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**Design, Construction
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a Differential
Electrochemical Mass
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S. J. Ashton

Design, Construction and Research Application of a Differential Electrochemical Mass Spectrometer (DEMS)

Doctoral Thesis accepted by
the Technical University of Munich, Germany

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ISSN 2190-5053

ISBN 978-3-642-30549-8

DOI 10.1007/978-3-642-30550-4

Springer Heidelberg New York Dordrecht London

ISSN 2190-5061 (electronic)

ISBN 978-3-642-30550-4 (eBook)

Library of Congress Control Number: 2012941303

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Printed on acid-free paper

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Parts of this thesis have been published in the following journal articles

Ashton, S.J., Arenz, M. (2012) “Comparative DEMS Study on the Electrochemical Oxidation of Carbon Blacks” *Journal of Power Sources* (accepted Jun. 2012)

Ashton, S.J., Arenz, M. (2011) “A DEMS study on the electrochemical oxidation of a high surface area carbon black” *Electrochemistry Communications* 13(12): 1473–1475

Electrochemistry is the science which deals with the conversion of matter to electricity; and/or electricity to matter.

Kyvstiakovsky (L. Antropov, Theoretical Electrochemistry) 1910

Supervisor's Foreword

Sean Ashton began his doctoral thesis in my Emmy Noether electrocatalysis research group in the Department of Physical Chemistry at the Technische Universität München in late 2007, where he was given the challenge of designing and constructing a so-called DEMS (Differential Electrochemical Mass Spectrometer) instrument and applying it to investigate proton exchange membrane fuel cell (PEMFC) catalysts. His work and corresponding doctoral thesis were exceptionally well formulated, and he has provided my laboratory with a beautifully designed, effective research tool.

In this thesis, Sean first presents the broader significance of the electrocatalysis research topic of my group (now part of the University of Copenhagen), which concerns itself with the fundamental investigation and development of fuel cell electrocatalyst materials. He then presents and discusses the prior DEMS instrument designs and their research applications, carefully compiling and evaluating the crucial information contained in prior DEMS literature. The thesis then documents, in detail, the design of the instrument he constructed (which does not simply replicate earlier instruments) presenting and discussing the design considerations of both hardware and software. After constructing a functional instrument, Sean did not impetuously dive into performing research studies but instead took the time to develop methods of characterising and optimising the various components, which are documented in his thesis. Finally, the research capability of the DEMS instrument is then demonstrated, revealing new insights in two key areas of fuel cell related research. The first study concerns methanol oxidation, whereby the stark contrast in the potential dependent conversion of methanol to CO_2 on Pt and PtRu catalysts is clearly revealed. The second study involves the investigation of industrial fuel cell catalyst support oxidation, where DEMS is able to evaluate the quantity and rate of the electrochemical oxidation of carbon supports, separating complete and partial oxidation currents.

Overall, the information that Sean presents in this thesis, which is largely unpublished, is not only exceptionally useful to those wishing to construct a similar instrument, but is also of great interest because of the insights and their context that were obtained.

Copenhagen, Denmark, March 2012

Matthias Arenz

Acknowledgments

I would first and foremost like to thank Prof. Matthias Arenz, whom will likely recall that in the interview and presentation for the Ph.D. position, I had to rather awkwardly respond to almost all questions regarding my master thesis with “I’m really sorry but I can’t say. It’s confidential”. Despite that, he decided to patiently guide me through my work and moulded me into an ‘electrochemist’ for which I am truly grateful.

This work, however, would not have even begun on the right track if it was not for the kind advice of Dr. Zenonas Jusys, whose knowledge and experience in DEMS is unrivalled. I would also like to thank Dr. Karl J.J. Mayrhofer whose enthusiasm provided me with a firm foundation in electrochemistry, and also Dr. Gustav Wiberg because when he wasn’t occupied finishing his own work, or singing in a choir (or the lab...), he was most likely teaching me Labview programming; without his influence I would almost certainly still be treating and analysing data today. There are also the remaining members of the electrochemistry group whom supported my work, namely Katrin and Markus to thank, particularly for the good-times we had setting up the laboratory in Copenhagen with Neuhavn and The Moose being special highlights. I would also like to express my appreciation to Prof. Ulrich Heiz and his research group for the pleasant working environment, the TU-München Mechanische Werkstatt for their meticulous fabrication of the DEMS components, and the Elektronik Werkstatt for regularly letting me ‘borrow’ things.

