Study of methanol reforming using Differential Electrochemical Mass Spectrometry (DEMS)

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ΕΑΑΟΡ - 4 Athens 2015

4 European Conference on Environmental Applications of Advanced Oxidation Processes

21-24 October 2015, Athens - Greece

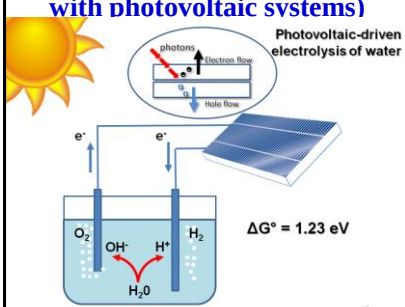
The Hydrogen

H_2

- **promising energy carrier**
- **No production of CO_2**

Hydrogen can be produced

- **chemically**
- **Electrochemically (combined with photovoltaic systems)**



Alternatively we can use light alcohols such as methanol, ethanol, glycerol etc. One of the advantages of methanol reforming is the lower energy demand ascribed to the electrolytic production of hydrogen.

Hydrogen production by methanol–water solution electrolysis is suitable for portable power applications because methanol–water solution electrolysis can start up and shut down in a moment and can produce hydrogen at a low temperature.

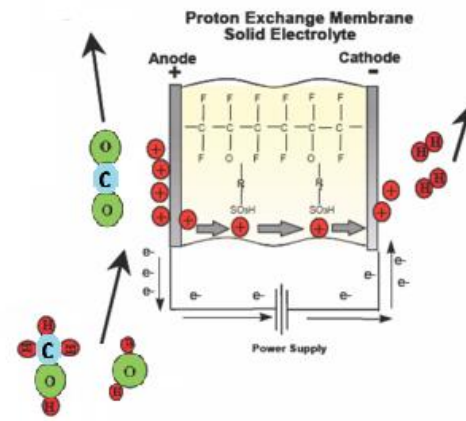
Electrochemical reforming of methanol

In this study the reforming was carried out in a polymer electrolyte membrane (PEM) cell using PtRu based electrodes as anodes and carbon supported Pt based electrodes as cathodes. An aqueous solution of methanol was used as anode fuel while pure He was fed to the cathode.

During the electrolysis process protons are produced in anode $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$

and transferred to the cathode through the proton exchange membrane. Hydrogen is then evolved at the cathode via $2H^+ + 2e^- \rightarrow H_2$

The membrane also separates the hydrogen from the anode gas mixture helping us to receive pure H_2.



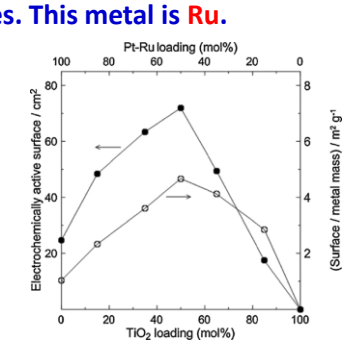
The Catalyst - Why Pt-Ru-TiO_2?

- 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_2

- 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_2 Loading on Pt-Ru Catalysts During Alcohol Electrooxidation, Electrochim. Acta 179 (2015) 578

The electrodes used

3 MEAs prepared using three different anodes

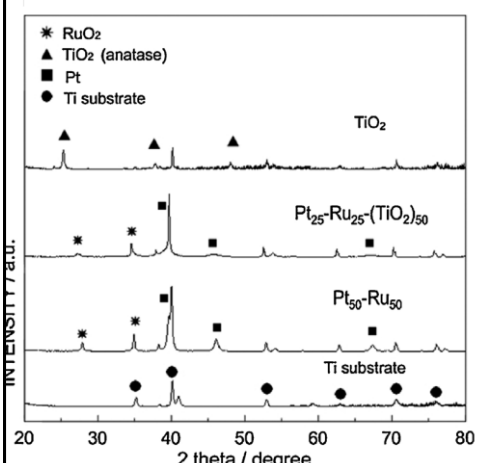
Anodes: 2 home-made PtRu/Ti and $PtRuTiO_2$/Ti
1 commercial PtRu/C

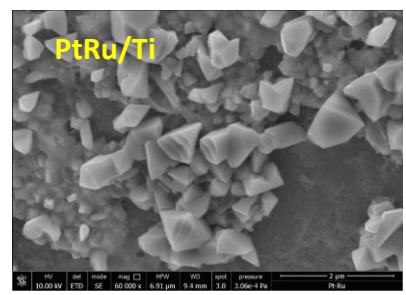
Cathode: Pt/carbon cloth 0.5 mg cm^{-2}

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





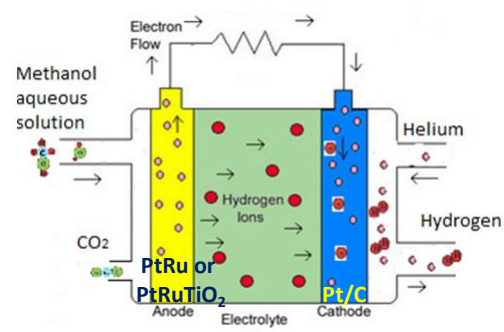
XRD and SEM results verify the lower dimensions of nanoparticles Pt/Ru in the presence of TiO_2

The cell setup

With the MS we monitor the cathode.

