Second International Workshop
Durability and Degradation Issues in PEM Electrolysis Cells and its Components

February 16-17, 2016 Freiburg, Germany

Degradation Mechanisms and Enhanced Stability of PEM Electrolysis Cells Using Low Catalyst Loadings and Novel Type of Membranes

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Hydrogen and renewable energy sources

- "Green" hydrogen can be produced from renewable energy sources by water electrolysis.
- A synergy between green hydrogen, electricity and renewable energy sources is needed for a sustainable development.
- Hydrogen can play an important role in the future as an energy carrier, for transportation and energy storage.

Electrohypem

http://www.electrohypem.eu/

Aricò, A.S., Siracusano, S., Briguglio, N., Baglio, V., Di Blasi, A., Antonucci, V. Polymer electrolyte membrane water electrolysis: Status of technologies and potential applications in combination with renewable power sources (2013) Journal of Applied Electrochemistry, 43 (2), pp. 107-118.

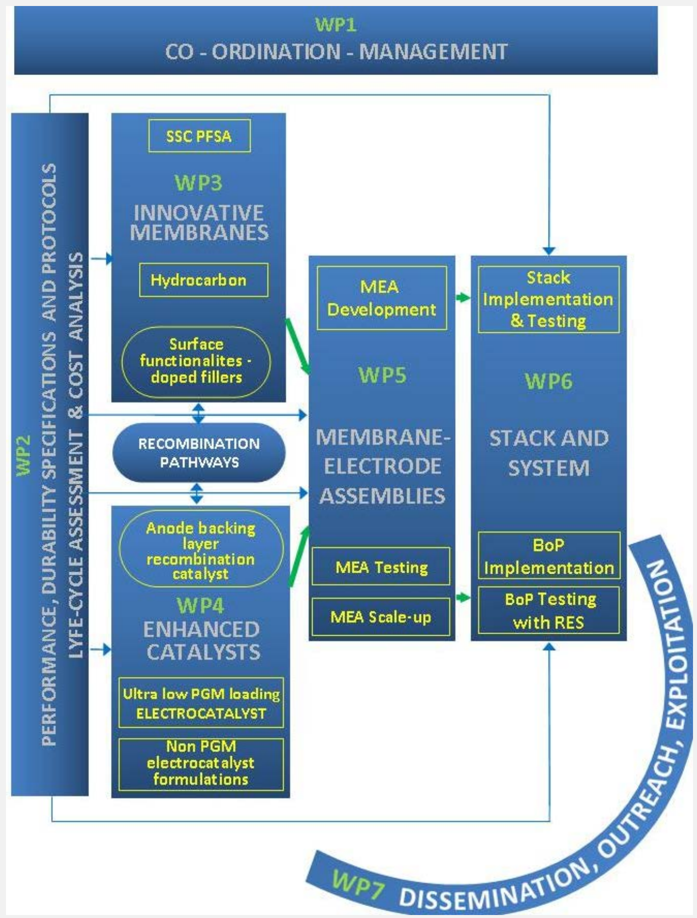
Electrohypem

Project & Partnership description

Enhanced performance and cost-effective materials for long-term operation of PEM water electrolysers coupled to renewable power sources

7th European Framework Programme of the FCH Joint Undertaking

Beneficiary name	Country	Partner type
CONSIGLIO NAZIONALE DELLE RICERCHE (**CNR-ITAE**)	Italy	Research
JOINT RESEARCH CENTRE, INSTITUTE FOR ENERGY AND TRANSPORT (**JRC-IET**)	Belgium	Research
CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE (**CNRS**)	France	Research
SOLVAY SPECIALTY POLYMERS ITALY S.P.A. (**SLX**)	Italy	Industry
ITM Power (Trading) Ltd (**ITM**)	United Kingdom	Industry
TOZZI RENEWABLE ENERGY (**TRE**)	Italy	Industry



http://www.electrohypem.eu/

ELECTROHYPEM objectives

The overall objective of the ELECTROHYPEM project was to develop cost-effective components for proton conducting membrane electrolysers with enhanced activity and stability in order to reduce stack costs and to improve efficiency, performance and durability.

The project mainly concerns with low-cost electrocatalysts and membrane development by addressing the validation of these materials in a PEM electrolyser (1 Nm^3 H_2/h) operating in the presence of renewable power sources.

The aim is to contribute to the road-map addressing the achievement of a wide scale decentralised hydrogen production infrastructure.

Aricò, A.S., Siracusano, S., Briguglio, N., Baglio, V., Di Blasi, A., Antonucci, V. Polymer electrolyte membrane water electrolysis: Status of technologies and potential applications in combination with renewable power sources (2013) Journal of Applied Electrochemistry, 43 (2), pp. 107-118.

PEM Electrolyzers

- **Electrolysis of water using *renewable energy sources* has significant advantages:**
  - **Production of high purity «green» hydrogen**
  - **High efficiency (>70 % vs. LHV)**
  - **Energy storage, Grid-balancing service, hydrogen for FCEVs**
- **Several technologies are currently used for water electrolysis : *alkaline systems, solid oxide electrolyzers* and PEM electrolyzers → Very promising for grid stabilisation and coupling with renewable power sources**

Key features of PEM electrolysis

- High current densities at low cell voltages ≈ **High efficiency** (even at low temperatures); **Dynamic behaviour; Rapid start-up/response**
- High resistance to duty cycles
- **Eco-friendly system** with increased level of **safety** (no caustic electrolyte circulating)
- Smaller mass-volume characteristics: compact system
- High **differential pressure**, meaning reduced gas compression requirements for the produced hydrogen gas
- High degree of **gases purity** (≈ 5N)
- Possibility of combining fuel cell and electrolyzer (regenerative fuel cell)

Drawbacks of PEM electrolysis

- **High cost** (PFSA membranes, noble metal electrocatalysts, Ti bipolar plates, expensive coatings)

CAPEX

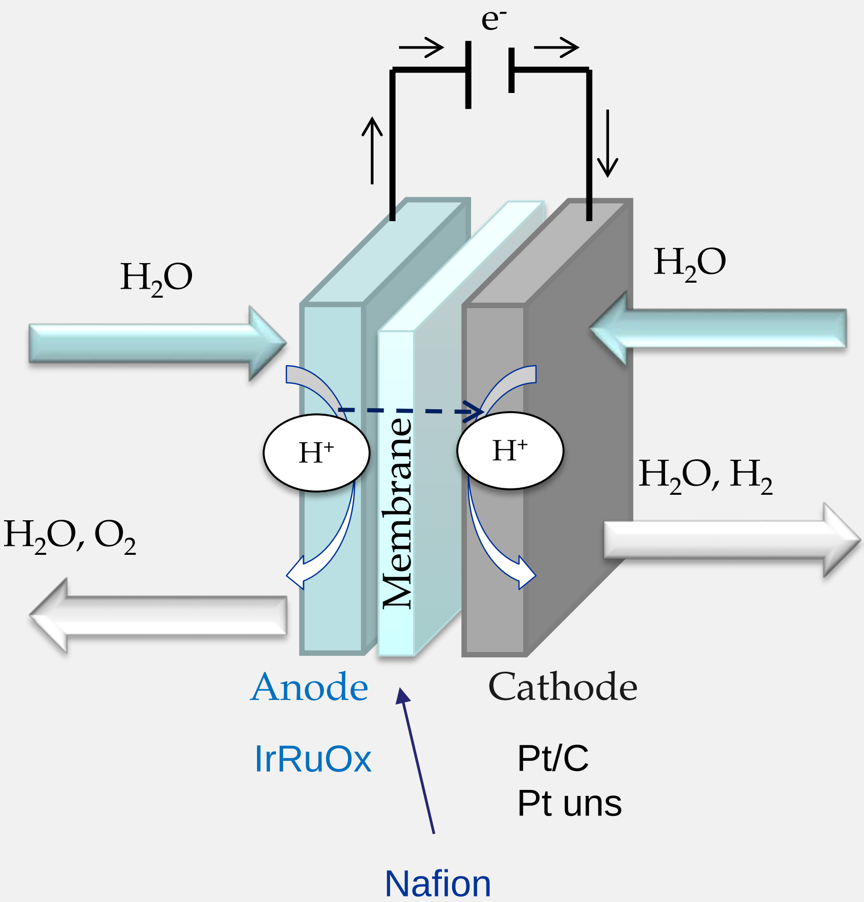
- Long-term durability > 100 khrs not yet achieved with low catalyst loadings

OPEX

PEM Electrolyzers

Drawbacks to overcome / Aspects to improve

- Slow oxygen evolution reaction rate
- Improvement of membrane properties
- Cost



Membrane Benchmark ⟹ Nafion®

- Excellent Performance
- Appropriate electrochemical Stability
- Suitable Mechanical Properties
- Rapid Start-up/ Rapid response
- Dynamic behaviour

