CLEAN HYDROGEN JU AEMEL PROJECT FINDINGS & JRC ELECTROLYSER DEGRADATION "2 IN 1" WORKSHOP

Accelerated stress test in PEM electrolysis

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H2020 FCH JU NEPTUNE
Project & Partnership description

Next Generation PEM Electrolyser under New Extremes **GA No. 779540**

Start → February 2018
End → April 2022

Overall objective:

To develop a set of breakthrough solutions at materials, stack and system levels to increase hydrogen pressure to 100 bar and current density to 4 A cm^{-2} for the base load, while keeping the nominal energy consumption <50 kWh/kg H_2

The aim of the project was to bring the new technology to TRL5

Analysis of performance degradation during steady-state and load-thermal cycles of PEM WE cells

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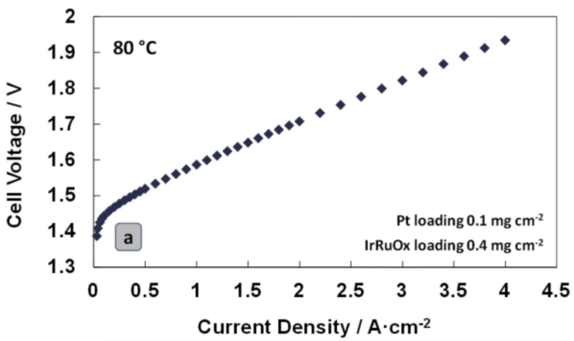
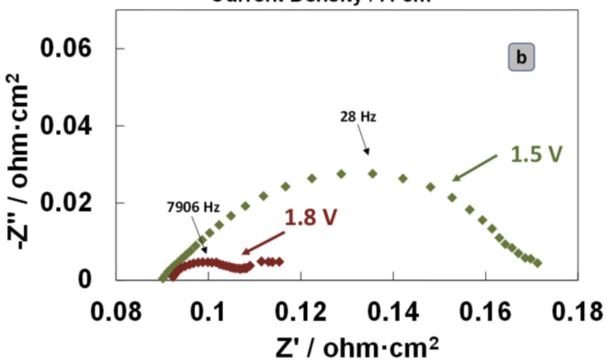
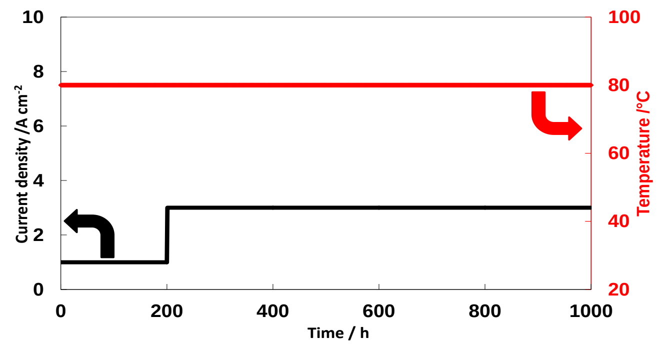
Electrochemical Characterization (BoL)





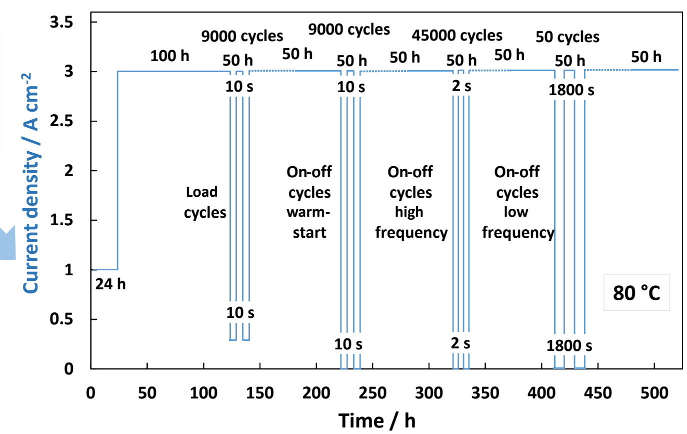
3 A cm^{-2}	*BoL*
Voltage Value	1.82
Voltage Efficiency / % (HHV)	81

