



# Differential Electrochemical Mass Spectrometry (DEMS) as a tool for reactions study. The case of hydrogen oxidation and methanol reforming.



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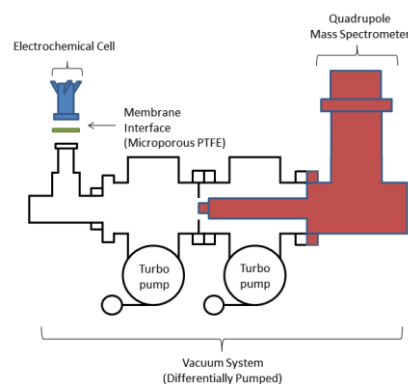
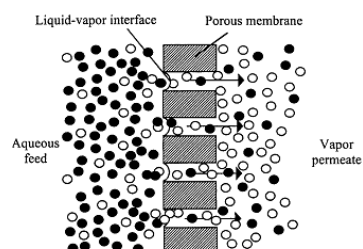


Project ARISTEIA No 3073



## What is DEMS

DEMS is the combination of electrochemical half-cell experimentation with mass spectrometry. This allows the in situ, mass resolved observation of gaseous or volatile electrochemical reactants, reaction intermediates and/or products.



The instrument essentially consists of three crucial components: an electrochemical half-cell, a PTFE membrane interface, and a vacuum system including the quadrupole mass spectrometer (QMS).

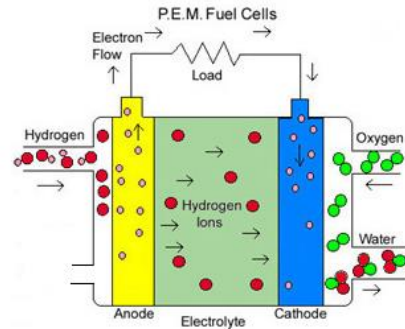


## What is DEMS

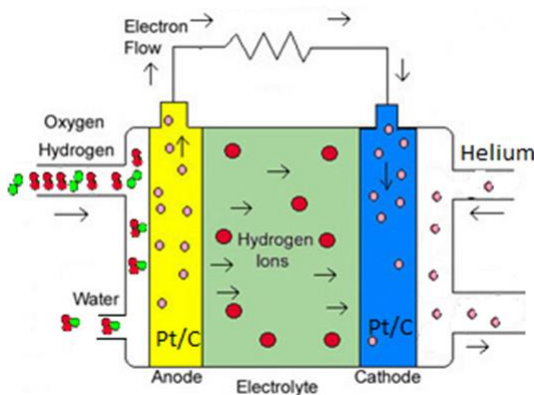


In this study we combine DEMS with a fuel cell

We start with a typical proton membrane electrochemical cell configuration and we can connect the MS either in **cathode** or **anode**. We can alter the MEAs, the feed and we can perform different types of chemical reactions.



## The Hydrogen – Oxygen Reaction



### Anode

Pt/C 0.5 mg/cm<sup>2</sup>

Feed H<sub>2</sub>/O<sub>2</sub>/He **saturated with H<sub>2</sub>O**

Total Flow 100 – 400 mL/min with different ratios of H<sub>2</sub>:O<sub>2</sub>

### Cathode

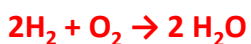
Pt/C 0.5 mg/cm<sup>2</sup>

Feed He saturated with H<sub>2</sub>O

Total Flow 60 mL/min

### Electrolyte

Nafion 117

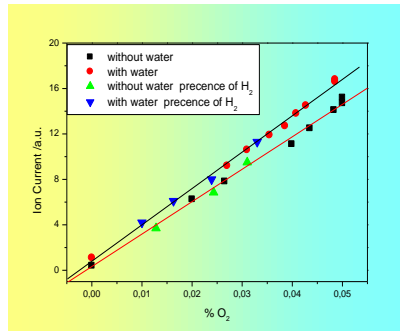
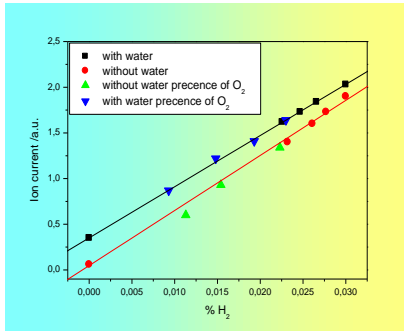