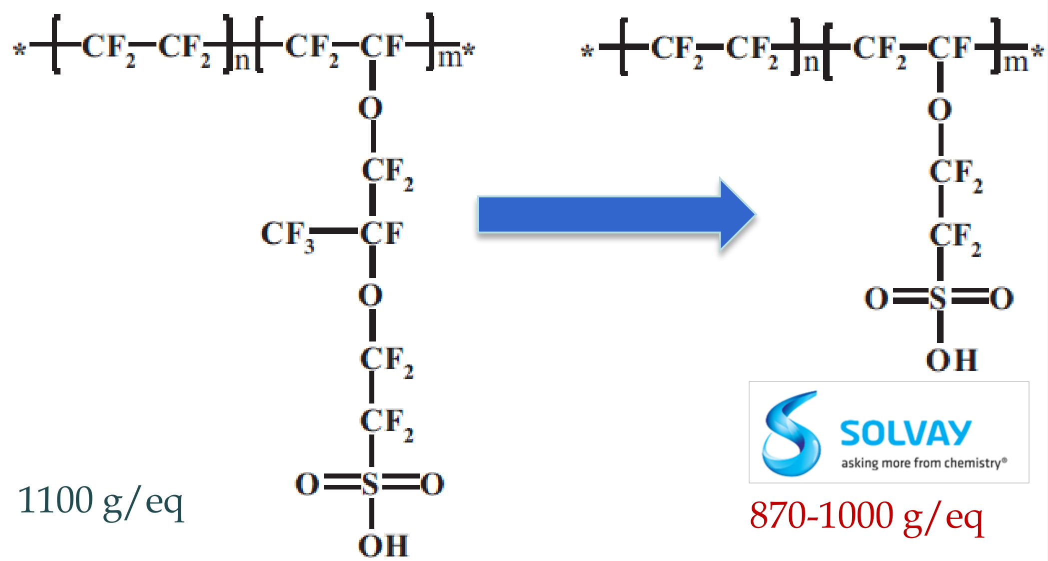
Cathode:

$$4H^+ + 4e^- \rightarrow 2H_2$$

Anode:

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

Advanced Membrane and Electro-catalyst



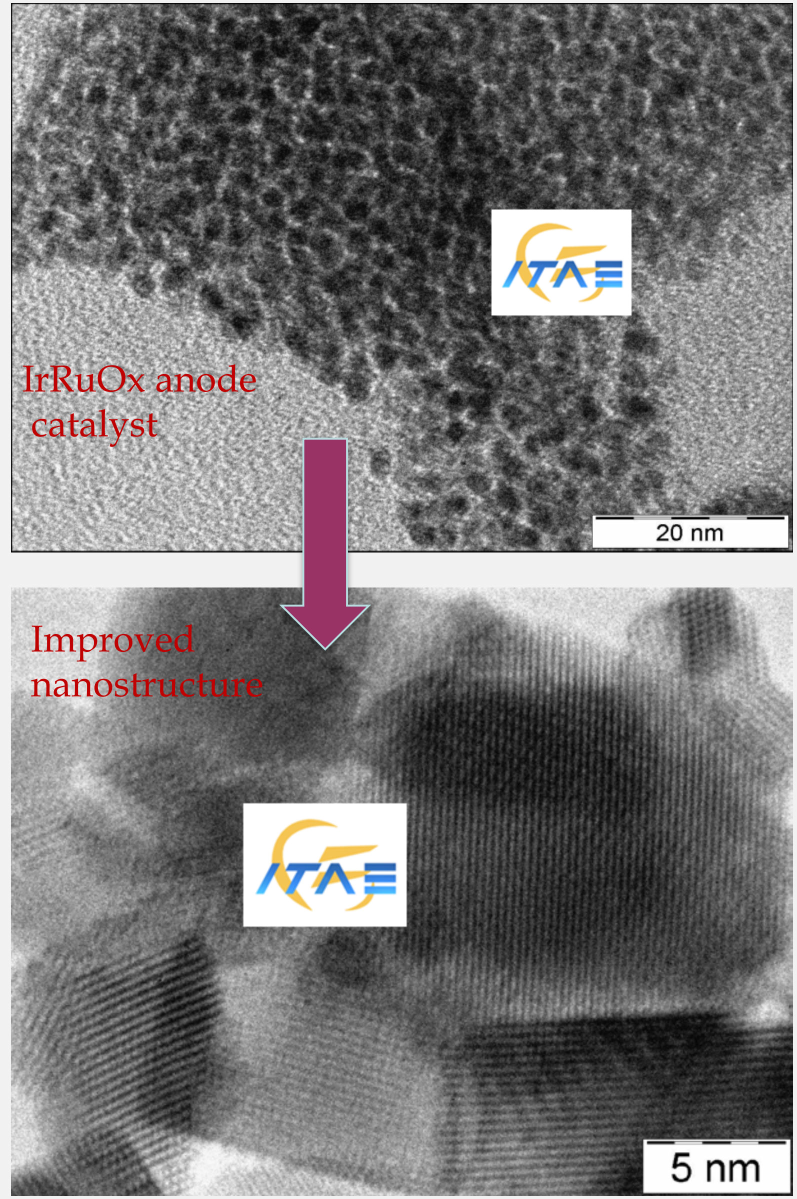
Nafion ®

Long side-chain ionomers

Aquivion ®

Short side-chain ionomer

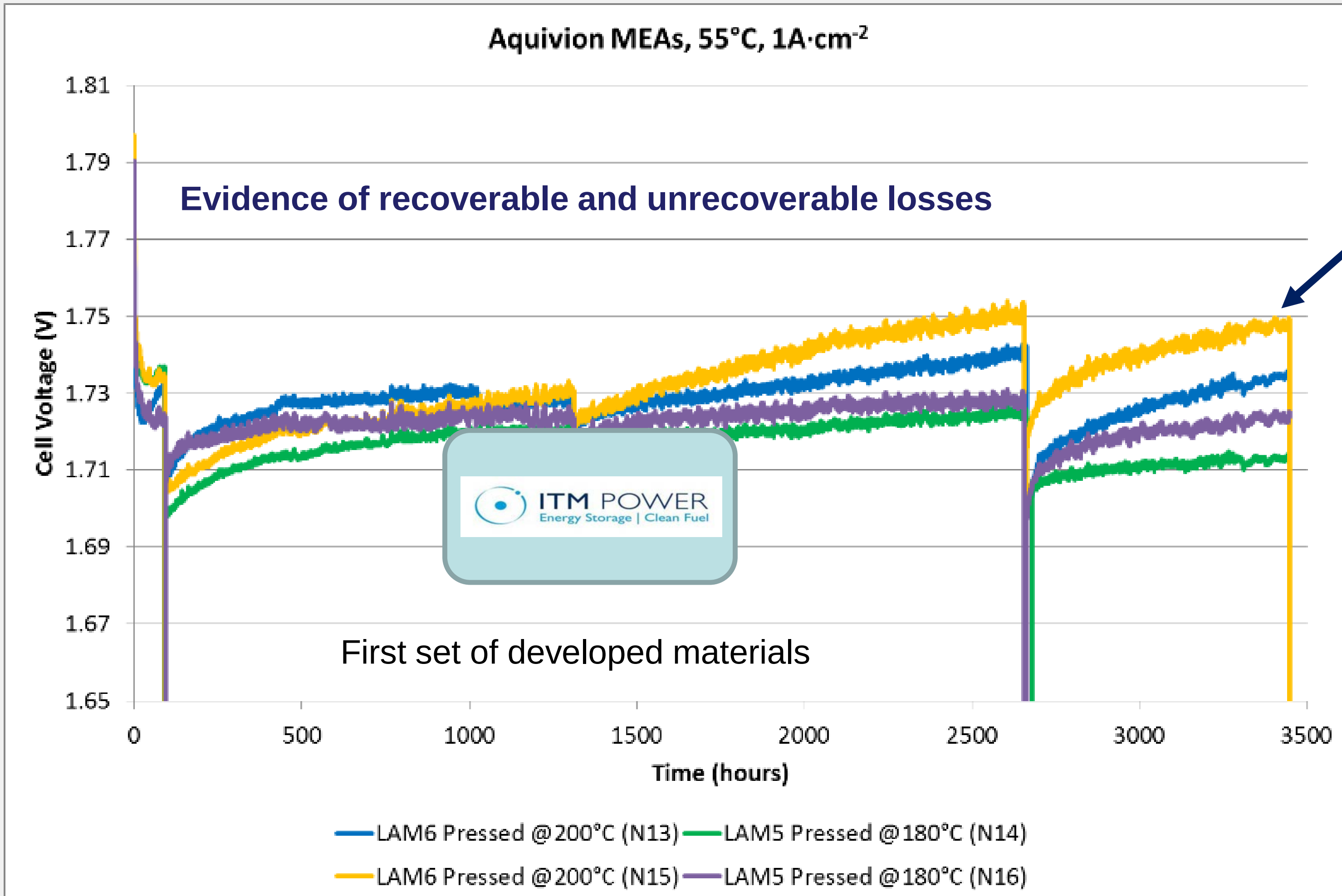
The Solvay Aquivion ionomer is characterized by both larger crystallinity and higher glass transition temperature than Nafion



