# UNIVERSITY OF SOUTHAMPTON

# FACULTY OF ENGINEERING, SCIENCE AND MATHEMATICS

4 HARRY R. S. K.

School of Chemistry

Development of a nanostructured palladium microelectrode for pH monitoring in scanning electrochemical microscopy

by

Kirsty-Jo Williams

Thesis for the degree of Doctor of Philosophy

June 2008

# UNIVERSITY OF SOUTHAMPTON <u>ABSTRACT</u> FACULTY OF ENGINEERING, SCIENCE & MATHEMATICS SCHOOL OF CHEMISTRY

#### Doctor of Philosophy

# DEVELOPMENT OF A NANOSTRUCTURED PALLADIUM MICROELECTRODE FOR PH MONITORING IN SCANNING ELECTROCHEMICAL MICROSCOPY

## by Kirsty-Jo Williams

This work describes the development of a nanostructured palladium microelectrode for use in scanning electrochemical microscopy. Once loaded with hydrogen to form the coexistent  $\alpha + \beta$  phase palladium hydride the potential of the nanostructured microsensor depends not on the H/Pd ratio, but on the activity of the protons in the solution. This thesis is focussed on extending the lifetime of the microsensor such that it can be successfully utilised in scanning electrochemical experiments.

The controlled potential method of loading the palladium film is investigated by application of a novel analytical technique. A measurement of the amount of hydrogen stripped from within the palladium lattice provides useful information on the efficiency of the controlled potential method of loading and on the amount of palladium remaining on the underlying disc. It has been shown that repeated use of the microsensor can lead to degradation of the palladium film.

A controlled current approach to loading the potential is introduced and many loading parameters are investigated including the loading current, loading time and solution pH. Also investigated are the film properties including film thickness, film freshness and the presence of the nanostructure. It is shown that controlled current loading can provide the required H/Pd ratio from first loading, even in a plain palladium film.

The use of the palladium microsensor in scanning electrochemical microscopy experiments is introduced. The microsensor is shown to be responsive to the changes in pH surrounding a platinum substrate undergoing cyclic voltammetry in a solution of  $0.5 \text{ M Na}_2\text{SO}_4$ . Well defined peaks which coincide with adsorption, evolution and consequent desorption of hydrogen on the Pt disc are seen in the potential, and pH measured by the tip. This shows that it is possible to use this nanostructured palladium hydride microsensor in scanning electrochemical microscopy experiments.

1. Introduction
1.1. pH Measurement at the Microscopic Level
1.1.1. Glass Electrodes 1 -
1.1.2. Field Effect Transistors 3 -
1.1.3. Polymer Films 4 -
1.1.4. Metal Oxides 5 -
1.1.4.1. Ruthenium 5 -
1.1:4.2. Tungsten 6 -
1.1.4.3. Platinum and Palladium 7 -
1.1.4.4. Antimony 8 -
1.1.4.5. Iridium9 -
1.2. Palladium Hydride 10 -
1.2.1. Phases 17 -
1.2.2. Hydrogen absorption 18 -
1.2.3. Palladium Hydride Electrodes 21 -
1.3. Fabrication of Nanostructured Films Using True Liquid Crystal
Templating 23 -
1.3.1. Lyotropic Liquid Crystals 23 -
1.3.1.1. Structure 23 -
1.3.1.2. Phases and Phase Diagrams 24 -
1.3.2. Plating Method 28 -
1.3.3. Previous Applications 30 -
1.4. Scanning Electrochemical Microscopy (SECM) 31 -
1.4.1. Historical Background 32 -
1.4.2. Principles of SECM 34 -
1.4.3. Potentiometric SECM 37 -
1.4.4. Applications 39 -
1.4.4.1. Concentration Measurement 39 -

-

1.4.4.2. Other Applications	41 -
2. Experimental	44 -
2.1. Reagents	44 -
2.2. Electrochemical Measurements	46 -
2.2.1. Instrumentation	46 -
2.2.1.1. Scanning Electron Microscope	46 -
2.2.1.2. Electrochemical Cells	46 -
2.2.1.3. Galvanostat Circuits	47 -
2.2.2. Experiment Design, Procedures and Protocols	49 -
2.2.2.1. Controlled Potential Experiments	49 -
2.2.2.2. Potentiometric Experiments	50 -
2.2.2.3. Galvanostatic Experiments	50 -
2.2.2.4. Scanning Electrochemical Microscopy (SECM)	51 -
2.3. Fabrication of Electrodes	52 -
2.3.1. Fabrication of Microelectrodes	52 -
2.3.2. Fabrication of Reference Electrodes	52 -
2.3.2.1. Saturated Mercurous Sulphate Electrodes	52 -
2.3.2.2. Saturated Calomel Electrodes	53 -
2.4. Deposition/Characterisation of Pd Films	53 -
2.4.1. Deposition	53 -
2.4.1.1. Deposition Procedure	53 -
2.4.2. Characterisation	55 -
2.4.2.1. Cyclic Voltammetry in $H_2SO_4$	55 -
2.4.2.2. Steady State Voltammetry in (NH <sub>3</sub> ) <sub>6</sub> Ru(III)Cl <sub>3</sub>	57 -
2.4.2.3. Roughness	59 -
<b>3. Potentiostatic Loading of Hydrogen into H<sub>1</sub>-e Pd</b>	60 -
3.1. Absorption behaviour	60 -
3.1.1. Q <sub>strip</sub> vs. Q <sub>Load</sub>	63 -
3.1.2. Loading Transient Analysis	68 -
3.2. Effect of E <sub>L</sub>	70 -

•

3.2.1. Stripping Analysis	71 -
3.2.2. Normalised Stripping Analysis	73 -
3.3. Nafion covered electrodes	76 -
3.4. Summary	81 -
4. Galvanostatic Loading of Hydrogen into H <sub>1</sub> -e Pd	8.
4.1. Loading Transients	
4.1.1. Effect of Loading Current	89 -
4.1.2. Effect of Loading Time	91 -
4.1.3. Effect of Oxygen	94 -
4.2. Loading / Stripping Analysis	96 -
4.2.1. Qstrip V QLoad	96 -
4.2.2. Effect of film thickness	98 -
4.2.3. Effect of film freshness	104 -
4.2.4. Effect of the nanostructure	107 -
4.2.5. Effect of pH	110 -
4.3. Summary	112 -
5. SECM	114
5.1. Experiment Set-up	115 -
5.2. Potentiometric Measurements in Aerated Solutions	120 -
5.2.1. Tip Potential	120 -
5.2.2. <i>pH</i> vs. <i>t</i>	123 -
5.2.3. Rate of Proton Release	127 -
5.2.4. Cyclic Voltammograms	132 -
5.3. Potentiometric Measurement in Deaerated Solutions	134 -
5.4. Summary	135 -
6. Conclusions/Further Work	137
	1/1

· · · · · ·

• ]

# Acknowledgements

I would firstly like to acknowledge the research carried out by **Dr. Toru Imokawa** prior to the research presented here. Although this thesis contains solely my own research, the work done by Dr. Imokawa provided a vital introduction to the research area.

**Dr. Guy Denuault** provided me with a fantastic opportunity to undertake my own research and gave up his time and knowledge to help me fulfil my potential. For this I will always be grateful and appreciative.

I would like to thank members of the Denuault & Bartlett research groups, particularly **Dr. David Cook** and **Dr. Liz Tull** for making my time enjoyable. Special thanks are reserved for **Dr. Maciej Sosna** who gave up his time and expertise on numerous occasions to help whenever needed.

The School of Chemistry has many superb members of support staff who go out of their way to make PhD lifer easier. I would specifically like to thank Alastair Clarke, Sally Dady, Karl Hagon and Bevy Price for their enthusiasm, assistance and guidance.

I would like to express my sincerest thanks to my parents who have been extremely supportive throughout my academic career. They have always encouraged me to be the best that I can and I hope they enjoy reading this thesis!

I cannot complete my acknowledgements without saying a huge thank you to my husband, the soon to be **Dr. Jonathan Williams** without whom I would not have embarked on a PhD and could not have completed it. His endless support, particularly over the past few months has been crucial to the completion of this thesis.

# **1. Introduction**

This thesis presents the research carried out into the development of nanostructured palladium hydride as a material for a micro pH sensor, particularly for use in scanning electrochemical microscopy (SECM). The research is picked up at a stage where a working pH sensor has been created and successfully used in a pH titration. The sensor has been shown to be reliable and theoretical – two very important characteristics. The current method for producing palladium hydride – potentiostatic loading – is investigated further and important conclusions are drawn and discussed in Chapter 3. These conclusions are particularly relevant when comparing with the new method of production – galvanostatic loading, as shown in Chapter 4. The new method also leads to a novel technique for analysis, which is applied retrospectively to the data recorded from potentiostatic loading, and also provides a greater insight into the palladium hydride system. Finally, in Chapter 5, the nanostructured palladium hydride is applied to SECM and the results are presented, along with proposed analysis.

# **1.1. pH Measurement at the Microscopic Level**

There is much need for pH measurements at localised positions and in small volumes of solution, especially in the field of life science and for clinical applications. This section details the current methods of the measurement of pH, particularly localised pH at the microscopic level.

# **1.1.1. Glass Electrodes**

Since the discovery of the ability of a glass membrane to determine hydrogen ion concentration, the glass electrode has been used in a wide range of applications, including chemical, biological and environmental studies. It was in fact the need for pH measurement and control in many areas of industry that lead to its development. The glass electrode has many properties that make it ideal for pH measurement. It can be used in solution containing oxidising or reducing agents; it is not poisoned by heavy

metals; and its use is not limited to aqueous media. Indeed, it can be used in several non-aqueous or partly aqueous media<sup>1</sup>.

One of the most common forms of the glass electrode consists of a thin glass membrane bulb inside which is mounted an internal reference electrode<sup>2</sup>. The reference electrode is immersed in an internal solution of constant pH containing the ion to which the inner reference electrode is reversible to; the reference electrode is often a silver chloride or calomel electrode and is immersed in either hydrochloric acid or a buffered chloride solution. The potential of the internal reference electrode is measured against that of an external electrode in contact with the analyte of interest. In combination pH electrodes, the reference electrode is actually built in with the glass electrode and connects with the analyte via a frit.

The ability of the glass membrane to determine the hydrogen concentration of a solution in which the electrode is immersed relies on the magnitude of the phase-boundary potential between the surface of the glass membrane and the solution. The phaseboundary potential is determined by the hydrogen ion activity in the solution. This happens since the glass functions as an ion-exchange material and an equilibrium is established between Na<sup>+</sup> cations on the surface of the glass and protons in the solution. As the pH of a solution changes from  $pH_1$  to  $pH_2$ , the potential of the glass membrane electrode changes according to the following relationship, derived from the Nernst equation.

 $E_2 - E_1 = -\frac{2.3RT}{F}(pH_2 - pH_1)$ 

# **Equation 1**

Thus the ideal pH response of the glass electrode is -59 mV per pH unit at 25 °C. However, in practice the glass electrode needs to be calibrated frequently using 2 (pH 4 and 10) or 3 (pH 4, 7 and 10) buffers. This ensures that the slope of the response is within 5% of 59 mV per unit. There are also limitations of the glass membrane electrode which prevent it obeying theoretical response. In very alkaline solutions (pH > 9) the potential recorded suggests a pH lower than expected, since the glass membrane suffers from partial substitution of H<sub>3</sub>O<sup>+</sup> ions by Na<sup>+</sup> or K<sup>+</sup>, resulting in the electrode

- 2 -

responding to these ions in the solution. It has been suggested by Michaelis that in alkaline solutions the sodium or other positive ions can also diffuse through the glass, thereby causing the deviations of the glass electrode at high pH<sup>3</sup>. This theory agrees with the observation that the smallest errors are observed when the glass membrane contains alkali metal cations of small radius and when the solution contains alkali metal cations of large radius<sup>2</sup>. As such, its effect can be reduced by using lithium glass (this reduces the error to approximately 50% of the sodium glass error) but cannot be removed.

Conversely, the potential recorded in very acidic solution (pH < 1) suggests a pH greater than expected. However, the cause of this so-called acidic error is not clear.

Glass membrane electrodes are effective. Despite their limitations, they are still the most popular pH sensor commercially available. However, there is considerable interest in the development of an alternative electrode for pH measurement; both from the view of eliminating these limitations and as the needs for smaller electrodes are ever increasing. Glass electrodes are not suitable for measurement of local pH, some more appropriate possibilities are suggested below.

## **1.1.2. Field Effect Transistors**

For approximately thirty years, the current flowing in tiny field effect transistors<sup>4</sup> (FET) has been used to probe ion concentrations, and in particular pH. Reasons for this include their small size, solid structure, and fast response. They also have low input impedance and simple instrumentation, the latter of which is especially important for a commercial pH sensor. FETs are made up of n-p-n semiconductors which form the source, gate, and drain respectively. The current between the source and the drain is influenced by a potential applied to the gate. In an ion selective field effect transistor (ISFET) an ion selective membrane acts as the gate, and as such the potential which acts upon the source-drain current depends on the amount of specific ions which have penetrated the membrane. Therefore by measuring the current, the concentration of ions can be measured. Both metal oxide field effect transistors<sup>5</sup> (MOSFETs) and reference field

- 3 -

effect transistors<sup>6</sup> (REFETs) have been used to measure pH. With the MOSFET it was found that there exists a linear relationship between the threshold voltage and pH only in the pH range from pH = 4 to pH = 7. When the pH range is extended, a non-linear relationship between pH and the threshold voltage is observed and this behaviour is explained in terms of deprotonation of different species of the native oxide surface. A combination of an IrOx microelectrode and a REFET was used to measure pH. A linear response with calibration curve slope of 69 mV pH<sup>-1</sup> was obtained<sup>6</sup>.

# 1.1.3. Polymer Films

Leopold et al<sup>7</sup> measured the local pH changes in the self oscillating Cu (II)-lactate system. This was done by coating a microband electrode with a pH sensitive conducting polymer, namely polyaniline (PANI), by electropolymerisation. It was assumed that local pH changes close to the electrode surface during reduction of the Cu (II)-complex to Cu were crucial to the oscillations and thus needed to be measured *in-situ*. The resulting pH sensitive electrode was calibrated by adding aliquots of 5 M NaOH to a solution of 0.6 M Cu (II) + 3 M lactate, between *pH* values of 9 and 13. The calibration curve had a slope of 65 mV pH<sup>-1</sup>.

Polyaniline is not the only polymer film to be used in pH measurement. Poly(1, 2diaminobenzene) electropolymerised onto the surface of a platinum film has been used as a potentiometric sensor to measure pH in an aqueous solution<sup>8</sup>. However, the electrode showed severe limitations. It is unstable at pH < 4, pH > 10 and results suggest that there are two linear regions in the calibration curve, with a changeover at pH = 6. Slopes of the curve are 45 mV pH<sup>-1</sup> for pH < 6 and 61 mV pH<sup>-1</sup> for pH > 6.

A pH responsive co-polymer poly(acrylic acid-co-isooctylacrylate) coated magnetoelastic sensor has been used for the wireless measurement of pH<sup>9</sup>. The sensor works over a  $1.3 - 7.5 \, pH$  range and is extremely robust, thus making it suitable for the measurement of gastric pH, to aid diagnosis of gastric diseases.

- 4 -

# 1.1.4. Metal Oxides

Many metal/metal oxide electrodes have been shown to have pH dependent potentials<sup>10</sup>. Among the wide range of metal/metal oxide electrodes that have been considered, Sb/SbOx, Ir/IrOx, W/WOx and Pd/PdOx microelectrodes have been used to measure local pH measurements, including SECM studies. Their attractiveness can be attributed to their ease of fabrication and their relatively robust structure. However, the potentiometric response of these metal/metal oxide electrodes does not show good accuracy or reproducibility. Also, their behaviour often varies between electrodes and as such it is normally required to calibrate the electrode before and after pH measurements. Some metal/metal oxide pH sensors and their properties are described below.

# 1.1.4.1. Ruthenium

Screen printed pH electrodes containing ruthenium dioxide, RuO<sub>2</sub>, have been created by Koncki and Mascini<sup>11</sup>. The pH sensitive layer of the screen printed electrode was prepared by hand-mixing graphite ink with RuO<sub>2</sub>, and was sandwiched between a conducting layer of silver ink and an insulating layer, with openings to allow contact. The calibration curve (*E* vs. *pH*) of this RuO<sub>2</sub> electrode yielded a slope of  $51.2 \pm 0.1$ mV pH<sup>-1</sup> when the graphite ink was doped with 9.8 % RuO<sub>2</sub>. The sensor showed good response for *pH* 2-7, but deviated from the expected response for *pH*  $\geq$  8. Response times were also longer for alkaline solutions, and reducing agents in solution adversely affected the response of the electrode. Applications for this type of pH sensor include pH measuring during enzymatic processes.

Sputtered thin-film RuO<sub>2</sub> electrodes were also used in a study by Kreider et al<sup>12</sup>, in a paper which also looked at platinum, palladium and iridium oxides. The study showed that RuO<sub>2</sub> electrodes produced by reactive sputtering at room temperatures, performed as well as or better than iridium oxide. The *E* vs. *pH* calibration plot produced a slope of  $54 - 59 \text{ mV pH}^{-1}$ , with no hysteresis. Prolonged exposure in buffered *pH* 10 solution caused a drop to  $52 - 54 \text{ mV pH}^{-1}$ , but no such effect was seen in acidic solutions.

- 5 -

#### 1.1.4.2. Tungsten

Tungsten oxide electrodes have been used in a variety of applications, including endothelial cells<sup>13</sup>, to monitor localised corrosion<sup>14</sup>, flow injection potentiometry<sup>15</sup> and for the pH monitoring of the heat transport circuits of thermal power plants<sup>16</sup>.

The exact method of formation and structure of tungsten oxide,  $WO_x$ , fabricated seems to vary across the reports. Yamamoto<sup>13</sup> et al cycled a tungsten wire in 2 M H<sub>2</sub>SO<sub>4</sub> between +1.0 and +2.0 V vs. Ag/AgCl to form WO<sub>3</sub>. Finally, the surface of the WO<sub>3</sub> was coated with Nafion to protect the film. The proposed potential determining reaction for a WO<sub>3</sub> electrode is shown in

$$WO_3 + nH^+ + ne^- \longrightarrow H_nWO_3$$
 Equation 2

The WO<sub>3</sub> electrode showed good linear response over the range pH 2 - 12, with a slope of  $53.5 \pm 0.5 \text{ mV pH}^{-1}$ .

pH sensors formed by oxidising a tungsten rod by heating in air were used to measure pH in high temperature aqueous environments<sup>16</sup>. The W/WOx electrode displayed a good linear response between pH 2 - 11. The slopes obtained, along with corresponding Nernstian slope values calculated from 2.330×RT/F, are shown in Table 1.

Table 1 Slopes of potential vs. pH curves for a WOx electrode at different temperatures. Taken from reference  $^{[16]}$ 

Temperature / °C	Nernstian slope / mV pH <sup>-1</sup>	WOx response / mV pH <sup>-1</sup>
212	96.3	95 ± 5
250	103.8	97 ± 5
300	113.7	104 ± 3

Dimitrakopoulos et al<sup>15</sup> immersed a tungsten wire in 1.0 M KOH overnight to establish a stable oxide film, thought to be either  $WO_2$  or  $W_2O_5$  due to the dark blue-brown colour. Proposed potential determining reactions for these electrodes are shown in Equation 3 and Equation 4.

- 6 -

$$WO_2 + 4H^+ + 4e^- \longrightarrow W + 2H_2O$$
 Equation 3  
 $W_2O_5 + 2H^+ + 2e^- \longrightarrow 2WO_2 + H_2O$  Equation 4

The electrode exhibited good linear response over the *pH* range 2 – 11, with a slope of  $44.8 \pm 0.5 \text{ mV pH}^{-1}$  in steady state mode and  $42.4 \pm 0.9 \text{ mV pH}^{-1}$  in flow injection mode.

# 1.1.4.3. Platinum and Palladium

Platinum and palladium oxide have both been studied as potential pH sensors<sup>12</sup>. Whilst PdOx has shown promising results, PtOx electrodes show limitations to their use. They suffer from a severe drop in sensitivity after long term use, from 50 mV pH<sup>-1</sup> to 24 mV pH<sup>-1</sup> after just 2 hours in a *pH* 2 solution. They also show a large hysteresis during pH cycling.

A number of methods for the formation of PdOx for use as a pH sensor have been proposed. These include anodisation in molten NaNO<sub>3</sub>/LiCl (98:2 by weight)<sup>17</sup> (electrochemical anodisation), oxidation of NaOH covered Pd wires at high temperatures<sup>18, 19</sup> (thermal oxidation), and thick-film sputtering onto silicon or aluminium<sup>12</sup>. The proposed potential determining reaction of PdOx is shown in Equation 5.

$$PdO + 2H^+ + 2e^- \longrightarrow Pd + H_2O$$
 Equation 5

The Pd/PdO electrodes formed by oxidation of NaOH covered Pd wires at high temperatures showed the best results. The *potential* vs. *pH* slope yielded a Nernstian response of  $59 \pm 1.2$  mV pH<sup>-1</sup>, and were shown to be stable in water for up to 6 years. However, the electrodes were sensitive to the presence of reducing agents in the solution.

Palladium / palladium oxide electrodes have been applied to the pH measurement of blood and extracellular fluids<sup>17</sup>.

- 7 -

# 1.1.4.4. Antimony

Antimony is second only to iridium when it comes to use as a metal/metal oxide pH sensor.

Antimony electrodes can be used as pH sensors without pre-oxidization of the surface<sup>20, 21</sup>, however thermal oxidation can be achieved by covering a pre-cleaned antimony electrode in powdered KNO<sub>3</sub>, and placing in a furnace at 500 °C for 2 hours under air atmosphere<sup>22, 23</sup>. The electrodes themselves tend to be fabricated by either a capillary melt method or by sealing monocrystalline antimony pieces in epoxy resin and grinding and polishing to expose the metal surface. The potential determining reaction of antimony electrodes was suggested by Bates<sup>2</sup> to arise from an oxidation-reduction reaction between the antimony metal and the surface oxide, Sb<sub>2</sub>O<sub>3</sub>, as shown in Equation 6.

 $Sb_2O_3 + 6H^+ + 6e^- \longrightarrow 2Sb + 3H_2O$  Equation 6

This reaction was verified in later studies by Ha and  $Wang^{23}$  by comparing the measured potential difference for 2 antimony electrodes, fabricated by different methods with the standard electrode potentials of different antimony oxide reactions.

As with all metal/metal oxide electrodes, it is expected that the antimony electrode will follow Nernstian behaviour, i.e. the potential of the antimony electrode should be a function of the activity of hydrogen ions as shown in Equation 7.

$$E_{Sb} = E_{Sb}^0 + \frac{RT}{F} \ln a_H$$

#### **Equation 7**

Given that  $pH = -\log_{10} a_H$  this would lead to a *E* vs. *pH* calibration plot slope of 59 mV pH<sup>-1</sup>. However, in practice, Sb/SbOx electrodes tend to show sub-Nernstian behaviour with reported calibration slopes of 50 – 55 mV pH<sup>-1</sup>. Even in agar media, antimony electrodes show a linear response of potential with pH<sup>22</sup>. The calibration curves, *E* vs. *pH*, show super-Nernstian behaviour, with a slope value of 71.9 mV pH<sup>-1</sup>.

- 8 -

Antimony electrodes, regardless of preparation, work over a large pH range. They have been shown to have a linear response across the pH range 2 – 10 in aqueous media<sup>21, 23</sup> and up to 4 – 7 in agar media (further pH values were not tested).

The rapid response and rugged structure of the antimony electrode make it useful for continuous industrial recording when great accuracy is not required. It is suitable for use at high temperatures and can be used in basic solutions with cells of the simplest design. Sb/SbOx microelectrodes are especially useful in biosystems where their small size, mechanical strength and chemical stability are required. To date they have been used to measure both bloodstream and myocardial  $pH^{20}$ , the pH change in agar media during plant tissue culture<sup>22</sup> as well as many other bioapplications.

# 1.1.4.5. Iridium

Iridium oxide electrodes are extensively used as pH sensors. Of recent literature on metal/metal oxide pH sensors, iridium oxide features more often than any other metal<sup>1</sup>. This is due to their low sensitivity to interference from redox agents, and the wide range of pH response (typically 2 - 12)<sup>24</sup>.

Iridium oxide can be prepared via a number of techniques. More traditional preparations of IrOx include electrochemical<sup>21, 25-27</sup> or thermal<sup>28</sup> oxidation of Ir electrodes. However, sputtering<sup>12</sup> of IrOx has been shown to be successful and recently the preferred method is the direct electrochemical electrodeposition of iridium oxide<sup>24, 29-32</sup>. It can be seen that the response of IrOx electrodes strongly depends on the preparation method. The widest pH range was found to be with electrodes formed by anodic electrodeposition of iridium oxide<sup>29</sup> (AEIROF). Some instances have been reported of iridium oxide showing two different linear regions of pH response, with a transition point at approximately  $pH = 6^{24}$ . However, most studies do not show this; instead they exhibit just one linear region in *E* vs. *pH* calibration curves. Iridium oxide pH sensors tend to exhibit Nernstian or super-Nernstian pH response, that is, the slope of the calibration curve is typically 59 – 90 mV pH<sup>-1</sup>. This suggests that the number of electrons

- 9 -

transferred for every proton varies, and is dependent on the method of preparation. Fog and Buck<sup>33</sup> first noticed that the difference in the measured potential difference can be indirectly attributed to the preparation. Vanhoudt<sup>25</sup> et al suggested potential determining reactions based on preparation methods. Sputtering and thermal oxidation methods of preparation tend to produce anhydrous iridium oxide IrO<sub>2</sub>, and tend to show calibration slope values of 59 mV pH<sup>-1</sup>. The potential determining reactions can be explained by Equation 8 or Equation 9.

$$IrO_{2} + H^{+} + e^{-} \longrightarrow IrO \cdot OH$$
 Equation 8  
$$2IrO_{2} + 2H^{+} + 2e^{-} \longrightarrow Ir_{2}O_{3} + H_{2}O$$
 Equation 9

However, electrochemically oxidised iridium tends to produce iridium oxides that are hydrated to various degrees. These have calibration slope values of up to 90 mV pH<sup>-1</sup>, suggesting that 1.5 electrons are transferred for every H<sup>+</sup>. A possible potential determining reaction for the hydrated iridium oxide  $[IrO_2(OH)_2 \cdot 2H_2O]^{2-}$  is shown in Equation 10

$$2[IrO_{2}(OH)_{2} \cdot 2H_{2}O]^{2-} + 3H^{+} + 2e^{----}[Ir_{2}O_{3}(OH)_{3} \cdot 3H_{2}O]^{3-} + 3H_{2}O \quad \text{Equation 10}$$

Interference studies<sup>33</sup> on iridium oxide electrodes show no interference from cations such as  $Li^+$ ,  $K^+$  or Na<sup>+</sup> or from anions such as  $F^-$ ,  $Cl^-$  or Br<sup>-</sup>. AEIROF electrodes have also been shown to be insensitive to most complexing agents<sup>21</sup>.

Applications of IrOx microelectrodes include SECM experiments<sup>24</sup>, to study the pH profile across a denitrifying biofilm<sup>25</sup>, to monitor cell metabolism<sup>27</sup> and for the fabrication of a wireless microanalysis system<sup>34</sup>.

# **1.2. Palladium Hydride**

Since Graham<sup>35</sup> first noted that huge amounts of hydrogen could be absorbed into a palladium tube, the palladium hydride system has been the subject of many research

- 10 -

papers and reviews. It has also been utilised in many applications including, but not limited to, hydrogenation of edible oil<sup>36</sup>, the manufacture of semi conductors and the cooling of power station alternators. The palladium hydride system is also of much interest in structure and materials chemistry; where there has been much work done with a purely academic interest. More recently, the ability of palladium to adsorb large amount of hydrogen has led to a huge interest in the use of palladium hydride as a hydrogen storage material, which could be of great use in fuel cells<sup>37</sup>.

The palladium hydride system has also been used as a model<sup>38</sup> for other metal hydride systems as it represents a classic example in the general area of the removal of gases from binary solid phases from simple stoichiometric ratios. In particular, the dependence on temperature and equilibrium pressures of the gaseous component of the system has been investigated and results show much reliability and reproducibility.

Hydrogen is generally introduced into the palladium via the gas phase, where the reaction  $H_2 \rightarrow 2H$  will readily occur so long as the surface of the palladium is sufficiently clean. The loading of hydrogen into palladium for use as a palladium electrode is discussed in more detail in 1.2.3 "Palladium Hydride Electrodes".

A commonly used representation of the palladium hydrogen phase relationship is the hydrogen pressure-hydrogen content-temperature (p-c(n)-T) plot, often shown in the form of p-c(n) isotherms, as shown in Figure 1.



**Figure 1** p-c(n) isotherms of palladium/hydrogen system. Phase transitions are shown are represented by a dashed line. Taken from ref  $[^{39}]$ .