# The Hydrogen – Oxygen Reaction



## Calibration Curves



The presence of  $H_2O$  influences the signal of  $H_2$  and/or  $O_2$

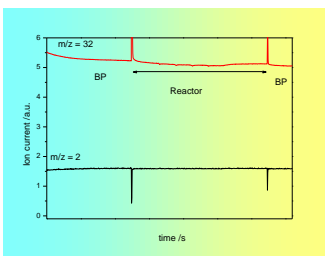
Simultaneous presence of  $H_2$  and  $O_2$  does not affect their response factors



# The Hydrogen – Oxygen Reaction

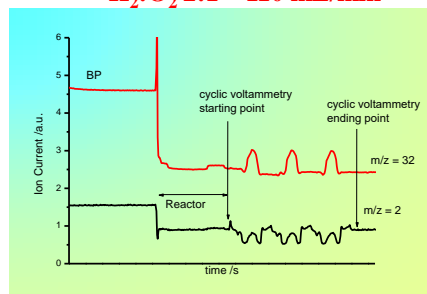


No reaction without catalyst

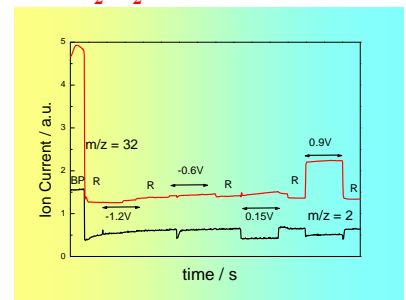


In the presence of Pt the reaction is very fast and vigorous.

$H_2:O_2$  2:1 110 mL/min



$H_2:O_2$  2:1 110 mL/min



For catalytic rates always

$$r_{H_2} = 2 r_{O_2}$$



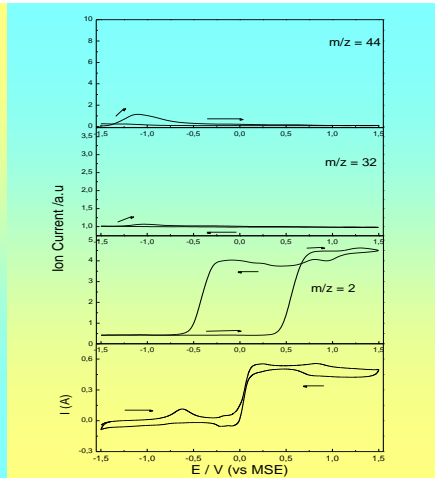
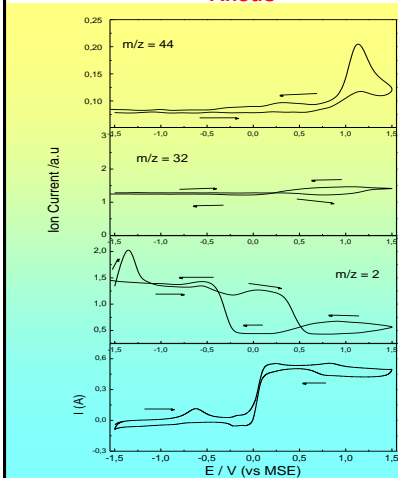
## The Hydrogen – Oxygen Reaction



**H<sub>2</sub>:O<sub>2</sub> 6.4:1 110 mL/min**

**Anode**

**Cathode**



Positive going scan

**Anode:**

Increase of  $I$  is followed by a decrease of the ion signal of  $m/z=2$  (H<sub>2</sub>) for H<sub>2</sub>:O<sub>2</sub> 6.4:1. The opposite behavior is observed for the signal of  $m/z=32$  (O<sub>2</sub>). The sharp increase of the signal of  $m/z=44$  (CO<sub>2</sub>) can be attributed to the oxidation of the carbon cloth (which is part of the anodic electrode) at potentials higher than 1V.

