Durability of PEM-FCs: studies on freezing conditions and H_2 crossover

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Catalytic **R**eaction **E**ngineering for **E**nergy and **E**nvironment
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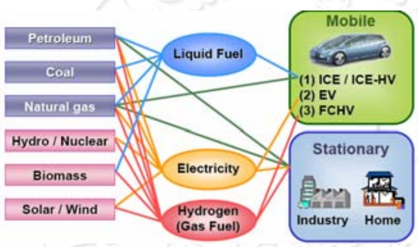
Viña del Mar, 28/10/2009

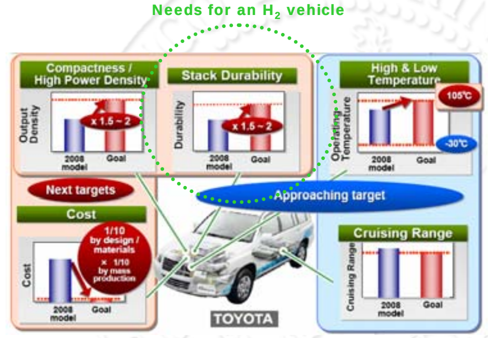
- **Durability of PEM-FCs**
- **Experimental activities on PEM-FCs**
  - Testing in subfreezing conditions
  - Testing o H_2 crossover evaluation
- **Future perspectives**
- **Acknowledgements**

Concept of energy source utilization for transportation



Electricity and hydrogen are expected to be alternatives to liquid fuel.

Needs for an H_2 vehicle



An H_2 vehicle on the road: major constrains

Starting failure at cold start:

- **Freeze during OFF** ➔ unable to start operation due to freeze of remaining water during OFF
- **Freeze after starting** ➔ unable to continue operation due to freeze of generated water before FC temperature exceeds 0 °C

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy
Fuel Cell Technologies Program

FC power systems ➔ durable and reliable as current automotive engines

- **5,000 hour lifespan or 150,000 miles equivalent**
- able to **function** over the full range of external environmental conditions, **–40 to +40 °C**

Table 3.4.3 Technical Targets: 80 kW$_e$ (net) Transportation Fuel Cell Stacks Operating on Direct Hydrogen [a]

Characteristic	Units	2003 Status	2005 Status	2010	2015
Cold start-up time to 50% of rated power					
@ –20°C ambient temperature	seconds	2	20	30	30
@ +20°C ambient temperature	seconds	<1	<10	5	5
Start up and shut down energy [f]					
from -20°C ambient temp	MJ	N/A	7.5	5	5
from +20°C ambient temp	MJ	N/A	N/A	1	1
Unassisted start from low temperature [j]	°C	N/A	-20	-40	-40

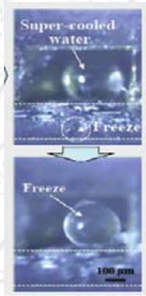
Durability of PEM FCs

Several factors affect the durability of PEM FCs:

- catalyst layer degradation
- gas diffusion layer degradation
- carbon support corrosion
- degradation of the polymeric membrane

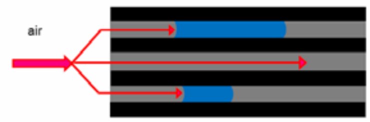
Components and interfacial damage caused by freezing water.

- Water redistribution and frost heave caused by capillarity forces drawing water to the freezing interface
- delamination of GDL into flow field channels
- morphology changes
- flow fields channels blocked by ice

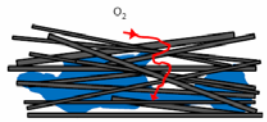


Flooding and water hold-up in PEM FCs

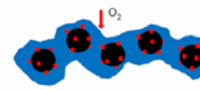
Channel Flooding



GDL Flooding



Catalyst layer flooding



Durability – general questions

Materials:
How **freeze** and **start cold transient operations** affect the FCs/MEAs components integrity, performance, durability

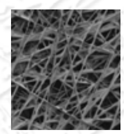
System/Engineering:
How the engineering solutions (start-up/shit-down, type of purge, transients, heating) impact on FCs/MEAs

- **freeze start related issues** can be addressed through **system operation/engineering solutions**
- **materials** can be affected by **freeze start or harsh transients**