MEA Durability

Optimisation of MEA manufacturing conditions

1st set of MEAs



Degradation study presented here is focused on the less stable MEA

Anode: IrRuOx

Cathode: Unsupported Pt black

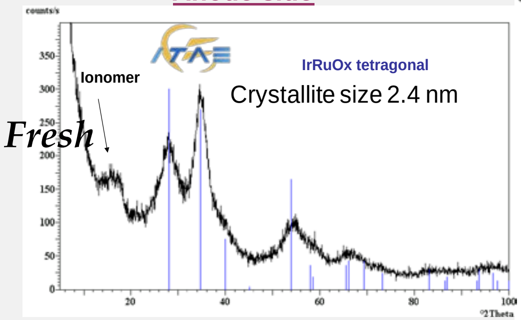
Membrane and ionomer: First supply of Aquivion

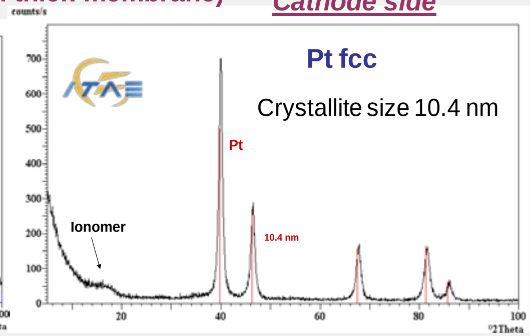
XRD

Structural and morphological analysis

Anode side 1A new (90 µm thick membrane) Cathode side

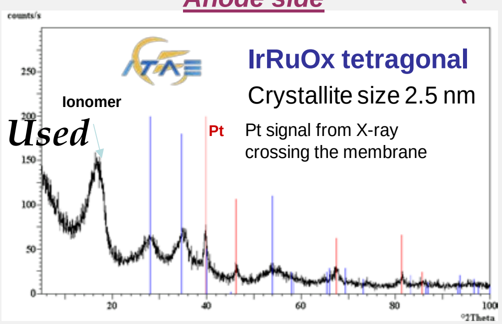
Fresh

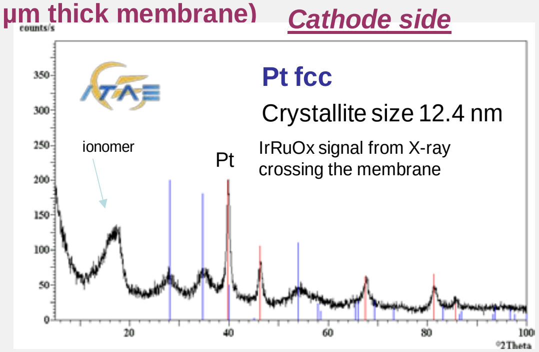




Anode side 1B used (40 µm thick membrane) Cathode side

Used





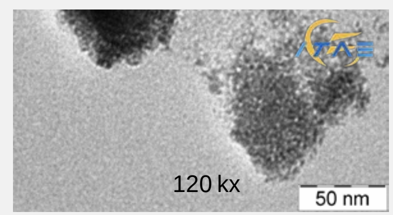
- No dramatic change in crystallite size, for both anode and cathode, in used samples.
- Increase of ionomer scattering in XRD of used samples is due to the membrane response

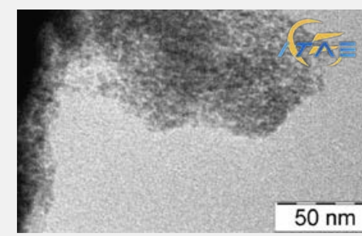
Used MEA: >3500 hrs operation

No morphology modifications in the catalytic layer

TEM

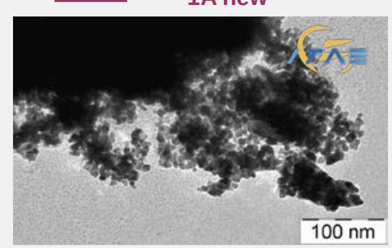
Fresh Used

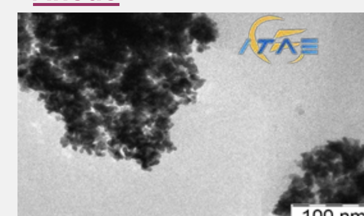




Anode 1A new

Anode 1B used





Cathode 1A new

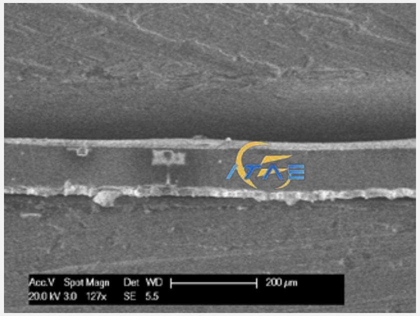
Cathode 1B used

Both unsupported

SEM – EDX

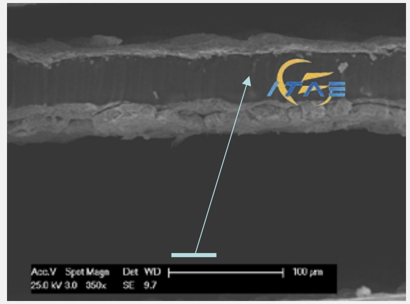
1A new

Section View



1B used

Section View

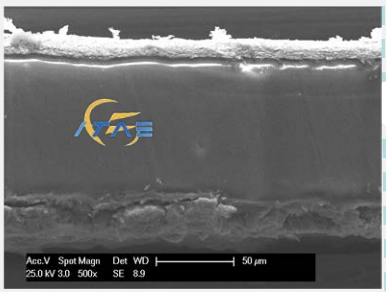


Section View

PtB →~ 13 µm

Aquivion → ~ 90 µm

IrRuOx→ ~ 33 µm

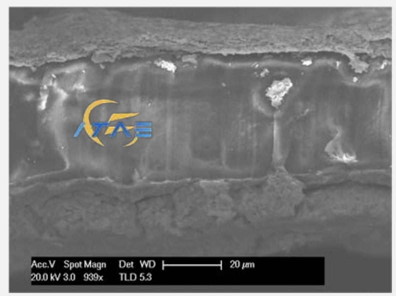


PtB →~ 13 µm

Aquivion 42 µm

1B used

IrRuOx→ ~ 28 µm



The specific MEA1B based on the first supply of Aquivion (3500 hrs) showed the presence of impurities, e.g Fe, at both electrodes and membrane;

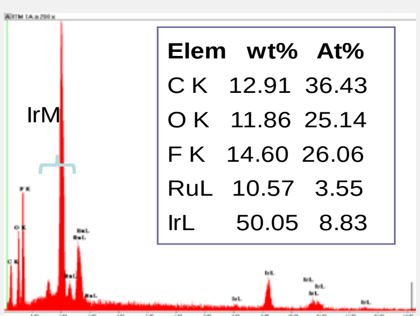
Some Ru dissolution was also evident

Slight decrease of the ionomer signal in elemental analysis of catalytic layer

Thinning effects are also detected

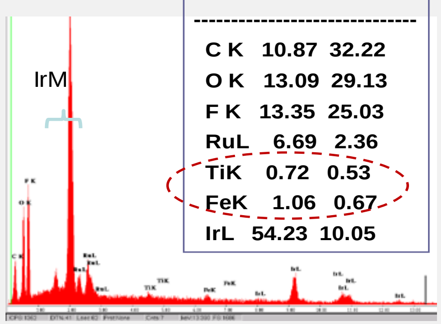
Anode side

Front View **1A new**



Elem	wt%	At%
C K	12.91	36.43
O K	11.86	25.14
F K	14.60	26.06
RuL	10.57	3.55
IrL	50.05	8.83

1B used



Elem	Wt %	At %
C K	10.87	32.22
O K	13.09	29.13
F K	13.35	25.03
RuL	6.69	2.36
TiK	0.72	0.53
FeK	1.06	0.67
IrL	54.23	10.05

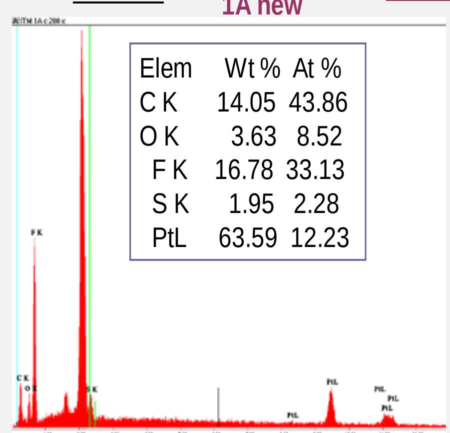
Elem	At%
RuL	28.67
IrL	71.83

$2.8 \cdot 10^{-3}$ % at. Ru/h loss

Elem	At%
RuL	19.01
IrL	80.09

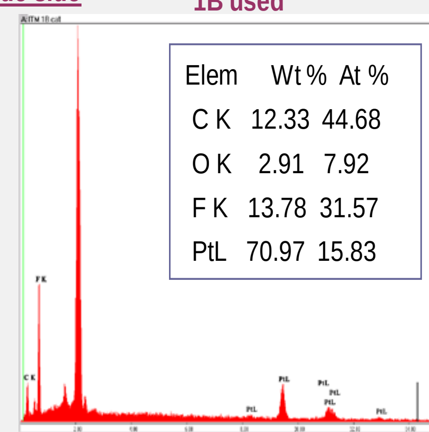
Cathode side

Front View **1A new**



Elem	Wt %	At %
C K	14.05	43.86
O K	3.63	8.52
F K	16.78	33.13
S K	1.95	2.28
PtL	63.59	12.23