**Cathode:**

The opposite behavior is observed, if we follow the cathodic gases.



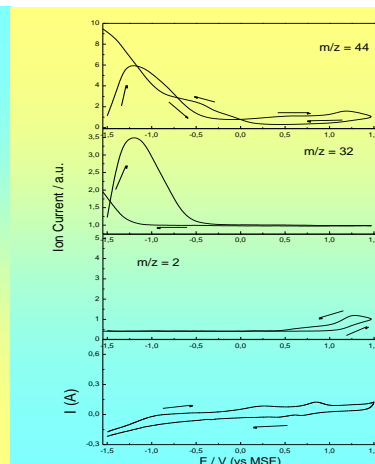
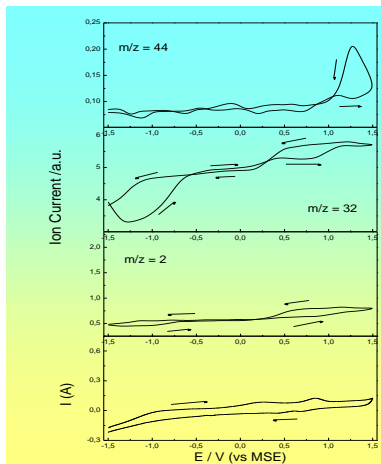
## The Hydrogen – Oxygen Reaction



**H<sub>2</sub>:O<sub>2</sub> 1:1 110 mL/min**

**Anode**

**Cathode**



Positive going scan

**Anode:**

In the case of H<sub>2</sub>:O<sub>2</sub> 1:1,  $I$  and  $m/z = 2$  changes are negligible due to the full conversion of H<sub>2</sub>. Increase of  $I$  is followed by an increase of the signal of  $m/z=32$  (O<sub>2</sub>). The sharp increase of the signal of  $m/z=44$  (CO<sub>2</sub>) can be attributed to the oxidation of the carbon cloth (which is part of the anodic electrode) at potentials higher than 1V.

**Cathode:**

The opposite behavior is observed, if we follow the cathodic gases.

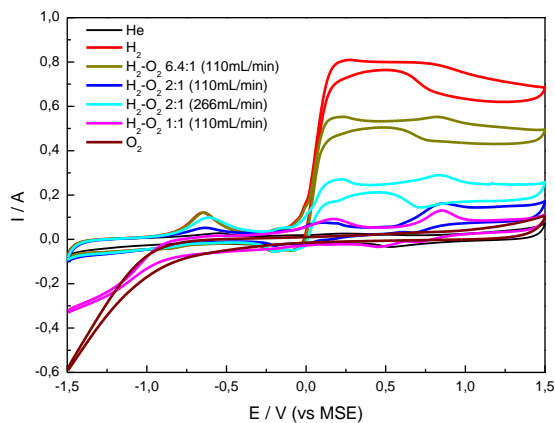




## The Hydrogen – Oxygen Reaction



### Cyclic Voltammetry under different reaction conditions



The cyclic voltammograms (CVs) under various reaction conditions are very different. The faradaic currents observed under cyclic voltammetry are dramatically affected both by the  $\text{H}_2:\text{O}_2$  ratio and the flowrate of the reactants. Higher flowrates or higher reducing mixtures result in lower values of hydrogen consumption and thus higher amounts of available hydrogen to be transferred to the cathodic side through the polymeric membrane



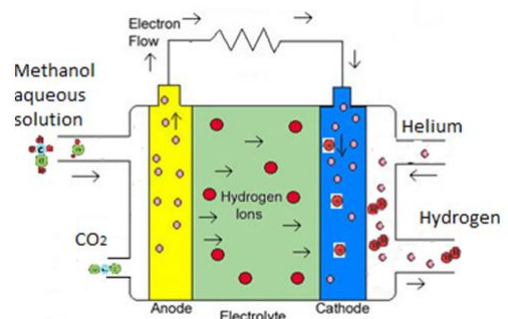
## Electrochemical reforming of methanol



The second case is Methanol electrolysis. With the MS we monitor the cathode.

