Anode Degradation Effects in PEMFC Stacks by Localized Fuel Starvation

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Outline

- Ciemat: spanish goverment center for energy research
- Ciemat FC Unit (L Daza):
  - High temperature fuel cells: SOFC (M Escudero)
  - Systems integration (T González)
  - Low temperature fuel cells: PEMFC (A M Chaparro)

Outline

PEMFC group activities:

- Basic electrocatalysis
  - RDE, EQCM, Membrane inlet mass spectrometry…
- Catalyst layers preparation
  - Electrospray deposition → Today, LRD43-4
  - Electrochemical deposition
- Single cell testing
  - Member of IEC/TC 105, WG1, WG11
- Small stacks mounting and characterisation

Other activities

Spanish Fuel Cell Association (APPICE) www.appice.es

National Congress on Fuel Cells: CONAPPICE 2010 (Seville, 2010)

Outline

- **Introduction**
- **Objectives**
- **Experimental procedure**
- **Results and Discussion**
- **Conclusions**

Degradation in PEM fuel cells (I)

- Increasing the durability in PEMFCs is a major challenge for the commercialization of this technology
- The main degradation mechanisms affect:
  - **Membrane** (mechanical failure, chemical contamination, electrochemical polarization, thermal decomposition)
  - **Catalyst** (Pt agglomeration, Pt migration, contamination, support corrosion)
  - **GDLs** (corrosion, chemical degradation with loss of hydrophobicity)
  - **Joints** (chemical degradation)
  - **Bipolar and end plates** (corrosion)

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Degradation in PEM fuel cells (II)

- Harsh operation conditions may accelerate usual degradation mechanisms or force new degradation processes.
- Starvation events occurring in anodic and/or cathodic electrodes are among the main causes for irreversible damage in the cells.
- Fuel/oxidant depletion or electrodes flooding are some of the causes of these episodes.

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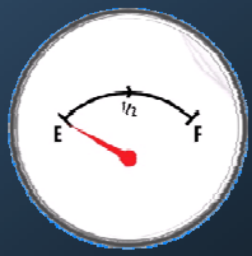
Objectives of the study

1. Analyzing the effects originated by localized fuel starvation due to flooding.

2. Analyzing the effects originated by the fuel tank depletion in a PEMFC stack.



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Stacks assembly

- PEMFC stacks integrated by 5 and 8 elements have been assembled:
  - Electrodes: E-TEK 0.25 $mg_{Pt}\cdot cm^{-2}$
  - Active area: 15.21 cm^2
  - PEM: NRE212
  - BP: graphite plates with double-path serpentine flow field

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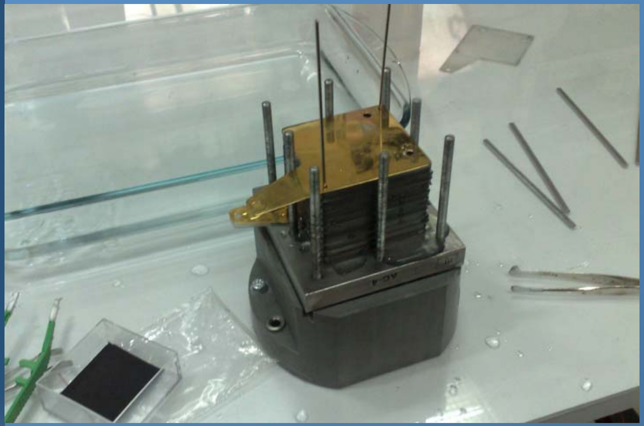
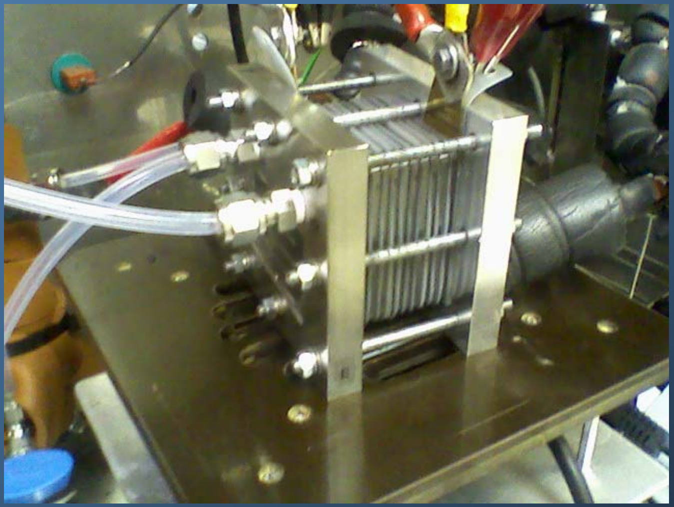
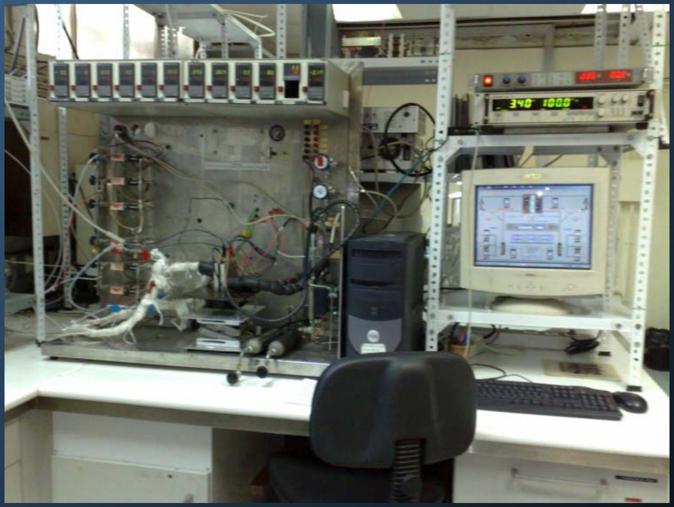
Stack assembly verification



