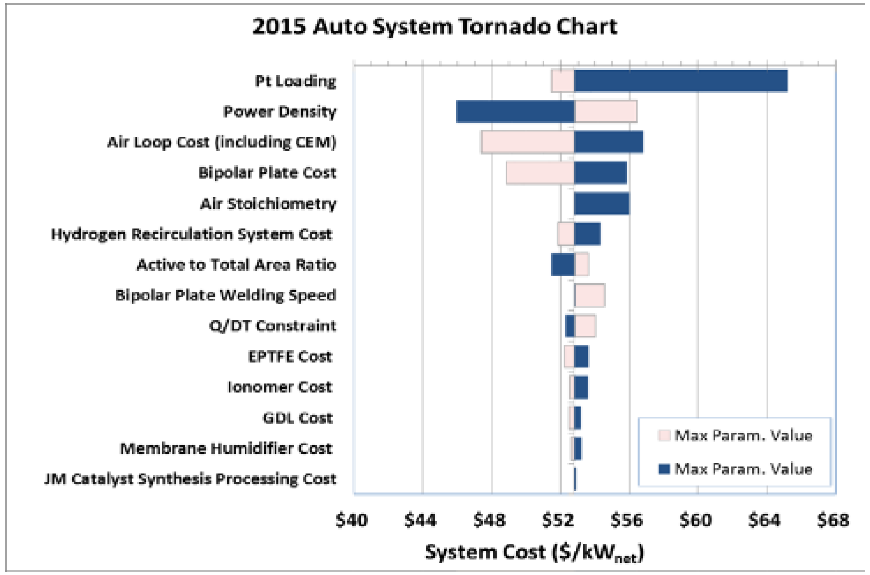
Magnus Thomassen
Senior Scientist, SINTEF Materials and Chemistry

PEM fuel cell status and cost



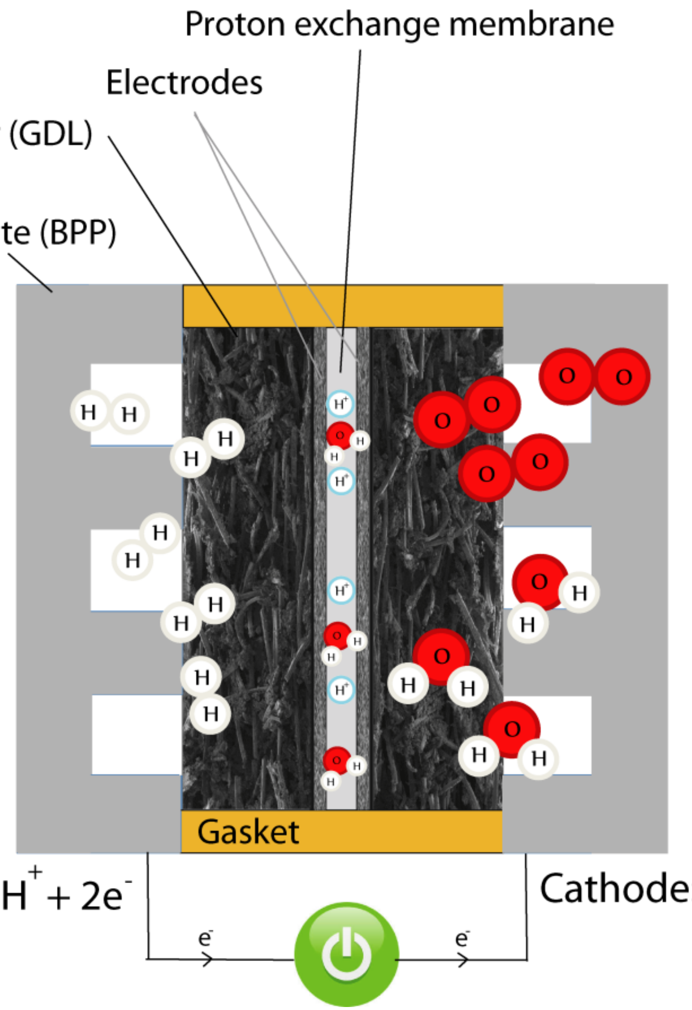






https://www.hydrogen.energy.gov/pdfs/review15/fc018_james_2015_o.pdf

PEM fuel cells and electrolysers



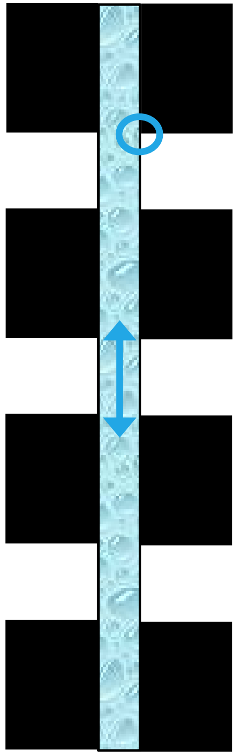
Anode: $H_2 \rightarrow 2H^+ + 2e^-$

Cathode: $2H^+ + 2e^- + 1/2\ O_2 \rightarrow H_2O$

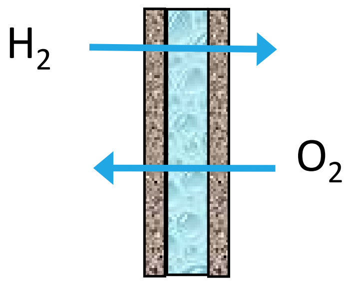
Membrane - Mechanical degradation

- 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?)

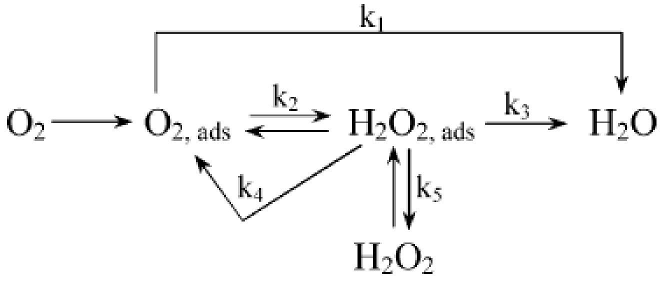
Fukuoka electrolyser accident



Membrane - Chemical Degradation



Gas crossover & chemical reaction



Oxygen reduction

- Peroxide formation "fingerprint" for chemical degradation of ionomer

H_2O_2
•OH
•OOH

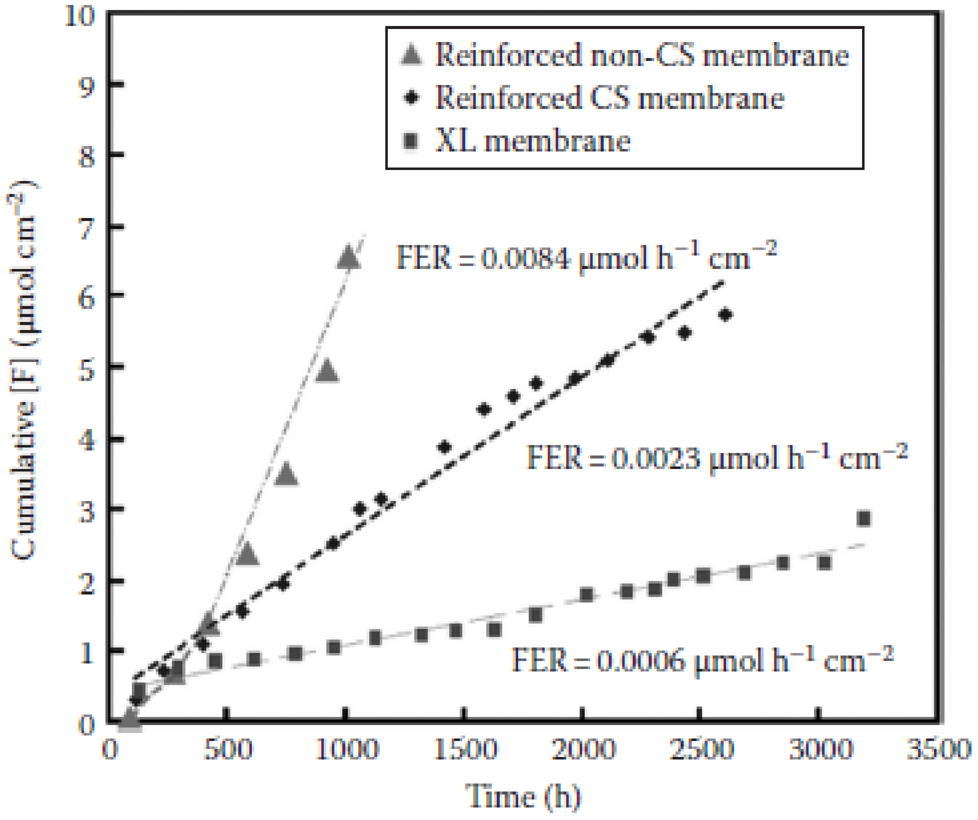
$$S + H_2O \rightleftharpoons S - OH_{ads} + H^+ + e^-$$
$$S - OH_{ads} \rightleftharpoons S - O + H^+ + e^-$$
$$2S - O \rightarrow 2S + O_{2(g)}$$

Oxygen evolution

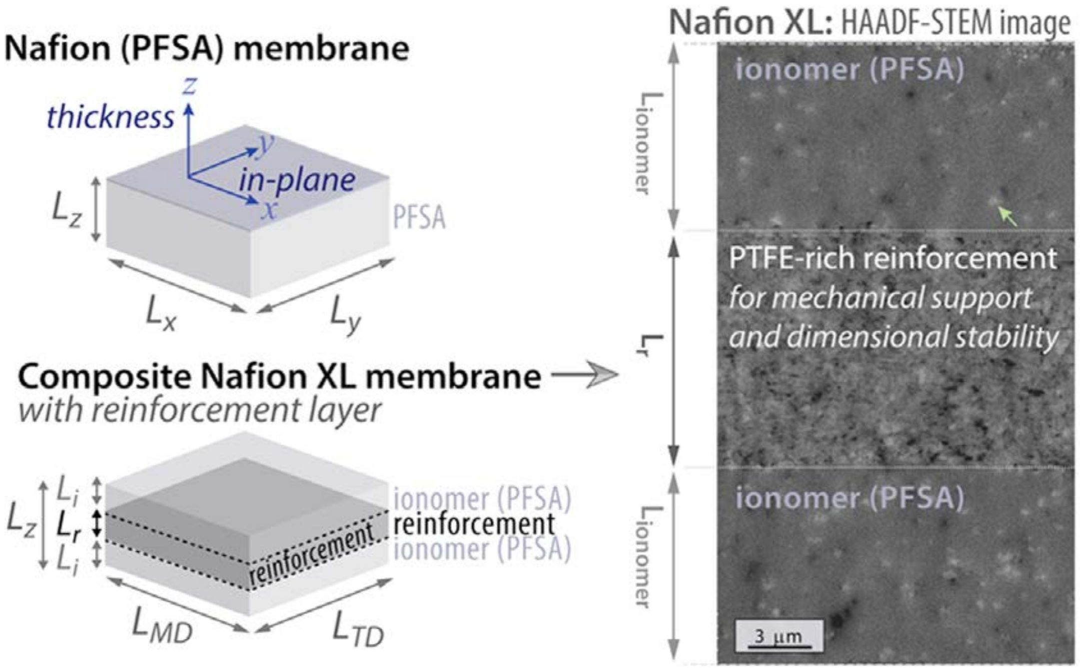
$Rf - CF_2COOH + \cdot OH \rightarrow Rf - CF_2\cdot + CO_2 + H_2O$
$Rf - CF_2\cdot + \cdot OH \rightarrow Rf - CF_2OH \rightarrow Rf - COF + \underline{HF}$
$Rf - COF + H_2O \rightarrow Rf - COOH + \underline{HF}$

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

Introduced mitigation strategies



Chapter 21. Handbook of Membrane Separations: Chemical, Pharmaceutical, Food and Biotechnological Applications



S. Shia, A. Z. Webera, A. Kusoglu Journal of Membrane Science Volume 516, 15 October 2016, Pages 123–134

AST protocol for membrane chemical stability

- PEM Fuel cells:
  OCV hold & RH cycling

- PEM Electrolysers: ?