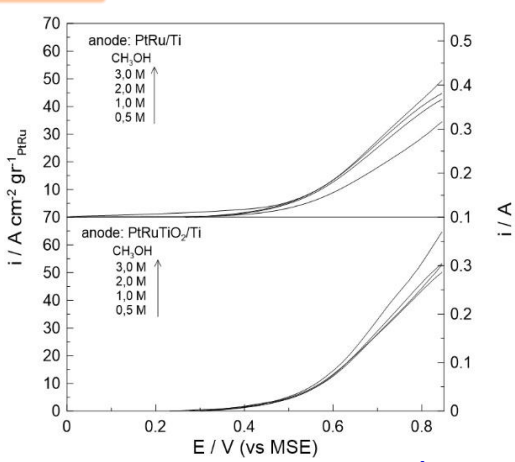
The anode feed is a methanol aqueous solution (C=0.1M – 3M). *Uo* = 5 mL/min
Temperature ranges between 25°C – 60°C.
The cathode is He with Uo= 60 mL/min

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

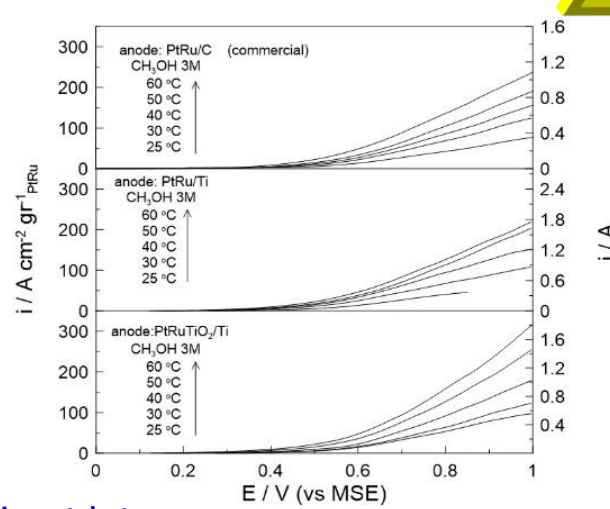


$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$ $\quad 6H^+ + 6e^- \rightarrow 3H_2$

Electrocatalytic activity



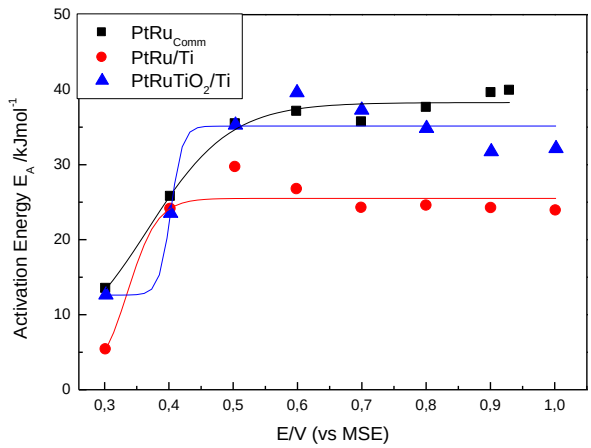
Current density (i.e. electro-catalytic activity) slightly increases with concentration



The most effective catalyst is the $PtRuTiO_2$/Ti

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

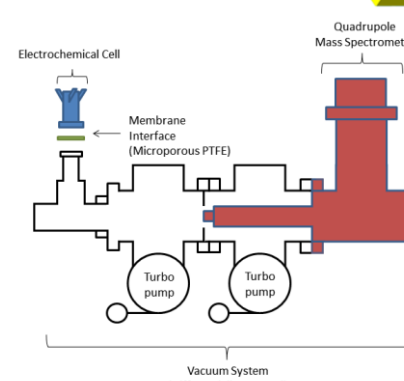
Electrocatalytic activity

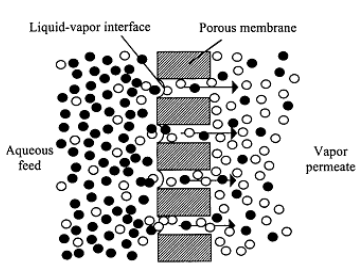


At about 0.3 -0.4 V there is a sharp increase in E_A. For higher values of potential the E_A is constant. Lower potential: the value of E_A indicates physical phenomena. The E_A for PtRu/Ti is rather low probably due to significant mass transfer phenomena.

