Cathodic precipitation of ceramic precursor materials

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Cathodic Precipitation of Ceramic Precursor Materials

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A Doctoral Thesis Submitted in Partial Fulfilment of the Requirements for the Award of Doctor of Philosophy at Loughborough University

To My Mum and Dad for Their Love and Support
Abstract

An electrochemical technique has been developed for the production of precursors to ceramic films on hydrogen sorbing metal substrates. It involves the electrolysis of aqueous metal salt solutions which yields hydrogen at the cathode, resulting in local generation of base (hydroxide ions) around this electrode. Such conditions promote the precipitation of metallic hydroxides from a suitable electrolyte. If the local alkaline environment is not disrupted by convective or other forces, then a solid phase accumulates near the cathode, and forms an adherent gel-like structure on its surface. In order to maintain deposition, it is essential that gaseous hydrogen evolution is minimised, and preferably eliminated. This can be achieved by use of a hydrogen sorbing cathode material, such as palladium. The electrode, and adherent film (or, in appropriate circumstances, the deposit alone) can then undergo a subsequent calcination treatment to yield the ceramic layer. It is possible to generate both porous and compact structures by this method, depending on the potential programme employed during deposition.

Research has been conducted into the understanding of mechanisms involved in porosity control of films deposited during different potential regimes, with view to establishing routes to layers of predetermined physical structure. In-situ optical methods were employed to complement the electrochemical techniques, providing valuable insight into the initial mechanisms of film formation and the subsequent thickening processes.

The utility of the precipitation process was illustrated by the fabrication of films which demonstrated a variable conductivity over a range of humidities appropriate to sensing application.
Investigation into the use of a bipolar palladium electrode as an aid to generating thick film deposits was carried out. The device comprised a palladium plate, operated as a bipolar electrode in aqueous electrolyte. Under suitable conditions, the negative face of this electrode can be made to generate and absorb hydrogen, whilst simultaneously, the positive face oxidises hydrogen transported across the bipolar substrate by diffusion. Thus the cathode face is a non-gassing electrode on which thick deposits of metal hydroxide can be grown.

This line of research lead to the realisation of a self-feeding hydrogen anode at the electrode's positive face. Further research was undertaken to assess the electrochemical properties of this anode. The effective operating window for hydrogen oxidation was investigated, and the effect of prolonged potential cycling, elevated temperature and bipolar plate thickness on this region was also considered.
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What's done we partly may compute,
But know not what's resisted.

Robert Burns (1759 - 1796)
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Chapter 1

Introduction
Chapter 1 : Introduction

Ceramic /si' ræmik, ki- /adj. & n. • adj 1 made of (esp) clay and permanently hardened by heat (a ceramic bowl). 2 of or relating to ceramics (the ceramic art). • n. 1 a ceramic article or product. 2 a substance, esp. clay, used to make ceramic articles [Gk keramikos f. keramos pottery][1]

1.1 : The Importance of Ceramics

As early as 6000 BC ancient civilisations of the Near East (the area around Syria and Asia Minor) discovered that clay, dug from the soil, could be fired to give a hardwearing brittle material; and thus, man-made ceramics were born [2,3]. Since then, ceramics in one form or other have played a key role in the everyday lives of most civilised communities. The peoples of ancient Greece (from where the word ceramic originates - keramos, meaning potter's earth), Egypt and China (to name but a few) used clay-based ceramics to fabricate domestic implements for use in cooking, food storage and a vast array of ornamentation. Many pieces still survive to this day - priceless artefacts which in some cases give us the only insight we have into the type of lives lead by the civilisations who created them.

More recently, ceramics have been employed for architectural applications. Ceramic bricks, cements and concretes were (and still are) used as the premier choice of building material by most modern communities. The materials used are usually referred to as traditional ceramics; having naturally occurring sources. This group, which also comprises glass and refractories, offers an often more resilient and cost-effective alternative to other natural resources such as metals and timber.
A new class of high purity/high performance ceramic has become increasingly more important in the latter part of this century. Termed advanced ceramics [4,5] these materials, often high purity oxides with tailored morphology and stoichiometry, are employed in numerous areas of engineering, industry, electronics and medicine. Examples of their use include coatings for heat and corrosion protection [6,7], electronics devices such as resistors and semiconductors, gas and humidity sensors [8], and shaped, high temperature bodies (including engine components) which replace traditional metals where greater resistance to corrosion, temperature and stress from a lighter component is required. Their ability to be mixed with microfibres (of for example glass or carbon) to increase their inherent strength and reduce the likelihood of stress fractures [9,10], and the possibility of inclusion of lubricating materials [11,12] within their porous structures, thereby creating self-lubricating surfaces, means they are increasingly employed as better alternatives to more conventional materials. The strength, machineability and biocompatibility of certain ceramics has also made them suitable materials for repair or replacement of diseased or damaged human body parts. Termed bioceramics [13-15], this class of materials presently includes a number of single crystal and polycrystalline ceramics, glasses, glass ceramics and composites. Specifically, high density/high purity alumina is used in artificial hip joints and knee prostheses, jaw bone reconstruction, segmental bone replacements, middle ear bone substituents, corneal replacements and dental implants. Various glass ceramics have proved useful in facilitating the bonding of prostheses and implants to both bone and tissue. Calcium phosphate based ceramics (in particular hydroxyapatite) have been used in a number of surgical implants where high stress loadings are not expected; these include replacement of middle ear and dental components and coatings on metal implants which aid acceptance of the artificial body part by the surrounding organic tissue. Porous calcium phosphates have also been employed in aiding bone rejuvenation, where bone is able to grow into the ceramic's
pores, allowing segmental replacement or strengthening of damaged bone via bridging with the ceramic material. These bioceramics often provide their recipients with extended relief from otherwise debilitation medical conditions.

The success enjoyed in the scientific community by ceramics in recent years is evident in the ever increasing number of journals, publications and conferences devoted solely to this group of materials. However, the discovery of high temperature superconductivity in Ba-La-Cu oxide ceramics in 1986 by Bednorz and Müller [16,17] making the possibility of transmitting electricity with zero power loss an achievable goal, has brought the exciting new prospects of ceramic technology to the general public. There is still enormous scope for improvement in the performance of present ceramic devices, and new applications will be found which will enhance the already substantial mark these materials have made on our lives. By all accounts ceramics are here to stay.

1.2 : Conventional Routes to Oxide-based Advanced Ceramic Materials

There are, in general, three conventional routes to the generation of ceramic materials where controlled purity and/or morphology is of particular importance [18]. The method of choice for a given situation will depend on the degree of purity and homogeneity required of the ceramic product. Each fabrication process may be tailored to some extent to suit the needs of the user. However, as yet, there is no definitive process which satisfies all requirements.
1.2.1: Precipitation from Solution

This technique is particularly suited to the generation of single component ceramic powders from impure raw materials. In the case of alumina, the mineral bauxite is dissolved under pressure in sodium hydroxide which separates impurities such as TiO$_2$, SiO$_2$ and Fe$_2$O$_3$ from the resulting sodium aluminate solution. Autoprecipitation may then occur on neutralisation with CO$_2$ to give bayerite ($\beta$-Al$_2$O$_3$.3H$_2$O) or alternatively, seeding with gibbsite crystals ($\alpha$-Al$_2$O$_3$.3H$_2$O) may be preferred. The process is commonly known as the Bayer process [19]. The alumina particle size during crystallisation will depend to varying extents on the temperature, alumina supersaturation and the amount of seed. However, the product, invariably an agglomeration of particles, will require further processing (grinding or milling) in order to attain the desired particle size, or to prepare a powder that will sinter to a density close to the material's theoretical value. The very nature of this processing unfortunately introduces impurities into the product.

Further problems arise where mixed component powders are required. Coprecipitation from a multi-component solution rarely results in the generation of a homogeneous material since the individual species will precipitate out at different pH. The mechanical and electrical properties of the ceramic will be adversely affected by poor homogeneity. Hence, careful pH control is essential.

1.2.2: Powder Mixing

A more successful route to multi-component powders involves physical mixing of the starting materials. The individual oxides (or carbonates) are firstly blended together, to form a homogeneous mixture, prior to grinding or milling. The powder mixture is
then pressed (if required) and calcined (heated in an oxygen-rich atmosphere) to give the ceramic product. Pure starting materials are a necessity since, unlike the precipitation process, no substrate cleanup is carried out here. Unfortunately, the grinding/milling again results in the introduction of unwanted species.

Other problems include environmental hazards associated with powder handling, the sometimes insufficient mixing of components associated with ball-milling and the loss of volatile oxides at the high temperatures needed to sinter the components into a single mixed oxide. Hence, reproducibility is often lost, making powder mixing techniques an unsatisfactory route to some high performance devices including many electroceramics.

1.2.3: Fusion Techniques

Here, the reactants are first mixed as powders and then melted together. Nucleating agents are then added and the temperature adjusted until crystallisation occurs. The process is limited by the melting points of the reactants and, as with powder mixing, care must be taken with the more volatile oxides. Fusion techniques are employed, among other things, in the fabrication of window glass, glass ceramics [20] and abrasives.

1.3: Controlling Macro and Micro Morphology

There are a number of techniques commonly used in conjunction with powder mixing which allow a certain amount of control over parameters such as the macroscopic geometry, density, porosity and grain size of the resulting material. They provide a means of tailoring the mechanical, optical and electrical properties of ceramics,
although they offer little scope for purity enhancement. Of the techniques available, the following are of particular use in the fabrication of advanced materials:

**Solid-state Sintering**: involves the binding together of ceramic particles at elevated temperature by virtue of their strive towards reduced surface free energy by surface area loss. Generally, little densification occurs, since the particles bond at the point of contact where evaporation and condensation of the material is the only aid to pore size reduction.

**Uniaxial Pressing**: employs a steel die which is filled with dry powder (or powder containing several weight percent water). This is then pressed, allowing Van der Waals forces to aggregate the powder into a coherent compact. Organic binders and lubricants are often included to maintain structural integrity and aid homogeneous mixing of the reactants prior to firing. Upon firing the organics are removed by decomposition to gaseous products. The process is a valuable technique for the manufacture of simple ceramic bodies such as discs and rings.

**Hot Uniaxial Pressing (Hot Pressing)**: as its name suggests involves the use of elevated temperature during pressing. Powders are placed in a graphite (refractory) die and heated in an inert atmosphere after compaction. The resulting materials are of higher density and smaller grain size than those produced by uniaxial pressing alone. The reason being, that the applied pressure sets up stresses at the point of contact between particles and this increases the driving force for sintering, whilst the elevated temperature aids the evaporation/condensation process at these contact points. Hence, a very small particle size is not necessary in order to generate ceramics of acceptable density. In order to help attain theoretical density, low melting point oxides are often added to the powder mixture prior to pressing. These aid sintering by the formation of
a liquid phase between particles which promotes local dissolution-recrystallisation processes thereby bonding the particles together at lower temperatures. In addition, pore size reduction occurs by means of capillary action. Unfortunately, the introduction of additives means that the finished ceramic will have impurities at its grain boundaries, which will decrease its physical strength and introduce unwanted electrical or optical properties.

Hot pressing is particularly suited to the fabrication of plates, blocks and other simple shaped bodies.

**Cold and Hot Isostatic Pressing (HIPing):** both employ the use of a compression mould operated by the application of liquid to a surrounding pressure vessel. The powder placed in the mould can be pressed to give a ceramic of uniform density (after firing) conforming to the geometric shape of the mould. Initial application was seen in the cladding of nuclear fuel elements [21].

**Slip Casting:** involves the use of sub-micron particle suspensions of ceramics in liquid (usually water) - commonly referred to as slips. The slip is first poured into a porous mould (generally plaster of Paris) wherein the liquid is absorbed and the solid deposits on the wall of the mould. On draining the excess liquid, the ceramic precursor body is then removed and fired. The technique has found particular application in the manufacture of tableware and other domestic implements, in addition to ceramic tubes, crucibles and various housings for electronic devices. Care needs to be taken to ensure that the particles remain in suspension to allow even deposition at the mould walls to occur, and the slip viscosity must be low to prevent air bubble entrapment in the resulting body, whilst high particle loadings (>70% by weight) are preferred in order to aid the drainage process. To this end, deflocculating
agents (surfactants) are introduced into the slips and factors such as pH, ionic strength and particle size need to be addressed.

**Injection Moulding:** has the ceramic powder as a filler in an organic polymer matrix. The resulting plastic material is then injected under elevated temperature and pressure into the mould, where the thermoplastic polymer sets, yielding a ceramic composite body. The design complexity of the resulting body has few restrictions. However, the polymer is difficult to remove, and attempts to do this often result in the generation of cracks and voids in the ceramic product.