Needs for advanced materials

- **Freezing/ice** can cause fuel starvation on anode by locking parts of cell
- **Air** could be present on the anode after system purge upon shut-down (related problems: cell reversal or cathode C-corrosion)
- **Dead-ended anode operation** could lead to pressure decrease and water accumulation ➔ need periodical water removal for H2 access to anode to prevent anode starvation
- **PEM FCs operated with reformate**: CO adsorption increased ay low temperature ➔ need heat to restart "poisoned" anode (CO tolerant anodes); system heat

Materials:
- Thickness
- Porosity
- Pore size distribution
- Hydrophobic treatment



Experimental activities on PEM-FCs @ POLITO

POLITECNICO DI TORINO
DISMIC Department of Materials Science and Chemical Engineering
ELCHILAB
HYSYLAB
ENVIRONMENT PARK

- Synthesis of new electrocatalysts
- Preparation of MEAs
- MEAs testing and characterization
- Experimental activities in subfreezing conditions
- Experimental activities on H_2 crossover evaluation

SOTTOZERO
H2 crossover

MEA preparation: 5 cm² active area

INK PREPARATION

CATHODE: 0.015 g Pt/C 20%
0.130 g Nafion 5%
0.054 g H_2O
0.054 g isopropyl alcohol
Catalyst ink stirring for 3 h

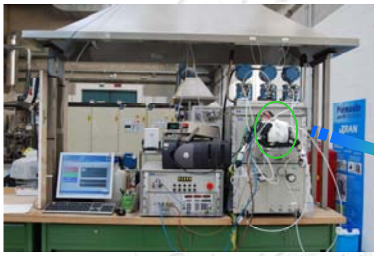
ANODE: 0.015 g Pt/C 20%
0.130 g Nafion 5%
0.054 g H_2O
0.054 g isopropyl alcohol
Catalyst ink stirring for 3 h

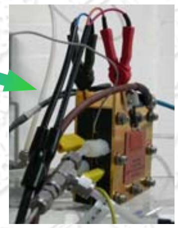
PAINTING DEPOSITION ON GDL
(LT 1200-W ELAT GDL E-TEK)
Pt load: 0.5 mg cm^{-2}

PAINTING DEPOSITION ON GDL
(LT 1200-W ELAT GDL E-TEK)
Pt load: 0.5 mg cm^{-2}

ELECTRODES HOT PRESSING
to Nafion 112/115/117
at 35 kg cm^{-2}, 120 °C, 2 min

PEM-FCs test rig @ HYSYLAB

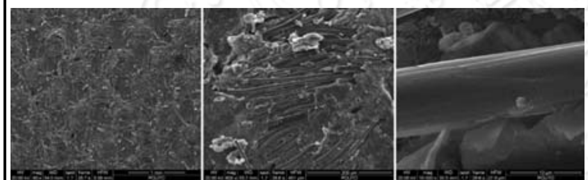




ElectroChem Power Station™ PSGDU-R 800W PEM FC: testing **up to 100 W**, from 5 cm^2 to 50 cm^2

SEM investigations on as-prepared MEAs

Nafion 115



80x 600x 10,000x

MEA without any damage, catalyst homogeneously distributed; integer GDL fibres

Effect of freezing conditions on MEAs

Freezing of water inside **PEM-FCs** could form **ice layers** in the electrodes and/or GDL. Cell reaction is limited/inhibited; the internal structure of the MEA could undergo **severe cracking**.

Thermostatic chamber (Angelantoni UC 600-70 model, useful capacity: 600 l, temp range: -70 ÷ +180 °C) to assure the complete ice formation within the MEA.

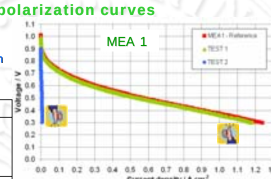
Studying the effect of sub-freezing conditions: **freezing/thawing** cycles: **+20 ÷ -10 °C & -10 ÷ +20 °C**
MEAs polarization curves evaluated after different isothermal conditioning.
Tested various **purging procedures**.

