



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



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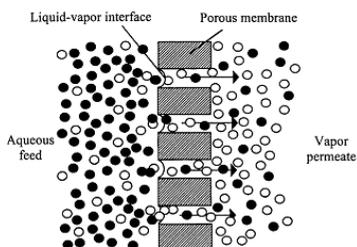
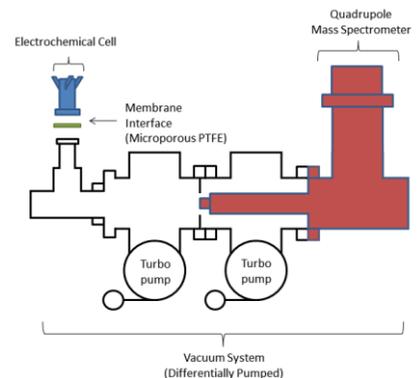
Project ARISTEIA No 3073



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).

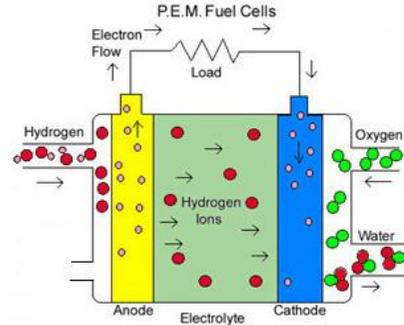


What is DEMS

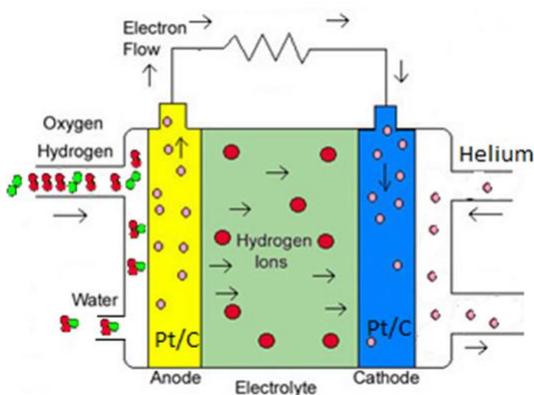


In this study we combine DEMS with a fuel cell

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/cm²

Feed H₂/O₂/He saturated with H₂O

Total Flow 100 – 400 mL/min with different ratios of H₂:O₂

Cathode

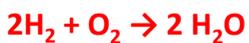
Pt/C 0.5 mg/cm²

Feed He saturated with H₂O

Total Flow 60 mL/min

Electrolyte

Nafion 117

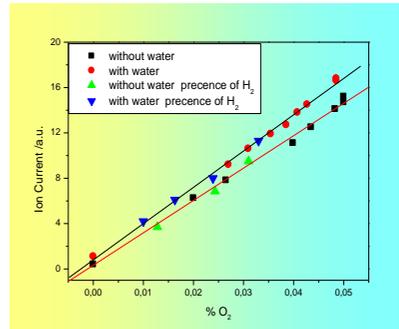
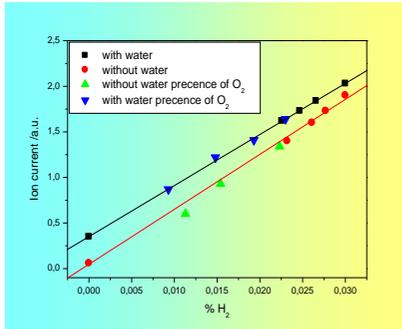




The Hydrogen – Oxygen Reaction



Calibration Curves



The presence of H₂O influences the signal of H₂ and/or O₂

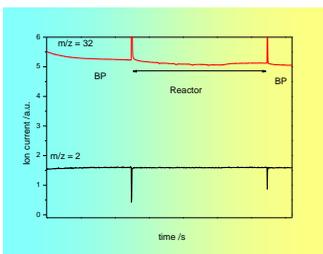
Simultaneous presence of H₂ and O₂ does not affect their response factors