**Extrusion:** involves a similar set of materials to injection moulding, however, it is applied to the fabrication of open-ended structures. Of particular note is its recent application in the manufacture of complex honeycomb catalyst supports for automobile catalytic converters.

1.4: Alternative Synthetic Routes

Where purity and homogeneity are paramount to the successful operation of a ceramic device, conventional fabrication techniques are often replaced by newer synthetic routes. An increasing number of such routes have been developed and tailored to the specific requirements of a vast array of advanced ceramic materials. Several key processes are outlined below.

1.4.1: Sol-gel Processes

At present, sol-gel technology provides perhaps the most versatile non-conventional route to ceramic materials [18]. Generally speaking, where ceramic fabrication is
concerned, there are two distinct groups of material to which the term sol is applied: liquids containing colloidally dispersed oxide (colloids being defined as having a dispersed phase with at least one dimension - here the particle diameter - between 1 nm and 1 μm in the dispersion medium) and those employing metal-organic compounds (e.g. alcoxides) as the dispersed phase.

In the former case, the colloidal oxide sol (containing various stabilising additives such as surfactants) is destabilised by the addition of excess water, whereupon the colloidal particles begin to form a network of loosely bound particulate aggregates with interstitial liquid. The resulting gelatinous material is referred to as the sol-gel. Rapid destabilisation generates sol-gels for use in the production of ceramic powders, whereas a more controlled rate, employing the slow uptake of atmospheric moisture by the sol, has proved a suitable route to fibres, monoliths and coatings. In order to obtain the ceramic end product, the liquid phase must first be removed, causing the gel to shrink and form a porous solid known as a xerogel.

Rapid removal at elevated temperature will result in the manufacture of fine particulates. Predetermination of particle size can be achieved by employing a gravity drop method involving two immiscible liquids. Here, the sol (liquid 1) is added dropwise to the top of a tower of solvent (liquid 2) into the bottom of which the hot solvent is pumped. As the sol falls, it meets the rising hot solvent which rapidly gels the sol droplets into spherical solid particles. Control over particle size is achieved by varying the dimensions of the sol inlet tube (which controls the droplet diameter) and the solvent type, density and temperature, in addition to its upward velocity.

Where monoliths and other complex structures are the desired product, the viscous gel (formed on slow destabilisation of the sol) may first be moulded, following which
a careful heating programme will be carried out in order to ensure that even shrinkage occurs and cracking is avoided. It is also essential that volatile organics are removed before the final firing stage, otherwise bubbles may be formed within the body of the device. In the case of powders and other structures, the final firing stage marks the conversion of the dry gel to the finished ceramic.

Where alcooxide sols are employed the processing stages are essentially the same as with colloidally dispersed oxide sols, with one fundamental difference. The initial sol is destabilised, on addition of water, by the hydrolysis and polycondensation of the alcoxides to give a polymeric gel known as an alcogel. Reactions occurring can be simplified as follows:

\[
\begin{align*}
\text{RO - M - OR} + \text{H}_2\text{O} & \rightarrow \text{ROH} + \text{RO - M - OH} \\
\text{RO - M - OH} + \text{RO - M - OR} & \rightarrow \text{ROH} + \text{RO - M - O - M - OR}
\end{align*}
\]

where \(-\text{M} - \text{OR}\) is an alcooxide with metal \(\text{M}\) and organic functional group \(\text{R}\).
It is possible to use sol-gel techniques to manufacture a vast array of precisely sized powders, fibres and contoured ceramic bodies. The very nature of the highly dispersed materials comprising the sols makes them excellent starting materials for ceramics with near total homogeneity and pre-defined physical properties. However, the obvious drawback is the cost of the high purity chemicals required to form the sols and dispersing solutions.

1.4.2: Hydrothermal Methods

Particularly suited to the manufacture of ceramic powders, hydrothermal techniques involve heating reactants such as metal salts, oxides and hydroxides in water (although other liquids have also been employed) at temperatures and pressures up to around 573 K and 100 MPa [18]. This can result in the generation of sub-micron ceramic particulates of controlled size and shape.

In the case of precipitation from aqueous solutions of metal salts, controlled addition of hydroxyl species may be carried out in order to give homogeneous nucleation of the insoluble metal hydroxide (ceramic precursor):

\[ M^{2+}(aq) + z\text{OH}^-(aq) \rightleftharpoons M(OH)_z(s) \]

Alternatively, forced hydrolysis at elevated temperature may be the preferred route to homogeneous nucleation. Here, hydrolysis leads to the deprotonation of bound water molecules, generating hydroxide ligands:

\[ [M(H_2O)_x]^{2+} \rightleftharpoons [M(H_2O)_{x-y}(OH)_{y}]^{(2-y)+} + yH^+ \]
Hydrolysis of all attached water molecules results in the nucleation of insoluble metal hydroxide species, giving rise to the generation of a ceramic precursor sol.

An alternative method of generating hydroxide ceramic precursors is to introduce chelated metal ions into a solution of sodium hydroxide and reducing agent at elevated temperature. On reduction, the metal ion is released into the high pH solution environment where it precipitates out as the corresponding metal hydroxide. This route also leads to the formation of hydroxide sols.

In both cases, the particle size and morphology of the resulting precursor (and therefore the ceramic) may be controlled by variation of temperature, pressure and solution concentration. Where hydrolysis of metal salts is concerned, the choice of anion will also allow morphological control: employing anions (e.g. sulphate and phosphate) which promote polymerisation through co-ordination with polynuclear species may result in the generation of amorphous precipitates, whereas simpler anions not affecting polymerisation, will lead to crystalline products. When using chelated metal ions as starting materials, choice of chelating and reducing agents may also affect changes in crystal morphology.

Both routes offer the prospect of manufacturing single and homogeneous mixed oxide powders from relatively cheap starting materials.

1.4.3: The Citrate Gel Process

Developed by Marcilly et al. [22], this method is particularly useful for the manufacture of high surface area ceramics. In the case of stabilised zirconias, citric acid is mixed with zirconyl and (for example) Gd(III) nitrates in solution (ca 2:1 mole
ratio acid/metal) the pH of which was previously increased to between 6 and 7.5 with \( \text{NH}_3\text{OH} \) in order to form an organometallic complex. A viscous mixture results when rapid partial dehydration occurs. The resulting material may be dried (ca. 373 K) to give an amorphous gel. On further heating, this ceramic precursor swells because of decomposition of \( \text{NH}_4\text{NO}_3 \), following which the metallo-organic complex decomposes exothermically. On calcination at 923K a high surface area (ca. 58 m\(^2\) g\(^{-1}\)) "tissue-like" stabilised zirconia is formed. The process is of significant use where porous, high surface area mixed oxides with excellent homogeneity are required.

1.4.4: Freeze-Drying

The drying of hydroxide or oxide slurries prior to firing may lead to the formation of large agglomerations of particles of the ceramic precursor. When manufacturing powders, these clusters must first be broken up and sieved before pressing in order to reduce the occurrence of large voids in the resulting ceramic. A more effective method of generating fine particulates for powder pressing is that of spray-drying. Here, the liquid slurry is atomised into an air stream where the water contained in the slurry droplets rapidly evaporates leaving behind spherical particulates. The hardness of these spheres may, however, lead to the formation of voids during pressing.

Freeze-drying offers a yet more successful route. In this case the liquid is converted to a solid phase by rapid cooling in liquid nitrogen. The solvent may then be sublimed from solid by heating under reduced pressure. This method is capable of generating soft agglomerates which can easily be broken down to give powders that sinter without void formation. Freeze-drying of mixed salts solutions is a method of retaining the solution homogeneity in the freeze-dried salt. This may then be thermally decomposed to give homogeneous mixed oxide particulates.
1.4.5: Vapour Deposition

The process of forming ceramics from the vapour phase [4] is particularly suited to the application of ceramic coatings to particulates and fibres. The process offers the ability to generate deposits of theoretical density with controlled grain-growth and orientation, as well as good adherence and throwing power. It involves the condensation, from the vapour phase, of a compound or compounds, onto the substrate, whereby the condensate forms an adhesive coating. Techniques are classed as physical (PVD) or chemical (CVD) depending, respectively, on whether simple evaporation/deposition alone occurs or chemical reaction between substrate and condensing vapour takes place to yield the deposited coating. Vapour deposition is commercially applied in the generation of coatings containing metals, borides, carbides, silicides and a selection of oxides including \( \text{Al}_2\text{O}_3 \), \( \text{SiO} \) and \( \text{SiO}_2 \).

This versatile process is capable of generating coatings with thickness from as little as 0.1 \( \mu \text{m} \) up to several centimetres for protection of substrates from wear, oxidation or corrosion or to enhance various physical, optical or electronic properties such as tensile strength, surface reflectance and conductivity respectively. However, disadvantages include the use of high temperatures which limit the choice of substrate and can lead to its unwanted physical or chemical modification.

1.4.6: Electrochemical Routes

In addition to the physical and chemical techniques described above for the generation of ceramic bodies, wet electrochemical methods have also proved successful. Though not strictly employed in the generation of ceramics, a method for the electrochemical fabrication of nickel hydroxide electrodes for nickel-based batteries was reported by
Pickett [23] in 1974. Now known as the Air Force process, his method employed sintered nickel plates, immersed in an ethanol-water solution of nickel nitrate at near boiling point temperatures. The plates were cathodized at a constant current density (ca. 50 mA cm\(^{-2}\)) for around 100 minutes. The current density chosen was sufficient to cause electrochemical decomposition of the supporting electrolyte, thereby liberating hydroxide ions:

\[2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^-\]

or by reduction of the nitrate ion, yielding a range of products in addition to hydroxide ions, for example:

\[\text{H}_2\text{O} + \text{NO}_3^- + 2e^- \rightarrow \text{NO}_2^- + 2\text{OH}^-\]

or

\[7\text{H}_2\text{O} + \text{NO}_3^- + 8e^- \rightarrow \text{NH}_4^+ + 10\text{OH}^-\]

On diffusion away from the electrode, the hydroxide ions react with nickel ions in the electrolyte, thereby precipitation of nickel hydroxide occurs within the pores of the nickel plate:

\[\text{Ni}^{2+} + 2\text{OH}^- \rightarrow \text{Ni(OH)}_2\]

Later research by Pickett and Maloy [24] outlined further scope for the Air Force method in the coprecipitation of cobalt and nickel hydroxides from a mixed nitrate electrolyte. They also postulated that potentiostatic control of the deposition process
would allow a certain amount of control over the extent of hydration of the resulting material. Green hydrated nickel hydroxide was observed when high current densities (high cathodic potentials) were used. This occurred since the growing deposit was generated at greater distances from the electrode surface, allowing hydroxide precipitation in a water-rich environment. Less hydrated Ni(OH)₂ was formed at lower current densities (lower cathodic potentials) since growth was restricted to the area close to the ion-rich diffusion layer at the nickel surface. Thus, this research hinted at a possible electrochemical route to mixed and composite materials with predetermined morphology.

In 1987, Switzer reported [25] the electrochemical generation of ceramic films and powders from aqueous metal salt solutions. In order to obtain thin films he employed a redox change method, whereby a metal, pre-plated onto an electrode surface, was anodised whilst the electrolyte pH was adjusted in order to ensure that the lower oxidation state remained stable, whilst allowing the higher oxidation state to be readily hydrolysed to the corresponding hydroxide or oxide. The resulting material formed as a thin film deposit on the anode surface.

Switzer also employed the electrochemical reduction of water, nitrate, bromate or a number of organic solvents as a means of generating base near a cathode surface. Combination of base with metal ions or complexes in solution then lead to the precipitation of metal hydroxide near the electrode surface (a method similar to the Air Force process [23]). Filtration of the precipitate from solution, followed by further treatment (calcination) of the hydroxide material made the manufacture of fine ceramic powders achievable.
Other researchers have applied various techniques of cathodic precipitation of metal hydroxides from aqueous electrolytes to the manufacture of precursors to superconducting oxides [26-29], preshaped ceramic bodies [30] and electrochromic devices [31-34].

Electrochemical methods offer a new and versatile non-conventional route to ceramic bodies, particles and coatings. Manipulation of electrolyte component concentrations, temperature and mobility, and the overall electrochemical regime should allow a degree of structural and morphological control over the resulting ceramic as yet unattained by most conventional and non-conventional routes. The low cost and ease of use of electrochemical methods should see their increased employment as more practical alternatives to the presently favoured chemical and physical routes to ceramic materials.