Of course, the completion of this work was unachievable without the support of my friends and family. I owe an awful lot to Gustav, Martin and Aras for providing mutual distraction from the highs and lows of our Ph.Ds. It was always great to get away from the relentless grinding of vacuum pumps, whether it was off to a Biergarten, the calmness of a snooker table, or even a trip to the ski slopes. Finally, I would like to especially thank my Mum and Dad, Jason and Jasmine for their unconditional love and support, and Bärbel, Steffi, Marga and Horst for their unreserved kindness. Thank you all.

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Abbreviations

AO	Analogue output
AFM	Atomic force microscopy
ATR-FTIR	Attenuated total reflection fourier transform infrared
ASA	Active surface area
AST	Accelerated stress testing
BET	Brunauer-emmett-teller
CB-IS	Cross beam (electron impact) ion source
CE	Counter electrode
CEEC	Chemical-electrical energy conversion
CO	Carbon monoxide
COR	Carbon oxidation reaction
CPU	Central processing unit
CV	Cyclic voltammetry/cyclic voltammogram
DAC	Digital-analogue-converter
DAQ	Data acquisition
DDE	Dynamic data exchange
DEMS	Differential electrochemical mass spectrometry
DMFC	Direct methanol fuel cell
DMSO	Dimethyl sulphoxide
ECSA	Electrochemical surface area
EOSA	Electrochemically oxidisable surface area
EQCM	Electrochemical quartz crystal microbalance
FC	Fuel cell
FTIR	Fourier transform infrared
GC	Glassy carbon
GUI	Graphical user interface
HClO ₄	Perchloric acid
HER	Hydrogen evolution reaction
HOR	Hydrogen oxidation reaction
H ₂ SO ₄	Sulphuric acid
HPLC	High-performance liquid chromatography

HSAC	High surface area carbon
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
KF	Klein flange
KOH	Potassium hydroxide
LSV	Linear sweep voltammogram
LT	Lifetime testing
MEA	Membrane electrode assembly
MID	Mass ion detection
MIMS	Membrane introduction mass spectrometry
MOR	Methanol oxidation reaction
MSCV	Mass spectrometric cyclic voltammogram
MWE	Multiple working electrode
NID	Negative impedance device
OER	Oxygen evolution reaction
ORR	Oxygen reduction reaction
PC	Propylene carbonate
PCTFE	Polychlorotrifluoroethylene
PEM	Polymer electrolyte membrane
PEMFC	Polymer electrolyte membrane fuel cell
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene Fluoride
QMA	Quadrupole mass analyser
QMS	Quadrupole mass spectrometer
RE	Reference electrode
RDE	Rotating disk electrode
RDS	Rate determining step
RHE	Reversible hydrogen electrode
SCE	Standard calomel electrode
SCSI	Small computer system interface
SDEMS	Scanning DEMS
SEM	Secondary electron multiplier
SHE	Standard hydrogen electrode
SPAIRS	Single potential alteration infrared reflectance spectroscopy
SWE	Single working electrode
TOC	Total organic carbon
TEM	Transmission electron microscopy
VI	Virtual instrument
WE	Working electrode
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction spectroscopy

Abstract

Electrochemical half-cell studies on industrial electrocatalysts contribute significantly towards our understanding of fuel cell processes. However, the study of complex, often overlapping reactions using standard methods is limited to the interpretation of a single electrode current. Presented here are details of the design, construction and characterisation of a differential electrochemical mass spectrometer (DEMS) that enables the in-situ elucidation of electrode currents. The capability of the instrument is demonstrated in two studies. In the first, DEMS is used to resolve the conversion of the methanol oxidation reaction to carbon dioxide on high surface area carbon (HSAC) supported Pt and PtRu catalysts, whilst the second focuses on the corrosion of industrial HSACs, separating partial and complete oxidation processes. Despite that both systems have long since been studied, new insights and understanding can be obtained using DEMS.

Chapter 1

Introduction

At the beginning of a thesis dedicated to the construction of a differential electrochemical mass spectrometer (DEMS), it is essential to first present the broader significance of the instruments intended application in the fundamental study of fuel cell relevant electrochemical reaction processes.

