Active concentration sensor developments for tritium balance dynamic control strategies in ITER

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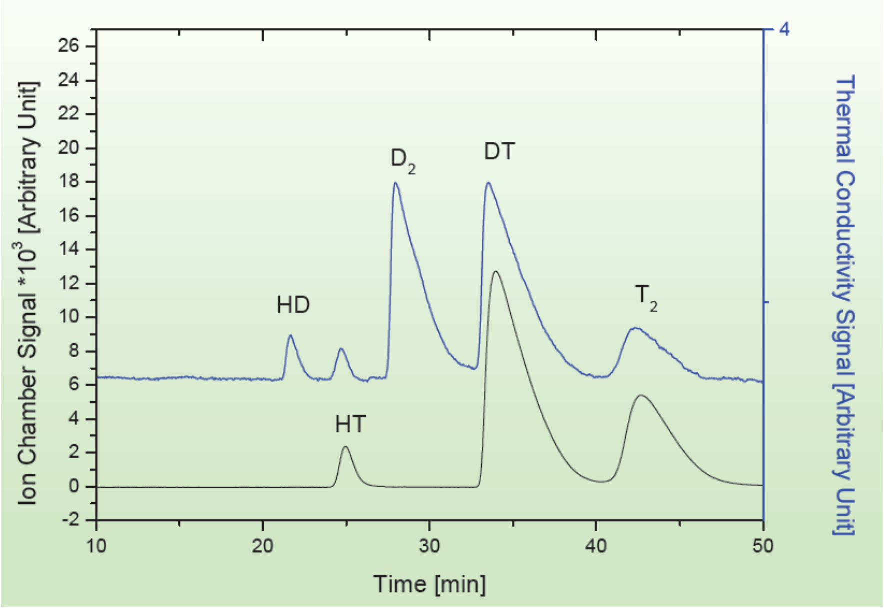
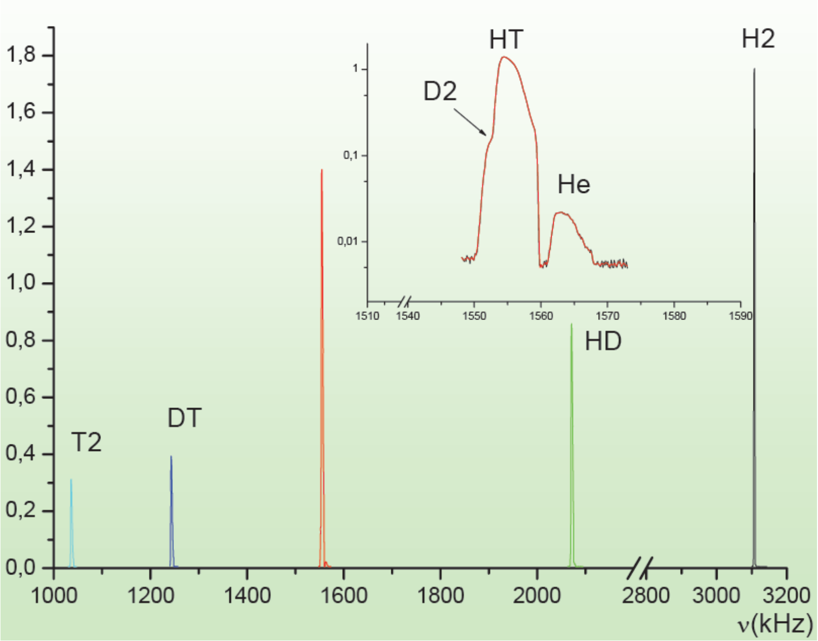
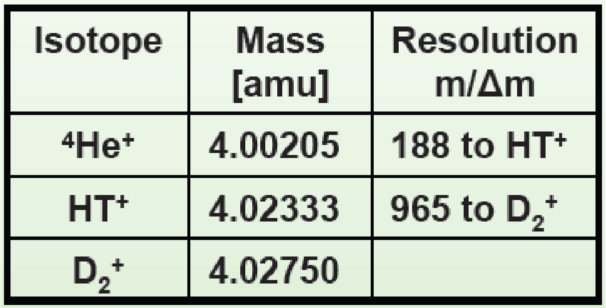
Analytical techniques for tritium determination

- Gas Chromatography (CG): method to separate components of a fluid mixture in a column by selective mixing with a carrier



Mass Spectroscopy: Omegatron type ion cyclotron resonance mass spectrometers or Fourier Transform Mass Spectrometry

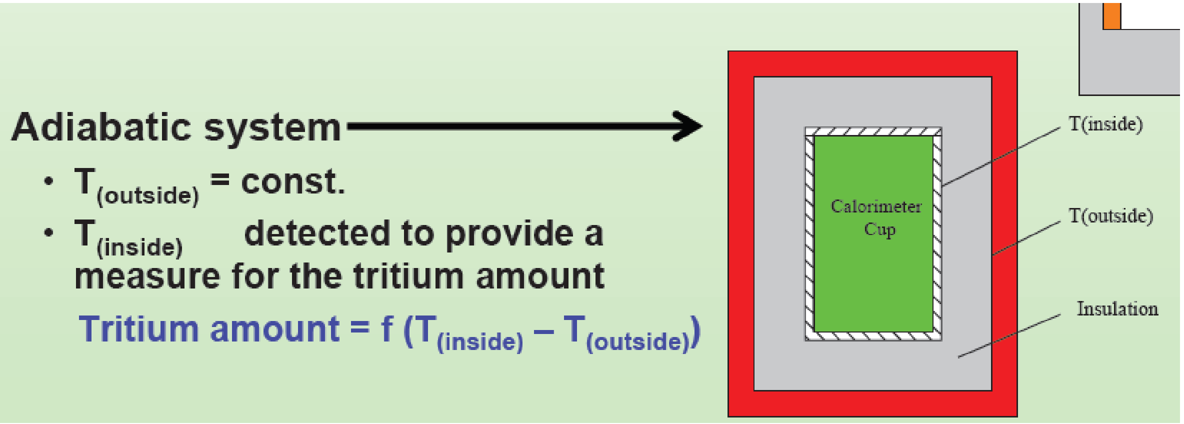




Isotope	Mass [amu]	Resolution m/Δm
$^4He^+$	4.00205	188 to HT^+
HT^+	4.02333	965 to D_2^+
D_2^+	4.02750	

Resolution required for separation

- Calorimetry: Thermal power produced by tritium ß-decay is used to measure the amount of tritium



Adiabatic system

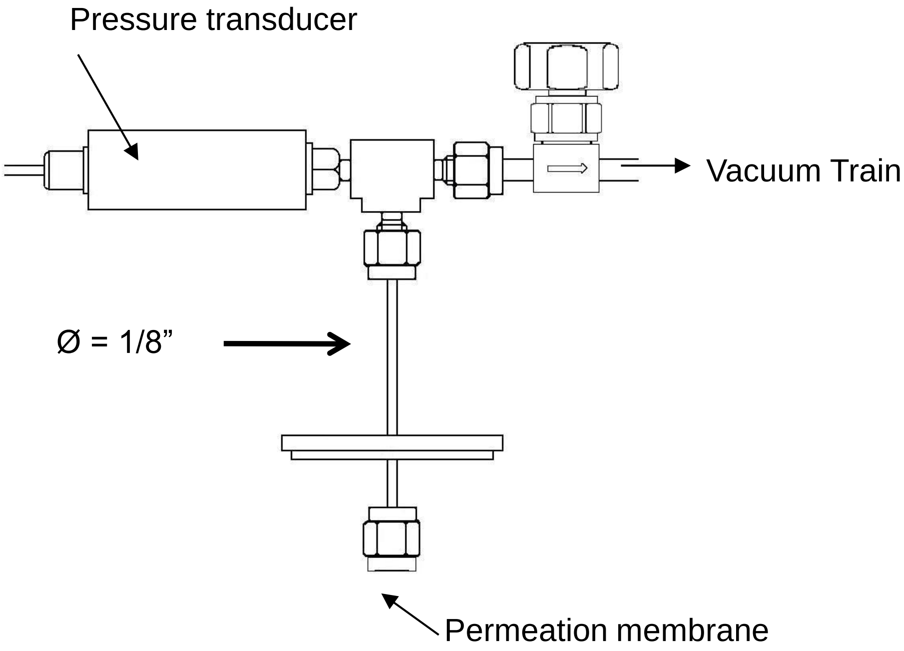
- $T_{(outside)}$ = const.
- $T_{(inside)}$ detected to provide a measure for the tritium amount