The anode feed is a methanol aqueous solution ( $C=0.1\text{M} - 3\text{M}$ ).  
Temperature ranges between  $25^\circ\text{C} - 60^\circ\text{C}$ .

We used PtRu based electrodes as anodes and carbon supported Pt based electrodes as cathodes.

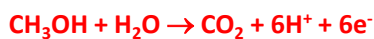




## Electrochemical reforming of methanol



During the electrolysis process protons are produced in anode via:

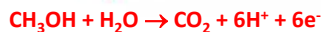
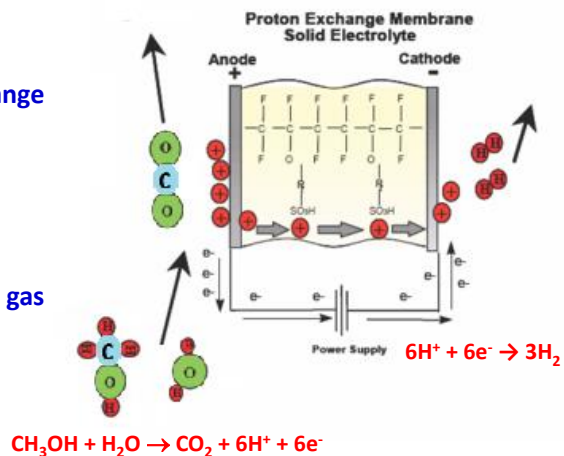


and transferred to the cathode through the proton exchange membrane.

Hydrogen is then evolved at the cathode via:



The membrane separates the hydrogen from the anode gas mixture resulting in pure  $\text{H}_2$  production.



## The Catalyst - Why Pt-Ru-TiO<sub>2</sub>?



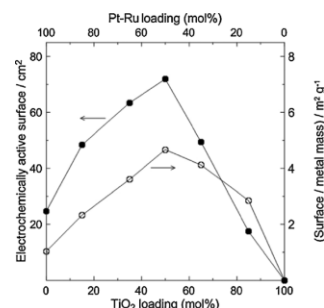
- Pt is the most effective metal for breaking the C-H bonds during the adsorption step
- Problem with the strongly adsorbed CO
- The OH adsorption from water dissociation is necessary to oxidize the strongly adsorbed CO species.

Thus, it is necessary to introduce another metal with the ability to decrease the coverage of CO adsorbed species and increase the coverage of OH species. This metal is **Ru**.

**Modification of Pt (or PtRu) anodes with TiO<sub>2</sub>**

- helps in mitigating the aggregation of Pt particles
- protects the Nafion membrane
- decreases the anode cost
- Increases the dispersion of Pt and/or Ru nanoparticles

B. Hasa, et al., Effect of TiO<sub>2</sub> Loading on Pt-Ru Catalysts During Alcohol Electrooxidation, *Electrochim. Acta* 179 (2015) 578





## The electrodes used



### 3 MEAs prepared using three different anodes

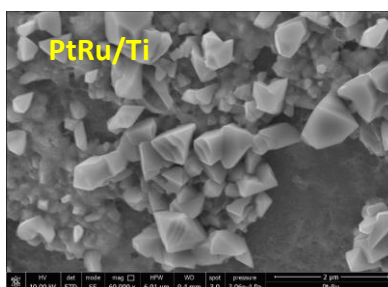
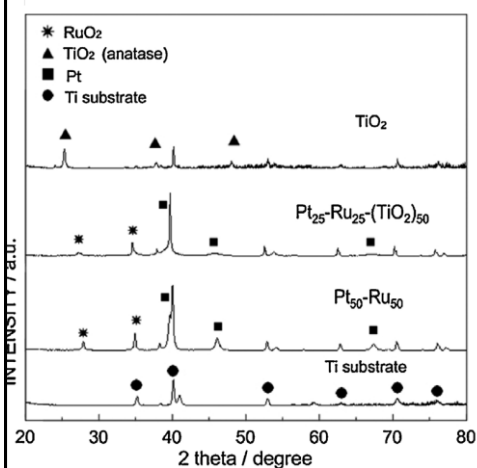
**Anodes:** 2 home-made PtRu/Ti and PtRuTiO<sub>2</sub>/Ti  
1 commercial PtRu/C

a/a	anodic electrode	Total metal loading	SSA (m <sup>2</sup> /g)
1	PtRu/Ti/C	1.45 mg cm <sup>-2</sup>	3.8
2	PtRuTiO <sub>2</sub> /Ti/C	1.07 mg cm <sup>-2</sup>	6.9
3	PtRu <sub>comm</sub> /C	1,0 mg cm <sup>-2</sup>	2.7

