COMPOSITE MEMBRANES FOR HIGH TEMPERATURE PEM FUEL CELLS: FROM SINGLE CELLS TO STACK

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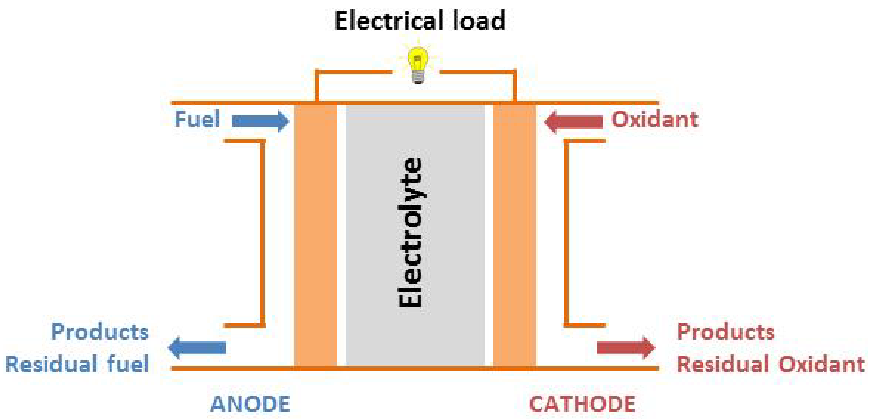
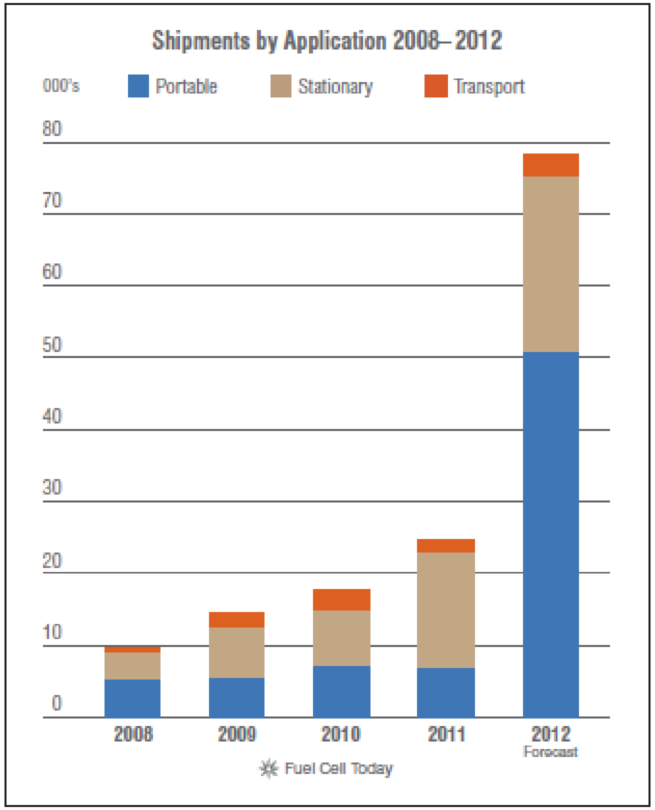
- **Introduction**
- **Objetives**
- **Results and discussion**
- **Conclusions**
- **Acknowledgements**

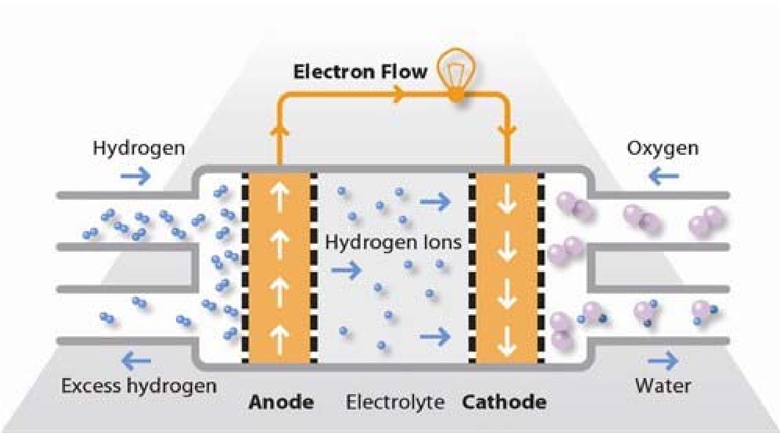


Device that converts the CHEMICAL energy of a fuel and a comburent DIRECTLY into ELECTRIC energy and HEAT

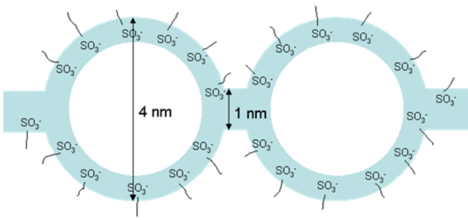


FUEL CELLS

- ✓**Polymer Electrolyte Membrane Fuel Cell (PEMFC)**
- ✓Phosphoric Acid Fuel Cell (PAFC)
- ✓Alkaline Fuel Cell (AFC)
- ✓Solid Oxide Fuel Cells (SOFC)
- ✓Molten Carbonates Fuel Cell (MCFC)



PEMFC ➡ **Most Extended Material** ➡ **NAFION**



Perfluorosulphonic Acid Membrane

Proton Conductivity
∝
Water Content

→ **Humidification**

T < 90 °C

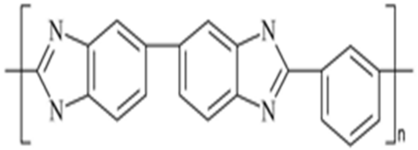
→

- ➢ **Sluggish kinetic of the cathodic reaction**
- ➢ **Low tolerance to fuel impurities**

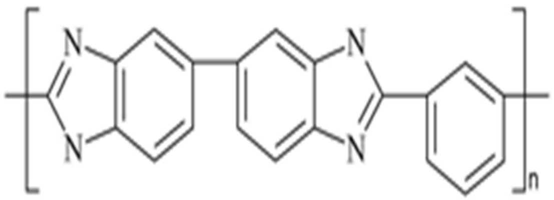
ALTERNATIVE → **INCREASE OPERATIONAL TEMPERATURE**
(T ≈ 100-200 ˚ C)

Polymeric Material
- ✓ **Thermal and Mechanical Resistance**
- ✓ **Proton Conduction**

PBI AS ELECTROLYTE MATERIAL FOR HT-PEMFC

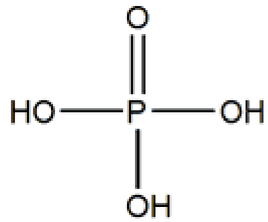


- **Excellent thermal resistance (> 550 ˚C in air)**
- **Low methanol crossover compared to Nafion®**
- **Acceptable mechanical properties**
- **No needs feed stream humidification**



PBI

+



H_3PO_4

↑ Conductivity

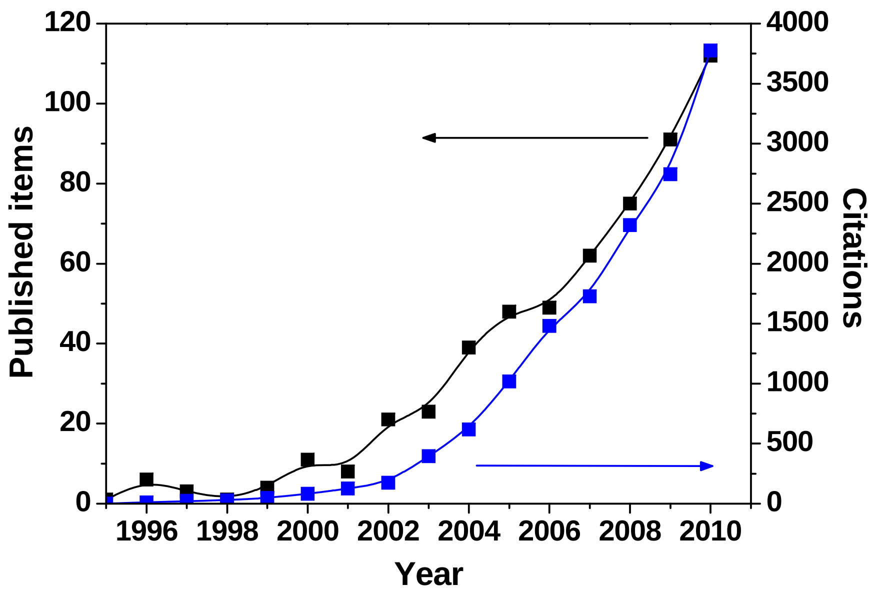
↓ Mechanical Properties

↓ FC Stability vs. Time

- ✓ High conductivity when doped with H_3PO_4 up to 200 °C

- ✓ Membrane becomes more plastic
- ✓ Acid leaching to electrodes → Electrodes deterioration
- ✓ …

Conventional PEM Fuel Cells	High temperature PEM Fuel Cells
▪ Nafion	▪ H_3PO_4-doped PBI
▪ Operating T: ~ 80 ºC	▪ Operating T: ~ 150 ºC
✓ Rapid start/stop	✓ Easier water management
✓ Higher durability	✓ Catalyst less sensitive to poisons
	✓ Waste heat recovery



Number of published item and citations per year of the topic "polybenzimidazole" and "fuel cell" classified within Web of Knowledge

Main drawback of PBI-HTPEMFC: **HIGH CELL VOLTAGE DEGRADATION RATE**

MAIN DEGRADATION MECHANISMS IDENTIFICATED

- **Leach of acid** → **MEMBRANE ELECTROLYTE ENHANCEMENT**
- **Catalyst sintering and agglomeration** → **CATALYST ENHANCEMENT**

CATALYST PROPERTIES ENHANCEMENT

MEMBRANE ELECTROLYTE PROPERTIES ENHANCEMENT

Service lifetime increase

Performance increase

Introduction

▶ Objetives

Results and discussion

Conclusions

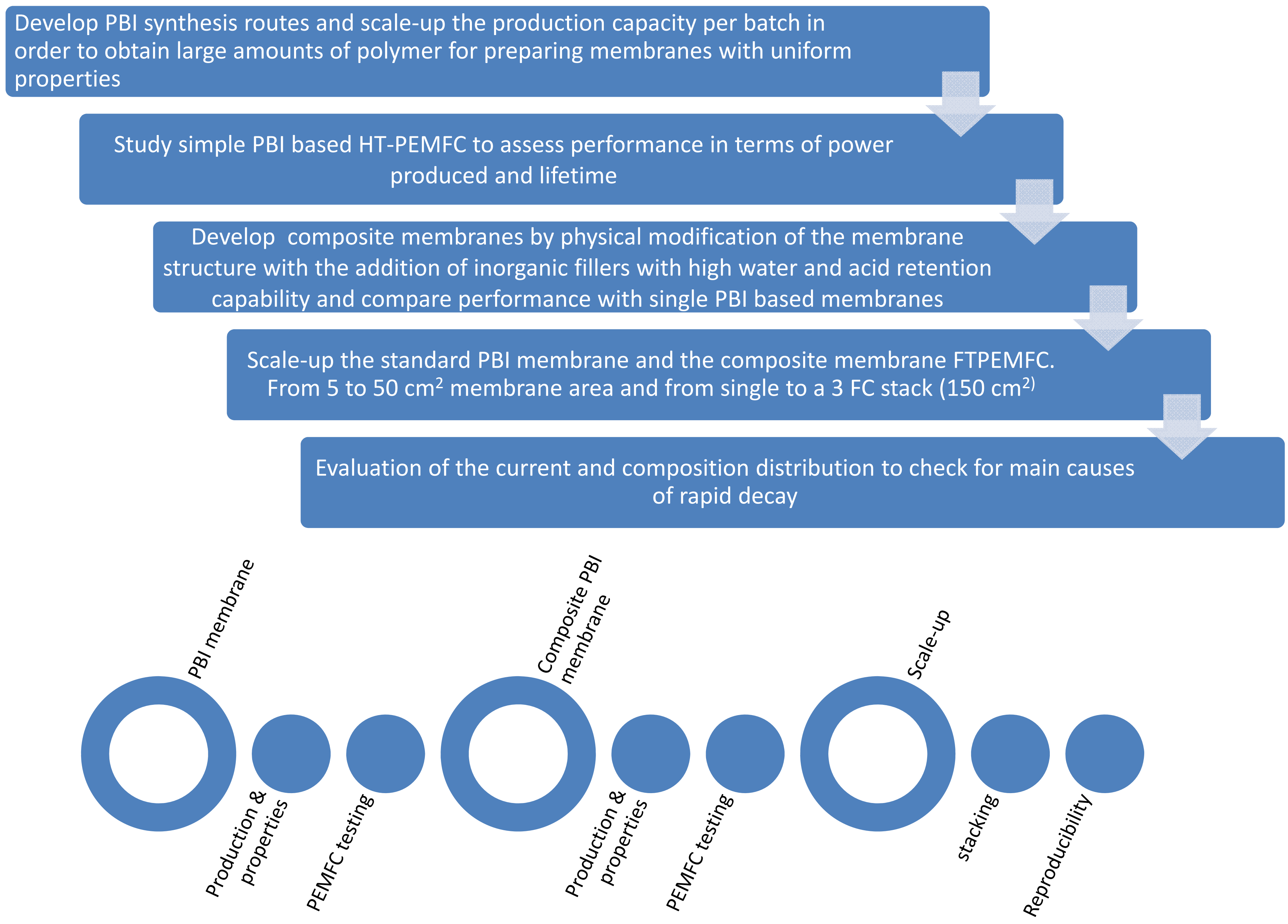
Acknowledgements

MEMBRANE ELECTROLYTE PROPERTIES ENHANCEMENT

Service lifetime increase

Performance increase

- ✓ Performance enhacement: how to obtain better membranes for HTPEMFC in order to increase service lifetime and get a better performance?
- ✓ Scale up concerns: Does size matter?
- ✓ Lack of reproducibility concerns: How to obtain better reproducibilities?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PEMFC testing
Composite PBI membrane
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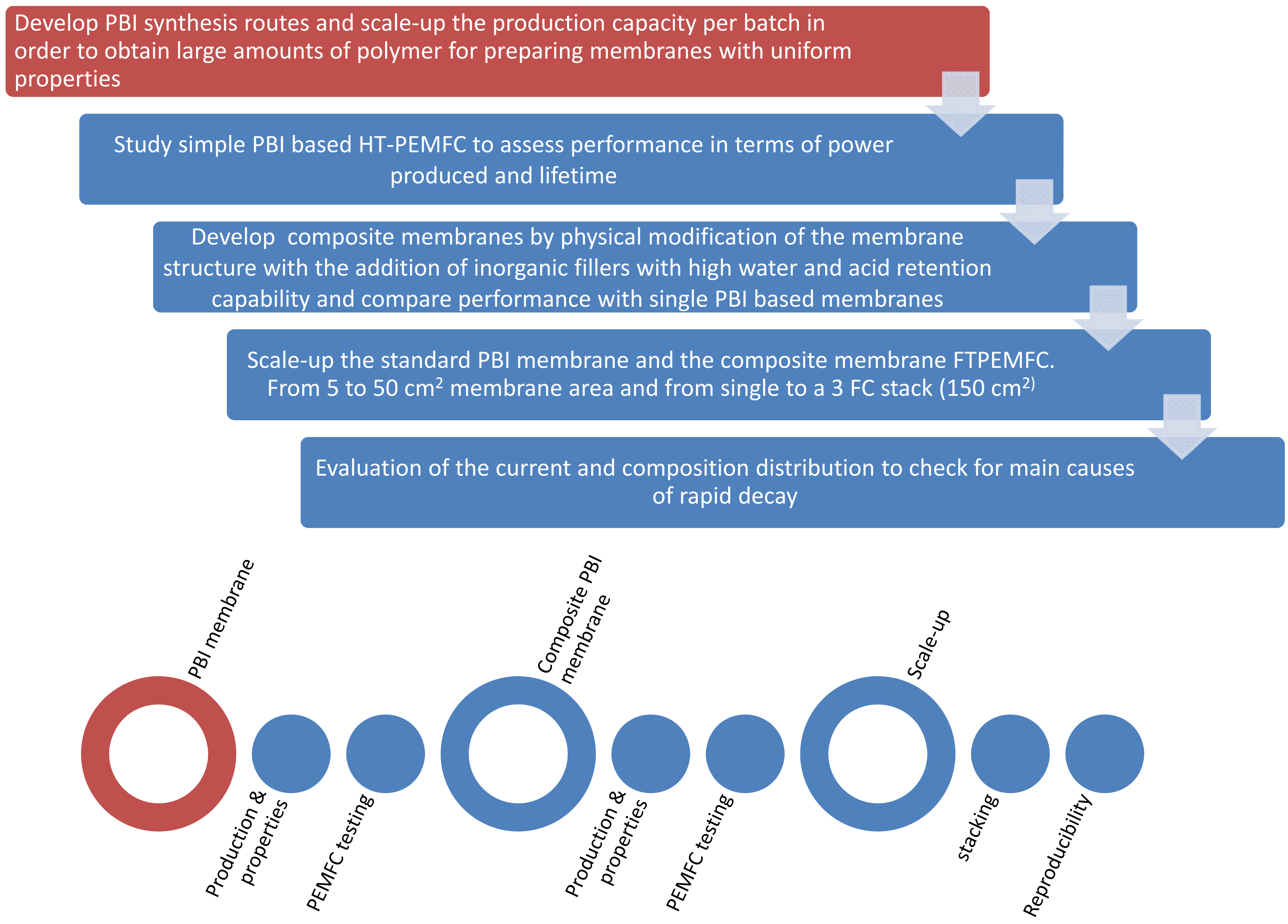
stacking
Reproducibility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Is it difficult to obtain the polymer to cast PBI membranes?

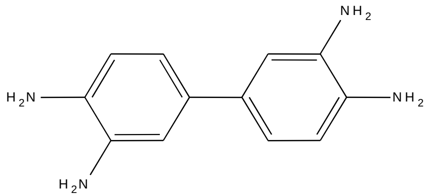
Previous remarks about PBI

Typical intrinsic viscosity of comercial PBI is around 0.8 (meaning molecular weights of around 140000 Daltons). **It is not designed for PEMFC application but for textile and chemicals production!!!!**

Very high molecular weights lead to insolubility of polymer but low molecular weights lead to bad mechanical properties. **Optimum value: 1.8-2.0 (according to our experience)**

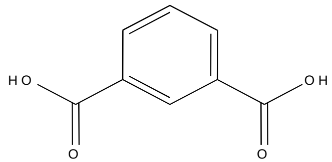
We have to develop our own synthesis route!

Procedure for manufacturing PBI



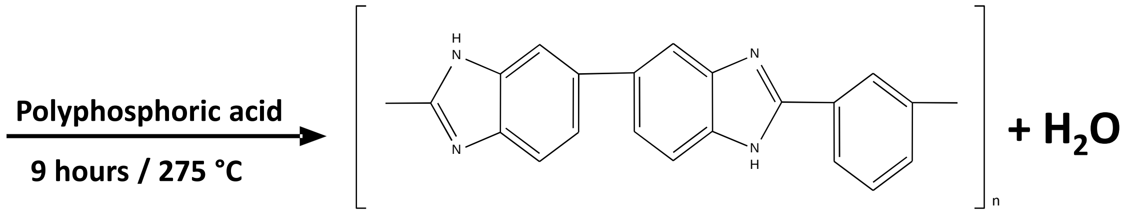
3,3'-Diaminobenzidine

+

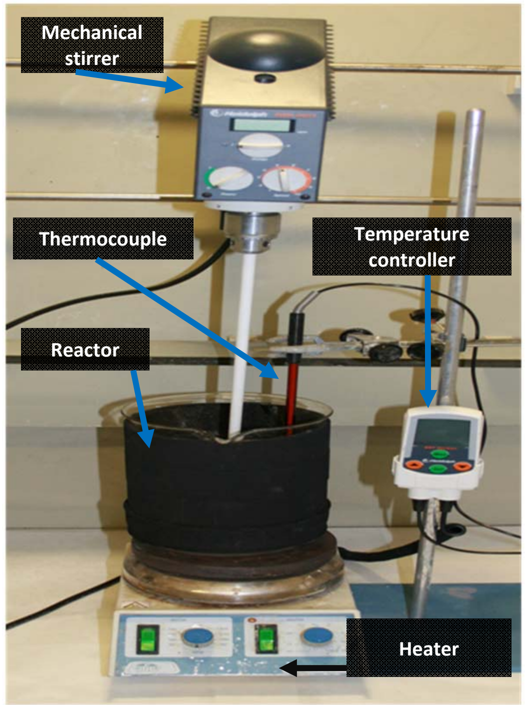


Isophthalic acid

Polycondensation of a triamine and aromatic diacid



Polybenzimidazole



USE OF SYNTHESIS METHOD FROM PREVIOUS STUDIES

Difficulties in mixing stages: HIGH VISCOSITY

≠

POLYMER QUALITY

First batches results:

- ✓ Sized for 4.5 g/batch. Only around 700 cm^2 membranes (50 μm thickness)/ batch (drawback for a later comparison of performance of HTPEMFC)
- ✓ Many experimental difficulties during the polymerization
- ✓ Not very high reproducibility
- ✓ Low molecular weight of the product

bach	Intrinsic viscosity	Molecular weight
1	1.03	197800
2	0.74	126000
3	0.71	119000
4	0.82	144900
5	0.81	142900
average	0.82	146120

Improvements for polymer resproducibility (test and errors):

- ✓ Vigorous stirring
- ✓ Strict thermal insulation
- ✓ High purity of monomers

Way to get more polymer

SCALED-UP 3-5 TIMES
ORIGINAL SINTHESIS PROCESS: further scale ups were very difficult because both heat transfer and kinetics were controlling mechanisms due to the difficulty of obtaining a uniform temperature in the polymerization reactor

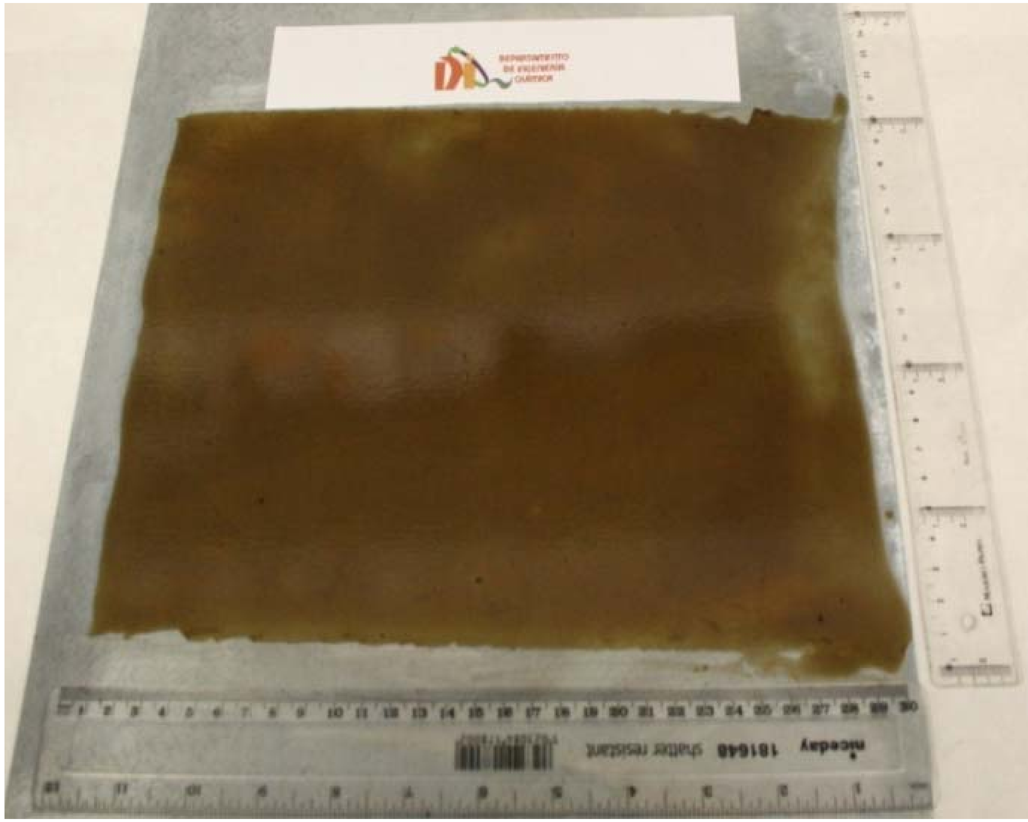
Batch number	Scale-up from the original process	Intrinsic viscosity (dl g^{-1})	PBI produced (g)
1	1:3	< 0.10	-
2	1:3	1.70	13.22
3	1:3	1.80	13.19
4	1:3	1.84	13.27
5	1:4	2.03	17.95
6	1:4	3.41	17.90
7	1:4	1.68	17.87
8	1:4	1.80	17.90
9	1:5	1.17	22.45

235 – 1013 kDa

Intermediate-high molecular weight

Molecular weight amplitude is acceptable although not excessively good (424 – 505 kDa)

Is it difficult to manufacture PBI membranes for HTPEMFC?