Tritium amount = $f\,(T_{(inside)} – T_{(outside)})$

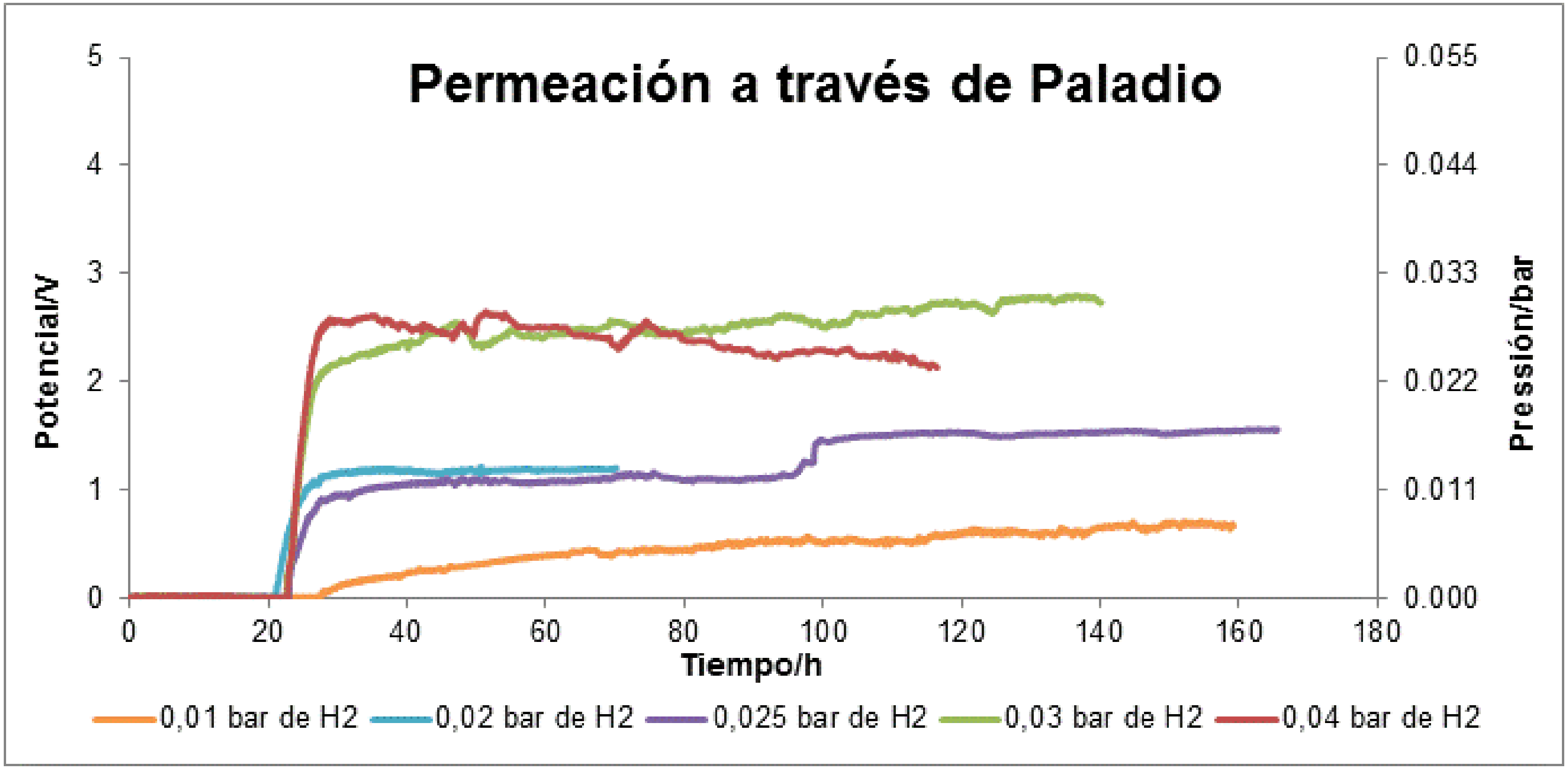
- Liquid scintillation counting: Conversion of beta particle energy by primary and secondary scintillators into light.
    - Primary scintillator provides mainly ultraviolet light
    - Secondary scintillator provides blue light
    - Liquid samples
    - Gaseous samples
    - Solid samples

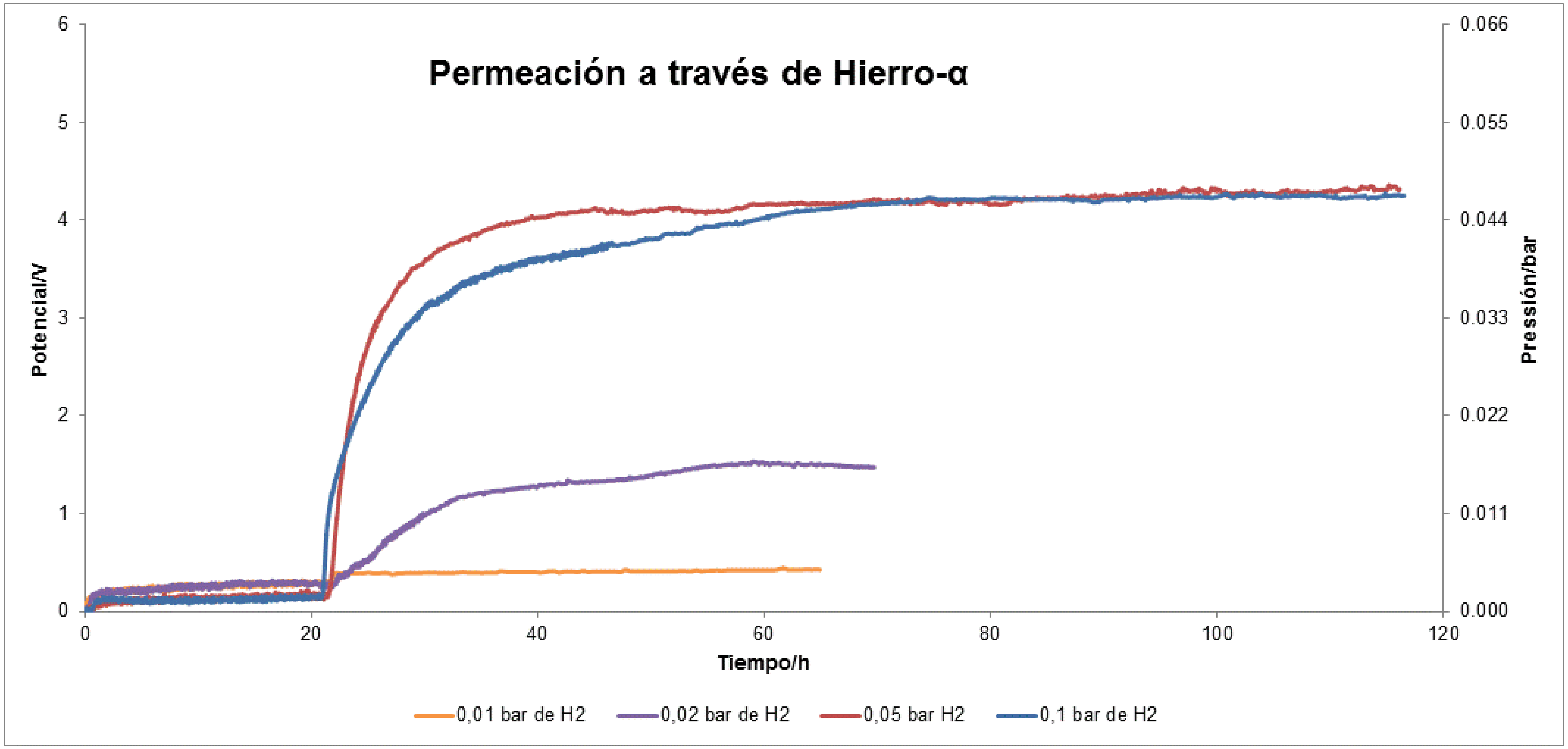
- Tritium (hydrogen) sensors: based on two different concepts, T diffusion-based membrane sensors and electrochemical sensors