The Hydrogen – Oxygen Reaction

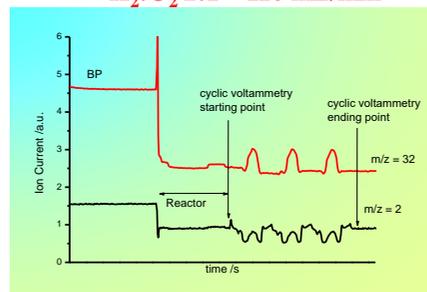


No reaction without catalyst

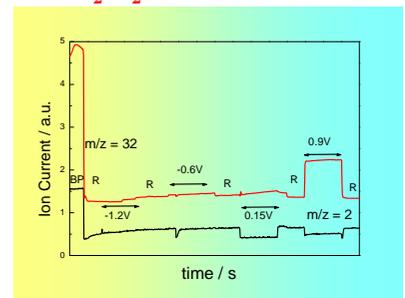


In the presence of Pt the reaction is very fast and vigorous.

H₂:O₂ 2:1 110 mL/min



H₂:O₂ 2:1 110 mL/min



For catalytic rates always

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



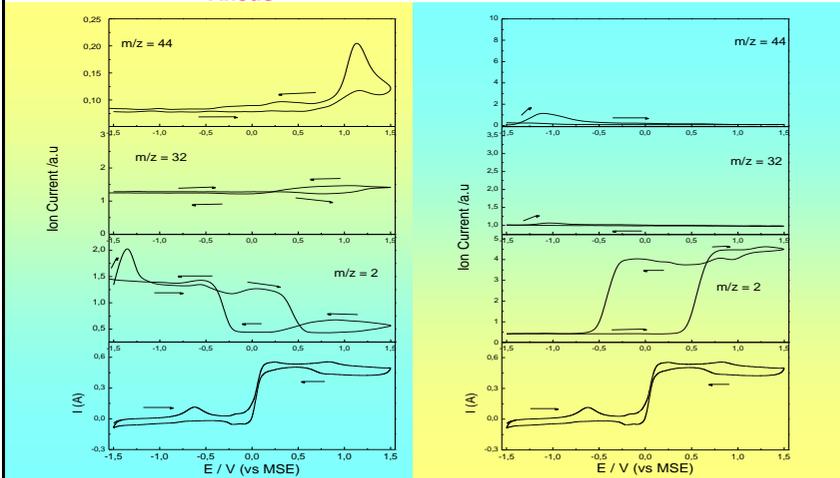
The Hydrogen – Oxygen Reaction



$\text{H}_2:\text{O}_2$ 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_2) for $\text{H}_2:\text{O}_2$ 6.4:1. The opposite behavior is observed for the signal of $m/z=32$ (O_2). The sharp increase of the signal of $m/z=44$ (CO_2) 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.



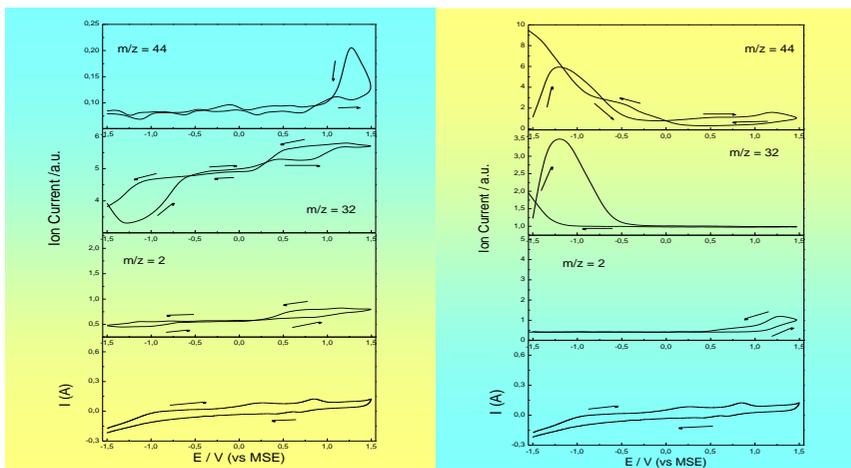
The Hydrogen – Oxygen Reaction



$\text{H}_2:\text{O}_2$ 1:1 110 mL/min

Anode

Cathode



Positive going scan

Anode:

In the case of $\text{H}_2:\text{O}_2$ 1:1, I and $m/z = 2$ changes are negligible due to the full conversion of H_2 . Increase of I is followed by an increase of the signal of $m/z=32$ (O_2). The sharp increase of the signal of $m/z=44$ (CO_2) can be attributed to the oxidation of the carbon cloth (which is part of the anodic electrode) at potentials higher than 1V.

Cathode:

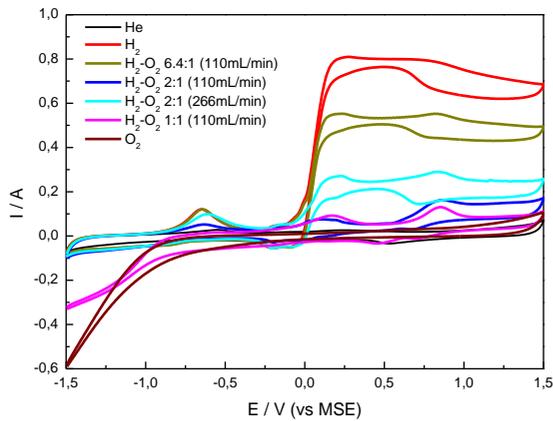
The opposite behavior is observed, if we follow the cathodic gases.



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

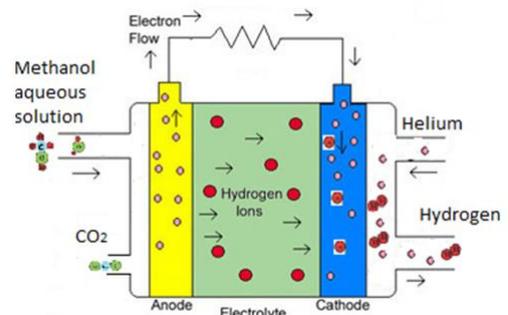


The second case is Methanol electrolysis. With the MS we monitor the cathode.

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:

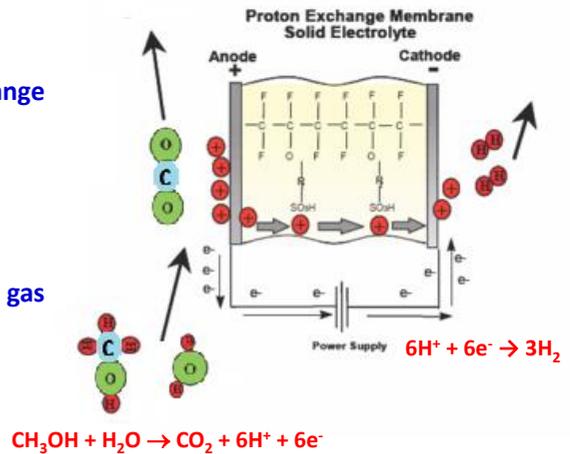


and transferred to the cathode through the proton exchange membrane.

Hydrogen is then evolved at the cathode via:



The membrane separates the hydrogen from the anode gas mixture resulting in pure H_2 production.



The Catalyst - Why Pt-Ru-TiO₂?



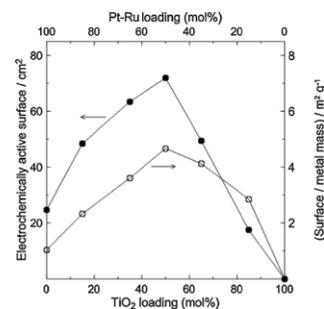
- Pt is the most effective metal for breaking the C-H bonds during the adsorption step
- Problem with the strongly adsorbed CO
- The OH adsorption from water dissociation is necessary to oxidize the strongly adsorbed CO species.