The p-c(n) isotherms shown in Figure 1 emphasise the existence of regions where the solid hydrogen content composition undergoes large changes, at effectively constant values of hydrogen gas pressure. These are shown in the diagram as the area between the dashed lines. These regions are widely characterised as the regions of coexistence of the  $\alpha$ -phase and  $\beta$ -phase hydrides, and exist below a critical value,  $T_c$ , of approximately 310 °C. It can be seen that the isotherm at 160 °C shows the largest region of  $\alpha$ -phase and  $\beta$ -phase coexistence, and is present for H/Pd ratios of approximately 0.04 – 0.5.

However, it can not be seen from these p-c(n) isotherms that there exists an hysteretic difference in the hydrogen pressure between the  $\alpha \rightarrow \beta$  and the  $\beta \rightarrow \alpha$  phase transition.

- 12 -

This hysteresis effect was seen early in the course of the presentation of p-c(n)-T isotherms. The pressure measured when the hydrogen content is being successively increased (absorption isotherm) shows a hydrogen pressure greater than when the hydrogen content is being successively removed (desorption pressure). This hysteresis effect can be shown in combined absorption/desorption isotherms, as in Figure 2.



Figure 2 A hysteresis cycle shown for palladium-hydrogen at 120 °C. A hysteresis scan is also shown starting from the decomposition plateau. Taken from reference  $[^{40}]$ 

The combined absorption/desorption isotherm in Figure 2 shows a hysteresis loop for the palladium hydrogen system at 120 °C. There is a marked difference of approximately 30 kPa between the adsorption isotherm and the desorption isotherm. However, repeated absorption-desorption cycles have been shown to reduce the extent of the hysteresis. The hysteresis is also reduced as the temperature is increased and it can be shown that at the critical temperature,  $T_c$ , there is no hysteresis. This fact can be used to determine the critical temperature. Possible reasons for the presence of hysteresis loops will be discussed in Section 1.2.1 "(Palladium Hydride) Phases".

Hydrogen can also be loaded into the palladium lattice by electrochemical methods, either under potentiostatic or galvanostatic control. The first noticeable feature of electrochemical loading is that the potential-hydrogen content isotherm shows a region where the solid hydrogen content composition undergoes large changes, at a constant value of chemical potential. An example of this is shown in Figure 3.



**Figure 3** Absorption ( $\longrightarrow$ ) and desorption ( $\longrightarrow$ ) relationships between the hydrogen content of palladium and electrodes potential, at a constant temperature of 25 °C. Redrawn from reference [<sup>41</sup>]

Figure 3 shows the approximate representation of the potential, *E*, during hydrogen absorption from a hydrogen-saturated solution, reported by Barton and Lewis<sup>41</sup>. As with the p-c(n) isotherms produced for loading from the gas phase, the plateaus produced at +0.050 V (absorption) and +0.060 V (desorption) are attributed to the coexistence of  $\alpha$  and  $\beta$  palladium hydride phases. The drop in potential prior to the +0.050 V plateau

was attributed to the pure  $\alpha$  phase, and the subsequent drop to 0 V to the pure  $\beta$  phase. Figure 3 also shows a hysteresis loop between the absorption and desorption loops, which highlights the similarities in the palladium hydride system, regardless of formation.

Studies have shown that hydrogen loading via a solution of dissolved hydrogen proceeds at a faster rate than loading via the gas phase, and at significantly lower temperatures. Electrolytically discharged hydrogen can be absorbed by palladium at temperatures close to 25 °C, compared with the generally slow rate of equilibration between palladium and hydrogen molecules at these temperatures<sup>41</sup>.

Many researchers of the palladium-hydrogen system have attempted to produce a method of measuring the hydrogen content in the palladium lattice in situ i.e. without removing the hydrogen. Many different studies have been undertaken, and include electrochemical quartz crystal microbalance (EQCM) method<sup>42-46</sup>, neutron diffraction, extended X-ray absorption fine structure (EXAFS) and X-ray diffraction (XRD) studies<sup>47</sup> and in situ resistance measurement<sup>41, 48, 49</sup> (ISRM).

There has been much research undertaken of the hydrogen palladium system by use of the electrochemical quartz crystal microbalance<sup>42-46</sup>. The EQCM is favoured since it can be used to measure mass changes in the order of ng cm<sup>-2</sup> accompanying electrochemical processes that occur in or on electrodes. The frequency change of the quartz crystal microbalance can be related to mass change via the Sauerbrey equation, as shown in Equation  $11^{50}$ .

$$\Delta f = \frac{-2f_0^2 mn}{\sqrt{\rho\mu}} = -C_f m$$

**Equation 11** 

where  $\Delta f$  is the frequency change, Hz

 $f_0$  is the fundamental frequency of the crystal, Hz m is the mass per unit area, g cm<sup>-2</sup> n is the harmonic number of the oscillation

- 15 -

 $\rho$  is the density of the quartz, equal to 2.648 g cm<sup>-3</sup>

 $\mu$  is the sheer modulus of quartz, equal to 2.947 g cm<sup>-1</sup> s<sup>-2</sup>

These constants are normally grouped together to give the sensitivity factor,  $C_f$ , which has the value of 42 Hz cm<sup>2</sup> µg<sup>-1</sup> for a 5 MHz crystal in aqueous solution.

The Sauerbrey equation is a theoretical relationship, and assumes that the electrode is free from stress. Authors agree that there is an overestimation of the mass obtained, however the extent of the overestimation varies greatly between authors and between the  $\alpha$ -phase and  $\beta$ -phase. In the case of hydrogen absorption into palladium the two most important factors affecting the response of the EQCM are (i) electrode mass changes (i.e. the amount of absorbed hydrogen) and (ii) stresses of the palladium lattice induced by the hydrogen absorption. Therefore Equation 12 can be applied.

$$\Delta f = \Delta f_{mass} + \Delta f_{stress}$$

#### **Equation 12**

Since Equation 12 has been shown to be valid<sup>44</sup>, the amount of hydrogen absorbed into the palladium lattice cannot be determined directly from the response of the EQCM. Also, the change in frequency due to stress,  $\Delta f_{stress}$ , is affected by many different factors including the amount of hydrogen absorbed, the type of palladium and is also sensitive to electrode ageing. Therefore, EQCM is not a valid method for the measurement of absorbed hydrogen in a palladium lattice.

In-situ resistance measurements use the relationship between the ratio of electrical resistances,  $\chi_R$ , and the hydrogen content, represented by the H/Pd ratio x. The ratio of electrical resistances of palladium loaded with hydrogen is related to the hydrogen content of the film, which is often expressed by Equation 13

- 16 -

$$\chi_{R} = \frac{R_{PdH_{x}}}{R_{Pd}}$$

#### **Equation 13**

The relationship between  $\chi_R$  and x increases linearly as the palladium film begins to absorb hydrogen into the  $\alpha$ -phase. As x increases and the Pd-H system passes from the pure  $\alpha$ -phase through to the  $\alpha + \beta$  mixed phase and finally through to the pure  $\beta$ -phase the rate of increase of  $\chi_R$  becomes slower until eventually the film is saturated and the resistance,  $\chi_R$ , is at its maximum. In high temperature or low pressure experiments, in which stoichiometric palladium hydride can be formed, it is shown that the resistance then decreases sharply.

However, experiments that have attempted to use this information in order to measure the resistance of the palladium film in-situ and therefore indirectly measure the hydrogen content, have encountered some problems. Among others, the inhomogeneous distribution of the hydrogen within the palladium lattice provides error in the measurement of the hydrogen content. These errors have been shown to be particularly significant in the areas of interest to this thesis, namely the  $\alpha + \beta$  mixed phase. Thus much care is needed if in-situ resistance measurements are used to calculate the hydrogen content.

#### **1.2.1. Phases**

It is generally accepted that palladium hydride undergoes phase transformations as it absorbs hydrogen. As the amount of hydrogen within the palladium increases, the phase transformation from  $\alpha$ -phase PdH to  $\beta$ -phase occurs. The phase transition occurs over a wide range of values of H/Pd ratio, and it is now known and accepted that there exists a region where the  $\alpha$ -phase and  $\beta$ -phase PdH can coexist. For all values of H/Pd ratio hydrogen is known to occupy the octahedral interstices of the original face centred cubic palladium lattice<sup>51</sup>.

It is commonly assumed that for very small values of the H/Pd ratio (pre  $\alpha$ -phase) the hydrogen is randomly distributed throughout the octahedral interstices. As the H/Pd ratio begins to increase the palladium retains its own face centred cubic lattice, but with increasing expansion.  $\alpha$ -phase palladium hydride is present for H/Pd < 0.1 and during

- 17 -

this time the hydrogen can be thought of as regions of solid solution within the palladium lattice. At H/Pd ratios > 0.1, however, the lattice becomes unstable and the original  $\alpha$ -phase is converted into a considerably expanded  $\beta$ -phase. This phase transformation sees the coexistence of the two distinct PdH phases and is completed when H/Pd reaches 0.5. For H/Pd > 0.5 i.e. pure  $\beta$ -phase, the palladium hydride structure corresponds to a defective sodium chloride structure with anionic hydrogen vacancies<sup>51</sup>. At a H/Pd ratio of 0.69 the palladium hydride system is in equilibrium with hydrogen gas at 1 atm pressure i.e. the palladium has absorbed the maximum amount of hydrogen<sup>52</sup>.

This information is summarised below in Table 2.

Table 2 Summary of the physical properties of the phases of palladium hydride. Taken partly from reference  $[^{53}]$ .

	Palladium	α-phase PdH	β-phase PdH
H/Pd Ratio		< 0.1	> 0.5
Lattice Structure <sup>54</sup>	f.c.c	f.c.c	f.c.c
Lattice Constant <sup>55</sup> / kx	3.882	3.882 - 3.886	4.017 - 4.031
Diffusion Coefficient of hydrogen <sup>54</sup> / cm <sup>2</sup> s <sup>-1</sup>	,	$\sim 2 \times 10^{-7}$	~2 x 10 <sup>-6</sup>

#### 1.2.2. Hydrogen absorption

The absorption of hydrogen by palladium cathodes during electrolysis was first noted by Graham<sup>35</sup>. The hydrogen evolution reaction on palladium takes place via a multistep reaction known as the Volmer-Heyrovski-Tafel route<sup>46, 56-58</sup>. The first step in this reaction scheme is the Volmer reaction (Equation 14) and is the adsorption of hydrogen onto the surface of the palladium

**Equation 14** 

where M represents the adsorption site on the Pd surface

MH<sub>ads</sub> is the hydrogen atom adsorbed on the surface

Once adsorbed, the hydrogen can form gaseous hydrogen following two processes. This can either be electrochemical desorption (Heyrovski reaction, Equation 15) or chemical recombination (Tafel reaction, Equation 16)

$$MH_{ads} + H_3O^+ + e^- \longrightarrow M + H_2 + H_2O$$
 Equation 15  
 $MH_{ads} + MH_{ads} \rightarrow H_2 + 2M$  Equation 16

Alternatively, the adsorption reaction (Equation 14) can be followed by an insertion process in the palladium leading to hydrogen absorption and diffusion of hydrogen into the bulk palladium. This is shown in Equation 17.

$$MH_{ads} \rightarrow MH_{abs} (surface) \rightarrow MH_{abs} (bulk)$$
 Equation 17

When studying the electrochemical reactions of the hydrogen/palladium system, it is important to be able to distinguish the hydrogen absorption / desorption currents, which are a few orders of magnitude higher than those of the surface processes. Studies have shown that when thin films<sup>59</sup> or small particles<sup>60</sup> of palladium (i.e. in the order of nm) are used as electrodes the adsorption and absorption processes can be distinguished from each other.

It is not yet known exactly how hydrogen atoms enter the bulk palladium. Different theories have been put forward for the mechanism of electrochemical loading of hydrogen into the palladium bulk. Two theories on the role of adsorbed hydrogen have been put forward<sup>58</sup>, namely the *diffusion controlled indirect hydrogen absorption reaction (har) model* and the *direct har model*. In the indirect har model, the hydrogen is first adsorbed onto the surface of the palladium via the Volmer reaction (Equation 14). Adsorbed hydrogen atoms then diffuse into the metal.

 $MH_{ads} \rightarrow MH_{abs}$ 

**Equation 18** 

The bulk diffusion of adsorbed hydrogen, Equation 18, is in competition with the Heyrovski reaction, (Equation 15) and Tafel reaction, (Equation 16). In the direct har model the hydrogen directly enters the metal, without passing through the adsorbed state.

$$H_3O^+ + M + e^- \rightarrow MH_{abs} + H_2O$$
 Equation 19

It has also been suggested that there exists a layer of hydrogen dissolved just beneath the surface<sup>61-63</sup>, known as "subsurface hydrogen". This subsurface layer, which can range from 20 - 50 nm, contains hydrogen that can be distinguished from bulk absorbed hydrogen. It has been suggested<sup>63</sup> that the absorption of hydrogen into the bulk palladium can be separated into the following four processes:

- (i) proton discharge and coupled chemisorption of H
- (ii) phase transfer of H from the surface to the subsurface
- (iii) transfer of hydrogen from (ii) to the bulk by diffusion along the chemical potential gradient of H
- (iv) parallel processes of desorption of H<sub>ads</sub> from the surface by either the Heyrovski (Equation 15) or Tafel (Equation 16) reaction.

Research by Czerwinski et al<sup>64-66</sup> also agrees with the theory of subsurface hydrogen. They showed that the H/Pd ratio in Pd limited volume electrodes (LVE), which was calculated from the charge of the hydrogen oxidation peak depends significantly on both the rate of the potential sweep and the thickness of the deposited layer of Pd. This experimental observation serves to endorse previous hypotheses about the presence of hydrogen absorbed into palladium as a subsurface layer phase. They also suggest that the subsurface layer exists not only during the absorption of hydrogen, but also during the desorption process. The general scheme for the desorption of hydrogen in an acidic (Equation 20) and basic (Equation 21) solution is shown below.

- 20 -

**Equation 20** 

$$H_{\beta} \leftrightarrow H_{\alpha} \leftrightarrow H_{sub} \leftrightarrow H_{ads} \rightarrow \qquad \rightarrow 1/2 H_{2}$$

 $\rightarrow^{k_2}$  H<sup>+</sup>+e<sup>-</sup>

 $\stackrel{k_1}{\longrightarrow} \frac{1}{2} H_2$   $\stackrel{k_2}{\longrightarrow} H_2 O + e^{-1}$ 

$$\mathrm{H}_{\beta} \leftrightarrow \mathrm{H}_{\alpha} \leftrightarrow \mathrm{H}_{\mathrm{sub}} \leftrightarrow \mathrm{H}_{\mathrm{ads}} \xrightarrow{\mathrm{OH}^{-}}$$

**Equation 21** 

The common theme between Equation 20 and Equation 21 is that in both cases it is the hydrogen present in the subsurface layer that is responsible for the generation of the adsorbed hydrogen, which can then undergo either electrochemical oxidation or recombination with other adsorbed hydrogen atoms. The thickness of the subsurface layer and the hydrogen content within it are both smaller in a basic solution when compared with an acidic solution. This is due to the presence of alkali metals in palladium, which are able to enter during hydrogen electrolysis.

# **1.2.3. Palladium Hydride Electrodes**

Palladium hydride electrodes have long been used as reference electrodes<sup>67, 68</sup>, by utilising the constant potential of the  $\alpha + \beta$  phase. The advantage of using palladium hydride over platinum hydride is that saturation of the electrolyte by bubbling hydrogen is not necessary with palladium hydride reference electrodes since they can carry their own hydrogen supply.

Since the potential measured depends on the hydrogen activity in the solution, palladium hydride electrodes have also been widely utilised as pH sensors<sup>68-71</sup>. There are many advantages to employing palladium hydride electrodes as pH sensors. The potentiometric response of palladium hydride pH sensors is rapid, stable and reproducible. They have been reported<sup>1</sup> to show almost theoretical potentiometric pH response i.e. the slope of the *potential-pH* calibration curve is close to the expected Nernstian value of -59 mV/pH at 25 °C. It is possible, therefore to conduct pH

measurements without calibration either before or after the pH measurements. A typical calibration curve is shown in Figure 4.



**Figure 4**  $E_{Pd-H}$  vs pH calibration curve obtained from a titration of a deaerated solution of 0.5 M Na<sub>2</sub>SO<sub>4</sub>.  $\bigcirc$ , forward titration (NaOH was added); , reverse titration (H<sub>2</sub>SO<sub>4</sub> was added);  $\bigtriangleup$ , in 0.5 M Na<sub>2</sub>SO<sub>4</sub> + 0.05 M phosphate buffer (before the titration);  $\bigstar$ , 0.5 M Na<sub>2</sub>SO<sub>4</sub> + 0.05 M phosphate buffer (after the titration). Taken from reference<sup>53</sup>

This is a rare characteristic for potentiometric micro pH sensor. Finally, due to their nature, palladium hydride pH sensors can be used in experiments where it is not possible to use conventional glass electrodes. For example, they can be used under conditions of high temperature or pressure, or can be used in fluoride solutions. They can also be used in strong alkaline solutions without interference from  $Na^+$  etc.

Historically, palladium hydride electrodes were prepared by loading a palladium wire with hydrogen directly from the gas phase. There is no special preparation of the palladium needed, other than being sufficiently free from grease and other surface contaminants. This should ensure that a rapid equilibrium is established between the gaseous hydrogen and the hydrogen dissolved in the palladium.

Recent research<sup>53</sup> has brought together the use of nanostructured palladium films with the pH-sensing ability of palladium hydride. The use of the nanostructure ensured that

microelectrodes could be used thus adding the advantages of microelectrodes into the mix.

Palladium hydride electrodes have been long used as both reference electrodes<sup>1</sup> and pH sensing electrodes<sup>2</sup> and have been applied to many systems. The ability of palladium to store vast amounts of hydrogen, up to 0.69 H per Pd atom, has also led to the use of palladium hydride in fuel cells. Nelson and Owen<sup>72</sup> utilised nanostructured palladium as the negative electrode in a high-performance supercapacitor/battery hybrid. The purpose of the research was not to suggest the use of palladium, an expensive material, commercially. Instead, by using palladium as the negative electrode they were able to make the performance of the device limited by the positive electrode and therefore study the positive electrode material, nanostructured Ni/Ni(OH)<sub>2</sub>.

# **1.3.** Fabrication of Nanostructured Films Using True Liquid Crystal Templating

True Liquid Crystal Templating (TLCT) is a templating method first published by Attard et al. in 1997<sup>73</sup>. It uses lyotropic liquid crystals as the template, reduces a metal salt around the template and then dissolves the template, leaving a metal film with a nanoscale structure.

# **1.3.1. Lyotropic Liquid Crystals**

#### 1.3.1.1. Structure

Lyotropic liquid crystals, otherwise known as surfactants, exhibit phase changes as the surfactant concentration is increased. The surfactants used in this study are amphiphiles meaning that they have both a hydrophobic and a hydrophilic section. A typical molecule is octaethylene glycol monohexadecyl ether (Figure 5), which consists of a hydrocarbon 'tail' and an ether headgroup.

- 23 -



Figure 5 Octaethylene glycol monohexadecyl ether  $C_{10}EO_8$ . (Grey = C, white = H, red = O)

On addition of water they remain as individual molecules until the critical micellar concentration (CMC) is reached, after which point the surfactant molecules aggregate into micelles. This happens since the ether headgroup is polar and as such favourably interacts with the water molecules. However, being non-polar and thus hydrophilic, the hydrocarbon tail is unable to favourably interact with the polar water molecule. The formation of the aggregated micelles represents the best alignment of the surfactant molecules so as to satisfy both the ether headgroup and the hydrocarbon tail. This is, in fact, true of all the phases formed as the concentration is increased.

# 1.3.1.2. Phases and Phase Diagrams

Below the critical micellar concentration the surfactant exists as individual molecules in which are soluble in water. However, since the hydrocarbon headgroup does not interact favourably with the surfactant forms a layer on the surface on the water, with the hydrocarbon tails out of the water. As the concentration of the surfactant increases, the surfactant molecules form micelles which are spheres of surfactant molecules in which the hydrocarbon tails are protected from the polar water molecules. As the concentration is increased further, this is no longer satisfactory and so the phase changes. Each new phase represents a method of protecting an increasing concentration of hydrocarbon tails.

Figure 6 shows the phases formed as the surfactant concentration is increased above the critical micellar concentration.



**Figure 6** Aggregation of surfactant molecules as the concentration is increased above the critical micellar concentration. Taken from reference [<sup>74</sup>]

The micellar solution  $(L_1)$  consists of spheres of surfactant molecules, arranged such that the hydrophobic tails are shielded from the water by the hydrophilic headgroups. When these arrange themselves onto a cubic lattice, this is known as the micellar cubic phase (I<sub>1</sub>). As the micellar concentration increases, the hexagonal phase (H<sub>1</sub>) is formed. This consists of cylinders of surfactant molecules sitting on a hexagonal lattice. Again the molecules are arranged so as to exclude water from the hydrophobic tail of the surfactant molecules. Figure 7 shows a close up view of the hexagonal (H<sub>1</sub>) phase.



Figure 7 A close up view of the arrangement of surfactant molecules in the H<sub>1</sub> (hexagonal) phase.

At concentrations greater than those required to form the hexagonal phase, surfactant molecules aggregate to from the cubic (V<sub>1</sub>) phase, lamellar phase (L<sub> $\alpha$ </sub>) and inverse phases, such as the inverse micellar phase (L<sub>2</sub>). Polarising optical microscopy can be used to distinguish between the different phases since the isotropic phases (e.g. L<sub>1</sub> & V<sub>1</sub>) do not show up in polarising optical microscopy and the non-isotropic phases show distinctive images. The method can be used to create a phase diagram, which shows the phases produced by varying surfactant concentrations and temperatures. It is produced by creating mixtures with various surfactant concentrations and observing under a microscope whilst altering the temperature with a microscope. The phases produced are also affected by the presence of the metal salt in the aqueous phase. Figure 8 shows a pseudobinary phase diagram constructed by Bartlett et al<sup>75</sup> of C<sub>16</sub>EO<sub>8</sub> in an aqueous solution of ammonium tetrachloropalladate, where the concentration of the palladium salt was kept constant at 1.40 mol dm<sup>-3</sup>.



Temp / <sup>o</sup>C

**Figure 8** Pseudobinary phase diagram of  $C_{16}EO_8$  and water in which the concentration of  $(NH_4)_2PdCl_4$  was kept fixed at 1.40 mol dm<sup>-3</sup>. H<sub>1</sub> is the hexagonal phase, V<sub>1</sub> the cubic phase, L<sub> $\alpha$ </sub> the lamellar phase and L<sub>1</sub> the micellar solution. Redrawn from reference [<sup>75</sup>]

It can be seen from Figure 8 that to achieve the hexagonal (H<sub>1</sub>) phase at room temperature, a surfactant concentration of between 40% and 80% is required. However, this range shrinks to between 45% and 60% at approximately 50  $^{\circ}$ C

In the previous and the current study, heptane is added to the mixture in order to swell and uniformise the pore size. As heptane is hydrophobic, is it attracted to the hydrocarbon tail of the surfactant and not the hydrophobic head-group. Although the phase diagram presented in Figure 8 does not contain heptane, is it not believed to be affected by the addition of heptane.

In this study, the mixture used is thermostated to a temperature of 25  $^{0}$ C and with a surfactant concentration of 47 wt. % which places firmly in the region of the hexagonal

- 27 -

phase. This is the only phase that will be used to create nanostructured films in the current study.

## **1.3.2. Plating Method**

In order to plate a nanostructured film onto the surface of an electrode, a templating mixture must be prepared using the information provided in phase diagrams, such as Figure 8. Firstly a metal salt, in this study ammoniumtetrachloropalladate, is added to water and this mixture is combined with the lyotropic liquid crystal in the required ratio. The final mixture is then electroplated onto the electrode by applying a constant potential for a desired time. This ensures that the metal salt, which is around the liquid crystal, is reduced and plated on the electrode.



Figure 9 A diagrammatic representation of the technique used to create a nanostructured film from a lyotropic liquid crystal template. Taken from reference  $[^{75}]$ .

Once the plating procedure is complete, the film is washed by stirring in plenty of water for two hours such that the surfactant is dissolved away. This leaves a metal film with pores where the lyotropic liquid crystal once was.

This relatively simple plating procedure means that once a templating mixture has been fabricated many palladium films can be created in a short space of time.

# **1.3.3.** Previous Applications

Since the original work, which deposited nanostructured Pt films onto 1 cm<sup>2</sup> gold electrodes<sup>73</sup>, lyotropic liquid crystals have been used as a template to produce a variety of nanostructured films, from metals such as platinum<sup>73, 76-78</sup> and palladium<sup>75, 79</sup> through to insulating 1,2-diaminobenzene polymer films<sup>80</sup> (denoted H<sub>1</sub>-eOPD). Recently, work has been reported of nanostructured CdTe films electrodeposited onto CdS electrodes for use in solar cell applications<sup>81</sup>. They suggested that nanostructured CdTe thin films would exhibit unusual charge carrier dynamics, improved collection of photogenerated carriers and thus enhanced solar conversion efficiencies.

Bartlett et al<sup>82</sup> have created nanostructured cobalt (H<sub>1</sub>-e Co) films from a deposition mixture of 56.05 % Brij 56 and 43.95 % aqueous solution containing CoAc<sub>2</sub> (0.4 M), KAc (0.51 M) and boric acid (0.16 M). The nanostructure was shown to have coercivity values 3-5 times greater than polycrystalline cobalt, which has very important implications for use in advanced storage media, since magnetic coercivity is the amount of energy required to alter the state of a magnet i.e. the higher a magnetic disc's coercivity index, the more data it can store.

Platinum nanostructured films have been used to study the electrochemical reduction of oxygen<sup>78</sup> and the detection of hydrogen peroxide<sup>77</sup>. In both cases the film was electroplated onto microelectrodes so as to benefit from the effects of using nanostructured films, whist retaining the valuable characteristics of microelectrodes. These nanostructured platinum films have also been used to monitor the local concentration of  $H_2O_2$  using scanning electrochemistry microscopy (SECM) in generation/collection mode. Evans et al<sup>77</sup> used a nanostructured platinum microelectrode scanned above a substrate of monolayer of glucose oxidase immobilised with polyphenol, in a *pH*-7 buffered solution. The activity of the substrate was modified with the tip by electrochemically generating OH near the surface. The local increase in pH severely lowered the activity of the enzyme beneath the tip and significantly decreased the flux of  $H_2O_2$  from this region. This is clearly seen as a bright spot in the image produced by the scanning electrochemical microscope. This is the first known
example of the use of nanostructured films in SECM. Evans et al<sup>83</sup> also used a similar SECM tip to enable the fabrication, functionalisation and characterisation of biologically active microspots. The generation/collection mode of the SECM and the nanostructured tips were able to provide a very reliable detection of the hydrogen peroxide generated by biotin labeled glucose oxidase thus yielding a chemical image of the fabricated microspot.

A previous study<sup>75</sup> was undertaken into the electrochemical behaviour of nanostructured palladium. In particular the study looked at the effect the nanostructure has on the hydrogen absorbing ability of palladium, especially when compared to that of bulk palladium. Voltammograms of nanostructured palladium in sulphuric acid were presented and compared to that of plain palladium films. In particular the formation of adsorbed and absorbed hydrogen were readily distinguished with the nanostructured palladium; due to the extremely high surface area to volume ratio of the H<sub>1</sub>-e Pd and the fast kinetics for the formation of  $\alpha$  and  $\beta$ -hydride phases. A similar study was performed more recently<sup>79</sup>, where nanostructured palladium was used to study the surface electrochemistry of palladium in aqueous sodium hydroxide. Contrary to palladium in acid, the hydrogen adsorption/desorption processes involve slow electron kinetics. Thus it can be assumed that the well defined peaks obtained in this study result from the high surface area to volume ratio and as such can be directly attributed to the nanostructure.

# **1.4. Scanning Electrochemical Microscopy (SECM)**

Scanning electrochemical microscopy (SECM) is a technique used to electrochemically image a surface by use of a microelectrode tip which is electrochemically controlled in the vicinity of the surface. This section will detail the historical background of the technique, the basic principle of SECM focussing on potentiometric probes and finish with a brief overview of some of its applications.

- 31 -

## **1.4.1. Historical Background**

In 1989, a paper by Bard's group<sup>84</sup> introduced the principle of Scanning Electrochemical Microscopy (SECM). The paper described the research done in creating a method of characterising processes and structural features of a surface immersed in a solution. However, work on scanning electrode surfaces and in-situ electrochemical STM studies were published up to 4 years earlier in simultaneous works by Engstrom<sup>85-88</sup> and Bard's group<sup>89-91</sup>. The development of SECM depended on the amalgamation of two separate issues of research. These were the use of microelectrodes in electrochemistry, and the application of piezoelectric elements to position a tip, as in scanning tunnelling microscopy (STM). Given that the use of microelectrodes in electrochemistry is a vast area of research, it transpires that SECM can also cover a wide range of experiments and techniques. In fact, it is worth noting that SECM is not an independent experiment, it relies on the electrochemical technique and almost any experiment available in electrochemistry is available to the SECM. Since its innovation, SECM experiments have advanced drastically and have been performed for a wide variety of applications, which make use of the many different modes of operation available to the scanning electrochemical microscope.