**Cathode:** Pt/carbon cloth 0.5 mg cm<sup>-2</sup>

**Electrolyte:** Nafion 117 membrane.

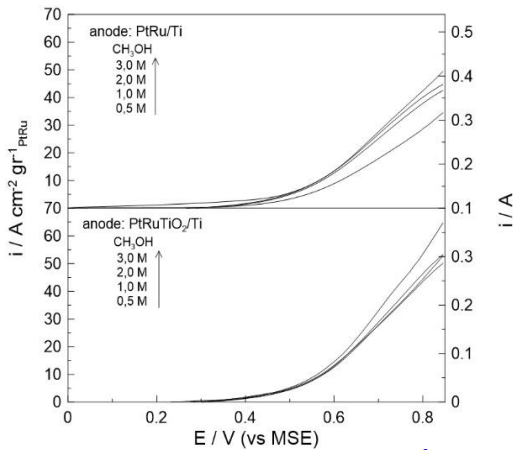
## XRD and SEM results



XRD and SEM results verify the lower dimensions of nanoparticles Pt/Ru in the presence of TiO<sub>2</sub>

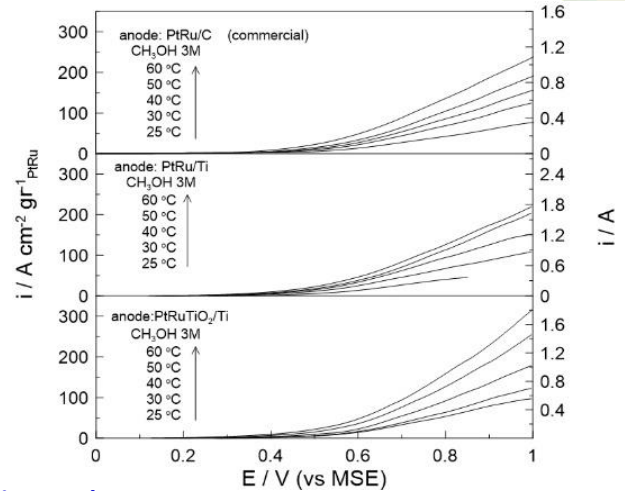


## Electrocatalytic activity



Current density (i.e. electrocatalytic activity) slightly increases with concentration

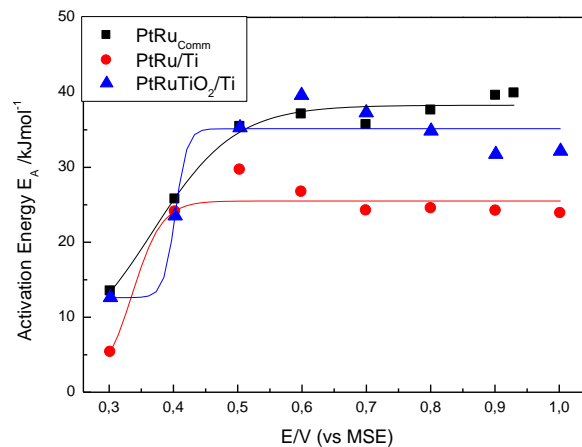
The most effective catalyst is the **PtRuTiO<sub>2</sub>/Ti**



Current density (i.e. electrocatalytic activity) increases with temperature



## Electrocatalytic activity



At about 0.3 -0.4 V there is a sharp increase in  $E_A$ . For higher values of potential the  $E_A$  is constant. Lower potential: the value of  $E_A$  indicates physical phenomena. The  $E_A$  for PtRu/Ti is rather low probably due to significant mass transfer phenomena.