1B used



Elem	Wt %	At %
C K	12.33	44.68
O K	2.91	7.92
F K	13.78	31.57
PtL	70.97	15.83

DEGRADATION MECHANISMS

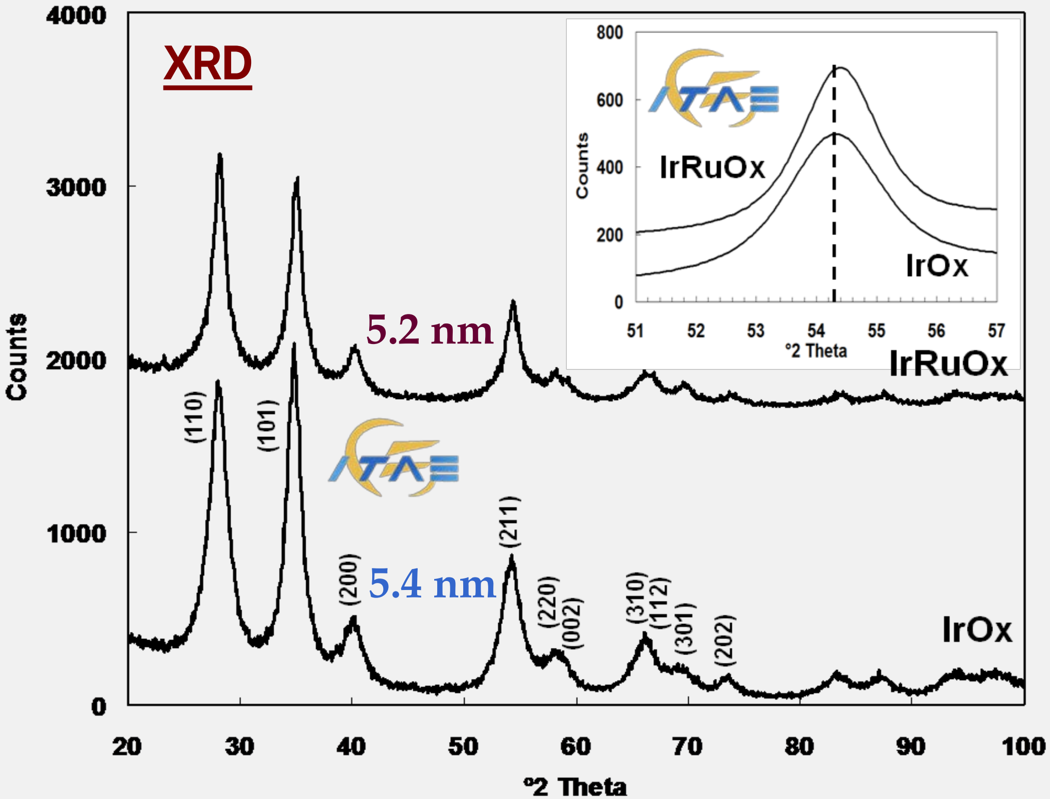
From the above analysis, the main sources of degradation for the first set of MEAs were individuated; these are reported below in order of relevance:

1) Presence of impurities of Na in the catalyst, Fe from the plant: these species affect ionic conductivity and accelerate membrane/ionomer degradation.
2) Ru dissolution from the IrRuOx catalyst (2.8 10^{-3} at. % Ru/h); it seems that the loss of Ru is not proceeding further when the Ru content reaches the level of 20% at. Probably, the fraction of Ru that is less alloyed or non-alloyed to Ir dissolves under operating conditions.
3) Ti plate degradation at the cathode side is another relevant source of performance decay and could be related to the release of fluorine species.
4) Ionomer content decreases, and probably gives rise to restructuring effects.
5) Membrane thinning and changes in the catalyst-membrane interface also occur and may affect hydrogen cross-over.

APPROACHES USED TO MITIGATE THE DEGRADATION MECHANISMS

- Catalysts were pre-leached in perchloric acid to remove all impurities
- The degree of alloying in the mixed oxide catalysts has been improved (XRD)
- Ir surface enrichment in the outermost layer of IrRuOx (verified by XPS)
- Unsupported cathode catalyst was replaced with supported Pt/C catalyst
- Chemical stabilisation of membrane and ionomer (lower release of fluorine)
- Further development of the coatings of Ti plates

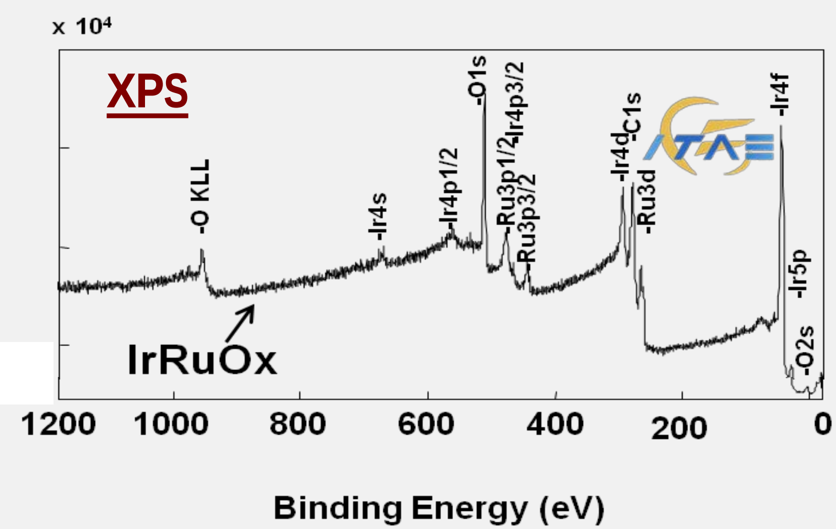
From IrOx to $Ir_{0.7}Ru_{0.3}Ox$ Anode Electro-Catalysts



A lattice contraction indicates the formation of a solid solution

Pre-requisite to Enhance the stability of Ru

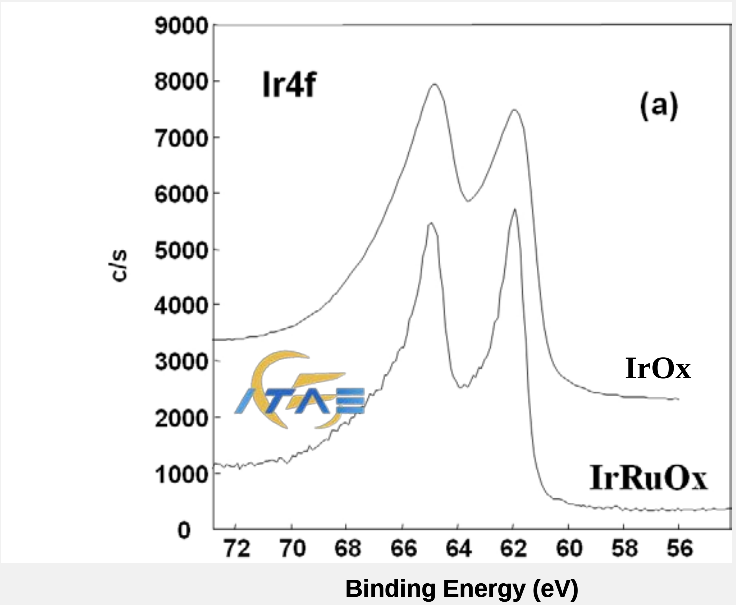
XPS: No impurities are present on the surface

