

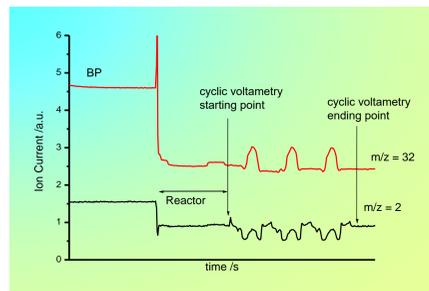
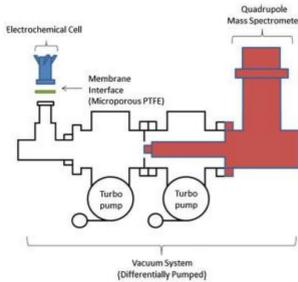
Introduction

What is DEMS

Differential Electrochemical Mass Spectrometry (DEMS) is a new technique which has been developed during the last decades [1-8] and used to study various electrocatalytic systems. DEMS allows for the **on line detection** of reaction products using **mass spectrometry** during **electrochemical processes**.

The term "differential" is used to emphasize the ability of the technique to provide kinetic information. DEMS has proven a highly valuable method for the direct, qualitative and quantitative measurement of dissolved gasses and volatile intermediates and products formed at electrode surfaces during potential sweep, potentiostatic and galvanostatic experiments.

In a typical DEMS experiment the ion current of one or more species involved in an electrochemical reaction are selectively measured as a function of time or varying the electrode potential. Plots of intensity versus electrochemical potential are called mass spectrometric voltammograms (MSVs).

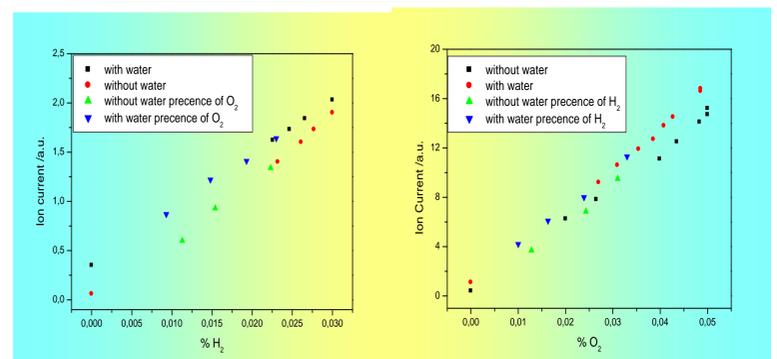


The Reaction

The $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ was used as a model reaction in order to demonstrate the functionality of a new DEMS set up which was built up at University of Patras. The catalytic reaction was taking place in a polymer electrolyte membrane (PEM) electrocatalytic cell.

Various $\text{H}_2:\text{O}_2$ mixtures saturated with H_2O with total flowrate between 100 and 400 cm^3/min were fed at the anodic part of the cell (catalyst: Pt/C with loading $0.5 \text{ mg}/\text{cm}^2$). Pure helium saturated with water was used to feed the cathode. Anode and cathode was separated with a Nafion 117 membrane while both were connected to a potentiostat/galvanostat (Autolab, PGSTAT 302 N). A mass spectrometer (Extrel, MAX 300-LG) was used to analyze the anodic or cathodic gases.

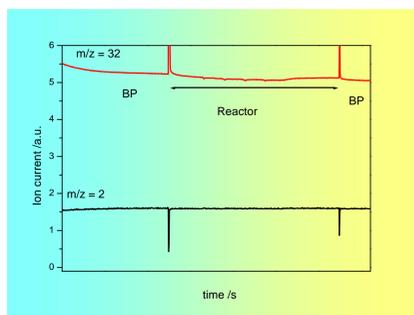
Calibration Curves



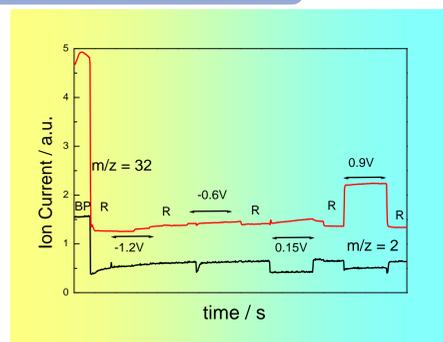
The calibration of signal was carried out by using known H_2 ($m/z = 2$) and O_2 ($m/z = 32$) gas mixtures (balance He). The simultaneous presence of H_2 and O_2 didn't affect the signal. On the other hand water, if present, can alter significantly the measured ion current and thus the calculated amount of H_2 and O_2 .

- We can monitor either the **anode** or the **cathode** of the reactor
- We can change the reaction mixture **composition** and **flow**

Results



There is no reaction without Pt catalyst. In the presence of Pt the reaction is very fast and vigorous.