It is the aim of this thesis to report on a cathodic precipitation technique for the generation of films of alumina precursors at a hydrogen sorbing palladium electrode [35-37]. It will be demonstrated that control over the deposit's porosity and structural morphology may be achieved by manipulation of the deposition potential regime. Mechanisms for film compaction and pore size reduction will be proposed, and in-situ optical studies of film growth will be used in order to substantiate these mechanisms. Furthermore, application of the cathodic precipitation process to the manufacture of humidity sensing materials will be explored [38]. The response to changing atmospheric humidity of a device fabricated by this electrochemical method will be compared to that of a commercially available sensor. AC impedance techniques will be employed in order to probe the electrochemically generated sensor's conduction mechanisms at various humidity levels, and an equivalent circuit model will be proposed for the device.
Finally, it will be demonstrated that the cathodic face of a bipolar palladium plate may be employed as a non-gassing electrode for use in the manufacture of thick films of the alumina precursor. In addition, the properties of a self-feeding hydrogen anode created at the bipolar electrode’s anodic face will be investigated. Particular attention will be given to optimisation of the hydrogen oxidation performance of this electrode.
Chapter 2

Electrochemical Generation of Insoluble Hydroxide Layers
Chapter 2: Electrochemical Generation of Insoluble Hydroxide Layers

Electrolysis of aqueous metal salt solutions yields hydrogen at the cathode, resulting in the local generation of base (hydroxide ions) around this electrode. Such conditions will promote the precipitation of metallic hydroxides from a suitable electrolyte. If the local alkaline environment is not disrupted by convective or other forces, then a solid phase accumulates near the cathode, and forms a gel-like structure which will adhere to the electrode surface under appropriate conditions [30]. In order to promote such conditions, it is essential that gaseous hydrogen evolution is minimised, and preferentially eliminated. This may be achieved by use of a hydrogen sorbing cathode material, such as palladium. Gels thus formed by cathodic precipitation may, on calcination, be converted to the corresponding oxide or oxide ceramic and are therefore termed 'ceramic precursors'.

2.1: A Precursor to Alumina

For the purpose of the following experiments a two-armed, silica glass, electrochemical cell (Figure 2.1.1) was used as the reaction vessel. The working electrode consisted of a length of 2 mm diameter palladium rod (99.95%, Goodfellow) (Figure 2.1.2) set in a glass tube with quick-set epoxy resin, and silver soldered onto a copper contact wire. The exposed disc was abraded with P1200 grade silicon carbide paper to remove any epoxy resin from its surface, and then polished with 0.3 micron alumina (Buehler Alpha Micropolish Alumina) on wetted Selvyt cloth, prior to use. The counter electrode comprised a 100 mm length of 1 mm diameter platinum wire (99.95%, Johnson Matthey), coiled to give a loop of approximate diameter 30 mm, and set into the cell wall above the Luggin capillary.
All potentials were measured (and are quoted) with respect to a mercury, mercurous sulphate reference electrode \( (E^o = 0.615 \text{ V at } 25^\circ\text{C}) \) (Figure 2.1.3). Electrolyte solutions were prepared using HPLC grade water (Rathburn) and high purity (Analal grade) aluminium sulphate (BDH). Acid solutions were prepared using 98% sulphuric acid (Fisons). Voltammetric data (cyclic voltammograms) were recorded using a Schlumberger Solartron 1286 Electrochemical Interface and an Advance Bryans X-Y chart recorder. A Sycopel Scientific Electronic Integrator was used to monitor cathodic charge passed during deposition in order to ensure that different deposition programmes generated equal amounts of the ceramic precursor. A circuit diagram showing the Electronic Integrator connected to the cell circuit can be seen in Figure 2.1.4.

2.1.1 Choice of Materials

For the manufacture of precursors to alumina, aluminium sulphate solution was chosen as the electrolyte because of its high solubility \( (86.9 \text{ g in } 100 \text{ mls water at } 25^\circ\text{C}) \) and moderate pH at low concentration (very slightly acidic) allowing deposits to be generated in a stable, non-corrosive environment. From initial investigation, it was decided that an aluminium sulphate concentration of 0.01 M be used for all deposition experiments. This concentration proved sufficient to facilitate the generation of suitable hydroxide films under the chosen time constraints of polarisation.
Figure 2.1.1: Two-armed Silica Glass Electrochemical Cell

Working Electrode

Reference Electrode

Pt Counter Electrode

Sintered Glass Frit

Luggin Capillary

Side View

Gas Outlet

Gas Tap

To Potentiostat (Counter Electrode)

Luggin Capillary

21
Figure 2.1.2: 2 mm Diameter Palladium Working Electrode

- Copper Contact Wire
- Cylindrical Glass Casing
- Silver Solder
- 2 mm Diameter Palladium Rod (disk exposed)
- Quick-set Epoxy Resin
Figure 2.1.3: Mercury, Mercurous Sulphate Reference Electrode

Key:

- Mercury
- Mercurous Sulphate
- Glass Wool
- Platinum Wire with Silver Solder Contact
2.1.2: Degassing

Prior to each new deposition experiment, the palladium working electrode required degassing of hydrogen in order to ensure that its concentration and eventual outgassing did not occur during film growth, and that the electrode surface closely resembled that employed during other runs. A suitable degassing potential was chosen by firstly introducing hydrogen into the electrode substrate by cathodic polarisation in 0.01 M aluminium sulphate electrolyte (cell configuration as in Figure 2.1.1), followed by anodic polarisation under cyclic voltammetry to oxidise the absorbed hydrogen. A potential of +0.50 V (vs reference) was chosen as the degassing potential. This corresponded to the anodic current peak for electrochemical hydrogen oxidation.

Hence, all degassing was carried out, in the aluminium sulphate electrolyte (following physical removal of surface hydroxide film, and dissolution of any residual deposit in
1.0 M sulphuric acid), by polarisation of the working electrode at +0.50 V until zero current was recorded.

2.1.3: Constant Potential Deposition

Employing the cell described in Figure 2.1.1 (connected to the Electronic Integrator as shown in Figure 2.1.4) with 0.01 M aluminium sulphate as electrolyte, the palladium working electrode was polarised to -3.20 V (versus reference) for 0.37 C charge passed (a period of approximately 30 minutes). A potential of -3.20 V was chosen because, following initial nucleation of the hydroxide film, the working electrode was effectively coated with a resistive layer, which increased in thickness as polarisation continued and thereby limited the cell current. Therefore, a high cathodic potential was required to allow continued growth of the deposit throughout the polarisation period.

Following deposition, the electrode and hydrated aluminium hydroxide deposit were removed from the electrolyte, and allowed to dry in air for 2 hours. The deposit was then removed from the palladium surface, desiccated, and submitted for SEM analysis. A selection of micrographs can be seen in Plate 2.1.1. The film produced by this method proved to have little structural integrity; fragmenting significantly on removal from the working electrode surface. Plate 2.1.1(a) shows a scanning electron micrograph of three of the larger fragments from the film. They are, at most, 0.5 mm across. On closer inspection of these fragments (Plate 2.1.1(b)), it can be seen that the deposit has a fairly open, porous structure. This undoubtedly accounts for the lack of structural integrity observed.
Plate 2.1.1: Scanning Electron Micrographs of the Hydroxide Film Generated by a Unipotential Deposition Program

(a)

(b)
2.1.4: Cycled Potential Deposition

Following cleaning and degassing, the 2 mm diameter palladium working electrode was subjected to 100 (linear ramp) potential cycles (in fresh 0.01 M aluminium sulphate electrolyte), each having sweep limits of -3.20 V and +1.00 V and scan rate 100 mVs\(^{-1}\). The initial scan was in the negative direction from 0.00 V. The quantity of charge passed during the cathodic part of each cycle was summed for the 100 cycles, and recorded as being 0.37 C. Hence, the charge passed during constant potential deposition was set to this value in order to ensure equal quantities of the deposit were generated by the two methods.

On completion of cycling, the electrode and its surface film were removed from the electrolyte and allowed to dry in air for 2 hours. The deposit was then removed from the palladium surface and scanning electron micrographs were taken (see Plate 2.1.2). In contrast to constant potential deposition, cycled potential deposition appeared to generate a much more structurally sound deposit; it was removed from the palladium substrate almost intact (Plate 2.1.2(a)). Close inspection of the surface under the scanning electron microscope (Plate 2.1.2(b)) also showed the deposit to be less porous than the film produced by unipotential deposition. It is believed that an electrochemical dewatering mechanism is responsible for the characteristics of the deposit generated during cycling.
Plate 2.1.2: Scanning Electron Micrographs of the Hydroxide Film Generated by a Cycled Potential Deposition Program

(a) 

(b)
2.1.5: Electrochemical Densification and Water Exclusion

From the cyclic voltammograms recorded during deposition (Figure 2.1.5), four key electrochemical processes were identified as follows:

1. Hydrogen generation coupled with hydroxide deposition

2. Oxidation of absorbed hydrogen

3. Hydrogen oxidation coupled with oxygen evolution

4. Reduction of adsorbed oxygen

On consideration of the processes occurring throughout the 100 potential cycles, the following mechanism was proposed for the observed deposit morphology:

Hydroxide is deposited on the palladium surface during the cathodic part of the first potential cycle. The layer is hydrated and porous, containing electrolyte and water.

During the anodic part of this cycle, hydrogen (absorbed as a result of the cathodic process) is oxidised. This causes the pH at the electrode/deposit interface to decrease as protons are released back into the electrolyte. Hence partial dissolution of the deposit occurs.
Figure 2.1.5: Selection of Cyclic Voltammograms Recorded During Deposition
During the cathodic portion of cycle 2, hydrogen generation is partly sustained by electrolytic decomposition of water within the remaining deposit causing water depletion. Simultaneously, base is generated in the structure, allowing free $\text{Al}^{3+}$ to precipitate here as hydroxide, thus reducing pore size. The area of electrode surface which was stripped of hydroxide by acid dissolution is now recoated in fresh deposit.

Once again, anodic hydrogen oxidation will release protons into the deposit, causing its partial dissolution. However, the area of deposit surviving the first dissolution process will be more dense than other areas, and therefore more resistant to dissolution. Hence, this material will preferentially be left at the electrode surface, along with a small portion of the fresh deposit. The denser aluminium hydroxide remaining from the first cycle will also present a barrier to current flow within the system, thereby decreasing the number of protons released on the second cycle. This will ensure that an increasing amount of deposit is left at the palladium surface, with increasing cycle number, following the anodic hydrogen oxidation process.

On cycle 3, fresh deposit will again be generated at the bare palladium areas of the electrode surface, and the material remaining from the partial dissolutions of cycles 1 and 2 will be further densified by hydroxide precipitation within the pores of the deposit.

It is also noted that at the anodic extreme of each cycle, oxygen evolution will also cause water depletion. Its subsequent reduction will generate base, giving rise to further hydroxide precipitation, and further pore size reduction.
The overall result is water removal and densification, sustained by diffusion of bulk electrolyte through the growing film, generating a less porous and more structurally sound deposit than the one produced by unipotential deposition.

In contrast, during constant potential deposition, initial nucleation of hydroxide deposit is followed by a continued build-up of the gelatinous precipitate. As the film thickness increases, the deposit is continually generated from a water-rich environment. Hence, there is no inherent process to promote the densification or pore-size reduction of the film. Therefore, the deposit generated is more porous and less mechanically stable than the one produced by a cycled potential programme.

2.1.6: Conclusions

It has been demonstrated that a precursor to alumina can be generated at the surface of a hydrogen sorbing electrode, by cathodic precipitation, from aqueous electrolyte. Furthermore, it has been shown that manipulation of the deposition potential regime provides a means of controlling the structural morphology of the manufactured deposit. It should therefore be possible, by employing a combination of constant, cycled and pulsed potential programmes, to generate precursors to ceramic films with predetermined physical structure and properties.
Chapter 3

in-situ Optical Study of Film Growth
Chapter 3 : in-situ Optical Study of Film Growth

3.1 : Cell Design

In order to substantiate the predicted mechanisms affecting hydroxide film growth morphology during different deposition regimes, it was decided that a series of in-situ optical studies should be carried out. For the purpose of this investigation, two new cells were employed. The first (Plate 3.1.1) comprised a glass body (70 mm inner diameter, with a depth of 40 mm, and an approximate electrolyte capacity of 200 ml) with openings for working and reference electrodes and a 100 mm length of platinum wire (1.0 mm diameter, 99.95%, Johnson Matthey), coiled to give loop of approximately 20 mm diameter, and set into the cell wall as the counter electrode.