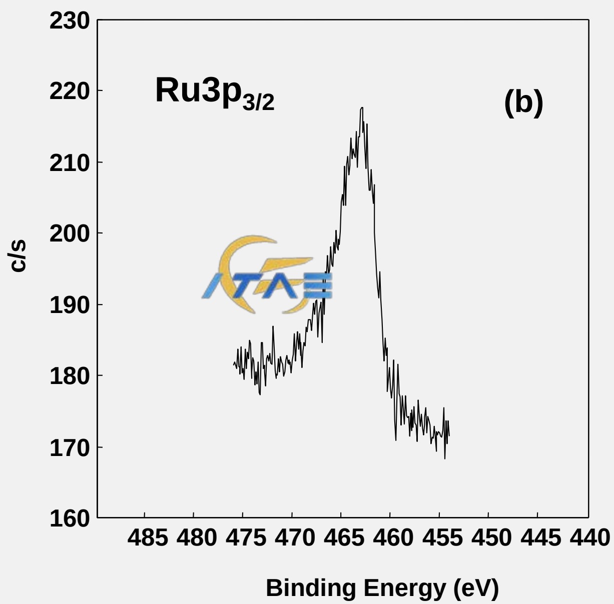


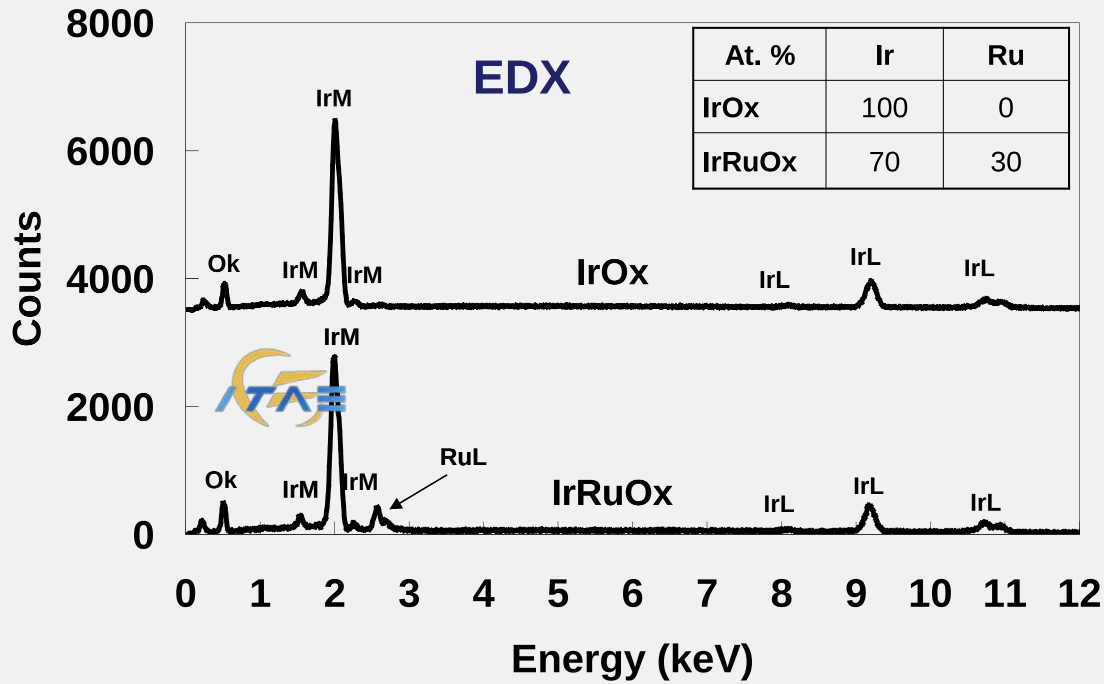
Siracusano, S., Van Dijk, N., Payne-Johnson, E., Baglio, V., Aricò, A.S. Nanosized IrOx and IrRuOx electrocatalysts for the O2 evolution reaction in PEM water electrolysers (2015)
Applied Catalysis B: Environmental, 164, pp. 488-495

From IrOx to $Ir_{0.7}Ru_{0.3}Ox$ Anode Electro-Catalysts

Bulk and surface characteristics







At. %	Ir	Ru
IrOx	100	0
IrRuOx	70	30

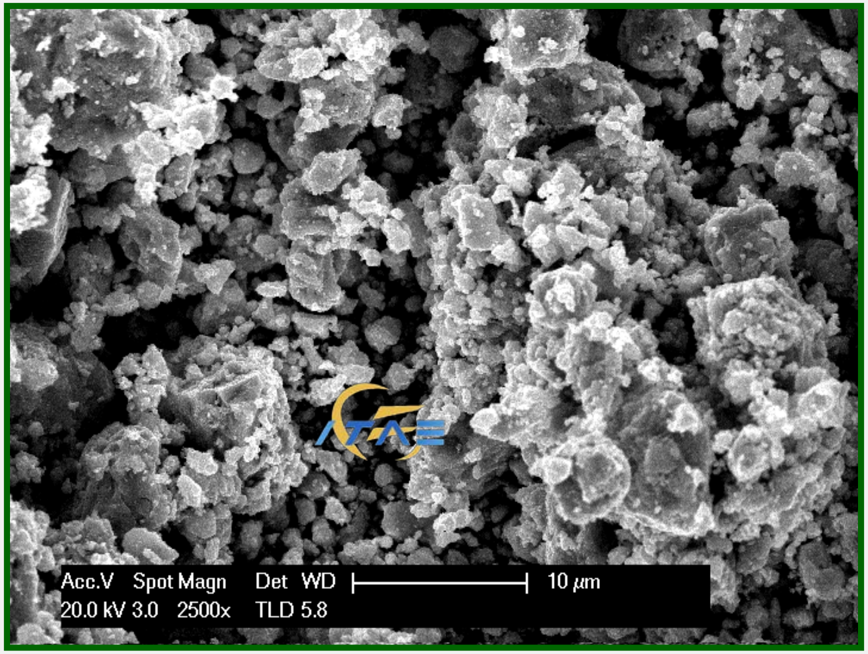
- ✓ Bulk atomic composition Ir:Ru = 70:30 (EDX)
- ✓ Surface atomic composition Ir:Ru = 80:20 (XPS)
- ✓ After sputtering with Ar^+ ions at 5 kV for 30 min approaches the bulk composition

Evidence of segregation of Ir on the surface

Catalyst Characterization: Large batch $Ir_{0.7}Ru_{0.3}Ox$ Anode

Morphological properties: SEM and TEM

SEM

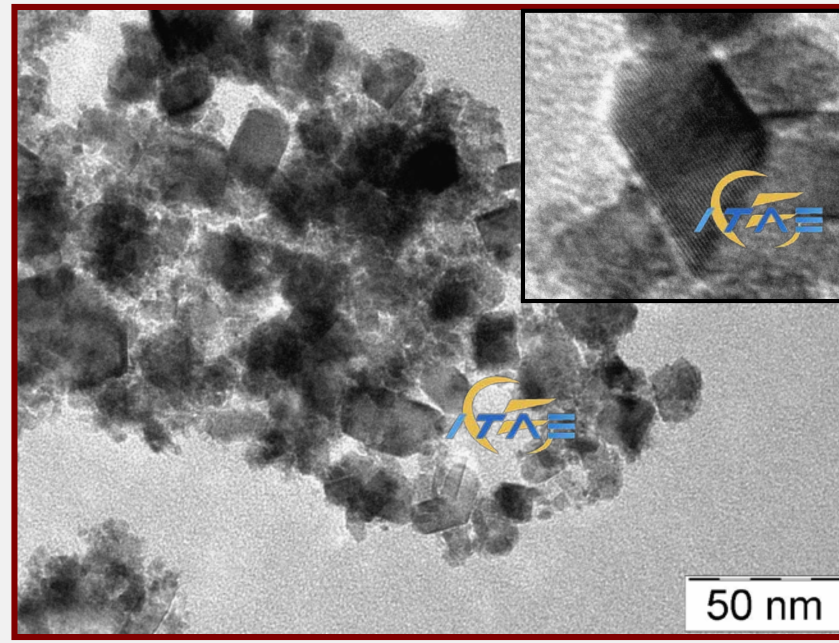


SEM-EDX:

$Ir_{0.7}Ru_{0.3}O_x$ (70:30 at.%)

(no impurities)

TEM



Several particles show a rectangular shape and a significant fraction of these particles are faceted than round (spherical)

The inset shows the crystalline lattice of the primary particles

Cathode electro-catalyst: 30% Pt/C

Sulfite-complex route

$H_2PtCl_6 + Na_2S_2O_5/NaHSO_3$

↓

$Na_6Pt(SO_3)_4$ + Vulcan

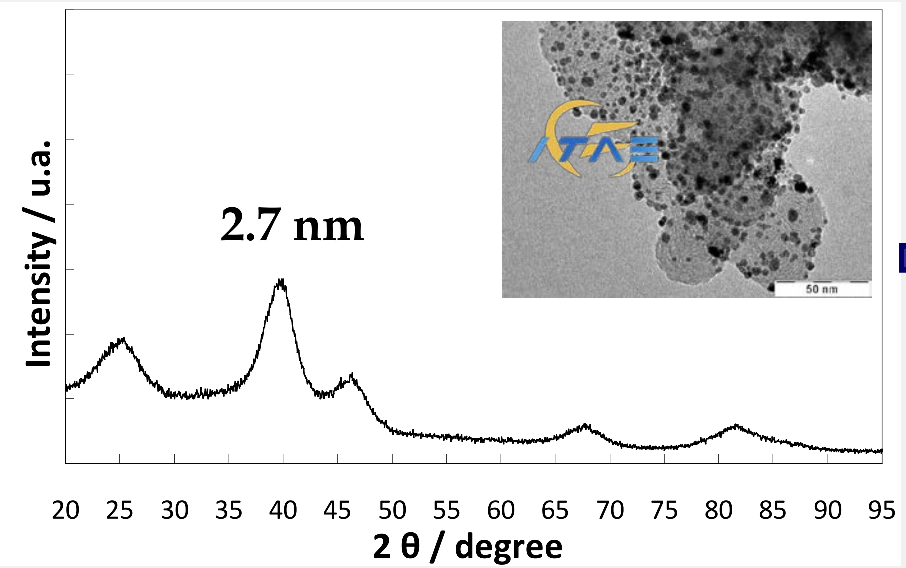
The Pt-sulfite complex/Vulcan slurry was decomposed by adding H_2O_2