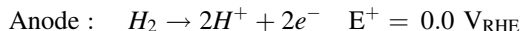
1.1 Background

Rising concerns over climate change and future oil and gas supply security are stimulating a political and economic shift towards a policy of sustainable energy [1]. In order to achieve sustainable energy consumption, aspects of both renewable energy and energy efficiency are required to be developed and encouraged. Sources of renewable energy are, however, not necessarily new concepts with wind-turbines having been present across the landscape for some time. Nevertheless, changing the way in which we produce and supply energy is only one aspect; the energy must also be stored and used efficiently. It is in energy efficiency, therefore, that more efficient chemical-electrical energy conversion (CEEC) devices such as the fuel cell, will play an essential role in replacing today's inefficient energy conversion devices, such as the combustion engine [2]. In contrast to the combustion engine, CEEC devices are not restricted by the Carnot efficiency limitations and can therefore offer higher energy conversion efficiency for the endeavour of sustainable energy [3].

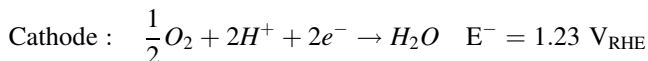
1.1.1 Fuel Cell Technology

The fuel cell CEEC device essentially converts chemical energy (contained in a fuel and oxidant) directly into electrical energy, and crucially does not involve any combustion. In principle, the device operates in a similar manner to an everyday CEEC, the battery; however, in contrast to the battery in which a limited quantity of the chemical energy source is stored internally, a fuel cell uses an external source of fuel and oxidant. An overview of the principle operation of a proton exchange membrane fuel cell (PEMFC) is depicted in Fig. 1.1.

The PEMFC consists of two platinum (Pt) electrodes: an anode and cathode which are separated by a proton exchange membrane (PEM) barrier. The device takes an external source of fuel and oxidant, in this case hydrogen (H_2) and oxygen (O_2), and generates electricity by electrocatalytically converting them into water. This process is a result of two electrochemical reactions which occur at each of the electrodes. At the anode electrode, the hydrogen is oxidised to produce protons and electrons:



Once generated, both protons and electrons travel from the anode to the cathode electrode; however, they must do so via two different paths imposed by the properties of the PEM. On one hand, the PEM is ion conducting and therefore the protons created at the anode simply pass through the membrane barrier to the cathode. On the other, the PEM is an electrical insulating barrier which means that the electrons must travel to the cathode via an alternate electron conducting pathway through which the current is harnessed. The protons and electrons are then consumed at the cathode electrode in the reduction of oxygen in the following reaction:



The only emission from the hydrogen fuelled PEMFC, therefore, is water vapour. The efficiency of the conversion of chemical into electrical energy in a fuel cell is determined by the potential difference between the anode and cathode electrode potentials. Theoretically, the maximum is 1.23 V determined by the difference between the thermodynamic half-cell potentials (i.e. $E^- - E^+$). Unfortunately, kinetic constraints for both anode and in particular, the cathode electrochemical reactions make it impossible for the thermodynamic reversible potential to be realised and large electrode overpotentials result, decreasing the energy conversion efficiency of the fuel cell CEEC device, as depicted in Fig. 1.2.

In order to achieve acceptable energy conversion efficiency (i.e. improve the cell potential), a significant quantity of expensive Pt electrocatalyst must be incorporated into the fuel cell membrane electrode assembly (MEA) to reduce the electrode overpotentials, particularly for the oxygen reduction reaction (ORR) at the cathode. In addition to that, is an extra quantity of Pt electrocatalyst required to ensure that the fuel cell also performs acceptably over its intended lifetime because

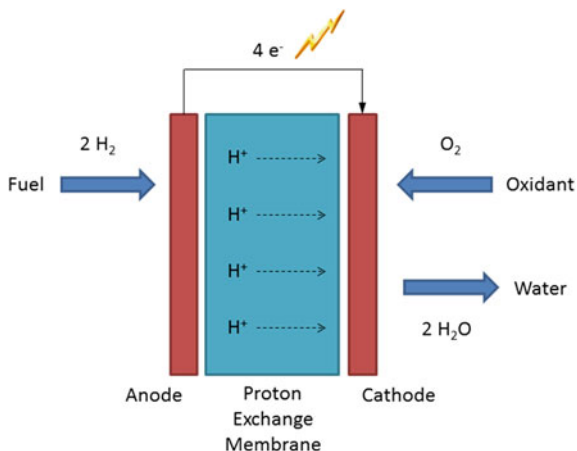


Fig. 1.1 A diagram illustrating the principles behind operation of the hydrogen fed PEMFC. The CEEC device possesses two electrodes that are separated via a proton exchange membrane, and converts an external supply of fuel (H_2) at the anode, and oxidant (O_2) at the cathode, into electricity and water (H_2O)