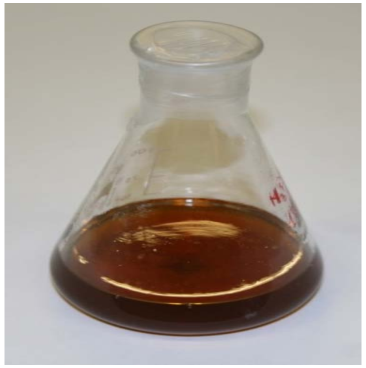
PBI membrane

Membrane Casting

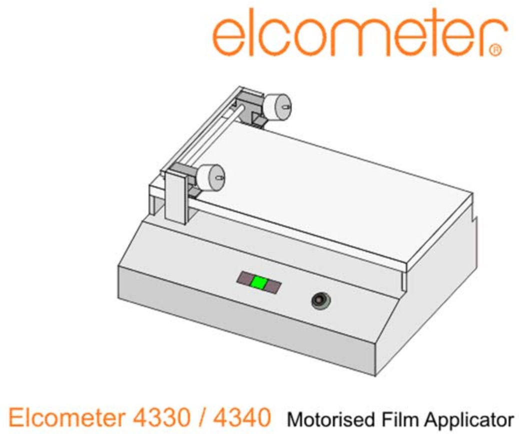
PBI powder

Dissolution in N,N'-dimethylacetamide at 5% wt.

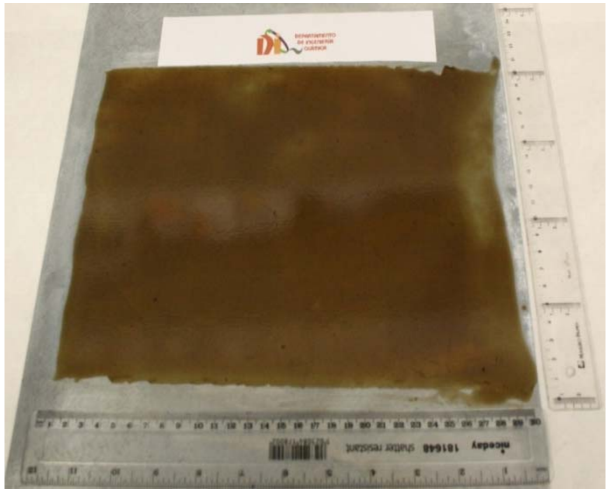
Vigorous stirring / 80-100 °C



PBI solution



Temperature ramp to evaporate the solvent and immersion in water → peeling-off the plate & washing



PBI membrane

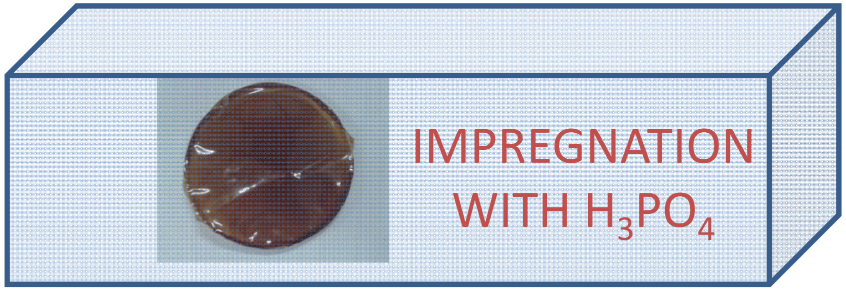
Key facts:

- Not difficult to obtain membranes up to 30 x20 cm^2 (DIN A4 size)

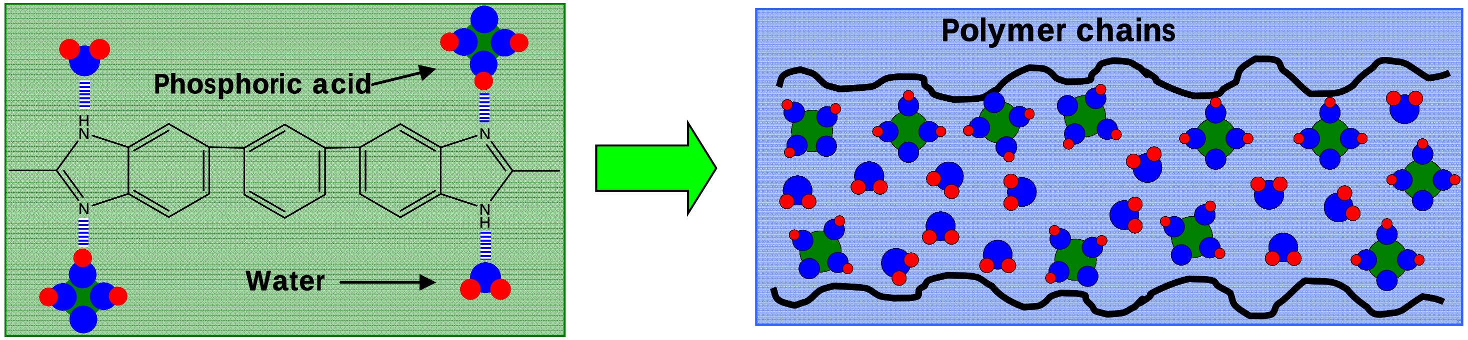
- A typical size for a membrane in a 5kW PEMFC stack could be around 200 cm^2 because larger areas lacks of:

- ✓ Robustnest (affecting lifetime)
- ✓ uniform properties (affecting current distribution and, hence, efficiency)

Membrane impregnation



Phosphoric acid bath



❖ Chemical interaction between the polymer and the acid → 2 molecules per PBI repeating unit

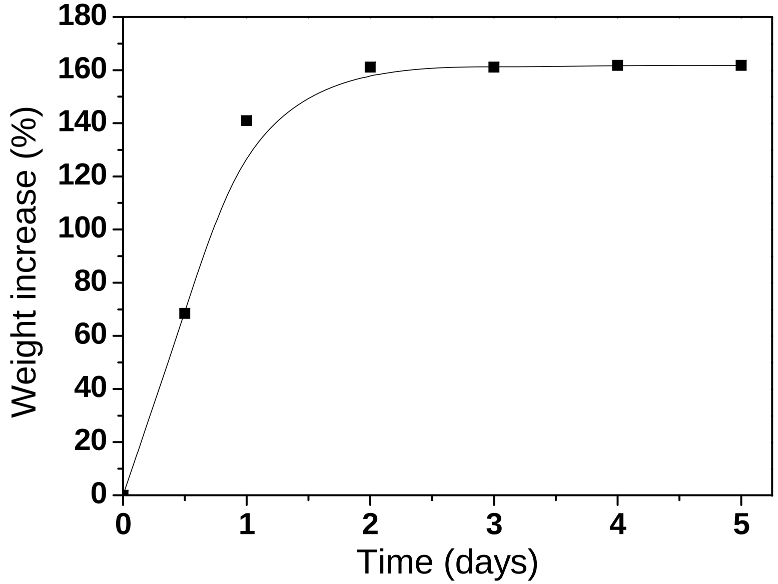
❖ More acid is placed between the polymer chains → swelling of the membrane

H_3PO_4 bath solution (wt. %)	H_3PO_4 uptake (mol · repeat unit PBI^{-1})	H_2O uptake (mol · repeat unit PBI^{-1})
75	5.3	5.9
85	11.3	11.6

High acid bath concentration

The higher the acid bath concentration, the higher the amount of absorbed acid per repeat unit of polymer

What about inmersion time?



Time-course of the PBI membrane (thickness: 60 μm) weight increases over time after 85 wt. % H_3PO_4 solution bath immersion

Stationary value achieved in 2 days of immersion

Ensure the entire H_3PO_4 absorption

Membranes immersion ≥ 5 days in the acid bath

ACID LEACH

Phosphoric acid remained in PBI membranes after leaching and previously doped into different H_3PO_4 bath concentration solutions

Sample	H_3PO_4 bath solution (wt. %)	Remaining Acid (mol · repeat unit PBI^{-1})
PBI·5.3 mol H_3PO_4	75	0.62
PBI·11.3 mol H_3PO_4	85	0.89

≈ 90 %

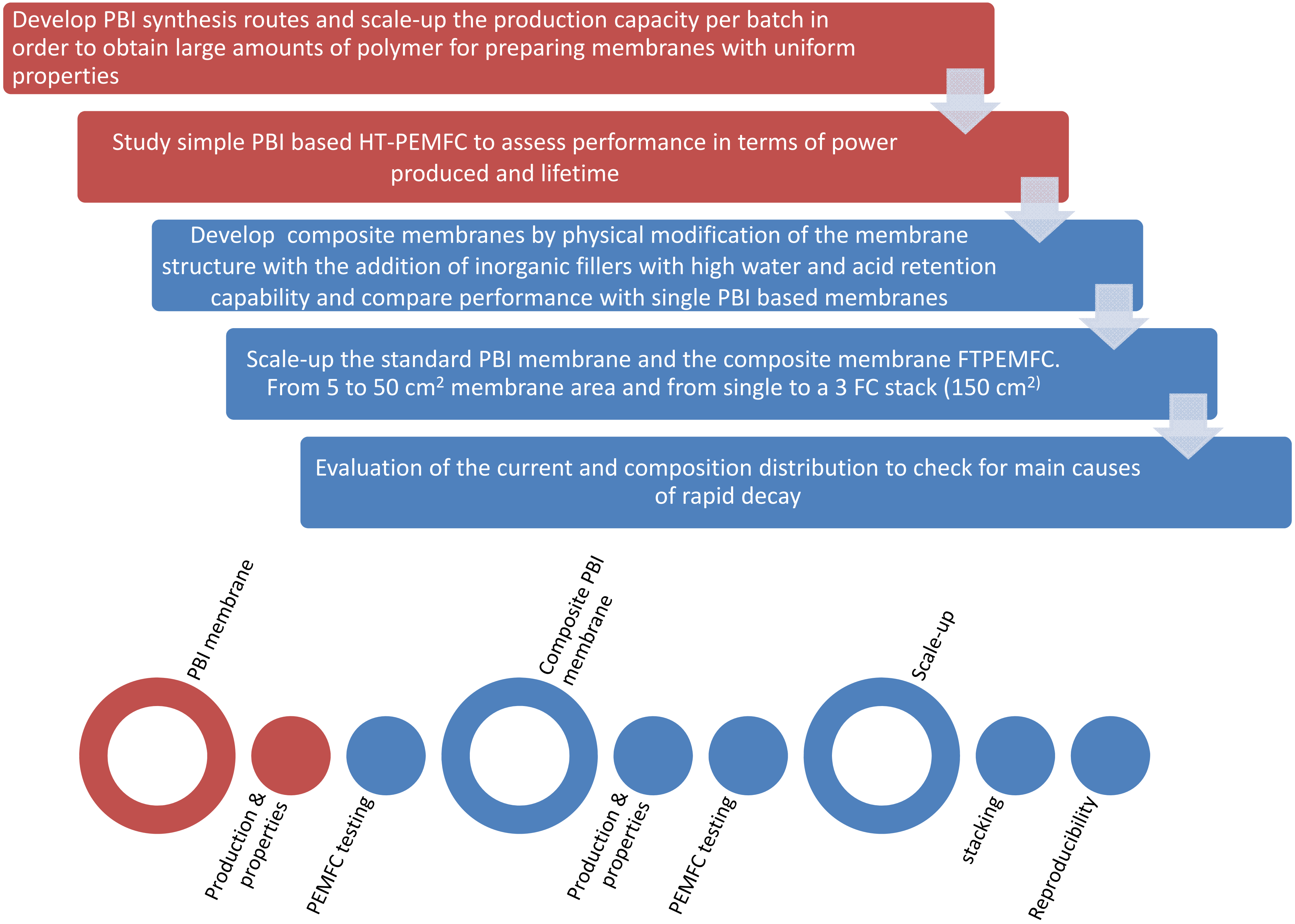
Membranes lost most of the acid after being washed with hot water → The "free" H_3PO_4 absorbed by the membrane is softly linked to the polymer backbone

MECHANICAL STRENGHT

Mechanical properties of the PBI membranes at different doping levels. T = 125 ºC

Sample	Stress at break (MPa)	Elongation (%)
PBI	446.0	40.1
PBI·5.3 mol H_3PO_4	34.9	275.2
PBI·11.3 mol H_3PO_4	22.2	289.8

Membranes become softer and plastic when are doped



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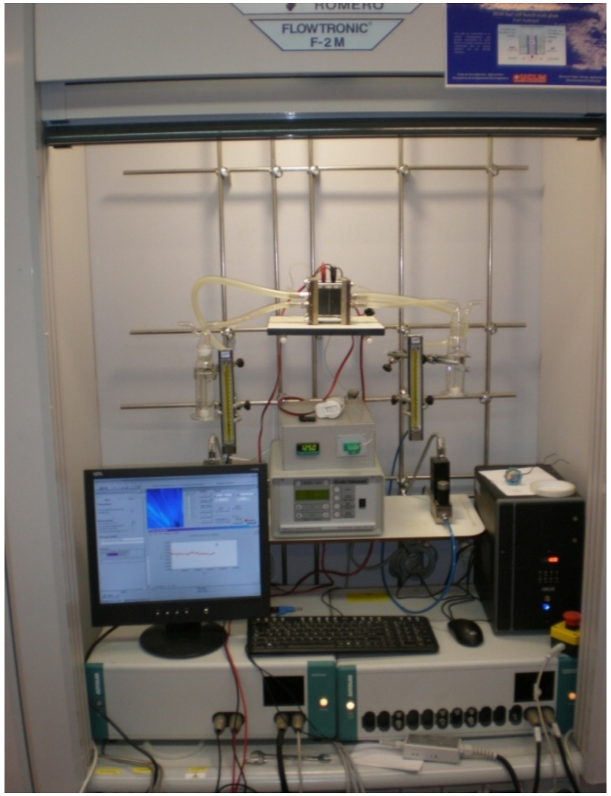
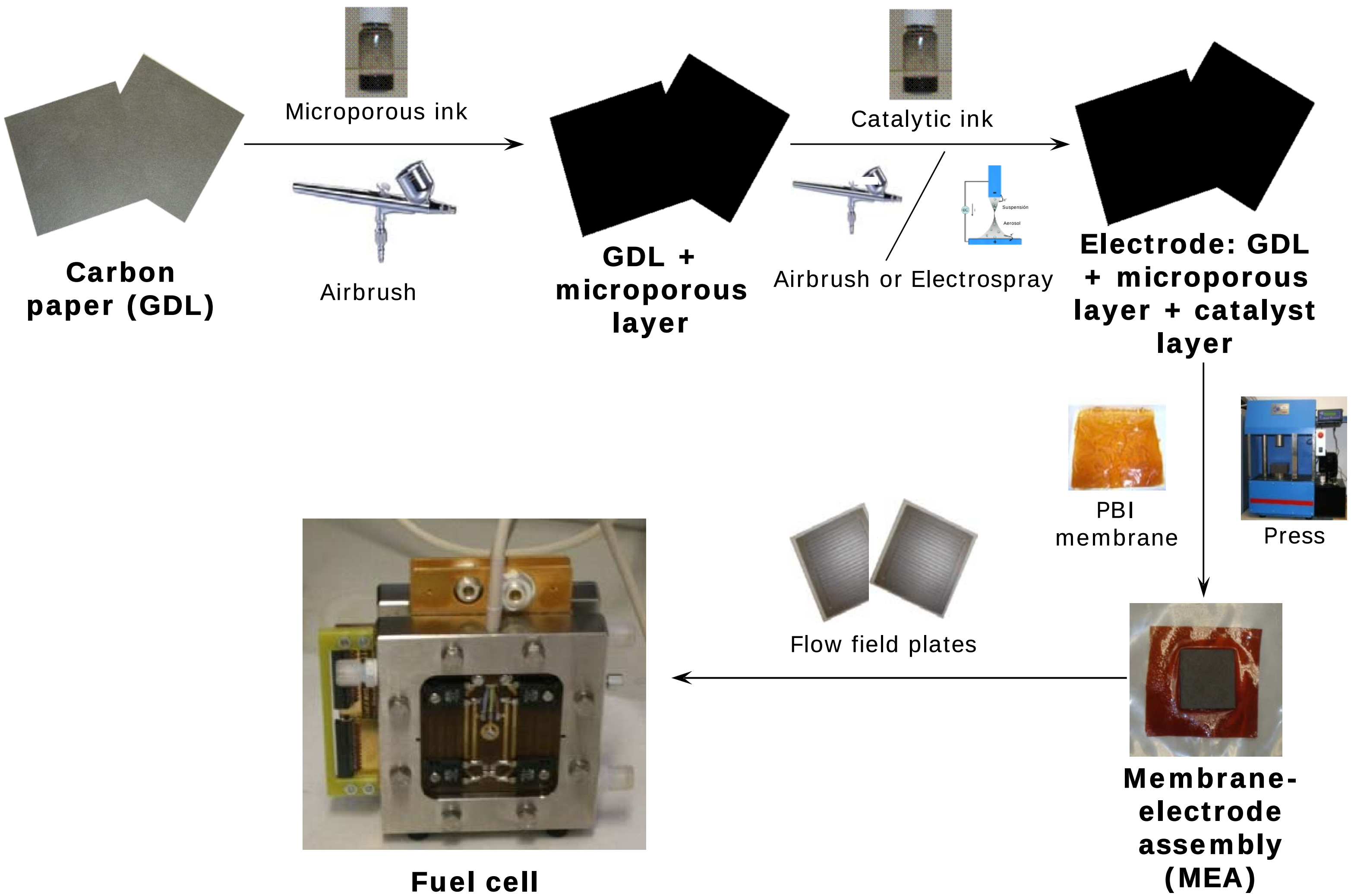
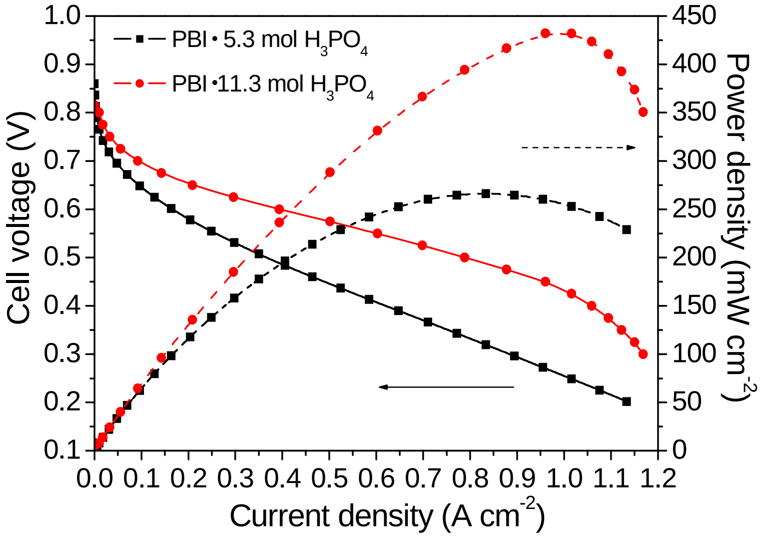
How do HTPEMFCs equipped with PBI membranes perform?



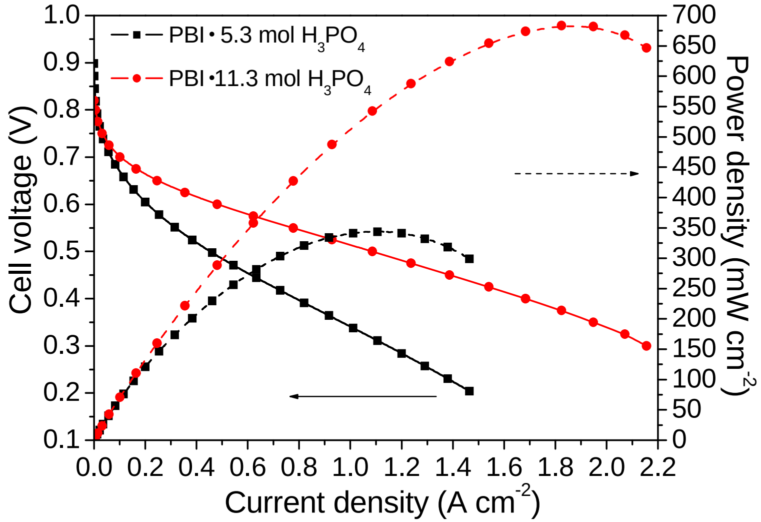
Preparation of MEAs



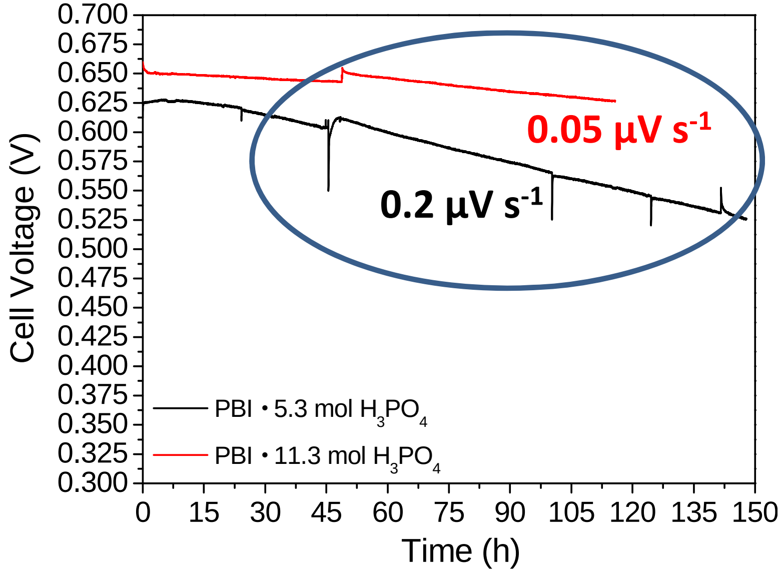
Fuel cell tests with PBI membranes



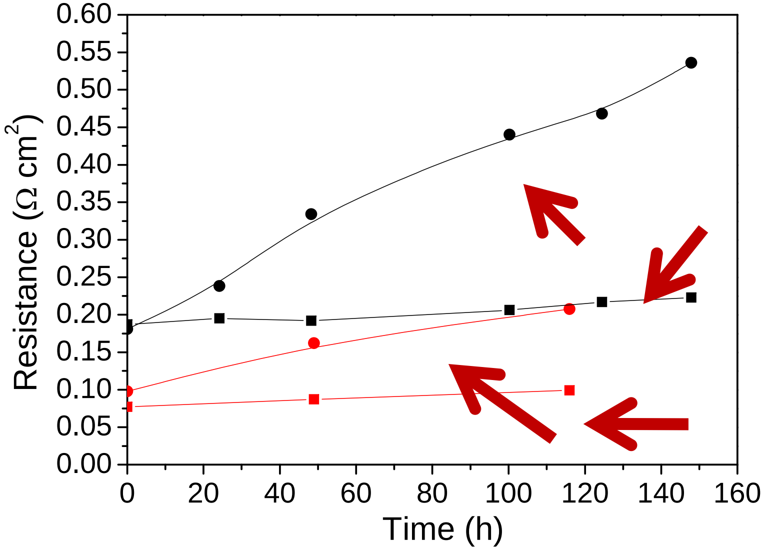
Polarization curves of PBI based fuel cells. T= 125 °C



Polarization curves of PBI based fuel cells. T= 175 °C



Fuel cell life test with PBI membranes impregnated into different acid bath concentrations studied in this Chapter. Voltage degradation versus time at 0.2 A cm^{-2} and T = 175 °C.