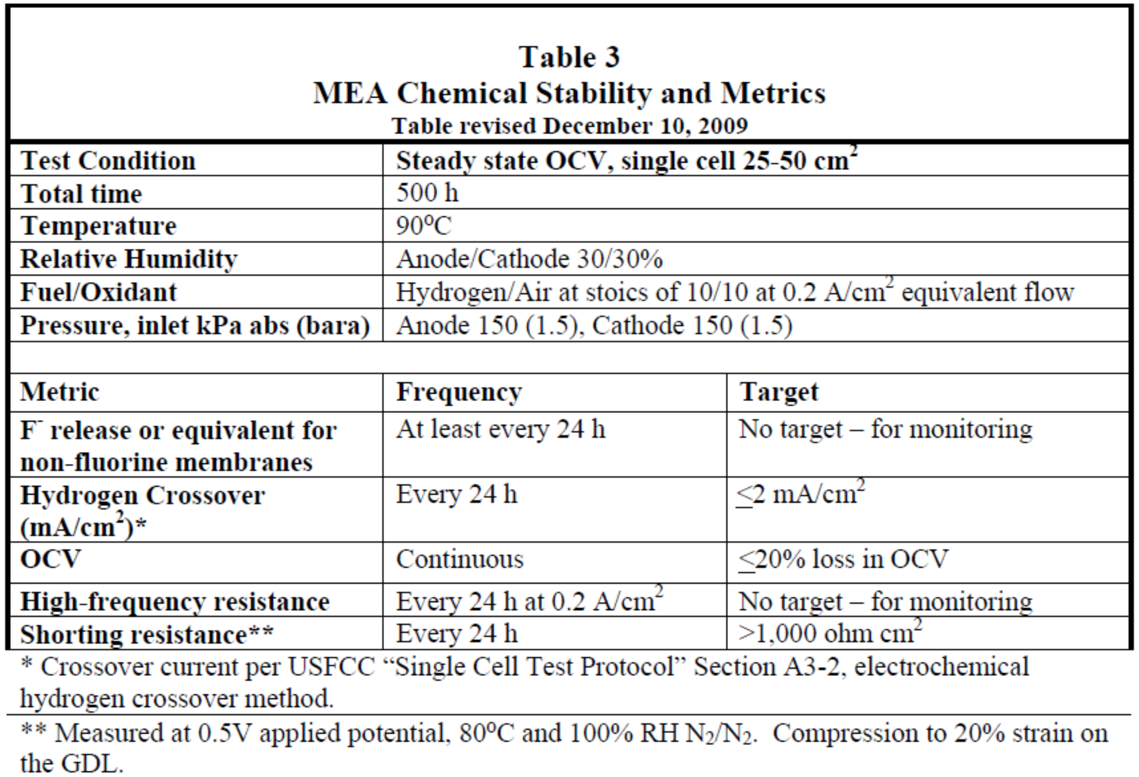


Table 3
MEA Chemical Stability and Metrics
Table revised December 10, 2009

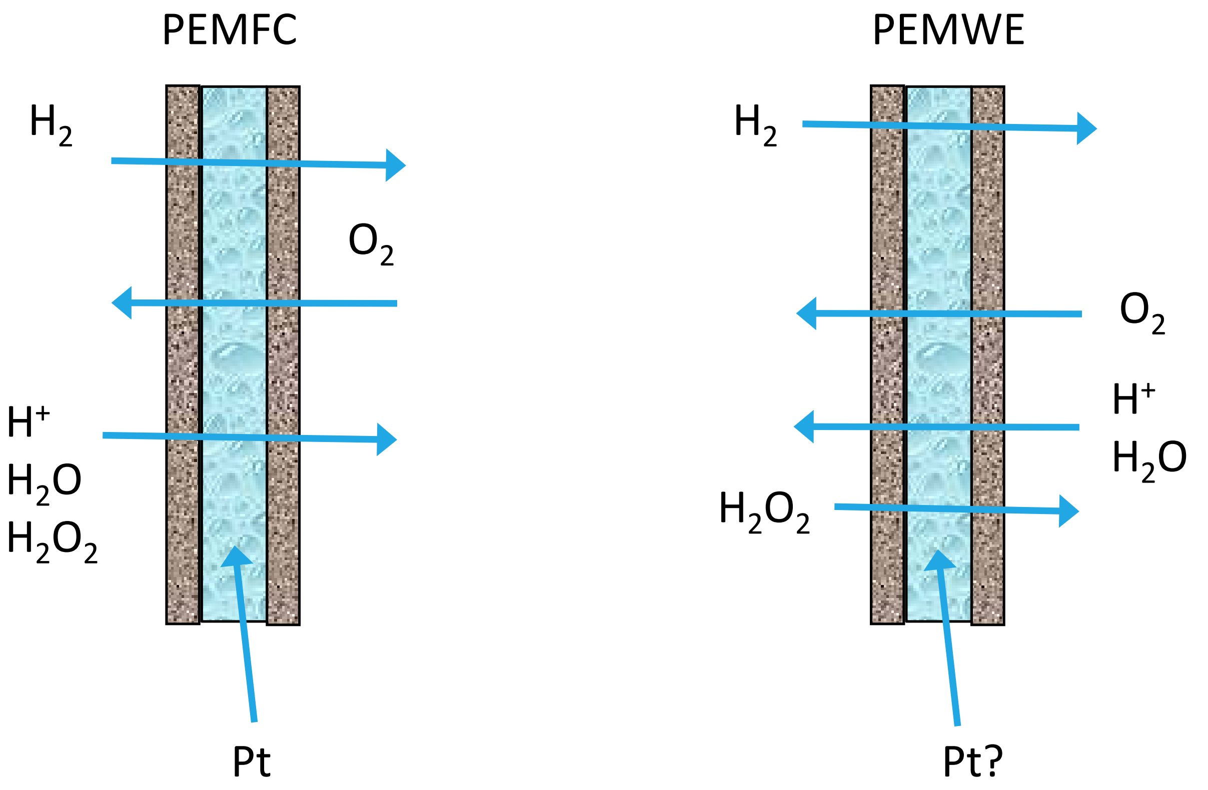
Test Condition	**Steady state OCV, single cell 25-50 cm^2**	
Total time	500 h	
Temperature	90°C	
Relative Humidity	Anode/Cathode 30/30%	
Fuel/Oxidant	Hydrogen/Air at stoics of 10/10 at 0.2 A/cm^2 equivalent flow	
Pressure, inlet kPa abs (bara)	Anode 150 (1.5), Cathode 150 (1.5)	
Metric	**Frequency**	**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.

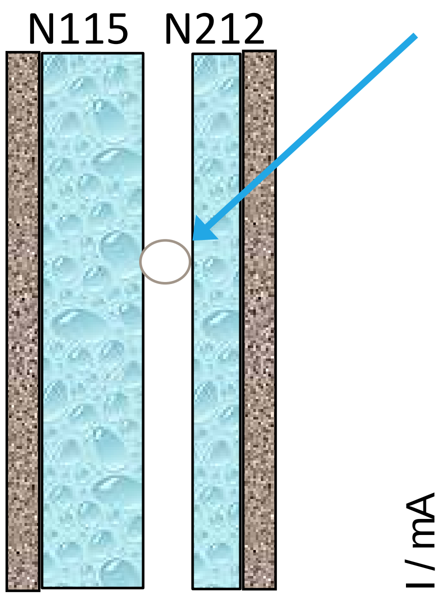
** Measured at 0.5V applied potential, 80°C and 100% RH N_2/N_2. Compression to 20% strain on the GDL.

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

PEM Fuel cells vs. PEM electrolysers

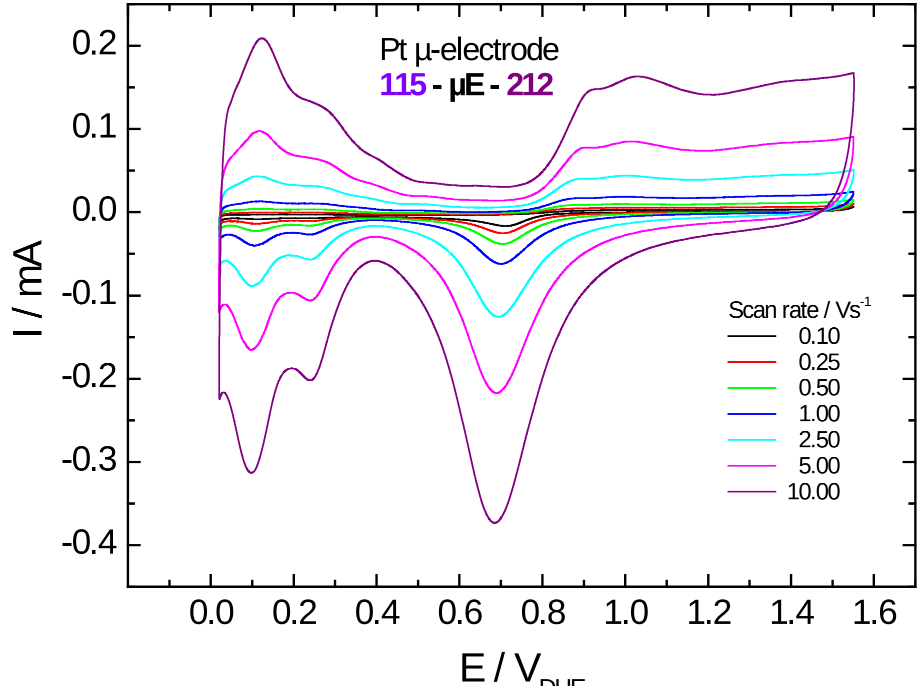


Peroxide detection using µ-electrodes.

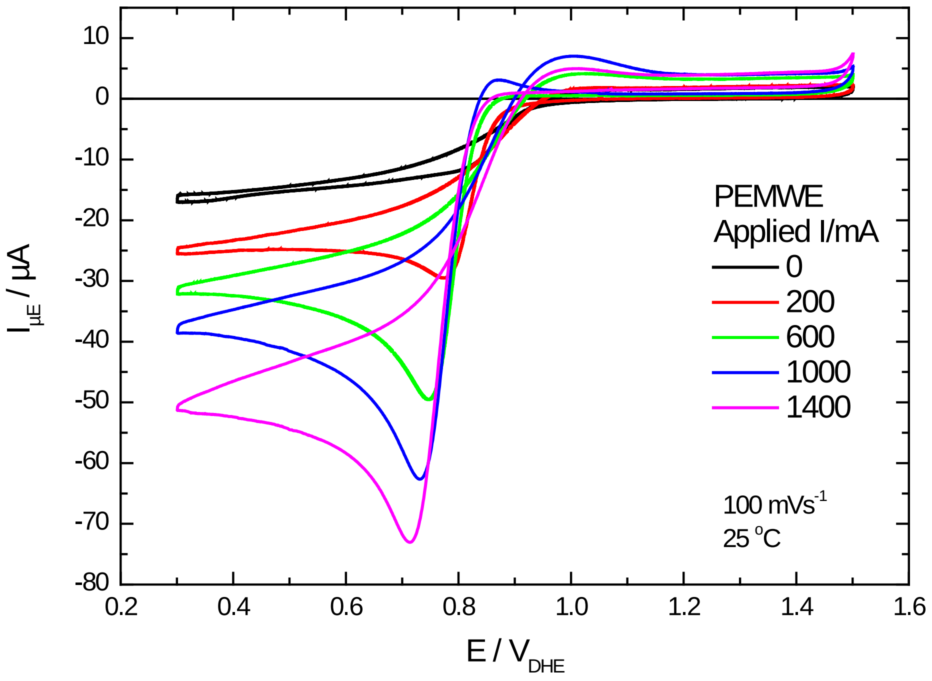


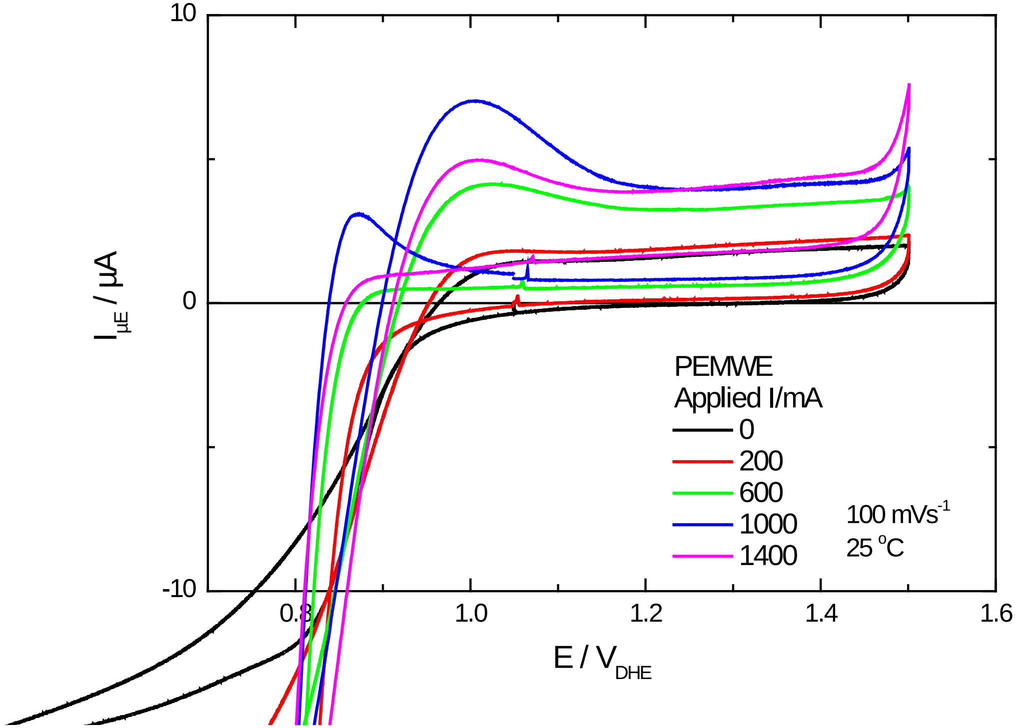
Pt wire 50 µm
PTFE insulated

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



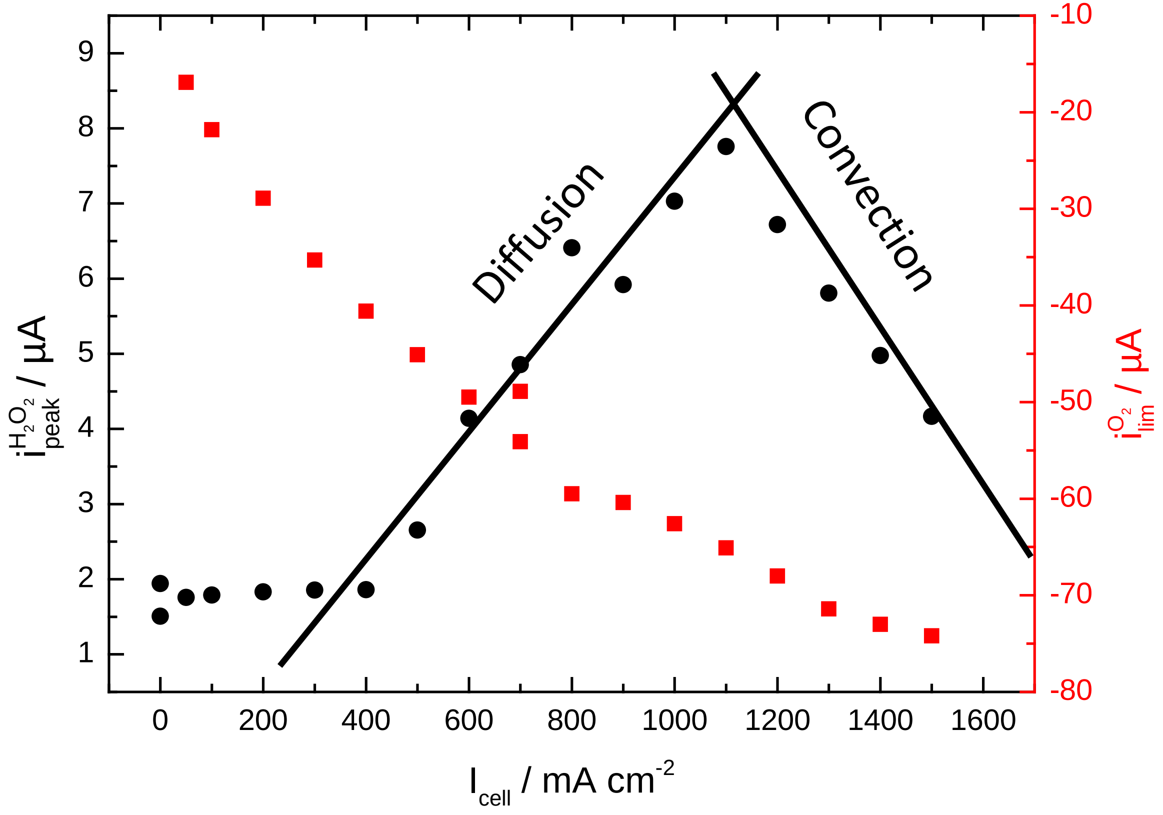
Peroxide detection using µ-electrodes.