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 TiO₂

- 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 TiO₂ 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 PtRuTiO₂/Ti
1 commercial PtRu/C

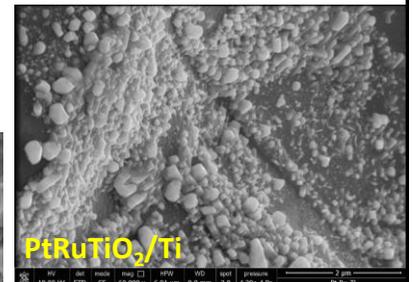
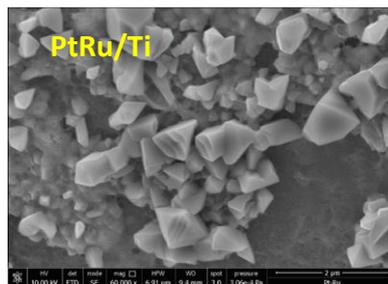
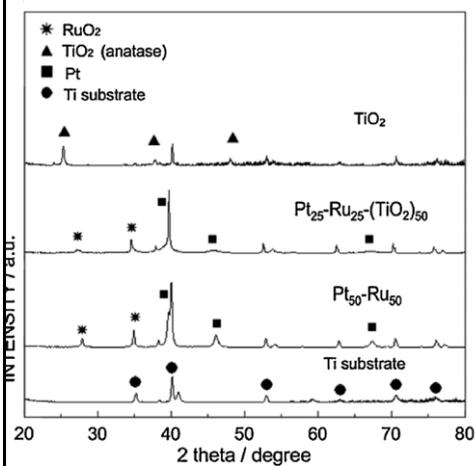
Cathode: Pt/carbon cloth 0.5 mg cm⁻²

Electrolyte: Nafion 117 membrane.

a/a	anodic electrode	Total metal loading	SSA (m ² /g)
1	PtRu/Ti/C	1.45 mg cm ⁻²	3.8
2	PtRuTiO ₂ /Ti/C	1.07 mg cm ⁻²	6.9
3	PtRu _{comm} /C	1,0 mg cm ⁻²	2.7



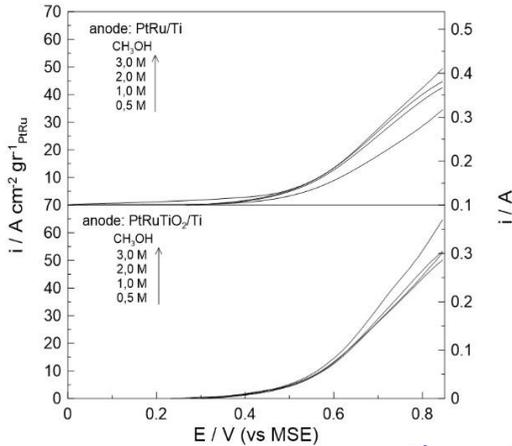
XRD and SEM results



XRD and SEM results verify the lower dimensions of nanoparticles Pt/Ru in the presence of TiO₂