↓

✓ **PtO_x/Vulcan**

Carbothermal reduction in inert (Ar) atmosphere at 600 °C

✓ **Pt/Vulcan**



XRD: Pt cubic and C support hexagonal crystallographic structures

TEM: Proper metal particle dispersion and good homogeneity

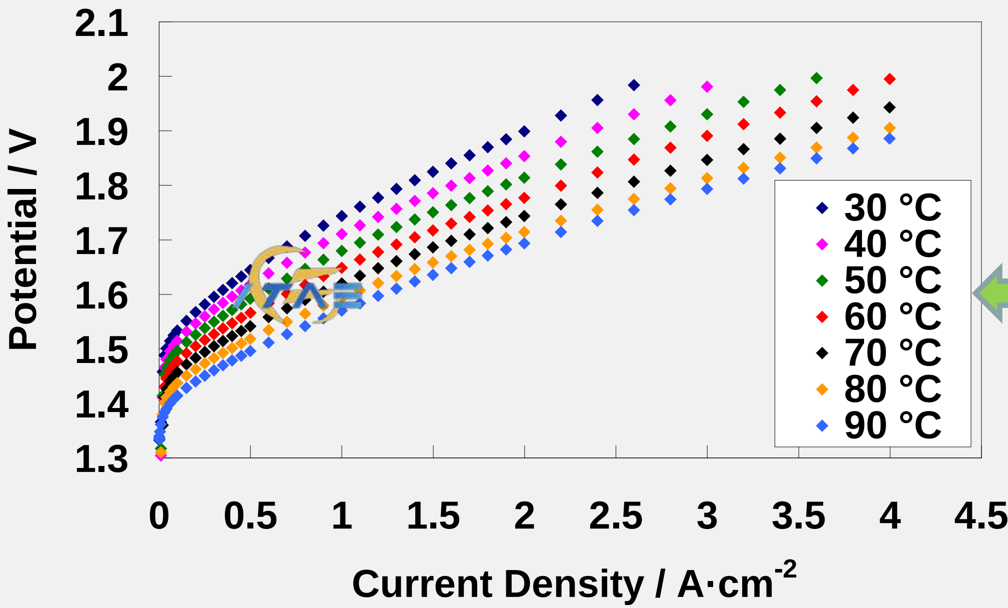
New MEAs
using different catalysts loading

MEA Catalysts Loading:

2 mg·cm^{-2} →	**Anode: 1.5 mg $Ir_{0.7}Ru_{0.3}O_2$ cm^{-2}** **Cathode: 0.5 mg Pt cm^{-2}**
1.6 mg·cm^{-2} →	**Anode: 1.5 mg $Ir_{0.7}Ru_{0.3}O_2$ cm^{-2}** **Cathode: 0.1 mg Pt cm^{-2}**
0.5 mg·cm^{-2} →	**Anode: 0.4 mg $Ir_{0.7}Ru_{0.3}O_2$ cm^{-2}** **Cathode: 0.1 mg Pt cm^{-2}**

Low catalyst loading MEA configuration: 0.44 mg cm^{-2} total noble metal (Ir, Ru, Pt) loading

MEA Catalysts Loading: 2 mg·cm^{-2}

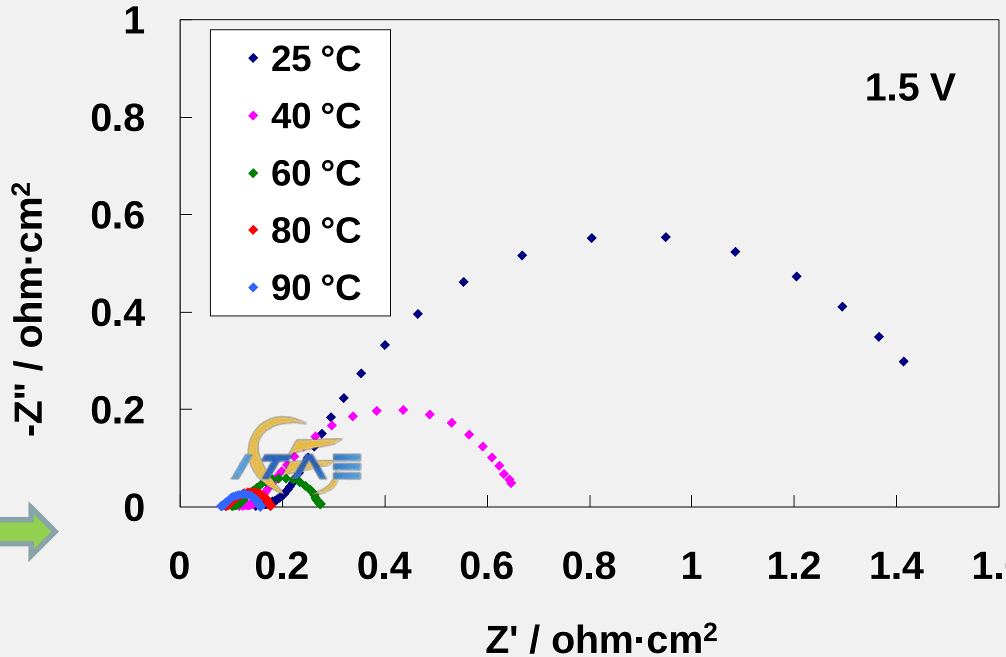


T / °C	A.cm^{-2} @ 1.6 V	A.cm^{-2} @ 1.8 V
30 °C	0.32	1.4
40 °C	0.42	1.6
50 °C	0.55	1.9
60 °C	0.70	2.2
70 °C	0.85	2.6
80 °C	1.04	3
90 °C	1.2	3.2

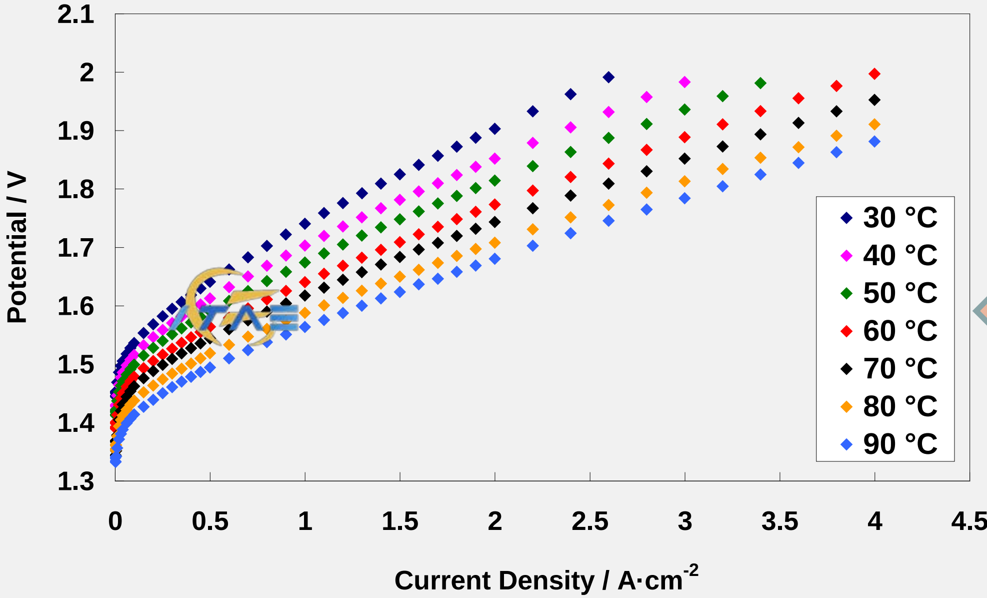
Cathode: 30% Pt/C
Membrane: E100-09S
Anode: IrRuOx

Anode: 1.5 mg·cm^{-2}
Cathode: 0.5 mg·cm^{-2}

T / °C	Rs / mΩ.cm^2	Rp / mΩ.cm^2
25 °C	150	1350
40 °C	117	530
60 °C	100	175
80 °C	90	88
90 °C	80	78



MEA Catalysts Loading: 1.6 mg·cm^{-2}



T / °C	A·cm^{-2} @ 1.6 V	A·cm^{-2} @ 1.8 V
30 °C	0.35	1.4
40 °C	0.45	1.65
50 °C	0.6	1.9
60 °C	0.75	2.3
70 °C	0.9	2.6
80 °C	1.1	3
90 °C	1.3	3.2