$\text{H}_2:\text{O}_2$ 6.4:1 110 mL/min
Anode

$\text{H}_2:\text{O}_2$ 6.4:1 110 mL/min
Cathode

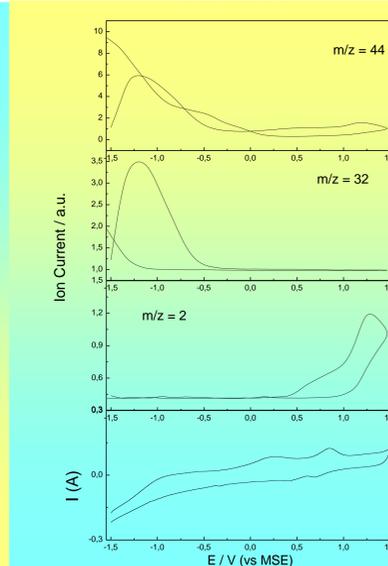
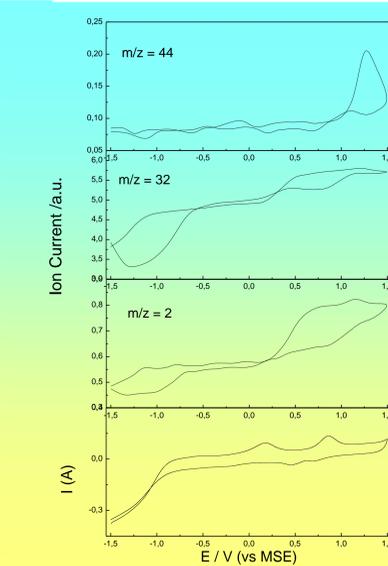
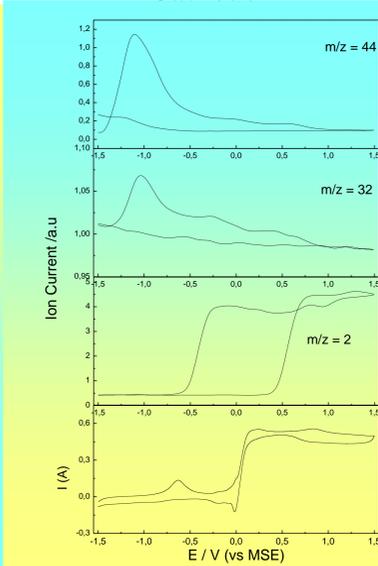
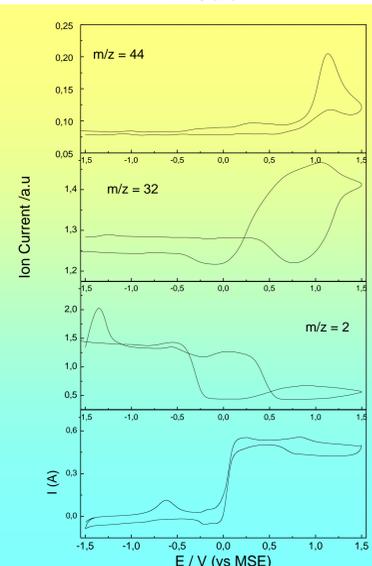
$\text{H}_2:\text{O}_2$ 1:1 110 mL/min
Anode

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

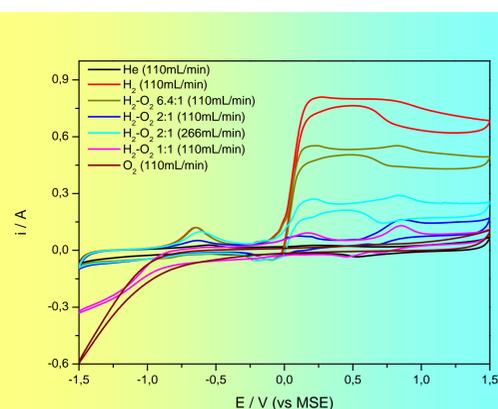
Positive going scan
Anode:

Increase of I is followed by a decrease of the ion signal of $m/z=2$ (H_2). 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 exact opposite behavior is observed, verifying the H^+ transfer through the Nafion membrane.



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



Conclusions

- DEMS can be used for monitoring the above reaction.
- The presence of H_2O affect the signals of the H_2 and O_2 .
- The present system is still under investigation and further study is necessary to explain the observed behavior.

References

- [1] S.J. Ashton, Design, Construction and Research Application of a Differential Mass Spectrometer (DEMS), 2012, ISBN: 978-3-642-30549-8
- [2] H. Baltruschat, Journal of American Society for Mass Spectrometry, 15 (2004) 1693-1706.
- [3] S. Wasmus, S.R. Samms, R.F. Savinell, Journal of Electrochemical Society, 142 (1995) 1183-1189.
- [4] J. Gun, S. Bharathi, V. Gutkin, D. Rizkov, A. Voloshenko, R. Shelkov, S. Sladkevich, N. Kyi, M. Rona, Y. Wolanov, D. Rizkov, M. Koch, S. Mizrahi, P.V. Pridkochenko, A. Modestov, O. Lev, Israel Journal of Chemistry, 50 (2010) 360-373.
- [5] C. Cremers, D. Bayer Polymer Electrolyte Membrane and Direct Methanol Fuel Cell Technology, (2012), 65-86.
- [6] C. Niether, M.S. Rau, C. Cremers, D.J. Jones, K. Pinkwart, J. Tübke Journal of Electroanalytical Chemistry, 747 (2015) 97
- [7] H. Oberacher, F. Pitteri, R. Erb, S. Plattner, Mass Spectrometry Reviews, 34 (2015) 64-92
- [8] Wei Chen, Qian Tao, Jun Cai, Yan-Xia Chen Electrochemistry Communications, 48 (2014) 10-121111