Ohmic (R_{Ω}, Squares) and charge transfer polarization ($R_{pol, ct}$, Circles) resistances variation for the different fuel cell in the life test. Black: PBI·5.3 mol H_3PO_4; Red: PBI·11.3 mol H_3PO_4

Irreversible voltage degradation

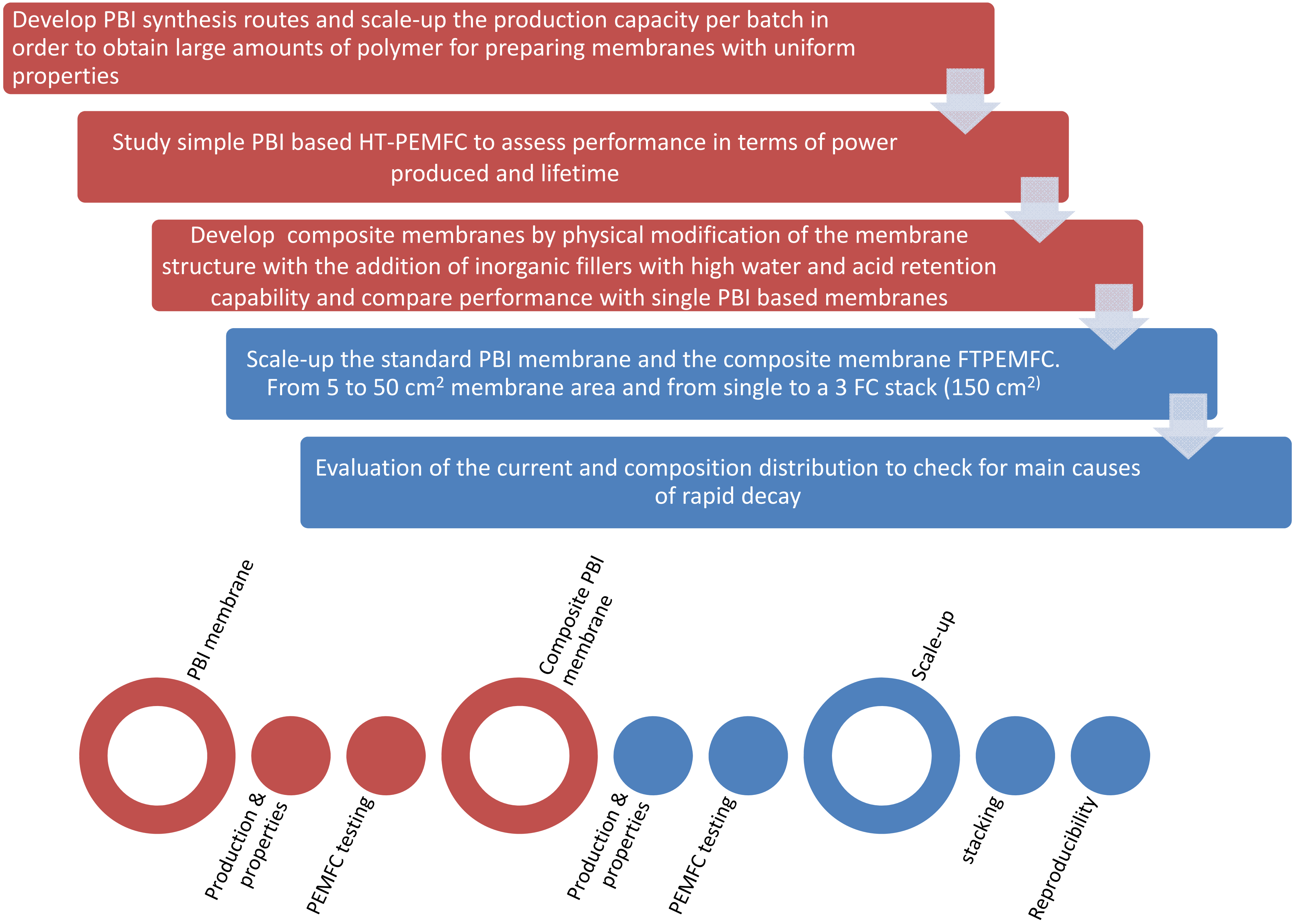
↑PBI·5.3 mol H_3PO_4 → PBI·11.3 mol H_3PO_4

↑ Acid loss →

Sample	R_{Ω} (mΩ cm^2 h^{-1})	$R_{pol, ct}$ (mΩ cm^2 h^{-1})
PBI·5.3 mol H_3PO_4	0.23 (r^2 = 0.941)	2.34 (r^2 = 0.984)
PBI·11.3 mol H_3PO_4	0.19 (r^2 = 0.999)	0.93 (r^2 = 0.964)

Low acid content → Acid / Electrolyte loss is more noticeable along time

└→ **Worse kinetic for the reactions**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Can we do something to increase service life and/or improve performance?

Inorganic fillers

- TiO_2 →
  - Amphoteric and hydrophilic character:
  - ✓ increase the acid doping level of the membrane
  - ✓ membrane acid-retention capabilitity
  - ✓ minimizing the acid loss during operation in the fuel cell
- $TiOSO_4$ →
  - Synergistic effect:
  - ✓ filler is a TiO_2 precursor
  - ✓ contains sulfates

Procedure to manufacture composite PBI membranes

PBI solution

+

TiO_2 / $TiOSO_4$

2, 4, 8 ó 16 % p/p

TiO_2 (anatase, d_m = 1,14 µm)

$TiOSO_4$ (≥ 29% Ti as TiO_2, d_m = 2,30 µm)

Ultrasonicated
2 h

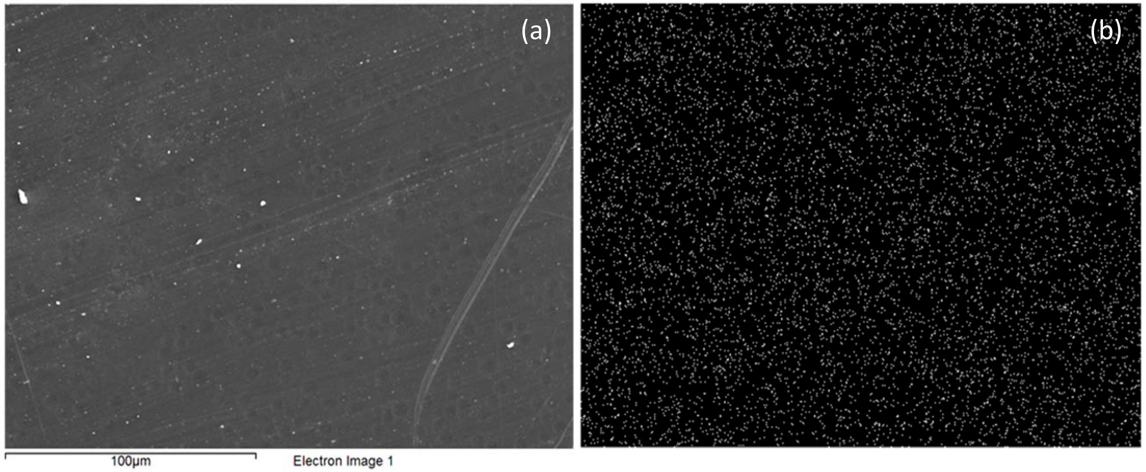
Mecanized
T = 80 °C
t = 8 h

Washing with water

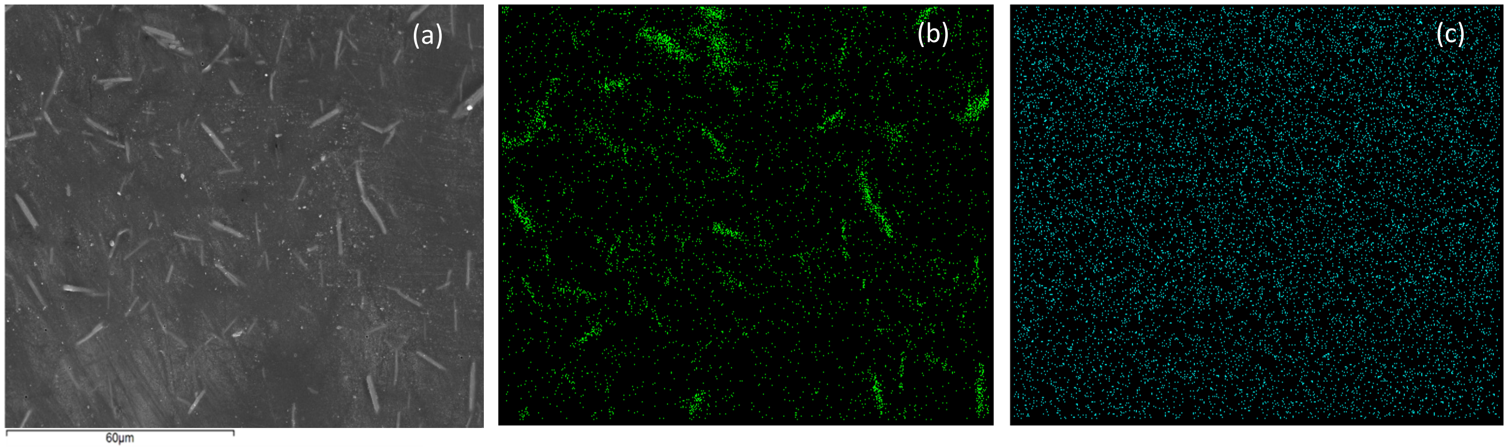
(a) (b) (c)

Pics of membranes obtained after mechanical process. (a) PBI Standart membrane; (b) PBI membrane with 16 % p/p TiO_2; (c) Pbi membrane with 16 % p/p $TiOSO_4$

SEM Y EDS



SEM micrographs of 2 % p/p en TiO_2 compose membrane surface (a) and distribution of titanium (b) in the membrane, obtained by mapping with EDS



SEM micrographs of 2 % p/p $TiOSO_4$ composite membrane surface (a) and distribution of titanium(b) and sulfur (c) in the membrane, obtaine by mapping with EDS

Composite PBI Membrane impregnation

Impregation

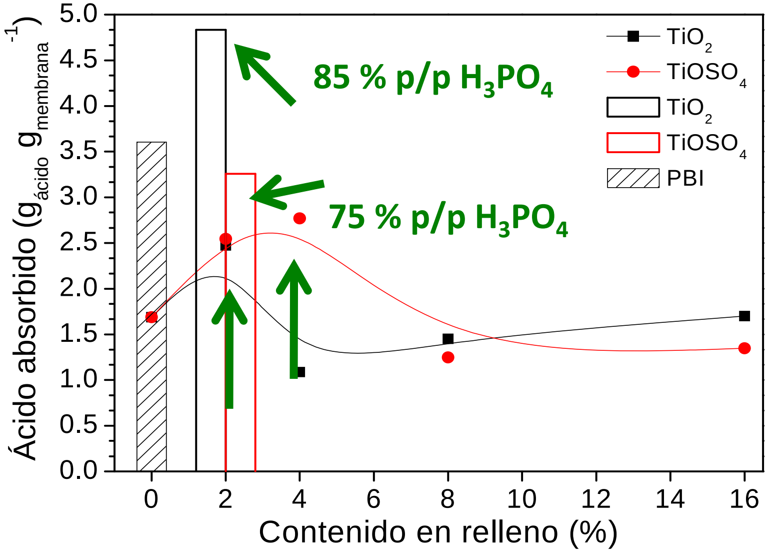
75 % p/p H_3PO_4

85 % p/p H_3PO_4

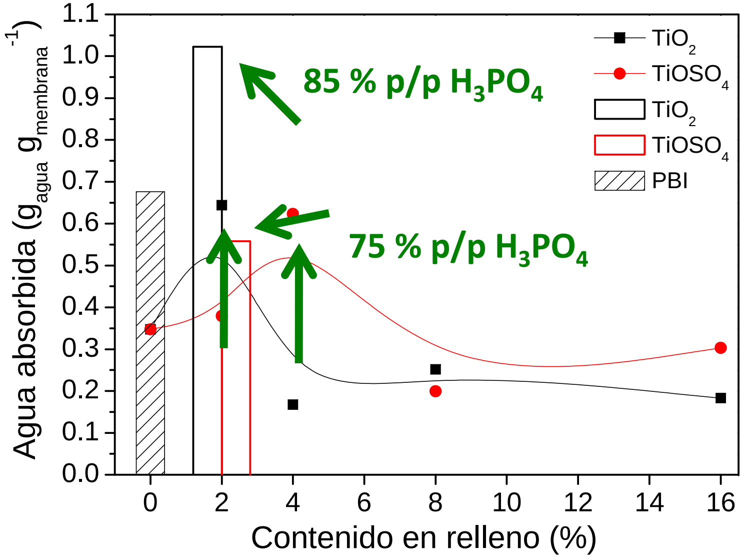
2, 4, 8 or 16 % p/p TiO_2
2, 4, 8 or 16 % p/p $TiOSO_4$

Best results →

2 % p/p TiO_2
2 % p/p $TiOSO_4$



Acid absorbed by different composite and standart PBI.
Lines: membranes doped into 75 % p/p H_3PO_4 solution.
Columns: membranes doped into 85 % p/p H_3PO_4 solution.



Water absorbed by different composite and standart PBI.
Lines: membranes doped into 75 % p/p H_3PO_4 solution.
Columns: membranes doped into 85 % p/p H_3PO_4 solution.

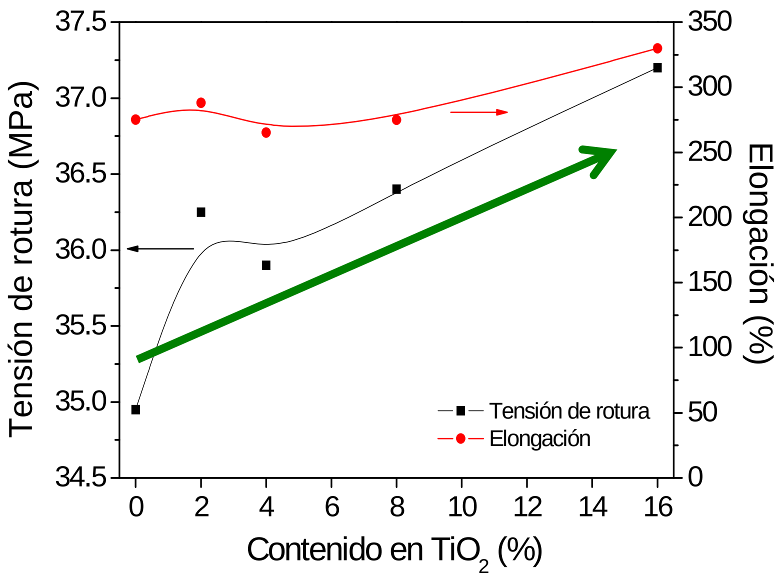
✓ 2 % p/p TiO_2 or 4 % p/p de $TiOSO_4$ into the polymer matrix were enought to retain higher amounts of acid and water than PBI.

✓↑ Filler concentration → Agglomerate formation →
→ ↓ active surface for acid and water absortion by the fillers

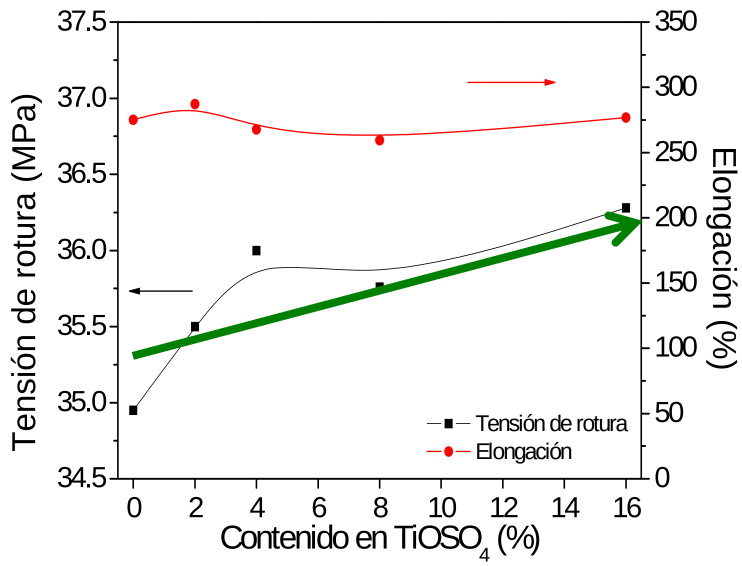
✓TiO_2 membrane→ ↑ Acid concentration → ↑ Doping level

✓$TiOSO_4$ membrane → ↑ Acid concentration → ≈ Doping level

Mechanical stress



Breaking stress and y elongation for composite PBI membranes with TiO_2 and standart. Impregnation bath: 75 % p/p H_3PO_4. T = 125 °C

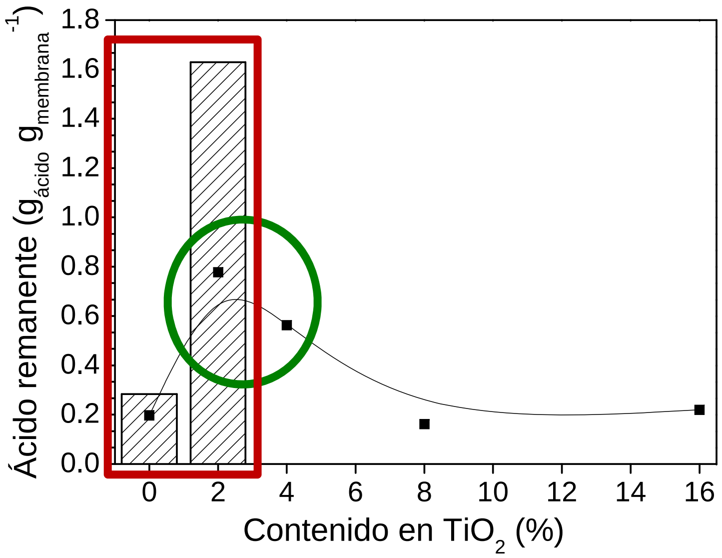


Breaking stress and y elongation for composite PBI membranes with $TiOSO_4$ and standart. Impregnation bath: 75 % p/p H_3PO_4. T = 125 °C

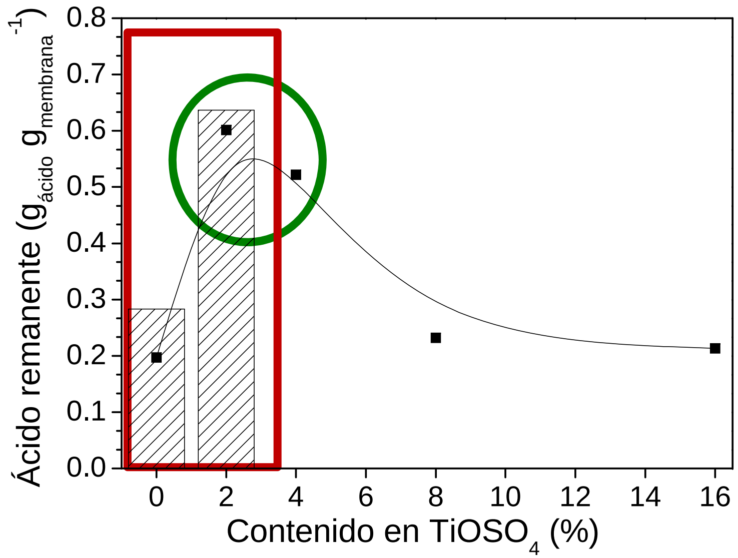
↑ x % TiO_2 / $TiOSO_4$ → **↑ Breaking stress**
↑ Elongation

✓↓ Weakness for composite membranes due to the inorganic reinforcing presence.

ACID LEACH



Phosphoric acid retained by TiO_2 composite membranes after lixiviation process. Lines: membranes doped with 75 % p/p H_3PO_4 solution. Columns: membranes doped with 85 % p/p H_3PO_4 solution.



Phosphoric acid retained by TiOSO composite membranes after lixiviation process. Lines: membranes doped with 75 % p/p H_3PO_4 solution. Columns: membranes doped with 85 % p/p H_3PO_4 solution.