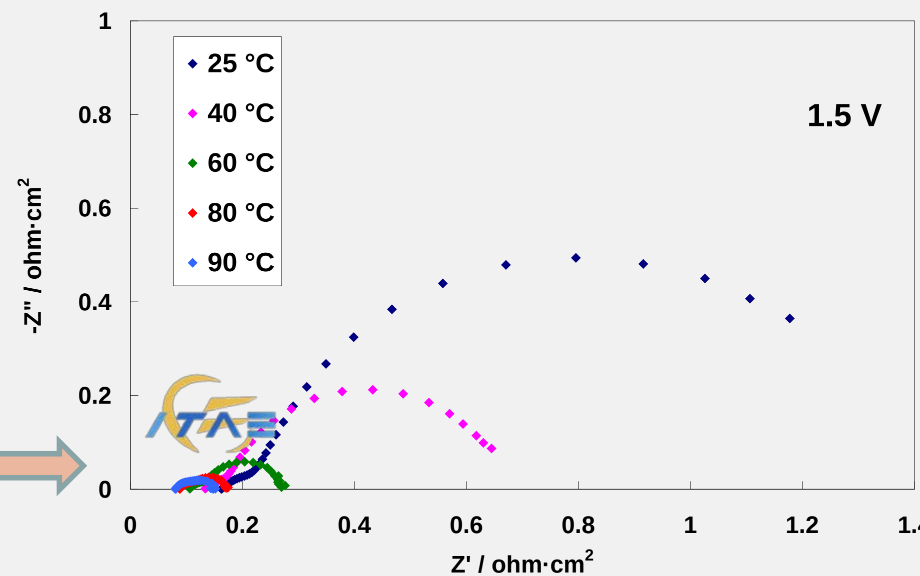
Cathode: 30% Pt/C
Membrane: E100-09S
Anode: IrRuOx

Anode: 1.5 mg·cm^{-2}
Cathode: 0.1 mg·cm^{-2}

Only cathode loading was decreased in this MEA

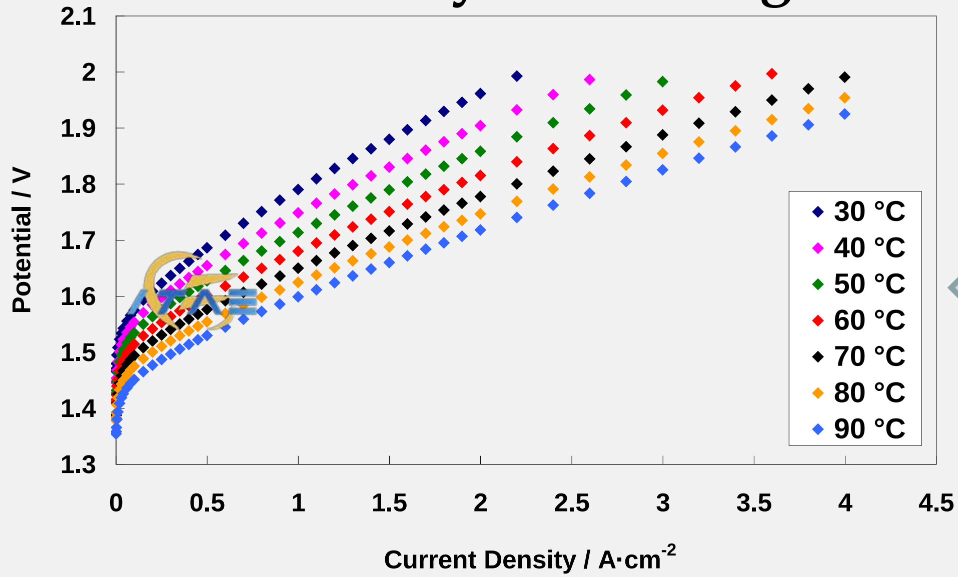
A thinner cathode catalyst is beneficial for mass transport

T / °C	Rs / mΩ.cm^2	Rp / mΩ.cm^2
25 °C	162	1200
40 °C	133	512
60 °C	106	164
80 °C	88	84
90 °C	81	67



Low catalyst loading configuration

MEA Catalysts Loading: 0.5 mg·cm^{-2}

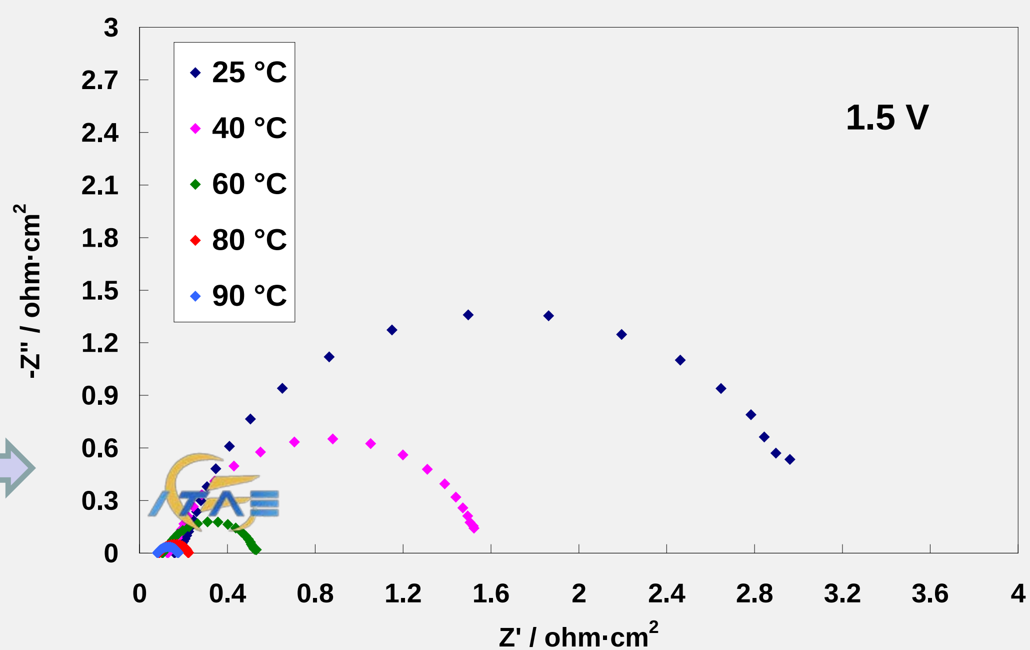


T / °C	A.cm^{-2} @ 1.6 V	A.cm^{-2} @ 1.8 V
30 °C	0.2	1.1
40 °C	0.25	1.3
50 °C	0.4	1.6
60 °C	0.5	1.9
70 °C	0.7	2.2
80 °C	0.8	2.5
90 °C	1	2.8

Cathode: 30% Pt/C
Membrane: E100-09S
Anode: IrRuOx

Anode: 0.4 mg·cm^{-2}
Cathode: 0.1 mg·cm^{-2}

T / °C	Rs / mΩ.cm^2	Rp / mΩ.cm^2
25 °C	158	2800
40 °C	128	1390
60 °C	105	425
80 °C	88	135
90 °C	82	94



Effect of total catalyst loading

Comparison of polarization curves and impedance spectra for different types of MEAs indicate:

Decrease of cathode catalyst loading of **5 times** does not cause significant change (better mass transport)

Decrease of anode catalyst loading of **3 times** causes a loss of 30-40 mV in the range 2-4 A cm^{-2} at 80 °C

- Decrease of cathode catalyst loading of **5 times** causes a sligth increase of the high frequency polarisation resistance (charge transfer) (first semicircle) but significantly lower polarisation resistance at lower frequencies (mass transport)

- Decrease of anode catalyst loading of **3 times** causes a significant increase in polarisation resistance (charge transfer associated to oxygen evolution)

Siracusano, S., Baglio, V., Moukheiber, E., Merlo, L., Aricò, A.S. Performance of a PEM water electrolyser combining an IrRu-oxide anode electrocatalyst and a short-side chain Aquivion membrane (2015) International Journal of Hydrogen Energy, . Article in Press. DOI: 10.1016/j.ijhydene.2015.04.159

Durability vs. catalyst loading

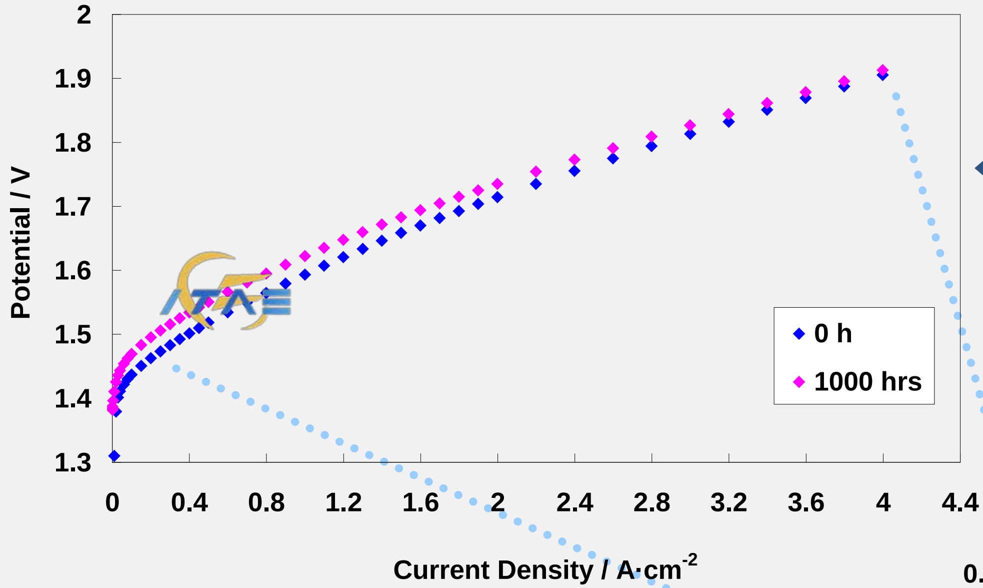
1000 hrs, 1 A cm^{-2} at 80 °C

Cathode: 30% Pt/C
Membrane: E100-09S
Anode: IrRuOx

Anode Loading mg cm^{-2}	Cathode Loading mg cm^{-2}	MEA Loading mg cm^{-2}	Total regression µV/h	Regression excluding the first 100 hrs µV/h
0.4	0.1	0.5	21	17
1.5	0.1	1.6	7	5
1.5	0.5	2.0	22	17