Air tightness: < 5 $mbar \cdot min^{-1}$

- After passing air-tightening and crossover tests, they have been operated in a home made test bench under predetermined conditions





Stack operation

Forced fuel starvation conditions

- **8-elements stack**:
  - Continuous operation at low current densities (<0.2 A•cm-²) under an anode stream with low excess for H_2 stoichiometry to favor anode flooding

- **5-elements stack:**
  - Operation under load and fuel substoichiometric conditions for a long period by simulating the depletion of the H_2 feeding source

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Stack operation

Cell voltage reversal cannot occur in single cell operation because the cell reaction would be endothermic ($\Delta G>0$). An external energy supply is required for cell voltage reversal.

In a cell operating inside a stack, cell voltage reversal may occur under fuel starvation of that cell (V_i), forced by the energy supplied from side cells (V_{side}).

$$I \cdot R_L = V_i + V_{side}$$

Current will be flowing while $V_i+V_{side} > 0$, so the maximum attainable cell voltage reversal is $-V_{side}$.

Stack operation

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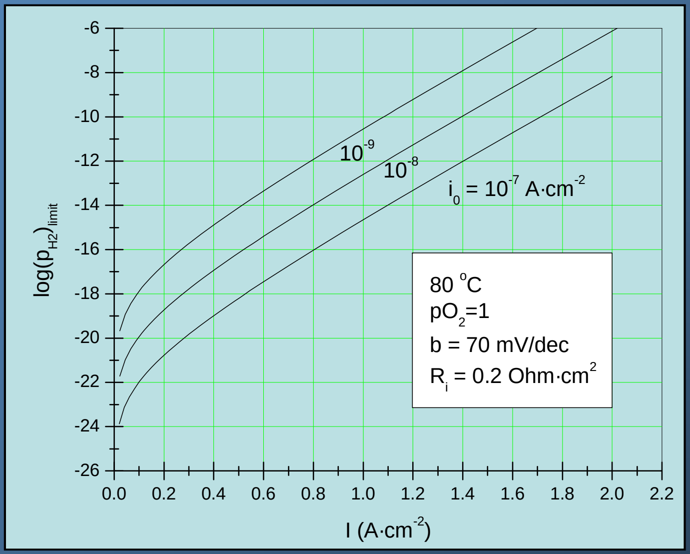
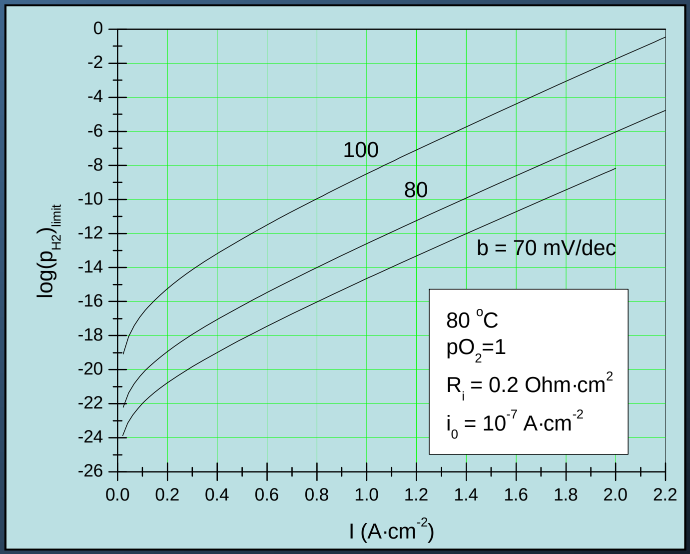
Cell voltage reversal

The limiting H_2 pressure for voltage reversal is a function of current and cell kinetics:





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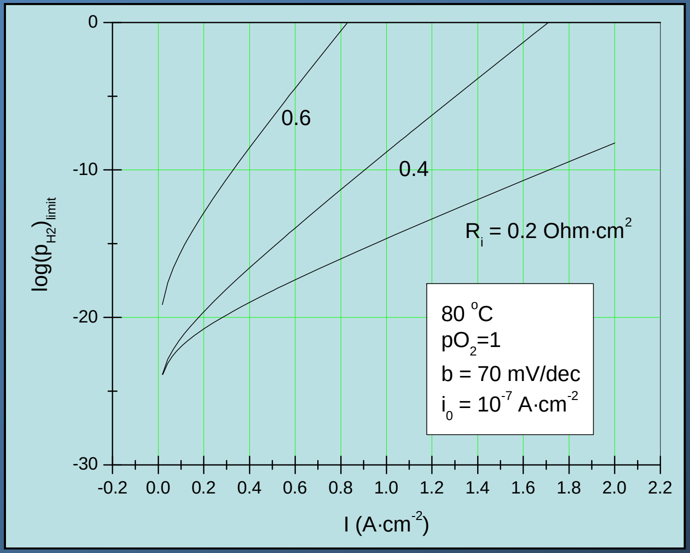
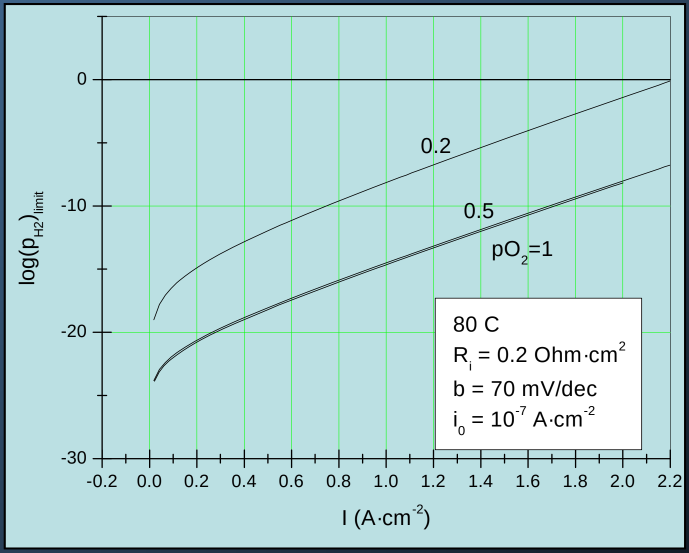
Cell voltage reversal

The limiting H_2 pressure for voltage reversal is a function of cell internal resistance and O_2 partial pressure in cathode:





Stack operation

Plausible reactions taking place on fuel starved cells are:

Water oxidation:

$H_2O = ½ O_2 + 2H^+ + 2e^-$ $E_{298K} = +1.23$ V vs RHE

$H_2O = ½ H_2O_2 + H^+ + e^-$ $E_{298K} = +1.77$ V vs RHE

Carbon degradation:

$C + 2H_2O = CO_2 + 4H^+ + 4e^-$ $E_{298K} = +0.207$ V vs RHE

$C + H_2O_2 = CO + H_2O$ $\Delta G_{298K} = -241$ kJ·mol^{-1}

PTFE/PFSA degradation

Performance analysis and characterization

In-situ:

- periodic performance evaluation by means of **polarization curves.**

Ex-situ:

- electrodes **TPO** (TG-MS analysis)
- **XPS** analysis of the electrodes surface

8-elements stack: forced anode flooding

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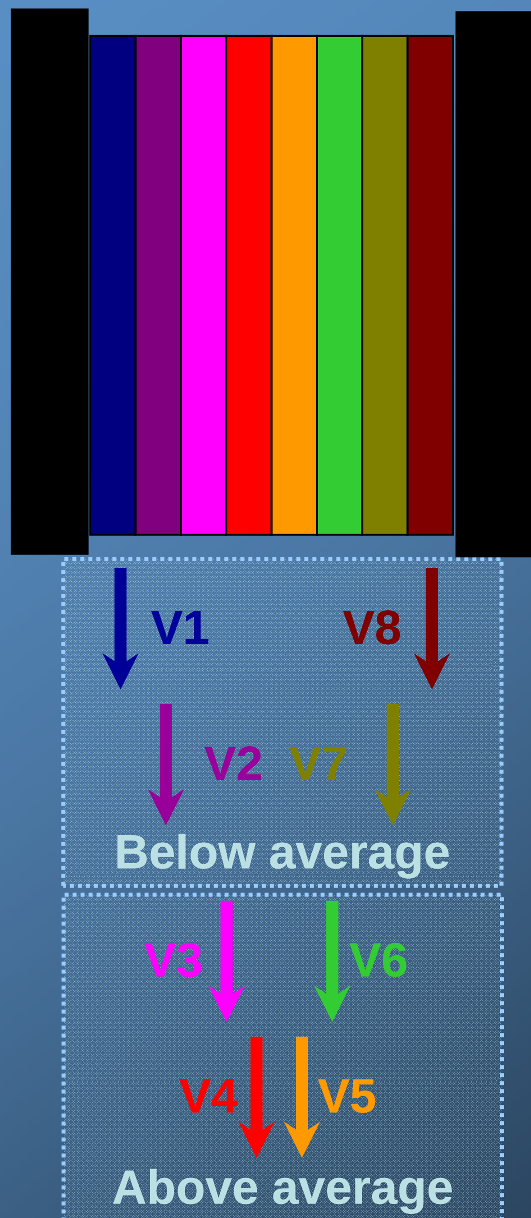
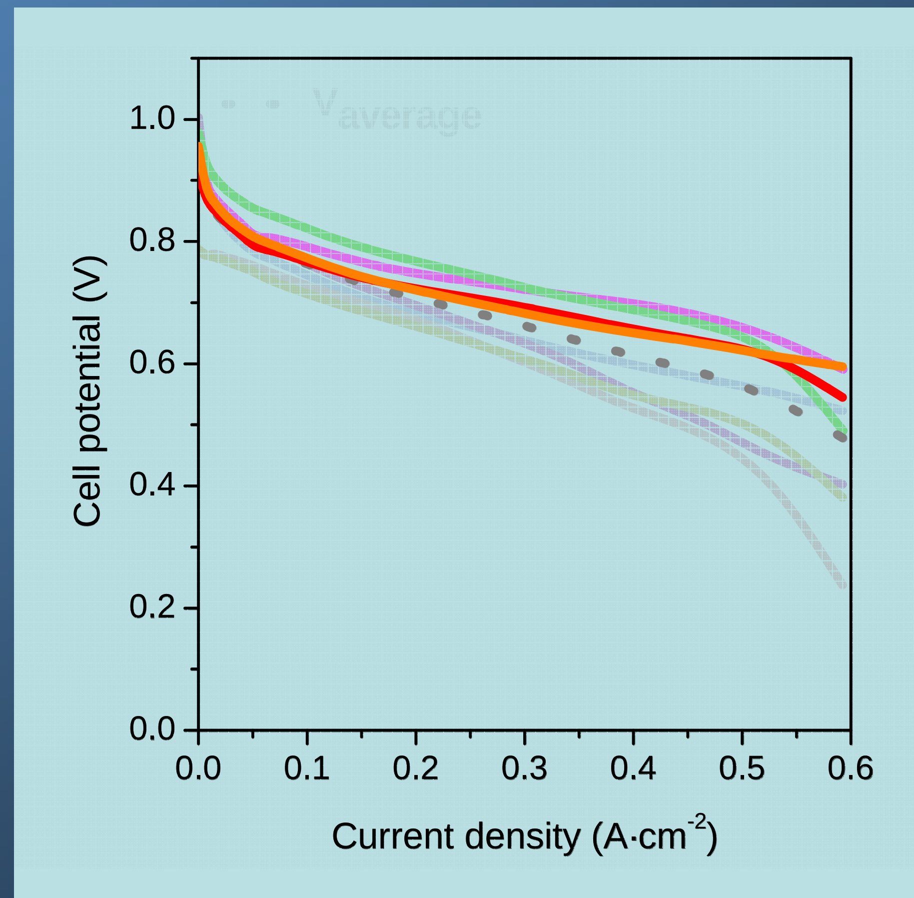
$\lambda_{H_2} / \lambda_{O_2} = 1.3 / 9.0$