Protocols



MEA durability test: steady-state

MEA durability test: load cycles



S. Siracusano, S. Trocino, N. Briguglio, F. Pantò, A. S. Aricò. Analysis of performance degradation during steady-state and load-thermal cycles of proton exchange membrane water electrolysis cells. Journal of Power Sources 468 (2020) 228390

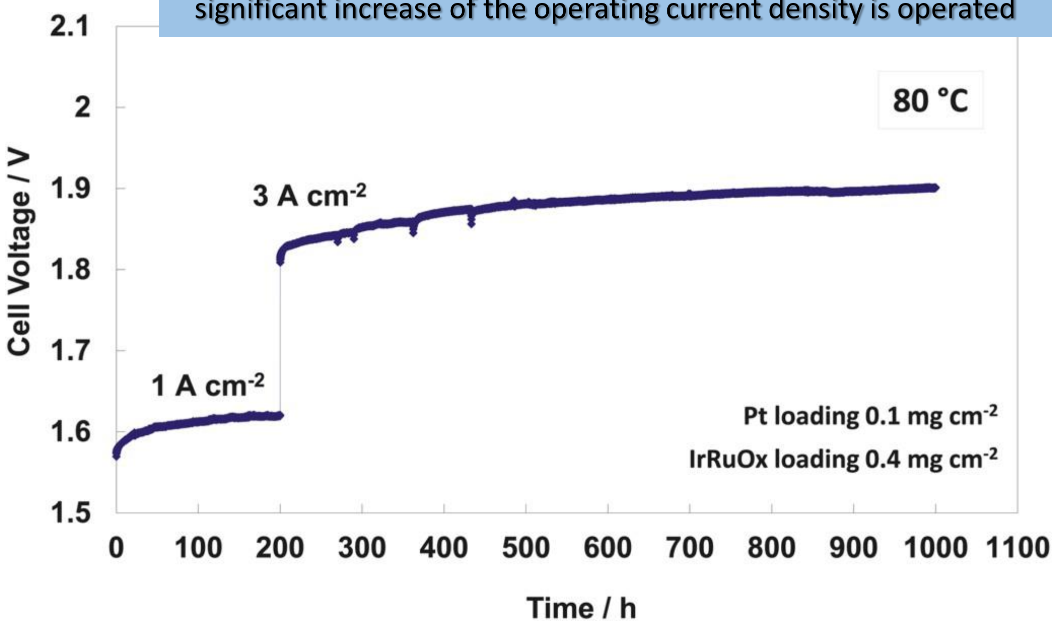
S. Siracusano, S. Trocino, N. Briguglio, V. Baglio A. S. Aricò. Electrochemical Impedance Spectroscopy as a Diagnostic Tool in Polymer Electrolyte Membrane Electrolysis. Materials 11 (2018) 1368

Specific conditions:

high current density and low PGM loading

MEA durability test: Steady-State

No stabilisation of cell voltage occur immediately when a significant increase of the operating current density is operated