The working electrode consisted of a palladium flag (5 mm by 25 mm and 0.125 mm thick, 99.95% pure, Goodfellow). Having soldered a copper contact wire to one end, the flag was set in a glass tube with quick-set epoxy resin, leaving a length of 20 mm exposed (the double sided flag having a total area of approximately 2 cm²). The reference electrode was a mercury, mercurous sulphate electrode, as depicted in Figure 2.1.3. A square of plate glass (100 mm by 100 mm and 1.5 mm thick) was attached to the front of the cell with quick-set epoxy resin. This gave an undistorted view of the working electrode, allowing photographs to be taken of deposits precipitated at its surface. Photographs were taken with a Pentax SLR camera fitted with a 35 mm lens and extension rings allowing close-up focusing on the working electrode. Illumination of the growing film was achieved with the aid of a small Duracell torch, the light from which was shone through a dispersion grid (60 mm by 60 mm and 2 mm thick frosted perspex plate) and onto the electrode. The rear and sides of the cell were covered in black card in an attempt to prevent stray light from confusing the image. The camera lens was placed approximately 150 mm from the
front of the cell. A schematic diagram of the whole arrangement can be seen in Figure 3.1.1.

The second cell (Figure 3.1.2) consisted of a strip of palladium foil (20 mm by 1 mm and 0.125 mm thick), soldered at both ends to copper contact wires, bent over to a point at the centre of the strip, set in a glass tube (inner and outer diameters 13 mm and 16 mm respectively) with Araldite® resin, and polished down (P120 silicon carbide paper, followed by P1200 paper, then 0.3 micron alumina on wetted Selvyt cloth) to reveal two palladium strip electrodes (0.125 mm by 1 mm and approximately 1 mm apart). This twin electrode was then upturned and a collar of silicone rubber fitted to allow containment of electrolyte. One strip was employed as the cell’s working electrode and the other as the counter electrode. A pinhole was made in the cell’s silicone rubber wall, into which was inserted a length silver wire, employed as a reference electrode (0.5 mm diameter, 30 mm long, and soldered onto a copper contact wire which was then set in glass tubing with quick-set epoxy resin). Optical studies of deposit growth at the palladium strip working electrode were achieved with the aid of an Olympus BHM microscope incorporating a PM-10AK exposure body fitted with a C-35AD-4 autowind camera and a Recordata Back 4.
Plate 3.1.1: Electrochemical Cell with Flat Plate Glass Front

Figure 3.1.1: Experimental Set-up for the Recording of Optical Micrographs During Hydroxide Film Deposition at a Palladium Flag Electrode
Figure 3.1.2: Electrochemical Cell for the Recording of Detailed Optical Micrographs During Hydroxide Film Deposition at a Palladium Surface Under Microscope
3.2 : Optical Observations During Film Growth

3.2.1 : Constant Potential Deposition at a Pd Flag Cathode

For this experiment, the flat front cell (Plate 3.1.1) with 0.01 M aluminium sulphate electrolyte, 5 mm by 20 mm palladium flag working electrode, platinum wire loop counter electrode and mercury, mercurous sulphate reference electrode, was employed. With the camera lens focused on the edge (0.125 mm thick) of the working electrode, a potential of -3.20 V was applied to for a period of 30 minutes. During this period, a series of photographs of the growing deposit generated at the palladium flag surface were taken. In addition, images of the bare electrode (prior to polarisation) and of the deposited film after termination of polarisation were also acquired. A selection of these can be seen in Plates 3.2.1 to 3.2.6. Details of each plate are given in Table 3.2.1.

Table 3.1.1: Key to Plates 3.2.1 to 3.2.6:

<table>
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<th>Elapsed Deposition Time /Minutes</th>
<th>Approx. Magnification</th>
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<td>Prior to Deposition</td>
<td>x 5</td>
</tr>
<tr>
<td>3.2.2</td>
<td>5</td>
<td>x 5</td>
</tr>
<tr>
<td>3.2.3</td>
<td>10</td>
<td>x 15</td>
</tr>
<tr>
<td>3.2.4</td>
<td>20</td>
<td>x 5</td>
</tr>
<tr>
<td>3.2.5</td>
<td>27</td>
<td>x 5</td>
</tr>
<tr>
<td>3.2.6</td>
<td>Deposition Complete</td>
<td>x 5</td>
</tr>
</tbody>
</table>
Plates 3.2.1 to 3.2.6: Optical Micrographs of a Depositing Aluminium Hydroxide Film at a Palladium Flag Working Electrode Under Constant Potential Polarisation

Plate 3.2.1

Plate 3.2.2
Plate 3.2.2 shows a gelatinous precipitate encircling the palladium flag working electrode after a deposition period of 5 minutes. The deposit appears denser (less transparent) at the electrode surface than at the deposit boundary (approximately 0.8 mm from the palladium flag) where it is very transparent and has an irregular edge. Plates 3.2.3, 3.2.4 and 3.2.5 taken at 10, 20 and 27 minutes (respectively) from the start of deposition, clearly indicate that the inner and outer portions of the deposit continue to grow outwards into the electrolyte, and that the deposit’s outermost surface remains transparent and irregular. This observation is in keeping with the deduction in Chapter 2 that constant potential deposition yields open/porous structures by virtue of the deposit’s generation from a water-rich environment. The irregular outer surface is due to the break-up of the gelatinous precipitate at its interface with the electrolyte; small fragments were observed to spool away from the bulk material and fall to the bottom of the cell. This surface erosion is likely to be due to the poor coherence of the underlying deposit.

Following completion of the 30 minute polarisation period, the finished deposit (Plate 3.2.6) had acquired a maximum thickness of approximately 1 mm, demonstrating that relatively thick surface coatings of ceramic precursor could be quickly generated using cathodic precipitation. Surface irregularities and the apparent decrease in density of the material at increasing distance from the electrode indicate that more complex control over the deposition regime would be necessary in order to manufacture suitable deposits for protective surface coatings or ceramic bodies. Attempts to observe film growth under cycled and pulsed potential programmes proved somewhat difficult using the present experimental set-up. Reflected light within the cell, poor magnification and focusing problems obscured physical changes in the growing deposits which were considerably thinner than the one produced under constant potential. Therefore, a cell that was viewable under a microscope (Figure 3.1.2) was employed in subsequent optical investigations.
3.2.2: Constant Potential Deposition at a 0.125 mm by 1 mm Palladium Strip Electrode

For this experiment, the microscope-viewable cell (Figure 3.1.2) incorporating 1 mm by 0.125 mm palladium strip working and counter electrodes and silver wire reference electrode (reference potential -0.20 V vs mercury, mercurous sulphate reference in 1.0 M H₂SO₄ electrolyte), and containing approximately 1 ml of 0.01 M aluminium sulphate, was employed. The electrolyte level was adjusted with the aid of a glass teat pipette to ensure that the meniscus curvature did not distort the image of the palladium strip working electrode as seen under the microscope. With the cell connected to the 1286 Electrochemical Interface, a potential of -3.00 V was applied to the palladium working electrode (equivalent to -3.20 V vs mercury, mercurous sulphate reference) for a period of 30 minutes. Throughout this period, the growing deposit was observed under the microscope with a x10 objective lens. A series of photographs were taken at various stages of deposition, a selection of which can be seen in Plates 3.2.7 to 3.2.18. These were taken using 100 ISO slide film with the microscope illumination set to level 5. Following processing, the slides were photographed using a Panagor zoom slide duplicator which allowed two-fold magnification of the original images. Prints were taken from negatives of the magnified images. The current-time profile (Figure 3.2.1) during polarisation was also recorded, as a data file, with the aid of a Viglen Dossier 486 PC Notebook connected via a serial port lead to the 1286 Electrochemical Interface. Communication between machines was achieved by employing Microsoft Windows Terminal Version 3.1 (a text communications package) with a baud rate setting of 9600. The acquired text data file was then exported to Microsoft Excel 5.0 for plotting.
Plates 3.2.7 to 3.2.18: Optical Micrographs of an Aluminium Hydroxide Film Depositing at a Palladium Working Electrode Under a Constant Potential Regime

Plate 3.2.7

Plate 3.2.8
Table 3.2.2: Key to Plates 3.2.7 to 3.2.18:

<table>
<thead>
<tr>
<th>Plate Number</th>
<th>Elapsed Deposition Time</th>
<th>Approx. Magnification</th>
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<td>3.2.7</td>
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<td>x 220</td>
</tr>
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<td>3.2.8</td>
<td>8 seconds</td>
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</tr>
<tr>
<td>3.2.9</td>
<td>14 seconds</td>
<td>x 220</td>
</tr>
<tr>
<td>3.2.10</td>
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</tr>
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<td>3.2.12</td>
<td>50 seconds</td>
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</tr>
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<td>3.2.13</td>
<td>1 minute 30 seconds</td>
<td>x 220</td>
</tr>
<tr>
<td>3.2.14</td>
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<td>10 minutes</td>
<td>x 220</td>
</tr>
<tr>
<td>3.2.17</td>
<td>20 minutes</td>
<td>x 220</td>
</tr>
<tr>
<td>3.2.18</td>
<td>Deposition Complete</td>
<td>x 220</td>
</tr>
</tbody>
</table>
Figure 3.2.1: Current-time Profile During Constant Potential Deposition - Correlated with the in-situ Optical Micrographs Taken
Plate 3.2.7 shows the bare palladium working electrode surface, as seen through the electrolyte solution, prior to polarisation. At 8 seconds from the onset of deposition (Plate 3.2.8) a slight clouding of the electrode surface is observed. This observation marks the initial nucleation of aluminium hydroxide near the palladium surface. At 14 seconds (Plate 3.2.9) the surface is covered in transparent islands of deposit which are separated by areas of bare palladium. The hydroxide film at this stage takes on a 'crazy paving' appearance. By 18 seconds (Plate 3.2.10) the islands appear more pronounced and at 30 seconds (Plate 3.2.11) dark areas are visible at the edge of the deposit where the islands have merged and the porous material begins to increase in thickness. After 50 seconds (Plate 3.2.12) the dark areas have increased in size; there are however still cracks (areas of bare palladium) in the deposit surface. On continued deposition the 'cracks' become narrower as hydroxide islands at the centre of the deposit begin to merge. 5 minutes from the start of polarisation (Plate 3.2.15), a continuous film covers the entire palladium surface. The darker translucent areas along the edge of the film mark thicker patches of the hydroxide material indicating that the rate of deposition is greater here than at its centre. As the deposition time increases further, the film begins to overspill onto the Araldite surface. On termination of polarisation (30 minutes, Plate 3.2.18) some areas of the film are close to twice the width of the deposition electrode. However, the film surface appears to be very uneven; a mixture of light and dark area indicate its varying thickness and density. It is noted that the current decreases continually during deposition for the first 24 minutes, as expected from an electrochemical system where the product is an adherent resistive film. However, there is a sharp rise in current following this period. This is almost certainly due to the breakaway of deposit from the electrode surface, decreasing the deposit resistance at that point and therefore allowing further (higher current) deposition to occur. Deposit break-up may be due to the excessive build-up of
hydrogen within the palladium electrode substrate, allowing eventual outgassing to 'blow off' fragments of the film. However, it is more likely that the sheer bulk of the deposit and its porous, non-coherent nature is responsible for any surface fragmentation.

Overall, the constant potential regime gives rise to uncontrolled hydroxide film growth at the palladium surface. The precipitation of material outside the electrode area confirms that the deposit is continually generated from a water-rich environment as discussed in Chapter 2 and section 3.2.1 of this chapter. Thus, a high degree of porosity and poor structural integrity is expected from the final deposit. In order to obtain deposits suitable for electronic, engineering or sensor applications, it is therefore essential that a more complex potential regime, allowing control of hydroxide nucleation and growth and pH cycling, be employed during the deposition period.

3.2.3: Cycled Potential Deposition at a 0.125 mm by 1 mm Palladium Strip Electrode

Prior to optical investigation of film growth under a cycled potential regime, the working and counter electrode assembly was first cleaned and degassed. With the silicon rubber collar off, any visible hydroxide deposit was removed by gentle polishing on tissue paper. The exposed palladium surface was then immersed in 1.0 M sulphuric acid solution for one minute (with the assembly agitated throughout) in order to dissolve off any remaining deposit. The surface was then washed in HPLC grade water. Having removed the hydroxide film, the two palladium strips were both connected to the working electrode terminal of the 1286 Electrochemical Interface
(via the copper wire contacts) and this new twin working electrode placed in a two armed cell (Figure 2.1.1) containing 0.01 M aluminium sulphate electrolyte, platinum wire loop counter electrode and mercury, mercurous sulphate reference. Hydrogen degassing was then carried out at a potential of +0.50 V vs reference until zero current. The palladium surface was then washed, following which, polishing was carried out with 0.3 micron grade alumina on wet Selvyt cloth. After a final washing, the electrode surface was allowed to dry in air and the silicone rubber collar was refitted.