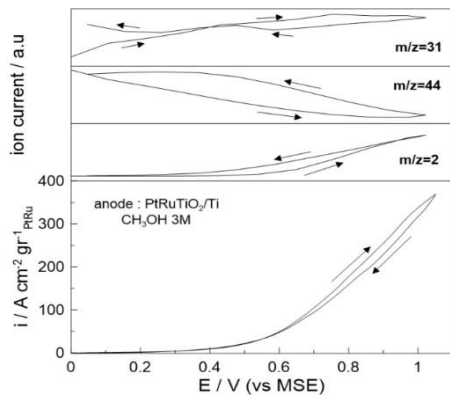
## DEMS

Using DEMS, we can record the gaseous or volatile compounds with very little time delay. Exploiting DEMS data, it is possible to give answers on the mechanism of the reaction. In this study we **monitor the cathode**.



### Typical Mass Spectrometer Cyclic Voltammograms, MSCVs

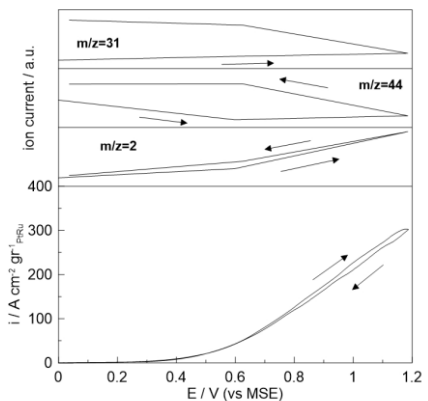
PtRuTiO<sub>2</sub>/Ti



We applied potential and follow the current and the signal for:  
**m/z=2, (H<sub>2</sub>) product in cathode,**  
**44 (CO<sub>2</sub>) product in anode**  
**and 31 (methanol) reactant in anode**

As potential increases:  
**Current and H<sub>2</sub> increases too,**  
**CO<sub>2</sub> decreases**  
**Methanol is not shown any trend**

PtRu/Ti

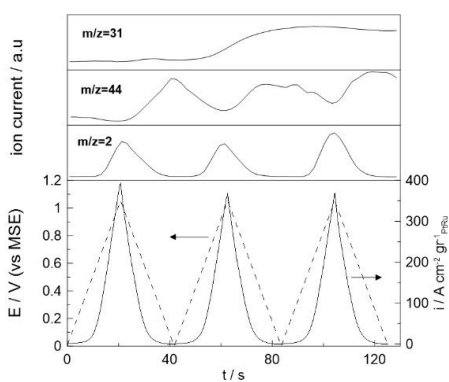


## DEMS

We can also have the profiles of the desire mazes with time when we apply several cycles of cyclic voltammetry

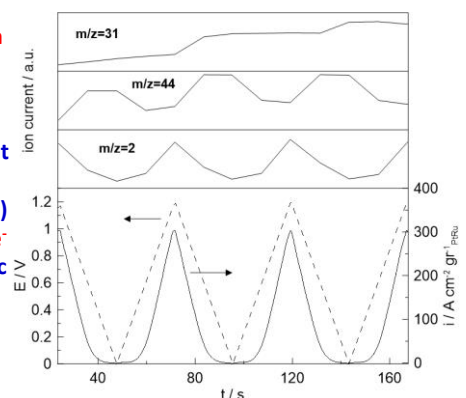


PtRuTiO<sub>2</sub>/Ti



**Maximum H<sub>2</sub> production at cathode observed at maximum current and potential.**  
**Cathode half reaction**  
 $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$   
**At minimum current significant CO<sub>2</sub> detection probably due to crossover. (anode half reaction)**  
 $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^-$   
**Methanol didn't show periodic trends**  
**(Methanol is a reactant)**

PtRu/Ti





## Conclusions



- DEMS can be applied to follow the reactants/products of an electrochemical process in a fuel cell type electrochemical cell.
- For the successful use of DEMS the cell and the experimental conditions must be first design with accuracy.



*Thank you for your attention*

### Acknowledgements

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