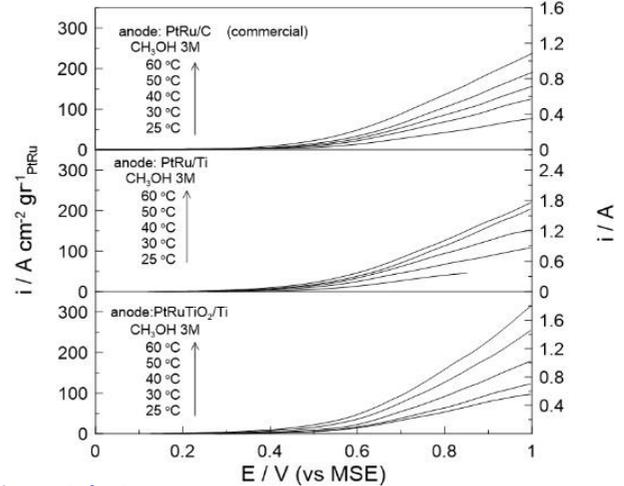


Electrocatalytic activity



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

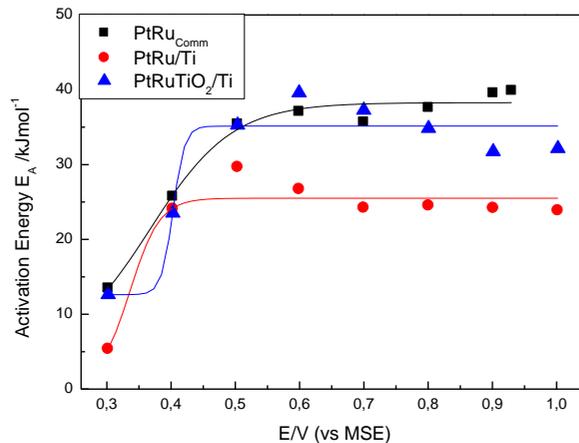
The most effective catalyst is the PtRuTiO₂/Ti



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.



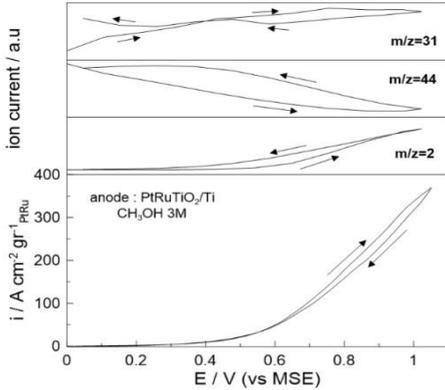
DEMS

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

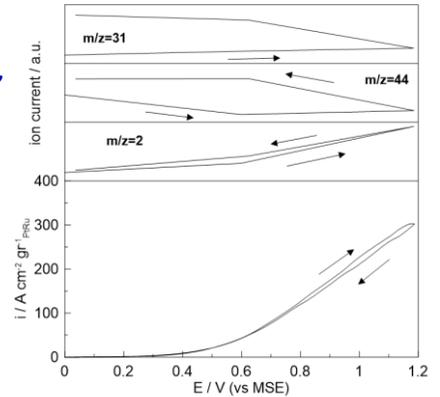
PtRuTiO₂/Ti



We applied potential and follow the current and the signal for: **m/z=2**, (H₂) product in cathode, **44 (CO₂)** product in anode and **31 (methanol)** reactant in anode

As potential increases:
Current and H₂ increases too,
CO₂ decreases
Methanol is not shown any trend

PtRu/Ti

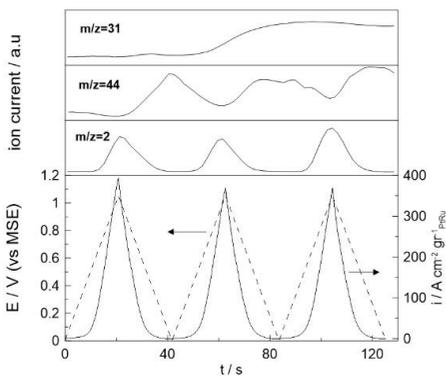


DEMS

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

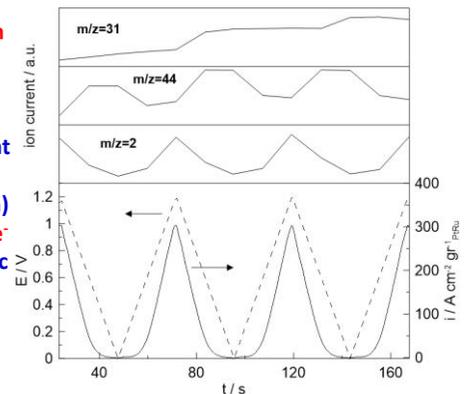


PtRuTiO₂/Ti



Maximum H₂ 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 CO₂ 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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Με τη συγχρηματοδότηση της Ελλάδας και της Ευρωπαϊκής Ένωσης