$P_{an} = P_{cath} = 1\ bar_r$

$T_{stack} = 50°\ C$; $T_{an\ sat} = T_{cath\ sat} = 30°C$





8-elements stack: forced anode flooding

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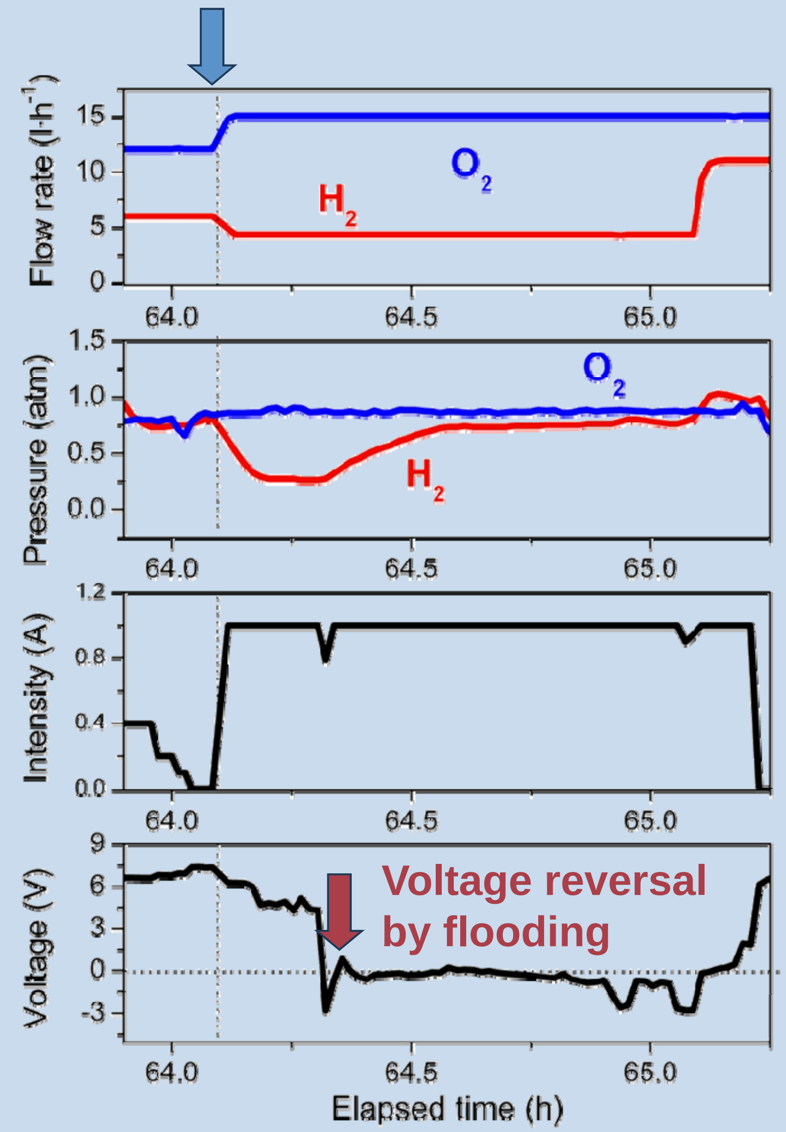
Low H_2 stoichiometry and load increase