2 y 4 % TiO_2 / $TiOSO_4$

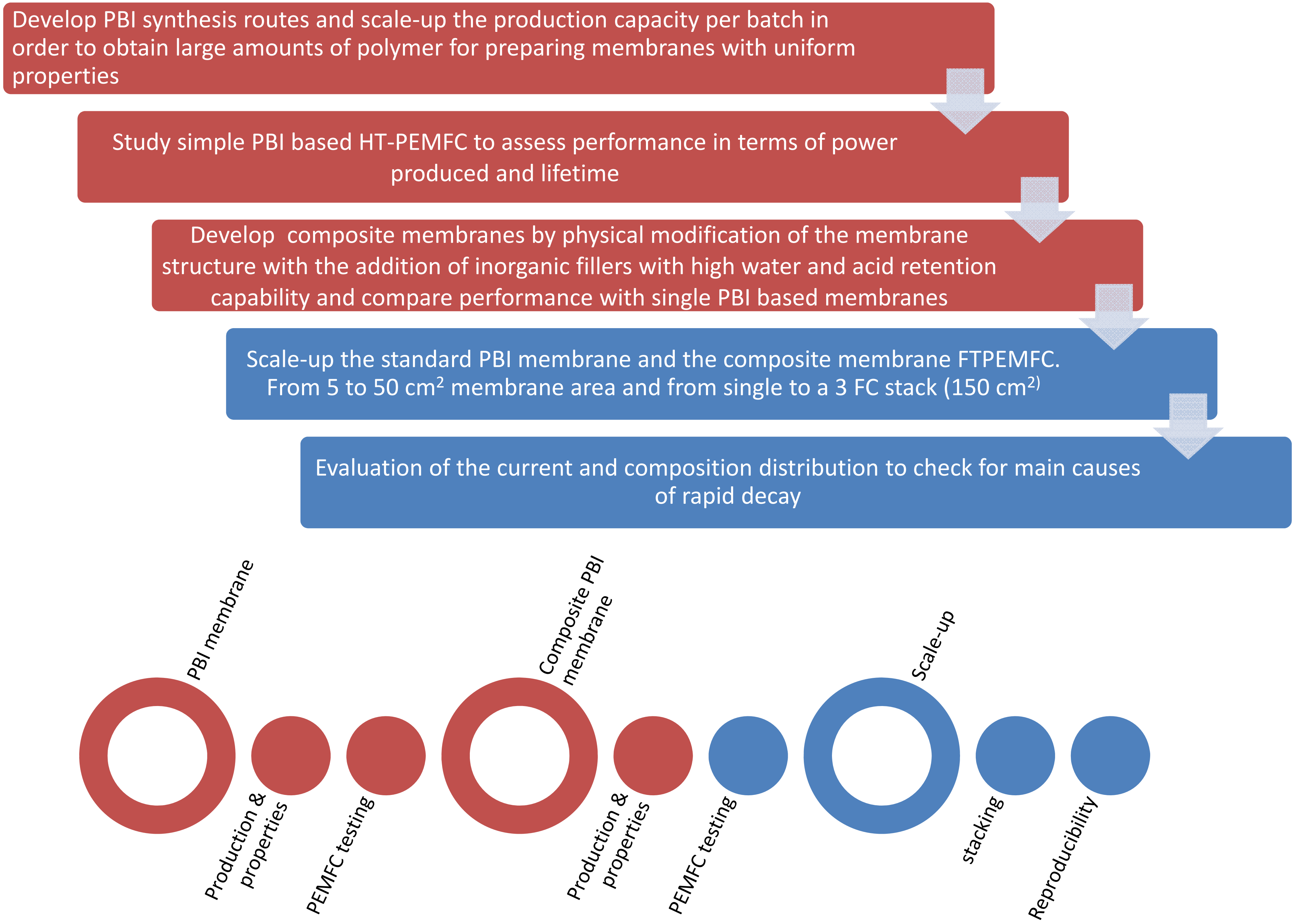
Impregnated with [H_3PO_4] = 75 % p/p

2 % TiO_2 / $TiOSO_4$

Impregnated with [H_3PO_4] = 85 % p/p

↑ Higher capability retention

2 % TiO_2-PBI → Higher capability retention
+ 5 times lesser than standart PBI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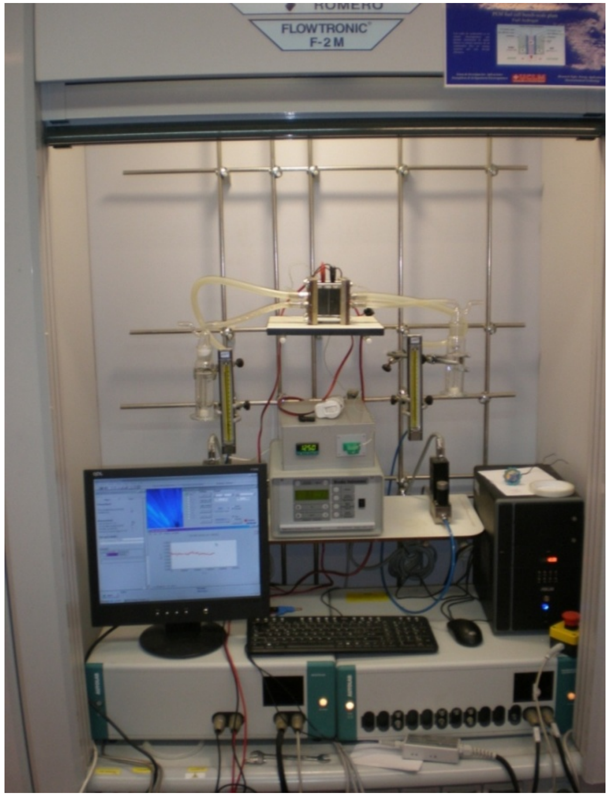
PBI membrane
Production & properties
PEMFC testing
Composite PBI membrane
Production & properties
PEMFC testing
Scale-up
stacking
Reproducibility

How do HTPEMFCs equipped with composite PBI membranes perform?



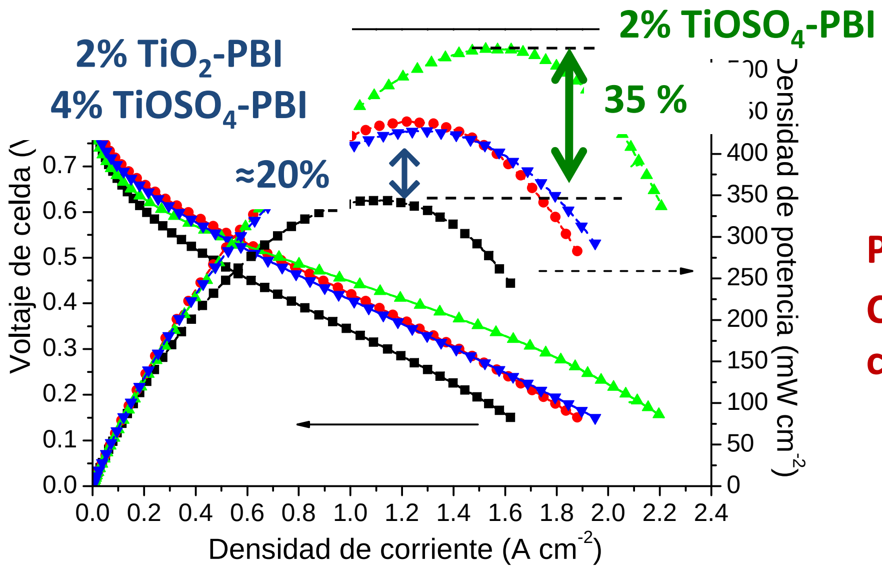
Fuel cell tests with composite PBI membranes

Membranes which were expected to have better performances in HTPEMFC

2 % TiO_2-PBI | **2 y 4 % $TiOSO_4$-PBI**

- ✓ larger acid and water absorption .
- ✓ higher acid retention capabilities .
- ✓ highest ionic conductivities.

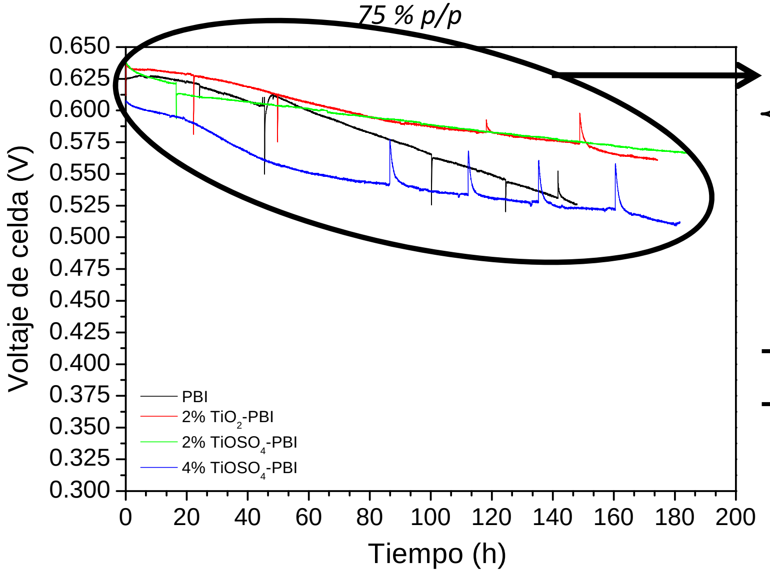
Membrane doped with 75 % p/p H_3PO_4



Polarization curves for fuel cells with Standart PBI and TiO_2 y $TiOSO_4$ composite membranes. T = 175 °C. [H_3PO_4]= 75 % p/p

Performance:

Composite PBI cells> standard PBI cells



Life test carried out for fuel cells operating with the differents membranes. Voltage vs time at 0.2 A cm^{-2} , T = 175 °C. [H_3PO_4]= 75 % p/p

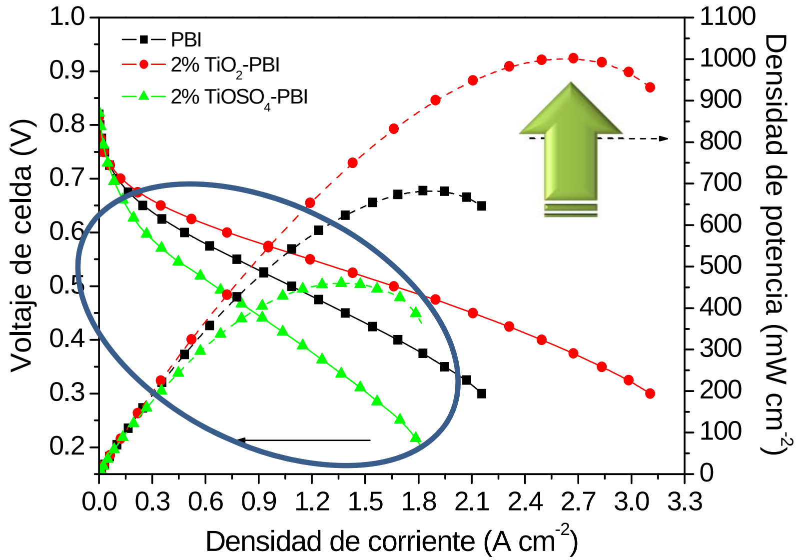
PBI: 0,2 µV s^{-1}

2% TiO_2-PBI: 0,12 µV s^{-1}

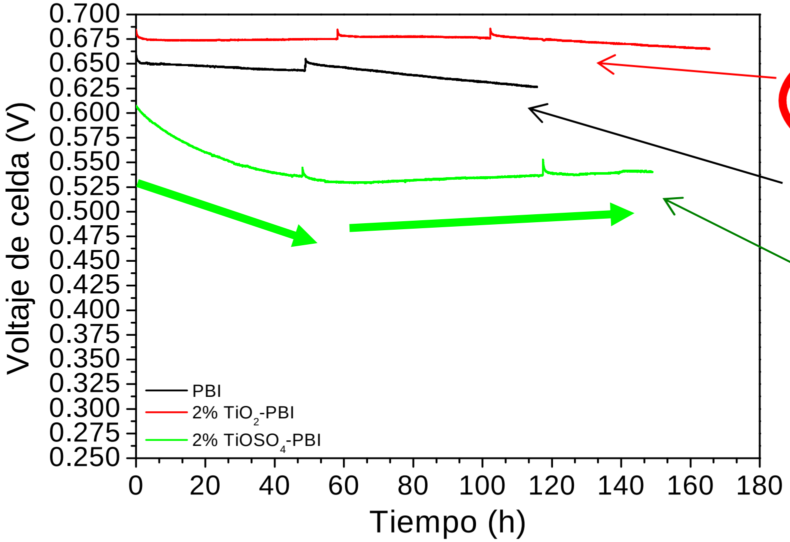
2% $TiOSO_4$-PBI: 0,09 µV s^{-1}

4% $TiOSO_4$-PBI: 0,13 µV s^{-1}

Sample	R_{Ω} (mΩ cm^2 h^{-1})	$R_{pol, ct}$ (mΩ cm^2 h^{-1})
PBI	0,23 (r^2 = 0.941)	2,34 (r^2 = 0.984)
2 % TiO_2-PBI	0,09 (r^2 = 0.939)	1,17 (r^2 = 0.844)
2 % $TiOSO_4$-PBI	0,11 (r^2 = 0.978)	0,26 (r^2 = 0.670)
4 % $TiOSO_4$-PBI	0,19 (r^2 = 0.990)	2,40 (r^2 = 0.860)



Polarization curves for fuel cells with standart PBI and composite TiO_2 and $TiOSO_4$ membranes. T = 175 °C. $[H_3PO_4]$= 85 % p/p



Life test carried by fuel cells operating with the different membranes. Cell voltage vs time 0.2 A cm^{-2} , T = 175 °C. $[H_3PO_4]$= 85 % p/p

0.01 μV s^{-1}

0.05 μV s^{-1}

0.06 μV s^{-1}

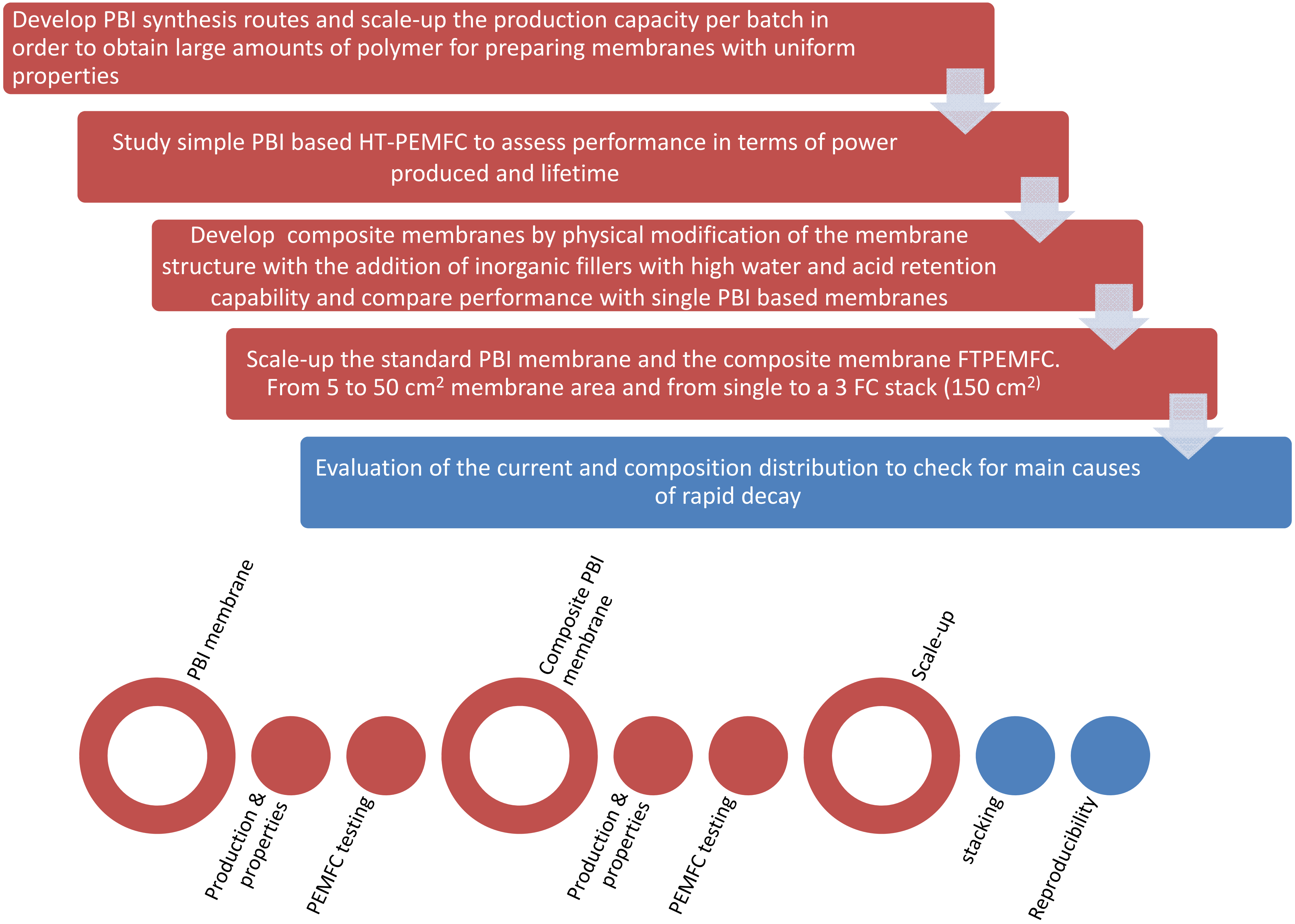
Membrane doped with 85 % p/p H_3PO_4

Worst performance: 2% $TiOSO_4$-PBI

Best performance: 2% TiO_2-PBI

1 W cm^{-2}

Extrange behaviour: 2% $TiOSO_4$-PBI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Production & properties
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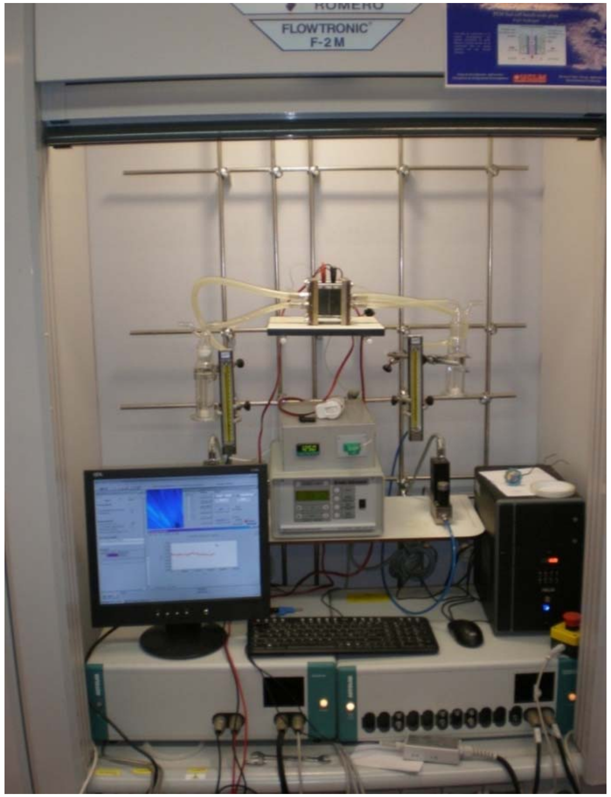
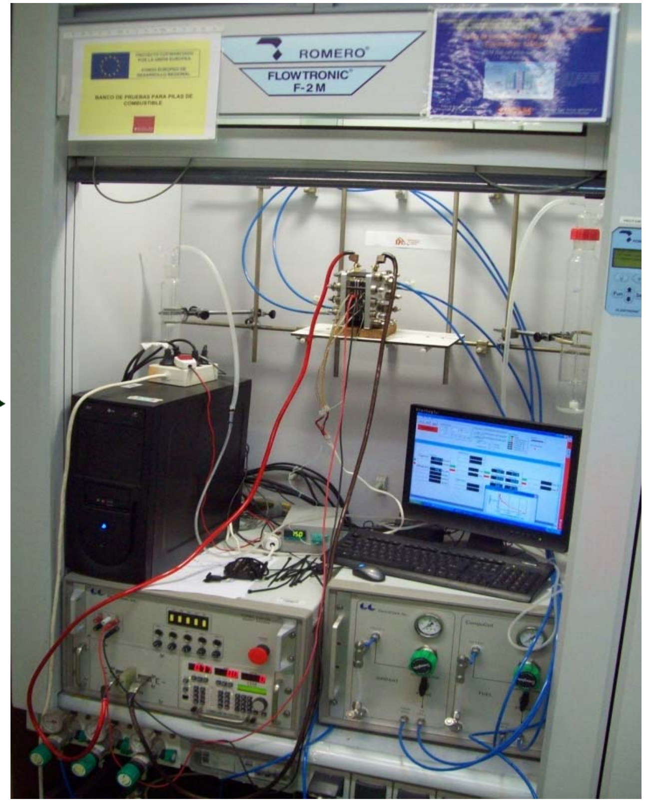
Scale-up
stacking
Reproducibility

Does size matters?



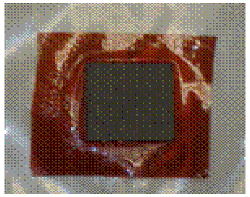
POTENCIOSTAT/GALVANOSTAT
FOR FUEL CELL
CHARACTERIZATION(20 A)



WORK STATION FOR FUEL CELL
CHARACTERIZATION (150 A)

Scale up of HTPEMFC

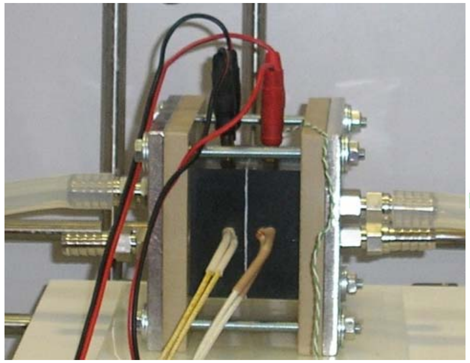
1) Increase cell size



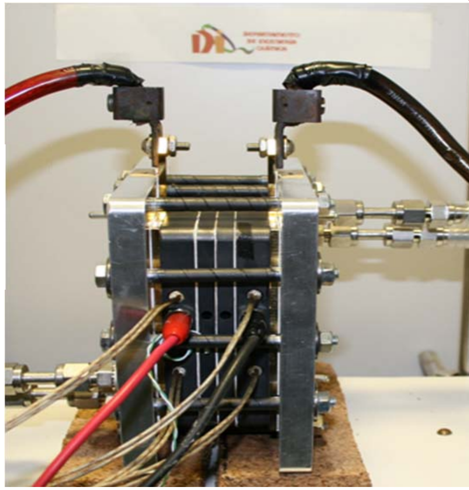
Area: 5 cm^2

Area: 50 cm^2

2) stacking



SINGLE CELL (1 MEA)



STACK (3 MEA)

Manufacturing of two fuel cell stacks

Fuel cell with doped PBI membrane $[H_3PO_4]$ = 75 % p/p (SFCS)

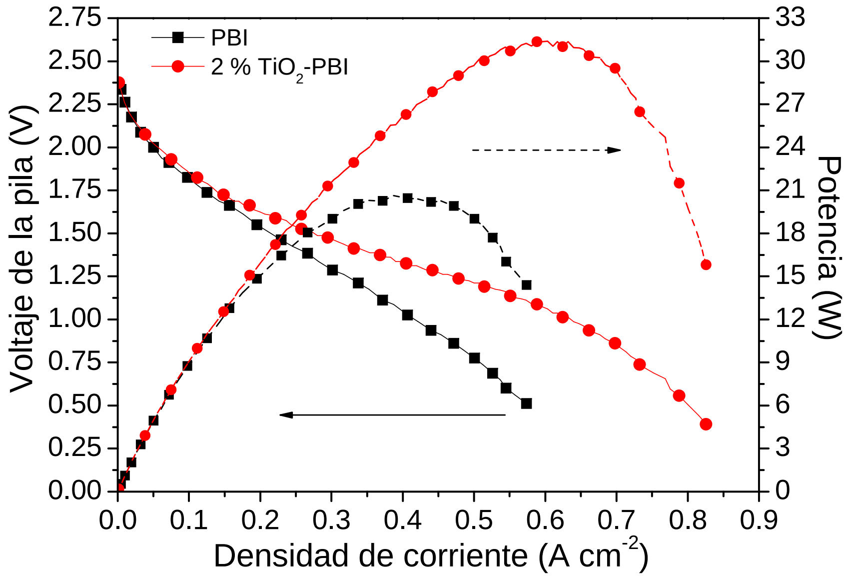
- ✓ Reference technology

Fuel cell with membrane 2 % TiO_2-PBI doped with $[H_3PO_4]$ = 85 % p/p (CFCS)

- ✓ Acid Absorption (+ adsortion)
- ✓ Acid retention
- ✓ Proton conductivity
- ✓ Performance in a fuel cell
- ✓ Stability in a fuel cell

- ✓ 3 cells
- ✓ 50 cm^2 / Cell
- ✓ total: 150 cm^2

Performance of stack



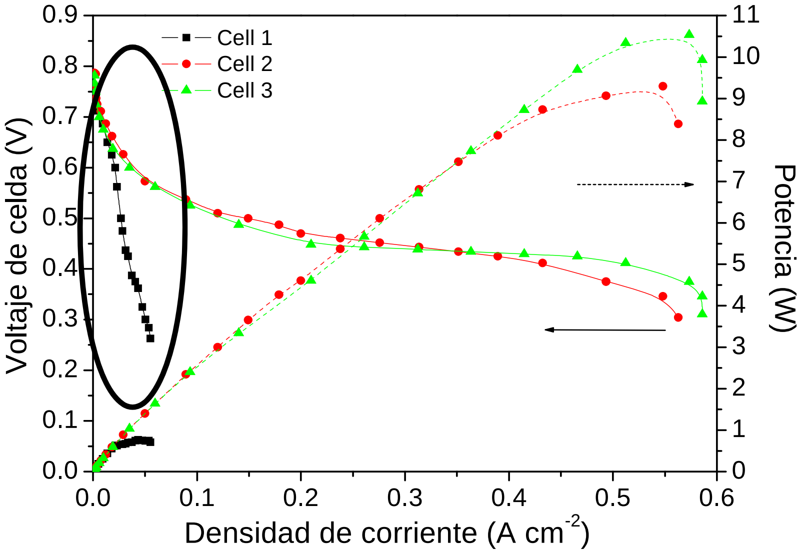
Polarization curves of SFCS and CFCS. λ_{H_2} = 2, λ_{O_2} = 3; T = 125 °C; P = 1 atm

Previous test:

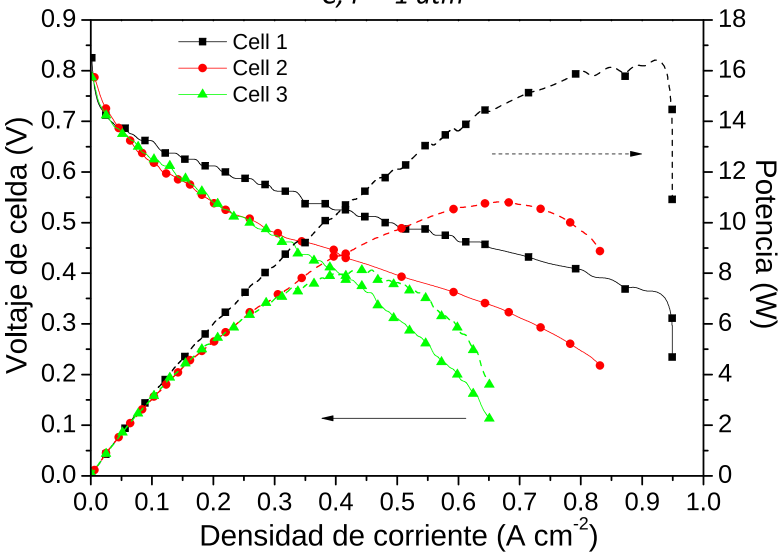
1) **conditioning stage**
2) **shut-down stage**

Best performance: HTPEMFC - 2% TiO_2-PBI (CFCS)

Performance of cells inside the stack



Polarization curves of each cell SFCS . λ_{H_2} = 2, λ_{O_2} = 3; T = 125 °C; P = 1 atm



Polarization curves of each cell of CFCS . λ_{H_2} = 2, λ_{O_2} = 3; T = 125 °C; P = 1 atm

Different performance of cells in the stack

↓

Low reproducibility for scale up

Cell 1 (SFCS) → worst performance

deactivation of the catalyst?