- H diffusion-based membrane sensors:
  - ✓ Experimental set-up



  - ✓ Membrane materials: Pd, α-Fe


Permeación a través de Paladio
Potencial/V
Presión/bar
Tiempo/h
0
1
2
3
4
5
0.000
0.011
0.022
0.033
0.044
0.055
0
20
40
60
80
100
120
140
160
180
0,01 bar de H2
0,02 bar de H2
0,025 bar de H2
0,03 bar de H2
0,04 bar de H2


Permeación a través de Hierro-α
Potencial/V
Presión/bar
Tiempo/h
0
1
2
3
4
5
6
0.000
0.011
0.022
0.033
0.044
0.055
0.066
0
20
40
60
80
100
120
0,01 bar de H2
0,02 bar de H2
0,05 bar H2
0,1 bar de H2

Electrochemical H sensors

Electrochemical sensors based on solid state electrolytes can be used for hydrogen monitoring. Their characteristics are optimum for these type of measurements:

- ✓ Short response time
- ✓ Elevated working temperatures
- ✓ Resistance against harsh environments

Perovskite type ceramic materials can be used as a proton selective conducting solid state electrolyte.

- Two different concepts:
  - ✓ Potentiometric sensors:
    - Based on proton conductive ceramics
    - Non-commercial ceramics
    - H electrochemical concentration cell

$$H_2(p_{H_2,I}),\ Pt\,|\,Electrolyte\,|\,Pt,\ \ H_2(p_{H_2,II})$$

$$V_{EMF} = -\frac{RT}{2F}\ln\frac{p_{H_2,I}}{p_{H_2,II}}$$

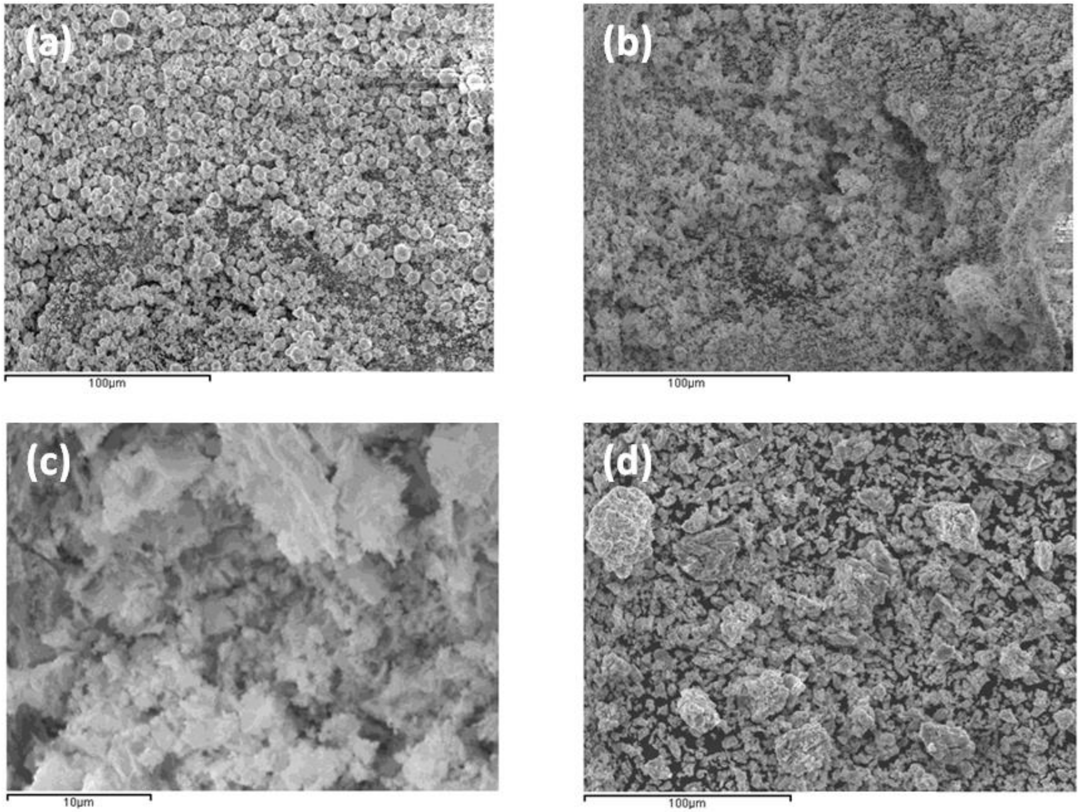
✓Amperometric sensors:

- Based on proton conductive ceramics
- Non-commercial ceramics
- H ionic conduction through the ceramic

$$\mathrm{i(t)} = \frac{n \cdot F \cdot A \cdot D_o^{1/2} \cdot C_o}{\pi^{1/2} \cdot t^{1/2}}$$

- Perovskite type ceramics synthesised

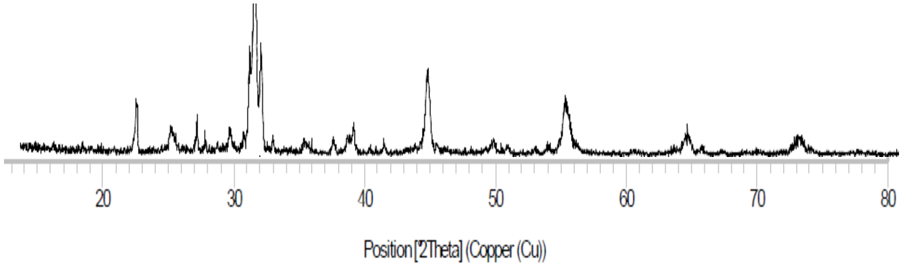
Formulation	Formulation
$Ba_3Ca_{1.18}Nb_{1.82}O_{9-\delta}$	$SrCe_{0.9}Y_{0.1}O_{3-\alpha}$
$CaZr_{0.9}In_{0.1}O_{3-\alpha}$	$Sr_3Fe_{1.8}Co_{0.2}O_{7-\delta}$
$Sr_3CaZr_{0.9}Ta_{1.1}O_{8.55}$	$BaCe_{0.6}Zr_{0.3}Y_{0.1}O_{3-\delta}$
$SrCe_{1-x}Yb_xO_{3-\delta}$	$Sr(Ce_{0,9}\text{-}Zr_{0,1})_{0,95}Yb_{0,05}O_{3-\alpha}$
$BaCeO_3$	$BaZr_{0,9}Y_{0,1}O_3$
$BaCe_{0.9}Y_{0.1}O_{3-\alpha}$	$Sr(Ce_{0,6}\text{-}Zr_{0,4})_{0,9}Y_{0,1}O_{3-\alpha}$



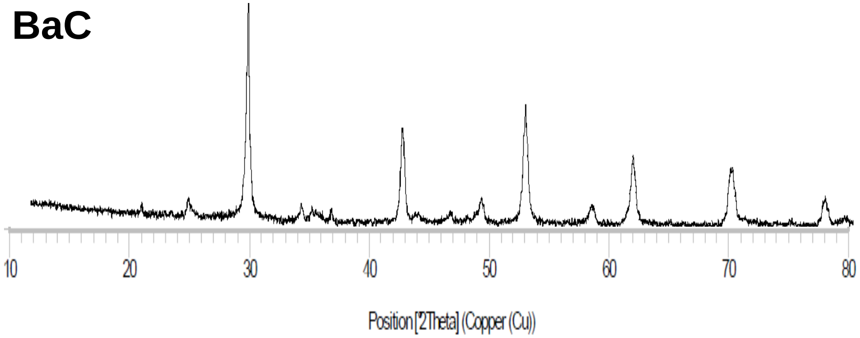
SEM images of BaZrY (a), BaCeZrY (b), SrCeZrY (c) and SrFeCo (d) in powder form after sintering at 1300°C.