$\lambda_{H_2} / \lambda_{O_2} = 1.3 / 9.0$

High H_2 comsumption causes p_{H_2} to decrease

Current is maintained

but voltage becomes unstable and is occasionally reversed

8-elements stack: forced anode flooding

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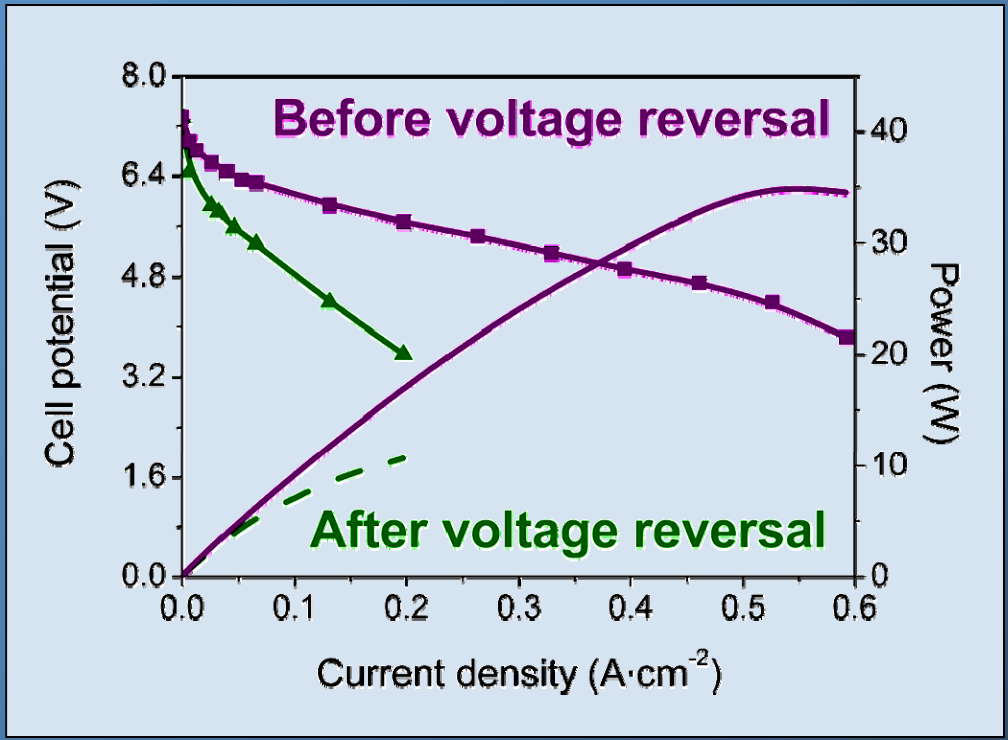


$\lambda_{H_2} / \lambda_{O_2} = 1.5 / 3.0$

T_{stack}=50ºC

This event causes an irreversible performance decay

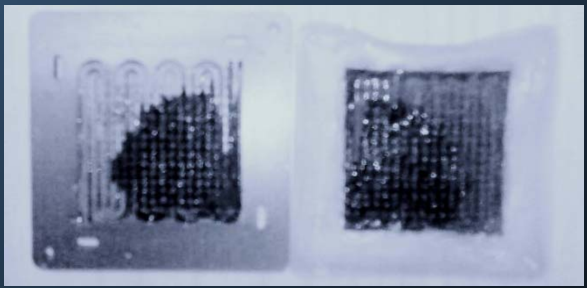
After disassembling the stack, some cells are observed to be degraded.