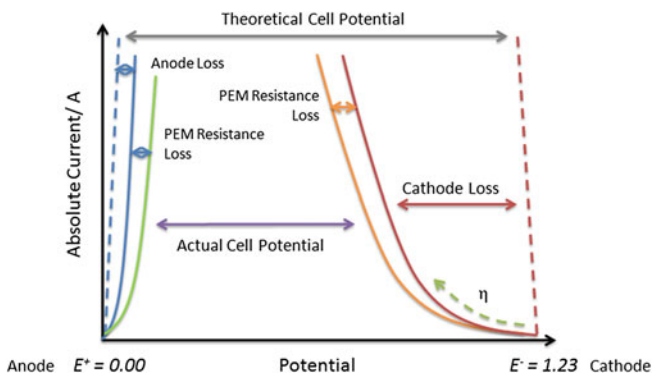


Fig. 1.2 A graph highlighting the origins of PEMFC performance losses. The practical cell potential (ca. 0.6 V) is significantly lower than the theoretical cell potential (~ 1.23 V) resulting in a loss in the energy conversion efficiency. A significant proportion of these losses arise from cathode due to the significant overpotential (η) required for the oxygen reduction reaction on Pt

the Pt electrocatalyst performance is not static but unfortunately deteriorates through use [4, 5]. Although adding Pt electrocatalyst can indeed provide an efficient and reliable PEMFC device, the net result of the significant Pt content required is a rather expensive and non-commercially viable CEEC device. Consequently, there is more than a strong incentive to develop electrocatalyst materials that are more active, more durable and less expensive than today’s state-of-the-art Pt based fuel cell electrocatalysts [6, 7].

1.1.2 Electrocatalyst Development

There are two feasible approaches to the screening and characterisation of prospective PEMFC electrode materials, whereby the performance of an electrocatalyst is either evaluated in-situ, as part of the MEA of a fuel cell; or ex-situ, in a three-electrode electrochemical half-cell setup, typically employing a rotating disc electrode (RDE) [7].

In the in situ approach, the electrocatalyst is fabricated into the MEA, and its performance is assessed by measuring the current–voltage characteristics (or polarisation curves) of the cell. The exact potentials of the anode and cathode in such measurements are in general not known precisely, only their potential difference. A simplified diagram illustrating the experimental parameters involved in such an experimental setup is depicted in Fig. 1.3.

In order to assess the performance of an electrocatalysts in an MEA, meticulous control over the MEA fabrication and experimental variables such as fuel and oxidant pressure, flow rate, humidity, and fuel cell operating temperature is required. The cell performance of a particular MEA is typically often published, together with details of the operating temperature, reactant pressure, stoichiometry, MEA preparation, and cell construction etc. Whilst there is no doubt that the assessment of the performance of an electrocatalyst in the fuel cell environment is the ultimate test an electrocatalyst materials performance; controlling every aspect of the MEA fabrication and experimental parameters in order to deduce the performance of the electrocatalyst alone is far from trivial. Not only does the preparation of an MEA require great effort in the research environment, but there are also numerous MEA preparation methods which are often performed by-hand, with questionable reproducibility [8]. It is therefore even more difficult to compare in situ electrocatalyst performance measurement observations between different research groups, and it has been suggested that the incorporation of a prospective electrocatalyst in an MEA should perhaps rather be left to experts in MEA fabrication [9]. The substantial effort, cost and difficulties associated with fabricating MEAs and reproducing experimental conditions with relatively slow accumulation of data, suggests that the in situ assessment of electrocatalyst performance alone is ambiguous, and neither an intuitive nor cost effective approach to the screening and characterisation of prospective fuel cell electrocatalyst materials.