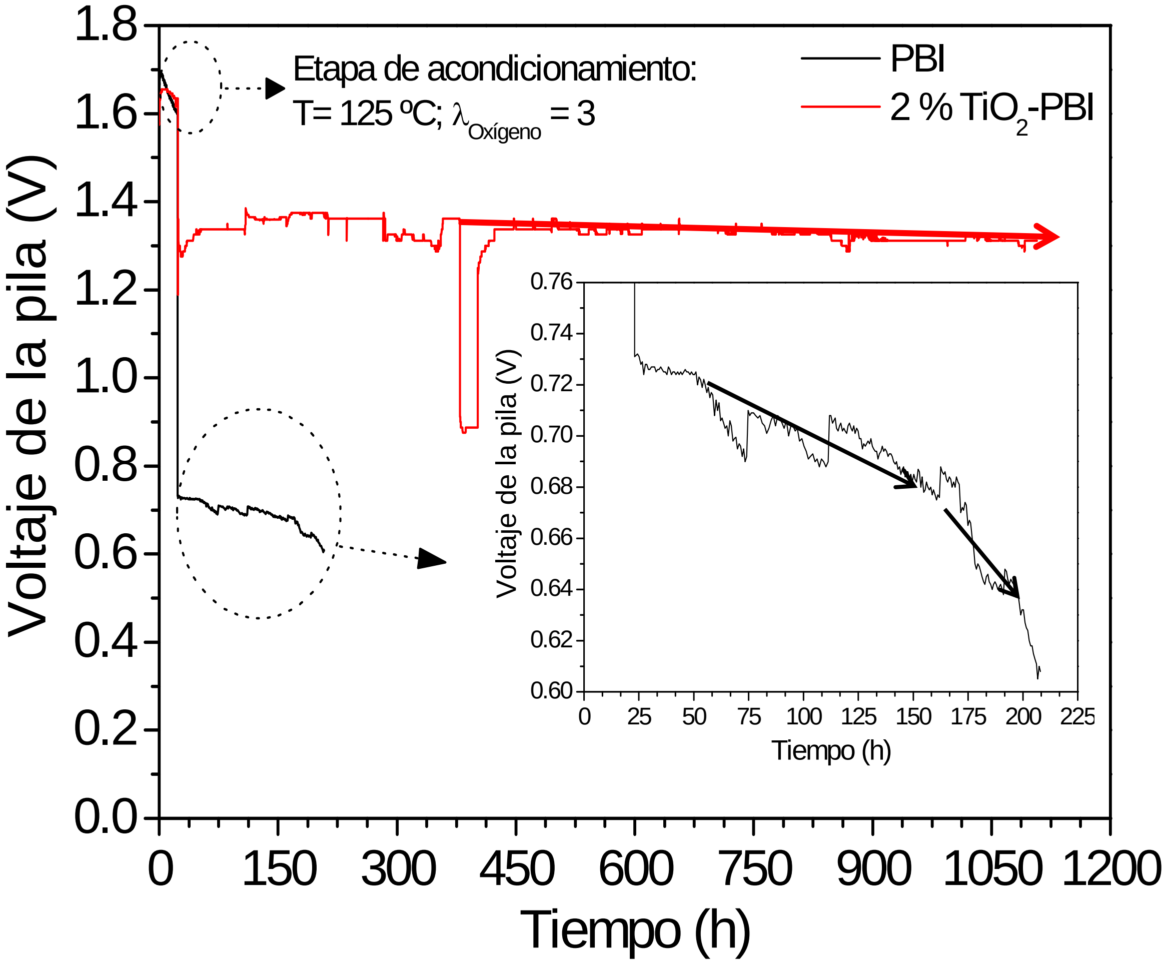
mechanical damage of the membranes?

Where& When?:

- **manufacturing of MEA**
- **asembling**
- **stacking**
- **conditioning**

Lifetest

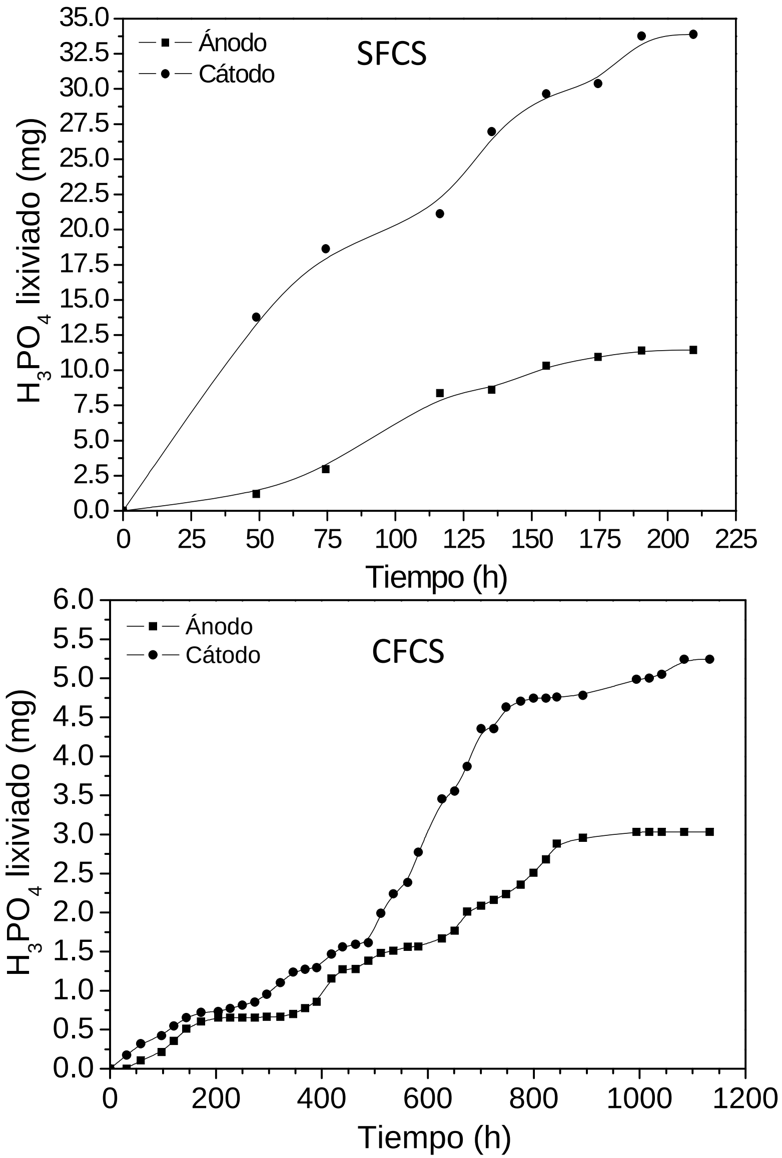
CFSF and SFCS operated at constant current density (0,2 A cm^{-2})



Voltage variation in life test (conditioning stage included). Current density= 0.2 A cm^{-2}; λ_{H_2} = 2, λ_{Aire} = 3; T = 150 °C; P = 1 atm

Performance decay < 2 % after 1100 h operation (total time: 1.700 h de estudio including testing and shut ups)

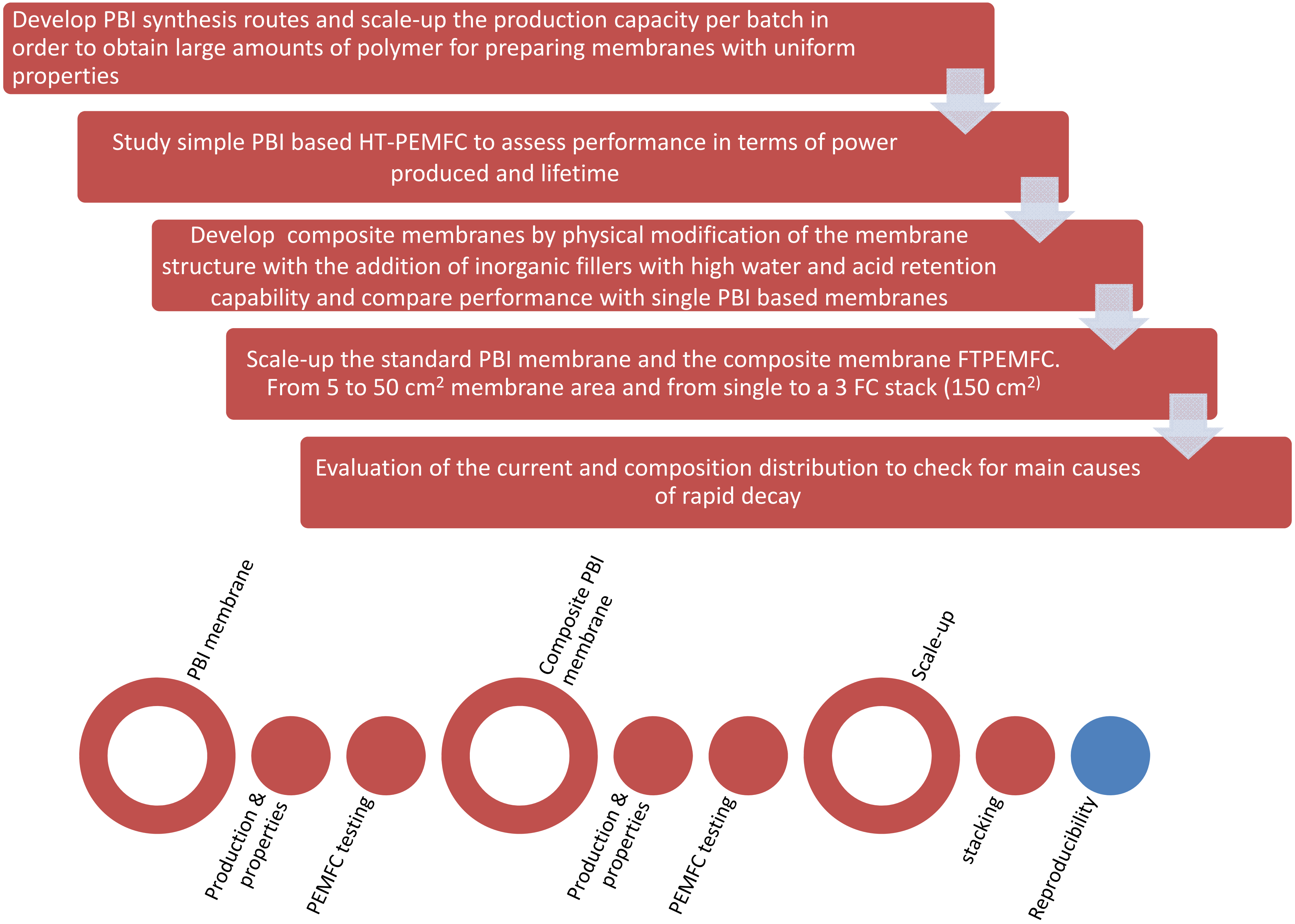
Acid leached during lifetest



H_3PO_4 lixiviated of anode and cathode for each fuel cell during the operation at constant load.

- ↑ acid leach more from the cathode side than from the anode side → water vapour generated in the reaction on the cathode side dragged part of the phosphoric acid outside the fuel cells

- CFCS total acid leached< 0,6 %
- SFCS total acid leached= 2 %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Production & properties
PEMFC testing
Composite PBI membrane
Production & properties
PEMFC testing
Scale-up
stacking
Reproducibility

What's the matter with reproducibility?

deactivation of the catalyst?

mechanical damage of the membranes?

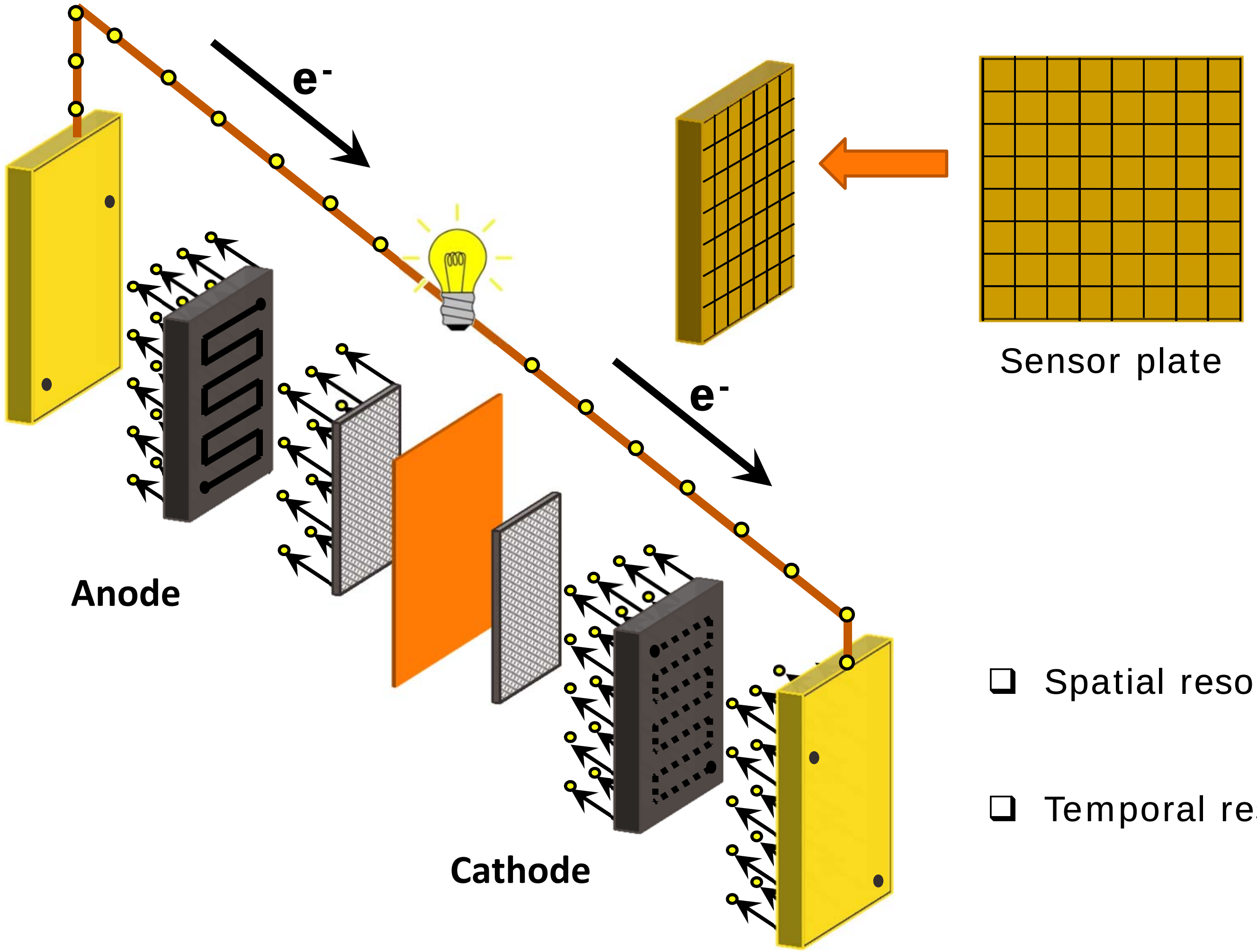
Where & When?:

- **manufacturing of MEA**
- **asembling**
- **stacking**
- **conditioning**

How to get a uniform behaviour?

Could current distribution measurement help to understand this low reproducibility?

➢ Apparatus – Placement of the measuring device



- ❑ Spatial resolution
- ❑ Temporal resolution

Lifetest I: airbrush; anode: 0.25 mg Pt cm-2 ; cathode: 0.25 mg Pt cm-2

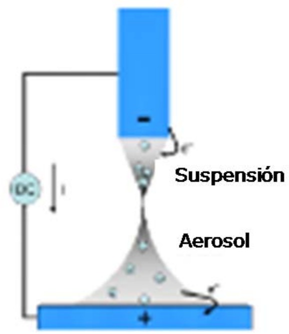
Lifetest II: electrospray; anode: 0.25 mg Pt cm-2 ; cathode: 0.25 mg Pt cm-2

Lifetest III: airbrush; anode: 0.10 mg Pt cm-2 ; cathode: 0.15 mg Pt cm-2

Lifetest IV: electrospray; anode: 0.10 mg Pt cm-2 ; cathode: 0.15 mg Pt cm-2

Spread catalytic ink technique:

airbrush



electrospray

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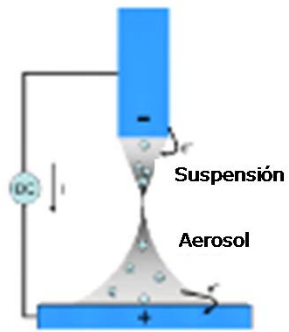
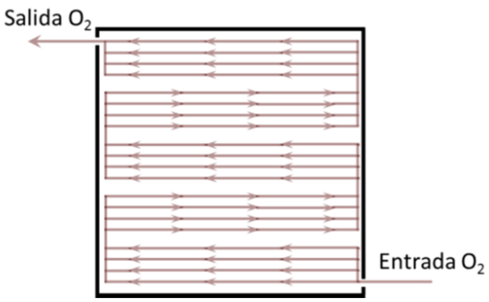
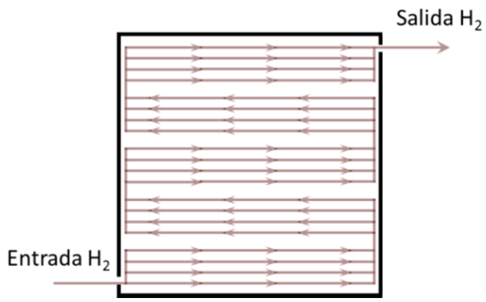
Spread catalytic ink technique:

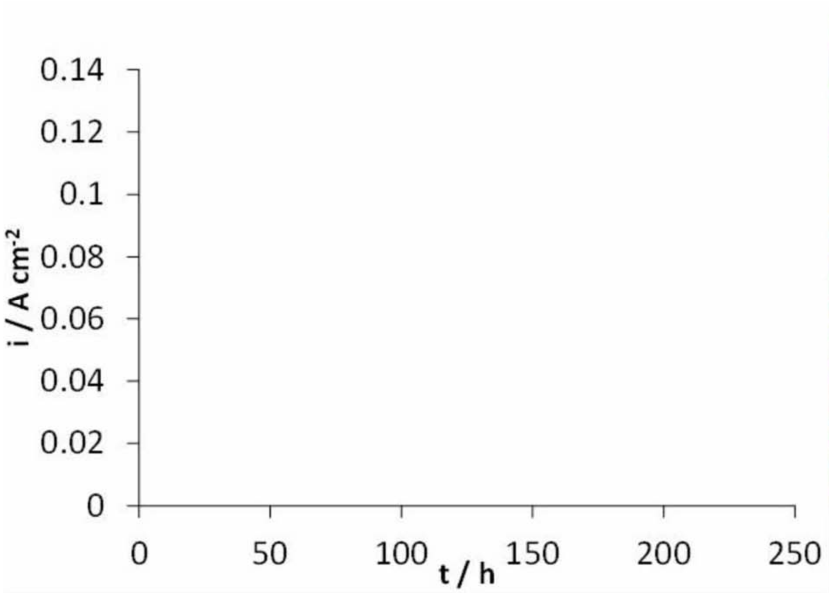
airbrush

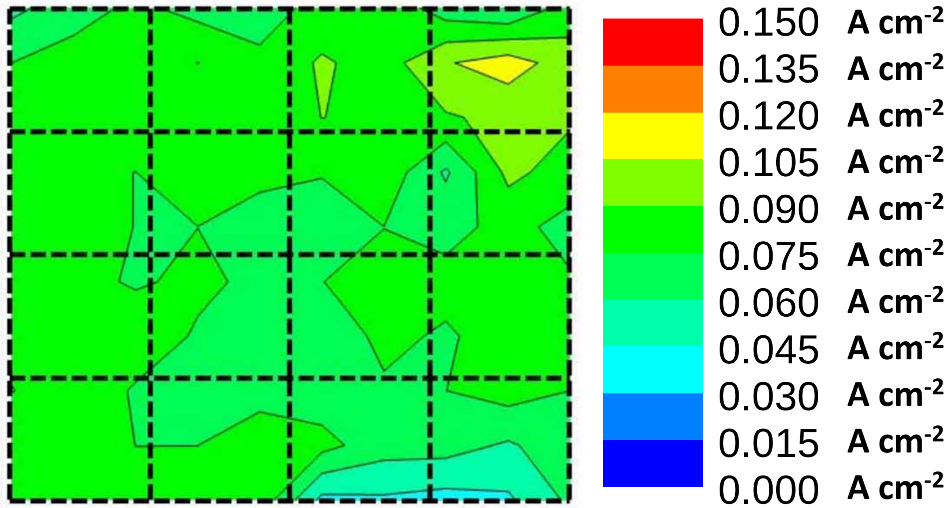


electrospray

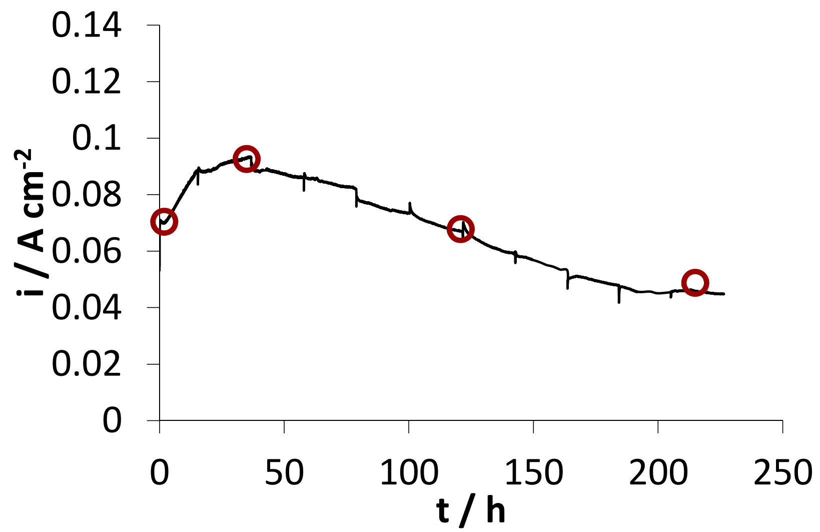


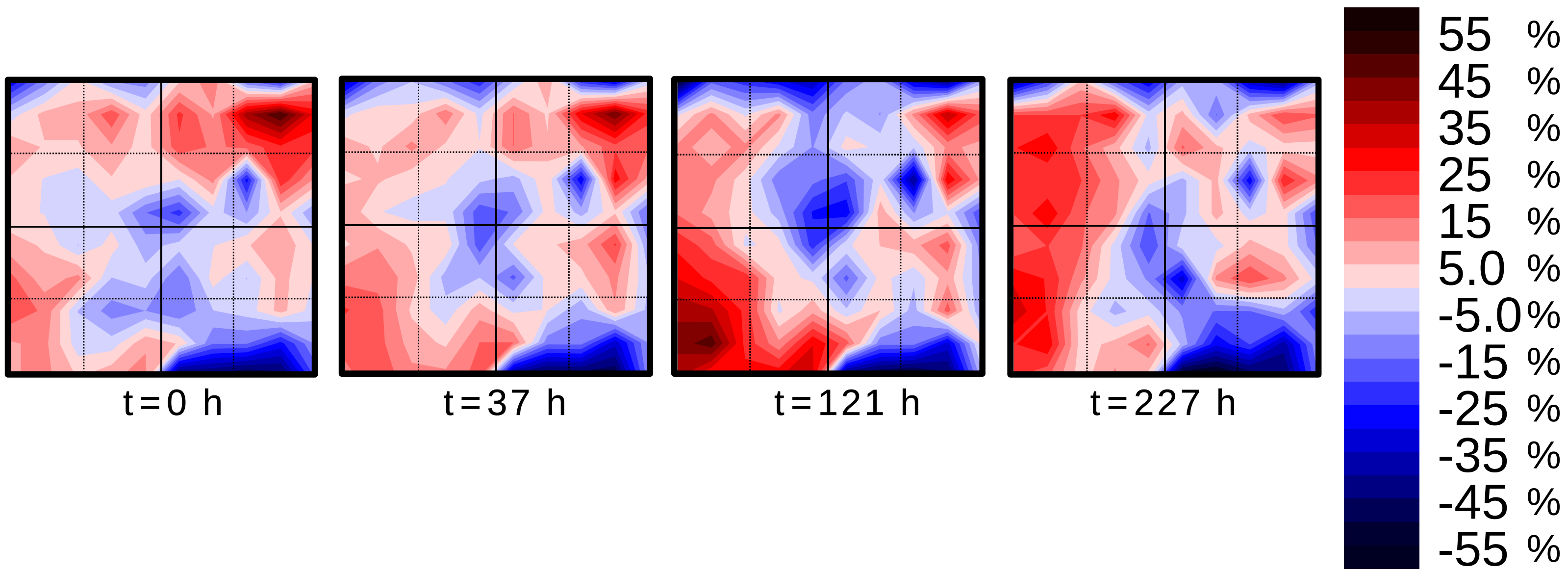






- ❑ Two different stages: activation and decay
- ❑ Current distribution is uneven and changes significantly during the lifetest
- ❑ No aparent influence of the reagents' inlets and outlets



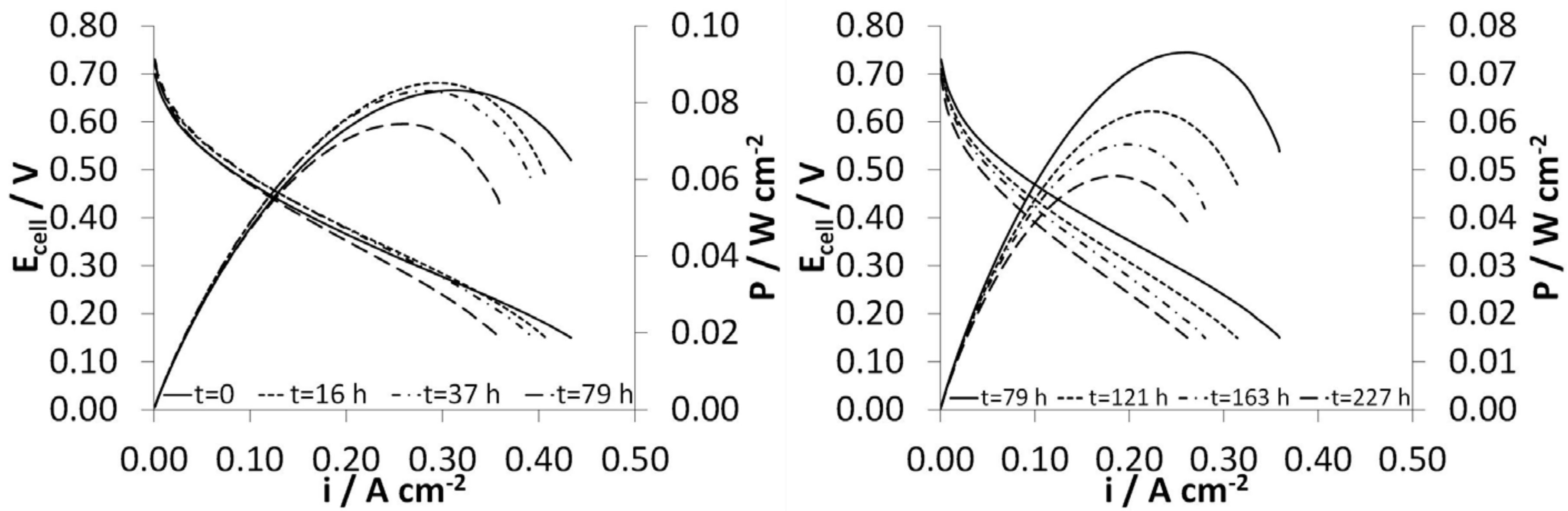


Significant change of the current distribution map during the lifetest.

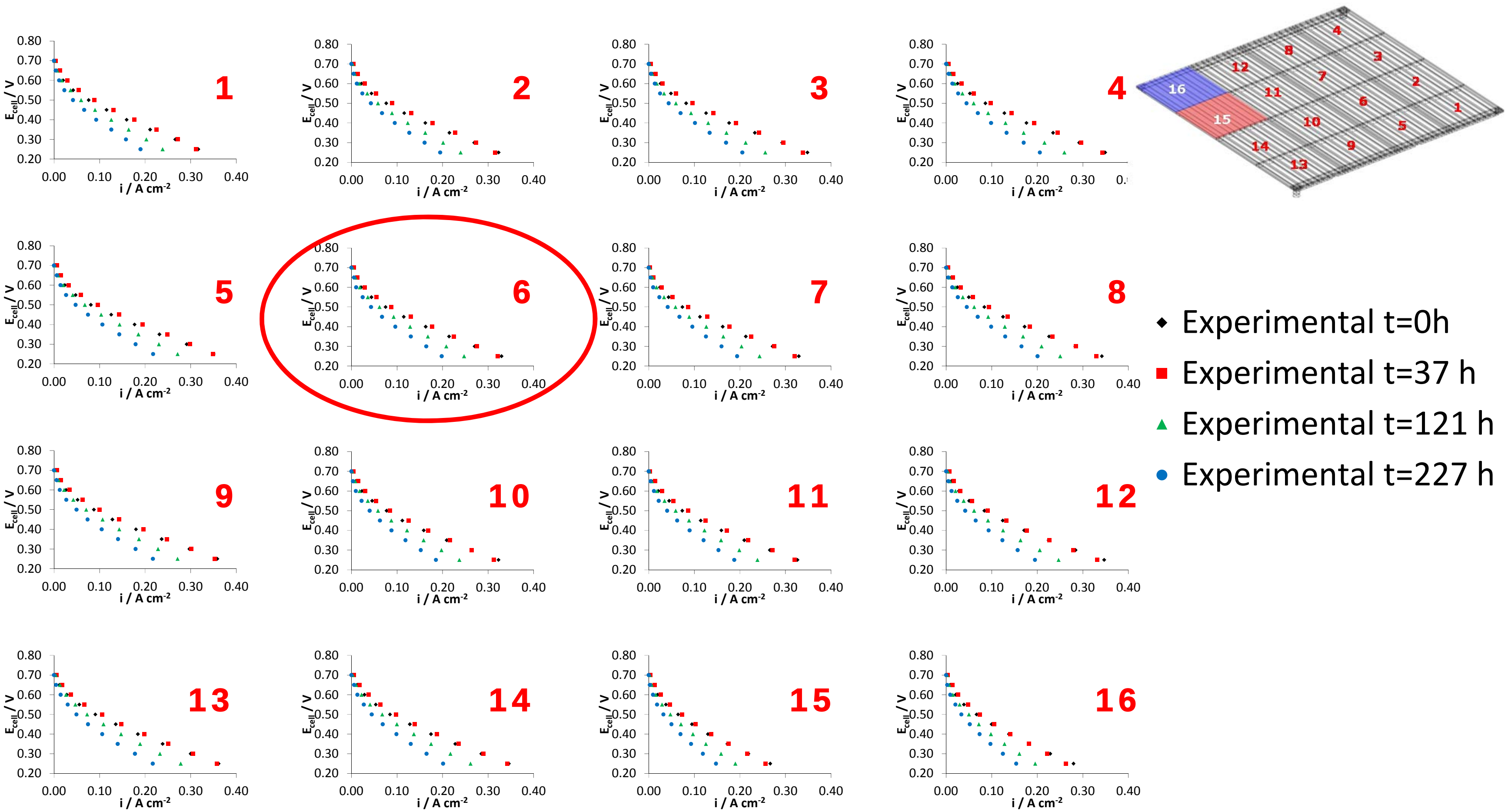
Differences are much higher at the end of the test

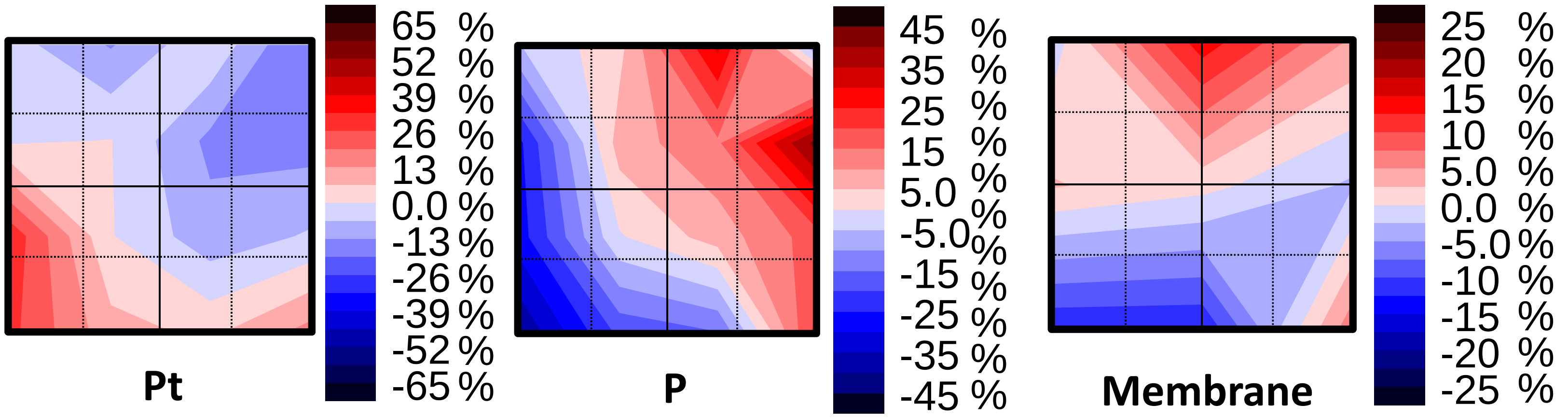
Keep in mind that average current decreases in the second state and maps reflects only changes

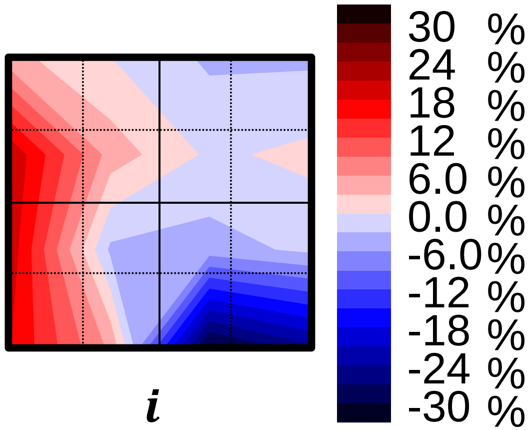
- Global polarization curves

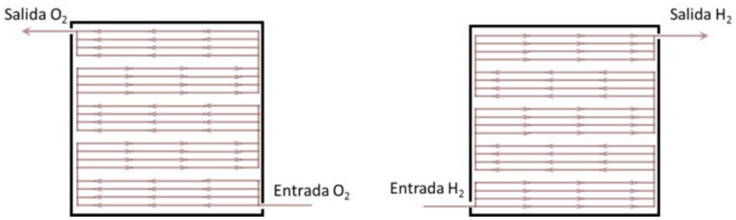


o Local polarization curves









- **Catalyst distribution**
  - Electrode manufacturing
  - Particle agglomeration
- **Water distribution**
  - Flooding
- **Temperature distribution**
  - Design
- **Reagent distribution**
  - Mass transport
  - Flow channels
- **Conductivity distribution**
  - Assemblage

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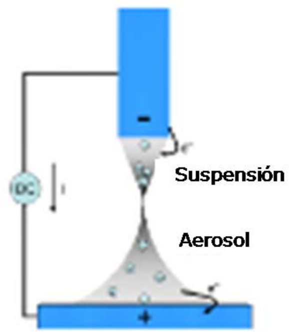
Spread catalytic ink technique:

airbrush



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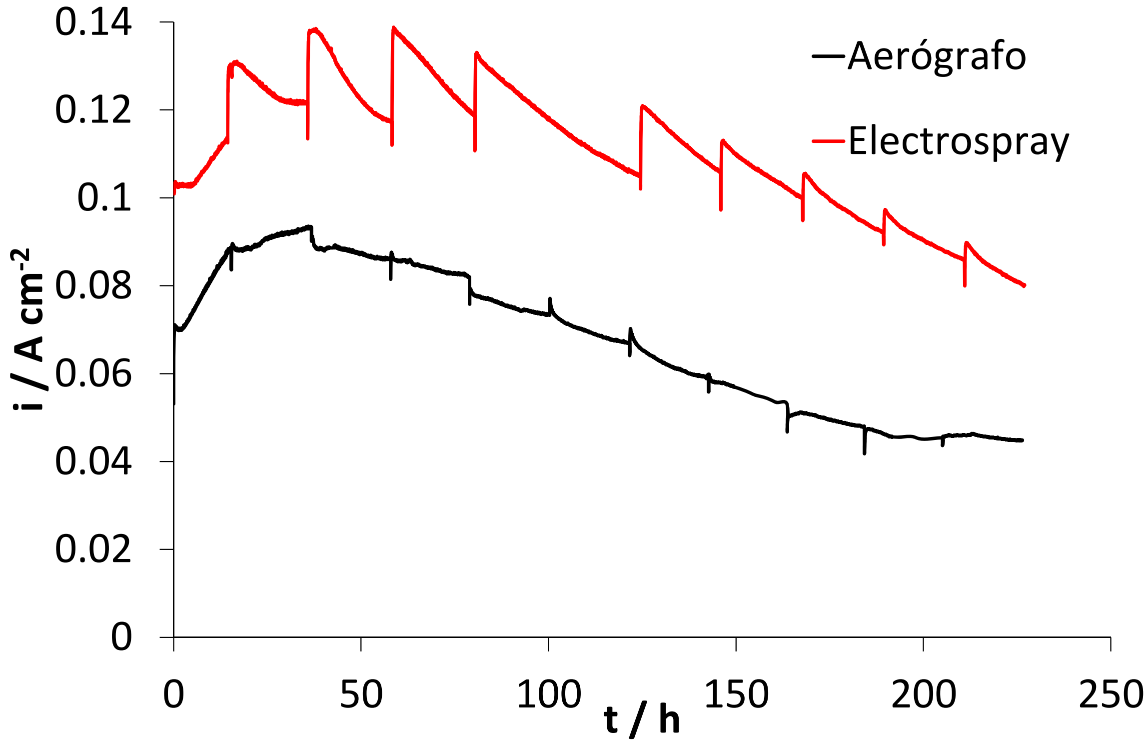
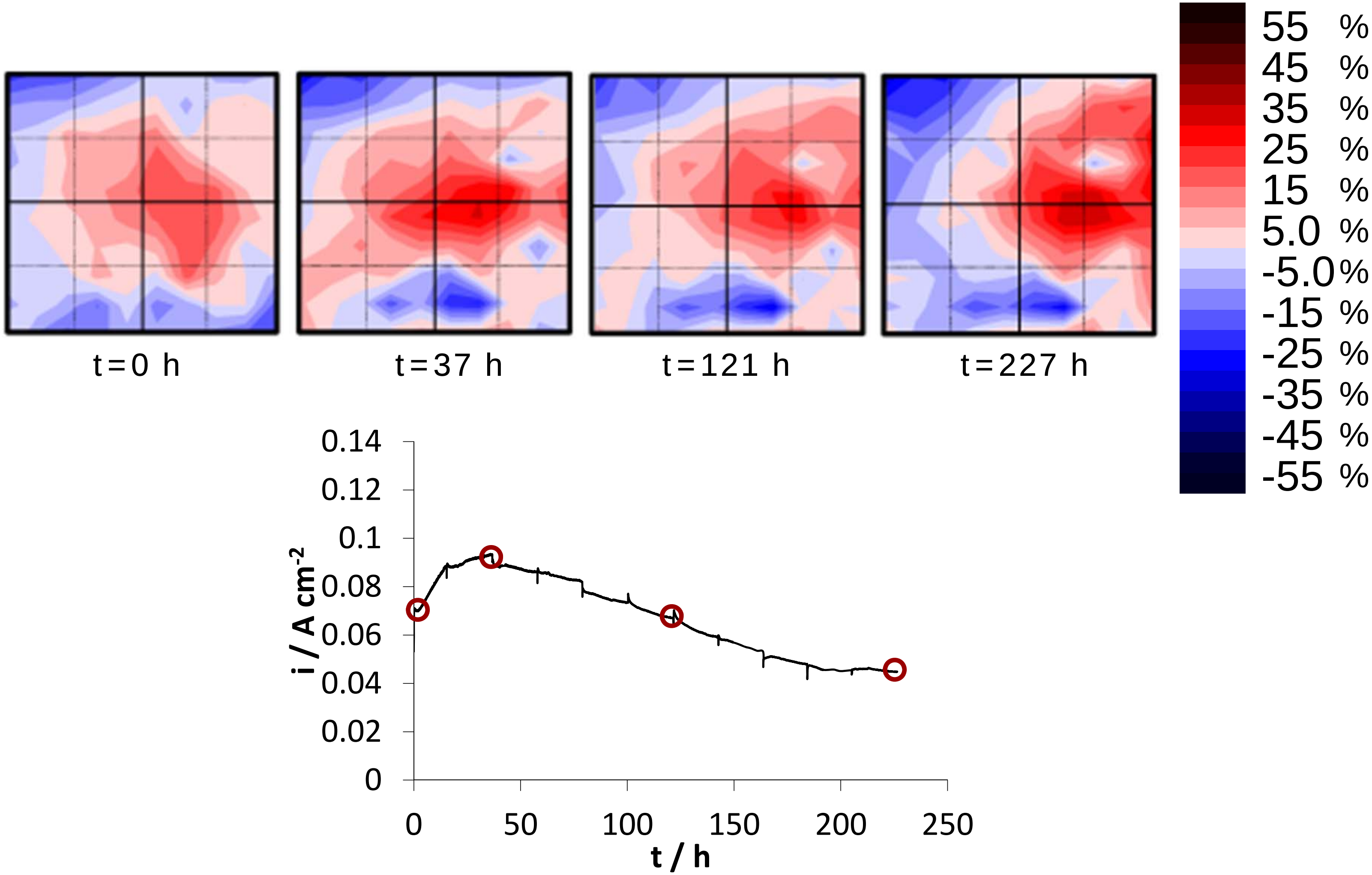


Differences in the current values not in the way in which they change: same stages during the lifetest: activation and decay (no influence of the catalyst deposition technique)

o *i* vs *t*



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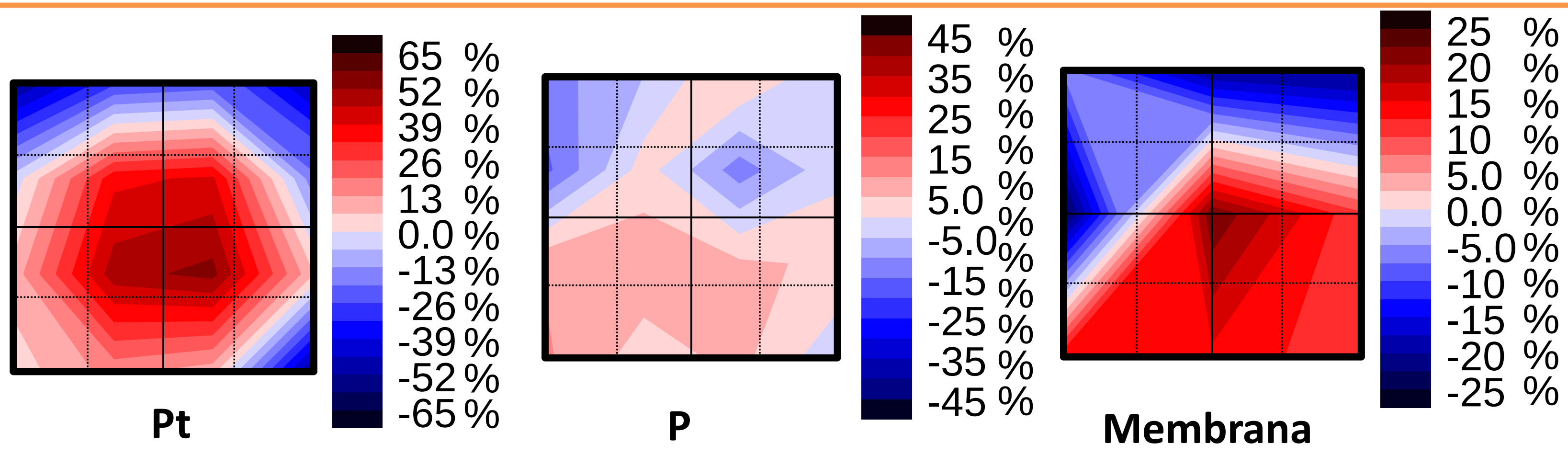