With approximately 1 ml of 0.01 M aluminium sulphate electrolyte in the cell, it was again placed under the microscope and the proper connections made to the palladium working and counter electrodes and the silver reference. The electrolyte level was also adjusted, as before, in order to attain the best possible view of the working electrode surface. A series of linear ramp potential cycles were initiated with limits of -3.00 V and +1.20 V vs silver reference (equivalent to -3.20 V and +1.00 V vs mercury, mercurous sulphate reference) and scan rate 100 mVs⁻¹. The initial scan was negative from a starting potential of +0.20 V. Changes in film growth characteristics during cycling were observed under microscope with a x10 objective lens fitted. A series of optical micrographs were taken during cycles 1 and 2. A selection of these can be seen in Plates 3.2.19 to 3.2.35, a key to which is given in Table 3.2.3. Cyclic voltammetric data was recorded with the aid of a serial interfaced PC (as before) and data was plotted using Microsoft Excel. Cyclic voltammograms of cycles 1 and 2 with correlation to the micrographs taken can be seen in Figure 3.2.2.
Plates 3.2.19 to 3.2.35: Optical Micrographs of an Aluminium Hydroxide Film Depositing at a Palladium Working Electrode Under a Cycled Potential Regime

Plate 3.2.19

Plate 3.2.20
Plate 3.2.35
### Table 3.2.3: Key to Plates 3.2.19 to 3.2.35:

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<thead>
<tr>
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<th>Electrochemical Process Involved</th>
<th>Approximate Magnification</th>
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<td>2 (71)</td>
<td>+0.90</td>
<td>DG/Ö₂ Gen</td>
<td>x 220</td>
</tr>
</tbody>
</table>

DP = Deposition

H₂ Gen = Hydrogen Generation

DG = Degassing

H₂ Ox = Hydrogen Oxidation

DG/Ö₂ Gen = Degassing Coupled with Oxygen Generation
Figure 3.2.2: Cyclic Voltammograms Recorded During Cycled Potential Deposition - Correlated with in-situ Optical Micrographs Taken

(a) Cycle 1
Plate 3.2.19 shows the bare palladium electrode surface prior to the onset of polarisation. As the applied potential is scanned negative, little change is observed until around -2.30 V (Plate 3.2.21) where clouding of the palladium surface occurs as hydroxide nucleation begins. Bands at the edge of the metal strip would seem to indicate preferential nucleation here as opposed to the central region. By -2.80 V (Plate 3.2.22) the palladium surface is covered in small nodular deposits similar to the islands observed in the initial stages of hydroxide precipitation under a constant potential programme. However, the gradual increase in deposition potential achieved with potential cycling allows a much finer grain deposit to form since the nucleation process will be much slower under such conditions. At -1.70 V (Plate 3.2.23) on the reverse scan the nodules have merged into larger islands separated by a network of areas of bare palladium surface which appear as cracks in the deposit. However, a continuous film seems to be present at the electrode edges where initial nucleation preferentially occurred.

Throughout deposition, the palladium electrode substrate absorbed hydrogen generated at its surface, thereby preventing it from disturbing the hydroxide growth process. As this electrode begins to oxidise its absorbed hydrogen at +0.30 V (Plate 3.2.24) protons are released into the deposit, lowering the pH at the electrode/deposit interface and partially dissolving the hydroxide material. Thus, the islands at the centre of the electrode begin to decrease in size, exposing more of the palladium surface. It is noted that the continuous deposit at the edges remains intact since it formed at an earlier stage than other areas and will therefore be denser and more resistant to acid dissolution. As hydrogen oxidation continues (Plates 3.2.25 and 3.2.26) the hydroxide islands further decrease in size exposing greater areas of the electrode surface. The outermost deposit however, remains unaffected. Close to the end of cycle 1, at a potential of +1.00 V (Plate 3.2.27) hydroxide dissolution becomes less prominent.

66
During the forward scan of cycle 2, hydroxide precipitation again occurs. Plates 3.2.28 to 3.2.32 show the islands of deposit increasing in size and once again reducing the areas of bare palladium to mere cracks in the surface film. In addition, dark areas begin to appear at the deposit edges as deposition occurs both within the porous film and at its interface with the electrolyte. Consequently the film increases in density and thickness. By -1.70 V on the reverse scan (Plate 3.2.32) a near continuous deposit is present over the entire electrode area containing only a few narrow regions of bare palladium (or cracks). On hydrogen oxidation at positive potentials (Plates 3.2.33 to 3.2.35) the cracks begin to widen as hydroxide is dissolved from newly deposited areas of the film. The denser film edges, as before, remain untouched.

Further cycling sees a continuation of the processes observed here, allowing a dense, compact deposit to form by means of pH cycling and pore size reduction as discussed in Chapter 2.

3.2.4: Pulsed Potential Deposition at a 0.125 mm by 1 mm Palladium Strip Electrode

For reasons which will become clear in section 4.2.5, it was decided that the effect on the film growth process of potential pulsing into deposition and degassing should also be investigated.

Following cleaning and degassing of the palladium surfaces as described in section 3.2.3, the silicone rubber collar was refitted and electrode connections made to the 1286 Electrochemical Interface. Again, the cell was filled with approximately 1 ml of 0.01 M aluminium sulphate electrolyte and placed under microscope (×10 objective); the electrolyte level being adjusted for viewing clarity as before. A series of potential
pulses were then applied to the working electrode: the potential was stepped from an open circuit of +0.210 V (vs silver reference) to -3.00 V at 100 Vs\(^{-1}\) and held there for a period of 40 seconds. The potential was then stepped up to +0.70 V (+0.50 V vs mercury, mercurous sulphate reference - the potential at which the maximum rate of hydrogen oxidation was found to occur) at 100 Vs\(^{-1}\) where it was held for 40 seconds. These two potential steps constituted one pulse cycle. A total of 20 pulse cycles were applied to the working electrode, during which time, a series of optical micrographs of the growing deposit were taken and the current-time profile was recorded as a data file on the serial interfaced PC. A selection of micrographs taken at various stages of deposition during cycles 1 to 20 can be seen in Plates 3.2.36 to 3.2.57 (see Table 3.2.4 for a key to these Plates) and the current-time profile with correlation to these is shown in Figure 3.2.3.

Plate 3.2.36 shows the bare working electrode surface prior to pulse cycling. 10 seconds into the first deposition pulse the palladium surface (as in the early stages of constant potential deposition) becomes clouded over as hydroxide nucleation begins (see Plate 3.2.37). After 20 seconds (Plate 3.2.38), islands of deposit cover the electrode area, separated by narrow regions of bare palladium. 30 seconds (Plate 3.2.39) sees the islands increase in size and merge at the electrode edges giving rise to dark areas of thicker deposit. Pulsing into hydrogen oxidation (Plates 3.2.40 to 3.2.42) generates protons at the electrode/deposit interface which partially dissolves the hydroxide film, decreasing the size of the islands of deposit and exposing larger areas of bare palladium. 30 seconds into the degassing pulse (Plate 3.2.42) only a few patches of deposit remain on the electrode surface, most of which are situated at its edges.
Plates 3.2.36 to 3.2.57: Optical Micrographs of an Aluminium Hydroxide Film Depositing at a Palladium Working Electrode Under a Pulsed Potential Regime

Plate 3.2.36

Plate 3.2.37
Table 3.2.4: Key to Plates 3.2.36 to 3.2.57:

<table>
<thead>
<tr>
<th>Plate Number</th>
<th>Pulse Cycle Number (and Cycle Time Elapsed /seconds)</th>
<th>Electrochemical Process Involved</th>
<th>Approximate Magnification</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2.36</td>
<td>Prior to Deposition</td>
<td>N/A</td>
<td>x 220</td>
</tr>
<tr>
<td>3.2.37</td>
<td>1 (10)</td>
<td>DP (H2 Gen)</td>
<td>x 220</td>
</tr>
<tr>
<td>3.2.38</td>
<td>1 (20)</td>
<td>DP (H2 Oen)</td>
<td>x 220</td>
</tr>
<tr>
<td>3.2.39</td>
<td>1 (30)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.2.40</td>
<td>1 (50)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.2.41</td>
<td>1 (60)</td>
<td>DG (H2 Ox)</td>
<td>x 220</td>
</tr>
<tr>
<td>3.2.42</td>
<td>1 (70)</td>
<td></td>
<td>x 220</td>
</tr>
<tr>
<td>3.2.43</td>
<td>2 (10)</td>
<td></td>
<td>x 220</td>
</tr>
<tr>
<td>3.2.44</td>
<td>2 (20)</td>
<td>DP (H2 Gen)</td>
<td>x 220</td>
</tr>
<tr>
<td>3.2.45</td>
<td>2 (30)</td>
<td></td>
<td>x 220</td>
</tr>
<tr>
<td>3.2.46</td>
<td>2 (50)</td>
<td></td>
<td>x 220</td>
</tr>
<tr>
<td>3.2.47</td>
<td>2 (60)</td>
<td>DG (H2 Ox)</td>
<td>x 220</td>
</tr>
<tr>
<td>3.2.48</td>
<td>2 (70)</td>
<td></td>
<td>x 220</td>
</tr>
<tr>
<td>3.2.49</td>
<td>3 (10)</td>
<td></td>
<td>x 220</td>
</tr>
<tr>
<td>3.2.50</td>
<td>3 (20)</td>
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<td>x 220</td>
</tr>
<tr>
<td>3.2.51</td>
<td>3 (30)</td>
<td></td>
<td>x 220</td>
</tr>
<tr>
<td>3.2.52</td>
<td>3 (50)</td>
<td></td>
<td>x 220</td>
</tr>
<tr>
<td>3.2.53</td>
<td>3 (60)</td>
<td>DG (H2 Ox)</td>
<td>x 220</td>
</tr>
<tr>
<td>3.2.54</td>
<td>3 (70)</td>
<td></td>
<td>x 220</td>
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<tr>
<td>3.2.55</td>
<td>4 (30)</td>
<td>DP (H2 Gen)</td>
<td>x 220</td>
</tr>
<tr>
<td>3.2.56</td>
<td>4 (70)</td>
<td>DG (H2 Ox)</td>
<td>x 220</td>
</tr>
<tr>
<td>3.2.57</td>
<td>20 (10)</td>
<td>DP (H2 Gen)</td>
<td>x 220</td>
</tr>
</tbody>
</table>
Figure 3.2.3:  Current-time Profile During Pulsed Potential Deposition - Correlated with in-situ Optical Micrographs Taken

(a) Pulse Cycles 1 to 3
(b) Pulse Cycles 1 to 20
During the second pulse cycle, the processes discussed are repeated. On pulsing to the deposition potential (Plates 3.2.43 to 3.2.45), the islands of hydroxide material begin to reform on the bare palladium surface and the few remaining from the previous cycle increase in thickness as more hydroxide is precipitated at the interface between deposit and electrolyte. On hydrogen oxidation (Plates 3.2.46 to 3.2.48), the islands begin to dissolve as protons are again released into the deposit. Continued pulse cycling (Plates 3.2.49 to 3.2.57) facilitates the gradual build-up of a dense thin film of aluminium hydroxide at the palladium surface. The dissolution/recrystallisation process which takes place during pulse cycling allows weakly held porous areas of the film to be continually stripped away and replaced by denser material, whilst areas left behind are further densified by deposition within the porous structure. The overall decrease in current (see Figure 3.2.3) during pulsing, occurring as a result of the resistive film growing at the working electrode, means that less hydrogen is oxidised on each successive pulse cycle. This ensures that less deposit is dissolved as the cycle number increases and that overall the film continues to grow and increase in density. Following pulse cycle 20, the deposit is a coherent surface film which appears mostly opaque when viewed under the microscope. It is worth noting that because the dissolution/recrystallisation process occurs at the electrode/deposit interface, material closest to the electrode surface will be denser than material nearer the deposit/electrolyte interface. Thus, films generated by this type of potential regime will have an underlying compact layer on top of which lies more porous material. They should therefore make excellent gas and humidity sensors (see Appendix 2).

3.3: Conclusions

The in-situ optical micrographic study undertaken here substantiates the proposed film growth mechanisms discussed in Chapter 2. It has been shown that hydroxide
film growth under a constant potential regime occurs from a water-rich environment which generates a bulky, porous and poorly coherent deposit. On the other hand, it was demonstrated that cycling or pulsing the applied potential into regions of hydrogen generation (hydroxide precipitation) and oxidation allowed a much more compact, coherent and less porous deposit to be generated. The compaction mechanism was proven to be hydroxide dissolution and recrystallisation at the palladium surface by means of pH cycling. It was expected that deposition within the pores of the growing deposit also plays a part and this may be seen from the darkening of the remaining areas of film following each dissolution/recrystallisation cycle.