The second approach concerning fuel cell electrocatalyst development are ex-situ methods that typically involve fundamental research using an electrochemical half-cell in aqueous electrolyte, such as the three-electrode RDE setup depicted in Fig. 1.4. The three-electrode electrochemical half-cell setup consists of a working electrode (WE), counter electrode (CE) and reference electrode (RE), each of which are submerged in a conducting aqueous electrolyte. In this setup, the potential of the WE is controlled relative to the RE using a potentiostat. The RE is itself an electrochemical half-cell, whose potential remains at a constant, fixed value. The potentiostat therefore can be used to precisely manipulate the potential of the WE electrode relative to the RE using electroanalytical techniques such as

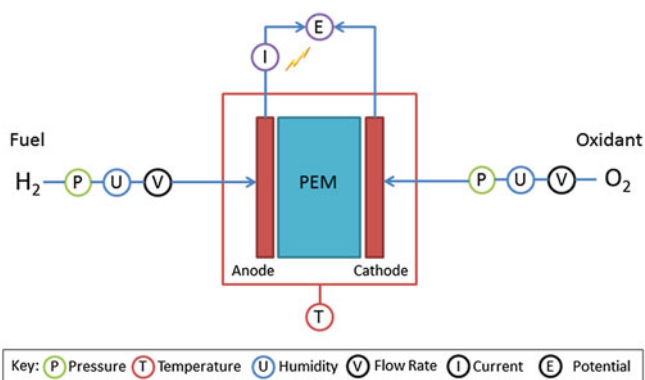
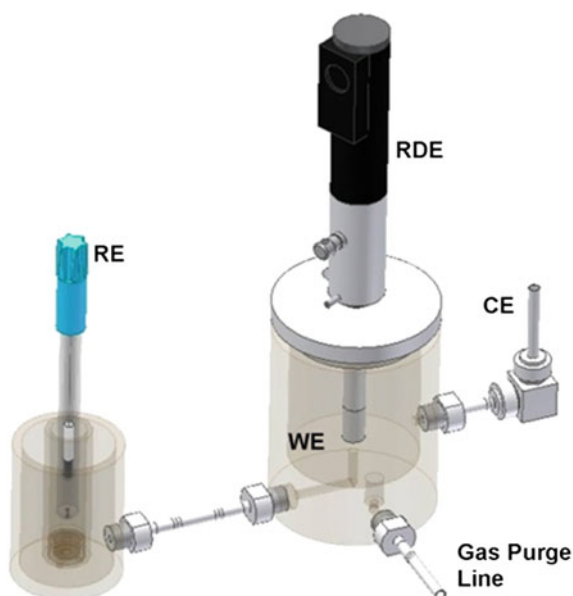


Fig. 1.3 An outline of the experimental setup and the numerous parameters that must be controlled during an in situ MEA experiment for the characterisation of electrocatalyst materials. The electrocatalyst must be fabricated into an MEA and the current is measured as a function of cell potential. These types of experiments are rather complicated and assessing the performance of the electrocatalyst alone is far from trivial

Fig. 1.4 An illustration of an electrochemical half-cell RDE setup that may be employed to characterise the performance of a PEMFC electrocatalyst material ex-situ. The electrocatalyst material is simply deposited on a WE substrate (i.e. no MEA fabrication is required). The setup is rather straightforward compared to in situ methodologies with fewer experimental variables, and the current and WE potential relationship may be measured precisely through the use of a RE



cyclic voltammetry (CV) to study electrochemical processes. The CE meanwhile is required to balance the current flowing through the WE (no current flows through the RE).

The performance and characteristics of electrocatalyst materials can then be accurately evaluated by measuring the current and WE potential relationship of the electro catalytic reaction. The principle advantage of the ex-situ three-electrode

electrochemical half-cell over the in situ MEA approach, in terms of electrocatalyst development, is essentially its capability to investigate model electrocatalyst materials. These experimental setups have, for example, been utilised in a number of fundamental studies with particular focus on the electrocatalysis of fuel cell reactions, typically the ORR [7, 10], hydrogen oxidation reaction (HOR) and methanol oxidation reaction (MOR) [11], which have been extensively studied on model electrodes such as polycrystalline [10], single crystal [12] and well-characterised alloy [11, 13–16] Pt surfaces, in order to gain a fundamental understanding of the reaction mechanisms and the relationship between catalyst structure and activity.