$3\ A\ cm^{-2}$	*Degradation Rate*
All test	90 µV/h
Last 300 h	33 µV/h

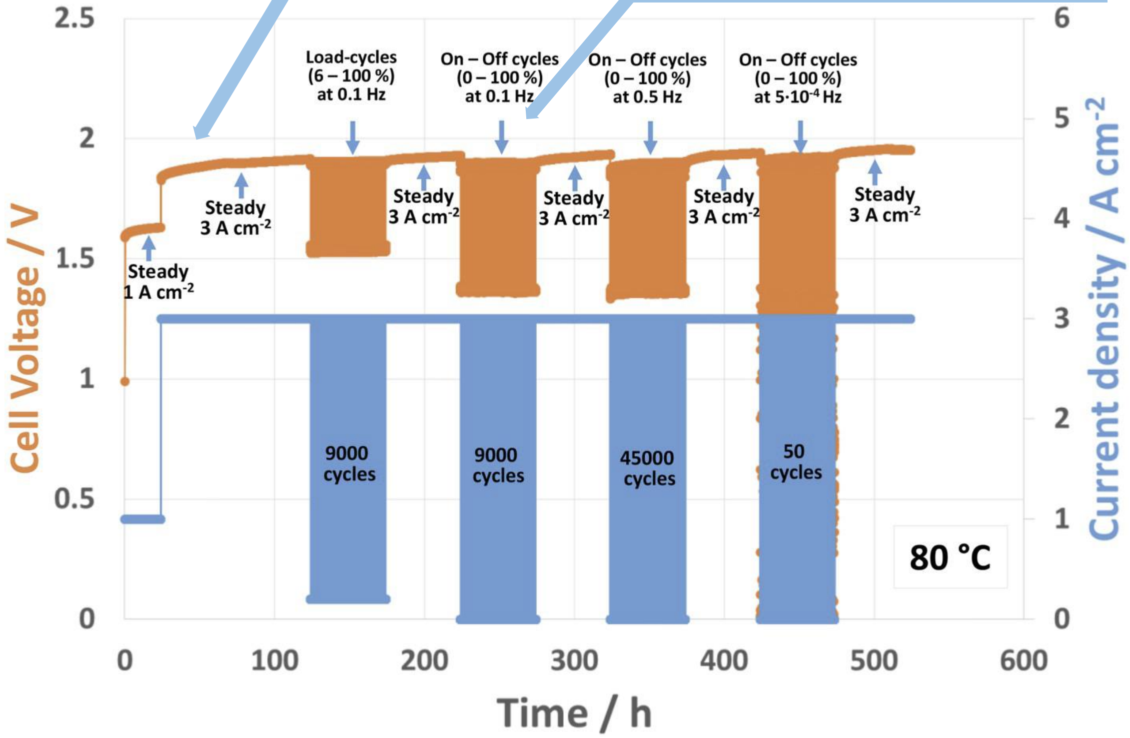
Reversible losses associated to mass transport issues

Modification in oxidation state at the anode surface or accumulation of the evolved gases in the catalyst micropores forming a diffusion barrier for the produced gas to escape from the catalytic layer. In fact, the occurrence of such supersaturation of dissolved gas in the catalyst layer seems to originate from mass transfer limitations during operation

MEA durability test: Load Cycles

Performance decay at fixed current

Lower decay during cycled operation steps



- A periodic decrease of the operating current density can mitigate performance losses by <u>producing only a recover of reversible degradation</u>

A lower reversible cell degradation is therefore foreseen during cycled operation in grid balancing service

MEA durability test: Load and Thermal Cycles

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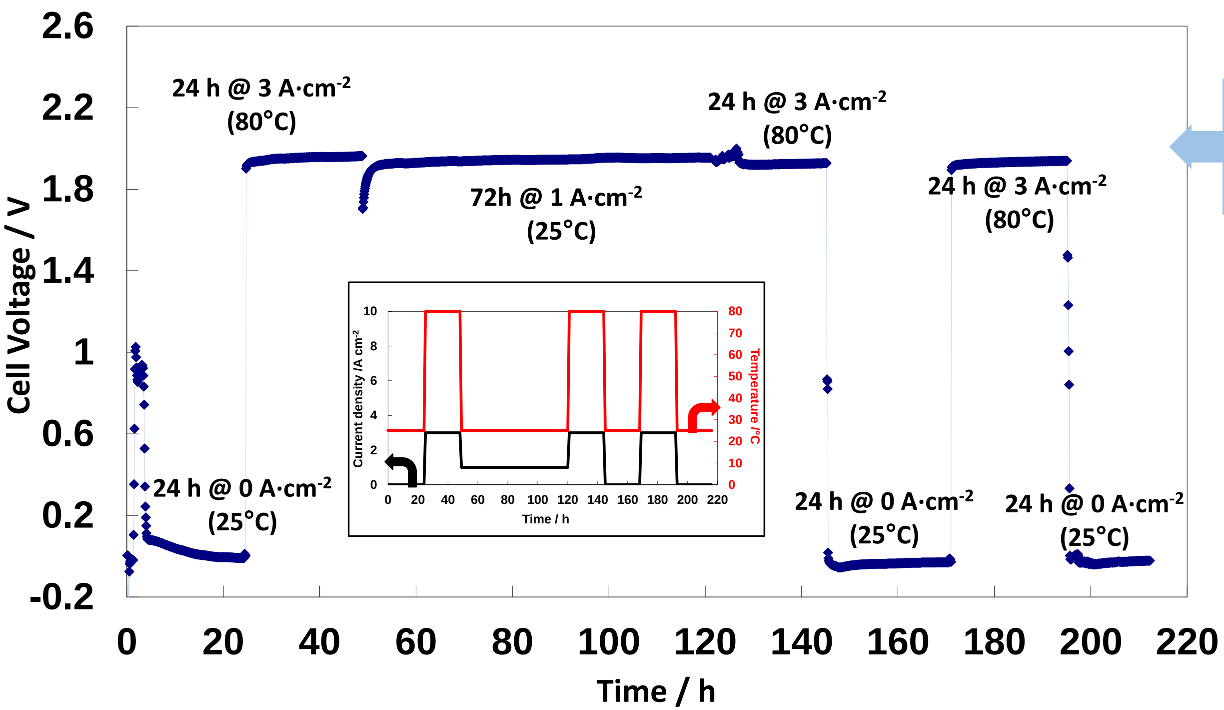
After the Load Cycles