- A single perovskite-type phase was confirmed for all ceramic elements by X-ray diffraction (XRD)

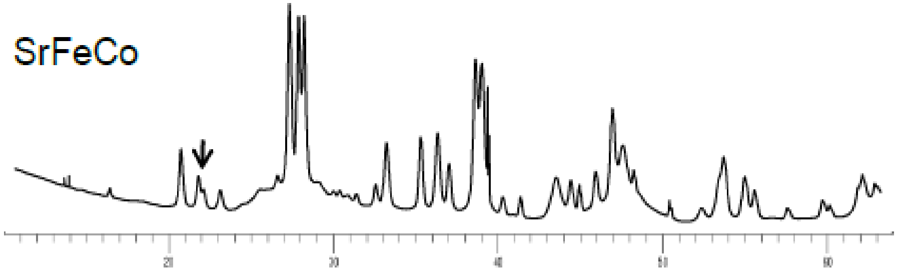
BCN18



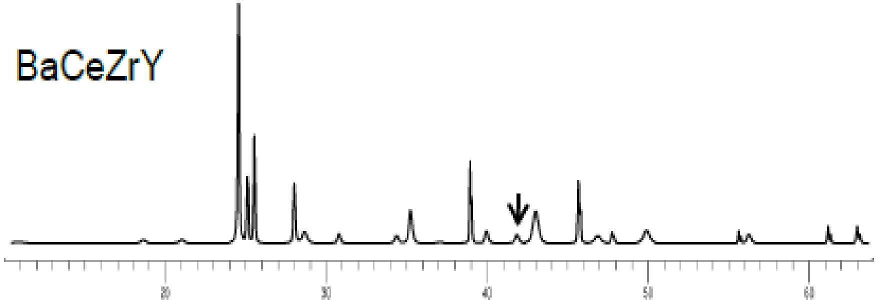
BaC



SrFeCo



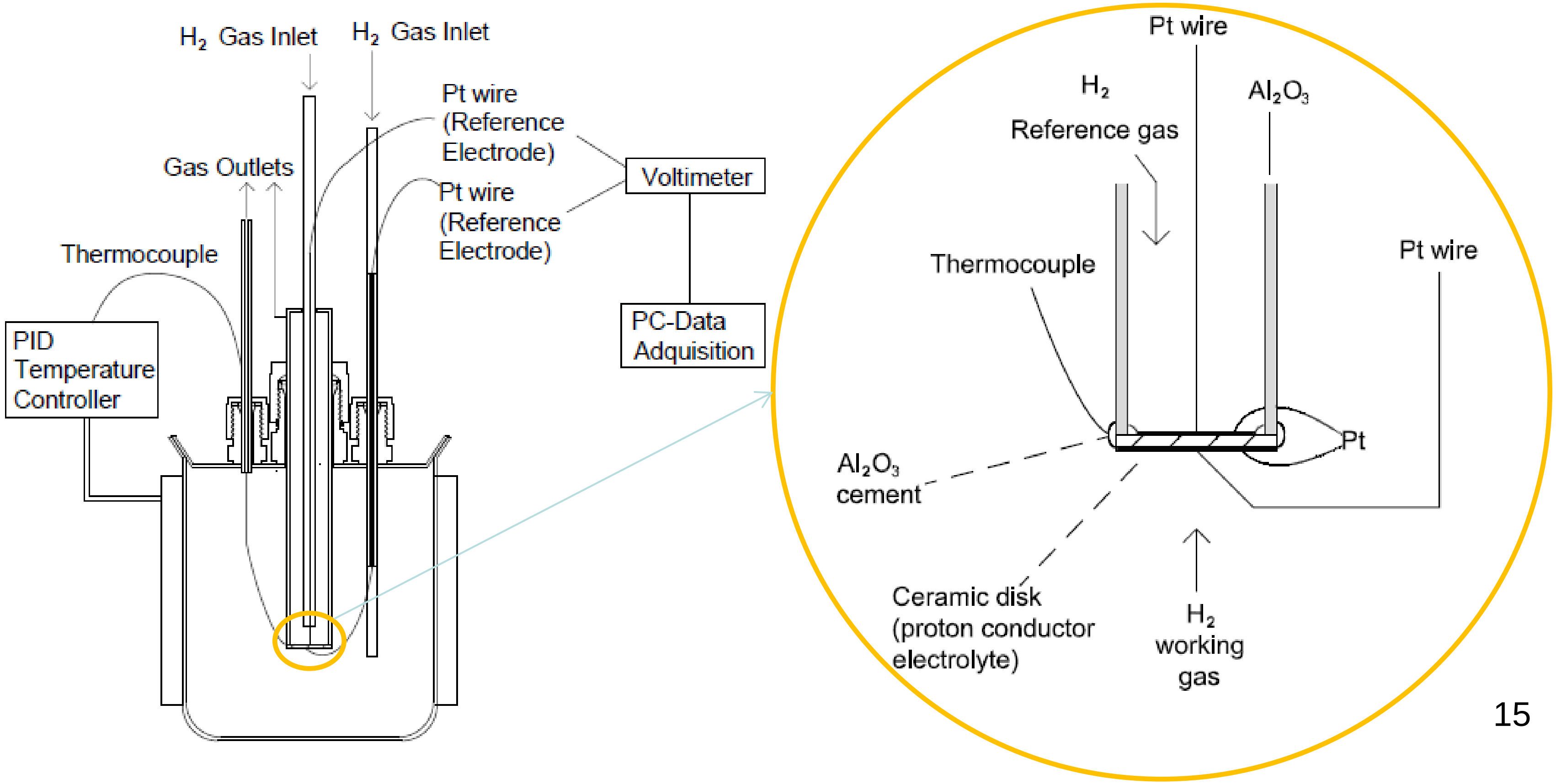
BaCeZrY



Experimental set up to test the proton conducting ceramic elements

- Reactor design

H_2(Ref.)||solid state electrolyte||H_2(Work.)