Scanning electrochemical microscopy came from the awareness of the fact that the steady state current of a microelectrode is affected by the presence of the substrate, when the substrate is within the diffusion layer of the tip. Redox mediators in the solution are used to transfer information between the substrate surface and the tip. There are three models for the diffusion of an electroactive species towards or away from a microelectrode. These are quasi-hemispherical diffusion (for a tip in the bulk solution), hindered diffusion (for a tip close to an insulating surface) and feedback diffusion (for a tip close to a conducting surface). These are shown in Figure 10.

- 32 -



**Figure 10** Diffusion of the redox mediator a) in the bulk, b) close to an insulator and c) near to a conductor. Arrows pointing toward the tip indicate the diffusion of O, whereas arrows pointing away indicate the diffusion of R. Taken from reference [92]

SECM has been used extensively to measure the concentration of various species such as  $H_2O_2^{83,93}$ ,  $Ag^+$  and  $I^{-94}$  and  $H^{+95-98}$ . It has also been possible to indirectly measure the dissolution of MnS from stainless steel. Paik et al<sup>99</sup> used  $I^{7}I_{3}^{-}$  as a redox mediator to measure the product of dissolution, HS<sup>-</sup> and  $S_2O_3^{2^-}$ . Scanning electrochemical microscopy has also been used extensively for electrodeposition of metals<sup>100-103</sup>, metal oxides<sup>104</sup> and biological substances<sup>105-107</sup>.

One of the more unusual applications of SECM is the creation of a method of "writingreading-erasing" on tungsten oxide. Turyan et al<sup>108</sup> used the feedback mode of SECM to write, read and erase onto tungsten oxide, WO<sub>3</sub>, films. A platinum tip was used to reduce WO<sub>3</sub> in localised regions and being electrochromic, this was accompanied by a colour change. By holding the tip above the substrate they fabricated spots with a diameter of approximately 200  $\mu$ m and created lines thickness approximately 100  $\mu$ m by moving the tip at a speed of 5  $\mu$ m s<sup>-1</sup>.

The acronym SECM is used interchangeably to describe the instrument (the microscope) or technique (microscopy).

### **1.4.2.** Principles of SECM

The scanning electrochemical microscope belongs to the group of scanning probe microscopes, a group that also includes scanning tunnelling microscopy (STM) and atomic force microscopy (AFM). Like these techniques, the SECM consists of a tip (in this case a microelectrode) that is held by a three dimensional micropositioner above the sample surface (substrate). Both the tip and substrate are immersed in a solution which contains an electrolyte and a redox mediator. The fundamental principle of the technique is to control the electrochemistry of the tip, bring the tip close to the surface of the substrate and then monitor the interaction between the tip and the substrate by measuring the electrochemical response.

Historically, movement of the tip around the substrate was achieved by use of inchworm drivers or inchworm drivers combined with piezoelectric pushers which allows the user to work in nm resolution. However, it is much more common for users to use stepper motors to move the microscope. The method of moving the tip is vital, since the positioner is very important in determining the scanning range, the hysteresis and accuracy of positioning.

The substrate used in SECM experiments can be any number of solid surfaces, e.g. metal, glass, polymer, biological material, or even liquid e.g. mercury or immiscible oil. In fact since SECM probes an interface, it can also be a gas in the case of a liquid/gas interface. It simply needs to be able to perturb the electrochemical response of the tip, or to itself be perturbed by a change in its local environment, caused by the presence of the species generated by the tip.

The SECM tips can be divided into two section; namely active or passive probes. Early SECM techniques utilised passive probes, which like their name suggests, do not electrochemically perturb the substrate, but instead assess the localised electrochemical activity of the substrate by mapping the potential distribution above the substrate. A large subsection of passive probes are ion-selective electrodes (ISE) which were initially developed by biologists for the purpose of measuring concentrations of various species within biological tissues. These ISE provide a Nernstian relationship between the electrode potential and the concentration of the redox species. These fall under the banner of potentiometric probes and will be discussed in 1.4.3. The most popular solid electrodes used for SECM are microdisc electrodes with diameter of  $0.6 - 25 \ \mu m^{109}$ , which are fabricated by sealing a microwire into a glass capillary and polishing the end flat. The ratio of the diameter of the entire tip (electrode plus glass) to the electrode is typically in the order of 10.

The main advantages of active probes over passive probes is that rather than be responsive to just one ion species, active probes can be adjusted to respond to various redox mediators. Active probes can be used to generate powerful reductants or oxidants and on diffusion away from the tip and toward the substrate these species perturb the surface of the tip. This allows for reactions on the surface of the substrate that are both highly controlled and highly localised, which can be used for the formation of specific designs during deposition or etching.

SECM with active probes is a highly versatile technique. Figure 11 shows the various modes of a SECM (taken from an SECM review paper by Mirkin and Horrocks<sup>110</sup>).

- 35 -



Figure 11 Schematic diagram showing the various types of SECM experiment. Taken from a review article by Mirkin and Horrocks<sup>110</sup>

Quantitative theoretical models have been developed for each of the modes of operation. By far the majority of SECM experiments are used with the tip in amperometric mode, which is shown in parts 1 - 5 of Figure 11. In particular the feedback mode, part 1, is greatly used. As shown in Figure 10 the diffusion of the redox active species in the reaction  $O + ne^- \rightarrow R$  to/from the SECM tip is affected by the presence of a substrate. When the substrate is insulating (Figure 10b), e.g. glass or plastic, the substrate impedes the diffusion of O to the tip and as such the current is less than in Figure 10a (negative feedback). However, when the substrate is conducting (Figure 10c) although the diffusion of O is still hindered, there is oxidation of the product ( $R \rightarrow O + ne^-$ ) back to O. The O generated at the substrate increases the amount of O at the tip and therefore the current detected is greater than in Figure 10a (positive feedback). Understanding the current recorded at the tip requires knowledge of the electrochemical behaviour of a microelectrode, which is well documented<sup>111-113</sup>.

#### 1.4.3. Potentiometric SECM

Part 6 of Figure 11 shows the SECM tip in potentiometric mode, i.e. when the SECM tip is sensitive to ions being generated by the substrate. Besides the high selectivity of the potentiometric signal, the main advantage of potentiometric tips is that they are able to measure concentration of species that are not electroactive in aqueous media, unlike amperometric techniques. As an example, alkali and alkaline earth metal ion profiles are particularly important in experimental life science, but cannot be quantified by voltammetry in aqueous media<sup>114</sup>.

Potentiometric SECM electrodes are passive probes which unlike active probes do not affect the concentration profile of the species generated or consumed at the substrate. This means that the theory for potentiometric SECM is simpler than for amperometric SECM. The response of the sensor depends linearly on the logarithm of the activity of the potential determining ion in the presence of other ions, as shown in Equation 22 for  $H^+$ . However, deviation from the ideal electrode behaviour is common.

$$E = constant - \frac{RT}{F} \ln a_{H^+}$$

#### **Equation 22**

Potentiometric ion selective electrodes (ISE) are membrane-based devices with internal filling solution and internal reference electrode or with internal solid contact. The main type of membrane electrodes are:

- glass membrane electrodes
- crystalline (or solid state) membrane electrodes

- 37 -

liquid membrane electrodes

An example of the electrochemical notation of a complete potentiometric cell assembly is given as:

 Ag | AgCl, KCl | | salt bridge | | sample | membrane | internal solution, AgCl | Ag

 Reference Electrode
 Ion-selective electrode

 where vertical lines indicate phase boundaries while double lines mark a liquid/liquid interface.

In this case, the cell potential is the sum of a number of local potential differences generated at the solid/solid, solid/liquid and liquid/liquid interfaces within the cell and measured between the two reference electrodes. At zero current the cell potential,  $E_{cell}$ , is given by Equation 23.

$$E_{cell} = E_{ISE} - E_{ref} + E_{jnc}$$

**Equation 23** 

It is worth noting that the potentiometric ISE when used in SECM have several drawbacks, when compared to amperometric mode. Firstly, the fabrication of most potentiometric tips is a complex and lengthy procedure and it is often necessary to have the tip specially made. The response of the potentiometric tips is not always Nernstian and calibration is often required before and after use. It is even common for response to vary from one tip to another tip despite them being the same type. It is possible in amperometric mode to use feedback to measure the tip-substrate distance indirectly by measurement of the feedback current. However, this method for the measurement of tip-substrate distance is not possible, and whilst alternative techniques are available they are mostly unwieldy.

# **1.4.4. Applications**

## 1.4.4.1. Concentration Measurement

SECM has been used extensively for the localised detection of ions in the vicinity of a substrate. SECM tips have been used to measure the activity of a number of different ions directly (amperometric and potentiometric tips) and indirectly (amperometric tips). Amperometric probes have been used to measure the concentration profile of hydrogen peroxide,  $H_2O_2^{83, 93}$ . Evans et al<sup>83</sup> used a nanostructured Pt tip (diameter = 10 & 50 µm) initially to drive the deposition of a micrometre size spot of biotinylated polypyrrole. Subsequent reaction with avidin and a biotinylated enzyme enabled the construction of a "molecular sandwich" capable of producing  $H_2O_2$ . The nanostructured tip was then used to "read" the activity of the microspot by reliably detecting the localised production of  $H_2O_2$ . 200 µm x 200 µm SECM images of activity around a microspot were obtained by measuring the current at the nanostructured Pt tip held at + 0.6 V vs SMSE.

Amperometric probes can also be used to indirectly measure the concentration profile of a species. Paik et al<sup>99</sup> used scanning electrochemical microscopy to investigate the dissolution of MnS inclusion in stainless steels during initiation of pitting corrosion in an aqueous solution of 10 mM KI and 0.1 M NaCl. The dissolution products of MnS (HS<sup>-</sup> and S<sub>2</sub>O<sub>3</sub><sup>2-</sup>) were detected amperometrically at a carbon fibre SECM tip using  $I/I_3^-$  as the redox mediator, as shown in Figure 12.



**Figure 12** Schematic diagram of the SECM detection of  $S_2O_3^{2-}$  and/or HS<sup>-</sup> above a MnS inclusion in stainless steel. Taken from reference [<sup>99</sup>]

The iodide was oxidised at the tip to produce triiodide which further reacted with the sulphur species at the inclusion to regenerate  $\Gamma$ . The regenerated  $\Gamma$  was detected at the tip as an increase in the current.

Using this method, it was possible to create a 400  $\mu$ m x 400  $\mu$ m SECM image of an electroactive site on the stainless steel.

Potentiometric tips have been extensively to measure  $H^+$  as well as alkaline earth metal ions<sup>115-117</sup> such as  $K^+$ , and  $Ag^+$ . Potentiometric pH sensing materials, such as the metal oxide electrodes presented in section 1.1 can be miniaturised to produce SECM tips capable of measuring localised changes in pH. Horrocks et al used an antimony microelectrode (approximate diameter = 40 µm) to measure the pH profile around a Pt target reducing water (diameter = 25 µm) with a scan rate of 10 µm s<sup>-1</sup>. A peak in the modulus of the potential was clearly seen around the Pt substrate, corresponding to a localised area of high pH. As the hydroxide ions diffuse away the potential decreases thus indicating a pH increase. A similar experiment was used to measure the corrosion of silver iodide in aqueous cyanide. It has been suggested that a local pH change is due to the consumption of cyanide anion at an AgI surface by complexation with silver. Use

of the antimony tip (diameter = 15  $\mu$ m) above the AgI surface (diameter = 40  $\mu$ m) resulted in an area of low potential, and thus high pH, around the substrate.

A preferred tip for measurement of other cations appears to be Ag/AgCl. Denuault et  $al^{118}$  demonstrated the use of the potentiometric approach of SECM using the deposition and stripping of silver, by using a Ag/Ag<sup>+</sup> microindicator electrode (diameter = 50 µm). The potential of the substrate was stepped from 0 to + 50 mV vs. Ag wire for 2 s and then to - 50 mV for 4 s. the potential difference of the microindicator and a large Ag reference electrode in the bulk solution was measured and plotted as a function of time for several tip-substrate distances. The results shown indicate three features that concur with the theory for semi-infinite diffusion, as the tip-substrate distance increases. These are: (i) the tip potential peak moves to longer times; (ii) its amplitude decreases and (iii) the onset of the potential increase also moves to longer times.

#### 1.4.4.2. Other Applications

#### Corrosion

There is much interest in using scanning electrochemical microscopy to measure localised corrosion in metals, mostly iron (steel)<sup>99, 119-124</sup> and titanium<sup>125, 126</sup>.

The most popular method<sup>120, 121, 123, 124</sup> for the localised measurement of the corrosion process on steel (including coated steel) is to utilise a Pt microdisc (diameter = 10  $\mu$ m) under potentiostatic control. The Pt tip is held at a potential of + 0.6 V vs. Ag/AgCl/KCl (saturated) so as to ensure that all of the products of corrosion (Fe<sup>2+</sup>) are oxidised at the surface of the tip. The tip-substrate distance is typically 10  $\mu$ m. Successful studies using this procedure have produced 2-dimensional concentration profiles across a substrate and have demonstrated the ability to measure corrosion pits. It has also been suggested that the assessment of various coatings with the SECM can be compared to that of industrial salt spray tests, whilst offering faster continuous local measurement.

The corrosion of titanium foil with a native oxide layer  $(TiO_2)$  was measured by Casillas et al<sup>125, 126</sup>. The Ti/TiO<sub>2</sub> interface is highly susceptible to pitting corrosion, especially in I and Br<sup>-</sup> containing solutions. In the corrosion pits Br<sup>-</sup> is electrooxidised to Br<sub>2</sub>. The experiment utilised a carbon fibre tip (diameter = 8 µm) held at a potential of + 0.6 V vs. SCE. At this potential, Br<sub>2</sub> generated at the Ti/TiO<sub>2</sub> surface is reduced to Br<sup>-</sup>. An SECM image of the entire Ti/TiO<sub>2</sub> surface was created and local regions of Br<sub>2</sub> were detected. Therefore it was also possible to detect local regions of pitting corrosion.

#### • Electrochemistry in small volumes

A huge leap in the research of electrochemistry in small volumes was made with the creation of a single probe containing a carbon fibre microelectrode and a Ag/AgCl reference electrode in separate channels<sup>127</sup>. In previous studies where low-volume measurements have been made with the SECM, the probe has remained stationary. Using this probe, pH images of a substrate immersed in 70  $\mu$ L thick films of solution were obtained in the generator-collector mode of SECM using an iridium oxide modified microcell. This type of single probe has the advantage over separate tip/reference electrodes since there is no chance of collision which can damage both electrodes.

#### Surface Reactions

Scanning electrochemical microscopy can be used to study surface reactions<sup>95-97, 128</sup>. Tan et al<sup>128</sup> used a method based on tip-substrate voltammetry of SECM to study the surface reaction of LaNi<sub>5</sub> alloy during the discharge process in KOH. By using at Pt microdisc tip (diameter = 100  $\mu$ m) the Pt oxide formation-reduction is used as a pH dependent reaction, while the tip potential is held at a constant potential. The mechanism of the discharge process of the LaNi<sub>5</sub> alloy was analysed by comparing the tip current-substrate potential curve (which reflects the exchange of H<sup>+</sup> or OH<sup>-</sup> between the alloy surface and the solution), with the substrate current-tip potential curve (which reflects the exchange of H<sup>+</sup> or OH<sup>-</sup> between the alloy surface of electrons on the LaNi<sub>5</sub> alloy surface). The results showed that the OH<sup>-</sup> adsorption process occurs before the electron transfer process during discharge

- 42 -

and the adsorptive OH<sup>-</sup> aids the oxidation of the adsorbed hydrogen atom on the alloy surface.

Yang et al studied the adsorption and desorption of hydrogen and the formation and reduction of oxides on platinum electrodes in Na<sub>2</sub>SO<sub>4</sub> solution<sup>95, 97</sup> using SECM. A Pt tip (diameter =  $25 \mu m$ ) was used to probe the reactions on the surface of a Pt substrate (diameter = 0.5 mm). Experiments were carried out with the tip-substrate voltammetry where the faradaic current flowing to the tip is recorded against the potential of the substrate, whilst cycling the potential of the substrate, and with tip-substrate chronoamperometry where the faradaic tip current is recorded against time following the application of a potential step to the substrate. Results showed, among others, that both oxide formation and oxide reduction involve two stages. The study also showed that a pH decrease as high as 2.3 pH units occurs during hydrogen desorption, corresponding to a similar pH change for hydrogen adsorption. In a separate study<sup>96</sup>, the pH changes at a Pt electrode surface during potential cycling in a pH 4 solution of 0.5 M  $Na_2SO_4 + 10^{-4}$  M H<sub>2</sub>SO<sub>4</sub>. The results illustrated the presence of a pH decrease close to the substrate during hydrogen desorption, oxide formation and oxide evolution. Conversely a pH increase was observed during oxide reduction, hydrogen adsorption and hydrogen evolution. These pH variations were as large as one pH unit.

Chapter 2 indentifies all of the reagents, instrumentation and standard experimental procedures which are used throughout the thesis. Chapter 3 introduces palladium hydride as created via a potentiostatic method, and details the new analysis conducted. In addition to this, an investigation into the use of a membrane across the surface of the film is presented. Chapter 4 presents the novel technique of loading the nanostructured film galvanostatically, in order to create the required palladium hydride. It also incorporates the new analysis introduced in Chapter 3 as applied to the galvanostatic technique, and utilises this in order to analyse the film properties. Finally Chapter 5 details the work conducted into the development of SECM as an application of the  $H_1$ -e Pd film, and shows much analysis in to the resultant tip potential/pH and substrate current plots.

- 43 -

# 2. Experimental

This chapter contains the details behind all of the experiments undertaken. Unless otherwise stated, the following apply:

- All reagents were used as received without further purification. The details of each reagent are listed in Table 3
- All aqueous solutions were prepared using purified water (< 0.1 µS cm<sup>-1</sup>). Purification of water was accomplished in two steps. Water was first passed through a Whatman RO50 water filtering system. This filtered water was then deionised by passing it through a Whatman STILLplus carbon filter
- All glassware was soaked overnight in 5 % Decon 90 (BDH) solutions and rinsed thoroughly with purified water before use

# 2.1. Reagents

Table 3

Name	Chemical	Manufacture	Grade	Use
	Formula	r		
Alumina Powder	Al <sub>3</sub> O <sub>2</sub>	Buehler	1.0, 0.3 and 0.05	Polishing
			μm	electrodes
Ammonium	(NH <sub>4</sub> ) <sub>2</sub> PdCl <sub>4</sub>	Alfa Aesar	Premion®	Plating Mixture
Tetrachloropalladate				
Brij® 56 (C <sub>16</sub> EO <sub>n</sub> ;	C <sub>16</sub> H <sub>33</sub> (OCH <sub>2</sub>	Aldrich	n/a	Plating Mixture
n = 4 - 12)	CH <sub>2</sub> ) <sub>n</sub> OH			
Buffer Solution pH 4	n/a	Aldrich	n/a	Test Solution
Buffer Solution pH 7	n/a	Aldrich	n/a	Test Solution
Buffer Solution pH 10	n/a	Aldrich	n/a	Test Solution
n-Heptane	C <sub>7</sub> H <sub>16</sub>	Aldrich	HPLC 99+%	Plating Mixture
Hexaammine	Ru(NH <sub>3</sub> ) <sub>6</sub> Cl <sub>3</sub>	Aldrich	98%	Test Solution
Ruthenium (III)				
Chloride				
Indium	In	Aldrich	99.99%	Microelectrodes
Mercurous Chloride	Hg <sub>2</sub> Cl <sub>2</sub>			Reference `
				Electrodes
Mercurous Sulphate	Hg <sub>2</sub> SO <sub>4</sub>			Reference
				Electrodes
Mercury	Hg	Alfa Aesar	Electronic Grade	Reference
			99.9998%	Electrodes

Nafion	C <sub>7</sub> HF <sub>13</sub> O <sub>5</sub> S .	Aldrich	n/a	Protective
	$C_2F_4$			Membrane
Octaethylene Glycol	C <sub>16</sub> H <sub>33</sub> (OCH <sub>2</sub>	Nikko	n/a	Plating Mixture
Monohexadecyl Ether $(C_{16}EO_8)$	CH <sub>2</sub> ) <sub>8</sub> OH	Chemicals co		
Potassium Chloride	KCl .	Fluka	Trace Select > 99.5%(AT)	Electrolyte
Potassium Chloride	KCl	BDH	Analar	Reference Electrodes
Potassium Sulphate	K <sub>2</sub> SO <sub>4</sub>	BDH	Analar	Reference Electrodes
Sodium Carbonate	Na <sub>2</sub> CO <sub>3</sub>	BDH	Analar	Test Solution
Sodium Hydrogen Carbonate	NaHCO <sub>3</sub>	BDH	Analar	Test Solution
Sodium di-Hydrogen Orthophosphate 1- hydrate	NaH <sub>2</sub> PO <sub>4</sub> . H <sub>2</sub> O	BDH	Analar	Test Solution
di-Sodium Hydrogen Orthophosphate 12- hydrate	Na <sub>2</sub> HPO <sub>4</sub> .12H <sub>2</sub> O	BDH	Analar	Test Solution
Sodium Hydroxide	NaOH	BDH	Analar	Test Solution
Sodium Sulphate	Na <sub>2</sub> SO <sub>4</sub>	Sigma	Sigma Ultra min 99.0%	Electrolyte
Sulphuric Acid	H <sub>2</sub> SO <sub>4</sub>	BDH	Aristar	Test Solution

.

# **2.2. Electrochemical Measurements**

### 2.2.1. Instrumentation

In all experiments, the following instrumentation was used where appropriate. Potential was applied using a Hi-tek instruments waveform generator, PPR1 and current was measured using a TW Young home made current follower. In scanning electrochemical microscopy experiments the movement of the tip was controlled using a Burleigh 6000 inchworm controller. In all experiments the temperature of the electrochemical cell was controlled, via a water jacket, with a Grant W14 thermostat.

When fabricating reference electrodes<sup>\*</sup>, the potential difference between the home made reference electrode and the commercial reference electrode was measured with a ISOTECH IDM91E digital voltmeter (DVM).

## 2.2.1.1. Scanning Electron Microscope

The scanning electron microscope used was a XPhilips XL30 ESEM microscope. It was used predominantly in "wet mode" so as to prevent charging up of the glass surrounding the electrode. The detectors used were the back scattered electron (BSE) detector and the gaseous secondary electron (GSE) detector. The images were predominantly taken at three different angles; a top down view of the electrode, a view perpendicular to the electrode and a side view at approximately 75°.

### 2.2.1.2. Electrochemical Cells

The electrochemical cells to be used were made by the in house glass blower. All cells contained a water jacket which was connected to a water bath (W14, Grant) so as to maintain a constant temperature of  $25 \pm 1$  °C. The water around the cell was connected to the mains earth so as to remove electrical noise to the cell. The cell was shaped so as to promote a minimum distance between the electrodes, and the volume of the test

- 46 -

<sup>\*</sup> See 2.3.2 "Fabrication of Reference Electrodes"

solution was approximately 25 cm<sup>3</sup>. When necessary the solution was deaerated by bubbling argon gas (BOC) through the solution for 10 minutes before the experiment. The Ar flow was discontinued on commencement of the experiment, so as not to perturb the diffusion of the reactants to, or products from, the electrodes surface.

#### 2.2.1.3. Galvanostat Circuits

Galvanostats can be manufactured by utilising Ohm's law, which states that the input potential,  $E_i$  = current, *i* x resistance, *R*. Thus if a constant supply of potential is passed through a resistor with constant resistance then a constant current equal in magnitude to  $E_i/R$  is obtained. Advanced galvanostats can be constructed by using operational amplifiers<sup>50</sup>. A classic operational amplifier galvanostat is shown in Figure 13. The current through the cell is simply given by:

# $i = E_i / R$ Equation 24

The magnitude of the current can be altered by changing the value of R or  $E_i$  and the sign can be reversed by either switching the polarity of the input voltage or switching the cell connections. This circuit has an added advantage that the electrode connected to the summing junction is always at virtual ground potential, since the output of the operational amplifier ensures that the summing junction itself is at virtual ground.



**Figure 13** Single-amplifier galvanostat. In this circuit the current going through the cell is drawn from the output of the operational amplifier and it matches that which comes from the voltage source and goes through R, i.e. equal to  $E_i / R$ . The potential supply used was a PPR1;  $E_i$  is typically 0.5 V. With R = 10 M $\Omega$ , loading current,  $i_L$  is typically 50 nA<sup>50</sup>.

The circuit shown in Figure 13 should be adequate for low current applications; however, since the current is drawn directly from the voltage source, large currents may alter the input voltage,  $E_i$ . Thus  $E_i$  becomes slightly dependent on the resistance of the cell (which is estimated to be between 5 and 15 M $\Omega$  at the  $\alpha$ - to  $\beta$ -phase PdH transition<sup>†</sup>). Additionally, it is important to use a constant potential supply since if the voltage source is a battery then the potential of the battery will decrease over time if currents are being drawn from it. An alternative is to use a galvanostatic circuit where no current is drawn from the voltage source, as in Figure 14. Here  $E_i$  is connected to the infinite impedance of the non-inverting input. As such, the summing junction is no longer at virtual ground; instead it is maintained at potential  $E_i$  by the operational amplifier. The current supplied to the cell is given by:

# $i = -E_i / R$ Equation 25

and in this circuit there is no current being drawn from the voltage source. Again, the magnitude of the current can be altered by changing the value of R or  $E_i$  and the sign can be reversed by either switching the polarity of the input voltage or switching the cell connections.

<sup>&</sup>lt;sup>†</sup> Determined from experiment.



**Figure 14** Diagram showing the circuit used to create the alternative galvanostat. Here the potential supply is a battery. The operational amplifier provides a current to the cell equal to  $-E_i / R$ . Typically,  $E_i = 7.3$  V and  $R = 100 \text{ M}\Omega$ , giving loading current,  $i_L = 73$  nA.

The galvanostatic data presented predominantly uses the galvanostat shown in Figure 13. The voltage source used is a PPR1 waveform generator (HiTek) so as to avoid voltage drop over time, due to currents being drawn. Typically,  $E_i = 0.5$  V and R = 10 M $\Omega$ , therefore i = 50 nA.

# 2.2.2. Experiment Design, Procedures and Protocols

Unless otherwise stated, all experiments were done under the following conditions:

- Temperature controlled using a thermostat and water jacket to 25  $^{\circ}C$
- Conducted within a Faraday cage
- Connected using short, shielded cables

# 2.2.2.1. Controlled Potential Experiments

Controlled potential experiments, such as potential sweeps and potential steps were undertaken by using a two electrode system. The reference electrode was a homemade SCE or SMSE electrode, which also served as a counter electrode since the currents passing were small (in the order of  $\mu$ A). The fabrication of the homemade SCE and SMSE electrodes will be explained further in Section 2.3.2 "Fabrication of Reference Electrodes". The potential of the working electrode with respect to the reference electrode was controlled using a waveform generator (PPR1 from HiTek), while the current was recorded using a homemade current follower.

## 2.2.2.2. Potentiometric Experiments

Potentiometric experiments, where the open circuit potential of the solution was measured, were also undertaken using a two electrode system. The reference electrode, which also served as a counter electrode, was a SMSE electrode, the fabrication of which will be described Section 2.3.2 "Fabrication of Reference Electrodes". The potential of the solution was measured by using a home-made differential amplifier. The positive input of the differential amplifier was connected to the working electrode (the nanostructured PdH sensor) and the negative input and earth were connected to the SMSE electrode. The differential amplifier and potentiostat used in controlled potential experiments were connected to the working/reference electrodes via a switch since this required one connection to the acquisition software, they are not required simultaneously and there is often the need for a fast change between the two.

### 2.2.2.3. Galvanostatic Experiments

Galvanostatic experiments, which were used exclusively for loading of the palladium film by use of a constant current, were undertaken using two electrodes. The combined reference/counter electrode was a home made SCE/SMSE electrode; the fabrication of which will be described Section 2.3.2 "Fabrication of Reference Electrodes". The current across the palladium film was supplied by homemade galvanostat, the potential source of which was supplied by the potentiostat described in Section 2.2.1. The potential of the electrode was monitored by the differential amplifier used in the potentiometric experiments.

#### 2.2.2.4. Scanning Electrochemical Microscopy (SECM)

All SECM experiments were conducted in 0.5 M  $Na_2SO_4$ . Separate SMSE reference electrodes were used for the tip and substrate. The cell shape was that of a trough, with the substrate positioned vertically through the bottom of the cell. The substrate reference electrode was positioned far away from the surface of the substrate, in the bulk solution. However, the tip reference electrode was situated in close proximity to the tip and substrate.

The tip current was supplied by the galvanostat and the potential across the tip and reference electrode was measured by a home-made high input differential amplifier. After loading, the galvanostat was disconnected from the tip so as not to interfere with the potential measurement.

The potential of the substrate was controlled by a PPR1 and a home made current follower was used to measure the current following through the substrate. Thus the variables that need to be monitored or recorded are the substrate potential and current,  $E_{substrate}$  and  $i_{substrate}$ , and tip potential,  $E_{tip}$ . Due to the limitations of the number of inputs into the acquisition programme (2 plus a time counter), only  $E_{tip}$  and  $i_{substrate}$  were measured during the cyclic voltammetry. The potential of the substrate during cyclic voltammetry was not measured since the parameters of the cyclic voltammetry are known and as such the potential can be recreated from the time value. Although not ideal, it is not thought to affect the experiment since it can be verified by the cyclic voltammetry.