No relevant additional performance decay

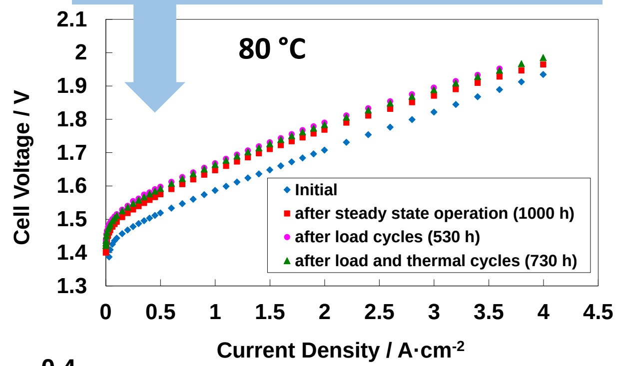
Test	*Degradation Rate*
Load cycles (Excluding the first 100 h)	95 µV/h
Thermal/load cycles	0 µV/h

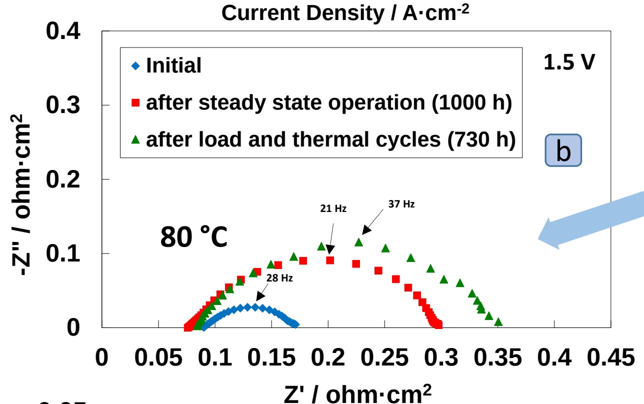
- These evidences indicate the occurrence of recoverable or reversible losses

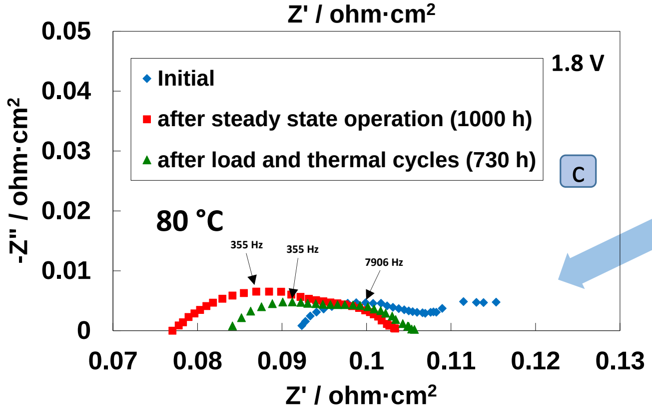
These are probably arising from mass transfer issues caused by gas evolution or by a modification of the anode oxidation state according to the specific operating potential window

MEAs electrochemical test: after steady state and load/thermal cycles

Cell voltage onset increased







3 A cm^{-2}	*BoL*	After Steady State	After Load and Load/Thermal Cycles
Voltage Value	1.82	1.87	1.89
Voltage Efficiency / % (HHV)	81	79	78