Some anodes (#3# and #4#) become thinner and partially adhered to BPs

AN#3#

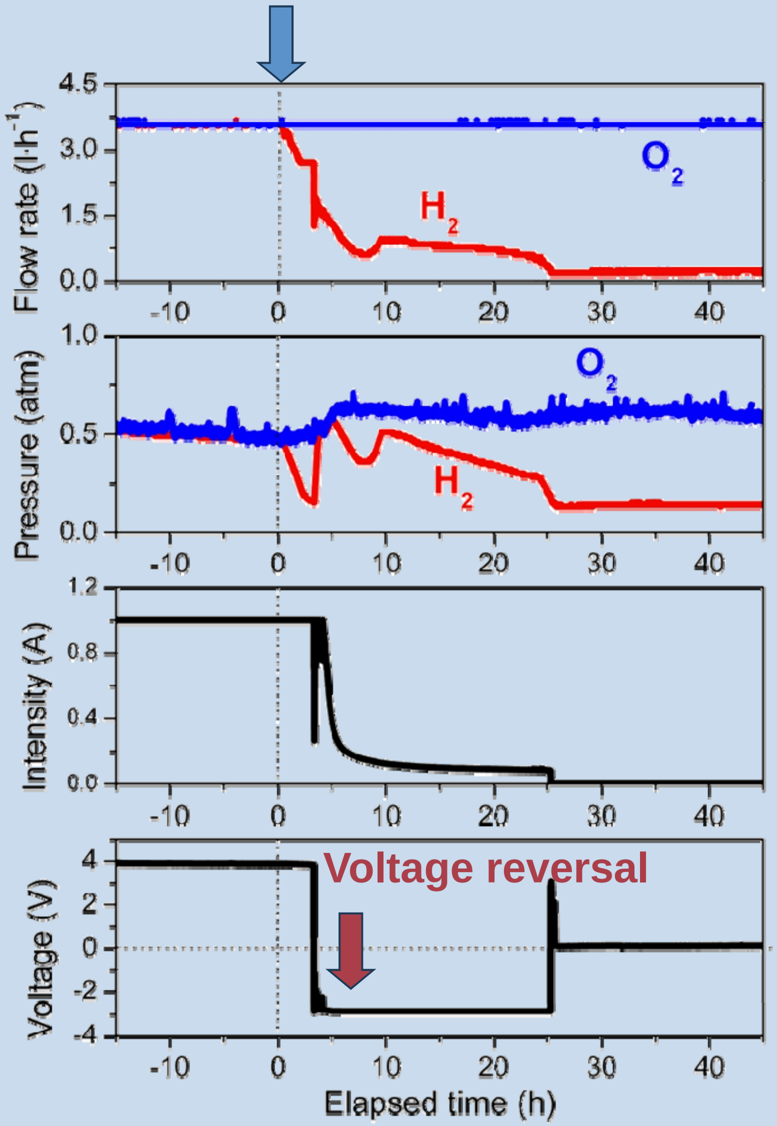
BP

MEA#3#



5-elements stack: forced fuel depletion

Operation under load and fuel substoichiometric conditions



$\lambda_{H_2} / \lambda_{O_2} = 7.2 / 14.4$

H_2 feeding is suddenly shut down at t=0.

H_2 flowrate and pressure decrease with oscillations

The load cannot be maintained at 1 A and suddenly decreases (I < 0.1 A)

After 3 min. the absence of H_2 originates a constant voltage reversal

The voltage is reset after removing the load.

5-elements stack: forced fuel depletion

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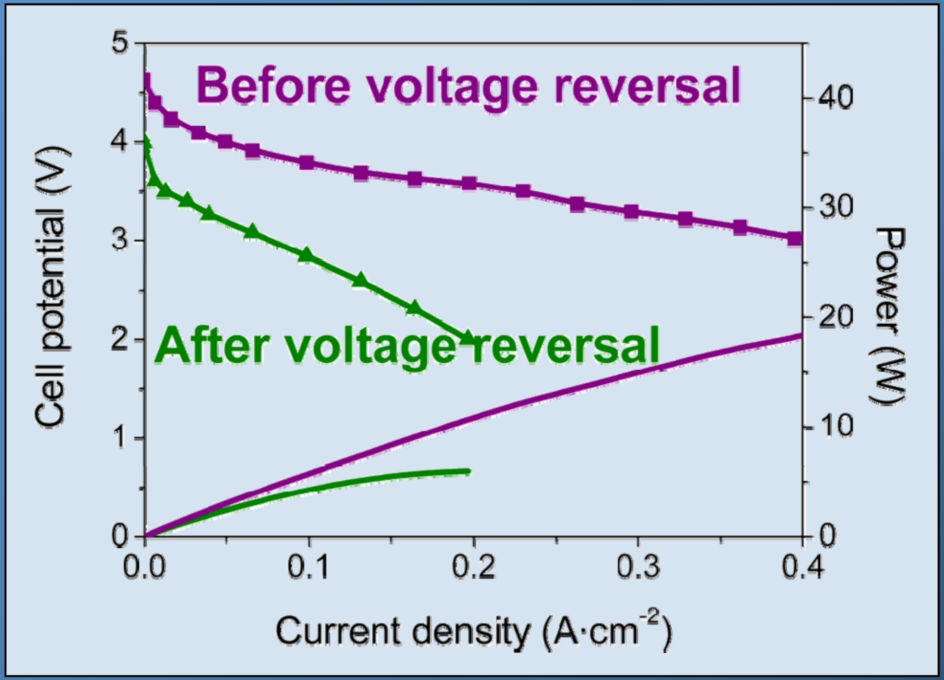
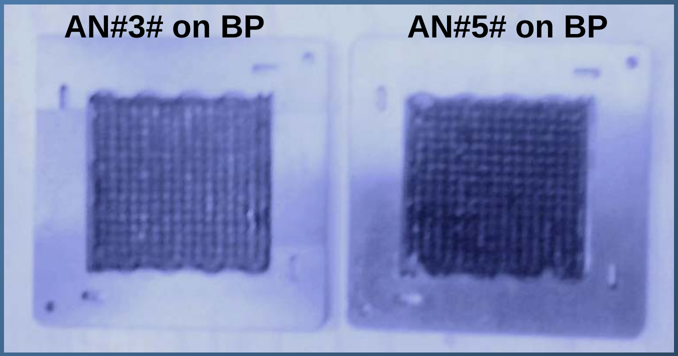