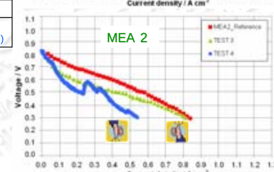
MEA activation:
8 h @ constant voltage (0.5 V)
Feeding: H_2 and O_2 100 Nl min^{-1} humidified 80%
Cell temperature: 70 °C

First attempts: MEAs polarization curves

Purging procedure: MEA 115 de-hydration by feeding **200 Nml min^{-1}** of **dry N_2 @ 70 °C** for **30 min** after testing before F/T cycles

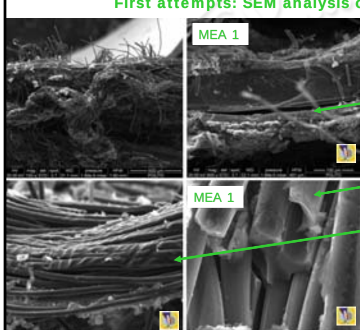
Test	MEA Status	Conditioning treatments
1	MEA 1 de-hydrated	48 h @ -10°C & 48 h @ +20°C
2	MEA 1 hydrated	
3	MEA 2 de-hydrated	8 h @ -10°C & 8 h @ +20 °C
4		4 consecutive F/T cycles (8 h @ -10°C & 8 h @ +20 °C)





Polarization curves:
- severe irreversible performance losses on **hydrated MEA1**, whereas **de-hydrated MEA1**, almost recovered its performance
- a certain decay of performance on **MEA2** with the increase of the F/T cycles

First attempts: SEM analysis on frozen MEA 1

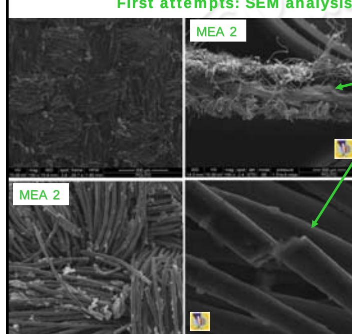


MEA 1 (hydrated) after test 2:

- Significant **damages** of both the membrane and backing layer
- **Catalyst delamination** from both the membrane and the GDL (leading presumably to H_2 crossover and consequent performance losses)
- **Cracks** and **fibers fractures**
- The fibers showed **plastic deformations** probably caused by the presence of the ice crystals

Possible strategy to avoid negative effects on MEAs: remove water from the FC before its complete shut-down

First attempts: SEM analysis on frozen MEA 2



MEA 2 (de-hydrated) after test 4:

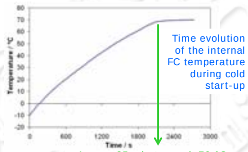
- After 4 F/T cycles, **modest catalyst delamination areas**
- No plastic deformations
- Less cracks and broken fibers

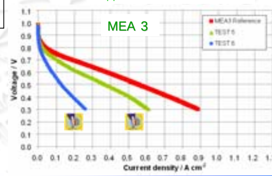
Anyway, the performance is not so good.

Second attempts: MEAs polarization curves

Purging procedure: MEA 115 de-hydration by feeding **200 Nml min⁻¹** of dry N_2 @ **70°C** for **30 min** after testing before F/T cycles.
All the assembled **MEA + FC test housing** was conditioned in the thermostatic chamber

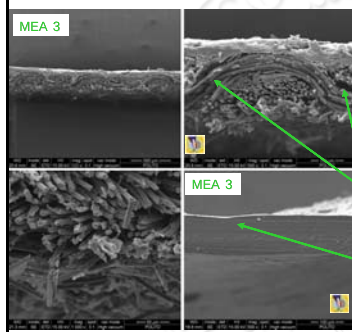
Test	MEA Status	Conditioning treatments
5	MEA 3: de-hydrated (with the FC test housing)	8 h @ -10 °C; cold start-up @ -10°C
6		3 consecutive F/T cycles (8 h @ -10°C and 8 h @ +20°C); 8 h @ -10 °C; cold start-up @ -10°C





Polarization curves:
- performance **degradation** very high. The purging method was inappropriate (maybe too low gas speed in the gas channels of the cell)
- Two mechanisms explaining why N_2 stream removes water from the FC stack: vaporization and physically pushing out liquid water droplets

Second attempts: SEM analysis on frozen MEA 3 after 4 F/T cycles



MEA 3 (de-hydrated) after test 6:

- Found some visible **traces of water in the flow fields** opening the FC housing (the adopted purging method was not sufficient to remove all the water present inside the FC housing)
- **Electrodes detached from the membrane** (total delamination phenomena occurred)
- Considerable **catalyst delamination** areas **from the GDL** (surely responsible for the performance losses)
- Catalytic layer pressed by crystal ices: different thickness along the membrane (10-50 μm)