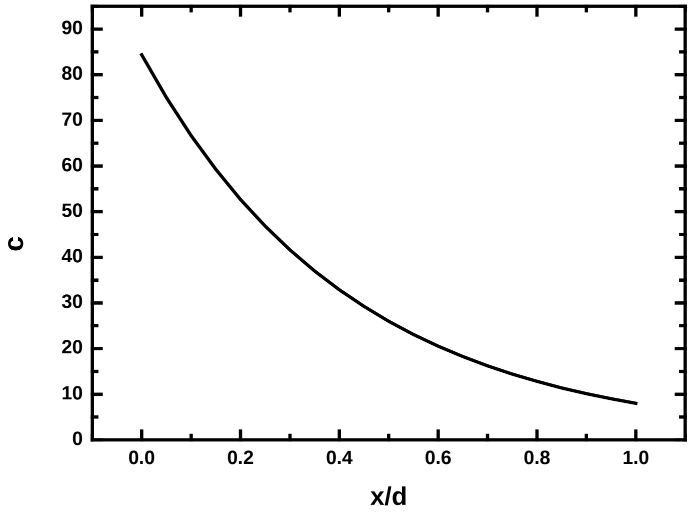




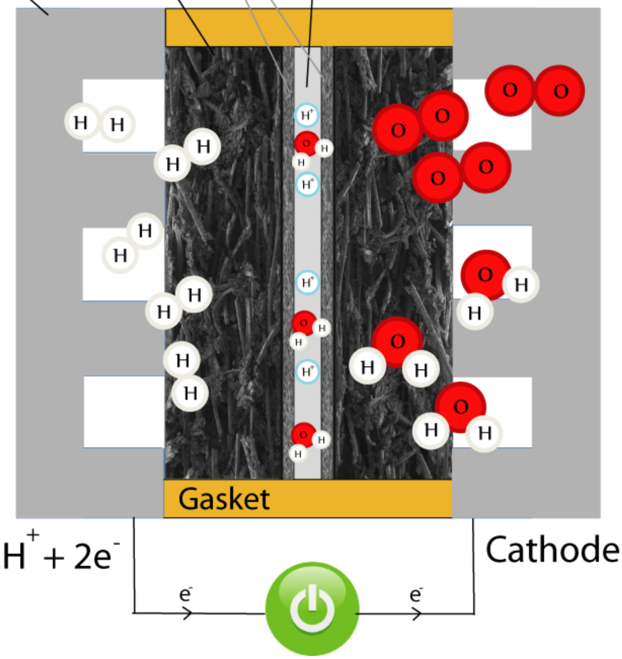
Peroxide detection using µ-electrodes.

- 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.





Bipolar plates for PEM fuel cells



Proton exchange membrane

Electrodes

Gas difusion layer (GDL)

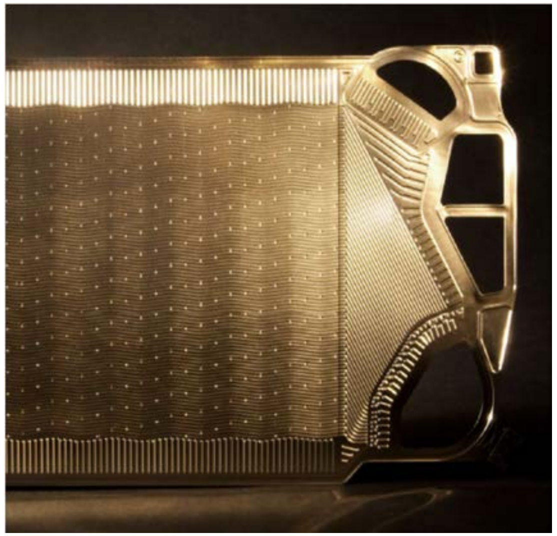
Bi-polar plate (BPP)

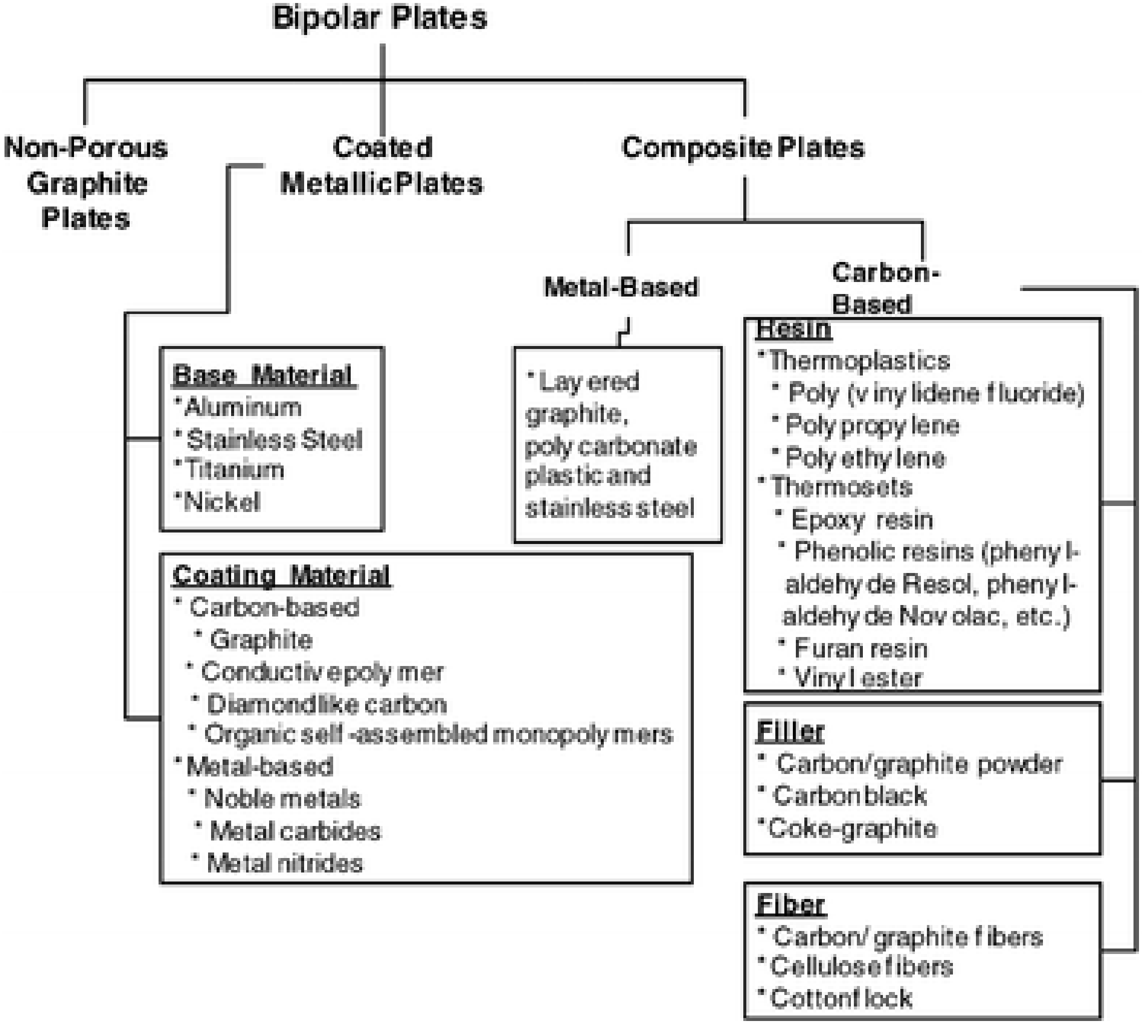
Gasket

Anode: $H_2 \rightarrow 2H^+ + 2e^-$

Cathode: $2H^+ + 2e^- + 1/2\ O_2 \rightarrow H_2O$

Bipolar plate materials

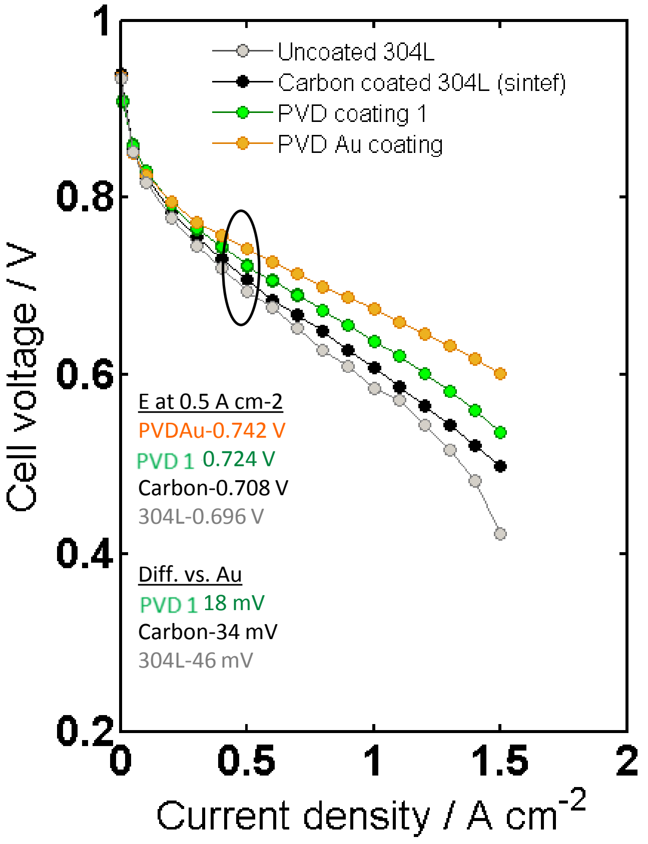


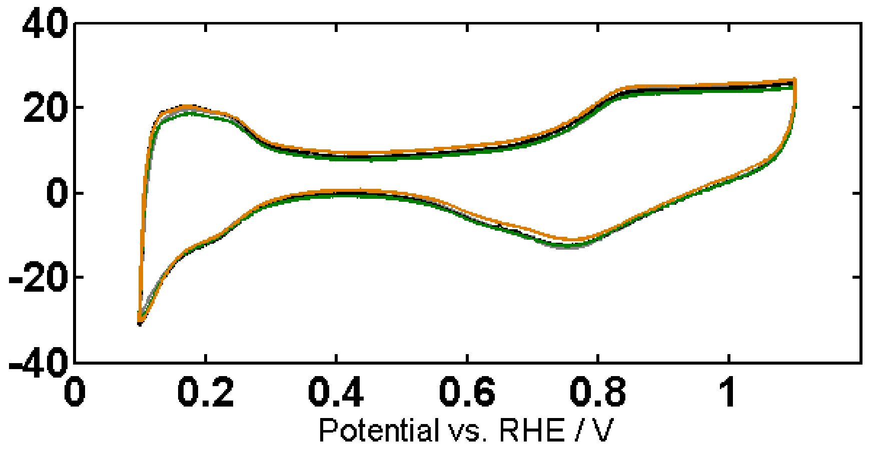


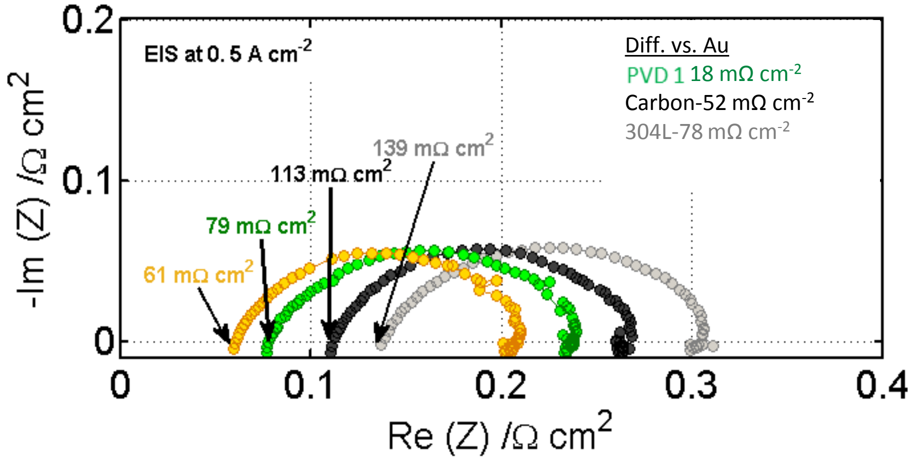
Bipolar Plates

- Non-Porous Graphite Plates
- Coated Metallic Plates
  - **Base Material**
    - Aluminum
    - Stainless Steel
    - Titanium
    - Nickel
  - **Coating Material**
    - Carbon-based
      - Graphite
      - Conductive polymer
      - Diamondlike carbon
      - Organic self-assembled monopolymers
    - Metal-based
      - Noble metals
      - Metal carbides
      - Metal nitrides
- Composite Plates
  - Metal-Based
    - Layered graphite, polycarbonate plastic and stainless steel
  - Carbon-Based
    - **Resin**
      - Thermoplastics
        - Poly (vinylidene fluoride)
        - Polypropylene
        - Polyethylene
      - Thermosets
        - Epoxy resin
        - Phenolic resins (phenyl-aldehyde Resol, phenyl-aldehyde Novolac, etc.)
        - Furan resin
        - Vinyl ester
    - **Filler**
      - Carbon/graphite powder
      - Carbon black
      - Coke-graphite
    - **Fiber**
      - Carbon/graphite fibers
      - Cellulose fibers
      - Cotton flock

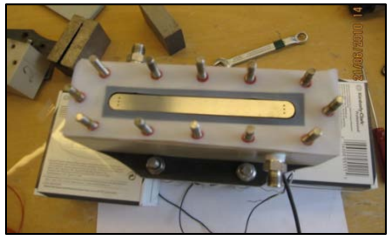
Fuel cell characterization of BPP







- Clear differences in HFR. Assuming membrane resistances are the same for all MEAs. Differences in HFR may be assumed to generated by the BPP