Further investigation into the effect of the controlled potential regime on film growth morphology should allow specific tailoring of the porosity and thickness and ultimately the stoichiometry and degree of crystallinity of the growing deposit. By employing electrolytes containing several species of precipitated metal ions, it will be possible to generate precursors to mixed oxide ceramics and laminated materials. Electrolyte additions of colloidal suspensions of particulates or fibres, which will become encapsulated in the growing deposit, should also provide a simple route to ceramic composites.

Although palladium metal was employed here as the deposition electrode substrate, other hydrogen-sorbing materials such as the Lanthanum-Nickel alloys [39,40] may also be used to the same effect. Indeed, the application of a thin film of hydrogen-sorbing material by, for example, electroplating or physical vapour deposition onto an electrode substrate should allow the generation of films of ceramic precursor on almost any surface, including non-conducting glasses and plastics. Cathodic precipitation therefore offers enormous scope for use in many areas of ceramic
technology including the manufacture of sensors, electronic junction devices, ceramic bodies and protective surface coatings.
Chapter 4

Application of Cathodic Precipitation in the Manufacture of Humidity Sensors
4.1 : Sensor Design and Fabrication

4.1.1 : Choice of Materials

It was decided that the application of cathodic precipitation to the manufacture of humidity sensing materials would be evaluated. It was reasoned that the electrochemical generation of ceramic precursors would be ideally suited in the fabrication of such devices since their sensing performance is firmly linked to the substrate porosity; a high degree of porosity is required in order to facilitate access of water vapour from the sensed atmosphere to the sensing material. For the purpose of the experiments conducted here, aluminium hydroxide was again the material of choice for deposition since alumina based humidity sensors are widely used and are well characterised devices [41-46].

4.1.2 : Electrodes/Sensor Substrates

In order to evaluate the performance of cathodically-precipitated materials for humidity sensing, it was essential to design an electrode which could act as both the depositing and testing medium. It was therefore decided that two closely spaced strips of palladium be employed, and a sensing film deposited such that it coated both surfaces and bridged the gap between the two. This would, in effect, produce a two electrode cell whose hydroxide electrolyte could be probed for impedance changes relating to the quantity of water adsorbed from the sensed atmosphere. The impedance would therefore relate directly to the relative humidity of that atmosphere.
The electrode (Figure 4.1.1) employed consisted of a strip of palladium (cut from 0.125 mm thick foil, 99.95% pure, Goodfellow) 1 mm by 30 mm and 0.125 mm thick, which was coated on half of one side by Lacomit insulator diluted with methylethylketone, and allowed to set in air. Copper contacts were then soldered onto each end, one of which was insulated with a length of heat-shrink. Araldite resin was then applied on top of the Lacomit and the strip folded over with the Lacomit insulator on the inside of the fold. The tip was then pressed in a vice between glass plates in order to allow the two halves of the strip to adhere together with an insulated gap of 0.01 mm between them. On hardening of the araldite (24 hours), the strip and its contacts were set in a silica glass tube (110 mm long with an outer diameter of 9 mm) with araldite resin (leaving approximately 50 mm of copper contact wire exposed). The resin was left to harden (a further 24 hours) and finally, the palladium end abraded with P120 silicon carbide paper to separate the two halves of the strip by removal of its folded tip. This was followed by polishing with P1200 grade paper and then 0.3 micron alumina (on wetted Selvyt cloth) in order to generate a reproducible surface onto which the sensing material could be deposited. Prior to each deposition experiment, the electrode surface was cleaned of any residual deposit (light polishing on tissue paper followed by immersion in 1.0 M sulphuric acid for 1 minute and finally by washing in HPLC grade water) and degassed at +0.50 V (vs mercury, mercurous sulphate reference) in 0.01 M aluminium sulphate electrolyte until zero current. The electrode surface was then repolished with 0.3 micron alumina and again washed in HPLC grade water.
The cell used for generation of the sensing material was the two armed cell depicted in Figure 2.1.1, with mercury, mercurous sulphate reference electrode and integrated platinum wire counter electrode. 0.01 M aluminium sulphate was again employed as electrolyte.

4.2 : Humidity Sensing

4.2.1 : Test Circuits

A Beckmann 3050 multimeter was used to monitor changes in DC resistance with humidity of the initially generated sensor. Later, the circuit shown in Figure 4.2.1 was used as a more accurate means of monitoring response to humidity changes. The circuit employed an ORTEC Brookdeal Signal Source 9472 signal generator and
Fylde 255DA buffer amplifier. The impedance of the test sensor (S) at a given humidity was determined by applying a known potential \((V_{in})\) at fixed frequency, across a series combination of the test sensor and a known resistance (R). The potential dropped across R \((V_{out})\) then relates directly to the sensor impedance \((S)\) as follows:

For the series combination of R and S

\[ V_{in} = V_{out} + V_s \]

where \(V_s\) is the potential dropped across the sensor.

The current \((i)\) through R and S will be equal, but will vary with the value of \(S\) (since R is constant).

Therefore, at any value of \(S\)

\[ i = \frac{V_{out}}{R} \quad \text{and} \quad S = \frac{V_{in} - V_{out}}{i} \]

Substituting for \(i\) in the equation for \(S\) gives

\[ S = \frac{V_{in} - V_{out}}{\frac{V_{out}}{R}} = \frac{R(V_{in} - V_{out})}{V_{out}} = \frac{R V_{in}}{V_{out}} - \frac{R V_{out}}{V_{out}} = R\left(\frac{V_{in}}{V_{out}} - 1\right) \]

and with an applied potential \((V_{in})\) of 1 V as used in the following experiments

\[ S = R\left(\frac{1}{V_{out}} - 1\right) \]
A Schlumberger Solartron 1250 Frequency Response Analyser was used (see circuit diagram, Figure 4.2.2) to obtain impedance spectra of the sensor at a range of humidities. This was connected, via serial ports, to a PC Notebook which logged the impedance spectra as a data file with the aid of Microsoft Windows Terminal Version 3.1 text communication package. The data was then processed and plotted, in complex plane form, with Microsoft Excel 5.0. Equivalent circuit modelling was carried out with the aid of the complex non-linear least squares impedance fitting programme LEVM 6.0 (J. Ross MacDonald, University of North Carolina, Chapel Hill, U.S.A.).
4.2.2: Controlled Humidity Environments

Humidity control was achieved by employing solutions of constant humidity salts [47,48] in sealed silica glass vessels. Evaporation/condensation processes at the liquid/vapour interface of a salt solution enclosed in a fixed volume will eventually reach equilibrium thereby generating a constant humidity atmosphere in the space above the solution. Variation of the solution concentration and/or the introduction of impurities into the enclosed space will allow the equilibrium water vapour pressure, and therefore the relative humidity, of the sealed atmosphere to be regulated. Therefore, a single salt solution may be employed in the generation of a wide range of humidified atmospheres. However, it is often more convenient to employ a range of different saturated salt solutions, each providing a specified relative humidity, since in
this case careful control of concentration of both salt and impurities is not required. Adding an excess of solute to the saturated solution ensures that it remains saturated and continues to generate a constant humidity environment even in the presence of minor impurities which may act as either source or sink of humidity.

For the purpose of experiments carried out here, five salts were chosen (see Table 4.2.1) whose saturated solutions would maintain constant humidity environments of approximately 6, 33, 51, 75, and 97 %RH. The vessels used as humidity chambers were cylindrical in shape with 72 mm inner diameter and height 145 mm. Access to the controlled humidity environment was facilitated by two ground glass joints incorporated into the top of each chamber. These were greased with Glisseal vacuum grease (Borer Chemie), and stopper adapters with o-ring seals of diameter 18 mm and 9 mm were fitted to allow insertion, with gas tight seals, of a reference probe and test sensor. The overall volume (taking into account the space immediately below the ground glass joints) was approximately 650 cm$^3$. Each solution was prepared by dissolving enough of the salt (at least 98 % pure, Aldrich) in 50 mls of HPLC grade water (Rathburn) at elevated temperature (80°C) to give a saturated solution. Each solution was then allowed to cool to room temperature, following which a further quantity of salt was added, sufficient to generate a salt layer of approximately 2 to 3 mm at the bottom of each vessel. A Vaisala HMI 31 humidity sensor, fitted with an HMP 35 humidity and temperature probe assembly, was used as a reference. The Vaisala sensor covered the full relative humidity range (0 to 100 %RH) with an accuracy of ±2% between 0 and 90 %RH and ±3% above 90 %RH. Over the temperature range 0 to 100°C it had an accuracy of ±0.1°C. A schematic diagram of a constant humidity chamber including salt, solution and both reference and test humidity sensors can be seen in Figure 4.2.3.
Table 4.2.1: Salts Employed in Controlled Humidity Environments

<table>
<thead>
<tr>
<th>Constant Humidity Salt</th>
<th>Expected Relative Humidity at 25°C / %RH</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBr</td>
<td>6</td>
</tr>
<tr>
<td>MgCl₂.6H₂O</td>
<td>33</td>
</tr>
<tr>
<td>Ca(NO₃)₂.4H₂O</td>
<td>51</td>
</tr>
<tr>
<td>NaCl</td>
<td>75</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>97</td>
</tr>
</tbody>
</table>

Figure 4.2.3: Schematic Diagram of a Constant Humidity Chamber
4.2.3 : Generation of Sensing Films

The constant and cycled potential deposition methods described in Chapter 2 were evaluated for use in the generation of sensing films at the surface of the electrode in Figure 4.1.1. With the two copper contacts shorted together allowing the two palladium strips to operate as a single working electrode, it was found that deposits produced by constant potential deposition (-3.20 V for 30 minutes) proved sufficiently open to bridge the two halves of the palladium working electrode. However, they were too structurally unstable and rapidly fell apart during use. Deposits generated by cycled potential deposition (between sweep limits of -3.20 V and +1.00 V at 100 mVs⁻¹) were more structurally stable with better adherence to the electrode surface. However, the compaction mechanism proved to be a problem when attempting to bridge the electrodes; separate deposits were always generated, with little or no material joining the two.

A combination of the two methods proved more promising. Firstly, a porous, bridging deposit was generated by polarisation of the twin working electrode at -3.20 V for 20 minutes in 0.01 M aluminium sulphate electrolyte. The deposit was then subjected to a series of 20 potential cycles each having sweep limits of -3.20 V and +1.00 V, with scan rate 100 mVs⁻¹ (initial scan negative from 0.00 V). This served to both reduce the pore size of the deposit, thereby increasing its structural integrity, and by partial dissolution (by pH cycling), cause a degree of compaction. On removal of the electrode and adherent film from solution, it was placed in HPLC grade water for 5 minutes in an attempt to remove any residual electrolyte from the deposit. It was then allowed to dry in air for one hour, following which, the sensor contacts were coupled to a digital multimeter.
It was discovered that the DC resistance of the deposit could be changed from greater than 20 MΩ (the multimeter's upper measurement limit) to 19 MΩ by lightly breathing on the film surface, and that hydration of the film with a small drop of water (ca. 1mm diameter) decreased its resistance to around 1 MΩ. This crudely demonstrated that cathodic precipitation could be employed in the fabrication of humidity sensing materials. The next step was to investigate the response of a similar sensor over a range of known humidities, and to compare this to the response of a commercially available sensing device.

4.2.4: Response of a Commercially Available Sensor

For the purpose of this investigation an NPH-50A sensor (Nemoto & CO. LTD.) was employed. In order to allow the device to be sealed in the test chambers, it was soldered to two copper contact wires (both of which were insulated with heat shrink sleaving) which were then set into a glass tube (170 mm long and 8 mm in diameter) with quick-set epoxy resin (see Figure 4.2.4).

The LiBr chamber (approximately 6 %RH) was chosen as the first controlled humidity environment. Both ground glass joints were fitted with greased glass stoppers to give gas tight seals. The chamber was then immersed in a water bath at 25°C for one hour to allow the atmosphere inside to equilibrate. The two sensors (NPH-50A test sensor and Vaisala reference sensor) were then inserted and sealed into the chamber with the o-ring sealed greased glass adapters. A further 30 minutes was allowed for re-equilibration of the humidified atmosphere, following which an AC signal, 1 V at 50 Hz, was applied to the test circuit connected to the NPH-50A device (Figure 4.2.1). The potential (V<sub>00</sub>) dropped across the measuring resistor R (where R = 46.8 kΩ) and the chamber's humidity (reference sensor reading) were then recorded. The
reference and test sensors were then transferred to the MgCl₂·6H₂O chamber, which had been previously sealed and immersed in the water bath at 25°C for one hour. Again, a further 30 minutes equilibration time was allowed before application of the same AC signal and measurement of $V_{\text{out}}$ and relative humidity. This process was repeated with the other three chambers in order of increasing humidity, following which a full repeat run was executed. The results can be seen in Table 4.2.2 below and in Figure 4.2.5.