# **2.3. Fabrication of Electrodes**

## 2.3.1. Fabrication of Microelectrodes

Microelectrodes were made in the lab using a well-known procedure<sup>112, 113</sup>. Firstly the microwire (approx. 2 cm) is placed in a soda glass pipette which had previously been cleaned and degreased using Decon 90<sup>®</sup> followed by acetone. The microwire is first sealed in the pipette by using a blowtorch flame, with care being taken to avoid over heating which would lead to bending of the pipette. The pipette is then further sealed by placing in a heating coil and slowly heated under reduced pressure, until all but 5 - 10 mm of the wire has been sealed. Small pieces of indium are then placed in the open end of the pipette, such that they surround the unsealed wire. The indium is slowly heated, and once melted a connecting wire is pushed to the bottom of the molten indium and twisted so as to ensure a sufficient connection has been made. On cooling, the indium will re-solidify and provide the connection between the connecting wire and the microwire. Finally, quick set epoxy resin is placed around the top of the pipette and connecting wire, so as to remove any strain on the connection. Before use, the microelectrode is polished on successive grades of silicon carbide paper (320, 600, 1200) on a polishing wheel, followed by successive grades of alumina (1.0, 0.3  $\mu$ m) so as to expose and clean the electrode surface.

### **2.3.2.** Fabrication of Reference Electrodes

Two different reference electrodes were used in this work; saturated calomel electrodes (SCE) were used for solutions containing chloride ions and saturated mercurous sulphate electrodes (SMSE) for all other solutions.

### 2.3.2.1. Saturated Mercurous Sulphate Electrodes

SMSE reference electrodes were home made and assembled using a known procedure<sup>129</sup>. Firstly, two pieces of glassware were obtained; a glass pipette with a frit at the bottom, and a tube of glass sealed at one end, with a connecting wire through the seal. A drop of mercury was placed in the tube until it covered the connecting wire. A paste consisting

of Hg and Hg<sub>2</sub>SO<sub>4</sub> was placed on top of the mercury drop and on top of this was a small amount of glass wool which had been soaked in saturated K<sub>2</sub>SO<sub>4</sub>. The glass pipette was filled with the same saturated K<sub>2</sub>SO<sub>4</sub> solution and the glass tube was fixed inside the glass pipette. The whole electrode was left standing in the remainder of the saturated K<sub>2</sub>SO<sub>4</sub>, such that the frit did not dry out. After soaking for 24 hours the electrode was tested with a commercial SMSE electrode, and was considered suitable for use if the potential was within 5 mV of the commercial electrode and stable. The SMSE electrode was regularly tested using this method.

#### 2.3.2.2. Saturated Calomel Electrodes

SCE electrodes were assembled using the same procedure as the SMSE electrodes. The difference is that  $Hg_2Cl_2$  was used in place of  $Hg_2SO_4$  and saturated KCl was used in place of saturated  $K_2SO_4$ . Again, once made the electrode was left to soak in the saturated solution for 24 hours before testing with a commercial SCE electrode and used only once the potential was stable and within 5 mV of the commercial electrode.

# 2.4. Deposition/Characterisation of Pd Films

## 2.4.1. Deposition

#### 2.4.1.1. Deposition Procedure

The electroplating was performed using a pre-determined and reliable method<sup>73, 130</sup>. A mixture of ammonium tetrachloropalladate, water, surfactant and heptane was made up according to Table 4 and used as the electroplating solution. The quantities were chosen such that the surfactant would form a hexagonal (H<sub>1</sub>) phase, with the Pd salt in the aqueous domain. The heptane was added so as to both increase and uniformise the size of the cylinders, and thus create bigger pores in the nanostructured palladium. Had excess heptane been added, an oily residue would be present in the mixture. The electrode to be plated was polished on 1  $\mu$ m and 0.3  $\mu$ m alumina powder before cycling in 1M H<sub>2</sub>SO<sub>4</sub>, until a stable voltammogram was obtained. Both the microelectrode and the reference electrode were covered with the plating solution before placing in the plating mixture. This was to ensure that the whole of the microelectrode was covered,

- 53 -

the microelectrode was not touching the bottom of the deposition cell and that there were no bubbles present. The presence of any of these would result in an uneven, patchy film. The electrodeposition was achieved by stepping the potential from the open circuit potential (approximately +0.3 V Vs SCE)<sup>53</sup> to -0.1V Vs SCE. The electrode was held at this potential until the charge passed,  $Q_{dep}$ , reached the required value, typically between 5 and 40  $\mu$ C. The film formed is known as a H<sub>1</sub>-e Pd film to signify its origin, with a subsequent A or B to signify the surfactant used – see Table 4.

	(NH <sub>4</sub> ) <sub>2</sub> PdCl <sub>4</sub>	Water	n-Heptane	C <sub>16</sub> EO <sub>8</sub>	Brij-56 <sup>®</sup>
H <sub>1</sub> -e Pd(A)	12%	39%	2%	47%	
H <sub>1</sub> -e Pd(B)	12%	39% .	2%		47%
Non- nanostructured Pd	40 mM	aqueous solution			

Table 4 Composition of plating solutions used.

Figure 15 shows a typical transient obtained during the plating of a H<sub>1</sub>-e Pd film onto a Pt microdisc. The temperature of deposition was always kept constant at 25  $^{0}$ C. It can be seen that when Brij-56<sup>®</sup> is used as the surfactant the loading time can be twice as long than when using C<sub>16</sub>EO<sub>8</sub>, caused by significantly lower currents. There is also a more gradual increase when using C<sub>16</sub>EO<sub>8</sub>.



**Figure 15** A typical transient obtained when palladium is plated onto a Pt microdisc (diameter = 25  $\mu$ m) using the (i) H<sub>1</sub>-e Pd (A) and (ii) H<sub>1</sub>-e Pd (B) mixture.  $Q_{dep} = 20 \mu$ C.

After depositing the film, the surfactant needed to be removed from within the pores of the palladium film. This was done by stirring the electrode in water for a minimum of two hours. The purpose of this was to remove the surfactant and heptane from within the pores, which was removed since the surfactant is soluble in water and the heptane is removed along with the surfactant. It was noted that the majority of the surfactant was removed within two hours, and although more could be removed for much longer times two hours was seen as a sufficient amount of time.

#### 2.4.2. Characterisation

### 2.4.2.1. Cyclic Voltammetry in H<sub>2</sub>SO<sub>4</sub>

Cyclic voltammetry in sulphuric acid can be used to calculate the electroactive area of an electrode. It can also be used to qualitatively assess the film. The cyclic voltammogram of a palladium film in  $H_2SO_4$  gives a fingerprint of the palladium surface redox processes. Figure 16 shows a typical cyclic voltammogram produced when a  $H_1$ -e Pd film is cycled in 1M  $H_2SO_4$ .

- 55 -



**Figure 16** Typical cyclic voltammogram for a H<sub>1</sub>-e Pd film electrodeposited onto a Pt microdisc ( $Q_{dep} = 20 \ \mu\text{C}, \ \varphi = 25 \ \mu\text{m}$ ) in 1M H<sub>2</sub>SO<sub>4</sub> (deaerated), with oxide stripping peak labelled (peak A). Scan rate = 100 mV s<sup>-1</sup>.

The peak labelled as peak A in Figure 16 is the current peak associated with the stripping of the palladium oxide formed in the forward scan, represented by the peaks at E = 0.2 and 0.4 V vs SMSE. The charge associated with the removal of the oxide layer,  $Q_{oxstrip}$ , can be used to indirectly measure the electroactive area of the palladium film.  $Q_{oxstrip}$  can be calculated by taking the integral of peak A and dividing by the scan rate, v, of the cyclic voltammetry. Finally the electroactive area of the film can be calculated by dividing  $Q_{oxstrip}$  by a conversion factor, since it is known that 424 µC of oxide stripped away for every 1 cm<sup>2</sup> of the palladium surface<sup>131</sup>. This assumes that a monolayer of oxide is produced. As such it is important that the upper potential limit of the cyclic voltammogram in controlled so that only a monolayer is produced. Investigations<sup>‡</sup> have shown that at an upper limit of 0.6 V vs SMSE is suitable for providing a monolayer of oxide.

<sup>‡</sup> Results not included in thesis

Typical values of for the electroactive area of a H<sub>1</sub>-e Pd film on a Pt microdisc ( $\varphi = 25$  µm) plated using  $Q_{dep} = 20 \ \mu\text{C}$  are  $6.5 \times 10^{-3} \text{ cm}^2$  and  $2.8 \times 10^{-3} \text{ cm}^2$  when the surfactant is C<sub>16</sub>EO<sub>8</sub> and Brij 56<sup>®</sup> respectively.

It is possible to calculate the geometric area of the film using two different methods. Both methods obtain an accurate measurement of diameter from which the area can easily be calculated. Firstly, steady state voltammetry can be used to measure the diffusion controlled limiting current, which is directly proportional to the film radius and secondly, scanning electron microscopy can be used to directly measure the diameter of the film.

#### 2.4.2.2. Steady State Voltammetry in (NH<sub>3</sub>)<sub>6</sub>Ru(III)Cl<sub>3</sub>

The steady state voltammetry is performed in  $(NH_3)_6Ru(III)Cl_3$ . Using potential limits of 0.05 – -0.4 V vs. SMSE and a slow scan rate, typically 2 mV s<sup>-1</sup>, a steady state voltammogram is achieved. The limiting current of this steady state voltammogram is related to the geometric diameter,  $\varphi$ , of the film by Equation 26.

$$i_{Limit} = 4nFDCa$$
 Equation 26

where *n* is the number of electrons transferred, *F* is the Faraday constant, *D* is the diffusion coefficient, *C* is the concentration of the redox species, and *a* is the radius of the microdisc, equal to  $\frac{1}{2} \varphi$ . The diffusion coefficient, *D*, was calculated by using plain electrodes of known diameter and plotting  $i_{Limit}$  against *a*. From the gradient of this slope, D was discovered to be  $8.8 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup>, which is in close agreement with a reported value of  $8.0 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup> <sup>132</sup> obtained under similar conditions. Thus in a solution of 10 mM (NH<sub>3</sub>)<sub>6</sub>Ru(III)Cl<sub>3</sub>, the geometric diameter of the film can be related to the limiting current,  $i_L$ , by Equation 27.

- 57 -

$$\varphi = i_L / 1.70 \times 10^{-5}$$

**Equation 27** 

where  $\varphi$  is the diameter / cm

 $i_L$  is the limiting current / A

## 2.4.2.3 Scanning Electron Microscopy (SEM)

Figure 17 shows a typical SEM image of a 25  $\mu$ m Pt disc plated with an H<sub>1</sub>-Pd film, obtained as described in Section 2.2.1.1. As can be seen, the typical film diameter, when plated onto a 25  $\mu$ m diameter microdisc is approximately 30  $\mu$ m. SEM can also be used to subjectively assess the quality of the film.



Figure 17 A typical SEM image of an H<sub>1</sub>-ePd film plated on a 25  $\mu$ m Pt disc.  $Q_{Dep} = 20 \mu$ C

In order to calculate the geometric area,  $G_A$ , the diameter of the film taken from either the SEM image or the steady state voltammogram is applied to Equation 28.

# $G_A = (\pi \varphi^2)/4$

#### **Equation 28**

It should be noted that films with an unexpected diameter or with a large disagreement between the diameter obtained via steady state voltammetry and that obtained from SEM were discarded.

A typical value of the geometric area of a film is  $9.7 \times 10^{-6}$  cm<sup>2</sup> when fabricated using C<sub>16</sub>EO<sub>8</sub> and  $9.2 \times 10^{-6}$  cm<sup>2</sup> when using Brij 56<sup>®</sup>.

#### 2.4.2.3. Roughness

The roughness factor,  $R_F$ , is the ratio of the electrochemical area,  $E_A$ , to the geometric area,  $G_A$ . Typical roughness factors are 3 for a plain polished electrode, 8 for a plain film, 670 for a nanostructured film made with  $C_{16}EO_8$ , and up to 305 for a nanostructured film made with Brij<sup>®</sup> 56. This is similar to previous research undertaken<sup>53</sup>.

The following chapter details the investigations into the potentiostatic loading research with has already been initiated, development of a new technique for analysis and the introduction of a membrane covering as a solution to the limited lifetime of the pH sensor.

# **3.** Potentiostatic Loading of Hydrogen into H<sub>1</sub>-e Pd

This chapter extends the previous research completed on the potentiostatic loading of an H<sub>1</sub>-e Pd film with hydrogen. In addition to recapping on the important aspects of potentiostatic loading, this chapter also introduces new analysis on the data obtained. This new analysis becomes particularly important in Chapter 4 when analysing the data obtained from galvanostatic loading. It is important to remember that in potentiostatic loading it is the driving force (potential) behind the insertion reaction that is predetermined and applied to the nanostructured palladium and that the rate of insertion adapts itself, according to the external parameters. The effect of some of these external parameters on the rate of insertion has been previously studied and will not be repeated, however, important conclusions will be referred to. This chapter reviews the effect of changing the loading potential and observes the effect of the film thickness on the insertion of hydrogen into the film. Also included is a description of the method used to characterise the H<sub>1</sub>-e Pd films once they have been loaded with hydrogen. By stripping the hydrogen back out from within the palladium lattice, it is possible to obtain a valuable measure of the relationship between the amount of hydrogen initially loaded, and how this compares with the charge measured during loading. This characterisation is described in Section 3.1.1, and used in Section 3.2. It should be noted that the results presented in this chapter are typical of the results obtained; these experiments are highly reproducible.

# **3.1.** Absorption behaviour

Hydrogen can be inserted into a  $H_1$ -e Pd film using potential as the driving force. It can be seen from a simple voltammogram that as potential is swept toward more negative values, the reaction proceeds through three steps; strong hydrogen adsorption, weak hydrogen adsorption and hydrogen absorption. When loading a film to form palladium hydride, however, it is more suitable to subject the film to a potential step. This ensures that the hydrogen is loaded to a maximum H/Pd ratio before hydrogen evolution occurs on the surface. However, the cyclic voltammogram obtained can be used to assess the most appropriate starting and final potentials. A typical cyclic voltammogram for a  $H_1$ -e Pd film in a *pH* 2 solution of  $H_2SO_4$  + Na<sub>2</sub>SO<sub>4</sub> is shown in Figure 18.



**Figure 18** Plot showing the three important areas in a cyclic voltammogram of an H<sub>1</sub>-e Pd(B) film on a Pt microdisc ( $Q_{dep} = 20 \ \mu\text{C}$ , Pt disc  $\varphi = 25 \ \mu\text{m}$ ) in a test solution (example here is 0.5 M Na<sub>2</sub>SO<sub>4</sub> + 0.05 M H<sub>2</sub>SO<sub>4</sub>, pH = 1.88). Scan rate = 100 mV s<sup>-1</sup>. Point A is the potential at which the electrode is held before stepping to a value within the double layer region, region B is the area at which hydrogen absorption/adsorption would be expected to occur and point C is the potential of the upper limit of the anodic stripping sweep.

When considering the potential limits to use, the three important areas are A, B and C as shown in Figure 18. A and C are both in the double layer region. The region identified as B denotes the region in which H adsorbed onto / absorbed into the nanostructured palladium.

The starting potential is chosen from the double layer region on the reverse sweep i.e. point A of Figure 18. In cases such as this where the double layer regions of the forward and reverse scans do not overlap greatly, or even not at all, a cyclic voltammogram will be run and paused in the double layer region on the reverse sweep, before commencing with the potential step loading. The potential is then stepped such that it lies within region B in Figure 18. This is the region in which hydrogen is firstly adsorbed, and then absorbed into the palladium lattice. Point C is important when looking at the removal of the absorbed hydrogen using a potential scan method and will be discussed and referred to further on in this chapter.

Using the cyclic voltammogram in Figure 18 as the guide, suitable starting and final potential for the potentiostatic loading into initial experiment into the H<sub>1</sub>-e Pd film are - 0.35 and -0.75 V vs. SMSE respectively. When hydrogen is potentiostatically loaded into a H<sub>1</sub>-e Pd film, the current of the film during the insertion process is measured. This creates a loading transient, or chronoamperogram, and for the conditions mentioned above, this transient is shown below in Figure 19.



**Figure 19** A typical chronoamperogram recorded when an H<sub>1</sub>-e Pd(B) film on a Pt microdisc ( $Q_{dep} = 20 \mu$ C, Pt disc  $\varphi = 25 \mu$ m) is potentiostatically loaded with hydrogen in a solution of 0.5 M Na<sub>2</sub>SO<sub>4</sub> + 0.05 M H<sub>2</sub>SO<sub>4</sub>, *pH* = 1.88. Loading potential,  $E_L$ , = -0.75 V vs. SMSE.

The loading transient shown in Figure 19 has a very distinctive shape: analysis is shown in section 3.1.2. The first 2 seconds of the loading transient sees a sharp peak in the current, which is followed by a long current plateau. This current plateau lasts for approximately 50 seconds after which time the current begins to slowly decrease again. This then yields to a second current plateau, which sees very small currents (~10 nA) pass through the film.

Anodic stripping voltammetry (ASV) has been used to study systems for many decades. By passing an anodic current through an electrode, a material can be completely stripped from the electrode surface. The charge required to remove this material can be found by integrating the current transient recorded, and apply Faraday's Law to calculate the amount of material stripped.

In the case of the palladium hydrogen system, the hydrogen within the palladium film can be measured using this method. It is useful to compare the charge required to completely strip the hydrogen from the lattice,  $Q_{strip}$ , with the charge applied when loading the film,  $Q_{Load}$ . This will give a measurement of the efficiency of a particular system, since in a perfectly efficient system these two values would be equal.

Therefore in order to fully understand the shape of the loading transient, a useful experiment is to look at the amount of hydrogen within the palladium lattice. This can be done by comparing the charge passed in two separate experiments, and is explained in the next section.

### 3.1.1. Q<sub>strip</sub> vs. Q<sub>Load</sub>

It needs to be emphasised that the amount of hydrogen loaded into the palladium cannot be fundamentally determined from the loading transient. It may be possible to calculate the amount of hydrogen from the charge underneath<sup>§</sup> the loading transient, by application of Faraday's Law which is expressed in Equation 29.

¢.

<sup>&</sup>lt;sup>§</sup> i.e. between the loading transient and the baseline (i = 0 A)

$$Q = mnF$$

where Q is the loading charge / C

*m* is the number of mole of hydrogen loaded / mol

*n* is the number of electrons transferred during loading

F is the Faraday constant, equal to 96485 C mol<sup>-1</sup>

However, applying Equation 29 directly assumes that all of the charge produced during loading is attributable to the loading of hydrogen, i.e. that there are no other reactions occurring alongside hydride formation. The other reaction that may contribute to the loading charge is the evolution of  $H_2$  gas on the surface of the palladium electrode. In order to verify this assumption it is necessary to forcibly strip out the hydrogen from within the palladium lattice immediately after the loading is completed. This is achieved by sweeping the potential in a positive direction to force the desorption of hydrogen from the palladium film. The starting potential for the strip is chosen to be the same as the loading potential used to insert the hydrogen. Therefore if the film was loaded to a maximum amount of hydrogen for that potential, there can be no additional hydrogen inserted before the potential sweep begins. In deciding the final potential for the sweep, again the cyclic voltammogram in Figure 18 needs to be referred to. It is important that all of the absorbed hydrogen is removed, but that the final potential is not significantly large such that the oxide formation reaction begins. Point C on Figure 18, which is placed within the double layer region is the best point to use, as it satisfies both of the criteria mentioned. In this case the final potential will be -0.3 V vs. SMSE. Figure 20 shows a typical hydrogen stripping sweep, and highlights the area used to calculate the stripping charge,  $Q_{strip}$ .



**Figure 20** A typical stripping voltammogram for a H<sub>1</sub>-e Pd film on a Pt microdisc ( $Q_{dep} = 20 \ \mu\text{C}$ , Pt disc  $\varphi = 25 \ \mu\text{m}$ ) in a solution of 0.5 M Na<sub>2</sub>SO<sub>4</sub> + 0.05 M H<sub>2</sub>SO<sub>4</sub>. The area marked is the area measured and referred to as "stripping charge",  $Q_{strip}$ .  $v = 10 \ \text{mV s}^{-1}$ .

In this case there will no contribution from other reactions as the  $H_2$  gas produced diffuses away from the electrode and cannot be oxidised back to  $H^+$ .

By comparing the loading charge with stripping charge at different loading times, it will be possible to state whether the loading charge is a suitable indicator for the amount of hydrogen absorbed into the palladium lattice. Figure 21 shows a plot of stripping charge,  $Q_{strip}$ , vs. the loading charge,  $Q_{Load}$ , for the insertion of hydrogen into an H<sub>1</sub>-e Pd film. In order to create the plot the film was loaded, by applying a potential step, for a set period of time. The loading was stopped and the stripping of hydrogen from within the pores began; starting from the potential reached during loading.



**Figure 21** Plot of stripping charge,  $Q_{strip}$ , vs. the loading charge,  $Q_{Load}$ , for the insertion of hydrogen into an H<sub>1</sub>-e Pd film on a Pt microdisc ( $Q_{dep} = 20 \,\mu$ C, Pt disc  $\varphi = 25 \,\mu$ m) from a solution 0.5 M Na<sub>2</sub>SO<sub>4</sub> + 0.05 M H<sub>2</sub>SO<sub>4</sub>. The loading was stopped at various times, and the stripping of hydrogen began immediately after, hence each data point corresponds to one loading/stripping experiment. Starting potential,  $E_i$ , is the value of the loading transient immediately before stripping began. Final potential,  $E_f$ , = -0.1 V Vs. SMSE,  $\nu = 100 \,\text{mV s}^{-1}$ .

It can be seen from Figure 21 that for values of  $Q_{strip}$  and  $Q_{Load} < 5 \ \mu\text{C}$  the relationship between the loading charge,  $Q_{Load}$ , and the stripping charge,  $Q_{strip}$ , is linear. This simple relationship is easy to explain since at low values of  $Q_{Load}$ , and thus H/Pd, the amount of H<sub>2</sub> being evolved off the surface of the palladium is negligible when compared with the amount of hydrogen being loaded into the palladium lattice. Thus the stripping charge increases proportionally with the loading charge. As the hydrogen absorption nears completion, however, the H<sub>2</sub> evolution reaction becomes more significant and as such more of the loading charge is used for this reaction than the hydrogen adsorption reaction. This is seen in Figure 21 by the change in the gradient at  $Q_{strip}/Q_{Load} \approx 5 \ \mu\text{C}$ . For values of  $Q_{strip}/Q_{Load} > 5\mu\text{C}$  the stripping charge is independent of the loading charge. This represents the point at which the palladium lattice is saturated with

- 66 -
hydrogen and as such the only reaction occurring is the hydrogen evolution reaction on the surface.

There are two further points that should be noted. Firstly, the gradient of the linear region should provide useful information. Since the gradient in Figure 21 is close to 1, this suggests that the efficiency of loading in potentiostatic mode is very high, and agrees with the 98% previously quoted<sup>53</sup>. Secondly, it should be mentioned that due to the nature of the experiment, it had been expected that there would be large errors in the calculated charges. However, the quality of data produced goes someway to dispelling the reservations.

Given that the loading charge can be used to measure the amount of hydrogen that has been loaded into the palladium lattice, it is possible to plot the current recorded during loading against the loading charge, which in turn can be converted into an H/Pd ratio. This can be achieved by applying Equation 30, which is a combination of Faraday's law (Equation 29) for both palladium and hydrogen, and is shown in Figure 22.

$$H / Pd = \frac{Q_{Load}}{Q_{Dep}} \times 2$$

#### Equation 30

The multiplier allows for the transfer of 1 electron during the insertion of hydrogen, but 2 electrons in the electrodeposition of the H<sub>1</sub>-e Pd film. Taking into account that the loading charge,  $Q_{Load}$ , can be assumed to be wholly attributable to hydrogen insertion, and that the H/Pd ratio can be directly calculated from this, it is now possible to plot  $Q_{Load}$  and H/Pd against the loading current, and thus qualitatively analyse the loading transient with respect to the amount of hydrogen present. Figure 22 shows the result of firstly determining the loading charge,  $Q_{Load}$ , and then applying Equation 30.



**Figure 22** Plot of  $Q_{Load}$  vs. *E* recorded during the potentiostatic loading of an H<sub>1</sub>-e Pd(B) film on a Pt microdisc ( $Q_{dep} = 20 \ \mu$ C, Pt disc  $\varphi = 25 \ \mu$ m). Solution is 0.5 M Na<sub>2</sub>SO<sub>4</sub> + 0.05 M H<sub>2</sub>SO<sub>4</sub>, *pH* = 1.88. The loading current is converted into H/Pd ratio (using Equation 30) and is also shown. Note that the values are only hold for H/Pd  $\leq 0.6$  and  $Q_{Load} \leq 6 \ \mu$ C.

#### **3.1.2. Loading Transient Analysis**

Following on from the analysis of the loading and stripping charge, the loading transient shown in Figure 19 can now be analysed. By looking at the loading charge, which can be related to the H/Pd ratio, sections of the transient can be labelled with the corresponding phase and phase transitions can be identified. This can be seen in Figure 23.



**Figure 23** A typical chronoamperogram recorded when an H<sub>1</sub>-e Pd(B) film on a Pt microdisc ( $Q_{dep} = 20 \mu$ C, Pt disc  $\varphi = 25 \mu$ m) is potentiostatically loaded with hydrogen in a solution of 0.5 M Na<sub>2</sub>SO<sub>4</sub> + 0.05 M H<sub>2</sub>SO<sub>4</sub>, pH = 1.88.

Figure 23 shows the hydrogen absorption processes and the centre of the potential range in which they occur. The three most important regions are:

- (i) the region in which  $\alpha$ -phase absorption occurs;
- (ii) the region in which the  $\alpha \rightarrow \beta$ -phase transition occurs; and
- (iii) the region in which  $\beta$ -phase is complete.

Region (i) is complete at the end of the pure  $\alpha$ -phase, which is known to occur at 0.05 < H/Pd < 0.1 This then leads into the  $\alpha + \beta$  mixed phase (region (ii)) which is known to be present when 0.1 < H/Pd < 0.5. The completion of the  $\alpha \rightarrow \beta$  phase transition occurs when H/Pd = 0.5. After this point the palladium hydride is in pure  $\beta$ -phase. These regions on the chronoamperogram can be identified by using the calculated H/Pd ratios in Figure 22.

## **3.2. Effect of EL**

The potential at which the hydrogen is loaded into the palladium lattice can affect the loading. For example if a potential is chosen that is too positive it may not be possible to load the hydrogen up to the required ratio. Alternatively, if a potential is chosen which is too negative for the system, the film may be damaged by excessive evolution of hydrogen on the surface of the film.

It is therefore important that the correct choice of loading potential,  $E_L$  is made. A range of loading potentials all within "region B" have been applied to a H<sub>1</sub>-e Pd film and the resulting loading transients are shown in Figure 24. The cyclic voltammogram for the loading solution is shown in Figure 18,



**Figure 24** The first 60 s of the current transient obtained when hydrogen is loaded into a H<sub>1</sub>-e Pd film on a Pt microdisc ( $Q_{dep} = 20 \ \mu\text{C}$ , Pt disc  $\varphi = 25 \ \mu\text{m}$ ). Loading potentials,  $E_L = (1) -0.81$ , (2) -0.79, (3) -0.77, (4) -0.75, (5) -0.73 and (6) -0.71 V vs. SMSE. Solution = 0.5 M Na<sub>2</sub>SO<sub>4</sub> + 0.05 M H<sub>2</sub>SO<sub>4</sub>, pH = 1.88.

As the loading potential becomes more negative, the driving force for the insertion reaction increases and as such the rate of insertion increases. It can also be seen that the current at which the two plateaus appear becomes more negative and the second plateau is reached more quickly. Indeed at loading potentials between -0.70 and -0.75 V vs. SMSE, the second plateau is not seen before 60 s. The important information, however, is not the current, but the H/Pd ratio that can be produced at these potentials. It is the amount of hydrogen loaded that will provide the best value of  $E_L$  to use. For this reason, it is important that we measure this accurately and the stripping analysis detailed in the previous section will be applied.

The second plateau which can be seen in the loading transient with a more negative  $E_L$ , corresponds to the current drawn during hydrogen evolution. As this plateau appears at more negative currents, more hydrogen is being evolved, and so the ideal value for the plateau is as close to 0 as possible. It has been suggested that this hydrogen evolution can also affect the stripping transient since the hydrogen evolved can become trapped in the bulk palladium<sup>47</sup>. On running the anodic stripping sweep, this hydrogen can be reoxidised. This means that the stripping charge measured,  $Q_{strip}$ , will be greater than the charge for removing the absorbed hydrogen leading to an error in the measurement of the amount hydrogen.

#### **3.2.1. Stripping Analysis**

As the loading potential,  $E_L$ , is changed the amount of hydrogen that is loaded into the nanostructured palladium film also changes. As mentioned before, it is possible to measure the amount of hydrogen that has been loaded by a reverse method. By stripping out all of the hydrogen loaded it is possible to relate the amount of hydrogen loaded to the loading potential used during the loading process. Figure 25 shows the effect of changing the loading potential on the amount of hydrogen stripped out, represented by  $Q_{strip}$ . The results of two separate H<sub>1</sub>-e Pd films are shown, having undergone the same the conditions.