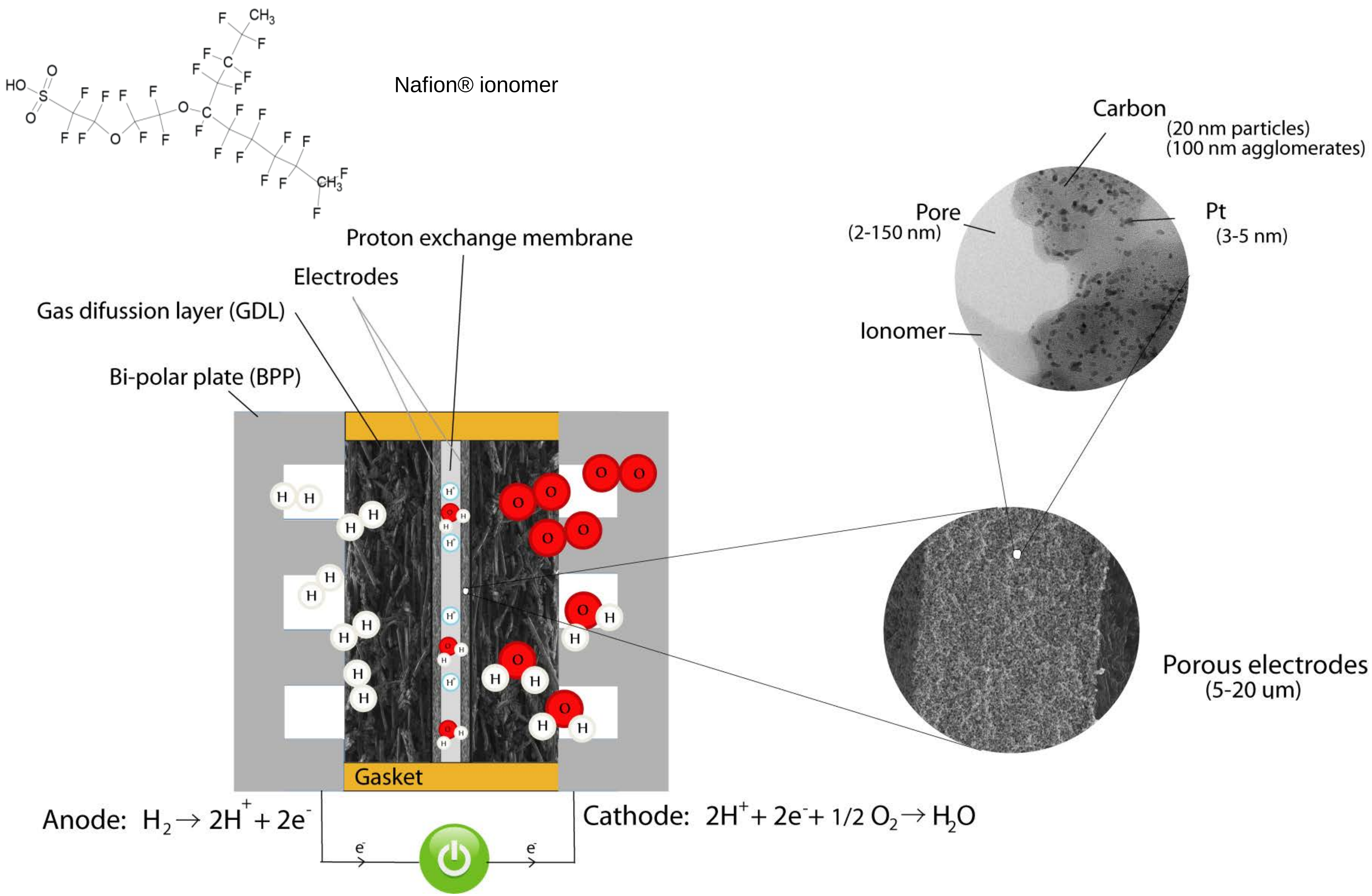
15 cm-2 active area

Bipolar plate requirements

Characteristic	**Units**	**2005 Status**	**2010**	**2015**
Cost	$ / kW	10	5	3
Total stack cost	$ / kW	65	30	20
MEA cost	$ / kW	50	15	10
Weight	kg / kW	0.36	<0.4	<0.4
H_2 permeation flux	cm^3 sec^{-1} cm^{-2} @ 80°C, 3 atm (equivalent to <0.1 mA / cm^2)	$<2 \times 10^{-6}$	$<2 \times 10^{-6}$	$<2 \times 10^{-6}$
Corrosion*	µA / cm^2	<1	<1	<1
Electrical conductivity	S / cm	>600	>100	>100
Resistivity (ICR)	Ohm cm^2	<0.02	0.01	0.01
Flexural Strength	MPa	>34	>25	>25
Flexibility	% deflection at mid-span	1.5 to 3.5	3 to 5	3 to 5
Durability	Hours			5000+

Requirements for PEM fuel cell bipolar plates from US Department of Energy
** 1 µA / cm^2 is eqvivalent to 11.5 µm y^{-1} for iron.*

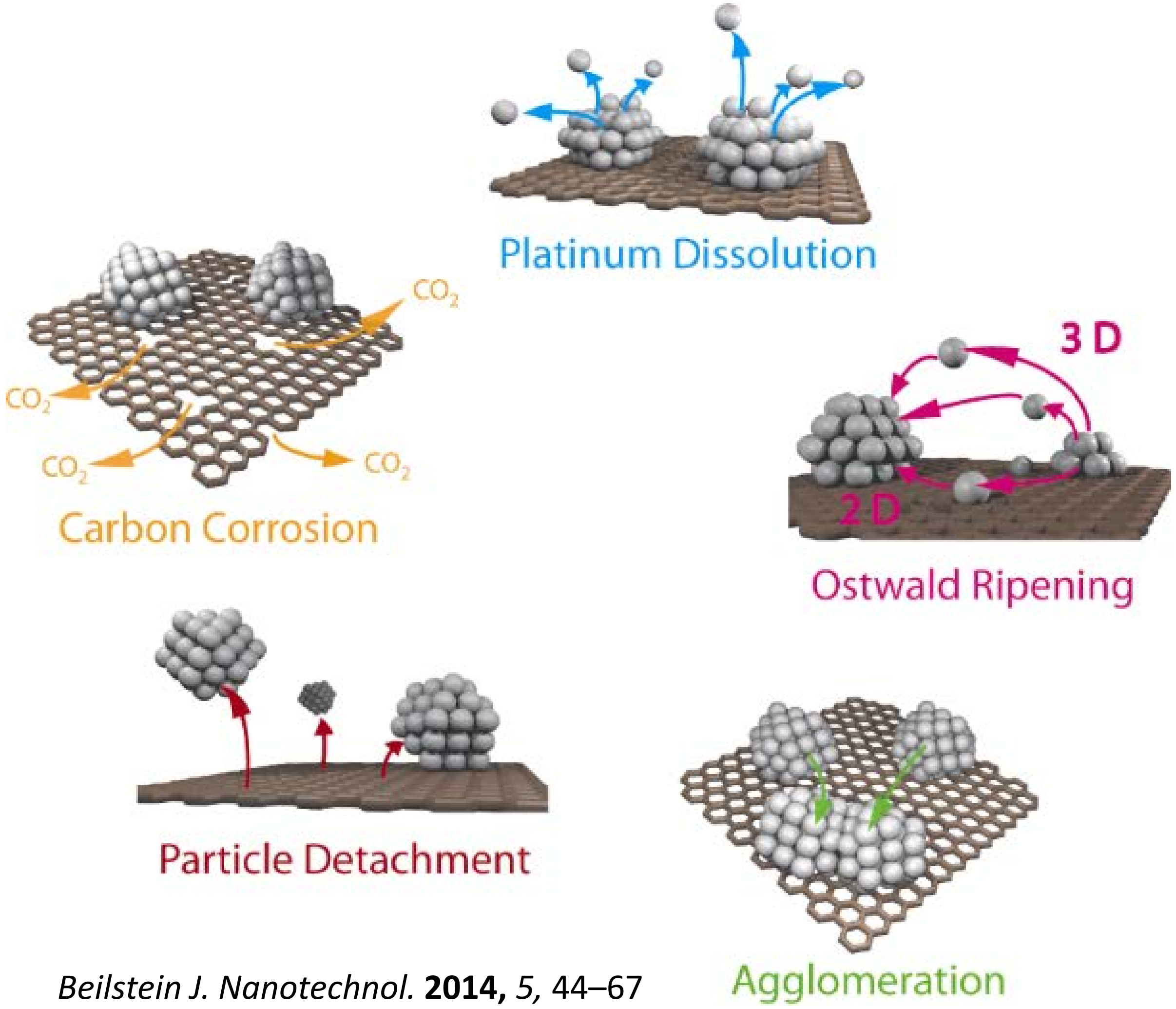
Electrodes for PEM fuel cells



Anode: $H_2 \rightarrow 2H^+ + 2e^-$

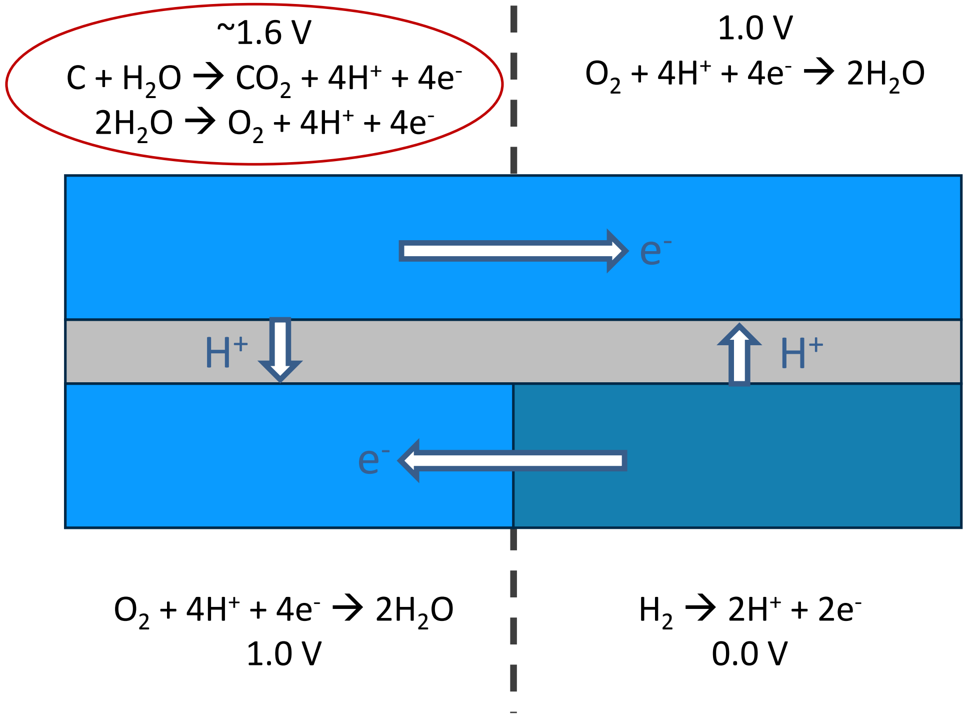
Cathode: $2H^+ + 2e^- + 1/2\ O_2 \rightarrow H_2O$

Degradation mechanisms



Beilstein J. Nanotechnol. **2014,** *5,* 44–67

The mechanism of carbon corrosion



~1.6 V
$C + H_2O \rightarrow CO_2 + 4H^+ + 4e^-$
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

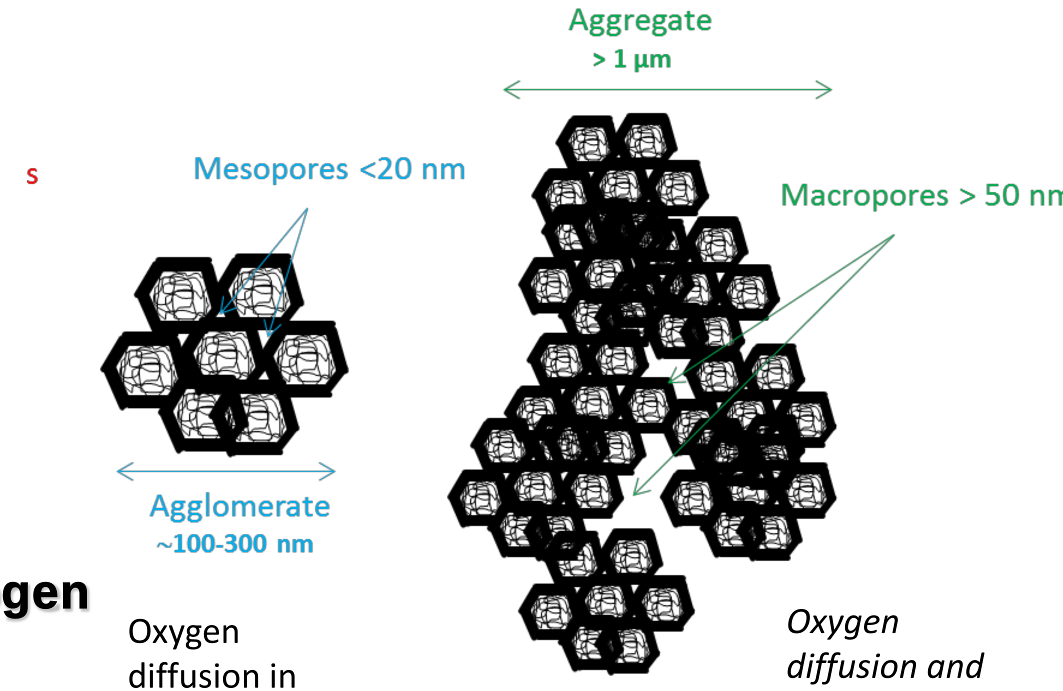
1.0 V
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
1.0 V