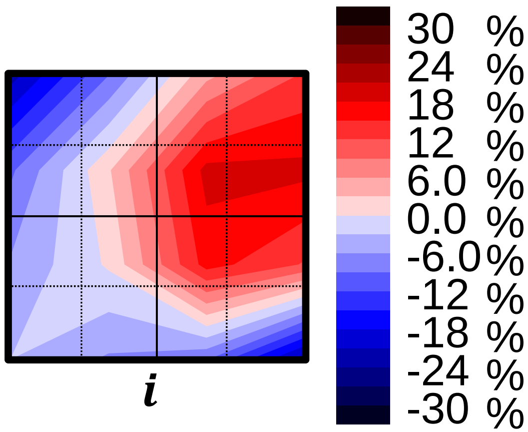

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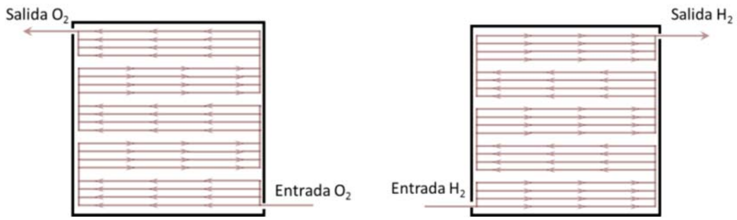

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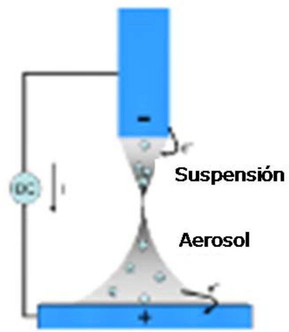
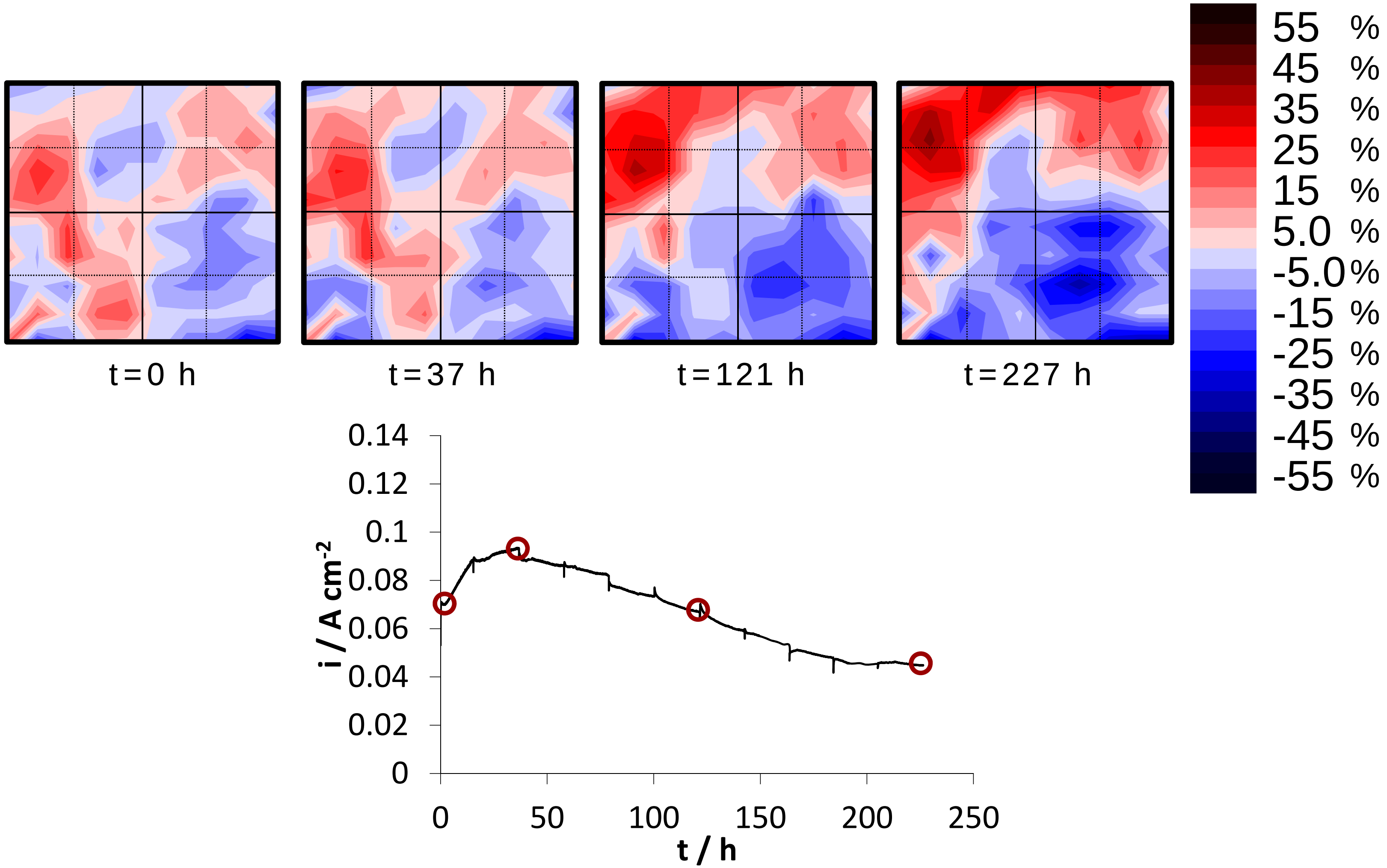
Spread catalytic ink technique:

airbrush



electrospray



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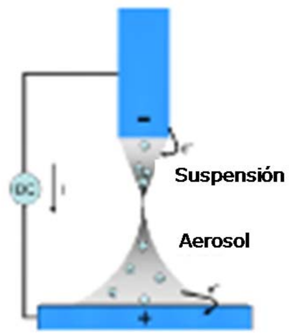

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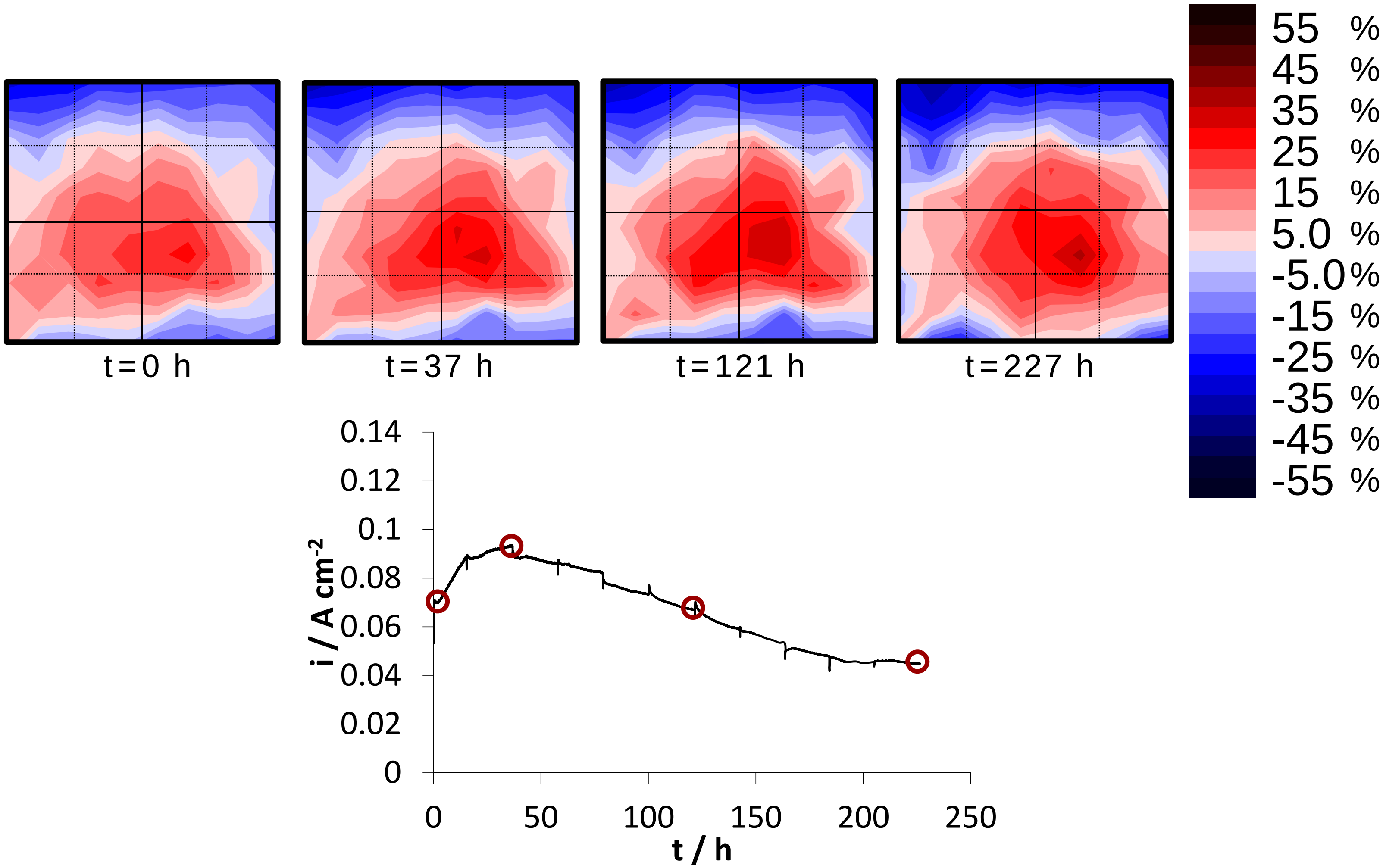
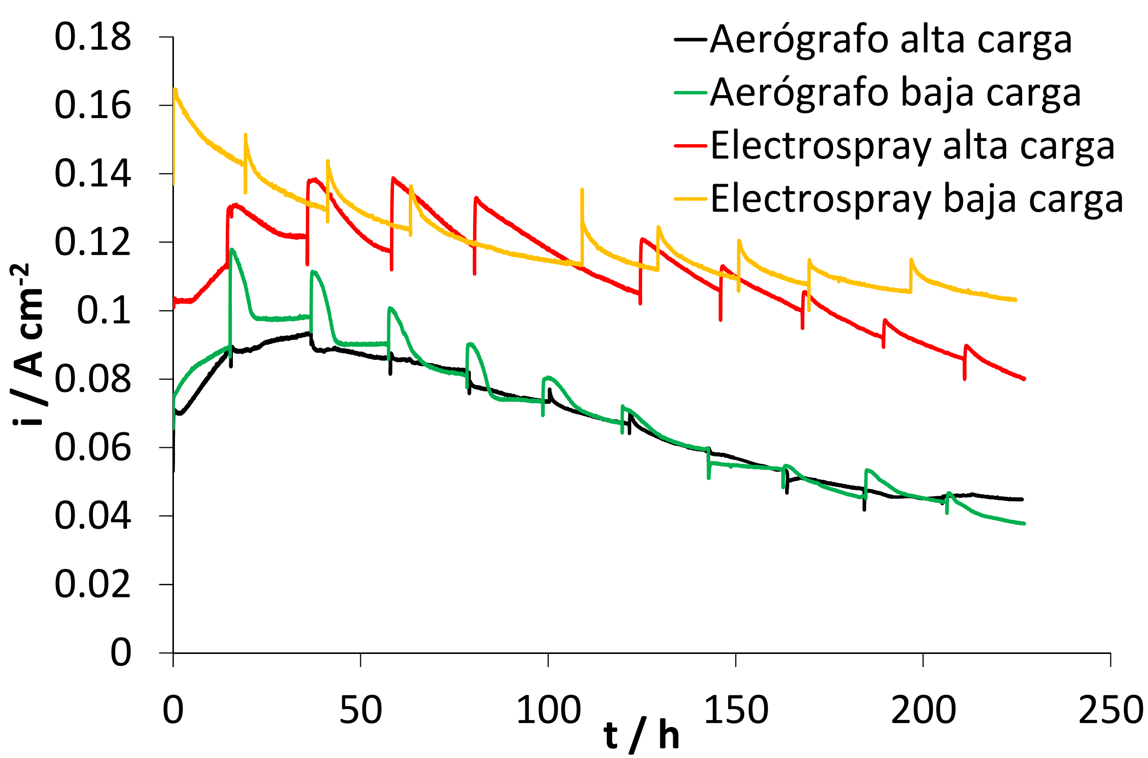
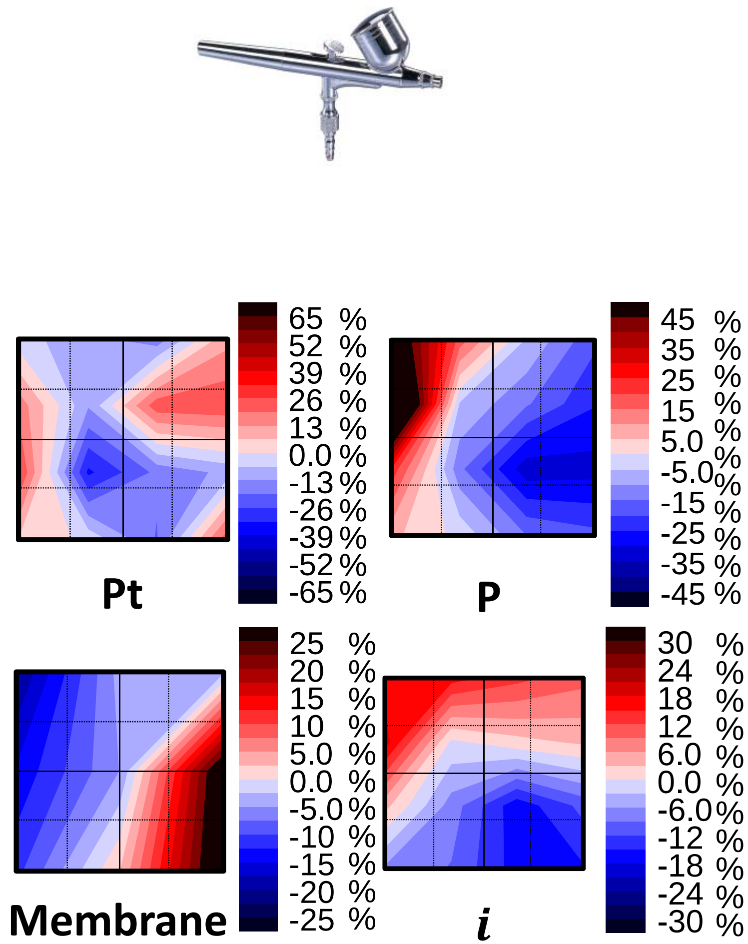


Significant change of the current distribution map during the lifetest. Differences are much higher at the end of the test

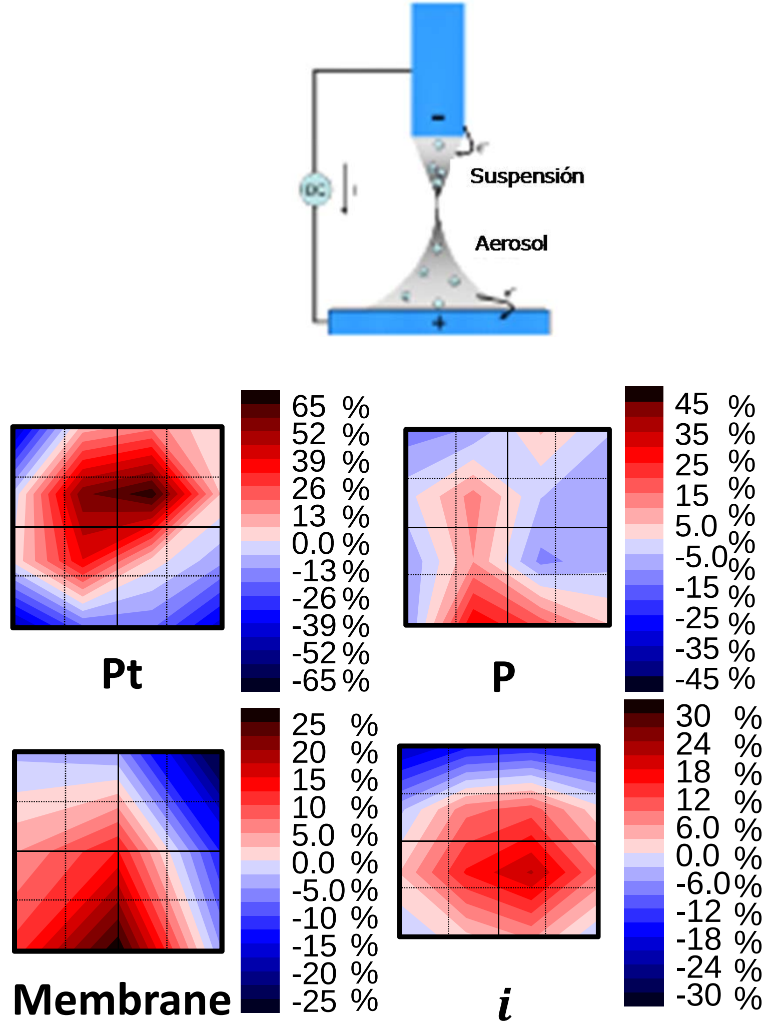
Keep in mind that average current decreases in the second state and maps reflects only changes



Differences in the current values not in the way in which they change: same stages during the lifetest: activation and decay (no influence of the catalyst deposition technique on the deterioration althought clearly better results of electrospray for the same catalyst content)



- ❑ No single relatioship can be appreciated



- ❑ Similarities between Pt and i

Concluding remarks

Manufacture of the components of PBI-HTPEMFC is not difficult but lack of reproducibility associated to the large number of manufacturing steps and the very different nature is inherent to the technology

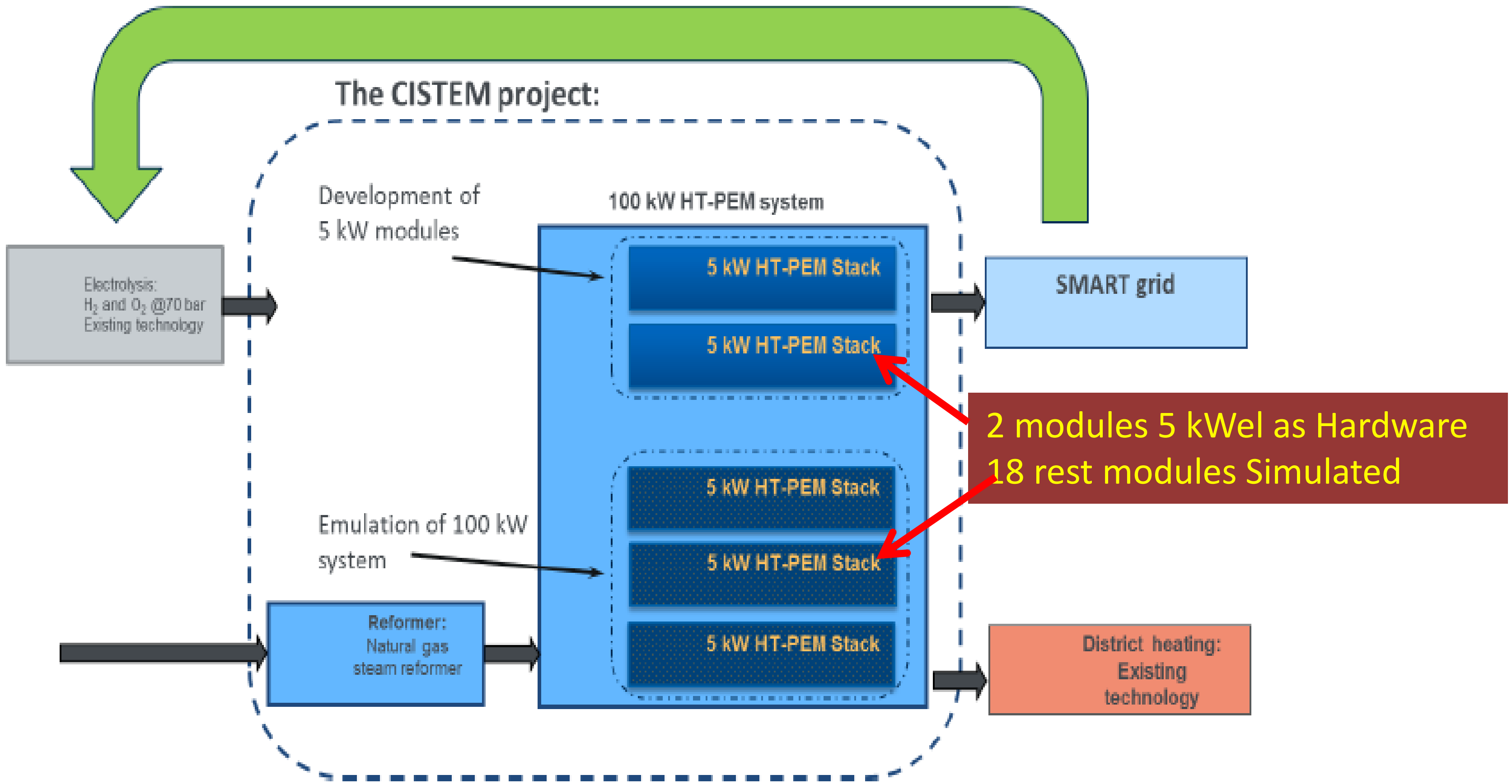
Composite membranes can help to increase service lifetime and enhance performance

Lifetime and reproducibility remains to be the key drawbacks in PBI-HTPEMFC technology. Non uniform behaviour can not directly be associated to a single parameter (catalyst, reagent distribution, temperature, membrane) to the joint effect of all of them.

Catalyst deterioration is the key to understand PBI-HTPEMFC performance decay . Leaching of phosphoric acid is a much less important problem

New materials beyond state of art are being developed including sulphonated compositte PBI Membranes which are showing very interesting results (CISTEM EU project)

CISTEM project: develop a new fuel cell (FC) based CHP technology, which is suitable for fitting into large scale peak shaving systems in relation to wind mills, natural gas and SMART grid applications.