**Figure 25** Plot of the hydrogen stripping charge,  $Q_{strip}$ , against the loading potential,  $E_L$ , for the loading of hydrogen into a H<sub>1</sub>-e Pd(B) film on a Pt microdisc ( $Q_{dep} = 20 \ \mu$ C, Pt disc  $\varphi = 25 \ \mu$ m) in a solution of 0.5 M Na<sub>2</sub>SO<sub>4</sub> + 0.05 M H<sub>2</sub>SO<sub>4</sub>, pH = 1.88. The amount of hydrogen loaded into the film was the maximum possible at each potential, and data shown is for two different electrodes under the same conditions. Each data point corresponds to an individual loading/stripping experiment.

Figure 25 is best analysed by considering the change in  $Q_{strip}$  as the loading potential,  $E_L$ , moves towards more negative values, i.e. moving from right to left. For values of  $E_L < -$ 0.55, there appears to a little or no hydrogen stripped from within the palladium lattice. When -0.65  $< E_L < -0.5$  there is a steady increase, followed by a region of slower increase. This region gives way at  $E_L \approx -0.71$  V vs. SMSE to a huge increase in stripping charge. This region is thought to correspond to the  $\alpha + \beta$  phase transition. Since the potential of the  $\alpha + \beta$  phase is not related to the H/Pd ratio, it transpires that there exists a potential at which many values of H/Pd are possible providing that the H/Pd ratio falls within range associated with the  $\alpha + \beta$  phase. Following this region, there are two separate regions. The first has a moderate increase, whereas the second region is a plateau at values much lower than the previous region. It is thought that they belong to a region of pure  $\beta$ -phase and trapped H<sub>2</sub> evolution respectively. However, this alone offers no explanation for the value of the second plateau.

#### **3.2.2.** Normalised Stripping Analysis

As has been previously mentioned, molecules of  $H_2$  gas that have been evolved on the palladium can be trapped within the lattice and reoxidised. It is thought that this process will lead to damage of the film, since the palladium lattice will undergo severe expansion and retraction. It is therefore suggested that the value of the plateau observed when  $E_L < -0.75$  V vs SMSE is due to damage of the palladium film. This would lead to either partial loss of Pd, or to a reduction of the electroactive area of the film. Either way this would explain a drop in the stripping charge,  $Q_{strip}$ , without a reduction in H/Pd. One way to investigate this theory is to assess the electroactive area of the palladium at various intervals. Figure 26 shows the result of the same experiment as in Figure 25, however the stripping charge,  $Q_{strip}$ , has been normalised by the area under the Pd oxide reduction peak. The area under the Pd oxide reduction peak was recalculated every 5 loading/stripping cycles by running a cyclic voltammogram of the H<sub>1</sub>-e Pd film in 1M H<sub>2</sub>SO<sub>4</sub>.



**Figure 26** Plot of the normalised hydrogen stripping charge,  $Q_{strip}$ , against the loading potential,  $E_L$ , for the loading of hydrogen into a H<sub>1</sub>-e Pd(B) film on a Pt microdisc ( $Q_{dep} = 20 \ \mu$ C, Pt disc  $\varphi = 25 \ \mu$ m) in a solution of 0.5 M Na<sub>2</sub>SO<sub>4</sub> + 0.05 M H<sub>2</sub>SO<sub>4</sub>, pH = 1.88. The amount of hydrogen loaded into the film was the maximum possible at each potential, and data shown is for two different electrodes under the same conditions. This is the same data as Figure 25, but with  $Q_{strip}$  divided by  $Q_{oxstrip}$ .

The effect of normalising the stripping charge,  $Q_{strip}$ , by the area under the Pd oxide stripping peak,  $Q_{oxstrip}$ , as shown in Figure 26 is to move the last plateau to a greater value than that for  $\beta$ -phase formation. There is also much greater agreement between the two different electrodes. This suggests that measurement of  $Q_{oxstrip}$  is a very good measurement of the volume of palladium left on the electrode surface. This can be rationalised by considering a unit cell of the nanostructured material, as shown below.

The volume of the unit cell is the area of the cross-section multiplied by the height, which can be written as:

$$V = \frac{\sqrt{3}}{2} \left(2r + w\right)^2 h$$

Given that  $2r \approx w$ , this can

be re-written as

The electroactive area can be assumed to be equal to the total surface area of the palladium, as can be expressed as in Equation 32. This equation consists of the area of the top surface of the film plus the area of the pore walls, and also makes the same assumption as Equation 31 that  $2r \approx w$ .

 $A = \sqrt{3}w^2 + \pi wh$ 

Equation 32

However, given that h >> w, this can be written simply as

**Equation 33** 

Combining Equation 31 and Equation 33, the surface area-volume ratio can be written as:

$$\frac{A}{V} \approx \frac{\pi w h}{\sqrt{3} w^2 h} = \frac{\pi}{\sqrt{3} w}$$

**Equation 34** 

Since the size of the unit cell is constant i.e. w is constant for a given film, the magnitude of the A/V is also constant; this implies that as the surface area (electroactive area) decreases, the volume of material also decreases proportionally. This, of course, assumes that the volume of material is lost uniformly from the surface.

This suggests that it is the degradation of the palladium film that leads to the reduction of  $Q_{strip}$ .

With respect to choosing the optimum loading potential, both Figure 25 and Figure 26 show the same information. As the aim of loading with hydrogen is to produce  $\alpha + \beta$  phase PdH, but without degrading the film, the ideal potential is one that consistently loads into the  $\alpha + \beta$  phase, but has zero chance of allowing hydrogen to evolve on the

 $V = \sqrt{3}w^2h$ 

Equation 31

surface. The chosen potential is therefore the potential just after the huge increase due to the  $\alpha + \beta$  phase (i.e. just into the pure  $\beta$ -phase PdH). In this case that equates to -0.72 V vs. SMSE, based solely on the stripping analysis.

### **3.3. Nafion covered electrodes**

The current lifetime<sup>133</sup> of palladium hydride pH sensors is approximately 1-1.5 hours in a deaerated pH 2 solution. One of the reasons the lifetime is much shorter than it would ideally be is due to the removal of hydrogen under open circuit conditions. At the open circuit potential, three main electrode reactions are thought to occur:

- 1. Oxidation of absorbed hydrogen; H (Pd-H)  $\rightarrow$  H<sup>+</sup> + e<sup>-</sup>(Anodic reaction)
- 2. Reduction of protons in the solution;  $H^+ + e^- \rightarrow H$  (Pd-H) (Cathodic reaction)
- 3. Reduction of oxygen dissolved in the solution (Cathodic reaction)

In deaerated solutions, the rate of reaction 1 is nearly equal to the rate of reaction 2, since no current is being drawn and the amount of oxygen in the solution is minimal. However, in aerated solutions, the rate of reaction 1 is equal to the rate of reaction 2 plus the rate of reaction 3. Therefore, the rate of reaction 1 with respect to the rate of reaction 2 is greater, and the lifetime of the electrode is shortened. For a 2-3  $\mu$ m thick H<sub>1</sub>-e Pd film on a 25  $\mu$ m diameter Pt microdisc, the lifetime is reduced to less than 10 minutes. To lengthen the lifetime of the electrode in aerated solutions, reaction 3 would need to be slowed down. One way to do this is to prevent or slow down the oxygen diffusing to the electrode by placing a barrier over the electrode. By coating the electrode with Nafion (a liquid membrane, in which the diffusion coefficient of oxygen is less than in water<sup>134</sup>), it should be possible to extend the lifetime of the electrode. The Nafion membrane should also slow down the rate of O<sub>2</sub> reduction at the surface of the electrode.

In order to do this, Nafion was added to the  $H_1$ -e Pd (B) film, by pipetting a few drops onto the tip of the electrode and allowed to dry, as this had been shown to be successful in previous studies<sup>13, 135</sup>. The electrodes were previously characterised as described in 2.4.2, and then re-characterised after adding the Nafion so as to ensure that the electrode properties themselves were not affected by the modification. Figure 27- shows the voltammogram obtained when a nanostructured palladium film is cycled in 0.5 M  $Na_2SO_4 + 0.05$  M  $H_2SO_4$  (*pH* 2) both before and after modifying with Nafion.



**Figure 27** Cyclic voltammogram of an H<sub>1</sub>-e Pd film electrodeposited onto a Pt microdisc electrode ( $Q_{dep} = 20 \ \mu\text{C}, \varphi = 25 \ \mu\text{m}$ ,) in a deaerated solution of 1 M H<sub>2</sub>SO<sub>4</sub> before (-----) and after (.....) covering with a Nafion film. Scan rate,  $\nu = 100 \text{ mV s}^{-1}$ .

It can clearly be seen from the cyclic voltammogram, Figure 27, that by modifying the nanostructured palladium film with the Nafion membrane, there is a decrease in the amount of activity taking place on the electrode surface. Since the cyclic voltammogram shows only surface processes, the reduction in the peak heights indicates a reduction in electroactive area. This would suggest that the reaction between the adsorbed hydrogen and oxygen in the solution is severely reduced without reducing the amount of hydrogen absorbed into the palladium lattice. This means that the removal of hydrogen from within the palladium lattice will proceed at a slower rate, and suggests a longer working life of the pH sensor. However, there may also be some problems with the potential measured for each pH, since the Nafion membrane also affects the proton movement through it. This may also mean that the times needed to load a given amount of

hydrogen into a Nafion covered  $H_1$ -e Pd film may be longer than with an uncovered film. However, analysis of the peak heights for oxide formation in cyclic voltammograms in Figure 27 suggests that the loading times will not be significantly lengthened. The loading of hydrogen involves H adsorption and H absorption and the peaks for these processes have not shrunk significantly; therefore the loading rate should not be considerably affected. Since it is shown that a Nafion modified nanostructured palladium film is able to absorb hydrogen by potentiostatic loading, it is now important to load such a film and compare the resulting chronoamperogram with one recorded with an unmodified film. The transients recorded whilst loading the film with hydrogen are shown in Figure 28.



**Figure 28** Loading transients recorded when a H<sub>1</sub>-e Pd film electrodeposited on a Pt microdisc electrode  $(Q_{dep} = 20.\mu C, \varphi = 25 \mu m)$  is loaded potentiostatically with hydrogen  $(E_L = -0.75)$  in a solution of 0.5 M Na<sub>2</sub>SO<sub>4</sub> + 0.05 M H<sub>2</sub>SO<sub>4</sub> (pH = 1.88). Dashed line (-----) represents a film modified with Nafion, solid line represents an unmodified film (----).

Qualitatively, the loading transients recorded do not vary much between the modified film and the film left uncovered, since both transients show similar features. Both transients show an initial peak in the current, which is thought to be predominantly due to hydrogen adsorption and  $\alpha$ -phase PdH formation, followed by a sudden decay. The subsequent plateau corresponds to the formation of  $\alpha + \beta$  phase PdH, which is completed by the end of the plateau. This is followed by a slower decay in the current that leads to a second plateau. The second plateau is thought to correspond to the evolution of H<sub>2</sub> gas. It would appear, from Figure 28, that there is more hydrogen absorbed into the Nafion modified film. This is because the plateau currents are very similar, however the duration of the plateau is longer in the presence of Nafion. However, whilst not ideal, the slight increase in loading time for the modified film should not impede on its ability to measure proton activity. This slight variation in the loading time would suggest that the film covered in Nafion would retain the absorbed hydrogen longer too. Figure 29 shows the anodic stripping voltammograms corresponding to the loading transients displayed in Figure 28.



**Figure 29** Stripping voltammogram recorded when hydrogen is stripped from an H<sub>1</sub>-e Pd film electrodeposited on a Pt microdisc electrode ( $Q_{dep} = 20 \ \mu\text{C}$ ,  $\varphi = 25 \ \mu\text{m}$ ) in a solution of 0.5 M Na<sub>2</sub>SO<sub>4</sub> + 0.05 M H<sub>2</sub>SO<sub>4</sub>. Dashed line (-----) represents a film modified with Nafion, solid line represents an unmodified film (----). Loading conditions:  $E_L = -0.75$  to max H/Pd.

It can be seen in Figure 29 that the film that is covered with the Nafion membrane has a larger stripping charge (area under the anodic stripping voltammogram). Using the  $Q_{strip}/Q_{Load}$  analysis previously presented, this would mean that the Nafion film has increased the amount of hydrogen that has been loaded into the palladium lattice, and confirms that analysis made of Figure 28.

The Nafion film is intended to extend the lifetime of the micro pH sensor. In order to ascertain if this is possible, a series of experiments was conducted comparing the lifetime of the Nafion covered film with that of an uncovered film. The results of such an experiment are shown below in Table 5.

- 80 -

Protective	Solution	Approximate	$t_1 / \min$	$t_2 - t_1 / \min$	Open Circuit
membrane	deaerated?	H/Pd			potential / V
used? (Y/N)	(Y/N)				Vs. SMSE
N	N	0.56	2.5	6	-0.698
N	Y	0.56	10.5	40	-0.703
Y	N	0.62	1.5	15	-0.698
Y .	Y	0.62	11.0	67	-0.703

**Table 5** Typical values of initial time,  $t_1$  and stable time,  $t_2$  for a H<sub>1</sub>-e Pd (B) film plated on a Pt microdisc (25 µm diameter) in 0.5 M Na<sub>2</sub>SO<sub>4</sub> + 0.05 M H<sub>2</sub>SO<sub>4</sub>.

It can be seen from the results in Table 5 that the Nafion membrane increases the stable time of the pH microsensor by approximately 50%, compared to the electrodes without the protective membrane. It also gave the open circuit potential expected in deaerated solutions, and therefore can function as a pH microsensor even with the Nafion protective covering on. In aerated solutions, however, the open circuit potential was more positive than expected, though this does not appear to be a problem limited to the Nafion protected electrodes.

#### **3.4. Summary**

The loading of hydrogen into a nanostructured palladium film via a potentiostatic method has been shown to be a successful approach. Stepping the potential means that the reaction is controlled and produces highly reproducible loading transients. The ideal loading conditions can easily be established by running a short series of experiments, which involve measuring the stripping charge associated with loading to a maximum H/Pd ratio for a given loading potential. Extracting the hydrogen and measuring the stripping charge,  $Q_{strip}$ , from the resulting stripping voltammogram can accurately determine the amount of hydrogen that has been loaded into the palladium lattice. However, the advantages that this method has make it unsuitable for the desired application. Since the driving force behind the reaction is controlled, the loading rate is

evolving with respect to time, so knowing when to stop loading so as to achieve a desired H/Pd ratio is difficult. Analysis has shown that the amount of hydrogen loaded into the nanostructured palladium lattice can be accurately established by measurement of the loading charge, however, at times after the initial loading the hydrogen will have

been desorbed from the palladium and this relationship no longer holds true. It is therefore required to strip the hydrogen completely from the film in order to measure the amount of hydrogen present. This method is enhanced by normalising the stripping charge,  $Q_{strip}$ , with the charge for reduction of Pd oxide,  $Q_{oxstrip}$ , which provides an accurate measure of the amount of Pd film remaining. This is a counter productive analysis technique and so this method does not lend itself to systematic reloading of the film. This chapter also introduces a novel analysis procedure that provides useful information about the hydrogen loading into the film. Comparison of the stripping charge,  $Q_{strip}$ , and the loading charge,  $Q_{Load}$ , provides a method of calculating the efficiency of loading. This new analysis will become essential in subsequent chapters.

Finally, the possibility of using a membrane across the surface of the film was investigated. This proposal proved to be successful, but not as successful as would have been expected. The working time of the film was extended by covering with Nafion, but it was still far less than required for many applications. By doing this work, it was also noted that there appeared to be a difference between the open circuit potentials of deaerated and aerated solutions. However, during use the test solutions need not be deaerated and so there will only be one type of solution for the microsensor to analyse. Covering the film with Nafion, or similar membrane, should not be dismissed, since there is an improvement and may be used in conjunction with another method to enhance it.

- 82 -

# 4. Galvanostatic Loading of Hydrogen into H<sub>1</sub>-e Pd

Galvanostatic loading, that is controlled current loading, can be used to load hydrogen into a palladium lattice. The method involves applying a current through the nanostructured film and measuring the potential difference between the film and the reference electrode. As this technique is much less common the potentiostatic loading a galvanostat had to be fabricated. The circuit of the galvanostat used is shown in Figure 14. This galvanostat was chosen because it was thought that this would supply a constant current and would not be subject to a drop in current. The advantages and disadvantages of using this method over the potentiostatic method will be discussed with reference to the results and data produced; however it should be noted that this method was investigated due to a perceived higher level of control within the  $\alpha + \beta$ mixed phase, where the potential is constant irrespective of the H/Pd ratio.

By far the majority of work done on electrochemical loading of hydrogen into palladium is done via a potentiostatic method. However, this method has a distinct disadvantage in that the loading cannot be controlled during the  $\alpha + \beta$  co-existent phase; since the potential is constant for all H/Pd ratios within this phase, any H/Pd ratio between 0.1 and 0.5 can be achieved with one potential. However, the amount of hydrogen loaded into the palladium lattice can be directly controlled using galvanostatic loading, particularly within the co-existent  $\alpha + \beta$  phase. This is significant since it is the range H/Pd = 0.1-0.5 that allows the palladium hydride to function as a pH sensor. This is because in this region the potential does not depend on the H/Pd ratio, only on the activity of protons within the solution. By supplying a controlled and constant current to the film the amount of hydrogen loaded can be controlled simply by the altering loading time and the resulting potential transient (chronoamperogram) can be used to monitor the loading progress. It is important that the hydrogen reservoir within the palladium lattice is a full as possible i.e. a H/Pd ratio of 0.5 is the ideal ratio. This allows for a long life of the pH sensor, since the whole range (0.1-0.5) is available.

The loading of a nanostructured palladium film by this method is a novel approach. Whilst the potentiostatic loading has been proved to be successful and results are enhanced by the nanostructure of the film, galvanostatic loading does not have the same reassurance. It is possible that the galvanostatic loading of a nanostructured will provide much better results than a plain film, as with potentiostatic loading, however the huge roughness of the film may also hinder the loading. This is because the potential is constantly changing, thus constantly affecting the double layer. This double layer increases with surface area and so may have more of an effect on nanostructured films than plain films. This will be discussed further later in this chapter, after the results have been presented. As with the results in the potentiostatic chapter it should be noted that the results presented in this chapter are typical of the results obtained; these experiments are highly reproducible.

### **4.1.** Loading Transients

There is much that can be drawn from the loading transient obtained when hydrogen is loaded galvanostatically into a nanostructured palladium film, both quantitatively and qualitatively. The following procedure was adopted for the galvanostatic loading of hydrogen into an  $H_1$ -e Pd film.

First, a fresh nanostructured palladium film was plated onto a Pt microdisc in the usual way, and characterised as previously described (Section 2.4.2). The film was held at the open circuit potential, such that there was no current flowing through the film. The hydrogen loading was started by applying the loading current,  $i_L$ , to the film whilst recording a chronopotentiogram. The current was held at this loading current for the loading time,  $t_L$ , until a stable potential was obtained. From analysis of the loading transients obtained when a H<sub>1</sub>-e Pd film is loaded potentiostatically with hydrogen, it is expected that after completion of hydrogen loading, there will be a plateau in the loading transient, corresponding to hydrogen evolution.

An example of the current transient produced during loading hydrogen at  $i_L = 48$  nA in shown in Figure 30. In this example, the potential stabilised in approximately  $t_L = 150$  s. The value of 48 nA was chosen such that  $i_L$  was both easily supplied and would provide an adequate time scale. A rough value for the time scale of the experiment could be calculated prior to the experiment, since the current/charge relationship can be applied: Q = it.



**Figure 30** Typical chronopotentiogram recorded when hydrogen is loaded into a H<sub>1</sub>-e Pd film electroplated onto a Pt microdisc ( $Q_{dep} = 20 \ \mu\text{C}$ ,  $\varphi = 25 \ \mu\text{m}$ ) at  $i_L = 48 \ \text{nA}$ , in a deaerated solution of 0.5 M Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> (pH = 1.88). Regions are: pre (i): H adsorption, (i):  $\alpha$ -phase PdH, (ii):  $\alpha + \beta$  mixed phase, (iii): pure  $\beta$ -phase and (iv): H<sub>2</sub> evolution.

Figure 30 shows a typical chronopotentiogram recorded when a H<sub>1</sub>-e Pd film is loaded with hydrogen at a constant current. The chronopotentiogram can be analysed by comparing with the chronoamperogram recorded during loading of hydrogen into a H<sub>1</sub>-e Pd film by applying a constant potential (Figure 19). There are four distinguishable regions, which correspond to (i) the formation of  $\alpha$ -phase PdH (including the adsorption of hydrogen); (ii) the coexistent phase of  $\alpha + \beta$  phase PdH; (iii) pure  $\beta$ -phase formation and (iv) H<sub>2</sub> evolution.

The steady current,  $i_L$ , applied to the electrode forces the reduction of the protons in the solution to occur at a constant rate via the Volmer reaction;

$$\mathrm{H_{3}O^{+} + e^{-} \rightarrow H_{ads} + H_{2}O}$$

The potential of the electrodes moves to a more negative value, characteristic of Equation 35 and this potential varies with time as the H/Pd ratio increases and H absorbs and the hydride evolves. The formation of hydrogen is thought to occur via two possible mechanisms<sup>56-58</sup>. One possible route may be by adsorbed hydrogen atoms, resulting from the Volmer reaction, diffusing into the metal

$$H_{ads} \rightarrow H_{abs}$$
 Equation 36

Another possible mechanism is hydrogen directly entering the metal without passing through the adsorbed state

$$H_3O^+ + e^- \rightarrow H_{abs} + H_2O$$
 Equation 37

Eventually the amount of hydrogen absorbed into the H<sub>1</sub>-e Pd film reaches its maximum, at approximately H/Pd = 0.69. At this point it is not possible to continue to load hydrogen and so the potential of the electrode rapidly shifts more negative such that a new reduction potential can be established. This second potential corresponds to the evolution of H<sub>2</sub> gas from the surface of the electrode either via the Heyrovski reaction (Equation 38) or the Tafel reaction (Equation 39), as shown below.

$$H_{ads} + H_{3}O^{+} + e^{-} \rightarrow H_{2} + H_{2}O$$
Equation 38
$$H_{ads} + H_{ads} \rightarrow H_{2}$$
Equation 39

The time taken to reach the point where the potential is required to change is called the transition time,  $\tau$ , and is measured from the moment the constant current is applied. The transition time is dependent on a variety of factors including proton concentration (pH),

film diameter ( $\varphi$ ) and thickness, and loading current ( $i_L$ ). The transition time is the chronopotentiometric analogue of peak or limiting current in controlled potential experiments. For simple reversible reactions, the transition appears as a near vertical drop in potential and so  $\tau$  can simply be read off the plot of loading transient. However, for more complex reactions this is not the case and so more care is needed when measuring  $\tau$ . For the potential transients obtained during galvanostatic loading of hydrogen into H<sub>1</sub>-e Pd films, the transition time will be measured by fitting the transition curve with a Boltzmann curve of the type

$$y = \frac{A_1 - A_2}{1 + e^{(t-\tau)/dx}} + A_2$$

**Equation 40** 

Where y is the electrode potential

t is the time,

 $\tau$  is the transition time, and

 $A_1$ ,  $A_2$  are adjustable parameters

For the loading transient in Figure 30, the transition time,  $\tau = 139$  s.

It is worth noting that since a constant current is applied the time scale can be directly converted into loading charge and H/Pd ratio, since this is calculated directly from loading charge. This aids in the analysis since we know the H/Pd values for given phases. Figure 31 shows a converted graph where the recorded loading potential is plotted as a function of loading charge,  $Q_{Load}$ , and H/Pd (assuming ~100% efficiency).



**Figure 31** Potential, *E*, as a function of loading charge,  $Q_{Load}$ , and H/Pd ratio, recorded when hydrogen is loaded into a H<sub>1</sub>-e Pd film electroplated onto a Pt microdisc ( $Q_{dep} = 20 \ \mu\text{C}$ ,  $\varphi = 25 \ \mu\text{m}$ ) at  $i_L = 48 \ \text{nA}$ , in a deaerated solution of 0.5 M Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> (pH = 1.88).

As can be seen, there are two plateaus. The first plateau runs approximately from a H/Pd ratio of 0.15 to 0.6, confirming the previous thought that this corresponds to the  $\alpha$  +  $\beta$  mixed phase. The second plateau occurs well after the accepted maximum for the amount of hydrogen loaded into palladium, and is thought to correspond to hydrogen gas evolving off the surface of the palladium electrode. It is important not to load too much into this region, since H<sub>2</sub> bubbles can get trapped in the Pd lattice and damage it. Trapped H<sub>2</sub> bubbles can also be oxidised and this can affect the analysis by stripping charge,  $Q_{strip}$ , since it is increased without increasing the amount of PdH formed.

- 88 -

#### **4.1.1. Effect of Loading Current**

It would be expected that changing the loading current,  $i_L$ , alters the timescale of the experiment; since the total amount of charge used to load the maximum amount of hydrogen into a nanostructured palladium film is constant. Since the loading charge,  $Q_{Load} = i_L \ge t$ ; as the loading current is increased, the loading time will decrease proportionally.

Figure 32 shows the chronopotentiograms obtained when the loading current used is a) 14.9 nA and b) 149 nA.



**Figure 32** Chronopotentiograms recorded during the galvanostatic loading of hydrogen into a H<sub>1</sub>-e Pd film plated onto a Pt microdisc ( $\varphi = 25\mu$ m) in a solution of 0.5 M Na<sub>2</sub>SO<sub>4</sub>. Loading current was (a) 14.9 nA and (b) 149nA.

Qualitatively these two chronopotentiograms show similar features, features which can be assigned to the different phases of palladium hydride as in the discussions of Figure 30. The two main points of note, however, are i) the potential values are much more negative for the loading at 149 nA than at 14.9 nA and ii) although the current is altered by a factor of ten, the time taken for the loading at 14.9 nA to reach the same point as the loading at 149 nA is less than ten times greater.

A possible explanation for the difference in the potential of the two chronopotentiograms lies in the application of the moving boundary mechanism  $(MBM)^{136, 137}$ . This is when the current supplied  $(i_L - \text{galvanostatic loading})$  or measured (potentiostatic loading) is analogous to the rate of the movement of the  $\alpha/\beta$  phase boundary through the palladium film. For galvanostatic systems, as the loading current,  $i_L$ , increases so does the rate of movement of the phase transition throughout the film, and as such a more negative potential is required to generate this rate. This also explains why, in potentiostatic loading, as the loading potential,  $E_L$ , is made more negative, the plateau current measured is also more negative.

The difference between the current change and the corresponding time change could be attributed to the diffusion process. When a higher current is used the protons in the pores undergo reduction to form the hydride faster than when a lower loading current is used. As such the hydride formation occurs faster than the diffusion of the protons from the bulk solution down the pores, and so less of the pore is being used for high values of  $i_L$ . Therefore, despite the fact that a higher current is used, the palladium hydride formation is less efficient due to the slow diffusion down the pore.

It is important to note that although a constant current is applied, the potential is changing, and so the applied current can be split into two sections, the faradaic current,  $i_f$ , and the double layer charging current,  $i_c$ . The double layer charging current is dependent on the area of the electrode and the change in potential and thus can be written as:

Equation 41

$$i_c = -AC_d \frac{dE}{dt}$$

where:

A is the area of the electrode /  $cm^2$ 

 $C_d$  is the differential capacitance of the double layer / F cm<sup>-2</sup>

Given that the applied current,  $i_L$ , is constant and  $i_c$  is a function of dE/dt, it transpires that the faradaic current,  $i_f$ , must also be a function of dE/dt, since  $i_f = i_L - i_c$ . Also, since dE/dt is a function of time  $i_c$  and  $i_f$  are also functions of time, even though i is constant. The size of the effect of the double layer charging current will be seen when comparing the galvanostatic loading of a nanostructured film with that of a plain film, since here the area, A, of the film is dramatically different. It would therefore be expected that there will be a dramatic difference in the loading. This will presented in Section 4.2.4.

#### 4.1.2. Effect of Loading Time

If the loading current is kept constant then the charge passed is proportional to the loading time. Also, since the charge passed is directly related to the amount of hydrogen loaded into the film, it is possible to choose the palladium hydride phase by altering the loading time. A series of experiments were run in a solution with a given pH with a given loading current, where only the loading time was altered. Immediately after loading, the hydrogen was stripped out of the film potentiostatically and a stripping charge,  $Q_{strip}$  was measured. This was compared with the loading charge,  $Q_{Load}$ , as calculated from loading current,  $i_L$  x loading time,  $t_L$ . For a perfect system,  $Q_{Load} = Q_{strip}$ , however it is already known, from previous experiments, that some of the loading current is used for other processes e.g. hydrogen evolution. Also it is suspected that there is a portion of the loading current that is used for charging the double layer. Figure 33 shows a plot of  $Q_{strip}$  against  $Q_{Load}$  for a a nanostructured palladium film loaded with hydrogen at a loading current of 73 nA in a solution of 0.5 M Na<sub>2</sub>SO<sub>4</sub> with (a) pH 7 buffer (5% v/v) and (b) pH 10 buffer (5% v/v).