$H_2 \rightarrow 2H^+ + 2e^-$
0.0 V

🟦 **Air**

🟦 **Hydrogen**



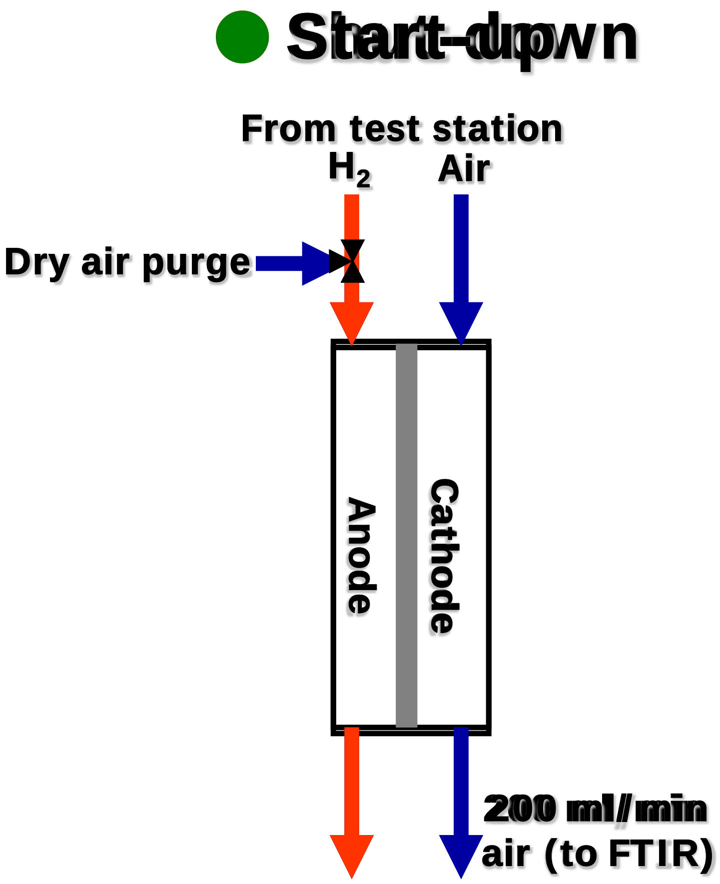
Oxygen diffusion in the agglomerate

Oxygen diffusion and water management in catalyst layer

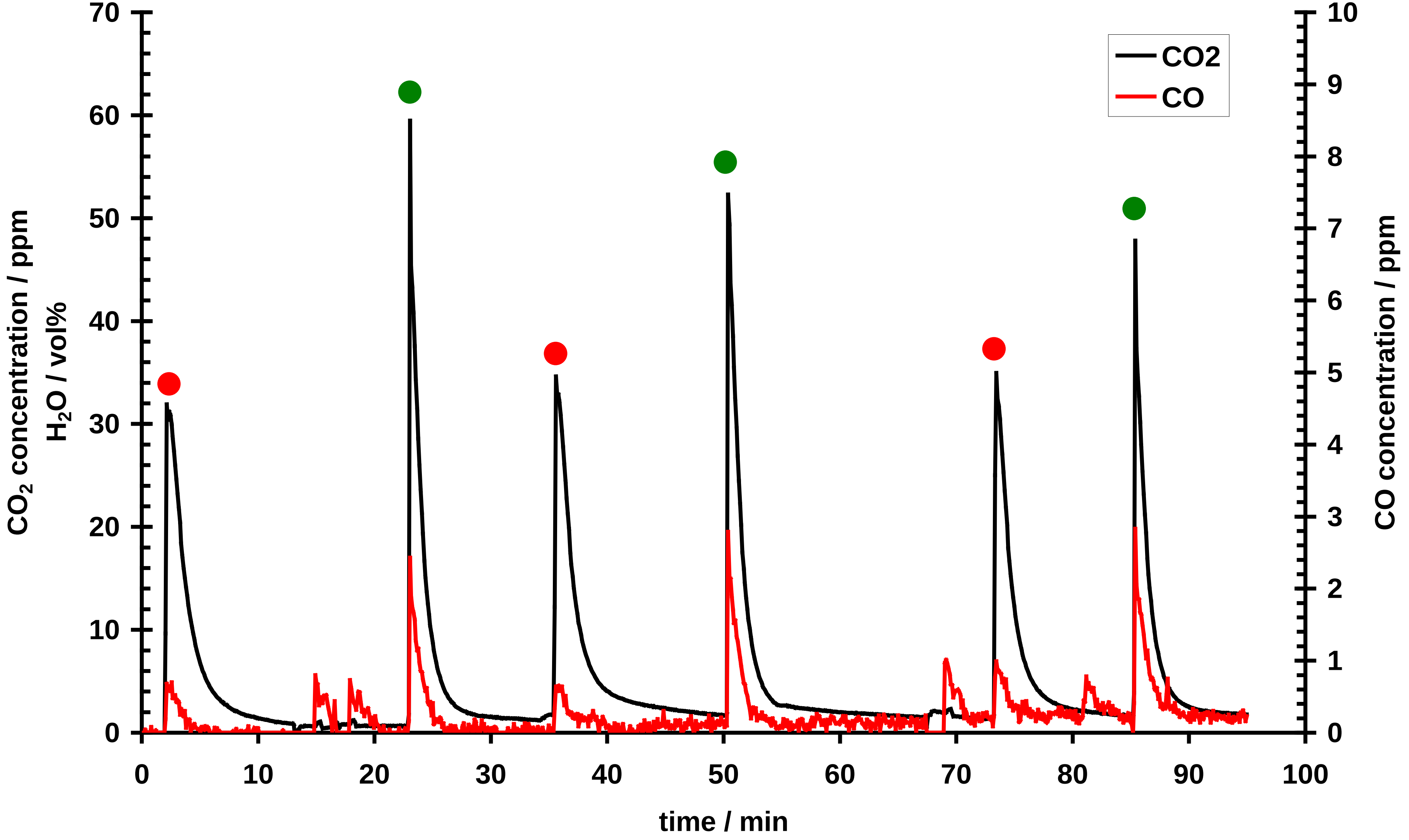
C.A. Reiser, L. Bregoli, T.W. Patterson, J.S. Yi, J.D. Yang, M.L. Perry and T.D. Jarvi, Electrochem. Solid-State Lett., 8, A273 (2005).

In situ carbon corrosion measurement by FTIR

- The fuel cell operates at **open circuit** at the start-up conditions.
- Gas flows are **not stopped** during shut-down.
- Purge air is either dry or passed through the anode humidifier.

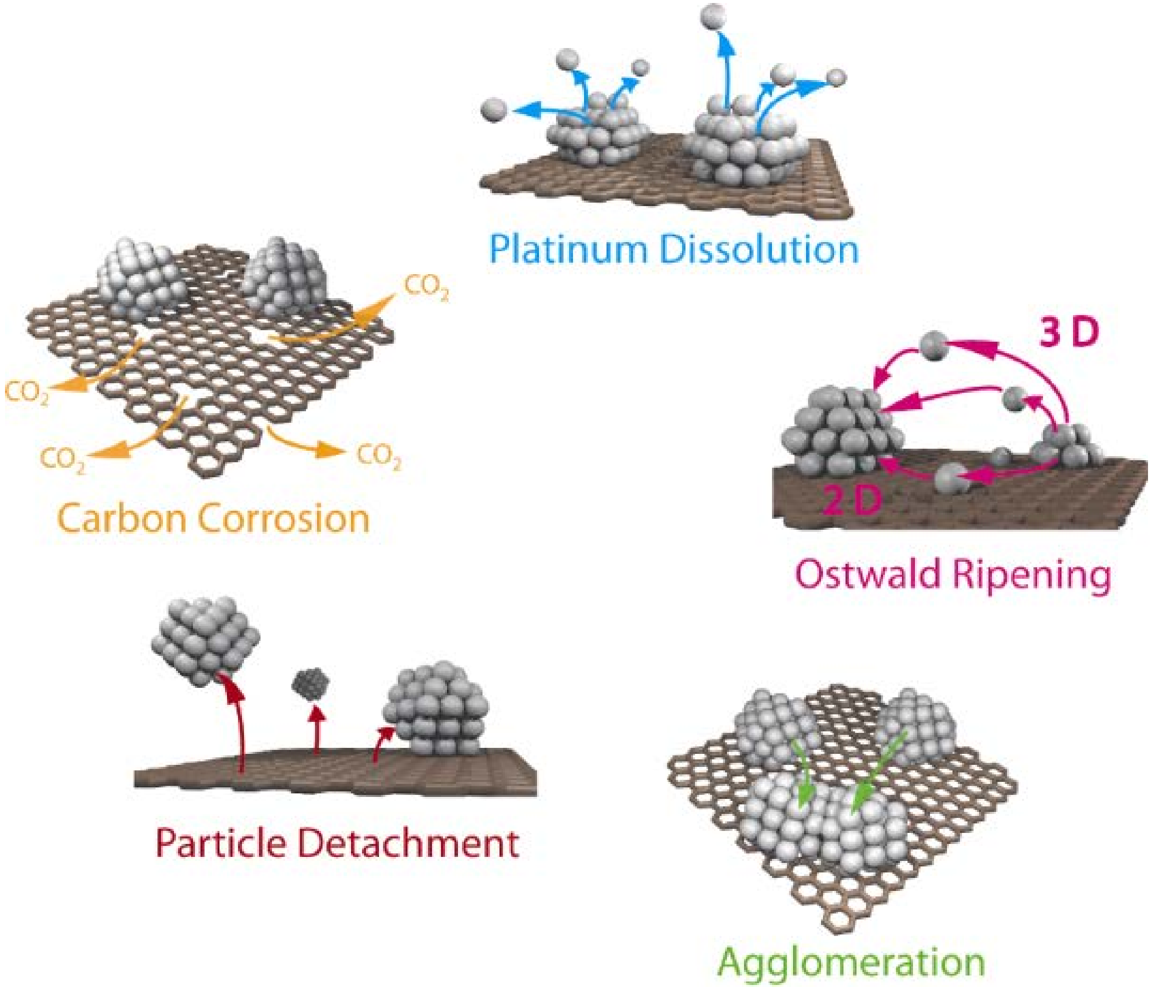


Results

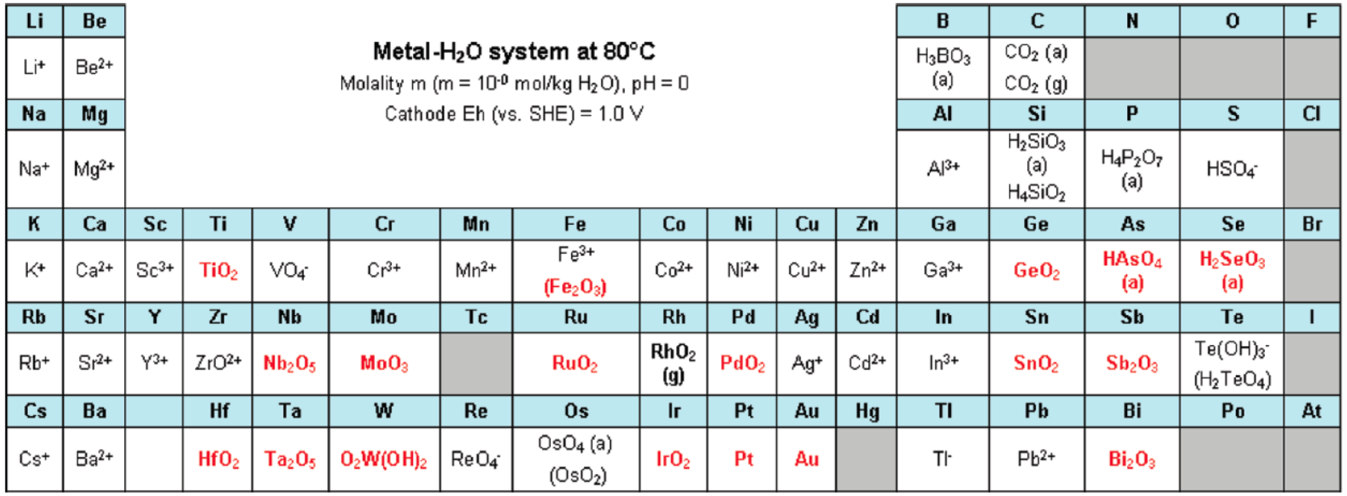


70
60
50
40
30
20
10
0
CO_2 concentration / ppm
H_2O / vol%
10
9
8
7
6
5
4
3
2
1
0
CO concentration / ppm
0
10
20
30
40
50
60
70
80
90
100
time / min
CO2
CO

Oxide supports



Criteria for selecting the support



Metal-H_2O system at 80°C

Molality m (m = 10^{-0} mol/kg H_2O), pH = 0

Cathode Eh (vs. SHE) = 1.0 V

Li	**Be**											**B**	**C**	**N**	**O**	**F**
Li^+	Be^{2+}											H_3BO_3 (a)	CO_2 (a) CO_2 (g)			
Na	**Mg**											**Al**	**Si**	**P**	**S**	**Cl**
Na^+	Mg^{2+}											Al^{3+}	H_2SiO_3 (a) H_4SiO_2	$H_4P_2O_7$ (a)	HSO_4^-	
K	**Ca**	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Ga**	**Ge**	**As**	**Se**	**Br**
K^+	Ca^{2+}	Sc^{3+}	**TiO_2**	VO_4^-	Cr^{3+}	Mn^{2+}	Fe^{3+} **(Fe_2O_3)**	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Ga^{3+}	**GeO_2**	**$HAsO_4$ (a)**	**H_2SeO_3 (a)**	
Rb	**Sr**	**Y**	**Zr**	**Nb**	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**	**Cd**	**In**	**Sn**	**Sb**	**Te**	**I**
Rb^+	Sr^{2+}	Y^{3+}	ZrO^{2+}	**Nb_2O_5**	**MoO_3**		**RuO_2**	**RhO_2 (g)**	**PdO_2**	Ag^+	Cd^{2+}	In^{3+}	**SnO_2**	**Sb_2O_3**	$Te(OH)_3^-$ (H_2TeO_4)	
Cs	**Ba**		**Hf**	**Ta**	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	**Hg**	**Tl**	**Pb**	**Bi**	**Po**	**At**
Cs^+	Ba^{2+}		**HfO_2**	**Ta_2O_5**	**$O_2W(OH)_2$**	ReO_4^-	OsO_4 (a) (OsO_2)	**IrO_2**	**Pt**	**Au**		Tl^-	Pb^{2+}	**Bi_2O_3**		

K. Sasaki et al, ECS Trans., 2010, 33(1), 473-482

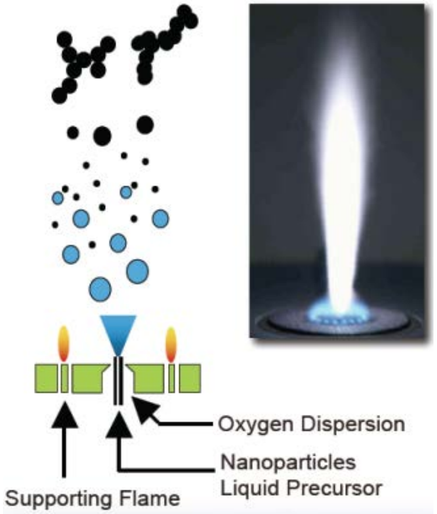
1. BET Surface Area (SA_{BET}): >50 m^2g^{-1}
2. Conductivity (σ): At least 0.01-0.1 Scm^{-1} for support and >1 Scm^{-1} for supported electrocatalyst
3. Microstructure – Pore Size Distribution (PSD), 20 – 150 nm

SnO_2-based support

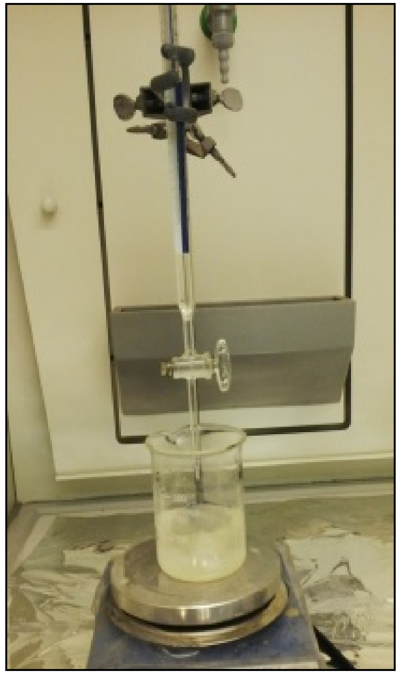
1. Thermodynamically stable
2. Low electrical conductivity
    Dope with n-type dopants (Sb and Nb)
3. Defined Microstructure
4. Use of different synthesis methods