$\lambda_{H_2} / \lambda_{O_2} = 1.5 / 3.0$

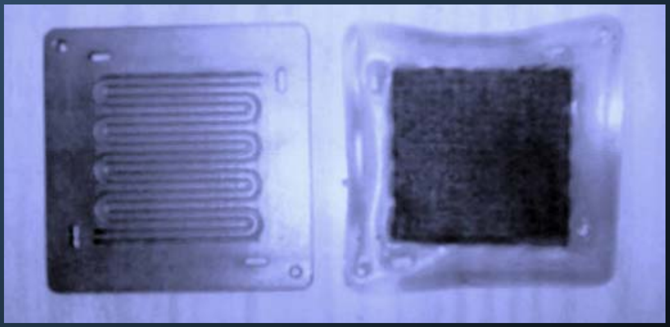
T_{stack}=50ºC

This event causes an irreversible performance decay

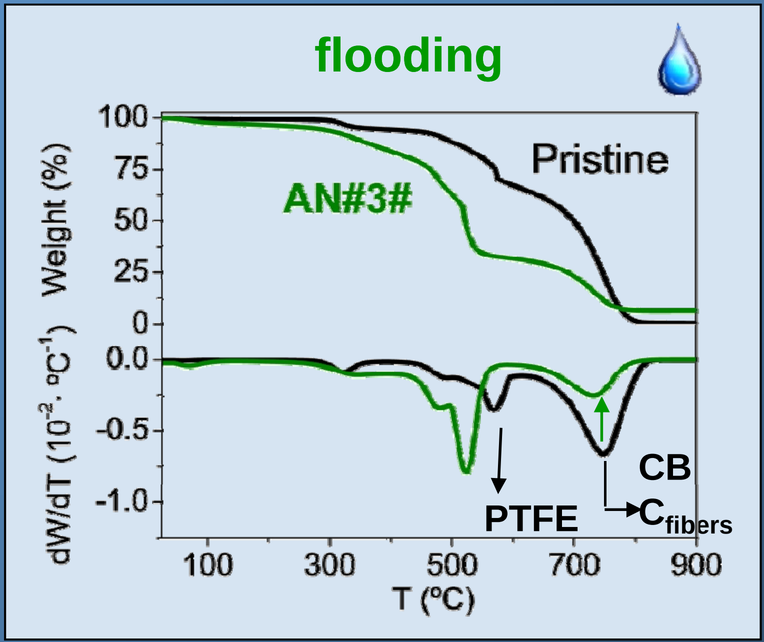


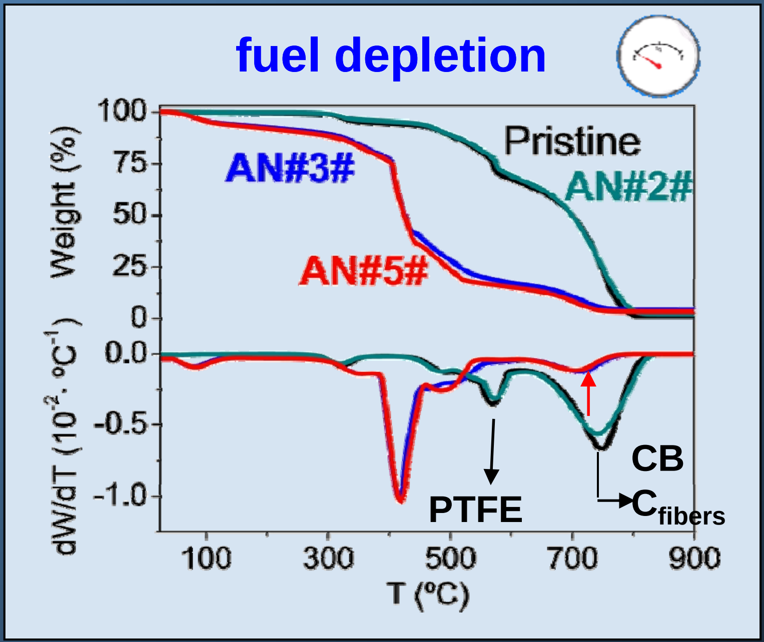
Two anodes (#3# and #5#) thinner and completely adhered to BPs

All cathodes are apparently undamaged (CAT#5#)



Characterization of damaged anodes: Temperature programmed oxidation (TG)





The TPO of the degraded electrodes, which look thinner than the pristine ones, reveal the corrosion of the carbon in the macroporous and microporous layers of the gas diffusion layer (GDM).

Characterization of damaged anodes: Temperature programmed oxidation (MS)

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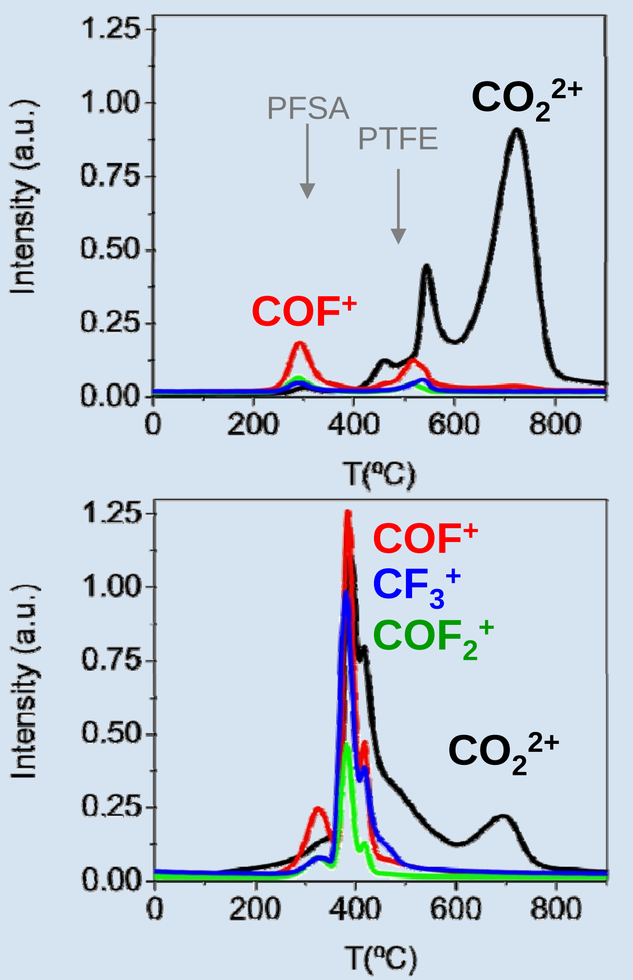
Fuel depletion

Undamaged anode (AN#2#)



Degraded anode (AN#3#)

PTFE is oxidized in pristine and apparently undamaged electrodes above 500ºC.