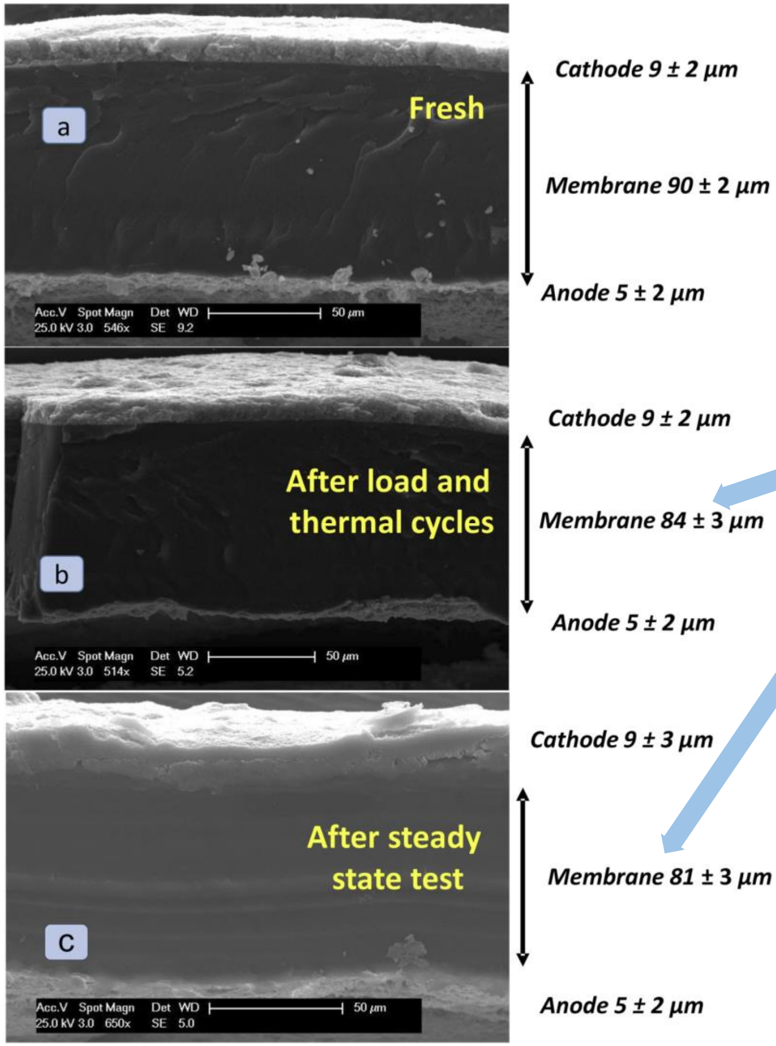
Increase of Rp ➔ catalyst degradation

Reduction of Rs ➔ cleaning and/or thinning of the membrane

Morphological Characterization

before and after steady state and load/thermal cycles

SEM cross-sections



Good adhesion of the electrodes to the membrane

Membrane thinning after both durability tests

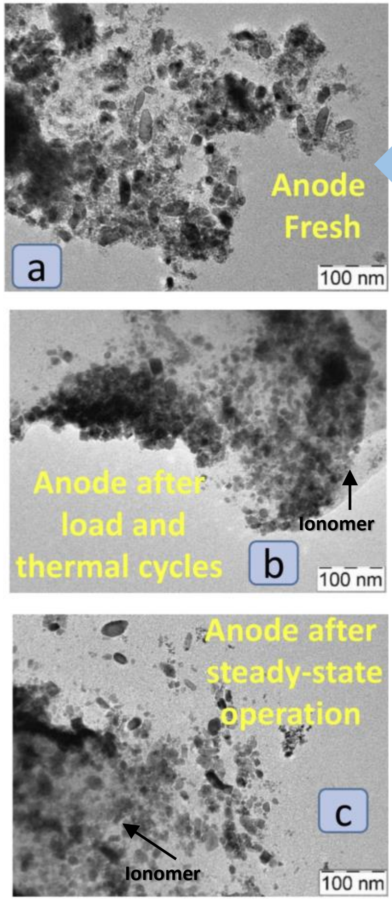
No significant change in the morphology of the catalytic layers both after the steady-state and load and thermal cycles tests