Support and catalyst synthesis

Flame spray pyrolysis



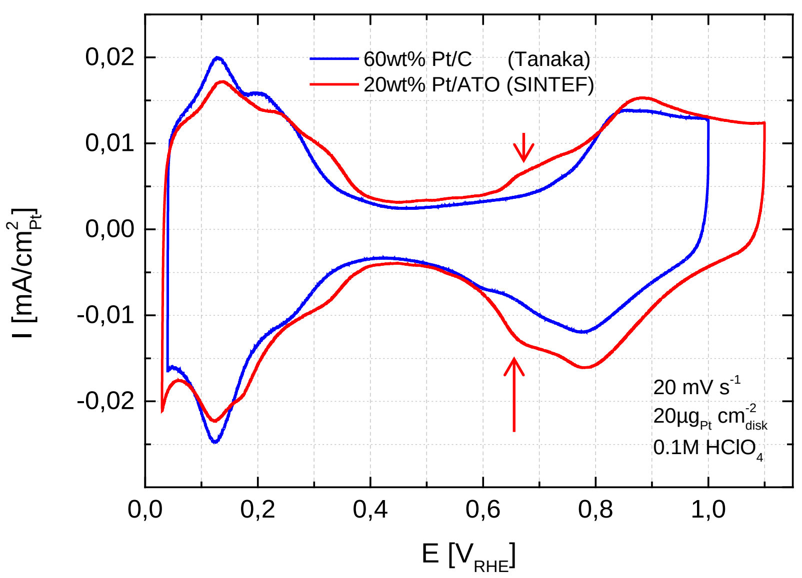
Co-precipitation

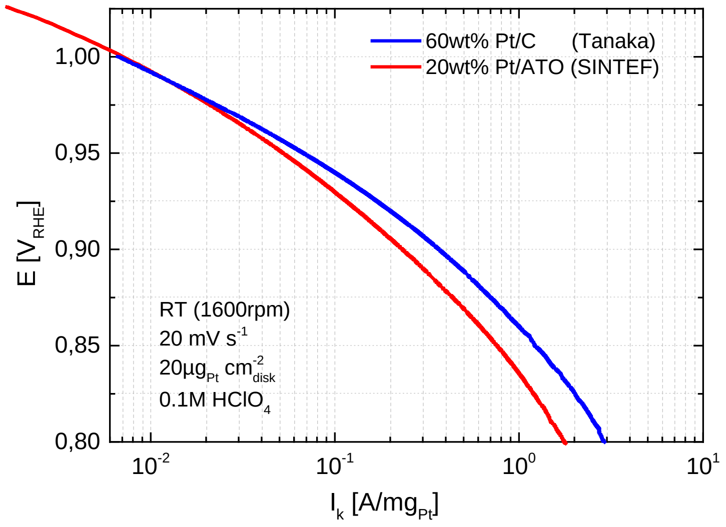


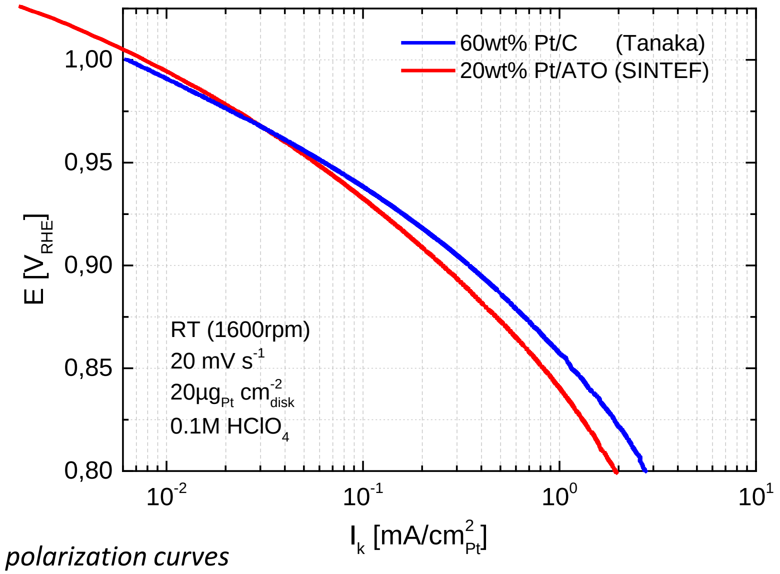
Session 5

Paul Inge Dahl: Supported catalyst particles for PEM fuel cells by one-step flame synthesis

Electrochemical characterization liquid electrolyte (RDE)





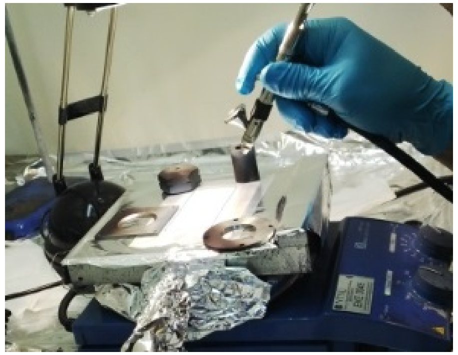


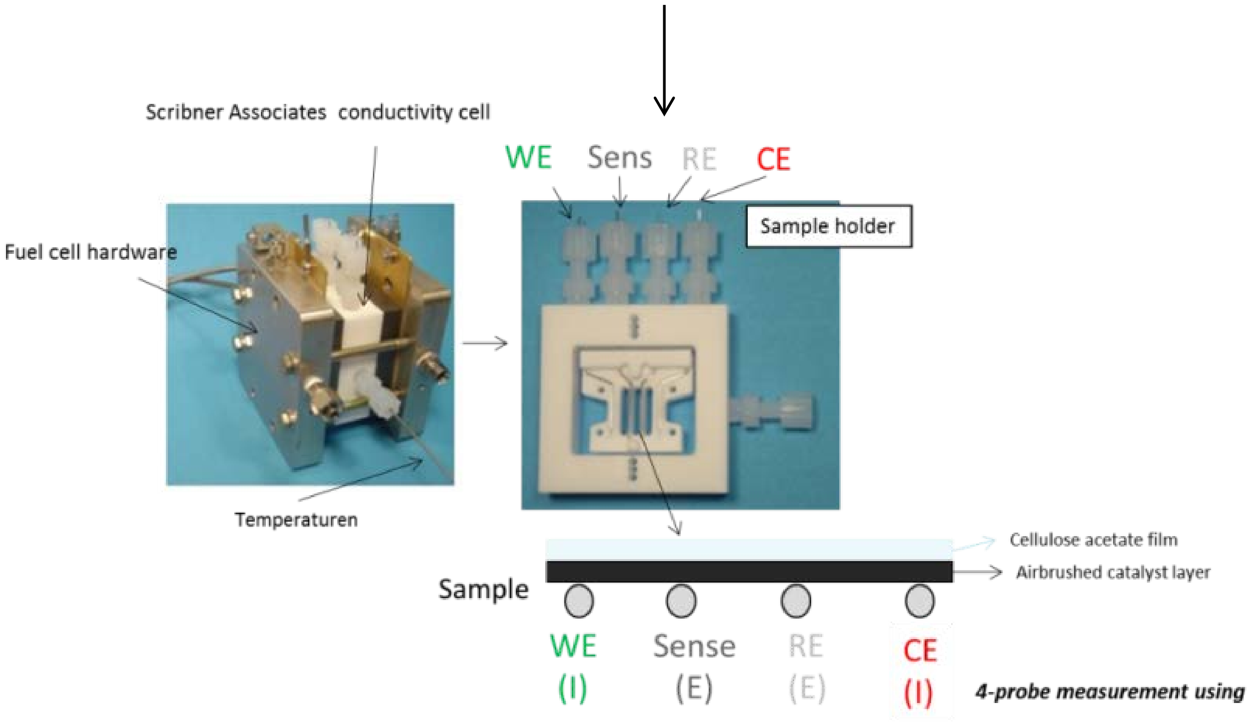
- Comparable CVs extra features on the H_{upd} region (Pt agglomeration)
- Sb oxidation reduction peaks

- Generally comparable activities as Pt/C possible differences in kinetics

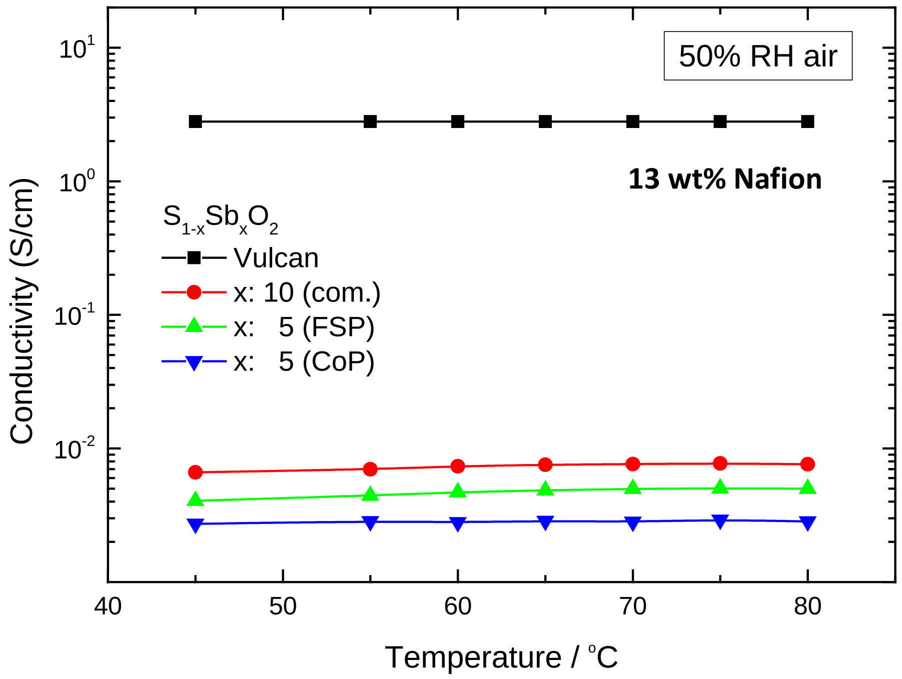
Mass transport and CV in N2 corrected polarization curves

Conductivity of oxide-based porous thin films




Scribner Associates conductivity cell
Fuel cell hardware
Temperaturen
WE Sens RE CE
Sample holder
Cellulose acetate film
Airbrushed catalyst layer
Sample
WE (I) Sense (E) RE (E) CE (I)

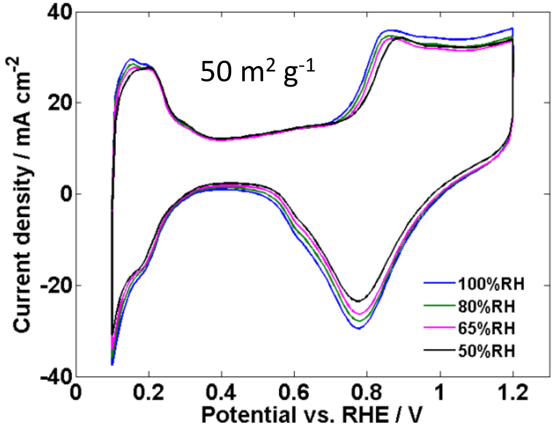
4-probe measurement using EIS



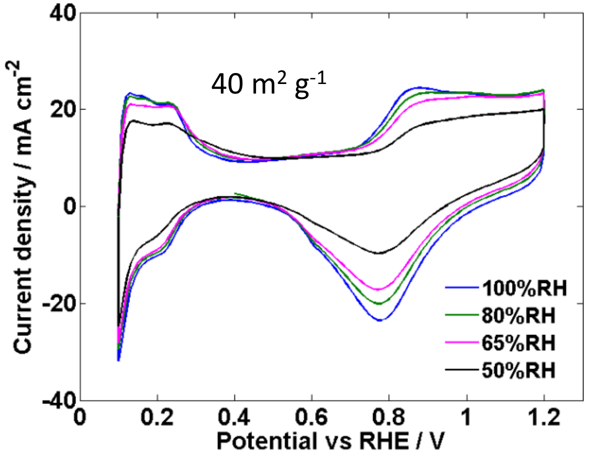
Conditions:
Temperature: cell 70 ^{o}C, pipes: 72^{o}C
Flowrate: Anode 0.2, cathode 0.1 l min^-1
Pressure: anode 1 barg, cathode 2barg
Gases: anode H2 and cathode N2
Sweep rate: 100 mV s-1
Ionomer/support ratio: Pt/C: 0.6, Pt/ATO:0.04

Fuel cell cyclic voltammetry

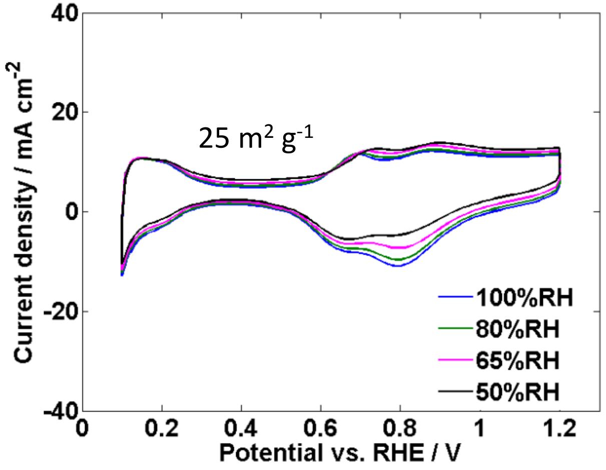
Commercial MEA-0.45 mgcm-2
35 µm membrane



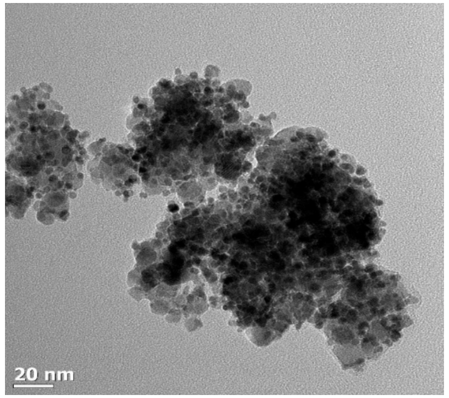
60wt% Pt/C-0.41 mgcm-2
50 µm N212 membrane (CCM)



20wt% Pt/5ATO-0.31 mgcm-2
50 µm N212 membrane (CCM)



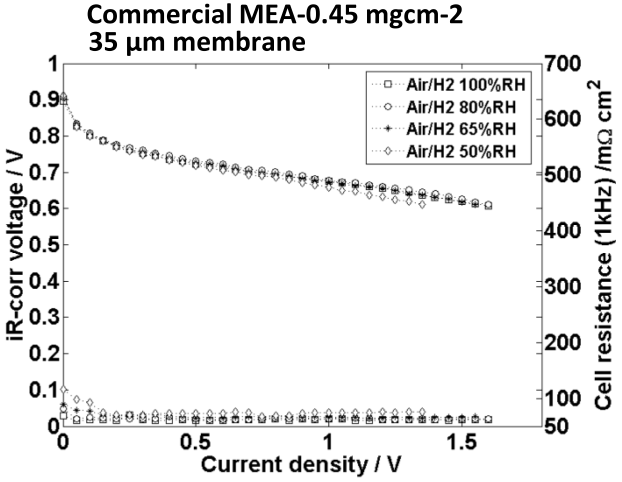
- Pt/ATO considerably lower ECSA
- Pt/ATO less define H_{upd} region
- Sb oxidation and reduction peaks present
- All three CL sensitive to low humidity.