Table 4.2.2(a): Impedance Response of NPH-50A Sensor to Varying Humidity (run 1)

<table>
<thead>
<tr>
<th>Constant Humidity Solution</th>
<th>Temperature °C</th>
<th>Relative Humidity %RH</th>
<th>$V_{\text{out}}$ /V</th>
<th>Sensor Impedance S /Ω</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBr</td>
<td>23.7</td>
<td>12.2</td>
<td>0.004</td>
<td>1.17x10⁷</td>
</tr>
<tr>
<td>MgCl₂·6H₂O</td>
<td>24.2</td>
<td>37.0</td>
<td>0.032</td>
<td>1.42x10⁶</td>
</tr>
<tr>
<td>Ca(NO₃)₂·4H₂O</td>
<td>24.7</td>
<td>48.5</td>
<td>0.093</td>
<td>4.56x10⁵</td>
</tr>
<tr>
<td>NaCl</td>
<td>23.8</td>
<td>74.5</td>
<td>0.764</td>
<td>1.45x10⁴</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>23.4</td>
<td>100.7</td>
<td>0.962</td>
<td>1.85x10³</td>
</tr>
</tbody>
</table>

Table 4.2.2(b): Impedance Response of NPH-50A Sensor to Varying Humidity (run 2)

<table>
<thead>
<tr>
<th>Constant Humidity Solution</th>
<th>Temperature °C</th>
<th>Relative Humidity %RH</th>
<th>$V_{\text{out}}$ /V</th>
<th>Sensor Impedance S /Ω</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBr</td>
<td>25.3</td>
<td>12.2</td>
<td>0.004</td>
<td>1.17x10⁷</td>
</tr>
<tr>
<td>MgCl₂·6H₂O</td>
<td>24.9</td>
<td>33.9</td>
<td>0.025</td>
<td>1.83x10⁶</td>
</tr>
<tr>
<td>Ca(NO₃)₂·4H₂O</td>
<td>24.8</td>
<td>48.4</td>
<td>0.095</td>
<td>4.46x10⁵</td>
</tr>
<tr>
<td>NaCl</td>
<td>25.0</td>
<td>71.1</td>
<td>0.764</td>
<td>1.45x10⁴</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>25.3</td>
<td>87.6</td>
<td>0.939</td>
<td>3.04x10³</td>
</tr>
</tbody>
</table>
Figure 4.2.4: NPH-50A Humidity Sensor
Figure 4.2.5: Humidity Response of the NPH-50A Sensor

(a) run 1
(b) run 2
Plots of $\log_{10}S$ versus relative humidity (Figures 4.2.5(a) and 4.2.5(b)) were linear as expected from the data sheet provided with the NPH-50A sensor (Farnell Technical Data Service). The data appears to be reproducible; the straight line plots for the first and second runs having equations (derived from the use of Microsoft Excel's linear regression tool) $y = -0.0447x + 7.70$ and $y = -0.0494x + 7.83$ respectively (where $x = \text{relative humidity (RH)}$ and $y = \log_{10}S$).

The above experiment demonstrates the successful operation of the humidity chambers, reference sensor and test circuit. It also provides a means of comparing the performance of cathodically precipitated sensors with that of a commercially available device.

4.2.5: The Generation of Humidity Sensing Materials by Pulsed Potential Deposition

It was successfully demonstrated in section 4.2.3 that a humidity sensing film of aluminium hydroxide could be generated across the gap between two 1.0 mm by 0.125 mm palladium strips placed 0.01 mm apart, by means of combined constant and cycled potential programmes. Therefore, it was reasoned that a pulsed potential regime, during which alternate deposition and degassing were carried out, would allow the generation of a similar deposit using a much simpler potential programme. An initial pulse to the deposition potential for a sufficient period would allow a gap-bridging deposit to form between the two palladium strips. Then, a pulse applied at the hydrogen degassing potential would partially dissolve the deposit at its weakest bound sites. Pulse cycling should then make it possible to gradually build up a gap-bridging film of sufficient density and structural integrity to be tested as a humidity sensing device.
Initial investigation concentrated on the effect of the number of pulses and the pulse width on the resulting deposit. It was discovered that alternate pulses into hydrogen generation (cathodic precipitation) at -3.20 V and hydrogen oxidation (degassing) at +0.50 V, 40 seconds pulse width at each potential for a total of 120 pulses (60 depositing and 60 degassing, 0.1 second step time between potentials) reproducibly generated a structurally sound bridging film of aluminium hydroxide, from the 0.01 M aluminium sulphate electrolyte, at the surface of the twin strip electrode (Figure 4.1.1). A deposit generated using these parameters, and placed in HPLC grade water for 5 minutes to remove any residual electrolyte prior to drying in a chamber containing silica gel desiccant, was then employed as the test sensor. Photographs of the electrode surface (taken under the Olympus BHM microscope with x10 objective) both before and after deposition of the sensing material can be seen in Plate 4.2.1.

Following a drying period of two hours, the aluminium hydroxide sensor was connected to the test circuit depicted in Figure 4.2.1. The value of R was chosen as 0.990 MΩ in order to allow greater sensitivity when measuring the sensor impedance (expected to be of the order of a few MΩ). The input signal was set at 1 V, 500 Hz. The test sensor and Vaisala reference sensor were then sealed into the LiBr humidity chamber which had previously been placed in a water bath at 25°C for one hour to allow equilibration of its humidified atmosphere. A further 30 minutes was allowed for re-equilibration, following which, readings of relative humidity, temperature and V_{out} were recorded. This procedure was repeated for the four remaining humidity chambers in order of increasing relative humidity as described in section 4.2.4. The whole testing process was then re-run a further five times. The resulting data can be seen in Table 4.2.3 and plots of V_{out}, S and log_{10}S vs relative humidity in Figure 4.2.6. Intervals between runs, during which the test sensor was placed in a desiccant chamber, were as stated in the Table.
Plate 4.2.1: Optical Micrographs of a Humidity Sensing Aluminium Hydroxide Film Generated by Pulsed Potential Deposition

(a) Part of the Bare Electrode Surface (Approximately x140 Magnification)

(b) Electrode Plus Bridging Deposit (Approximately x140 Magnification)
Table 4.2.3: Response of a Cathodically Precipitated (Pulsed Deposition) Film to Changes in Humidity

<table>
<thead>
<tr>
<th>Run No. (interval /hrs)</th>
<th>Constant Humidity Salt</th>
<th>Relative Humidity /%RH</th>
<th>Temperature /°C</th>
<th>V_{out} /V</th>
<th>Sensor Impedance, S/MΩ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>LiBr</td>
<td>10.7</td>
<td>24.8</td>
<td>0.143</td>
<td>5.93</td>
</tr>
<tr>
<td></td>
<td>MgCl$_2\cdot$6H$_2$O</td>
<td>30.9</td>
<td>25.0</td>
<td>0.134</td>
<td>6.40</td>
</tr>
<tr>
<td></td>
<td>Ca(NO$_3$)$_2\cdot$4H$_2$O</td>
<td>45.1</td>
<td>25.1</td>
<td>0.166</td>
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</tr>
<tr>
<td></td>
<td>NaCl</td>
<td>68.7</td>
<td>25.2</td>
<td>0.599</td>
<td>0.663</td>
</tr>
<tr>
<td></td>
<td>K$_2$SO$_4$</td>
<td>89.2</td>
<td>25.2</td>
<td>0.842</td>
<td>0.186</td>
</tr>
<tr>
<td>2</td>
<td>LiBr</td>
<td>10.9</td>
<td>25.3</td>
<td>0.095</td>
<td>9.43</td>
</tr>
<tr>
<td></td>
<td>MgCl$_2\cdot$6H$_2$O</td>
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<td>25.6</td>
<td>0.087</td>
<td>10.4</td>
</tr>
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<td>Ca(NO$_3$)$_2\cdot$4H$_2$O</td>
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<td>25.3</td>
<td>0.109</td>
<td>8.09</td>
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<td>NaCl</td>
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<td>25.2</td>
<td>0.385</td>
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<tr>
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<td>K$_2$SO$_4$</td>
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<td>25.4</td>
<td>0.824</td>
<td>0.211</td>
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<tr>
<td>(24)</td>
<td>LiBr</td>
<td>11.9</td>
<td>25.1</td>
<td>0.096</td>
<td>9.32</td>
</tr>
<tr>
<td></td>
<td>MgCl$_2\cdot$6H$_2$O</td>
<td>30.9</td>
<td>25.5</td>
<td>0.098</td>
<td>9.11</td>
</tr>
<tr>
<td></td>
<td>Ca(NO$_3$)$_2\cdot$4H$_2$O</td>
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<td>25.5</td>
<td>0.104</td>
<td>8.53</td>
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<td>NaCl</td>
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<td>25.1</td>
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<td>1.69</td>
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<tr>
<td></td>
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<td>25.2</td>
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<td>0.244</td>
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<tr>
<td>3</td>
<td>LiBr</td>
<td>11.6</td>
<td>24.6</td>
<td>0.089</td>
<td>10.1</td>
</tr>
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<td></td>
<td>MgCl$_2\cdot$6H$_2$O</td>
<td>31.8</td>
<td>24.6</td>
<td>0.092</td>
<td>9.77</td>
</tr>
<tr>
<td></td>
<td>Ca(NO$_3$)$_2\cdot$4H$_2$O</td>
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<td>24.9</td>
<td>0.097</td>
<td>9.22</td>
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<td>NaCl</td>
<td>67.8</td>
<td>25.2</td>
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<td>5.93</td>
</tr>
<tr>
<td></td>
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<td>LiBr</td>
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<td>24.0</td>
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<td></td>
<td>MgCl$_2\cdot$6H$_2$O</td>
<td>34.0</td>
<td>23.9</td>
<td>0.091</td>
<td>9.89</td>
</tr>
<tr>
<td></td>
<td>Ca(NO$_3$)$_2\cdot$4H$_2$O</td>
<td>51.9</td>
<td>23.8</td>
<td>0.098</td>
<td>9.11</td>
</tr>
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<td></td>
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<td>23.9</td>
<td>0.230</td>
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<tr>
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<td>LiBr</td>
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<td>25.0</td>
<td>0.086</td>
<td>10.5</td>
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<tr>
<td></td>
<td>MgCl$_2\cdot$6H$_2$O</td>
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<td>25.2</td>
<td>0.089</td>
<td>10.1</td>
</tr>
<tr>
<td></td>
<td>Ca(NO$_3$)$_2\cdot$4H$_2$O</td>
<td>45.4</td>
<td>25.4</td>
<td>0.091</td>
<td>9.89</td>
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<tr>
<td></td>
<td>NaCl</td>
<td>67.6</td>
<td>25.2</td>
<td>0.156</td>
<td>5.36</td>
</tr>
<tr>
<td>(108)</td>
<td>K$_2$SO$_4$</td>
<td>87.8</td>
<td>25.2</td>
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<tr>
<td>6</td>
<td>LiBr</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>MgCl$_2\cdot$6H$_2$O</td>
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<td></td>
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<td>K$_2$SO$_4$</td>
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Figure 4.2.6: Impedance Response of the Aluminium Hydroxide Film to Changes in Atmospheric Relative Humidity

(a)
From the plots of $\log_{10}S$ vs relative humidity (Figure 4.2.6(c)) it is evident that the aluminium hydroxide film does indeed exhibit sensitivity to changes in atmospheric humidity. The poor initial sensitivity over the range 0 to 40 %RH may be attributed [49] to the initial build-up of a monolayer of physisorbed water at the hydroxide surface, complete at around 40 %RH. When dealing with a dry film alumina humidity sensor, the formation of this monolayer is marked by the device’s most sensitive response to increasing atmospheric humidity. In this region of the relative humidity spectrum, the majority of current is carried by a phonon-induced electron tunnelling mechanism at the alumina surface (see Appendix 2). The magnitude of this current increases with the number of adsorbed water molecules which donate electrons to the substrate’s conduction bands. Once the monolayer is complete, the device responds, less sensitively, to further increases in atmospheric humidity by means of proton conduction (via the Grøthuss chain reaction [50] or ‘proton hopping’ mechanism) across a second physisorbed layer which now begins to form. However, in the case of an aluminium hydroxide sensor, it is reasonable to assume that near monolayer coverage of water may already have occurred before the device was exposed to a humidified atmosphere. This is probably the case since no calcination of the film was carried out and therefore, the hydroxide surface will continue to be hydrated until subjected to such a process. Thus, below 40 %RH the surface coverage of physisorbed water may be complete, giving rise to a sensor surface which is non-responsive to relative humidities of less than 40 %RH. Above this value, as with an alumina-based sensor, a second physisorbed layer will form and proton conduction will then explain the more sensitive nature of the device to high levels of humidity. At this higher end of the humidity range, solvated aluminium and sulphate ions (residual electrolyte, trapped in the hydroxide film during the deposition stage) also aid the conduction process and reduce the sensor’s impedance. Thus, over the 40 to 100 %RH range, the sensor demonstrates very good sensitivity to changes in relative
humidity; having a mean slope (in this range) of -0.0369 per 1 % change in %RH compared to -0.0508 for the commercially available NPH-50A device from Nemoto & CO. LTD. (see Table 4.2.4 for linear regression analysis of data obtained for NPH-50A and hydroxide film sensor in the 40 to 100 %RH region). Unfortunately, looking at the spread of the plots for the aluminium hydroxide sensor's humidity response, its precision does not appear to be particularly reproducible. This may be due to ageing of the hydroxide film during periods of desiccation between runs; gradual loss of chemisorbed water would result in a change in the overall stoichiometry [51,52] of the film giving rise to changes in its ability to take up water and thereby affecting its response to humidity.