**Figure 33** Plot of the anodic stripping charge,  $Q_{strip}$ , against the loading charge,  $Q_{Load}$  used for hydrogen absorption into an H1-ePd film electrodeposited onto a Pt microdisc ( $Q_{dep} = 20 \ \mu$ C,  $\varphi = 25 \ \mu$ m).  $i_L = 73$  nA, solution is (a) 0.5 M Na<sub>2</sub>SO<sub>4</sub> + pH 7 buffer and (b) 0.5 M Na<sub>2</sub>SO<sub>4</sub> + pH 10 buffer . Each data point corresponds to one loading/stripping experiment.

Figure 33 can be separated into two sections. Initially the plot follows the trend which can be written as

$$Q_{strip} = kQ_{Load}$$
 Equation 42

where k is a constant representative of faradaic efficiency

Following the linear section, there is a region where  $Q_{strip}$  is constant for any given  $Q_{Load}$ . The value at which  $Q_{strip}$  plateaus is indicative of the maximum amount of hydrogen that can be absorbed into the nanostructured palladium film, since

$$H / Pd = \frac{Q_{strip}}{Q_{dep}} \times 2$$
 Equation 43

An independent linear fit of the two plots in Figure 33 gave a gradient of 0.67. This means that 67% of the applied current,  $i_L$ , was used to load hydrogen into the nanostructured palladium film. That is to say the  $i_f = 67\% i_L$ . Using this value of  $i_f$ , it is possible to construct a plot showing potential, E, with respect to the H/Pd ratio. H/Pd ratio is calculated using

$$H / Pd = 0.67 \times \frac{Q_{Load}}{Q_{dep}} \times 2$$

**Equation 44** 

An example of this plot, for the pH 10 solution, is shown in Figure 34.



**Figure 34** Potential as a function of H/Pd ratio during the galvanostatic loading of hydrogen into a H<sub>1</sub>-e Pd film electrodeposited onto a Pt microdisc ( $Q_{dep} = 20 \ \mu\text{C}$ ,  $\varphi = 25 \ \mu\text{m}$ ) in a solution of 0.5 M Na<sub>2</sub>SO<sub>4</sub> + pH 10 buffer, with a loading current of 73 nA.

Figure 34 confirms the initial assumption shown in Figure 30. It is known that palladium hydride is in the  $\alpha+\beta$  phase whilst 0.1 < H/Pd < 0.5. It is also known that at

H/Pd values lower than this the palladium hydride is in the pure  $\alpha$  phase, which is itself preceded by hydrogen adsorption. Once the maximum H/Pd ratio (~0.69) is reached, the potential plateaus at a value where only H<sub>2</sub> evolution occurs. This can be seen more clearly in Figure 30 than in Figure 34, since Figure 30 is at pH = 1.88 (rather than pH 10) and as such there are more H<sup>+</sup> present.

#### 4.1.3. Effect of Oxygen

It should be noted that the chronopotentiograms recorded in Figure 32 were not recorded in deaerated solutions and as such there was oxygen in the solutions. This means the that some of the charge applied to the film may be used in the reduction of the dissolved oxygen in the system. This is more noticeable when very low values of  $i_L$  are used. Figure 35 shows the chronopotentiogram obtained when hydrogen is loaded galvanostatically into a H<sub>1</sub>-e Pd film with a loading current of 7.3 nA.



**Figure 35** Chronopotentiogram recorded during the galvanostatic loading of hydrogen into a H<sub>1</sub>-e Pd film electrodeposited onto a Pt microdisc ( $Q_{dep} = 20 \ \mu\text{C}$ ,  $\varphi = 25 \ \mu\text{m}$ ) in a 0.5 M Na<sub>2</sub>SO<sub>4</sub> + pH 7 buffer solution. Loading current was 7.3 nA. Solution was not deaerated in (a) but was deaerated in (b)

It can be seen that there is a great difference between the two chronopotentiograms. Since 7.3 nA is less than the measured<sup>\*\*</sup> limiting current for oxygen reduction on a 30  $\mu$ m palladium film, in an aerated solution all of the current is being used for this electrochemical process and so the potential drifts more positive, i.e. it is not possible to load in such a solution. In a deaerated solution, however, there is little or no oxygen to reduce and as such the hydrogen loading is seen as a negative drift in potential.

### 4.2. Loading / Stripping Analysis

#### 4.2.1. Qstrip V QLoad

To fully assess the efficiency of a given system the stripping charge,  $Q_{strip}$ , was measured and compared with the calculated value of the loading charge,  $Q_{Load}$ . The loading charge was calculated from the loading current using the equation

### $Q_{Load} = i_L t_L$

#### **Equation 45**

where:

 $i_L$  is the loading current applied  $t_L$  is the loading time.

By altering  $t_L$  and stripping immediately after loading, a range of values for  $Q_{Load}$  can be produced, along with corresponding values of  $Q_{strip}$ . This will lead to a plot of  $Q_{strip}$  V  $Q_{Load}$ , a typical example of which can be seen in Figure 36.

<sup>\*\*</sup> The limiting current measured in a 0.5 M  $Na_2SO_4 + pH 7$  buffer (5% v/v) solution was approximately 9.5 nA.



**Figure 36** A typical example of the plot produced when an H<sub>1</sub>-e Pd film is loaded galvanostatically with hydrogen and immediately stripped potentiostatically.  $Q_{strip}$  is measured by integrating the resulting stripping voltammogram,  $Q_{Load}$  is taken as the product of loading current,  $i_L$ , and the loading time,  $t_L$ . Each data point corresponds to one loading/stripping experiment. The straight line (a) represents the loading of hydrogen into the lattice, whilst (b) represents the hydrogen evolution on the surface of the palladium. Results presented are for a H<sub>1</sub>-e Pd film on on Pt microdisc ( $\varphi = 25 \,\mu$ m) in a solution of 0.5 M Na<sub>2</sub>SO<sub>4</sub> + 0.05 M H<sub>2</sub>SO<sub>4</sub>.

The resulting plot can be separated into two sections as shown in Figure 36. Section (a) represents the loading of hydrogen into the nanostructured palladium film up to the maximum H/Pd ratio of 0.6. It would be expected that during this time,  $Q_{strip}$  is directly proportional to  $Q_{Load}$ , since as the loading current is increased the amount of hydrogen loaded into the film increases proportionally. Therefore the amount of hydrogen stripped also increases proportionally. For a perfectly efficient system the gradient of the slope in section (a) is 1. It is expected that for galvanostatic loading of hydrogen into an H<sub>1</sub>-e Pd film the efficiency will be 90% or greater, since potentiostatic loading has been shown to be highly efficient.

Section (b) shows a plateau region, where the stripping charge has reached a maximum. This occurs once the maximum amount of hydrogen has been loaded into the nanostructured palladium film. During this stage, all supplied current is used to evolve  $H_2$  gas from the solution on the surface of the film. Since this  $H_2$  gas then diffuses away from the electrode it cannot be reduced back to  $H^+$  and so there is no stripping charge attributed to this process. The only stripping charge seen is that from the maximum amount of hydrogen loaded into the palladium film. The value at which section (b) plateaus is dependent on the amount of Pd plated onto the microelectrode surface. The maximum stripping charge can be calculated by multiplying the charge used to deposit the  $H_1$ -e Pd film,  $Q_{dep}$ , by 0.3, assuming a maximum H/Pd ratio of 0.6. This is because the reduction of Pd<sup>2+</sup> to electroplate Pd requires 2e<sup>-</sup>, whereas the number of electrons required to load H<sup>+</sup> into the nanostructured palladium film is 1. This relationship is derived in 4.2.2 "Effect of film thickness" and shown in Equation 48. Conversely, the maximum stripping charge,  $Q_{stripmax}$ , can be used to calculate the maximum H/Pd ratio using Equation 46.

$$(H/Pd)_{\rm max} = \frac{2Q_{\rm strip\,max}}{Q_{\rm Dep}}$$

#### **Equation 46**

For a typical film deposition of 20  $\mu$ C, a maximum stripping charge of 6  $\mu$ C would represent a maximum H/Pd ratio of 0.6.

By comparing the  $Q_{strip}$  vs.  $Q_{Load}$  plot in Figure 36 with the plot of potential, E vs.  $Q_{Load}$  and H/Pd in Figure 31 it can be seen that the initial analysis of the shape of the potential transient produced during loading Figure 36 is verified by the plateau formation. The point at which the plateau begins coincides with the point at which H<sub>2</sub> evolution was deemed to occur.

#### **4.2.2.** Effect of film thickness

The thickness of a H<sub>1</sub>-e Pd film can easily be altered by varying the deposition charge,  $Q_{dep}$ , during the electrodeposition process. For a given size of microdisc electrode, the thickness of the film will be roughly proportional to  $Q_{dep}$ , however as the deposition charge is increased the amount of palladium overspill is also expected to increase. As such the thickness will not be exactly proportional to the deposition charge,  $Q_{dep}$ .

Although the plating method did not depend on the deposition charge, care was taken with the thick film to ensure that all of the surfactant had been removed from the pores. Therefore once made, the electrodes were stirred overnight, instead of 2-4 hours which is normally sufficient. The  $H_1$ -e Pd films were characterised and the characterisation parameters were compared. Table 6 shows the characterisation parameters calculated for 3 different thicknesses of film.

	$Q_{dep} = 10 \ \mu C$	$Q_{dep} = 20 \ \mu C$	$Q_{dep} = 40 \mu C$
Diameter / µm	27.4	28.7	31.4
Thickness / µm	1.7	2.5	3.5
Geometric Area / cm <sup>2</sup>	5.9 x 10 <sup>-6</sup>	6.47 x 10 <sup>-6</sup>	7.74 x 10 <sup>-6</sup>
Electroactive Area / cm <sup>2</sup>	2.67 x 10 <sup>-3</sup>	4.76 x 10 <sup>-3</sup>	9.22 x 10 <sup>-3</sup>
Roughness Factor	453	736	1191

 Table 6 Typical properties of three different thickness nanostructured films.

As can be seen from Table 6, the diameter of the  $H_1$ -e Pd film plated onto the Pt microdisc electrode (with a constant diameter of 25 µm) increases with deposition charge. This leads to a small increase in the geometric area of the film, which is proportional to the square of the radius. However, the electroactive area of the film is almost directly proportional to the deposition charge and as such increases dramatically with each growth in deposition charge. The combination of these two effects leads to a vast increase in the roughness factor of the film as the deposition charge in increased.

Figure 37 shows the top view of the palladium film as imaged by scanning electron microscopy (SEM). As the images are all shown at the same magnification and scale, it can clearly be seen that as the deposition charge has increased, the diameter of the film is also increased.



**Figure 37** SEM images of an H<sub>1</sub>-e Pd film (various  $Q_{dep}$ ) plated onto a Pt microdisc ( $\varphi = 25 \ \mu$ m). Deposition charges are: (a) 10  $\mu$ C, (b) 20  $\mu$ C and (c) 40  $\mu$ C.

The effect of the film thickness on galvanostatic loading was studied. The film thickness was controlled by the deposition charge,  $Q_{dep}$ , which was set when depositing the film onto the microdisc.

It is worth noting at this stage that due to the high error incurred when measuring the thickness of the film on the scanning electron microscope, the deposition charge will be used in all data analysis as a more accurate representation.

Figure 38 shows how the chronopotentiogram obtained during galvanostatic loading in  $Na_2SO_4$  is affected by altering the thickness of the film.



**Figure 38** Plot showing the effect of film thickness (identified by the film deposition charge) on the loading transient obtained when a H<sub>1</sub>-e Pd (A) film on a Pt microdisc ( $\varphi = 25\mu$ m) is loaded with hydrogen under galvanostatic conditions. Solution = 0.5 M Na<sub>2</sub>SO<sub>4</sub> + 0.05 M H<sub>2</sub>SO<sub>4</sub>, *i*<sub>L</sub> = 50 nA.

It can be seen from Figure 38 that as the thickness of the nanostructured film is increased, the  $\alpha+\beta \rightarrow \beta$  transition time increases proportionally. This is to be expected for a galvanostatic loading, where the rate of the hydrogen loading is predetermined, and the potential alters to achieve the given rate.

It can also be seen that the potential at which the  $\alpha + \beta$  phase occurs becomes slightly more positive as the thickness of the film increases. This is contrary to expectations, since thicker films require more protons to achieve the same H/Pd ratio. This would cause a negative shift in potential as more protons would be removed from the solution thus leaving the solution more alkaline. In the  $\alpha + \beta$  phase, the phase rule says the potential is only a function of pH. However, it is thought that the phase rule will not apply during galvanostatic loading, since the system is not in equilibrium. Therefore the potential shift does not necessarily imply a shift in pH. When loading with a constant current, the potential alters to achieve the predetermined rate and as such results suggest that as the H/Pd ratio increases there requires more of a driving force to load into the thinner film than the thicker film. The relationship between the  $\alpha + \beta$  plateau potential and the deposition charge is shown to be linear.

It is possible that this is due to the rate of the hydrogen dispersion through the palladium lattice. Since the pores are deeper the loading of the hydrogen is sufficiently fast to ensure that the protons in the solution will not have time to diffuse along the length of the pore before it is electrochemically absorbed by the palladium film. This means that the hydrogen must diffuse in the direction of the film thickness for thicker films, and it follows that the thicker the film the more palladium that cannot be reached by the protons in solution.

In addition to the loading transient it is also possible to look at the effect of film thickness on the stripping charge. Figure 39 shows the maximum stripping charge,  $Q_{stripmax}$ , as a function of  $Q_{dep}$ . This is the stripping charge obtained when a nanostructured film is reoxidised immediately after the maximum loading is achieved. It can be found by plotting stripping charge,  $Q_{strip}$ , against loading charge,  $Q_{Load}$ , and reading off the point at which the graph plateaus (for example see Figure 35). This ensures that the film has not been loaded into the region where H<sub>2</sub> is evolved, can be trapped in the pores and reoxidised during stripping.


**Figure 39** A plot showing the maximum stripping charge obtained for H<sub>1</sub>e-Pd (A) films plated on a Pt microdisc ( $\varphi = 25\mu$ m) with varying thicknesses when loaded with hydrogen under galvanostatic conditions. Solution = 0.5 M Na<sub>2</sub>SO<sub>4</sub> + 0.05 M H<sub>2</sub>SO<sub>4</sub>, *i*<sub>L</sub> = 50 nA.

Analysis of Figure 39 provides a linear fit with gradient 0.3 and standard error of 0.001. This gradient is exactly as expected, since the ratio of  $Q_{stripmax}$  to  $Q_{dep}$  is representative of the maximum H/Pd ratio. We can therefore write:

$$\frac{Q_{strip\,\max}}{Q_{den}} = \frac{Q_{H\,\max}}{Q_{Pd}} = \frac{m_{H\,\max}n_{H}F}{m_{Pd}n_{Pd}F}$$

**Equation 47** 

where:

*m* is the number of moles (mol)

*n* is the number of electrons

F is the Faraday constant.

The number of electrons for each proton loaded is 1, and the number of electrons for each atom of Pd plated is 2. Also, we know that the maximum H/Pd ratio is 0.6, and so we can substitute  $m_H / m_{Pd} = 0.6$ . This gives us:

**Equation 48** 

$$\frac{Q_{strip\max}}{Q_{dep}} = 0.6 \times \frac{1}{2} = 0.3$$

The results from this section of work have been highly reproducible and provide yet more proof that the electrochemical loading of hydrogen into palladium, particularly nanostructured palladium, is well behaved and can be thought of as an ideal system. Thus a nanostructured palladium film could be utilised in a situation where a predetermined amount of hydrogen is needed to be removed, by simply controlling the size and thickness of the nanostructured film. This works especially well since the palladium film is supported by a Pt microdisc. This means that there is a reservoir of hydrogen which will not leak via the electrode. It will leak a small amount via the pores of the film, particularly in the presence of hydrogen scavengers or the due to the freshness of the film; the latter of which is discussed in the next section. Conversely a preloaded nanostructured film could be used to inject a known amount of protons into a solution. This will be important when trying to make a pH tip for SECM measurements. This series of experiments has also proved useful in accurately measuring the maximum H/Pd ratio for this system, which for other systems can be anything up to PdHx, where x = 1 according to various literature sources<sup>138</sup>.

#### 4.2.3. Effect of film freshness

One major advantage of using a film, be it plain or nanostructured, is that once the film is plated maintenance is relatively simple. Microdisc electrodes require an initial polish on alumina of grain sizes 1.0, 0.3 and 0.05 and before every experiment on 1.0 and 0.3. As well as being very time consuming, polishing a H<sub>1</sub>-e Pd film would result in the film being removed from the Pt microdisc. However, in order to keep an H<sub>1</sub>-e Pd film in good condition all that is needed is a few cycles in sulphuric acid, rinsing with water and to be stored in water. This works well for a nanostructured film which is only required for a short amount of time, however questions can be raised over the quality of a nanostructured film which has been loaded and stripped with hydrogen many times and has undergone many cycles in  $H_2SO_4$ . This is particularly vital for a palladium film since the palladium lattice is known to swell by 3.3% for an H/Pd ratio of 0.59<sup>47</sup>. This repeated cycle of expansion/contraction is a cause for concern for long term use of one nanostructured film. Nanostructured  $H_1e$ -Pt films show similar behaviour with the formation/reduction of Pt oxide during cycles in  $H_2SO_4$ . As a precaution, the electrochemical area of a nanostructured film was measured on each day of experimentation but this gives no clue as to the quality.

Images of the film as taken with the scanning electron microscope can give some information as to the physical quality of the film, but is unable to provide any details of the electrochemical quality of the film. Images taken of a fresh and an old film are shown in Figure 40.



**Figure 40** SEM pictures of an H<sub>1</sub>-e Pd(B) film electrodeposited on a 25  $\mu$ m Pt microdisc ( $Q_{dep} = 20 \mu$ C,  $\varphi = 33.1 \mu$ m) that has (from left to right) been freshly plated; undergone moderate use and undergone substantial use.

In order to assess the quality of the film, a loading/stripping experiment was run to compare the hydrogen loading ability of a fresh film and a well used film.

Figure 41 shows the stripping/loading data acquired for a) a newly plated film, and b) a film that has been well used. Since all experiments were run with relatively new films, a used film was replicated by subjecting a film to over a hundred loading/stripping cycles



**Figure 41** Plot showing the  $Q_{strip} \vee Q_{Load}$  plot for a) a newly plated film ( $\neg \bullet \neg$ ) and b) a film that has undergone over a hundred loading and stripping cycles ( $\neg \bullet \neg$ ).

As can be seen from Figure 41, the maximum stripping charge of the well used film is much less than that of the fresh film. The used film has a maximum stripping charge of  $3.26 \pm 0.03 \mu$ C compared to  $5.66 \pm 0.03 \mu$ C. This would suggest that either the electroactive area of the palladium lattice is partially blocked or that the amount of Pd in the film has decreased, i.e. a portion of the film has been lost. This leads to a reduction in the maximum amount of hydrogen. However, until the point when the maximum is first reached, the used film works as well as the new film. As mentioned before the gradient of the first linear section can be thought of as a measure of the loading efficiency of the nanostructured film. A gradient of 1 would imply 100% efficiency whereas a gradient of 0 (as at the plateau of maximum loading) suggests that all of the loading current applied is use for an alternative electrochemical reaction. The well used film has a gradient of 0.902  $\pm$  0.015 whereas the fresh film has a gradient of 0.898  $\pm$  0.013. Therefore it can be said that regardless of the freshness of the film, a nanostructured palladium film will galvanostatically load with hydrogen with a loading efficiency of 90%. This means that the freshness of a film does not affect its loading

ability up to its maximum load. This implies that the structure remains accessible, but that some Pd has been lost due to cycling.

#### 4.2.4. Effect of the nanostructure

Previous work<sup>53</sup> has studied the difference in the current transient observed when a plain palladium film is loaded potentiostatically with hydrogen compared with a H<sub>1</sub>-e Pd film. The results show that for the same loading potential,  $E_L$ , the currents produced during loading are much smaller for the plain Pd film than for the H<sub>1</sub>-e Pd film. This meant that the loading time of the plain Pd film was upto 15 times longer than the loading time of the nanostructured Pd film. However, if a more negative loading potential was applied then the loading time could be reduced. For example, at  $E_L = -0.75$  V vs. SMSE the loading time was 600 s. However, at  $E_L = -0.85$  V vs. SMSE the loading time was 600 s. It was also noted that the quality of the loading transients obtained with the plain palladium films were poor – particularly when compared to those obtained with the nanostructured palladium film.

A plain palladium film was fabricated by electrodeposition onto a Pt microdisc from an aqueous solution of ammonium tetrachloropalladate. The charge applied during deposition,  $Q_{dep}$ , was 20  $\mu$ C. This film was viewed under the scanning electron microscope (SEM) and qualitative comparisons were made between the surface of this film and that of an H<sub>1</sub>-e Pd film plated with the same deposition charge. The dimensions of each of the films were also compared. The SEM images obtained are shown in Figure 42.



Figure 42 SEM images of (a) a plain Pd film and (b) an H<sub>1</sub>-e Pd (A) film electrodeposited onto a Pt microdisc ( $\varphi = 25 \ \mu m$ )

Figure 42 shows clear differences in the quality of the films produced from aqueous solution and from a surfactant containing solution.

The film produced from the aqueous film is a thin film with a large edge effect. The film produced is so thin that the scratches produced by polishing the underlying Pt microdisc can be seen. Finally, the film appears to be made up of many small nuclei of palladium.

The film produced from the mixture containing the surfactant shows a very different texture. The film itself is much thicker, there is no detail from the underlying Pt microdisc, and as such the edge effect is less pronounced. There is also much more uniformity across the whole of the surface of the  $H_1$ -e Pd film.

The chronopotentiogram obtained during galvanostatic loading of hydrogen into a plain Pd film has been recorded, and compared to that recorded for a nanostructured Pd film, with the same deposition charge. These chronopotentiograms are shown in Figure 43.



**Figure 43** Chronopotentiogram recorded during the galvanostatic loading of hydrogen ( $i_{Load} = 50$  nA) into (i) a nanostructured Pd (H<sub>1</sub>-e Pd) film and (ii) a plain Pd film, both plated onto a Pt microdise ( $\varphi = 25 \mu m$ ). Solution = 0.5 M Na<sub>2</sub>SO<sub>4</sub> + 0.05 M H<sub>2</sub>SO<sub>4</sub>.

It can clearly be seen from Figure 43 that whilst the same qualitative shape is maintained, there is a difference between the chronopotentiogram recorded for a plain film compared to that of a nanostructured film. For the plain film, the chronopotentiogram appears to show no defined region for adsorbed hydrogen, which given the relatively low surface area of the film, is not unexpected. It can also be seen that whilst the time needed to complete the loading of  $\alpha$ -phase hydrogen is shorter, the time required to fully load into the plain film, compared with that of the nanostructured film, is longer. Again this is to be expected since the absence of the pores means that the hydrogen will have diffuse through from the top surface of the film all the way through its entire thickness. The third point of note is that the plateau potentials are radically different; -0.713 V vs SMSE for the nanostructured film and -0.740 V vs SMSE for the plain film. This is thought to be directly attributable to the nanostructure, or lack of it.

#### 4.2.5. Effect of pH

All of the galvanostatic loading experiments discussed in this thesis to date have been performed in mixed solution of Na<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> at *pH* 2. Potentiostatic loading has been achieved in a variety of different pH solutions ranging from *pH* 2 - *pH* 12. However, at *pH* > 3 the concentration of protons in the solution is very low, and as such the rate of hydrogen loading via the protons in the solution is limited. This can be overcome by setting the loading potential sufficiently negative so that the loading of hydrogen can be achieved by the reduction of water molecules. As such, as pH increases either the loading time must increase dramatically or the loading potential applied must become more negative, or both if the chosen potential is not negative enough.

The effect of a change in the pH of the loading solution is not expected to be as dramatic for galvanostatic loading as it is for potentiostatic loading. The time taken to load the film is expected to remain constant regardless of the pH, although the loading potential will logically move towards a more negative region. The advantage of galvanostatic loading over potentiostatic loading is that the loading potential is achieved rather than having to be predetermined.



**Figure 44** The loading transient obtained when a H<sub>1</sub>-e Pd (A) film electrodeposited on a Pt microdisc electrode ( $Q_{dep} = 20 \ \mu\text{C}$ ,  $\varphi = 25 \ \mu\text{m}$ ) is loaded galvanostatically with hydrogen. Loading current = 50 nA. Solution = 0.5 M Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> (pH 2) (----) and 0.5 M Na<sub>2</sub>SO<sub>4</sub> + NaOH (pH 12) (----).

Figure 44 shows the loading transient of the same H<sub>1</sub>-e Pd film in Na<sub>2</sub>SO<sub>4</sub> solutions at pH 2 and pH 12. Qualitatively, the shapes of the transients are similar but not exact. For example both have 2 plateaus as seen previously, one for the  $\alpha + \beta$  phase and one for hydrogen evolution. However, the  $\alpha + \beta$  plateau is more pronounced at pH 2 than at pH 12 but the  $\alpha$ -phase section is more pronounced at pH 12 than at pH 2. In terms of potential, the transient for the pH 12 solution is approximately 0.6 V more negative at pH 12 (-1.318 V vs SMSE) than at pH 2 (-0.713 V vs SMSE). This corresponds to a negative shift of 60 mV per pH unit and is the shift expected by applying the Nernst equation to the reduction of protons. However this is not thought to be due to the phase rule, since previous data has suggested that the phase rule does not apply during loading. The effect of altering the pH can also be studied by looking at the stripping charge,  $Q_{strip}$  vs. the loading charge,  $Q_{Load}$ . Using data obtained under the same conditions as in Figure 44, the  $Q_{strip}$  vs.  $Q_{Load}$  plot at pH 2 and pH 12 can be seen in Figure 45.



**Figure 45** Plot of the  $Q_{strip}$  vs.  $Q_{Load}$  for a H<sub>1</sub>-e Pd film electrodeposited onto a Pt microdisc ( $Q_{dep} = 20 \,\mu\text{C}$ ,  $\varphi = 25 \,\mu\text{m}$ ) loaded galvanostatically in a) 0.5 m Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub>, pH 2 ( $\neg$ ) and b) 0.5 M Na<sub>2</sub>SO<sub>4</sub> + NaOH, pH 12 ( $\neg$ ).

It can be seen from Figure 45 that whilst the maximum stripping charge is independent of the pH of the solution, the loading efficiency is less for the pH 12 solution than for the pH 2 solution. The gradient of the first linear section is  $0.766 \pm 0.014$  for the solution at pH 12, but this increases to the more usual value of  $0.898 \pm 0.013$  at pH 2. These results suggest that the loading efficiency is reduced at higher pH solution. This can also be seen in Figure 44, since the time taken to fully load at pH 12 is noticeably longer than at pH 2.

## 4.3. Summary

A novel approach to loading a nanostructured  $H_1$ -e Pd film with hydrogen has been proposed. This approach centres on loading the film by controlling the current through the film, and has shown to offer smooth, highly reproducible loading transients. The procedures used in this technique have been given, and immediate advantages have been seen, since the loading conditions do not need to be established as with potentiostatic loading. Instead, it is possible to decide on a suitable loading time and work backwards to calculate the loading charge, since these are interrelated. The potential required to produce this rate of loading is automatically achieved by the system.

An analysis of the loading transients has been provided, and reactions have been given for each of the different sections. The two plateaus on the loading transients have, as with potentiostatic loading, been attributed to the  $\alpha + \beta$  mixed phase followed by hydrogen evolution on the surface of the palladium.

The effects of the loading current,  $i_L$ , the loading time,  $t_L$  and the oxygen present in the system have all been investigated. It is noted that the relationship between the loading current and time taken to fully load the nanostructured film are not related by a simple inverse proportionality as expected, especially when there is a huge difference between the loading currents chosen. Several theories for this have been considered, including the moving boundary mechanism (MBM), the diffusion of protons in the solution and the effect of the double layer. Studies of the consequences of altering the loading time have been conducted. These studies have led to the reintroduction of the  $Q_{strip} \vee Q_{Load}$ 

analysis technique. This in turn has led to an awareness of the efficiency of loading and a knowledge of how the H/Pd ratio is changing with time. This knowledge reinforces the analysis of the loading transients and in particular the reactions occurring during the potential plateaus. Analysis of the potential produced at very low loading currents (~7 nA) show that the presence of oxygen in the solution means that the loading is not 100% efficient in that some of the loading current is used to reduce the dissolved oxygen.

The loading/stripping analysis was studied in more detail, and in particular, the effect of solution pH, the nanostructure, the freshness of the film and the thickness of the film were all investigated. The main conclusion that can be drawn from these investigations are that galvanostatic loading offers many advantages over potentiostatic loading. It is possible to load plain palladium films with hydrogen using galvanostatic loading, in fact there are only minor differences between the loading transient for a plain film, and one for a  $H_1$ -e Pd film. By passing a current through the film a known amount of protons can be removed from, or injected into, a solution, which cannot be accomplished by applying a potential across the film. This is interesting when considered with scanning electrochemical microscopy in mind.