Potentiometric Sensors. Electrochemical Results

- Gases
  - Reference electrode

    Calibration mixture: Ar+1000 ppm/v H_2

    P_{H2} = 0.001 bar / 0.0001 bar
  - Working electrode

    Gases Mixture: Ar + H_2

- Working temperatures
  - T=500 ºC
  - T=600 ºC

- Electrochemical potentials calculated using the Nernst equation

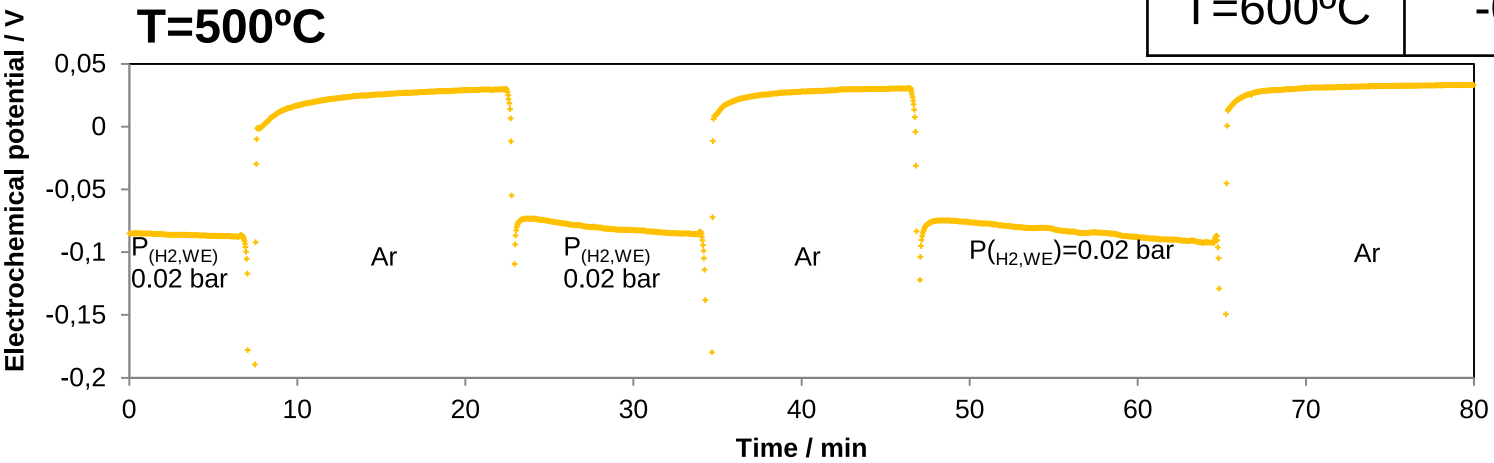
$P_{(H2,RE)}$=0.001bar

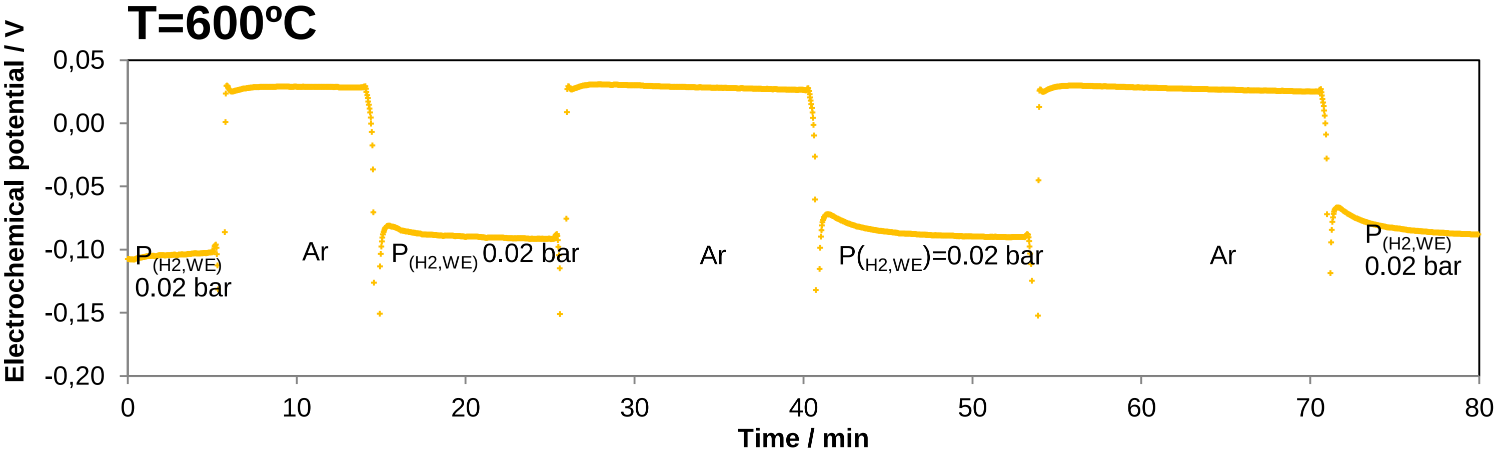
	P_{H2}=0.005 bar	P_{H2}=0.02 bar	P_{H2}=0.05 bar	P_{H2}=0.1 bar
T=500ºC	-0.054 V	-0.100 V	-0.130 V	-0.153 V
T=600ºC	-0.060V	-0.112 V	-0.147 V	-0.173 V

