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.

http://www.electrohypem.eu/

# 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

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<tr>
<th>Beneficiary name</th>
<th>Country</th>
<th>Partner type</th>
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<td>CONSIGLIO NAZIONALE DELLE RICERCHE (CNR-ITAE)</td>
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[http://www.electrohypem.eu/](http://www.electrohypem.eu/)
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.

**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:

\[ 2H_2O \rightarrow 4H^+ + 4e^- + O_2 \]
The Solvay Aquivion ionomer is characterized by both larger crystallinity and higher glass transition temperature than Nafion.
MEA Durability

Optimisation of MEA manufacturing conditions

Evidence of recoverable and unrecoverable losses

Degradation study presented here is focused on the less stable MEA

First set of developed materials

Anode: IrRuOx
Cathode: Unsupported Pt black
Membrane and ionomer: First supply of Aquивion
XRD

Structural and morphological analysis

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

- 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.
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
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 ($2.8 \times 10^{-3}$ 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.
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\textsubscript{0.7}Ru\textsubscript{0.3}Ox Anode Electro-Catalysts

A lattice contraction indicates the formation of a solid solution

Pre-requisite to Enhance the stability of Ru

XRD

XPS: No impurities are present on the surface

From IrOx to Ir$_{0.7}$Ru$_{0.3}$Ox Anode Electro-Catalysts

**Bulk and surface characteristics**

- 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$_{0.3}$O$_x$ 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

H₂PtCl₆ + Na₂S₂O₅/NaHSO₃ → Na₆Pt(SO₃)₄ + Vulcan

The Pt-sulfite complex/Vulcan slurry was decomposed by adding H₂O₂

✓ PtOₓ/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 Ir₀.₇Ru₀.₃O₂ cm⁻²
  - Cathode: 0.5 mg Pt cm⁻²

- **1.6 mg cm⁻²**
  - Anode: 1.5 mg Ir₀.₇Ru₀.₃O₂ cm⁻²
  - Cathode: 0.1 mg Pt cm⁻²

- **0.5 mg cm⁻²**
  - Anode: 0.4 mg Ir₀.₇Ru₀.₃O₂ 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$^{-2}$

<table>
<thead>
<tr>
<th>Temperature / °C</th>
<th>$A\cdot cm^{-2}$ @ 1.6 V</th>
<th>$A\cdot cm^{-2}$ @ 1.8 V</th>
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<tbody>
<tr>
<td>30 °C</td>
<td>0.32</td>
<td>1.4</td>
</tr>
<tr>
<td>40 °C</td>
<td>0.42</td>
<td>1.6</td>
</tr>
<tr>
<td>50 °C</td>
<td>0.55</td>
<td>1.9</td>
</tr>
<tr>
<td>60 °C</td>
<td>0.70</td>
<td>2.2</td>
</tr>
<tr>
<td>70 °C</td>
<td>0.85</td>
<td>2.6</td>
</tr>
<tr>
<td>80 °C</td>
<td>1.04</td>
<td>3</td>
</tr>
<tr>
<td>90 °C</td>
<td>1.2</td>
<td>3.2</td>
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Cathode: 30% Pt/C
Membrane: E100-09S
Anode: IrRuOx

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

<table>
<thead>
<tr>
<th>Temperature / °C</th>
<th>$Rs$ / mΩ⋅cm$^2$</th>
<th>$Rp$ / mΩ⋅cm$^2$</th>
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<tbody>
<tr>
<td>25 °C</td>
<td>150</td>
<td>1350</td>
</tr>
<tr>
<td>40 °C</td>
<td>117</td>
<td>530</td>
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<tr>
<td>60 °C</td>
<td>100</td>
<td>175</td>
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<tr>
<td>80 °C</td>
<td>90</td>
<td>88</td>
</tr>
<tr>
<td>90 °C</td>
<td>80</td>
<td>78</td>
</tr>
</tbody>
</table>
MEA Catalysts Loading: 1.6 mg·cm⁻²

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
Low catalyst loading configuration

**MEA Catalysts Loading:** 0.5 mg·cm⁻²

**Cathode:** 30% Pt/C

**Membrane:** E100-09S

**Anode:** IrRuOₓ

<table>
<thead>
<tr>
<th>T / °C</th>
<th>Rs / mΩ·cm²</th>
<th>Rp / mΩ·cm²</th>
</tr>
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<tbody>
<tr>
<td>25 °C</td>
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<tr>
<td>80 °C</td>
<td>88</td>
<td>135</td>
</tr>
<tr>
<td>90 °C</td>
<td>82</td>
<td>94</td>
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</table>

**Current Density / A·cm⁻²**

**Potential / V**

**Z' / ohm·cm²**

**Z'' / ohm·cm²**

- **Anode:** 0.4 mg·cm⁻²
- **Cathode:** 0.1 mg·cm⁻²

**Graphs and Tables**

- Graph showing current density versus potential at different temperatures.
- Table listing Rs and Rp values at different temperatures.
- Graph showing Z' and Z'' values at different temperatures.
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 slight 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)

Durability vs. catalyst loading

1000 hrs, 1 A cm⁻² at 80 °C

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

<table>
<thead>
<tr>
<th>Anode Loading (mg cm⁻²)</th>
<th>Cathode Loading (mg cm⁻²)</th>
<th>MEA Loading (mg cm⁻²)</th>
<th>Total regression (µV/h)</th>
<th>Regression excluding the first 100 hrs (µV/h)</th>
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</thead>
<tbody>
<tr>
<td>0.4</td>
<td>0.1</td>
<td>0.5</td>
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<td>17</td>
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<td>1.5</td>
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<tr>
<td>1.5</td>
<td>0.5</td>
<td>2.0</td>
<td>22</td>
<td>17</td>
</tr>
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</table>
MEA Catalysts Loading: 2 mg·cm^{-2}

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

- Decrease of Rs
- Increase of Rp
- Increase of onset
- Similar potential at high current

1.5 V
80°C
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$^{-2}$
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/
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, IrRuO\(_x\) 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 IrRuO\(_x\) with Ir surface enrichment
➢ Chemical stabilisation of membrane and ionomer (lower release of fluorine)
➢ MEA fabrication procedure optimised
The authors acknowledge the financial support of the EU through the FCH JU ELECTROHYPEM Project. “The research leading to these results has received funding from the European Community’s Seventh Framework Programme (FP7/2010-2013) for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement Electrohypem n. 300081.”