Finally, it is shown that when altering the pH of a solution, there need be no alterations to the procedure required for galvanostatic loading, since the potential is reached and not applied. This has huge advantages in a practical sense since the time of the experiment can always be predetermined and there are no preliminary experiments to determine the potential or current to be applied.

# 5. SECM

The ultimate application of the nanostructured PdH micro pH sensor has always been scanning electrochemical microscopy (SECM). The ability to measure the interfacial surface pH between a surface (SECM substrate) and the surrounding solution is an interesting, useful and highly challenging application. It can be used for both purely academic reasons, for example to provide the fundamental knowledge needed to explore and understand surface reactions and industrial reasons for example to obtain useful information about surfaces e.g. corrosion sites on a metallic surface.

The typical set up of an SECM experiment involves a substrate undergoing a reaction with the solution which is either monitored by or affected by the presence of a tip. The manner in which this is carried out varies enormously, with the more common methods detailed in Sections 1.4.1 and 1.4.2. The tip is usually a microelectrode with a diameter of up to 25  $\mu$ m. It is important that the tip is sufficiently small, since it is the tip diameter that is predominantly responsible for the resolution of the SECM experiment. Unlike conventional experiments with microelectrodes, it is also important that the diameter of the glass surrounding the microelectrode is also kept sufficiently small, typically 2-10 times the diameter of the electrode itself. This is to prevent the glass around the tip from shielding the substrate.

The chapter describes the research performed to measure the pH change of a solution near an electrode undergoing cyclic voltammetry. This experiment was chosen for a number of reasons. Firstly, research had previously been published<sup>95-97</sup> using SECM to perform a similar task; secondly, some qualitative information is already known about the movement of protons during the cyclic voltammetry; thirdly, it is thought that the experiment is relatively simple, whilst not being trivial. The previous work conducted in this area used an amperometric (active) sensor to measure the pH of the solution by running tip-substrate voltammograms. This current research utilises a potentiometric (passive) sensor to measure the pH of solution, and as such the substrate is a separate electrochemical entity to the tip and is not affected electrochemically by its presence. The cyclic voltammogram of the substrate, which is a 0.5 mm diameter platinum disc,

- 114 -

will be performed in 0.5 M Na<sub>2</sub>SO<sub>4</sub>. Cyclic voltammetry in this solution provides surface reactions which are known to produce significant changes in the surface pH. The results in this chapter are typical of those obtained; however the reproducibility of the experiments was not investigated systematically.

This application of the nanostructured micro pH sensor is an extremely challenging application and will test the possibility of the pH sensor as a commercial application.

# 5.1. Experiment Set-up

The first stage in the SECM experiment was to fabricate the tips. In this study the tips were either 10  $\mu$ m or 25  $\mu$ m Pt microdiscs, which had been previously plated with a nanostructured H1-e Pd film. The microdisc tips were fabricated as previously explained in Section 2 and sharpened such that the diameter of the entire glass tip, 2r<sub>g</sub>, was not more than 10 times the diameter of the film, 2a. The ratio of r<sub>g</sub>:a is given the term R<sub>g</sub>, and an R<sub>g</sub> value < 10 is typical for SECM experiments. The value of R<sub>g</sub> is kept as low as possible so as to reduce the amount of shielding caused by the glass. A typical SECM tip is shown in Figure 46.

115 -

 $2r_g < 10 \ge 2a$ 



**Figure 46** A typical tip used for SECM experiments. The electroactive area was an H<sub>1</sub>-e Pd film deposited onto a Pt microdisc ( $Q_{dep} = 20 \ \mu\text{C}$ ,  $\varphi = 25 \ \mu\text{m}$ ). The tips were sharpened such that  $R_g = 2r_g/2a < 10$ .

The nanostructured palladium tip was aligned above the substrate such that the centre of the tip was vertically above the centre of the substrate, as in Figure 47. In this study the SECM substrate was a platinum disc, with a radius of 0.5 mm, sealed into a glass pipette. The tip was brought down until almost touching the substrate, as observed under a stereo microscope, then brought up by  $10 \mu m$ .



Figure 47 Diagram to show the alignment of the SECM tip with respect to the substrate. The tip was centred over the substrate in the x and y planes, and moved in the z plane according to the stage of the experiment.

Both the nanostructured tip and the Pt substrate were placed into a trough which was filled with the solution and each was independently connected to an SMSE reference electrode. The substrate was introduced to the cell via an opening in the bottom of the cell and leaking was prevented by using a PTFE o-ring. This will be explained further when discussing the use of a covered cell for deaerated experiments. The substrate was connected such that it was always under potentiostatic mode, and only the current was measured and recorded. The substrate potential was recreated by using the predetermined potential limits and scan rate, due to limitations of the software which meant that only two channels could be recorded at any one time. These were used for the substrate current and the tip potential. The tip was connected such that the high input differential amplifier was always attached across the tip/reference electrode, and the galvanostat was connected during the loading process only.

The H<sub>1</sub>-e Pd tip was moved into the bulk solution and loaded galvanostatically with hydrogen until the palladium hydride was in the mixed  $\alpha + \beta$  phase, i.e. H/Pd = 0.5. Once the loading was complete the tip was moved closer to the substrate and at the same time the cyclic voltammetry on the substrate was begun. It is worth noting that loading of the tip could not be achieved whilst the substrate was undergoing cyclic voltammetry, regardless of the tip position, since there was interference between the two processes. As such it was important that the substrate voltammetry was ceased before loading or reloading was attempted. However, once loaded and the cyclic voltammetry on the substrate started, the tip was switched from galvanostatic mode to potentiometric mode. As such once the tip was sufficiently close to the substrate the change in local proton activity could be measured. The tip-substrate distance used in these experiments was less than 10 µm. It cannot be accurately measured, due to the limitations of potentiometric SECM tips, which cannot be used in feedback mode to measure tip-substrate distance.

Before each set of experiments, two control measures were taken. Firstly, the potential of the nanostructured tip in the bulk solution was measured and recorded and secondly the cyclic voltammogram of the substrate without the tip present was also recorded. This was to ensure that the cyclic voltammetry of the substrate was not affected by the presence of the tip. A typical cyclic voltammogram recorded for the 0.5 mm Pt disc in 1 M  $H_2SO_4$  is shown in Figure 48.



**Figure 48** Cyclic voltammogram of a SECM substrate, Pt disc – diameter,  $\varphi$ , = 0.5 mm, in 1M H<sub>2</sub>SO<sub>4</sub> (not deaerated). Scan rate; v, = 100 mV s<sup>-1</sup>.

The cyclic voltammogram shown in Figure 48 shows many distinguishing features, including the hydrogen adsorption/desorption peaks in the negative potential region and the platinum oxide formation/removal in the positive potential region. Those reactions which yield a positive current, namely the desorption of sorbed hydrogen and the formation of platinum oxide, produce protons and as such make the area surrounding the substrate more acidic. Conversely, the reactions which yield a negative current; the removal of platinum oxide and the formation of absorbed (and adsorbed) hydrogen remove the protons from the solution and make it more alkaline. The change in pH is expected to be significant, since for the formation/removal of platinum oxide, PtO, two protons per Pt atom can be released or consumed.

The potential of the tip in the bulk of the solution was recorded since this was a base point on the E vs. pH plot and all potentials were calculated relative to this point, using a slope value of -59 mV pH<sup>-1</sup>.

## **5.2.** Potentiometric Measurements in Aerated Solutions

The potential of the tip was measured whilst the substrate was undergoing cyclic voltammetry, and the tip-substrate distance was less than 10  $\mu$ m. The set up was analogous with that for a rotating ring-disk electrode. In this case the substrate is behaving as the disc and the tip is behaving as the ring.

The solution in this study was  $0.5 \text{ M } \text{Na}_2\text{SO}_4$  and was not deaerated before the SECM experiments were begun.

### 5.2.1. Tip Potential

The tip potential was plotted as function of time and shown with the simultaneous substrate current. This plot is shown in Figure 49. It should be mentioned that these were not the first cycles recorded.



**Figure 49** The potential of an H<sub>1</sub>-e Pd tip ( $Q_{dep} = 20 \ \mu$ C, Pt disc  $\varphi = 25 \ \mu$ m) during cyclic voltammetry of a Pt disc ( $\varphi = 0.5 \ m$ m) close to the tip (tip-substrate distance < 10  $\mu$ m) in a solution of 0.5 M Na<sub>2</sub>SO<sub>4</sub>.  $\nu = 50 \ m$ V s<sup>-1</sup>, -1.2 - 0.6 V vs. SMSE. Also shown is the current of the substrate measured at the same time. Data presented for two voltammetric cycles, bulk potential = -0.78 V vs. SMSE.

It can be seen from the plot of  $E_{tip}$  and  $i_{substrate}$  vs. t (Figure 49) that the tip potential shows dramatic, sharp changes during the adsorption and consequent desorption of hydrogen into the Pt disc, but less defined in the oxide formation/stripping region. The plot starts off at the positive end of the cyclic voltammogram, i.e. when the potential of the substrate was 0.6 and moves towards the negative end. At this stage the Pt disc has undergone oxide formation. As the time increases, the potential of the tip becomes more negative. This is due to the removal of the Pt oxide formed which consumes protons from the solution, as shown in Equation 49.

$$PtO + 2H^+ + 2e^- \rightarrow Pt + H_2O$$

**Equation 49** 

- 121 -

As the protons are consumed from the solution, the solution becomes more alkaline and as such the tip potential moves more negative. After the oxide removal, the Pt disc undergoes hydrogen adsorption followed by hydrogen evolution, which are shown in Equation 50.

$$Pt + H_3O^+ + e^- \rightarrow PtH_{abs} + H_2O$$
 Equation 50

These reactions also consume protons and as such there is another drop in the tip potential. However the tip potential is much more distinct during the hydrogen adsorption/evolution than for the oxide removal. The two separate processes for weak adsorption and strong absorption can be identified in the tip potential.

The desorption and removal of the hydrogen from the Pt disc is shown as two peaks in the substrate current, but only appears as one on the plot of potential tip. Since the substrate current,  $i_{substrate}$ , is a measure of the rate of electron transfer and the tip potential reflects the local change in H<sup>+</sup> activity, the combined plot suggests one of two conclusions. Either the desorption of hydrogen from the platinum surface proceeds as two steps with respect to the electron transfer but only one step with respect to the proton transfer, or the tip is not sensitive enough to detect the difference between an increase of proton activity due to strong hydrogen desorption and weak hydrogen desorption. Finally  $E_{tip}$  then begins to increase due to Pt oxide formation, which is shown in Equation 51.

## $Pt + H_2O \rightarrow PtO + 2H^+ + 2e^-$ Equation 51

As can be seen, the formation of Pt oxide releases protons into the solution and as such makes the solution more acidic. However, as with the oxide removal, the tip response is very broad, especially when compared with the response for the hydrogen reactions.

### 5.2.2. *pH* vs. *t*

The tip potential,  $E_{tip}$ , is a function of the logarithm of the proton activity, and as such is a linear function of pH. It is possible to obtain a plot of pH vs. t by applying the Nernst equation to the SECM system, as shown in Equation 52.

$$E = E^0 + \frac{RT}{F} \ln \frac{a_H}{a_{H(Pd-H)}}$$

Equation 52

Where  $E^0$  is the standard potential for the reaction / V

*R* is the universal gas constant, 8.314 J  $K^{-1}$  mol<sup>-1</sup>

T is the temperature / K

F is the Faraday constant, 96485 C mol<sup>-1</sup>

 $a_i$  is the activity of species i.

It is possible to rearrange Equation 52 and express the tip potential in terms of pH only. This can be achieved by applying the following four separate identities.

> (i) In dilute solutions, such as 0.5 M Na<sub>2</sub>SO<sub>4</sub>, the activity of ions is equal to the concentration of the ions

(ii) 
$$a_{H(Pd-H)} = 1$$

- (iii)  $pH = -log_{10} [H^+]$
- (iv) At room temperature, 2.3  $RT/F = 59.1 \text{ mV}^{\dagger\dagger}$

Thus Equation 53 can be applied to the system.

$$E = E^0 + 0.059 \, pH$$

#### **Equation 53**

 $E^0$  was determined experimentally so as to obtain an accurate value for this specific system. This was achieved by measurement of the potential in a number of solutions of

<sup>††</sup> Using R = 8.314 J K<sup>-1</sup> mol<sup>-1</sup>, T = 298 K, F 96485 C mol<sup>-1</sup> and that  $\ln(x) = 2.3 \log_{10}(x)$ 

- 123 -

known pH and plotting a calibration plot. This calibration plot can be used to solve Equation 53 for the unknown  $E^0$ . The calibration plot produced is shown in Figure 50.



Figure 50 Calibration plot obtained from measurement of potential in a solution of deaerated 0.5 M  $Na_2SO_4$  with  $H_2SO_4$  (acidic solutions) or NaOH (basic solutions).

Solving Equation 53 for the unknown  $E^0$  leads to Equation 54, which can be used to calculate the solution pH directly from the tip potential.

$$E = -0.59 + 0.059 \, pH$$
 Equation 54

The plot obtained when changing tip potential,  $E_{tip}$ , to pH is shown in Figure 51. As the tip potential becomes more negative, the solution becomes more alkaline and as such the pH increased. Thus the shape of the pH vs. t plot is the mirror image of the  $E_{tip}$  vs. t plot.

E/V vs. SMSE



**Figure 51** The pH measured by an H<sub>1</sub>-e Pd tip ( $Q_{dep} = 20 \ \mu$ C, Pt disc  $\varphi = 25 \ \mu$ m) during cyclic voltammetry of a Pt disc ( $\varphi = 0.5 \ \text{mm}$ ) close to the tip (tip-substrate distance < 10  $\mu$ m) in a solution of 0.5 M Na<sub>2</sub>SO<sub>4</sub>. v = 50 mV s<sup>-1</sup>, -1.2 - 0.6 V vs. SMSE. Also shown is the current of the substrate measured at the same time. Bulk pH = 5.4

The shape of the *pH* vs. *t* plot can be analysed as for the  $E_{tip}$  vs. *t* plot. It is also possible to analyse the peaks in a more quantitative way. The first definite peak in the plots is attributed to the Pt oxide reduction. This occurs at values of 22.9 & 92.8 s on the *i<sub>substrate</sub>* plot, but occurs at values of 27.2 & 97.0 s on the *pH* and  $E_{tip}$  plots. This 5 second delay may be attributed to the diffusion of the hydrogen, and this can be quickly proved or disproved by calculating the time taken for the protons in the solution to diffuse away from the tip toward the electrode. The diffusion layer,  $\delta$ , can be calculated by Equation 55 and this equation be rearranged to calculate the time taken for a species to diffuse a given distance as shown in Equation 56.

- 125 -

 $t = \frac{\delta^2}{D}$ 

 $\delta = \sqrt{Dt}$ 

**Equation 56** 

where  $\delta$  is the diffusion thickness / cm (i.e. the tip-substrate distance)

D is the diffusion coefficient / cm<sup>2</sup> s<sup>-1</sup>

t is time taken to diffuse the distance  $\delta$  / s

Substituting  $\delta = 10 \times 10^{-4}$  cm (the maximum tip-substrate distance) and using a H<sup>+</sup> diffusion coefficient of 7.7 x  $10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>, the time taken for diffusion is calculated as 13 ms. Even allowing for a huge error in tip-substrate distance and diffusion coefficient, it is clear that the time difference of 4.3 s between the *i<sub>substrate</sub>* peak and the *pH/E<sub>tip</sub>* peak cannot be attributed to the diffusion process. Similar studies can be performed on the other peaks, namely the hydrogen adsorption and desorption. These results are shown in Table 7.

Electrochemical process		<i>i<sub>substrate</sub></i> peak time /	$E_{tip}/pH$ peak time	Time difference /
Oxide	Cycle 1	22.9	27.2	4.3
Removal	Cycle 2	92.8	97	4.2
Hydrogen	Cycle 1	31.5/34.3	35.4	3.9/1.1
adsorption	Cycle 2	101.4/104.4	105.2	3.8/0.8
Hydrogen	Cycle 1	39.3/40.9	43.7	4.4/2.8
desorption	Cycle 2	109.3/110.9	112.9	3.6/2.0

 Table 7 Table containing the times of the peaks shown in Figure 51

It has been proposed by previous studies<sup>97</sup> that the desorption of hydrogen can be divided into to two sub-steps; the first being electron transfer and the second being the release of H<sup>+</sup> from the platinum surface. The current study is in agreement with the former study since the measure of electron transfer ( $i_{substrate}$ ) peaks well before the measure of proton release (*pH*). However, whilst the timescale of pH represents a timescale of proton release, it is worth remembering that pH = -log<sub>10</sub> [H<sup>+</sup>] and as such to

directly compare the rate of electron transfer with the rate of hydrogen release, the pH must be converted into  $[H^+]$  as shown in the following section.

### **5.2.3. Rate of Proton Release**

Since this SECM procedure is novel, the ideal representation of the data has not yet been established. Plots of  $E_{tip}$  and pH vs. t have been shown and compared with the simultaneous substrate current,  $i_{substrate}$ . Plots of  $\frac{d(E_{tip})}{dt}$  and  $\frac{d(pH)}{dt}$  have been also been created, but do not significantly add to the knowledge that can be concluded from other figures. Also, integrating the substrate current diminished the peaks. As mentioned previously, it is important to compare the **rate** of proton release with  $i_{substrate}$ , which represents the **rate** of electron transfer.

It is assumed that the pH sensor is monitoring all of the release and consumption of protons. However, it is important to note that the SECM solution is not deaerated and as such contains dissolved gases. Although the effect of dissolved  $O_2$  on the pH sensor is known, i.e. the lifetime is significantly reduced, the effect of other dissolved gases is not known. Specifically, dissolved  $CO_2$  in the solution can react with  $H_2O/OH^-$  to form  $HCO_3^-$  which affects the measured pH. Previous studies have shown that pH sensors can be dramatically affected by the presence of dissolved  $CO_2$  as this can act as a buffer, especially when close to *pH* 7. The dissolved  $CO_2$  reacts with the water via Equation 57.

$$CO_2 + H_2O \rightarrow H^+ + HCO_3^-$$
 Equation 57

The effect of Equation 57 is to make the solution slightly acidic. Previous work<sup>139</sup> has investigated this effect and the results of a pH titration curve is shown in Figure 52.



**Figure 52** *pH* titration curves for a bismuth electrode in a solution of increasing [OH] — theoretical response for a zero buffer capacity;  $\circ$  represent the pH response in the absence of CO<sub>2</sub>; • represents the response in presence of CO<sub>2</sub>. Taken from reference<sup>139</sup>

In can be seen from Figure 52 that the pH response in the presence of  $CO_2$  is much less than in the absence of  $CO_2$ , and that this difference is dependent on the value of pH. At a concentration of approximately 11 µmol dm<sup>-3</sup> the theoretical pH is 7, the response in the absence of  $CO_2$  is 5.7 and the response in the presence of  $CO_2$  is 4.8. Thus at pH 7 the  $CO_2$  has reduced the pH by almost 1 pH unit. The presence of  $CO_2$  in the solution therefore, is responsible for the acidity of the bulk solution (pH = 5.4) and may also contribute to the broadness of the tip response in the oxide formation region. The buffering capacity of CO<sub>2</sub> leads to some of the protons being released or consumed by the substrate not being measured by the tip; Figure 52 has shown that the greater difference between deaerated and CO<sub>2</sub> saturated is in the slightly alkali region (pH = 8-9).

In the conversion, shown in Figure 53 and Figure 54, the buffering capacity is not taken into account since the most affected region is not resolvable.



**Figure 53** The rate of change of proton concentration measured by an H<sub>1</sub>-e Pd tip ( $Q_{dep} = 20 \,\mu$ C, Pt disc  $\varphi = 25 \,\mu$ m) during cyclic voltammetry of a Pt disc ( $\varphi = 0.5 \,\text{mm}$ ) close to the tip (tip-substrate distance < 10  $\mu$ m) in a solution of 0.5 M Na<sub>2</sub>SO<sub>4</sub>.  $\nu = 50 \,\text{mV s}^{-1}$ , -1.2 – 0.6 V vs. SMSE. Also shown is the current of the substrate measured at the same time.

- 129 -

The plot of  $\frac{d[H^+]}{dt}$  vs. *t* compared with *i<sub>substrate</sub>* vs. *t* is shown in Figure 53. Whilst the oxide formation region is noisy and featureless, the oxide removal, hydrogen adsorption and hydrogen desorption regions give more information than the  $E_{tip}$  and *pH* plots. If the plot is enhanced around the area which contains these reactions, as in Figure 54, it can be seen that the two separate peaks for hydrogen adsorption and absorption have been resolved, as in the *i<sub>substrate</sub>* plot.



Figure 54 A close up view of the region of oxide removal (A), hydrogen adsorption (B), hydrogen absorption (C) and hydrogen desorption (D) as in Figure 53.

The enhanced plot, Figure 54, shows the four main resolvable peaks which correspond to oxide removal (A), adsorption of strongly bound hydrogen (B), adsorption of weakly bound hydrogen (C) and hydrogen desorption (D). Other peaks seen in the  $i_{substrate}$  plot were not seen in the  $\frac{d[H^+]}{dt}$  plot, due to this area of the plot being noisy and featureless.

- 130 -

It can be seen by eye that the time difference between the  $i_{substrate}$  and  $\frac{d[H^+]}{dt}$  is considerably less than for  $E_{tip}/pH$  and  $i_{substrate}$ . The precise time differences between these peaks have been calculated and are shown in Table 8.

Electrochemical process		i <sub>substrate</sub> peak time / s	$\frac{d[H^+]}{dt} \text{ peak}$ time / s	Time difference / s
Oxide	Cycle 1	22.9	23.5	0.6
Removal (A)	Cycle 2	92.8	93.4	0.6
H <sub>ads</sub> strong (B)	Cycle 1	31.5	32.2	0.7
× .	Cycle 2	101.4	102.0	0.6
H <sub>ads</sub> weak (C)	Cycle 1	34.3	34.3	0
	Cycle 2	104.4	104.1	0.3
Hydrogen	Cycle 1	39.3/40.9	37.8	-1.5/-3.1
desorption (D)	Cycle 2	109.3/110.9	107.5	-1.8/-3.4

Table 8

NB. All peak times are quoted to the nearest 100 ms, with an associated error  $\pm$  50 ms, which is the error incorporated by the resolution of the recording equipment, which is far greater than the expected experimental error.

The calculated time differences are indeed significantly shorter when considering  $\frac{d[H^+]}{dt}$ instead of  $E_{tip}$  or pH. These values are much more reliable since these convey

the time difference between the peak rate of e transfer and the peak rate of H<sup>+</sup> transfer. However, even with the reduced difference in peaks times this cannot be attributed solely to the rate of diffusion of H<sup>+</sup> since the time taken for proton transfer across the 10  $\mu$ m gap was estimated to be 13 ms, approx 40 times less than the observed peak separation. It can also be seen that in the hydrogen desorption reaction, the proton transfer now proceeds the electron transfer.

#### 5.2.4. Cyclic Voltammograms

Since previous work<sup>96</sup> has produced tip-substrate voltammograms, it has been thought that it would be beneficial to compare the tip potential (in the more meaningful form of pH) and the substrate current as a function of the substrate potential. The tip-substrate voltammograms in the literature show the tip current of an amperometric tip, with respect to the substrate potential, during cycling of the substrate potential. Figure 55 shows these two plots on separate axes.



**Figure 55** The pH of an H<sub>1</sub>-e Pd tip ( $Q_{dep} = 20 \ \mu$ C, Pt disc  $\varphi = 25 \ \mu$ m) during cyclic voltammetry of a Pt disc ( $\varphi = 0.5 \ \text{mm}$ ) close to the tip (tip-substrate distance < 10  $\mu$ m) in a solution of 0.5 M Na<sub>2</sub>SO<sub>4</sub>.  $\nu = 50 \ \text{mV s}^{-1}$ , -1.2 – 0.6 V vs. SMSE. Also shown is the current of the substrate measured at the same time. The pH of the tip was calculated from the potential using the Nernst equation. Bulk pH = 5.4.

The main features of the pH-potential plot of the Pt substrate are the two peaks in the potential region -0.7 - -1.2 V vs. SMSE. These highlight the changes in the pH caused by the removal of the PtO layer, and the formation of adsorbed hydrogen. It can also be

seen that due to the peak separation observed on the transients between the substrate response and the tip response, there are two loops of the pH-t plot.

The *pH-t* also highlights the lack of definition, particularly at pH < 5.75. However, it is not expected to affect the use of the tip as a pH sensor when used in pH mapping, provided the pH map is recorded at a significantly reduced speed.

#### **5.2.5.** Comparison with Previous Studies

The tip response obtained from previous studies show defined peaks in both the oxide formation/reduction region<sup>95</sup> and the hydride adsorption/desorption region<sup>97</sup> of the Pt cyclic voltammogram in 0.5 M Na<sub>2</sub>SO<sub>4</sub>, although this cannot be carried out in one experiment. In order to obtained defined peaks in the oxide formation/reduction region, the tip potential needs to be significantly higher ( $E_{tip} > 0$  V vs. SMSE) than for the hydride adsorption/desorption/desorption region ( $E_{tip} < -1.0$  V vs. SMSE).

Both the current study and the former study show a peak separation of greater than 1 s between the substrate and the tip response for strong  $H^+$  desorption. It has been shown that this cannot be attributable to the diffusion of  $H^+$  in the solution, since this is expected to be approximately 13 ms, rather than the 1.2 s experienced in the former study and 1.5 s experienced in this study. Both studies conclude that the sub-step for hydrogen adsorption/desorption occurs prior to the electron transfer step.

Neither the current study nor the previous study have taken into account the buffering capacity of dissolved  $CO_2$  in the solution. However, in the former study the solution had been deaerated before use, thus reducing the amount of  $CO_2$  in the solution. This may account for the greater pH swing observed (previous study – 2.3 pH units, current study – 1.3 pH units), and for the defined peaks in the oxide formation region.

## **5.3.** Potentiometric Measurement in Deaerated Solutions

It is known that the removal of hydrogen from within the palladium lattice is significantly enhanced in the presence of oxygen or other oxidants, and as such the lifetime of the micro pH sensor is significantly reduced. In order to produce SECM experiments over a long time a deaerated solution must be used. In order to achieve this, a few modifications to the current SECM set up were necessary. The SECM cell currently used was not suited to a deaerated experiment. The open trough-like shape meant that the dissolved oxygen would leave the solution easily, and that it would also be difficult to deaerate the whole solution. It was decided that the easiest method of modifying the cell would be to cover the top of the cell with a film with low permeability of oxygen, namely Parafilm. In addition to low oxygen permeability, it is also extremely impermeable to water. The solution was deaerated by purging with argon in a 3 necked, V-shaped cell and then transferred into the SECM cell. One of three necks was used as an inlet for the Argon which consisted of a thin tube placed through a rubber seal. Another of the necks was used to transfer the solution through to the SECM cell, and again consisted of a thin tube through a rubber seal. The middle of the three necks was used to control the procedure. Whilst the solution was undergoing purging, the middle neck was left open so as to allow the oxygen to leave the cell. Once the solution had been completely deaerated, the argon flow was reduced and the middle cell closed. This forced the solution to travel through the outlet and into the SECM cell. This would then provide the SECM cell with a full deaerated solution in which experiments could be performed.

However, it was at this point that the experiment began to fail. The force of the solution being transferred into the cell created a leak in the SECM cell usually, but not exclusively, around the point at which the electrode came up through the bottom of the cell. This then created a dilemma. If the cell was to be left uncovered then oxygen would return to the solution far too quickly, but if the cell was covered then solution leaked out of the cell. Partially covering the cell did not appear to ease the situation, since the cell continued to leak. It was therefore concluded that in order to perform

- 134 -

SECM experiments under deaerated conditions, a new SECM cell would need to be designed. This new SECM cell would have the SECM substrate being introduced into the cell via the side or top of the cell and the point at which the substrate and cell met would be higher than the level of the solution. Due to time pressures, this was not possible in this current research, however, it would provide an interesting topic for future research.

### 5.4. Summary

The use of a  $H_1$ -e Pd film on a Pt microdisc has been shown to be successful in monitoring the changes in proton concentration around a Pt disc undergoing cyclic voltammetry. The experiment required to achieve such results has been documented, and the issues faced have also been detailed. To perform such a novel, challenging application of a  $H_1$ -e Pd film new procedures have been created by combining a number of existing, well documented methods.

The potential of a  $H_1$ -e Pd film in the vicinity of a Pt disc undergoing cyclic voltammetry has been recorded. The results show that the tip potential shows well defined peaks which coincide with adsorption, evolution and consequent desorption of hydrogen on the Pt disc. The results also show a broad change in the potential of the nanostructured film, which corresponds with the formation and subsequent removal of a Pt oxide layer on the substrate surface. The two separate peaks for adsorption can be identified in both the tip potential and the substrate current. However, the desorption and removal of the hydrogen from the Pt disc is shown as two peaks in the substrate current, but only appears as one on the plot of potential tip. Combining the analysis of the two plots suggest that although the desorption of hydrogen from the platinum surface proceeds as two steps with respect to the electron transfer, it only proceeds via one step with respect to the proton transfer.