$Ba_3Ca_{1.18}Nb_{1.82}O_{9-\delta}$ – BCN18

$P_{H2,RE}$ = 0.001 bar

	P_{H2}=0.02 bar
T=500ºC	-0.100 V
T=600ºC	-0.112 V

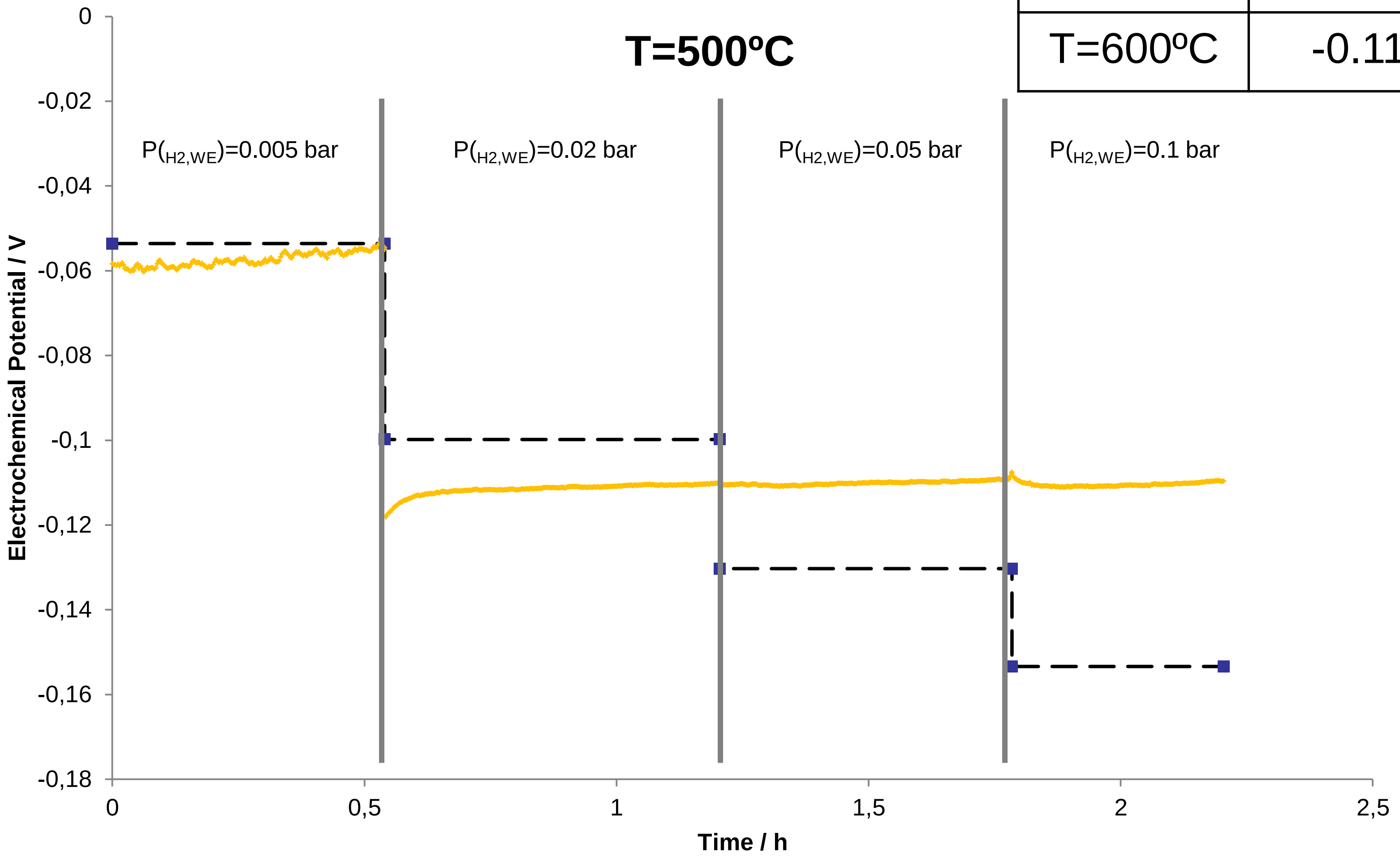




$Ba_3Ca_{1.18}Nb_{1.82}O_{9-\delta}$ – BCN18

$P_{H2,RE}$ = 0.001 bar

	P_{H2}=0.02 bar
T=500ºC	-0.100 V
T=600ºC	-0.112 V

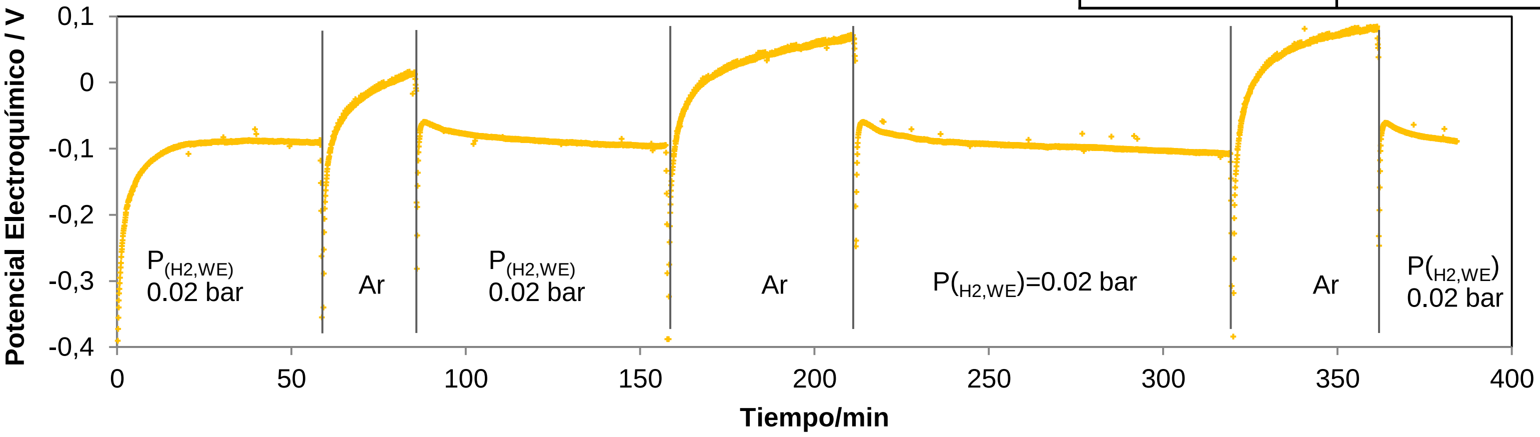


$BaCeO_3$ – BaC

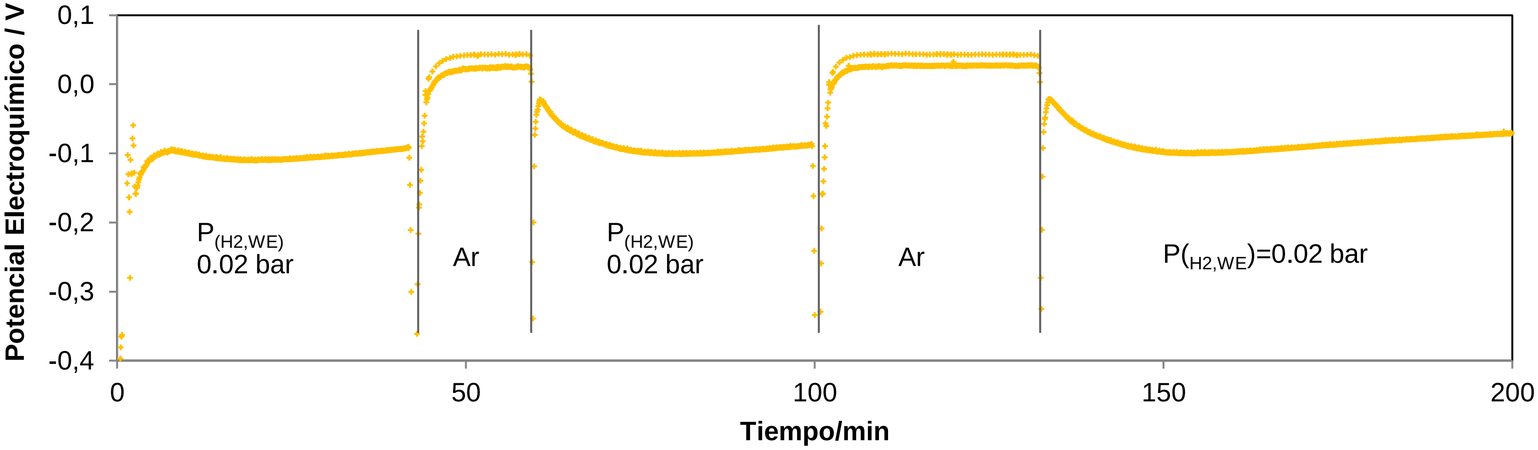
$P_{H2,RE}$ = 0.0001 bar

	P_{H2}=0.02 bar
T=500ºC	-0.176 V
T=600ºC	-0.199 V

T=500ºC



T=600ºC

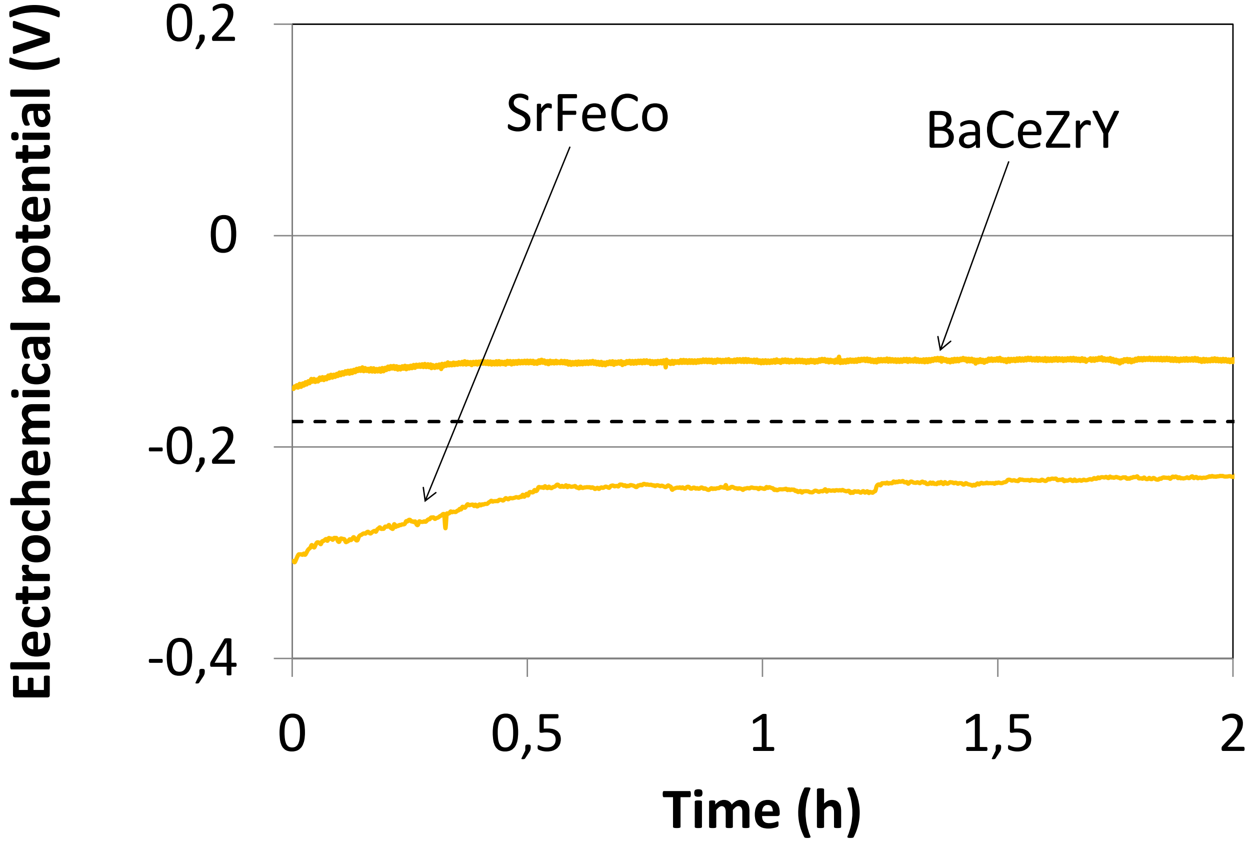


SrFeCo and BaCeZrY

$P_{H2,RE}$ = 0.0001 bar

	P_{H2}=0.02 bar
T=500ºC	-0.176 V
T=600ºC	-0.199 V

T=500ºC



Selected Ceramics

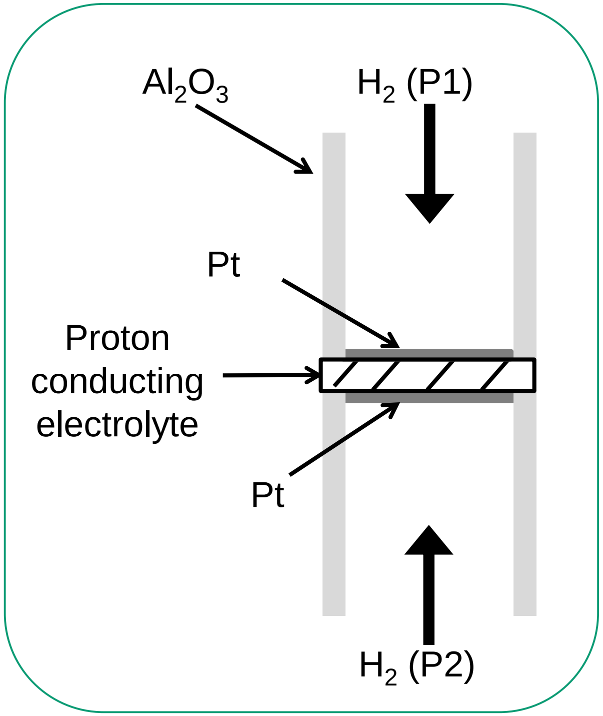
Highly Recommended

$Sr_3CaZr_{0.9}Ta_{1.1}O_{8.55}$	SCZT85
$SrCe_{0.9}Y_{0.1}O_{3-\alpha}$	SCY
$Sr_3Fe_{1.8}Co_{0.2}O_{7-\delta}$	SrFeCo
$BaCe_{0.6}Zr_{0.3}Y_{0.1}O_{3-\delta}$	BaCeZrY

Recommended

$Sr(Ce_{0,9}Zr_{0.1})_{0.95}Yb_{0.05}O_{3-\delta}$	SrCeZrYb