In damaged anodes, compounds originated from PTFE oxidation appear around 400ºC. PTFE degradation is probably the origin of this temperature decrease.

The CO_2 proportion originated from carbon black and carbon fibers is drastically reduced in damaged anodes.

CO_2^{2+}	(m/z=22)
COF^+	(m/z=47)
COF_2^+	(m/z=66)
CF_3^+	(m/z=69)

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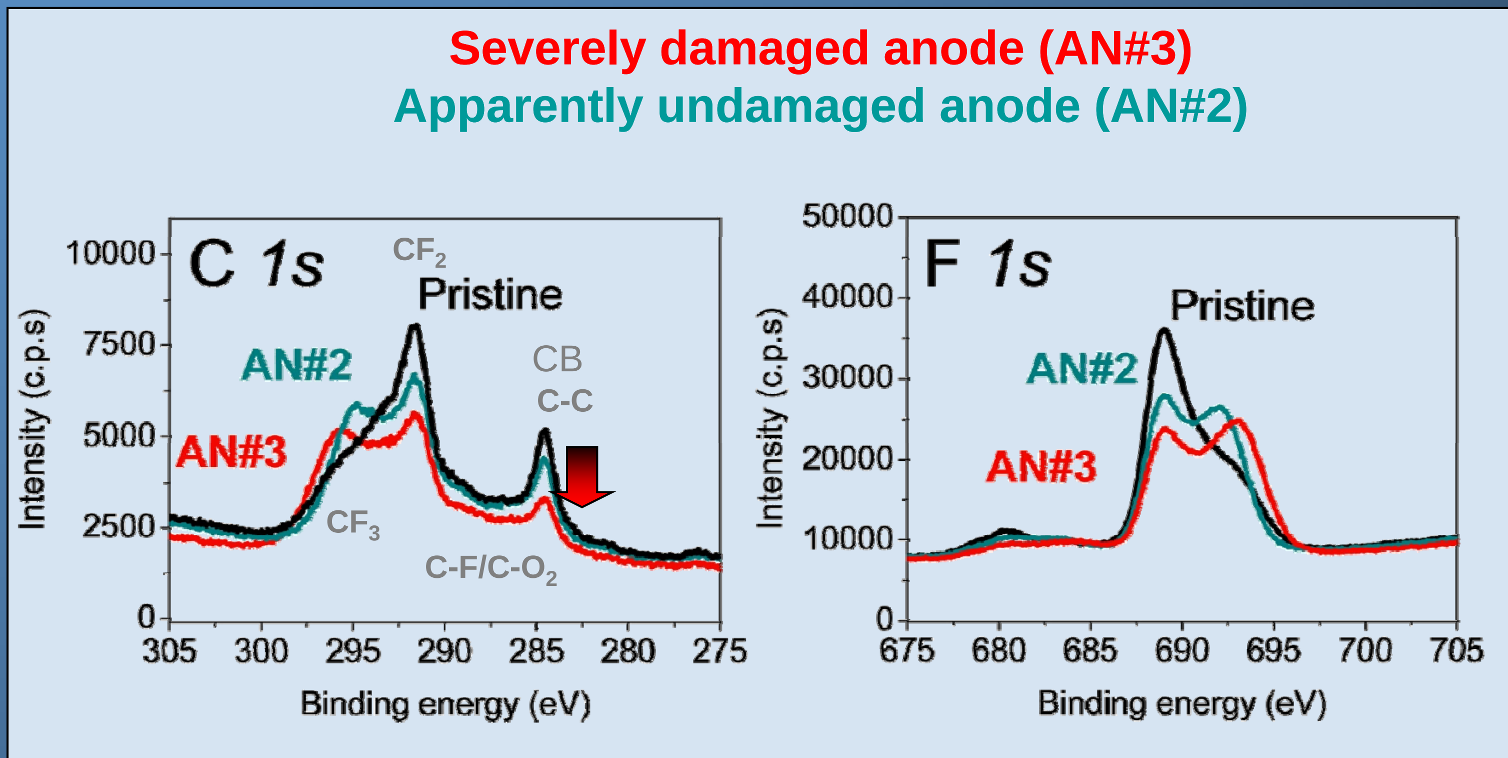
Characterization of damaged anodes: XPS analysis of the anodes surface

Fuel depletion



The C *1s* and the F *1s* signals obtained from the analysis of the anode surface reveal also the change on the catalytic layer of the damaged electrode.

Conclusions

- Fuel starvation due to electrodes flooding or fuel depletion originates similar irreversible damages in fuel cells.
- TG-MS analysis has revealed that the visible damaged cells have experienced an intense corrosion in the anode gas diffusion medium.
- This process contributes to slim the anodes and degrade the hydrophobic PTFE component.
- Losing hydrophobic properties causes corrosion to be concentrated at those initially damaged cells.

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Thank you for your attention

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