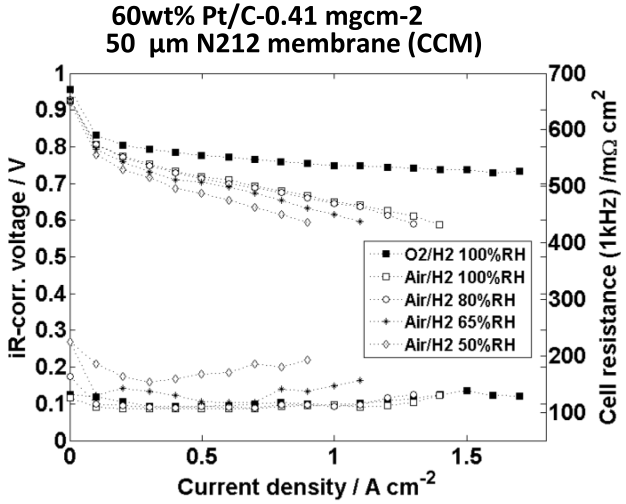


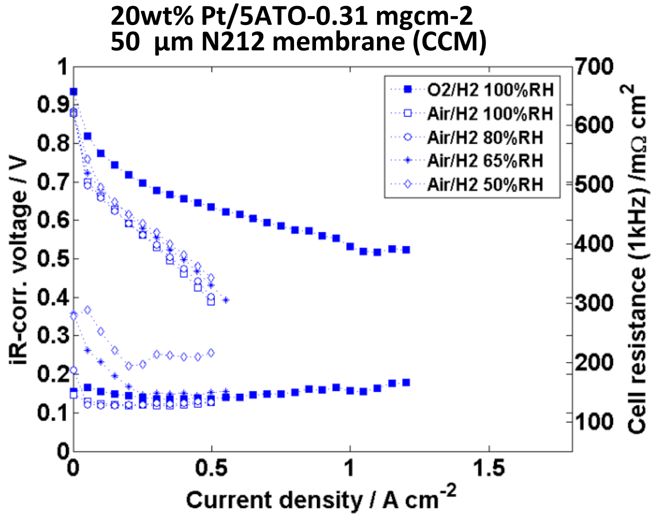
Average Pt particle size: 4.9 nm

Conditions:
Temperature: cell 70 °C, pipes: 72°C
Stoichiometry: Anode:2, cathode:4
Pressure: anode 1 barg, cathode 2 barg
Gases: O2/H2 and Air/H2
RH gases: 100, 80, 65, 50 %RH
Ionomer/support ratio: Pt/C: 0.6, Pt/ATO:0.04
Steady state galvanostatic measurements: 10 min/point

Fuel cell performance

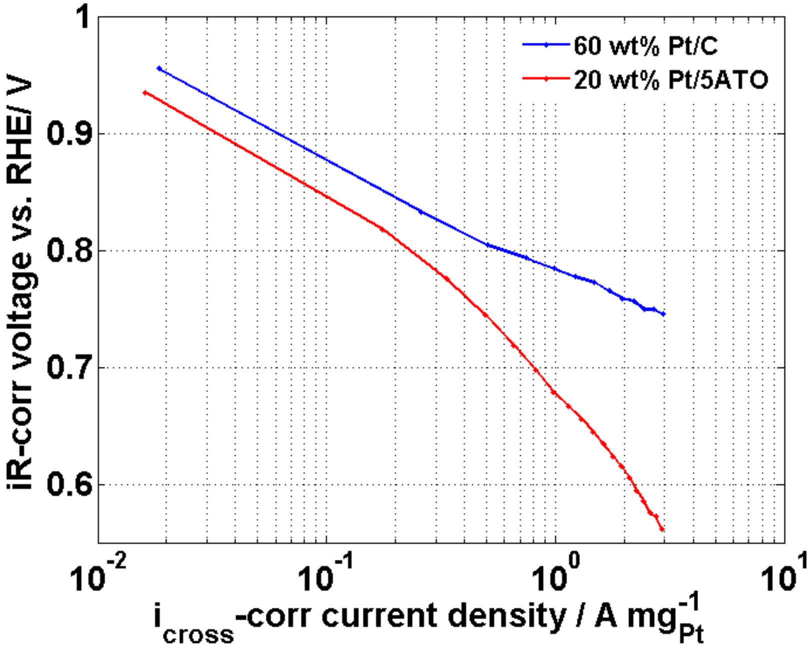

Commercial MEA-0.45 mgcm-2
35 µm membrane

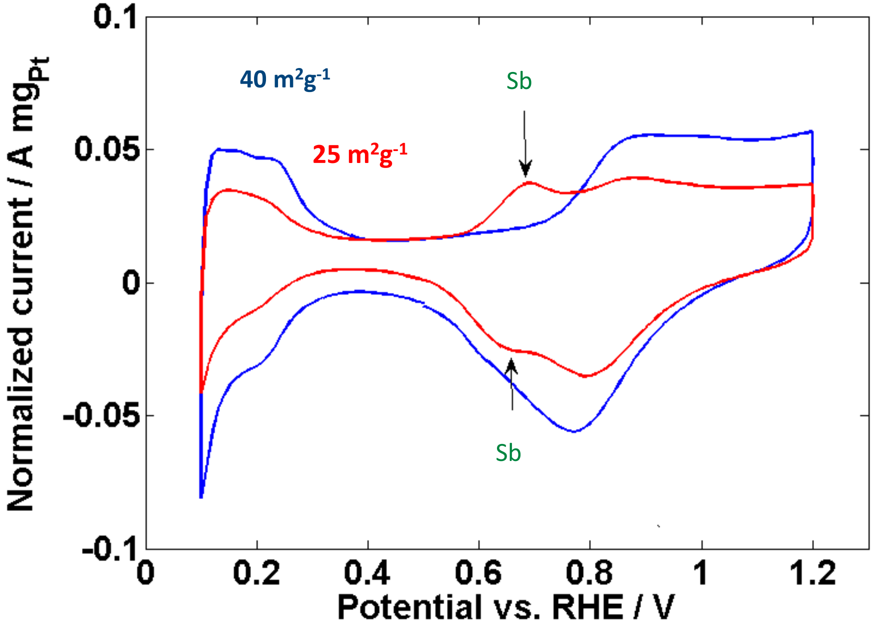

60wt% Pt/C-0.41 mgcm-2
50 µm N212 membrane (CCM)


20wt% Pt/5ATO-0.31 mgcm-2
50 µm N212 membrane (CCM)

- iR corrected performance in O_2/H_2 100%RH: 60wt% Pt/C: 0.78 V and 20wt% Pt/ATO: 0.63 V at 0.5 A cm^{-2} (**150 mV difference-**lower catalytic activity)
- **Cell resistance is not the main issue**, at 100%RH:Pt/C 100 mΩcm^2, Pt/ATO 132 mΩcm^2
- iR corrected performance in Air/H_2: Commercial: 0.73 V, 60wt% Pt/C: 0.72 V, Pt/ATO:0.39V at 0.5 A cm^{-2} (**330 mV difference**-a clear indication that mass transport is also present)
- Pt/ATO improves performance at low RH

Fuel cell specific activity and kinetics





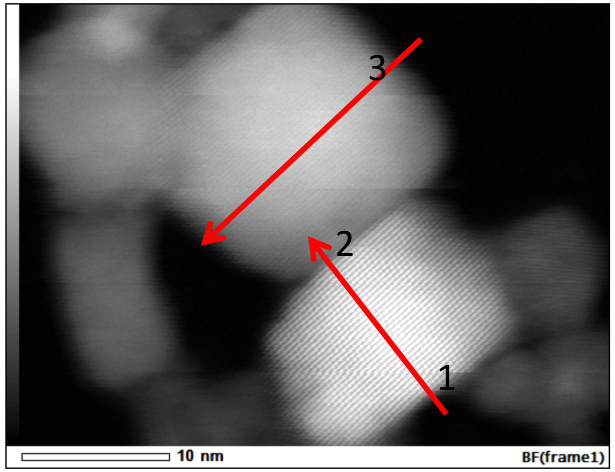
- Lower mass activity of Pt/ATO, may be attributed to lower surface area
- Kinetics completely changed after 0.8 V

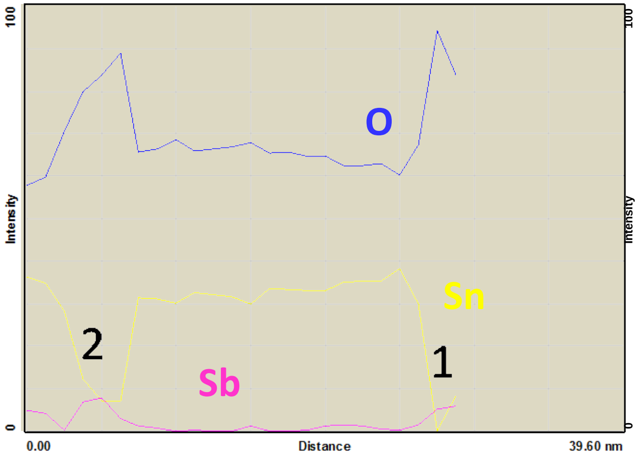
-Sb may have a blocking effect on ORR

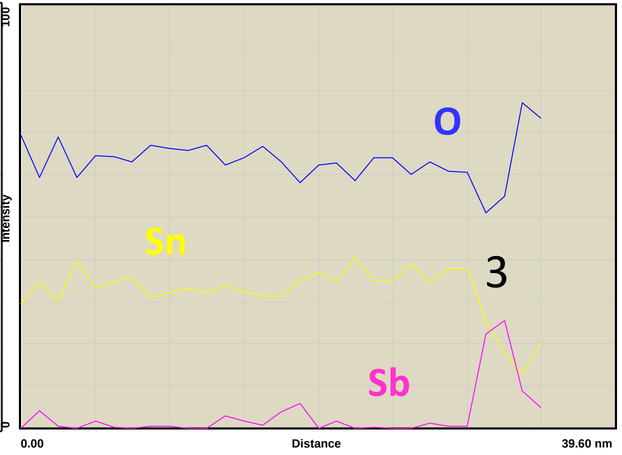
-low ECSA may induce mass transport

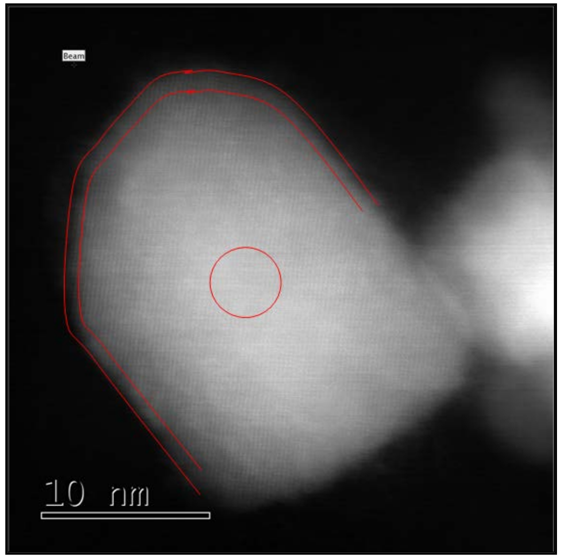
Conditions:
Temperature: cell 70 °C, pipes: 72°C
Stoichiometry: Anode:2, cathode:4
Pressure: anode 1 barg, cathode 2barg
Gases: CVs H2/N2 and **curves H2/O2**
RH gases: 100 %RH

Sb segregation with EDS





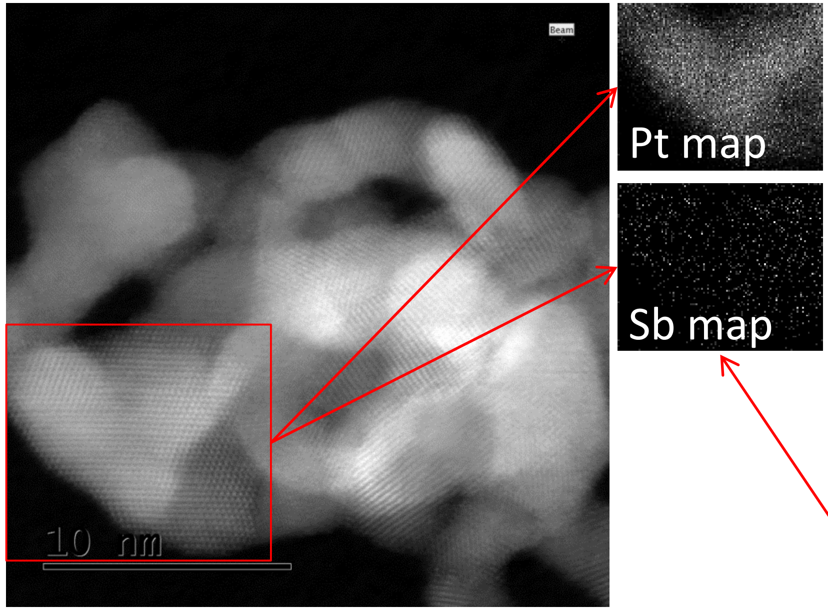




- *ATO particles give an <u>average chemical composition</u> of* $\mathbf{Sn_{0.91}Sb_{0.09}O_2}$ *in the center of the particles.*
- *<u>Outer 1 nm layer</u> of the same particles has an average composition of* $\mathbf{Sn_{0.55}Sb_{0.45}O_2}$

High intensity probe (electron beam less than 2 Å)