Fundamental studies on model catalysts, however, are not always entirely applicable to the more immediate concerns of fuel cell development, although in combination with theory [17] they do provide insights into how the ideal fuel cell electrocatalyst might be designed [11, 18, 19]. A more applied method, therefore, is to perform fundamental research studies in an electrochemical half-cell which directly approach problems associated with fuel cell development needs, such as the characterisation of the activity [7, 20–23], and durability [24, 25] of industrial fuel cell catalysts. In comparison to in situ methods, there are fewer experimental variables to control in the electrochemical half-cell, no MEA fabrication is required and the potential of the WE can be controlled and measured precisely. Consequently, the experiments are comparatively straightforward and cost effective, allowing the more rapid accumulation of experimental data. Electrochemical half-cell setups may therefore be considered as a rather intuitive methodology for effective fuel cell electrocatalyst material screening and characterisation, as well as for fundamental research studies on fuel cell relevant electrochemical processes. This is of course achieved at the expense of the electrocatalyst material being characterised in an aqueous rather than humid gas phase environment of the fuel cell, and consequently the extrapolation of ex-situ observations to the MEA is not necessarily straightforward. A rather complementary approach is therefore crucial toward developing characterisation methodologies to accelerate fuel cell electrocatalyst development.

It is the more applied ex-situ approach to the fundamental study of fuel cell relevant processes, and development of electrocatalyst characterisation methodologies in an electrochemical half-cell that is taken in our laboratory. Nevertheless, such studies using standard RDE setups are not without their own limitations and ambiguities. For example, the study of complex and frequently overlapping electrochemical reactions is in principle limited to the clouded interpretation of a single electrode current. Consequently, more sophisticated techniques that allow the in situ elucidation of electrochemical reactants, intermediates and products, in an electrochemical half-cell such as DEMS are an invaluable research tool.

1.2 Outline and Objectives

The objective of this dissertation was to essentially design, construct and characterise a DEMS instrument, intended for fundamental research studies on fuel cell relevant electrochemical reaction processes. The thesis is organised in the almost chronological order of the design, construction and development processes, followed by two demonstrations of the DEMS application in research.

In order to achieve this goal it was important to first acquire an overview of the DEMS literature, and evaluate the various DEMS design solutions that have appeared previously. A review of the DEMS literature, with particular focus on previous electrochemical cell design solutions is presented in [Chap. 2](#).

In [Chap. 3](#), an overview of the experimental setup along with the design of the critical components of the DEMS instrument built as part of this work is then presented. This section is extended to include necessary details of the hardware and software that were required, or indeed developed to improve the operation and usability of the DEMS instrument.

Once a working DEMS instrument was established, it was crucial to then understand the practical aspects of the instrument and its operation, which is covered in [Chap. 4](#). This includes the evaluation of the effect of experimental variables and a guide for optimising and calibrating the DEMS instrument.

In a first study, the research capabilities of the DEMS instrument is demonstrated in [Chap. 5](#) that revisits the MOR on HSAC supported Pt and PtRu catalysts. Using DEMS, we are able to observe MOR products and evaluate the conversion of methanol to CO_2 as a function of the WE potential using a variety of electro-analytical techniques.

Finally, in [Chap. 6](#) the electrochemical oxidation of various HSAC supports is examined and is a topic which has received relatively little attention using DEMS. In this study, we are able to elucidate electrode currents that arise from partial and complete oxidation of the HSAC supports, as well as the oxygen evolution reaction that occurs on the polycrystalline Au substrate or supported Pt particles.

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Chapter 2

Differential Electrochemical Mass Spectrometry

The intention of this chapter is to provide an overview of the DEMS technique, the instrument designs and example research applications. This involves the presentation and discussion of previous design solutions, which are separated into three parts: the electrochemical cell, membrane interface and the vacuum system of the mass spectrometer. Example experiments from the DEMS literature are then briefly described which highlight where a particular DEMS electrochemical cell design may be favoured. Ultimately, the appropriate design solution is determined by the intended research application of the DEMS instrument.

2.1 Principle of Operation

Differential Electrochemical Mass Spectrometry (DEMS) is essentially an analytical technique that combines 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. By correlating the faradaic electrode current with relevant mass ion currents, ambiguous electrochemical reaction processes can be elucidated, whereas standard electrochemical techniques such as the RDE are otherwise limited to the interpretation of a single electrode current. An overview of the DEMS instrument is depicted in Fig. 2.1.

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). The role of the electrochemical half-cell is to enable controlled electrochemical experimentation at a WE of interest, and to allow reaction products to be transported to the membrane interface. This interface consists of a microporous PTFE membrane that partitions the aqueous electrolyte of the electrochemical cell from the high vacuum conditions required