By changing the tip potential into pH, a more quantitative analysis of the peaks has been possible. The results suggest that for hydrogen desorption the electron transfer precedes the proton transfer, by comparing the peak separation of  $i_{substrate}$  and pH. However, in order to fully compare the rate of proton transfer with the rate of electron transfer, the

plot of  $\frac{d[H^+]}{dt}$  vs. time was produced and compared with the substrate current. This is a direct comparison of two rates. This shows that peak separation between the tip response and the substrate response cannot be attributed to the diffusion of the protons in solution to/from the tip. These results now suggest that the proton transfer precedes the electron transfer in the hydrogen desorption reaction. The tip and substrate response were also shown as voltammograms. These voltammograms highlight the lack of definition in the tip response, particularly in the region of oxide formation/removal. Finally the issues of using the current SECM cell design with a deaerated solution have been presented. It has been concluded that in order for a successful measurement of the proton changes around a Pt substrate undergoing cyclic voltammetry to be made, a novel cell needs to be fabricated. Ideally, this new cell would provide in-situ deaerating, and would be constructed such that the substrate would be introduced into the cell at a higher level than the solution, so as to avoid leaks in the system.

## 6. Conclusions/Further Work

There are two possible ways of loading hydrogen into a  $H_1$ -e Pd film, in order to create a palladium hydride pH sensor; potentiostatic and galvanostatic loading. This thesis has shown developed insight into an established method (potentiostatic loading), presented a novel method (galvanostatic loading) and then placed the sensor into an extremely challenging environment in order to test its credentials to move to a practical pH sensor (SECM).

The loading of hydrogen into a nanostructured palladium film via a potentiostatic method has been shown to offer advantages over other possible approaches. Stepping the potential means that the reaction is controlled and produces highly reproducible loading transients. The required loading conditions must be predetermined by running a short series of experiments, which involve measuring the stripping charge associated with loading to a maximum H/Pd ratio for a given loading potential. The loading of hydrogen into the same H<sub>1</sub>-e Pd film can also be achieved by galvanostatic loading. This approach centres on loading the film by controlling the current through the film, and has been shown to offer smooth, highly reproducible loading transients. Analyses of the loading transient for both galvanostatic and potentiostatic loading have been provided, and reactions have been given for each of the different regions. Both transients are strikingly similar, with both showing two clear plateaus. In both cases these have been attributed to the  $\alpha' + \beta$  mixed phase followed by hydrogen evolution on the surface of the palladium.

The immediate advantages of the galvanostatic method of loading were seen, since the loading conditions do not need to be established as with potentiostatic loading. Instead, it is possible to decide on a suitable loading time and work backwards to calculate the loading charge, since these are interrelated. The potential required to produce this rate of loading is automatically achieved by the system.

The advantages of the potentiostatic method become a barrier when the desired application is considered. In order to behave as a pH sensor, the H/Pd ratio must be between 0.1 and 0.5, ideally 0.5 such that the hydrogen reservoir is as full as possible. Since the driving force behind the reaction is controlled, the loading rate is evolving

with respect to time, so knowing when to stop loading so as to achieve a desired H/Pd ratio is difficult. With galvanostatic loading, however, the rate of hydrogen insertion is governed by the current, which is controlled. This means that any desired H/Pd ratio can be achieved simply by altering the loading current and/or the loading time. This procedure has been shown to work under various conditions using galvanostatic loading which has not been possible with potentiostatic loading. Without any pre-experimental calibrations, the galvanostatic technique can load hydrogen into a palladium film of any thickness and freshness and in a solution of any pH. This is because it is the rate that is controlled and not the driving force behind the reaction. Galvanostatic loading has even been successful in loading hydrogen into plain palladium film. In fact there are only minor differences between the loading transient for a plain film, and one for a H<sub>1</sub>-e Pd film. Previous research has shown that loading hydrogen into a plain palladium film is not reliably and reproducibly possible using potentiostatic control. Analysis has shown that the amount of hydrogen loaded into the nanostructured palladium lattice can be accurately established by measurement of (potentiostatic loading) or calculation of (galvanostatic) the loading charge. However, at times after the initial loading some hydrogen will have been desorbed from the palladium and this relationship no longer holds true. Regardless of the loading method, the only way of knowing the amount of hydrogen within the palladium lattice is to strip the hydrogen completely from the film.

Investigations into the potentiostatic loading of the nanostructured film led to a novel analysis that provided useful information about the hydrogen loading into the film, and was used extensively when examining galvanostatic loading. The comparison of the loading charge,  $Q_{Load}$  and the stripping charge,  $Q_{strip}$  can provide information about the loading efficiency of the system and how the H/Pd ratio changes with loading time,  $t_L$ . The effects of the loading current,  $i_L$ , the loading time,  $t_L$  and the oxygen present in the system have all been investigated. It is noted that the relationship between the loading current and time taken to fully load the nanostructured film are not related by a simple inverse proportionality as expected, especially when there is a huge difference between the loading currents chosen. Several theories for this have been considered, including the moving boundary mechanism (MBM), the diffusion of protons in the solution and
the effect of the double layer. Analysis of the loading potential produced at very low values of  $i_L$  (~7 nA) show that the presence of oxygen in the solution means that the loading is not 100% efficient in that some of the loading current is used to reduce the dissolved oxygen.

Also, the possibility of using a membrane across the surface of the film was investigated. This proposal proved to be successful, but not as successful as would have been expected. The working time of the film was extended by covering with Nafion, but it was still far less than required for many applications. It is thought that only in conjunction with another method will this method be suitable.

The creation of galvanostatic loading has led to the development of the nanostructured pH sensor as an SECM tip. This has led to the successful monitoring of the changes of the proton concentration surrounding a platinum disc during cyclic voltammetry. The results show that the tip potential shows well defined peaks which coincide with adsorption, absorption and consequent desorption of hydrogen on the Pt disc. The results also show a broad change in the potential of the nanostructured film, which corresponds with the formation and subsequent removal of a Pt oxide layer on the substrate surface. It is possible to see the two separate peaks for strongly and weakly adsorbed hydrogen in the tip potential-time plot. A more quantitative analysis of the peaks is possible by plotting pH against time. Comparing the peak separation of  $i_{substrate}$ and pH suggests that for hydrogen desorption the electron transfer precedes the proton transfer. In order to fully compare the rate of proton transfer with the rate of electron transfer, the plot of  $\frac{d[H^+]}{dt}$  vs time was produced and compared with the substrate current. This demonstrated that peak separation between the tip response and the substrate response cannot be attributed to the diffusion of the protons in the solution to/from the tip, and as such must be from the timing difference between the proton

transfer and electron transfer. These results also suggest that the proton transfer precedes the electron transfer in the hydrogen desorption reaction. The tip and substrate response were also shown as voltammograms. These voltammograms highlight the lack of definition in the tip response, particularly in the region of oxide formation/removal.

- 139 -

The issues of using the current SECM experiment set up with a deaerated solution have been presented. It has been concluded that in order for a successful measurement of the proton changes around a Pt substrate undergoing cyclic voltammetry to be made, a novel cell needs to be fabricated. Ideally, this new set up would provide in-situ deaerating, and would be constructed such that the substrate would be introduced into the cell at a higher level than the solution, so as to avoid leaks in the system.

It would be of great value to this area of electrochemistry if future work focussed primarily in two main areas.

Firstly, the use of the  $H_1$ - Pd film in SECM experiments needs to be developed further. Although the ground work has been set, future work can focus on successfully achieving a pH map of a substrate at varying potentials. This could then be followed up with a study of the pH changes of a single area of a surface whilst a corrosion pit is induced. This would lead to potential corrosion sites being identified long before they become visible.

Secondly, the use of recessed electrodes is an area that would have been investigated had time been permitting. This would work by creating a microelectrode in the usual manner and recessing the electrode by etching the metallic area of the electrode, but leaving the surrounding glass in place. A H<sub>1</sub>-e Pd film could then be plated on top of the recessed electrode, to the depth of the recess. It is thought that this would offer three major benefits. The greatest benefit is that a much thicker film can be plated, thus creating a large reservoir of palladium hydride. Current films are up to 4 µm thick, whereas the use of a recessed microelectrode could allow films up to 10  $\mu$ m in thickness to be plated onto the surface. The increase in the palladium hydride reservoir is a great advantage since the biggest constraint on the current system is the relatively short working time of the pH sensor, and a larger reservoir would vastly lengthen the working time of the sensor. Whilst it is currently possible to plate thick films, it is not possible to do so without increasing the diameter of the film. By using a recessed electrode it is possible to create a thick film which is contained and therefore has a diameter which is independent of the thickness and always equal to the diameter of the underlying electrode. An increase in the diameter in the film would lead to a decrease in the

resolution when used as a tip in scanning electrochemical microscopy, which is highly disadvantageous.

The second advantage is that the film would become much more durable. As the film is on the surface of the microelectrode, it can be removed simply by fouching the film. This means that whilst in use, the film can accidentally be detached from the microelectrode, especially when used as an SECM tip, as the tip is operating at a distance of less than 10  $\mu$ m from the substrate. The third advantage to using a recessed microelectrode is that it slows down the removal of hydrogen from the nanostructured palladium, albeit on a small scale. Hydrogen is removed from the film by dissolved oxygen/oxidants in the solution. Although the majority of this is from within the pores, there will be some hydrogen that is close to edge of the film and as such is removed from the perimeter of the film. If this is protected by way of glass from the electrode material then there will be less hydrogen removed. This again will lengthen the lifetime of the pH sensor.

## 7. References

- (1) Ives, D.; Janz, G *Reference Electrodes*; Academic Press, Inc.: New York, 1961.
- (2) Bates, R. G. *Determination of pH, Theory and practice*; John Wiley and Sons: New York, 1964.
- (3) Dole, M. Journal of the American Chemical Society 1931, 53, 4260-4280.
- (4) Janata, J. Analyst 1994, 119, 2275-2278.
- (5) Ashcroft, B.; Takulapalli, B.; Yang, J.; Laws, G. M.; Zhang, H. Q.; Tao, N. J.;
   Lindsay, S.; Gust, D.; Thornton, T. J. *Physica Status Solidi B-Basic Research* 2004, 241, 2291-2296.
- (6) Kim, Y. J.; Lee, Y. C.; Sohn, B. K.; Kim, C. S.; Lee, J. H. Electronics Letters 2003, 39, 1515-1516.
- (7) Leopold, S.; Herranen, M.; Carlsson, J. O.; Nyholm, L. Journal of Electroanalytical Chemistry 2003, 547, 45-52.
- (8) Heineman, W. R.; Wieck, H. J.; Yacynych, A. M. Analytical Chemistry 1980, 52, 345-346.
- Jain, M. K.; Cai, Q. Y.; Grimes, C. A. Smart Materials & Structures 2001, 10, 347-353.
- (10) Teixeira, M. F. S.; Ramos, L. A.; Neves, E. A.; Cavalheiro, E. T. G. Journal of Analytical Chemistry 2002, 57, 826-831.
- (11) Koncki, R.; Mascini, M. Analytica Chimica Acta 1997, 351, 143-149.
- (12) Kreider, K. G.; Tarlov, M. J.; Cline, J. P. Sensors and Actuators B-Chemical 1995, 28, 167-172.
- (13) Yamamoto, K.; Shi, G. Y.; Zhou, T. S.; Xu, F.; Zhu, M.; Liu, M.; Kato, T.; Jin, J.
   Y.; Jin, L. T. Analytica Chimica Acta 2003, 480, 109-117.
- (14) Luo, J. L.; Lu, Y. C.; Ives, M. B. Journal of Electroanalytical Chemistry 1992, 326, 51-68.
- (15) Dimitrakopoulos, L. T.; Dimitrakopoulos, T.; Alexander, P. W.; Logic, D.;
   Hibbert, D. B. Analytical Communications 1998, 35, 395-398.

- (16) Kriksunov, L. B.; Macdonald, D. D.; Millett, P. J. Journal of the Electrochemical Society **1994**, 141, 3002-3005.
- (17) Liu, C. C.; Bocchicchio, D. B.; Overmyer, P. A.; Neuman, M. R. Science 1980, 207, 188-189.
- (18) Grubb, W. T.; King, L. H. Analytical Chemistry 1980, 52, 270-273.
- (19) Kinoshita, E.; Ingman, F.; Edwall, G.; Glab, S. *Electrochimica Acta* **1986**, *31*, 29-38.
- Rosenfeldt, F. L.; Ou, R.; Smith, J. A.; Mulcahy, D. E.; Bannigan, J. T.; Haskard, M. R. Journal of Medical Engineering & Technology 1999, 23, 119-126.
- (21) Kinoshita, E.; Ingman, F.; Edwall, G.; Thulin, S.; Glab, S. *Talanta* **1986**, *33*, 125-134.
- (22) Wang, M.; Ha, Y. Biosensors & Bioelectronics 2007, 22, 2718-2723.
- (23) Ha, Y.; Wang, M. Electroanalysis 2006, 18, 1121-1125.
- Wipf, D. O.; Ge, F. Y.; Spaine, T. W.; Bauer, J. E. Analytical Chemistry 2000, 72, 4921-4927.
- (25) Vanhoudt, P.; Lewandowski, Z.; Little, B. Biotechnology and Bioengineering
   1992, 40, 601-608.
- (26) Li, J. P.; Du, Y. L.; Fang, C. Electroanalysis 2007, 19, 608-611.
- Ges, I. A.; Ivanov, B. L.; Schaffer, D. K.; Lima, E. A.; Werdich, A. A.;
   Baudenbacher, F. J. Biosensors & Bioelectronics 2005, 21; 248-256.
- (28) Hitchman, M. L.; Ramanathan, S. Analytica Chimica Acta 1992, 263, 53-61.
- (29) Bezbaruah, A. N.; Zhang, T. C. Analytical Chemistry 2002, 74, 5726-5733.
- Marzouk, S. A. M.; Ufer, S.; Buck, R. P.; Johnson, T. A.; Dunlap, L. A.; Cascio,
   W. E. Analytical Chemistry 1998, 70, 5054-5061.
- (31) Marzouk, S. A. M. Analytical Chemistry 2003, 75, 1258-1266.
- (32) Hassan, S. S. M.; Marzouk, S. A. M.; Badawy, N. M. Analytical Letters 2002, 35, 1301-1311.
- (33) Fog, A.; Buck, R. P. Sensors and Actuators 1984, 5, 137-146.
- (34) Morimoto, K.; Suzuki, H. Biosensors & Bioelectronics 2006, 22, 86-93.
- (35) Graham, T. Proceedings of the Royal Society 1869, 212-220.

- 143 -

- (36) Fernandez, M. B.; Tonetto, G. M.; Crapiste, G. H.; Ferreira, M. L.; Damiani, D.
  E. Journal of Molecular Catalysis a-Chemical 2005, 237, 67-79.
- (37) Korin, E.; Soifer, L.; Mogilyanski, D.; Bettelheim, A. Electrochemical and Solid-State Letters 2004, 7, A484-A487.
- (38) Lewis, F. A. Advances in Hydrogen Energy 1979, 1, 279-290.
- (39) Lewis, F. A. International Journal of Hydrogen Energy 1996, 21, 461-464.
- (40) Flanagan, T. B.; Oates, W. A. Annual Review of Materials Science 1991, 21, 269-304.
- (41) Barton, J. C.; Lewis, F. A. Talanta 1963, 10, 237-246.
- (42) Grden, M.; Kotowski, J.; Czerwinski, A. Journal of Solid State Electrochemistry 1999, 3, 348-351.
- (43) Grden, M.; Kotowski, J.; Czerwinski, A. Journal of Solid State Electrochemistry 2000, 4, 273-278.
- (44) Lukaszewski, M.; Czerwinski, A. Journal of Electroanalytical Chemistry 2006, 589, 87-95.
- (45) Grasjo, L.; Seo, M. Journal of Electroanalytical Chemistry 1990, 296, 233-239.
- (46) Gabrielli, C.; Grand, P. P.; Lasia, A.; Perrot, H. *Electrochimica Acta* 2002, 47, 2199-2207.
- (47) Rose, A.; Maniguet, S.; Mathew, R. J.; Slater, C.; Yao, J.; Russell, A. E.
   *Physical Chemistry Chemical Physics* 2003, 5, 3220-3225.
- (48) Zhang, W. S.; Zhang, Z. F.; Zhang, Z. L. Journal of Electroanalytical Chemistry 2002, 528, 1-17.
- (49) Barton, J. C.; Lewis, F. A.; Woodward, M. I. Transactions of the Faraday Society 1963, 59, 1201-1207.
- (50) Bard, A. J.; Faulkner, L. R. *Electrochemical methods : fundamentals and applications*, 2nd Edition ed.; New York : John Wiley, 2001.
- (51) Lewis, F. A. Zeitschrift Fur Physikalische Chemie Neue Folge 1985, 146, 171-185.
- (52) Hill, G. J.; Ives, D. J. G. In *Reference Electrodes*; Ives, D. J. G., Janz, G. J., Eds.; Academic Press Inc.: London, 1961, pp 71-126.
- (53) Imokawa, T. PhD, Southampton, 2003.

- (54) Lewis, F. The palladium hydrogen system; Academic Press: London, 1967.
- (55) Aben, P. C.; Burgers, W. G. Trans. Faraday Soc. 1962, 58, 1989-1992.
- (56) Zhang, W. S.; Zhang, X. W.; Li, H. Q. Journal of Electroanalytical Chemistry 1997, 434, 31-36.
- (57) Mengoli, G.; Bernardini, M.; Fabrizio, M.; Manduchi, C.; Zannoni, G. Journal of Electroanalytical Chemistry **1996**, 403, 143-151.
- (58) Lim, C.; Pyun, S. I. *Electrochimica Acta* **1994**, *39*, 363-373.
- (59) Baldauf, M.; Kolb, D. M. Electrochimica Acta 1993, 38, 2145-2153.
- (60) Tateishi, N.; Yahikozawa, K.; Nishimura, K.; Takasu, Y. *Electrochimica Acta* **1992**, *37*, 2427-2432.
- (61) Szpak, S.; Mosierboss, P. A.; Gabriel, C. J.; Smith, J. J. Journal of Electroanalytical Chemistry 1994, 365, 275-281.
- (62) Czerwinski, A.; Kiersztyn, I.; Grden, M. Journal of Solid State Electrochemistry 2003, 7, 321-326.
- (63) Conway, B. E.; Jerkiewicz, G. Journal of Electroanalytical Chemistry 1993, 357, 47-66.
- (64) Czerwinski, A.; Kiersztyn, I.; Grden, M.; Czapla, J. Journal of Electroanalytical Chemistry 1999, 471, 190-195.
- (65) Czerwinski, A.; Kiersztyn, I.; Grden, M. Journal of Electroanalytical Chemistry **2000**, 492, 128-136.
- (66) Lukaszewski, M.; Kusmierczyk, K.; Kotowski, J.; Siwek, H.; Czerwinski, A. Journal of Solid State Electrochemistry 2003, 7, 69-76.
- (67) Vasile, M. J.; Enke, C. G. Journal of the Electrochemical Society 1965, 112, 865-870.
- (68) Tseung, A. C. C.; Kelly, J. F. D.; Goffe, R. A.; (UK). Application: GBGB, 1982, pp 9 pp.
- (69) Macdonald, D. D.; Wentreek, P. R.; Scott, A. C. Journal of the Electrochemical Society 1980, 127, 1745-1751.
- (70) Dobson, J. V.; Brims, G. Electrochimica Acta 1987, 32, 149-153.
- Kihara, S.; Yoshida, Z.; Matsui, M. Bulletin of the Institute for Chemical Research, Kyoto University 1986, 64, 207-217.

- (72) Nelson, P. A.; Owen, J. R. Journal of the Electrochemical Society 2003, 150, A1313-A1317.
- (73) Attard, G. S.; Bartlett, P. N.; Coleman, N. R. B.; Elliott, J. M.; Owen, J. R.;
   Wang, J. H. Science 1997, 278, 838-840.
- (74) Guérin, S. PhD, University of Southampton, 1999.
- (75) Bartlett, P. N.; Gollas, B.; Guerin, S.; Marwan, J. *Physical Chemistry Chemical Physics* **2002**, *4*, 3835-3842.
- (76) Elliott, J. M.; Birkin, P. R.; Bartlett, P. N.; Attard, G. S. *Langmuir* **1999**, *15*, 7411-7415.
- Evans, S. A. G.; Elliott, J. M.; Andrews, L. M.; Bartlett, P. N.; Doyle, P. J.;
   Denuault, G. Analytical Chemistry 2002, 74, 1322-1326.
- (78) Birkin, P. R.; Elliott, J. M.; Watson, Y. E. Chemical Communications 2000, 1693-1694.
- (79) Denuault, G.; Milhano, C.; Pletcher, D. Physical Chemistry Chemical Physics 2005, 7, 3545-3551.
- (80) Elliott, J. M.; Cabuche, L. M.; Bartlett, P. N. Analytical Chemistry 2001, 73, 2855-2861.
- (81) Li, X. H.; Nandhakumar, I. S.; Gabriel, T.; Attard, G. S.; Markham, M. L.; Smith, D. C.; Baumberg, J. J.; Govender, K.; O'Brien, P.; Smyth-Boyle, D. Journal of Materials Chemistry 2006, 16, 3207-3214.
- (82) Bartlett, P. N.; Birkin, P. N.; Ghanem, M. A.; de Groot, P.; Sawicki, M. Journal of the Electrochemical Society 2001, 148, C119-C123.
- (83) Evans, S. A. G.; Brakha, K.; Billon, M.; Mailley, P.; Denuault, G.
   *Electrochemistry Communications* 2005, 7, 135-140.
- (84) Bard, A. J.; Fan, F. R. F.; Kwak, J.; Lev, O. Analytical Chemistry 1989, 61, 132-138.
- (85) Engstrom, R. C.; Strasser, V. A. Analytical Chemistry 1984, 56, 136-141.
- (86) Engstrom, R. C.; Weber, M.; Werth, J. Analytical Chemistry 1985, 57, 933-936.
- (87) Engstrom, R. C.; Weber, M.; Wunder, D. J.; Burgess, R.; Winquist, S. Analytical Chemistry 1986, 58, 844-848.

- 146 -

- (88) Engstrom, R. C.; Meaney, T.; Tople, R.; Wightman, R. M. Analytical Chemistry 1987, 59, 2005-2010.
- (89) Liu, H. Y.; Fan, F. R. F.; Lin, C. W.; Bard, A. J. Journal of the American Chemical Society **1986**, 108, 3838-3839.
- (90) Kwak, J.; Bard, A. J. Analytical Chemistry 1989, 61, 1794-1799.
- (91) Kwak, J.; Bard, A. J. Analytical Chemistry 1989, 61, 1221-1227.
- (92) Denuault, G. Electrochemistry Newsletter 1995, 82, 10-21.
- (93) Horrocks, B. R.; Schmidtke, D.; Heller, A.; Bard, A. J. Analytical Chemistry **1993**, 65, 3605-3614.
- (94) Shao, Y. H.; Mirkin, M. V.; Fish, G.; Kokotov, S.; Palanker, D.; Lewis, A. Analytical Chemistry 1997, 69, 1627-1634.
- (95) Yang, Y. F.; Denuault, G. Journal of Electroanalytical Chemistry 1998, 443, 273-282.
- (96) Yang, Y. F.; Denuault, G. Journal of the Chemical Society-Faraday Transactions 1996, 92, 3791-3798.
- (97) Yang, Y. F.; Denuault, G. Journal of Electroanalytical Chemistry 1996, 418, 99-107.
- (98) Klusmann, E.; Schultze, J. W. *Electrochimica Acta* 1997, 42, 3123-3134.
- (99) Paik, C. H.; White, H. S.; Alkire, R. C. Journal of the Electrochemical Society **2000**, 147, 4120-4124.
- (100) Hess, C.; Borgwarth, K.; Ricken, C.; Ebling, D. G.; Heinze, J. *Electrochimica Acta* **1997**, *42*, 3065-3073.
- (101) Ammann, E.; Mandler, D. Journal of the Electrochemical Society 2001, 148, C533-C539.
- (102) Tel-Vered, R.; Bard, A. J. Journal of Physical Chemistry B 2006, 110, 25279-25287.
- (103) Mandler, D.; Bard, A. J. Journal of the Electrochemical Society **1990**, 137, 1079-1086.
- (104) Shohat, I.; Mandler, D. Journal of the Electrochemical Society 1994, 141, 995-999.

- (105) Nowall, W. B.; Wipf, D. O.; Kuhr, W. G. Analytical Chemistry 1998, 70, 2601-2606.
- (106) Shiku, H.; Uchida, I.; Matsue, T. Langmuir 1997, 13, 7239-7244.
- (107) Shiku, H.; Takeda, T.; Yamada, H.; Matsue, T.; Uchida, I. Analytical Chemistry **1995**, 67, 312-317.
- (108) Turyan, I.; Krasovec, U. O.; Orel, B.; Saraidorov, T.; Reisfeld, R.; Mandler, D. Advanced Materials 2000, 12, 330.
- (109) Barker, A. L.; Gonsalves, M.; Macpherson, J. V.; Slevin, C. J.; Unwin, P. R. Analytica Chimica Acta 1999, 385, 223-240.
- (110) Mirkin, M. V.; Horrocks, B. R. Analytica Chimica Acta 2000, 406, 119-146.
- (111) Fleischmann, M., Pons, S., Rolison, D.R., Schmidt, P. P. Ultramicroelectrodes, 1 ed.; Scientific Publishing Division, 1987.
- (112) Zoski, C. G. Electroanalysis 2002, 14, 1041-1051.
- (113) Denuault, G. Chemistry & Industry 1996, 678-680.
- (114) Horrocks, B. R.; Mirkin, M. V.; Pierce, D. T.; Bard, A. J.; Nagy, G.; Toth, K. Analytical Chemistry **1993**, 65, 1213-1224.
- (115) Evans, N. J.; Gonsalves, M.; Gray, N. J.; Barker, A. L.; Macpherson, J. V.;
   Unwin, P. R. *Electrochemistry Communications* 2000, 2, 201-206.
- (116) Wei, C.; Bard, A. J.; Kapui, I.; Nagy, G.; Toth, K. Analytical Chemistry 1996, 68, 2651-2655.
- (117) Wei, C.; Bard, A. J.; Nagy, G.; Toth, K. Analytical Chemistry 1995, 67, 1346-1356.
- (118) Denuault, G.; Frank, M. H. T.; Peter, L. M. Faraday Discussions 1992, 23-35.
- (119) Zhu, Y. Y.; Williams, D. E. Journal of the Electrochemical Society 1997, 144, L43-L45.
- (120) Volker, E.; Inchauspe, C. G.; Calvo, E. J. Electrochemistry Communications 2006, 8, 179-183.
- (121) Souto, R. M.; Gonalez-Garcia, Y.; Gonzalez, S. Corrosion Science 2005, 47, 3312-3323.
- (122) Lister, T. E.; Pinhero, P. J. Analytical Chemistry 2005, 77, 2601-2607.

- 148 -

- (123) Souto, R. M.; Gonzalez-Garcia, Y.; Gonzalez, S.; Burstein, G. T. Corrosion Science 2004, 46, 2621-2628.
- (124) Bastos, A. C.; Simoes, A. M.; Gonzalez, S.; Gonzalez-Garcia, Y.; Souto, R. M. Electrochemistry Communications 2004, 6, 1212-1215.
- (125) Casillas, N.; Charlebois, S. J.; Smyrl, W. H.; White, H. S. Journal of the Electrochemical Society 1993, 140, L142-L145.
- (126) Casillas, N.; Charlebois, S.; Smyrl, W. H.; White, H. S. Journal of the Electrochemical Society **1994**, 141, 636-642.
- (127) Spaine, T. W.; Baur, J. E. Analytical Chemistry 2001, 73, 930-938.
- (128) Tan, Z.; Yang, Y.; Jiang, F.; Shao, H. Electrochimica Acta 2006, 52, 68-74.
- (129) Bartlett, P. N. In *Biosensors: A Practical Approach*; Cass, A. E. G., Ed.; Oxford University Press: Oxford, 1990, pp 47.
- (130) Guérin, S. PhD, Southampton, 1999.
- (131) Rand, D. A. J.; Woods, R. Journal of Electroanalytical Chemistry and Interfacial Electrochemistry 1972, 35, 209-218.
- (132) Pyo, M.; Bard, A. J. Electrochimica Acta 1997, 42, 3077-3083.
- (133) Imokawa, T.; Williams, K. J.; Denuault, G. Analytical Chemistry 2006, 78, 265-271.
- (134) Zimmerman, J. B.; Wightman, R. M. Analytical Chemistry 1991, 63, 24-28.
- (135) Jo, G. B.; Won, M. S.; Shim, Y. B. Electroanalysis 1999, 11, 885-890.
- (136) Millet, P.; Srour, M.; Faure, R.; Durand, R. Electrochemistry Communications
   2001, 3, 478-482.
- (137) Zhang, W. S.; Zhang, X. W.; Zhao, X. G. Journal of Electroanalytical Chemistry 1998, 458, 107-112.
- (138) Ash, R.; Barrer, R. M. Physics and Chemistry of Solids 1960, 16, 246-252.
- (139) Albery, W. J.; Calvo, E. J. Journal of the Chemical Society-Faraday Transactions I 1983, 79, 2583-2596.