A different purging procedure must be adopted

Improvement of the purging procedure

By purging, i.e. removing the water from the FC, the overall **R increases** drastically due to the decay of the proton conductivity inside the membrane. **Reference time**: the moment when the overall R increases

Relationship between drying N_2 flow and overall cell resistance R
(measured with Hioki 3560 Milliohm Hitester) used constant N_2 flow rates with the same **ratio anode/cathode = 1/3**

$$R_{measured} = R_{membrane}^{*} + R_{contact(flowfield/GDL)} + R_{contact(GDL/catalyst)}$$

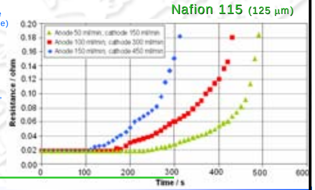
* Correlation to determine $R_{membrane}$ by knowing the membrane conductivity as a function of λ (ratio H_2O/SO_3^- in the membrane)

$$R_{mem}(T_{cell}) = \frac{z_{mem}}{\sigma(T_{cell})}$$

$$\sigma(T_{cell}) = \exp\left[1268\left(\frac{1}{303} - \frac{1}{273+T_{cell}}\right)\right] \times (0{,}005139\lambda - 0{,}00326)$$

* T. E. Springer, T. A. Zawodzinski, S. Gottesfeld, PEM-FC Model, J. Electrochem. Soc., 138 (1991) 2334 - 2342.

Nafion 115 (125 μm)



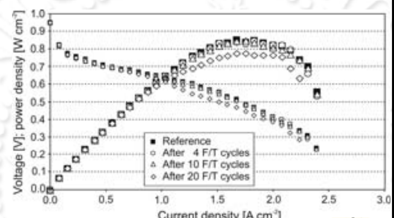
Selected **300 s** (5 min)
dry N_2 @ 70°C
150 Nml min⁻¹ @ anode side
450 Nml min⁻¹ @ cathode side

First new purging procedure (MEA1): dry N_2

MEA 112 de-hydration by feeding **dry N_2** @ **room temperature** for **4 min** after testing before F/T cycles

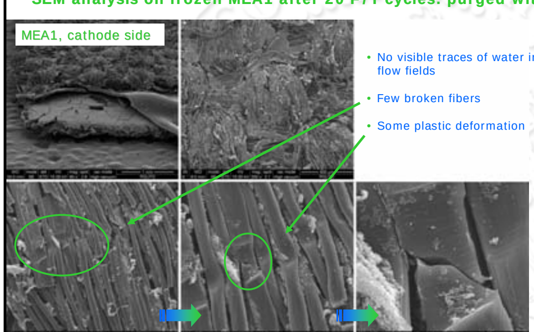
20 F/T cycles

MEA 112 re-activation at a constant tension of 0.5 V for 30 min, by feeding pure humidified H_2 and O_2, 100 Nml min⁻¹



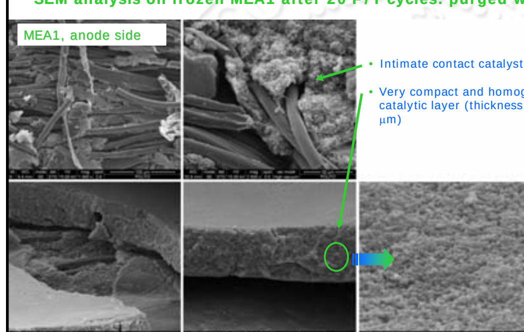
Polarization curves:
- **very limited performance loss** after 20 F/T cycles
- starting from a maximum value of power density equal to 0.859 W cm⁻² @ 1.67 A cm⁻² recorded for the reference MEA1, the **power density loss** was equal to **9.0%** after 20 F/T cycles, with 0.781 W cm⁻² @ 1.75 A cm⁻².