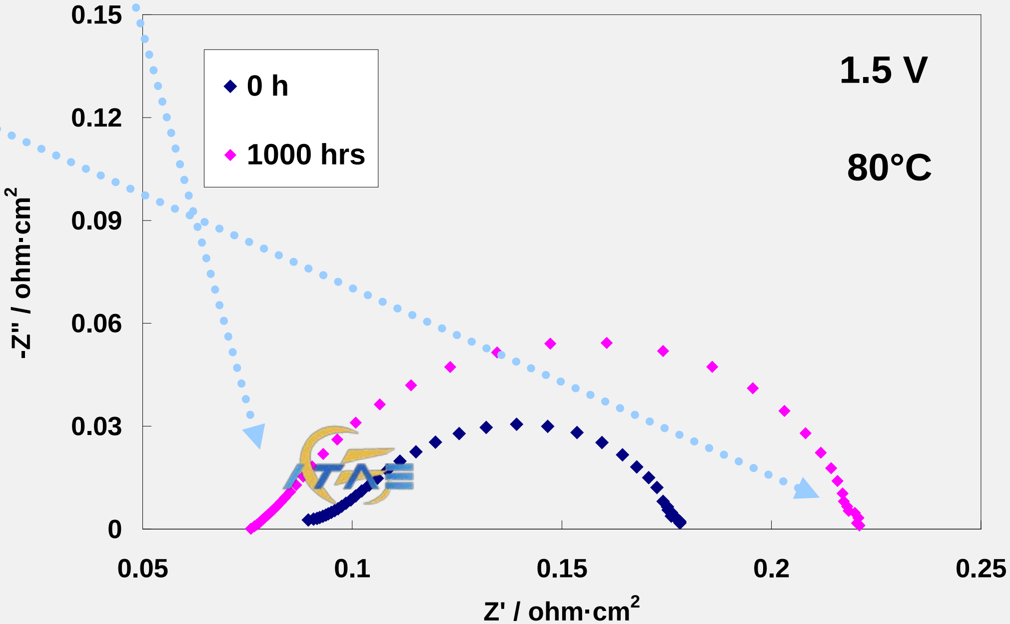
MEA Catalysts Loading: 2 mg·cm^{-2}

Comparison: before and after 1000 h at 1 A cm^{-2} time test

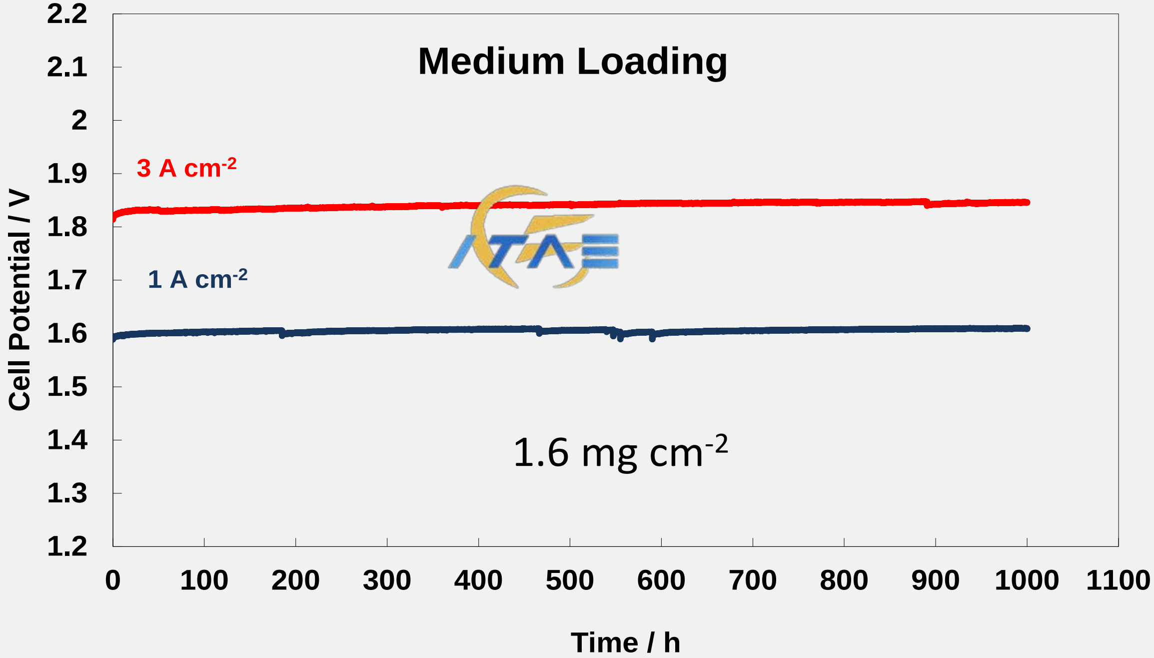


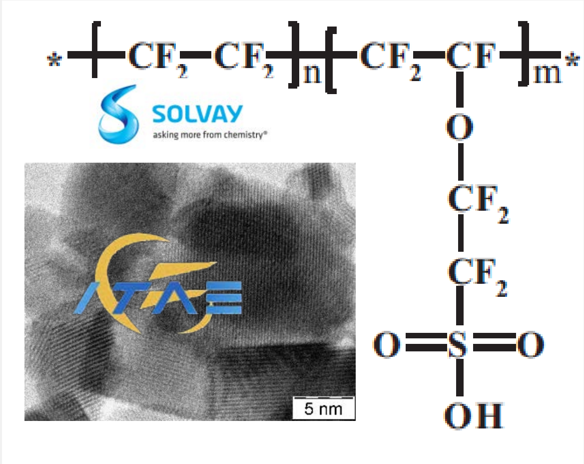
- ✓ Increase of onset
- ✓ Similar potential at high current

- ✓ Decrease of Rs
- ✓ Increase of Rp



Durability tests at 3 A cm^{-2}





Very low degradation rate also at high current density

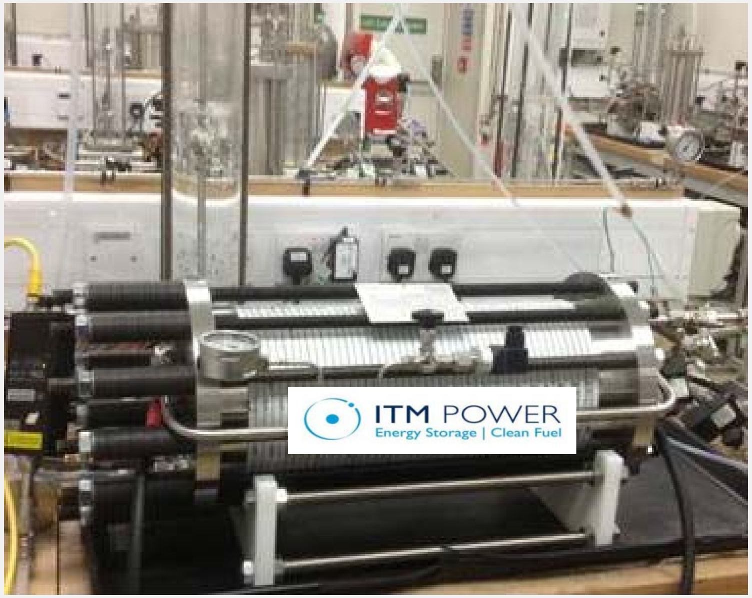
Comparable decay rate at 1 and 3 A cm^{-2}

FCH JU ElectroHypem Project

The enhanced materials have been produced on a suitable scale and validated in a 1.2 Nm^3 H_2/h PEM electrolyser at ITM in terms of performance, durability and dynamic behaviour

Solvay Aquivion® extrusion and hydrolysis plants

ITM PEM electrolysis stack developed for Electrohypem



http://www.electrohypem.eu/

Electrohypem

Conclusions

- ✓ Advanced membrane and electro-catalysts were developed for water electrolysis
- ✓ Performances of 3.2 A cm^{-2} at 1.8 V have been achieved
- ✓ The electrochemical activity was investigated in a single cell PEM electrolyzer consisting of a Pt/C cathode, IrRuOx anode and an Aquivion membrane;
- ✓ The optimized MEAs showed degradation rate less than 5 μV/h (1000 hrs) and no relevant degradation phenomena were present in the post-operation analysis.
- ✓ Excellent performance and moderate decay 15 μV/h (1000 hrs) was observed for the low catalyst loading (0.5 mg cm^{-2}) MEA

Mitigation strategies adopted

- ➢ Catalysts pre-leached in perchloric acid to remove all impurities
- ➢ Degree of alloying improved in IrRuOx with Ir surface enrichment
- ➢ Chemical stabilisation of membrane and ionomer (lower release of fluorine)
- ➢ MEA fabrication procedure optimised

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