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.





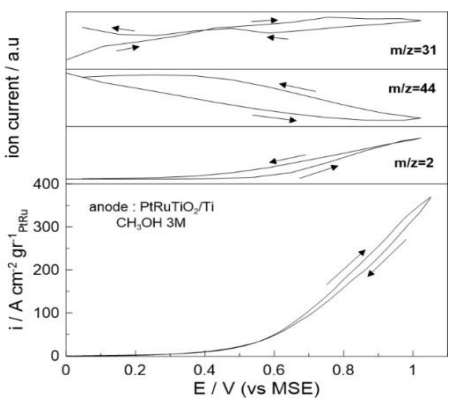
The instrument essentially consists of three crucial components: an electrochemical half-cell, a PTFE membrane interface, and a vacuum system including the quadrupole mass spectrometer (QMS).

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

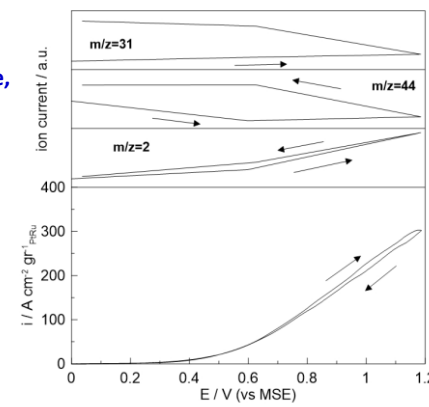
$PtRuTiO_2/Ti$



We applied potential and follow the current and the signal for:
m/z =2, (H_2) product in cathode,
44 (CO_2) product in anode
and 31 (methanol) reactant in anode

As potential increases:
Current and H_2 increases too,
CO_2 decreases
Methanol is not shown any trend

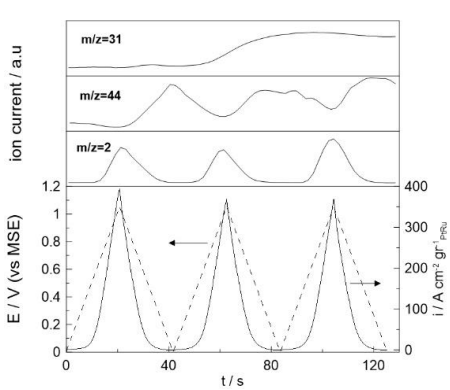
PtRu/Ti



DEMS

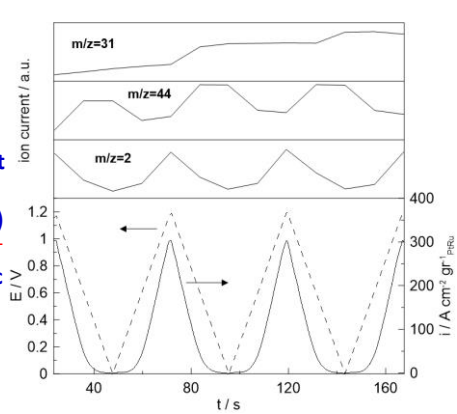
We can also have the profiles of the desire mazes with time when we apply several cycles of cyclic voltametry

$PtRuTiO_2/Ti$



Maximum H_2 production at cathode observed at maximum current and potential.
Cathode half reaction
$2H^+ + 2e^- \rightarrow H_2$
At minimum current significant CO_2 detection probably due to crossover. (anode half reaction)
$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$
Methanol didn't show periodic trends
(Methanol is a reactant)

PtRu/Ti



Conclusions

- Home-made MEAs based on PtRu and PtRu modified with TiO_2 anodes prepared and compared with commercial PtRu anodes during electrochemical reforming of methanol
- PtRu modified with TiO_2 anodes exhibit higher electrocatalytic activity for H_2 production
- DEMS was applied to follow the products of cathode. It is shown that DEMS can be useful for the study of gas crossover. It was found that there are significant crossover problems for methanol and CO_2
- Hydrogen production increases with potential. Calibration of the mass spectrometer is necessary to study the faradaic efficiency of the process

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Thank you for your attention

Acknowledgements
Work supported by the "ARISTEIA II" Action of the "Operational programme of education and lifelong learning" which is co-funded by the European Social Fund (ESF) and National Resources.