SEM analysis on frozen MEA1 after 20 F/T cycles: purged with N_2



- No visible traces of water in the flow fields
- Few broken fibers
- Some plastic deformation

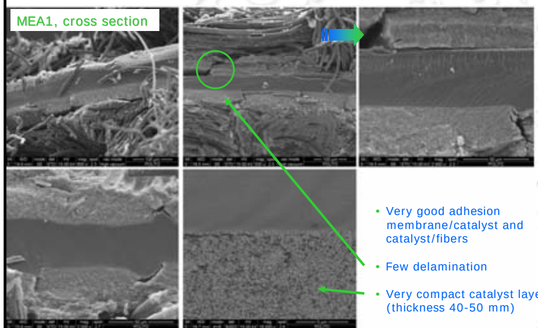
SEM analysis on frozen MEA1 after 20 F/T cycles: purged with N_2



- Intimate contact catalyst/GDL
- Very compact and homogeneous catalytic layer (thickness 40-50 μm)

SEM analysis on frozen MEA1 after 20 F/T cycles: purged with N_2

MEA1, cross section



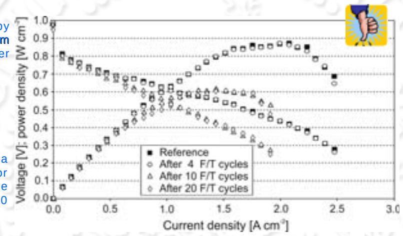
- Very good adhesion membrane/catalyst and catalyst/fibers
- Few delamination
- Very compact catalyst layer (thickness 40-50 mm)

Second purging procedure (MEA2): dry air

MEA 112 de-hydration by feeding **dry Air @ room temperature** for **4 min** after testing before F/T cycles

20 F/T cycles

MEA 112 re-activation at a constant tension of 0.5 V for 30 min, by feeding pure humidified H_2 and O_2, 100 Nml min^{-1}



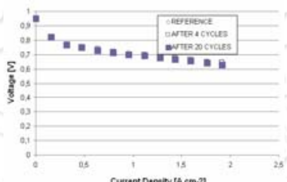
Polarization curves:
- **drastic power density loss** after only 10 F/T cycles; not so much from 10 to 20 F/T cycles
- starting from a maximum value of power density equal to 0.875 W cm^{-2} @ 2.07 A cm^{-2} recorded for the reference MEA2, the **power density loss** was equal to **30%** after 20 F/T cycles, with 0.602 W cm^{-2} @ 1.67 A cm^{-2}

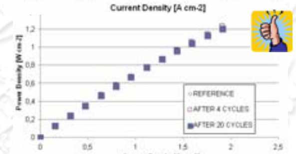
Third purging procedure (MEA3): H_2 @ anode % air @ cathode

MEA 112 de-hydration by feeding **dry Air at cathode side** & **dry H_2 at anode side** for **4 min** after testing before F/T cycles

20 F/T cycles

MEA 112 re-activation at a constant tension of 0.5 V for 30 min, by feeding pure humidified H_2 and O_2, 100 Nml min^{-1}





Polarization curves:
- **very limited performance loss** after 20 F/T cycles
- starting from a maximum value of power density equal to 1.202 W cm^{-2} @ 1.92 A cm^{-2} recorded for the reference MEA3, the **power density loss** was equal to **0.3%** after 20 F/T cycles, with 1.981 W cm^{-2} @ 1.92 A cm^{-2}.

SEM analysis on frozen MEA2 and MEA3

Still under investigation:

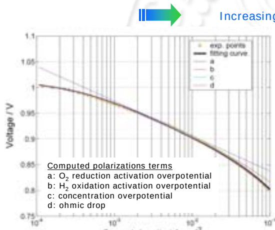
- Expected more delamination and plastic deformations on MEA2 due to the worsening in the performance (purging with air)
- Expected no damages nor delamination on MEA3 due to the very good performance (purging with air @ cathode side and with H_2 @ anode side)

H_2 crossover studies

When O_2 and H_2 permeate through the membrane and react directly with each other, the energy is lost as heat. This leads to the inefficiency of the FC.

In addition, such gases crossover leads to the formation of peroxide and hydroperoxide radicals which cause further deterioration of the membrane.

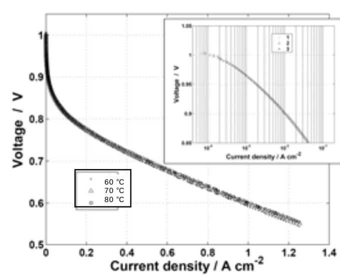
Increasing of H_2 **crossover** is a sign of MEAs deterioration



Proposed method: to take into account the OCV change following the oxidation of crossed H_2 at the O_2 electrode, with the assumption of a mixed electrode potential at the cathode involving the electrochemical reduction of O_2 and the oxidation of H_2 passing through the membrane.

Semi-empirical simplified mathematical model approach, based on analytical expressions of the polarization terms, to determine the H_2 crossover permeation rate, together with the evaluation of the electro-catalytic activity.