Sb segregation Pt/ATO



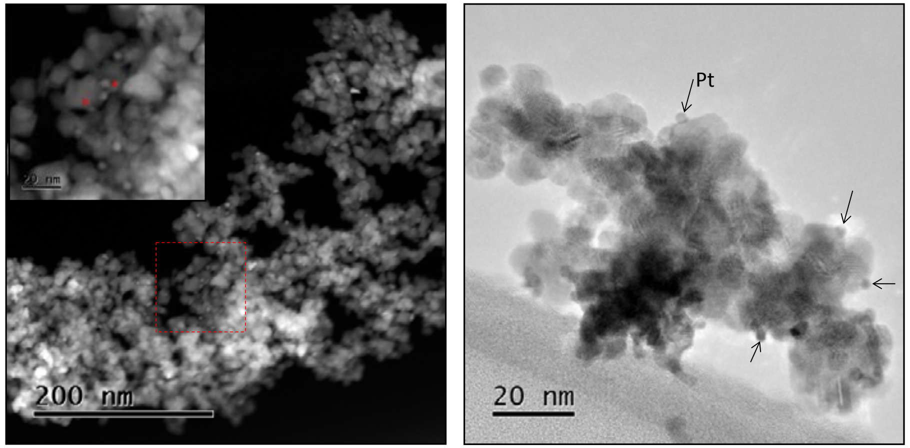
High Angle Annular Dark field Scanning Transmission Electron Microscopy (HAADF STEM) image

__After Pt deposition:__

Sb content in the ATO support is in the range 1.0 – 2.0 at.%

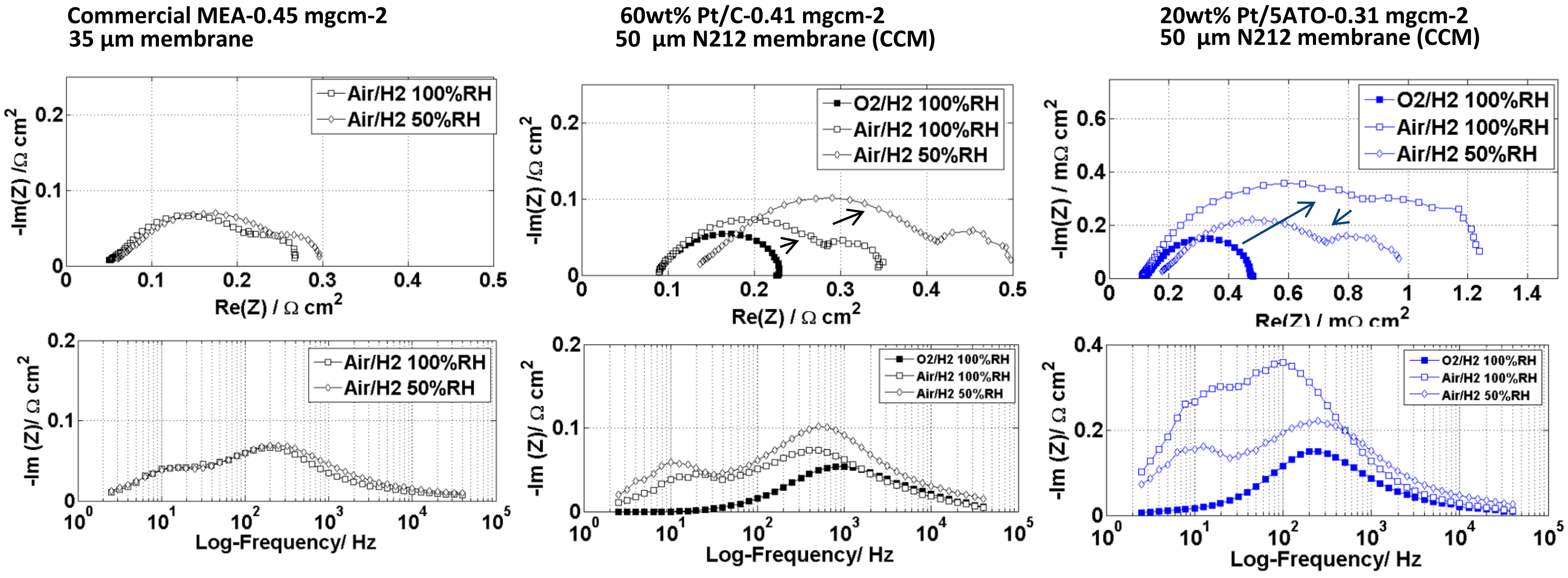
Thus, Average chemical composition of the ATO :

$Sn_{0.99}Sb_{0.01}O_2$ *instead of the nominal* $Sn_{0.90}Sb_{0.10}O_2$



- Element mapping by X-ray Energy Dispersive Spectroscopy (EDS).
- **In general, most of the Sb in ATO has diffused out of the support and concentrated in the ATO-Pt interface.**
- In some Pt particles, only Pt and Sb can be detected. In other Pt particles, minor amounts of O could be detected in addition to Pt and Sb. The average composition in the present map was found to be 95.4 at.% Pt, 2.6 at.% Sb and 2.0 at.% O.

Mass transport



Commercial MEA-0.45 mgcm-2
35 µm membrane

60wt% Pt/C-0.41 mgcm-2
50 µm N212 membrane (CCM)

20wt% Pt/5ATO-0.31 mgcm-2
50 µm N212 membrane (CCM)

- O2/H2 at 100%RH: Pt/ATO semicircles double the size of the Pt/C
- Air/H2 at 100 %RH:

-Difference between Air and O2 (channel, GDL, electrode transport)

-Pt/C slightly larger than commercial (electrode)

-Pt/ATO almost 4 times larger than Pt/C (electrode mass transport)

- Air/H2 at 50 %RH:

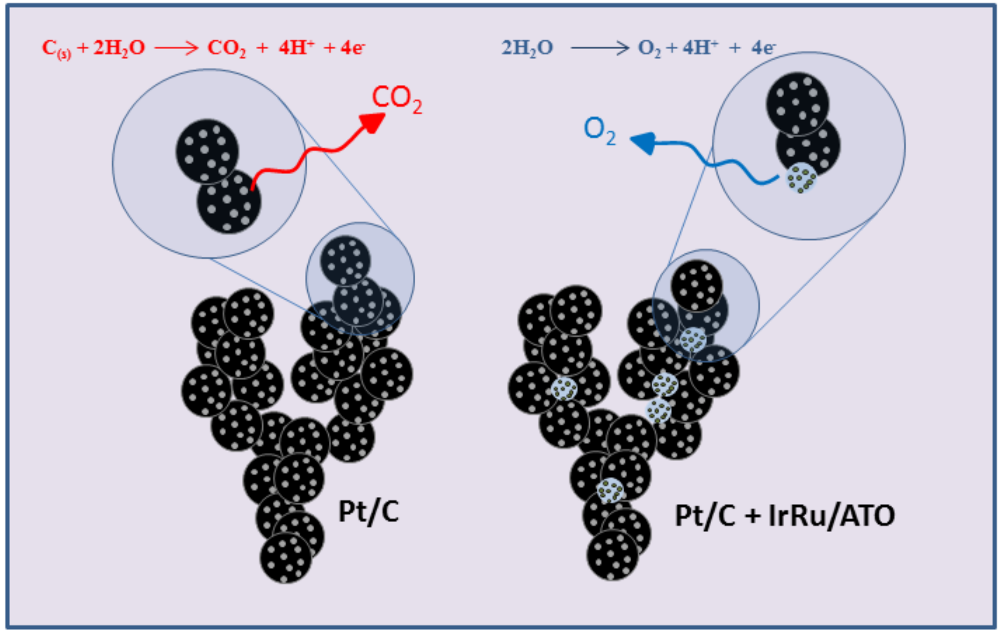
-Commercial and Pt/C impedance increases

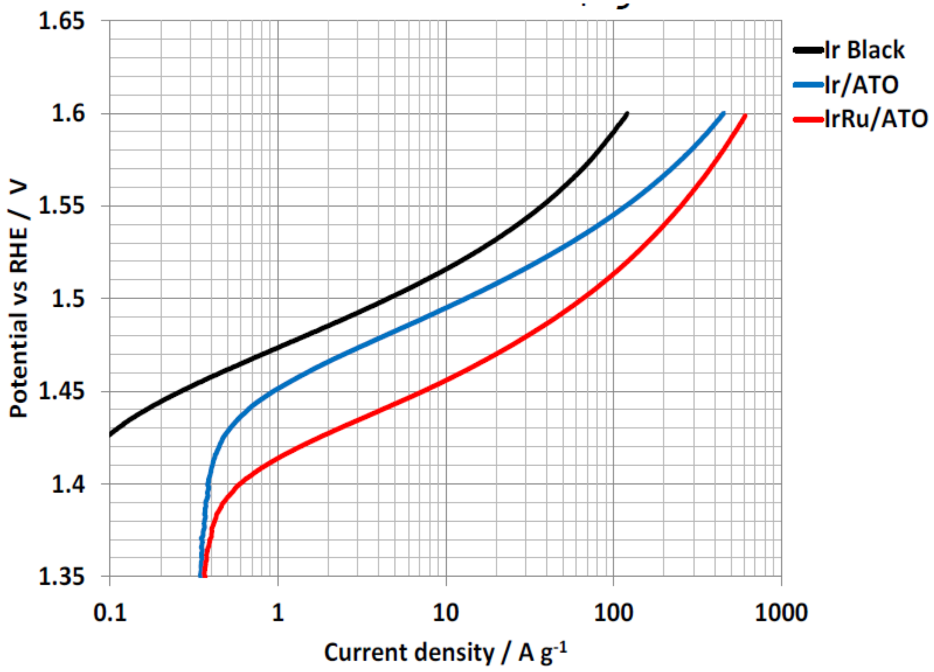
-Considerable decrease for the Pt/ATO (flooding)

Conditions:
Temperature: cell 70 °C, pipes: 72°C
Stoichiometry: Anode:2, cathode:4
Pressure: anode 1 barg, cathode 2barg
Gases: O2/H2 and Air/H2 at 0.5 A cm-2
RH gases: 100, 80, 65, 50 %RH

Alternative approach for increased stability

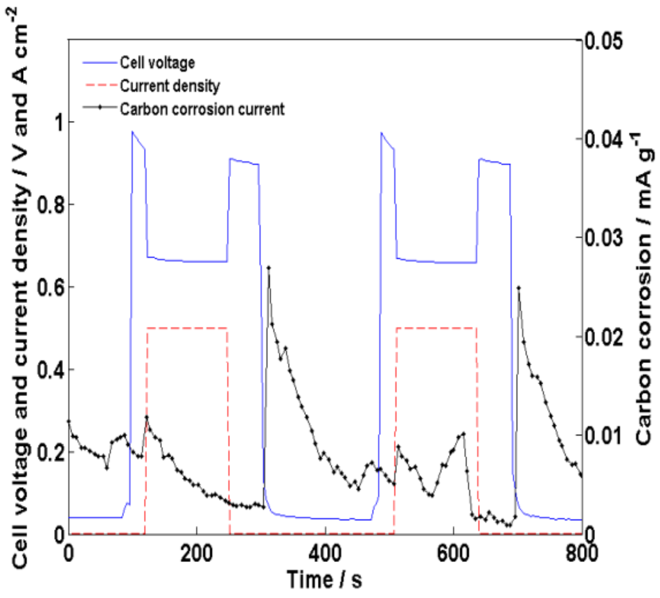
ATO based Oxygen evolution catalyst in PEM fuel cell cathodes



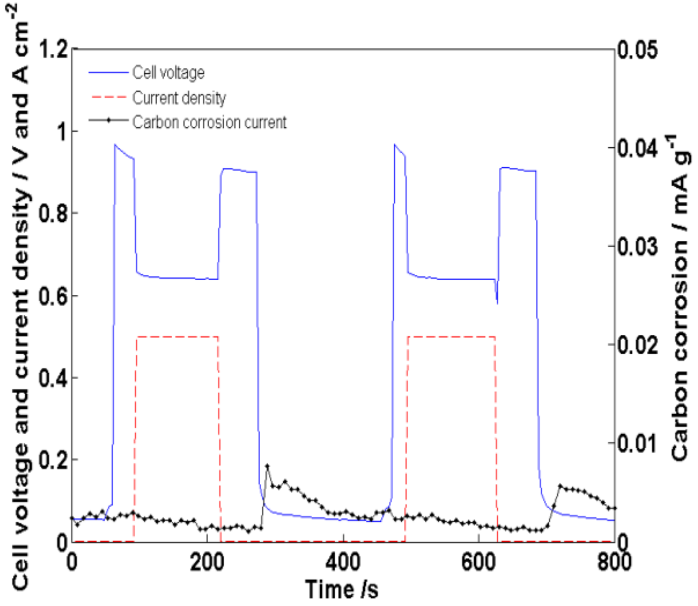


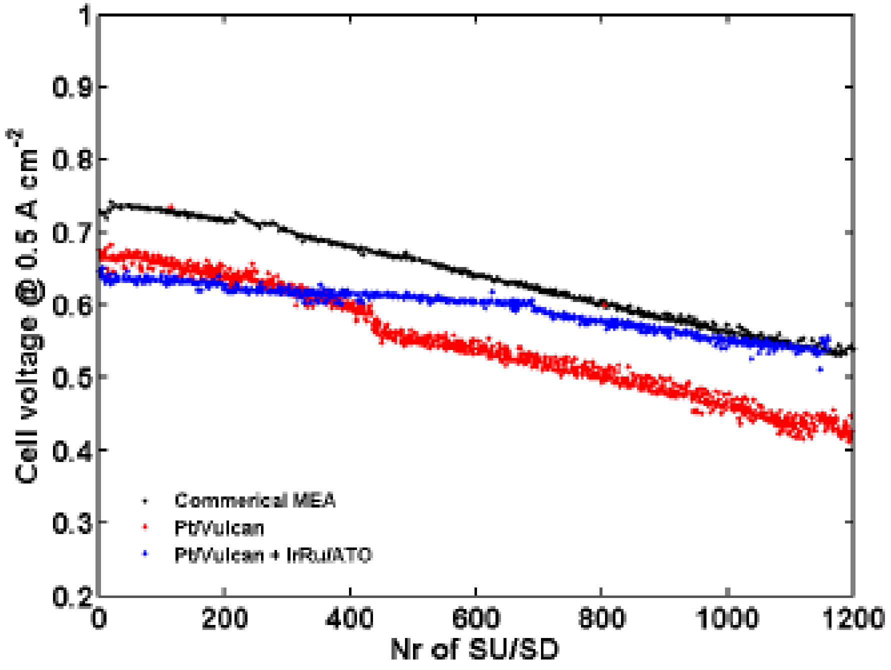
Reduced carbon corrosion – improved stability

Pt/C cathode



Pt/C + IrRu/ATO cathode





Summary

- PEM fuel cells and electrolysers are rapidly approaching mass marked applications
- Although many challenges have been solved, there are still opportunities for further material improvements
- Cost and durability as well as manufacturability is extremely important

Thank you for your attention

325327

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