Introduction

Objetives

Results and discussion

Conclusions

Acknowledgements

- The authors thank Spanish government for the research project CTM2010-18833

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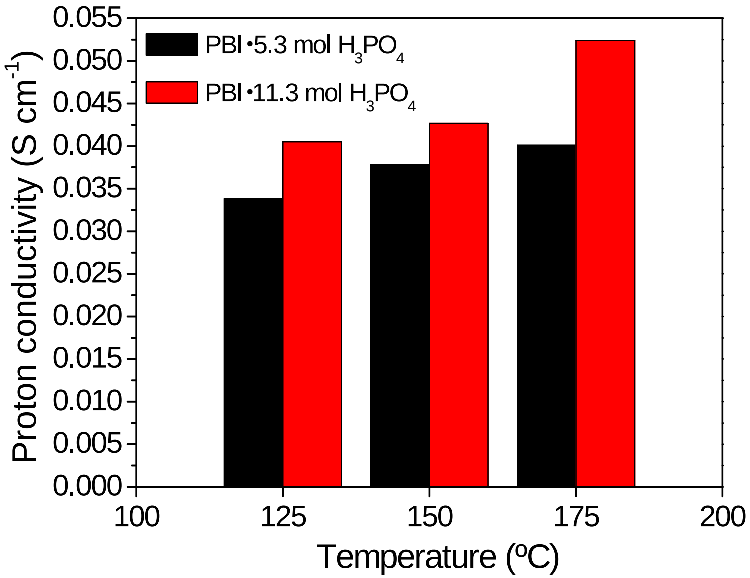
- Special thanks to the HYDROGEN DAYS organizers for their kindness and support of the research in hydrogen technology

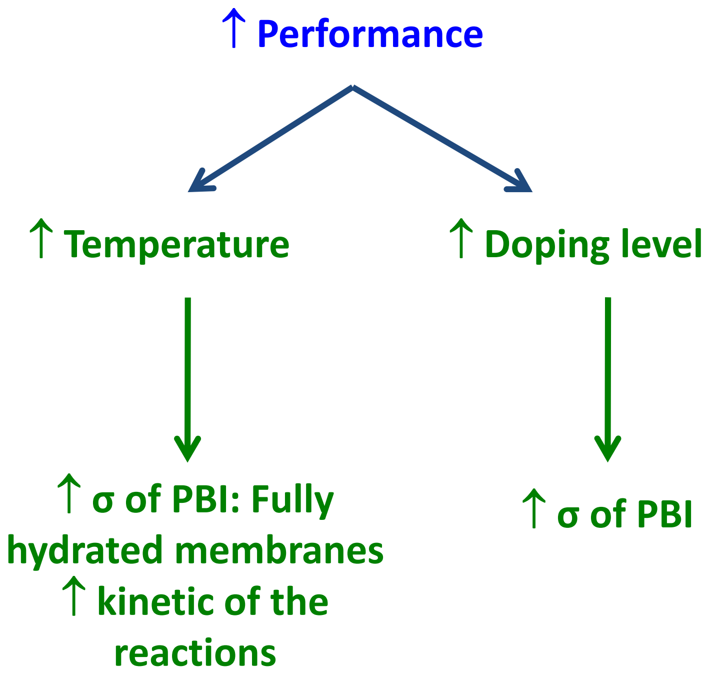
HydrogenDays 2014

Thank you for your kind attention!

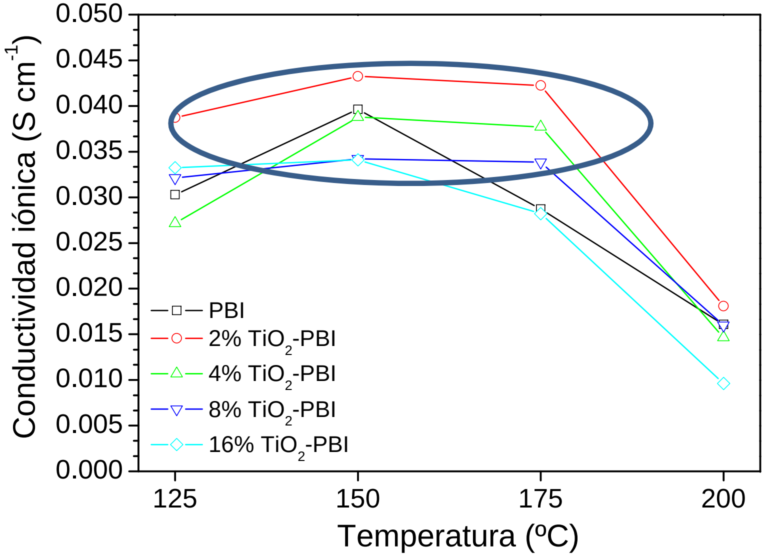
Composite membranes for high temperature PEM fuel cells: from single cells to stack. M.A. Rodrigo, J. Lobato, P. Cañizares, F.J. Pinar, H. Zamora and D. Úbeda



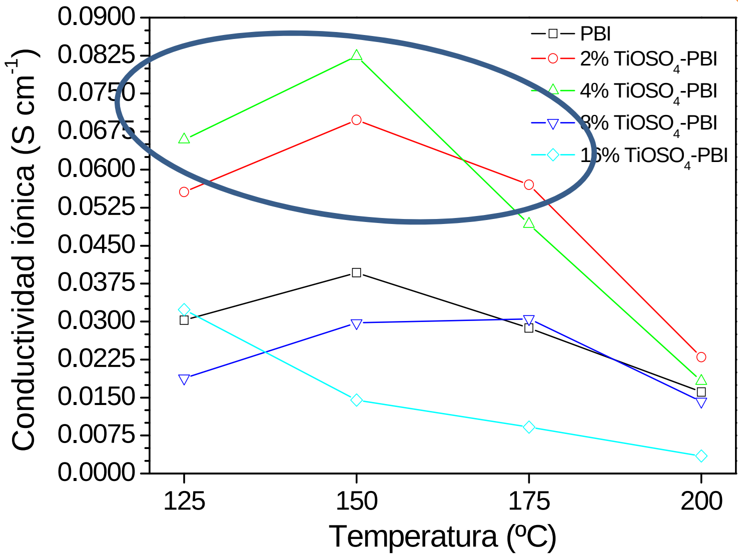
Influence of temperature on proton conductivity of PBI membranes used in fuel cell and doped into different H_3PO_4 bath solutions



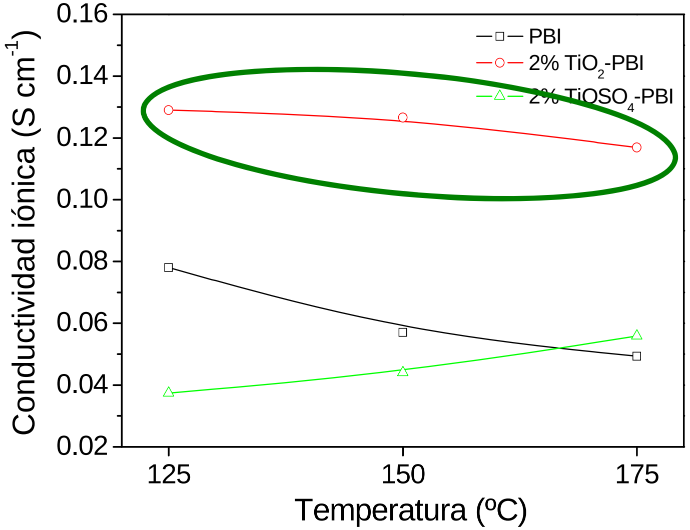
IONIC CONDUCTIVITY



Ionic conductivity for TiO_2 composite PBI membranes and Standart PBI membranes at differents temperatures. $[H_3PO_4]$= 75 % p/p



Ionic conductivity for $TiOSO_4$ composite PBI membranes and Standart PBI membranes at differents temperatures. $[H_3PO_4]$= 75 % p/p



Ionic conductivity of composite and standart membranes based PBI at differents temperatures. $[H_3PO_4]$= 85 % p/p

Composite membranes→↓ Decrease in σ with ↑Tª

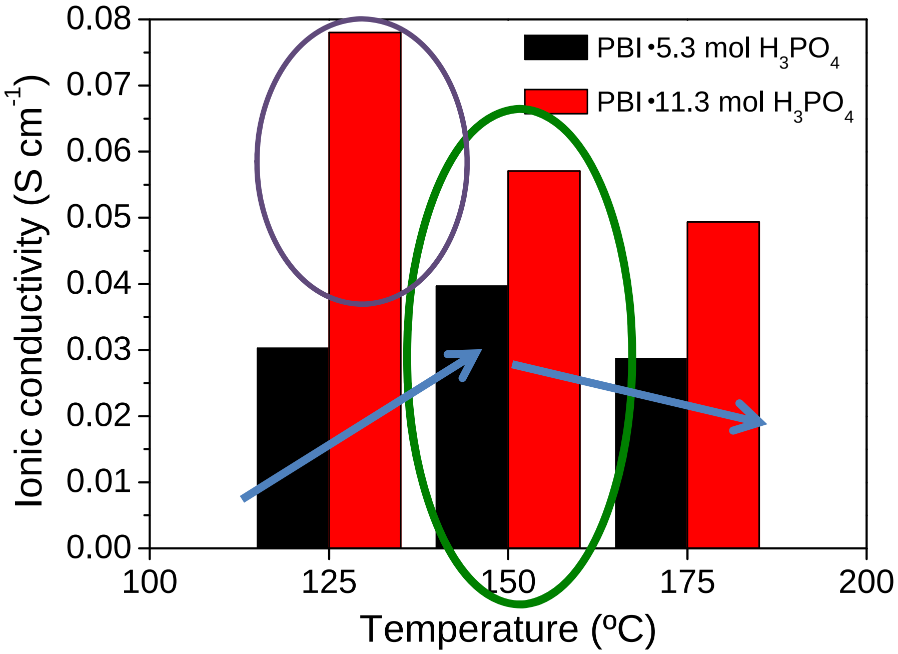
2, 4, 8 % TiO_2-PBI and 2, 4 % $TiOSO_4$-PBI **75 % p/p H_3PO_4** **↓** **σ↑**

PBI

2 % TiO_2-PBI → ↑↑σ

85 % p/p H_3PO_4

IONIC CONDUCTIVITY



Influence of temperature on ionic conductivity for PBI membranes doped into different H_3PO_4 bath solutions

✓ ↑ **Acid doping level →↑ Membrane conductivity → Larger amount of proton carriers (acid and water)**

✓ ↑ **Temperature →↑ Membrane conductivity → ↑Mobility of proton "carriers"**

✓ ↑**150 °C →↓ Membrane conductivity → Degradation of H_3PO_4:**

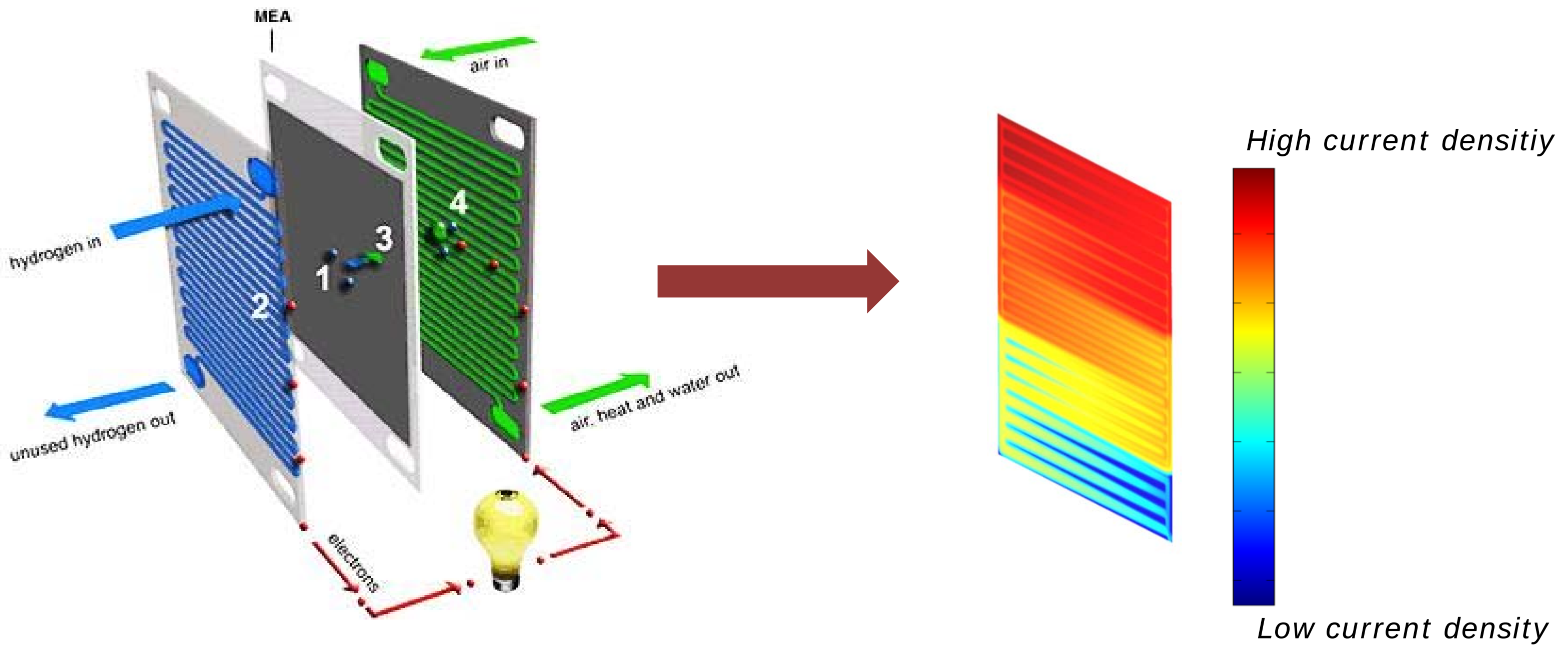
$$2\ H_3PO_4 \rightarrow H_4P_2O_7 + H_2O$$

✓ **PBI·11.3 mol H_3PO_4 →↑ conductivity at 125 °C→ Not totally dehydrated**

✓ **↓σ→↑Temperature → ↓ Relative Humidity**

Current density distribution in a PEM fuel cell

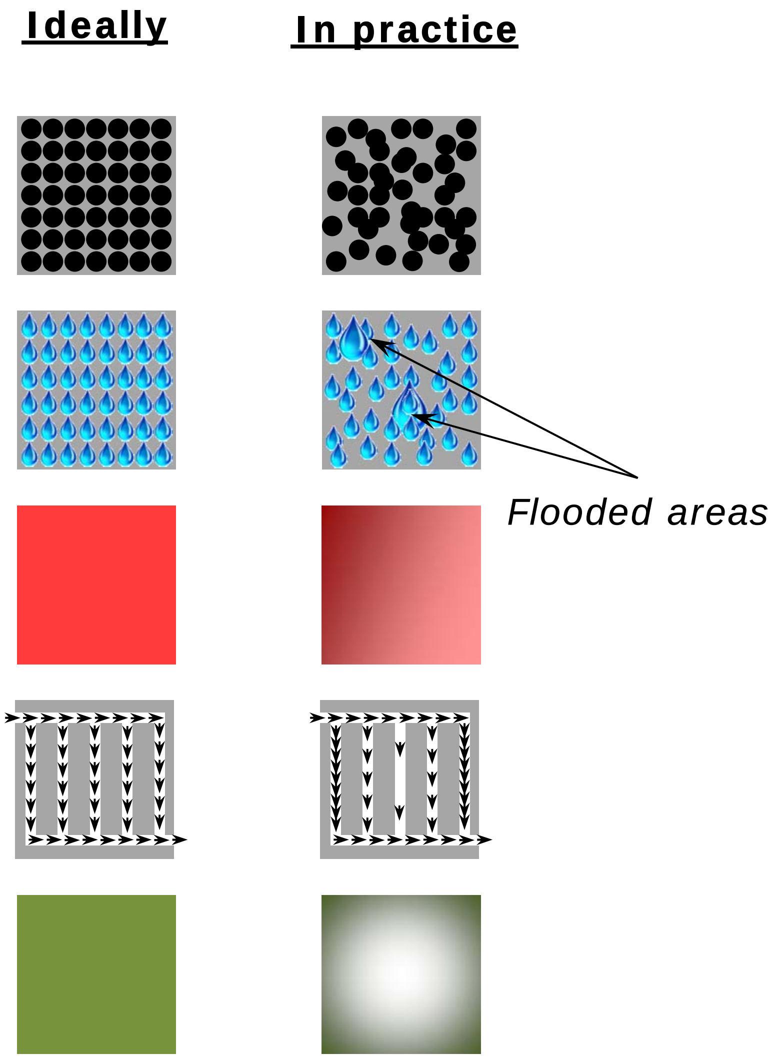
- Activation losses → Catalyst properties
- Ohmic losses → Electrolyte properties
- Concentration losses → Reagent concentration



❑ **In practice, current density distribution is not uniform**

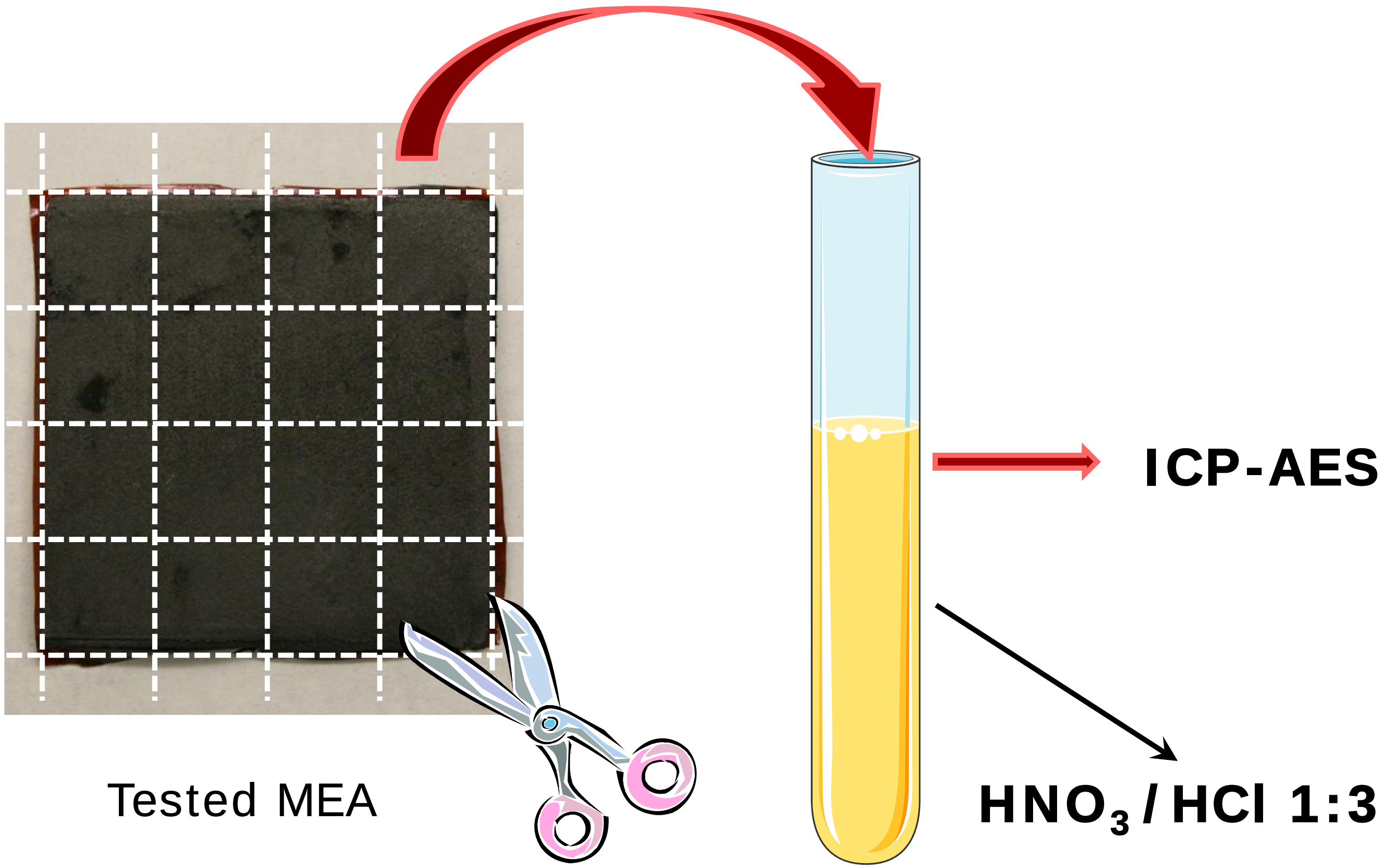
➢ Current density distribution in a PEM fuel cell

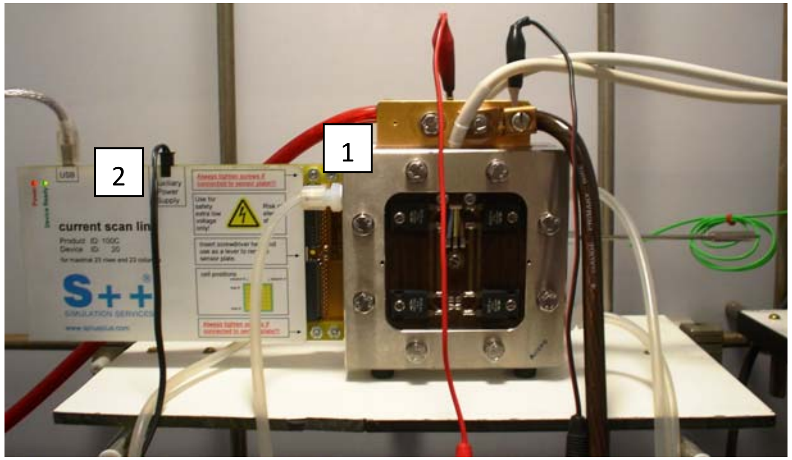
- **Catalyst distribution**
  - Electrode manufacturing
  - Particle agglomeration
- **Water distribution**
  - Flooding
- **Temperature distribution**
  - Design
- **Reagent distribution**
  - Mass transport
  - Flow channels
- **Conductivity distribution**
  - Assemblage



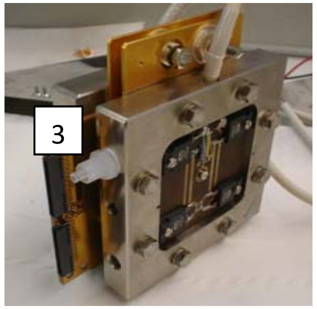
Post-mortem analysis

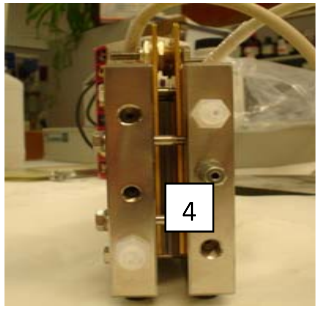
- **Analysis of Pt and P content**

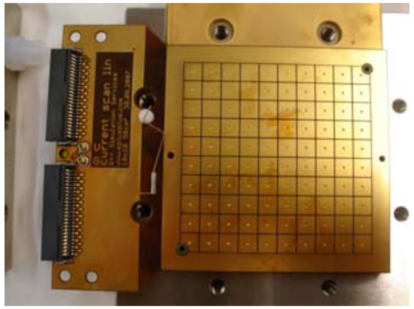




Element	Description
1	Fuel cell
2	Data acquisition board
3	Sensor plate
4	End plates







- ❑ Array of 10 x 10 sensors. Each sensor measures the electric current flowing through it.
- ❑ Measurement principle: varirion of the magnetic permeability