Determination of the polarization curves



Nafion® 112 @ 60 °C

Obtained by a slow potentiodynamic technique (AMEL potentiostat MOD 7050).

The current intensity was recorded by varying the cell voltage at a low scan rate (0.2 mV s^{-1}) from the OCV to 0.5 V and reverse.

Polarization curves traced at 3 different cell temperatures (60, 70 and 80 °C) for different MEAs (Nafion® 112, 115 and 117).

Very good reproducibility

Experimental activities on PEM-FCs @ POLITO

H2 crossover

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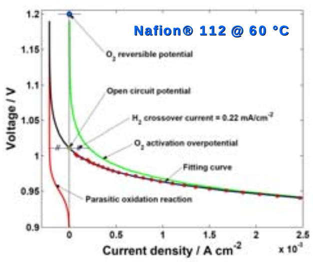
Determination of H_2 crossover rates



The anodic curve corresponding to the "parasitic oxidation reaction" was arbitrary and computed by best-fitting with the following equation:

$$V_s = V_{s0} + c_s \frac{RT}{F} \log\left(\frac{I_s}{I_{ls} - I_s}\right)$$

V_s: voltage for the parasitic reaction
I_s: current for the parasitic reaction
V_{s0}: half-wave potential of the curve
c_s: empirical coefficient (for the curve slope)
I_{ls}: limiting value for the oxidation reaction

The value of the current density for the parasitic reactions at the **open circuit potential** is taken as the **H_2 crossover rate**. (other oxidation reactions negligible)

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H2 crossover

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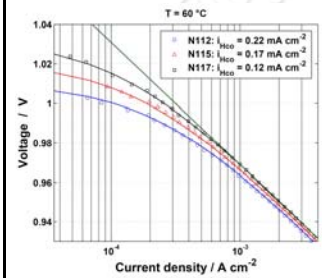
Obtained H_2 crossover current densities (mA cm^{-2})



Nafion®	60 °C	70 °C	80 °C
N117	0.12	0.19	0.24
N115	0.17	0.21	0.27
N112	0.22	0.25	0.32

H_2 crossover current densities raise by decreasing the thickness of the membranes and increasing the operative cell temperature.

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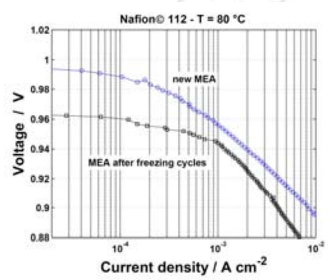
H_2 crossover current densities on degraded MEAs



New MEA Nafion® 112 tested @ 80 °C

→ H_2 crossover current density **0.32 mA cm^{-2}**

Aged MEA Nafion® 112 tested @ 80 °C after 20 freezing/thawing cycles

→ H_2 crossover current density **0.73 mA cm^{-2}**

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H2 crossover

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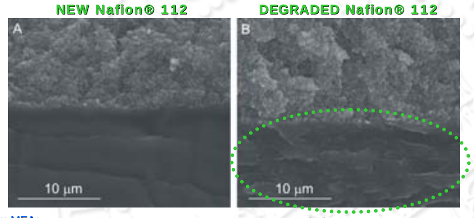
SEM investigations on new and degraded MEAs

NEW Nafion® 112 | **DEGRADED Nafion® 112**



New MEA:
→ perfect adhesion between the highly porous, catalytic layer and the membrane, without any area of delamination or fracture.
→ quite compact membrane, without any sign of deterioration.

Degraded MEA:
→ still good adhesion between the catalytic layer and the membrane
→ the membrane appeared altered compared to the new one (increased porosity?)

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Future perspectives

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Future perspectives

- Freezing studies: cold start-up
- H_2 crossover studies: influence of the pressure gas and further ageing

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Acknowledgements

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Acknowledgements

- **For projects funding:** SPH2 Sistema Piemonte Idrogeno; Europa – Gateway to the European Union
- **For kind cooperation:**
  - ✓ **CRE³ Group:** G. Gavello, V. Specchia & G. Saracco
  - ✓ **ElChiLab Group:** J. Zeng, C. Francia, N. Penazzi & P. Spinelli
  - ✓ **HySyLab:** U.A. Icardi & A. Graizzaro

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1859-2009
150 anni di Cultura Politecnica
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Acknowledgements
Muchas gracias por su gentil atenciòn
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