Morphological and Surface Characterization

before and after steady state and load and thermal cycles

ANODE: $Ir_{0.7}Ru_{0.3}Ox$

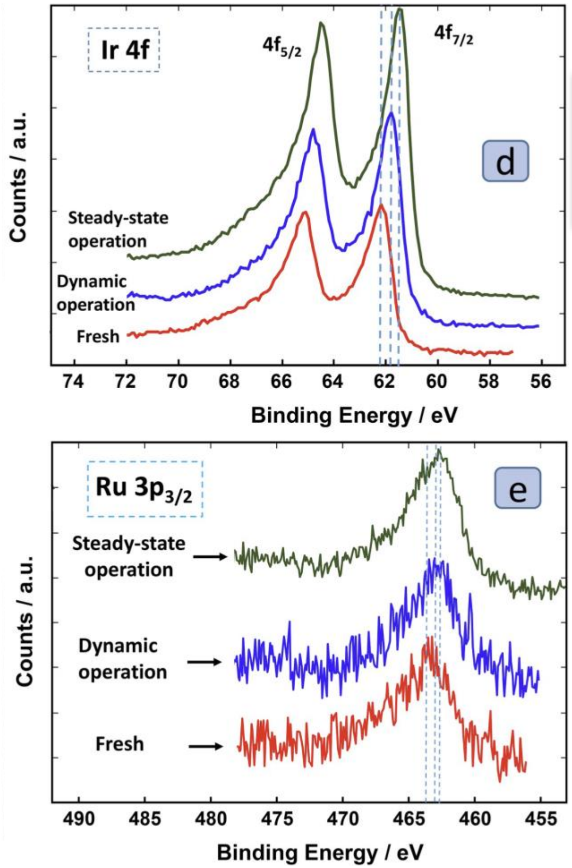
TEM



Mixture of nanosized irregularly shaped and faceted (squared and rectangular) particles

Less agglomerated

XPS



Shift to lower B.E. in the used sample ➔ Ir^{4+} to sub-stoichiometric Ir^{3+}

Ir sites having unsaturated coordination with oxygen species

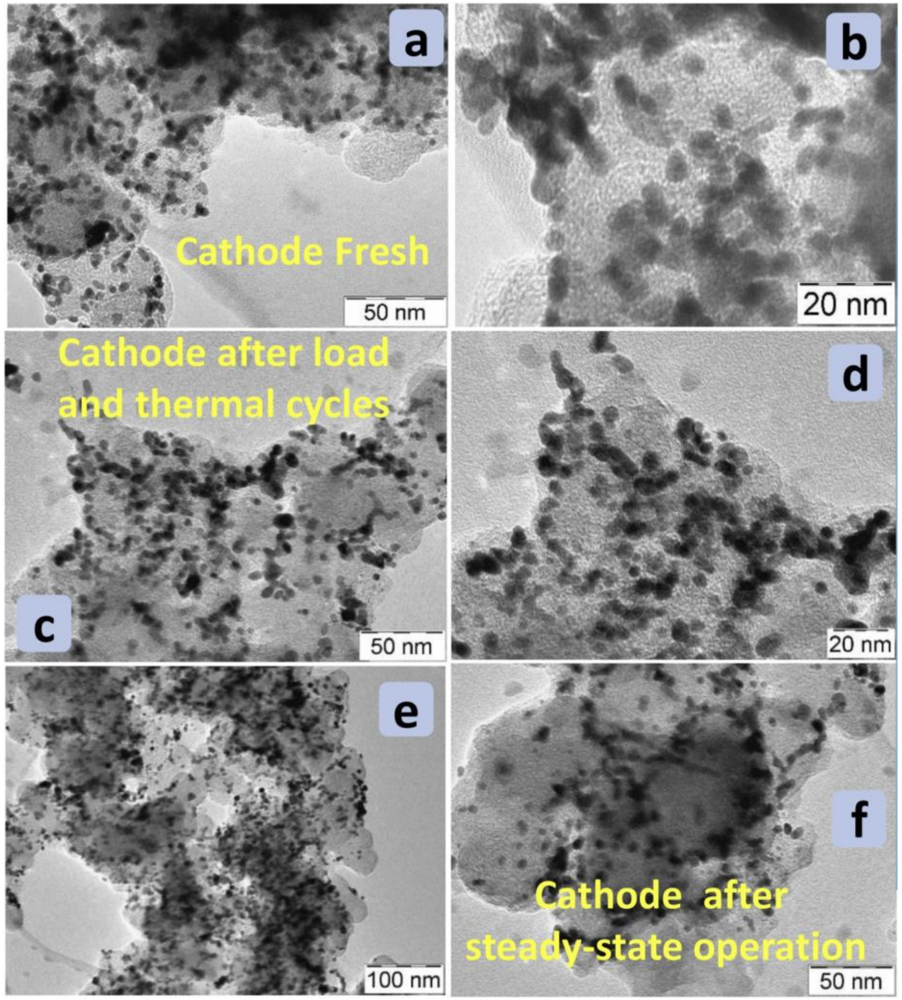
Shift to lower B.E. in the used sample ➔ Ru^{4+} to sub-stoichiometric Ru^{3+}