$BaCeO_3$	BaC
$BaZr_{0,9}Y_{0,1}O_3$	BaZrY
$Ba_3Ca_{1.18}Nb_{1.82}O_{9-\delta}$	BCN18
$CaZr_{0.9}In_{0.1}O_{3-\alpha}$	CZIn
$SrCe_{1-x}Yb_xO_{3-\delta}$	SCYb

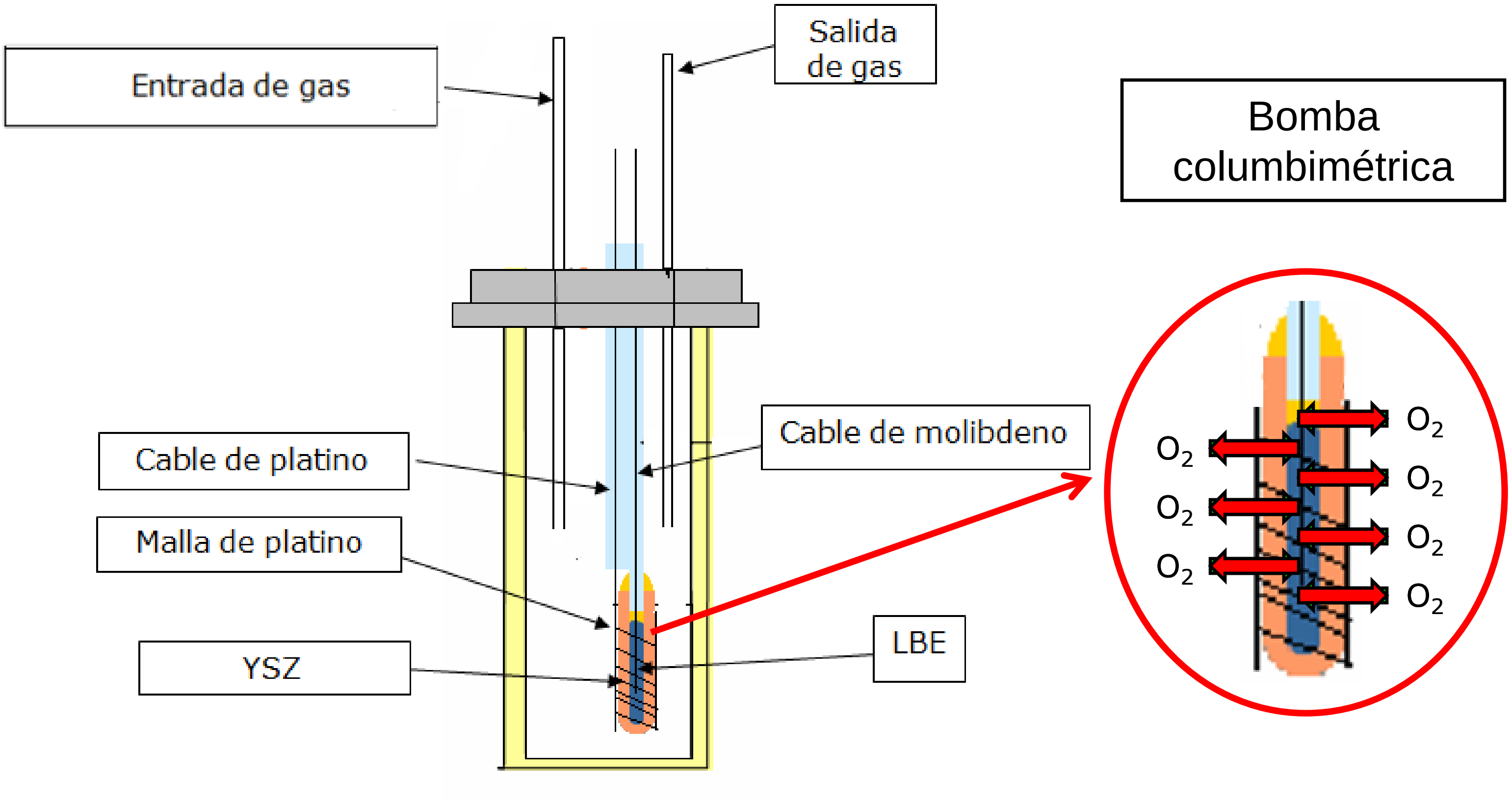
Amperometric H sensors



- Based on Coulometry
- Cottrell equation: Relationship electrochemical current vs concentration

$$\mathrm{i(t)} = \frac{n \cdot F \cdot A \cdot D_o^{1/2} \cdot C_o}{\pi^{1/2} \cdot t^{1/2}}$$

Coulometry experiments



Entrada de gas

Salida de gas

Bomba columbimétrica

Cable de molibdeno

Cable de platino

Malla de platino

YSZ

LBE

O_2

O_2

O_2

O_2

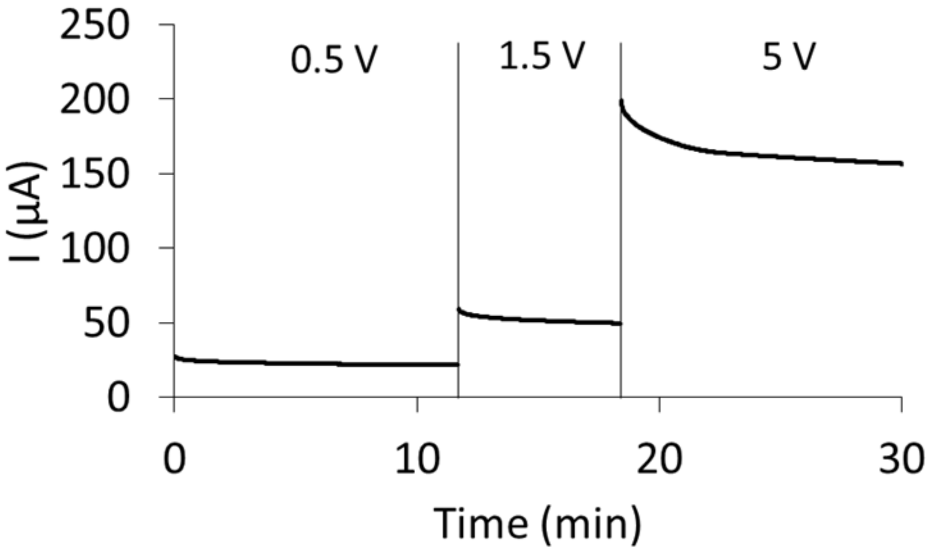
O_2

O_2

O_2

- Experimental set-up allowed working with controlled environments:
  - Solid Electrolyte $Sr(Ce_{0,9}Zr_{0.1})_{0.95}Yb_{0.05}O_{3-\delta}$
  - 500ºC, 575ºC and 650ºC
  - Applied potentials: 0.5 V, 1.5 V and 5 V
  - $P_{H2,anode} = 0.02$ bar
  - $P_{H2,cathode} = 0.010$ bar