Morphological Characterization

before and after steady state and load and thermal cycles

CATHODE: 40 % Pt/C

TEM



- No significant change in morphology after the durability tests

- Pt/C catalyst is embedded into the ionomer layer

- slight growth of the Pt particles upon cycled operation

Survey of main results from ex-situ physico-chemical analysis

ANODE: $Ir_{0.7}Ru_{0.3}Ox$

CATHODE: 40 % Pt/C

	Membrane thickness	Bulk elemental analysis of Ir and Ru metals in the anode layer SEM-EDX		Surface elemental analysis of Ir and Ru metals in the anode layer XPS		B.E. Ir $4f_{7/2}$	B.E. Ru $3p_{3/2}$	Mean particle size anode	Mean particle size cathode
Units	**µm**	**Ir at. %**	**Ru at. %**	**Ir at. %**	**Ru at. %**	**eV**	**eV**	**nm**	**nm**
FRESH MEA	**90 ± 2**	**70.1 ± 0.5**	**29.9 ± 0.5**	**75.4 ± 2.0**	**24.6 ± 2.0**	**62.18**	**463.48**	**6 ± 2.0**	**2.5 ± 0.5**
MEA operate in steady-state mode	**81 ± 3**	**70.7 ± 0.5**	**29.3 ± 0.5**	**76.2 ± 2.0**	**23.8 ± 2.0**	**61.50**	**462.67**	**6 ± 2.0**	**3.0 ± 0.5**
MEA operated with load and thermal cycles	**84 ± 3**	**76.7 ± 0.5**	**23.3 ± 0.5**	**80.3 ± 2.0**	**19.7 ± 2.0**	**61.82**	**462.84**	**5 ± 2.0**	**3.5 ± 0.5**

Beside the presence of a sub-stoichiometric oxide phase on the anode surface, the slight loss of Ru species may represent another cause of catalyst performance degradation especially associated to cycled operation as observed in the increase of polarization resistance in the activation region of the polarization curve

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Conclusions

Analysis of performance degradation during steady-state and load-thermal cycles under specific conditions (high current density and low PGM loading) was investigated

Reversible loss

- *Due to two different phenomena: changing the oxidation state on the surface according to the different potential window and accumulation of the gas molecules entrapped in the micro-pores forming a diffusion barrier to escape from the catalyst layer.* ***Decrease of the operating current density can mitigate performance losses can allow to recover part of the reversible losses.***

Irreversible loss

- *Irreversible catalyst degradation, caused by the substoichiometric oxide phase occurrence at the anode surface, upon prolonged operation and by the loss of Ru species, is causing an increase of polarization resistance in the activation region for the used MEAs.* ***This is slightly larger for the cycled MEA (due to higher loss of Ru species)****.*

The acquired knowledge may be helpful in designing more stable MEAs for operation under such harsh dynamic operating conditions by focusing on robust solid solutions of Ir and Ru oxides with tailored core-shell structures and enhanced morphologies for the catalyst layers

ACKNOWLEDGEMENT

Thank you for your kind attention!

Institute CNR-ITAE – Messina (Italy)