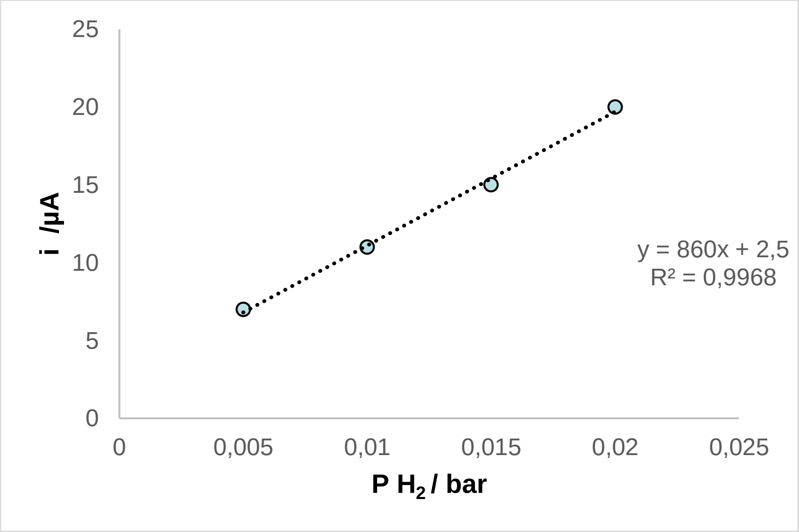
Amperometric Sensors. Electrochemical Results



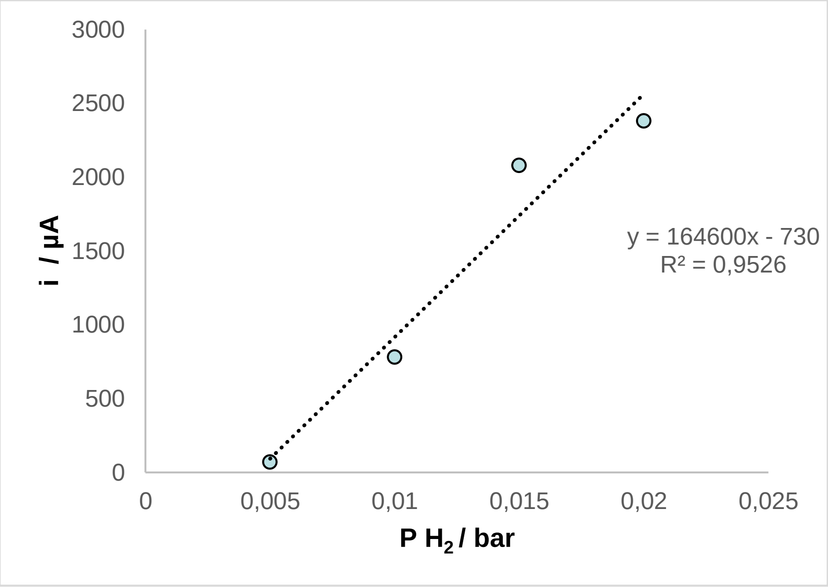
Amperometric records at 500ºC

Temperature / ºC	Applied Potential / V	Corrected Current / µA
500	0.5	4
	1.5	11
	5	40
575	0.5	131
	1.5	320
	5	780
650	0.5	960
	1.5	2840
	5	6600

500 ºC 1.5 V



575 ºC 5 V



Conclusions

- Solid state electrolytes (proton conducting) have been synthetized, characterized and tested in a potentiometric hydrogen gas sensor.
- Selected ceramics show small deviation between theoretical and experimental data (<100mV).
- Amperometric mode is an alternative to the potentiometric mode for very low hydrogen partial pressures.
- Electrochemical sensors can be considered as an promising tool for tritium control.

PROTOCODAC PROJECT

PROCON SYSTEMS

UPC

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PROTOCODAC PROJECT

- The aim of project **PROTOCODAC**, is for it to become a technological demonstration of a prototyping model of experimental instruments in conventional control systems suitable for advanced nuclear facilities.

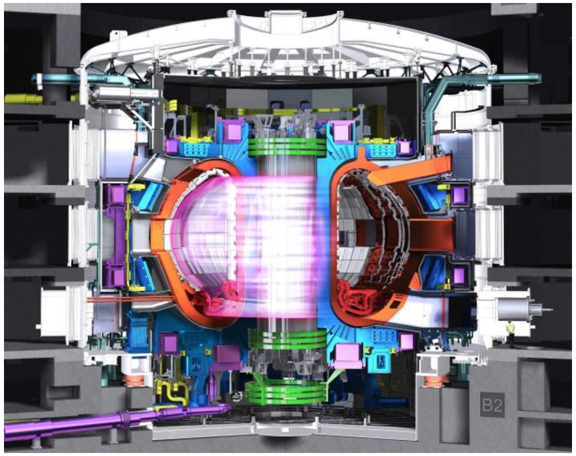
- This application will be valid for a wide range of scientific and nuclear installations, but for the technical feasibility assessment, the case of the ITER plant **Test Blanket Modules (TBM)** will be applied.

- The project is being developed in collaboration with the company **Procon Systems**, the **Universitat Politècnica de Catalunya (UPC)** and the **Institut Químic de Sarrià (IQS)**.

- The origin of the project is based on two premises:

  1 Innovative technical solutions to the monitoring of active concentrations of tritium.

  2. New developments in the field of the predictive simulation of tritium concentrations.



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PROTOCODAC PROJECT

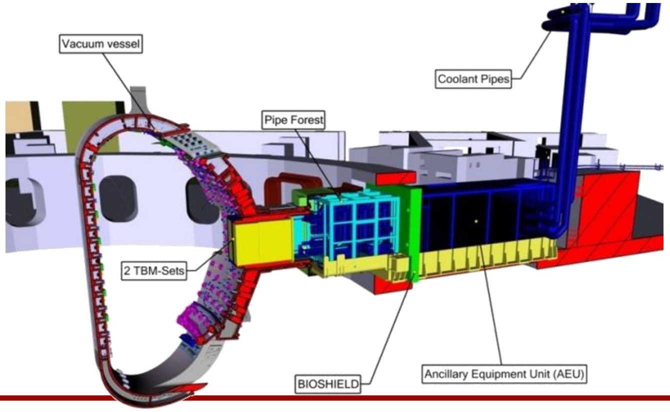
- The objectives of the project are to:

    1. Establish and lay the foundations of the conceptual design of: the Control System, Data Acquisition, and Monitoring & Diagnostic Instrumentation for the ITER TBM systems.

    2. Anticipate the key developments of the detailed engineering of such systems with regard to the strategic perspective of a future supply of principal facilities with TBM control

    3. Review existing Monitoring and Diagnostics solutions from the perspective of integration with the CODAC ITER TBM system.

    4. Contribute to specific developments of Instrumentation (on-line and real-time tritium concentration sensors) and their impact on new control strategies.



Acknowledgments

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