Directly following the end of run 6, during which (as with the previous 5 runs) the test sensor was exposed to increasing humidity, exposure to decreasing humidity was carried out in order to investigate any hysteresis problems with the device. As with all previous runs, one hour was allowed for equilibration of the humidified atmosphere contained in each chamber and a further 30 minutes for re-equilibration following insertion of the test and reference sensors. The results can be seen in Table 4.2.5 and Figure 4.2.7. From the plots of sensor impedance (S) and $\log_{10}S$ vs relative humidity (Figure 4.2.7(b) and 4.2.7(c) respectively) it can be seen that the response to decreasing humidity closely follows the response to increasing humidity under the conditions used in this particular test. Therefore, under such conditions, this type of sensing device does not appear to have significant hysteresis problems.
Table 4.2.4: Linear Regression of Impedance Data from Both the Aluminium Hydroxide and Commercial Sensor in the 40-100 %RH Region

<table>
<thead>
<tr>
<th>Sensor Device</th>
<th>Run No</th>
<th>%RH</th>
<th>( V_{\text{out}} / V )</th>
<th>( \log_{10}S )</th>
<th>Gradient</th>
<th>Intercept</th>
<th>Mean Gradient</th>
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<tbody>
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<td>A. H.</td>
<td>1</td>
<td>45.1</td>
<td>0.166</td>
<td>6.70</td>
<td>-0.0325</td>
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<tr>
<td></td>
<td></td>
<td>68.7</td>
<td>0.599</td>
<td>5.82</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>89.2</td>
<td>0.842</td>
<td>5.27</td>
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<td>0.385</td>
<td>6.20</td>
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<td>0.824</td>
<td>5.32</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>A. H.</td>
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<td>0.104</td>
<td>6.93</td>
<td>-0.0363</td>
<td>8.62</td>
<td></td>
</tr>
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<td>68.2</td>
<td>0.369</td>
<td>6.23</td>
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<td></td>
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<td>0.802</td>
<td>5.39</td>
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<tr>
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<td>8.82</td>
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<td></td>
<td></td>
<td>67.8</td>
<td>0.143</td>
<td>6.77</td>
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<tr>
<td></td>
<td></td>
<td>88.7</td>
<td>0.761</td>
<td>5.49</td>
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</tr>
<tr>
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<td>51.9</td>
<td>0.098</td>
<td>6.96</td>
<td>-0.0405</td>
<td>9.24</td>
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<td>75.7</td>
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<td>6.52</td>
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<td>0.902</td>
<td>5.03</td>
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<td>0.808</td>
<td>5.37</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>C.</td>
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<td>0.093</td>
<td>6.98</td>
<td>-0.0458</td>
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<tr>
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<td></td>
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<td>0.962</td>
<td>4.59</td>
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<tr>
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<td></td>
<td>87.6</td>
<td>0.939</td>
<td>4.81</td>
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</tbody>
</table>

A. H. = Aluminium Hydroxide
C. = Commercial
Table 4.2.5: Test for Hysteresis in Sensor Response to Increasing and Decreasing Humidity

<table>
<thead>
<tr>
<th>Constant Humidity Salt</th>
<th>Relative Humidity /%RH</th>
<th>Temperature /°C</th>
<th>Vout /V</th>
<th>Sensor Impedance, S /MΩ</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBr</td>
<td>12.8</td>
<td>25.0</td>
<td>0.086</td>
<td>10.5</td>
</tr>
<tr>
<td>MgCl₂·6H₂O</td>
<td>31.5</td>
<td>25.2</td>
<td>0.089</td>
<td>10.1</td>
</tr>
<tr>
<td>Ca(NO₃)₂·4H₂O</td>
<td>45.4</td>
<td>25.4</td>
<td>0.091</td>
<td>9.89</td>
</tr>
<tr>
<td>NaCl</td>
<td>67.6</td>
<td>25.2</td>
<td>0.156</td>
<td>5.36</td>
</tr>
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<td>K₂SO₄</td>
<td>87.8</td>
<td>25.2</td>
<td>0.808</td>
<td>0.235</td>
</tr>
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<td>MgCl₂·6H₂O</td>
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<tr>
<td>LiBr</td>
<td>13.1</td>
<td>25.3</td>
<td>0.092</td>
<td>9.77</td>
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Figure 4.2.7: Impedance Response of the Aluminium Hydroxide Sensor to Increasing and Decreasing Humidity - Test for Hysteresis

(a)
4.2.6: Impedance Analysis of the Cathodically Precipitated Sensor at a Range of Humidities

A brief introduction to the technique of impedance analysis is given in Appendix 3.

Following investigation of the aluminium hydroxide sensor's response to changing humidity, it was decided that an impedance analysis should be carried out at each of the five previously used humidity levels in order to further probe the processes involved in determining its response characteristics. Hence, the cathodically precipitated film was connected (via the electrode on which it was deposited) to the 1250 Frequency Response Analyser (FRA) as shown in Figure 4.2.2. The sensor was connected to the FRA's analyser channel 2 (measuring the potential dropped across it in volts), whilst a 0.958 MΩ resistor was connected to channel 1 (measuring the current, in amps, through the series circuit comprising it and the sensor). Hence, the FRA's output reading (the ratio of channel 2 over channel 1), once multiplied by a factor of $0.958 \times 10^6$, gave the sensor impedance (in complex number form) in ohms.

Beginning with the LiBr humidity chamber, previously sealed and placed in a water bath at 25°C for 1 hour, the test sensor (aluminium hydroxide) and Vaisala reference sensor were sealed inside and a period of 30 minutes allowed for re-equilibration of the humidified atmosphere. Following this a frequency scan was initiated with initial frequency 65 kHz and final frequency 100 mHz at an amplitude of 1 V. A large amplitude was required since the sensor has an unusually high impedance compared to most electrochemical systems (which require less than 100 mV amplitude to probe any electrochemistry occurring) and conduction within the device occurs at the porous surface of a poorly conducting deposit and not at a bare metal electrode. The scan was executed logarithmically with 10 steps per decade of decreasing frequency.
and an integration time (during which the impedance response was ‘averaged’) equivalent to 5 cycles at each frequency step, until 1 Hz when the integration time was set to 120 seconds per step. The impedance response was recorded as a three column data set: frequency, real part and imaginary part impedance by the serial interfaced PC. Temperature and relative humidity were recorded at the beginning and end of the frequency scan and an average value taken. The whole process was repeated in each of the four remaining chambers in order of increasing relative humidity, and following a period of 4 days, during which the test sensor was placed in the desiccant chamber, the entire experiment was repeated. Temperature and relative humidity readings at each phase can be seen in Tables 4.2.6(a) and 4.2.6(b), and visual representations of the impedance response of the sensor at each humidity level are shown, as complex plane plots, in Figure 4.2.8.
Table 4.2.6(a): Temperature and Relative Humidity Readings for the First Run of Impedance Analyses

<table>
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<th>Humidity Salt</th>
<th>Temperature °C</th>
<th>Relative Humidity /%RH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>Final</td>
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<tr>
<td>K₂SO₄</td>
<td>24.9</td>
<td>25.3</td>
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Table 4.2.6(b): Temperature and Relative Humidity Readings for the Second Run of Impedance Analyses

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<td>Ca(NO₃)₂·4H₂O</td>
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<td>NaCl</td>
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<tr>
<td>K₂SO₄</td>
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Figure 4.2.8: Impedance Spectra, in Complex Plane Representation, of the Aluminium Hydroxide Sensor at Various Relative Humidities

Run 1
(a) 12.5 %RH
(b) 31.2 %RH
(c) 48.2 %RH
(d) 69.8 %RH
(e) 91.7 %RH
Run 2

(f) 9.9 %RH

[Graph showing impedance vs. frequency with markers indicating low frequency region]
(g) 30.4 %RH

![Graph showing real impedance vs Imaginary impedance with Low Frequency indication]
(h) 45.8% RH
(i) 66.4 %RH
(j) 86.8 %RH

Real Impedance (ohms)

Imaginary Impedance (ohms)
The impedance spectra representing data acquired at the four lower relative humidity levels (Figures 4.2.8(a), (b), (c) and (d) for run 1 and (f), (g), (h) and (i) for run 2) clearly take the form of a double semicircle (although a certain amount of distortion is observed at 69.8 %RH). This is characteristic of a circuit having a series combination of two parallel RC circuits, as is the case with a system comprising two non-blocking electrodes. The non-zero intercept on the Z' axis of the high frequency semicircle indicates that an equivalent circuit model for this system must contain a third resistance in series with the two parallel RC combinations. Thus, the predicted model to which the experimental data must be fitted is as shown in Figure 4.2.9. This is similar to a model proposed by Jason and Woods [53,42] for a typical dry film alumina sensor (prepared by anodisation of an aluminium surface in acid electrolyte) shown schematically in Figure A2.1 in Appendix 2. Their model, which may be mathematically equated to the circuit depicted in Figure 4.2.9 has C1 and R1 equal to the capacitance and leakage resistance of a mixed air, alumina and water dielectric (the thickness of which is that of the porous oxide layer), R2 as the base resistance (relating to the coherent alumina film in contact with the aluminium surface), C2 as the corresponding capacitance and R3 as the resistance along the pore sides. The R2/C2 combination, being related to the aluminium/alumina interface, may also incorporate the double layer capacitance and charge transfer resistance arising from electrochemical processes occurring there. It is reasonable to assume that a similar analogy could be made for the aluminium hydroxide film under investigation here. However, R2 and C2 must now relate to the combined resistance and capacitance of two coherent hydroxide layers; one at the surface of each palladium electrode contact. The hydroxide deposit in contact with the palladium surface will be more compact than the material at its outermost surface because of pH cycling and the compaction mechanism described in Chapters 2 and 3. Therefore, this layer may be treated as analogous to the coherent base layer in an alumina-based device. The low frequency
A semicircle corresponding to these layers will, in the case of the hydroxide sensor, also relate to the double layer capacitance and charge transfer resistance of any palladium dissolution/plating or hydrogen absorption/desorption (via redox processes) occurring at the two palladium-aluminium hydroxide interfaces.

**Figure 4.2.9:** Predicted Equivalent Circuit Model of the Sensor in the Relative Humidity Range 10 to 70 %RH

![Equivalent Circuit Model](image)

Equivalent circuit modelling of impedance data obtained at each of the four lower humidity levels was carried out with the aid of J. Ross MacDonald’s LEVM 6.0 complex non-linear least squares immitance fitting programme. The programme’s circuit model K was employed, removing components as required in order to obtain the model circuit shown in Figure 4.2.9. Modelled data (along with the original experimental data) is displayed as a solid line in the respective plots of Figure 4.2.10. The fitting results can be seen in Table 4.2.7 and a summary of the model circuit component values is given in Table 4.2.8.
Figure 4.2.10: Complex Plane Representations of Experimental and Modelled Impedance Data Obtained from the Aluminium Hydroxide Sensor at Relative Humidities in the Range 10 to 70 %RH

Run 1
(a) 12.5 %RH
(b) 31.2 %RH
(c) 48.2 %RH

![Graph of real and imaginary impedance vs. frequency with fitted and experimental data, showing a low frequency region.](image)
(d) 69.8 %RH
Run 2
(e) 9.9 %RH
(f) 30.4 %RH

Graph showing real and imaginary impedance plotted against frequency. The graph includes two sets of data: fitted data and experimental data. A low frequency region is indicated on the graph.
(g) 45.8 %RH
(h) 66.4 %RH
Table 4.2.7(a): Example of Equivalent Circuit Fitting Results

LEVM : COMPLEX NONLINEAR LEAST SQUARES IMPEDANCE DATA FITTING PROGRAM
VERSION 6.0 - 2/18/93

**Impedance spectrum at 12.5 %RH (film 1, batch 1)\)**

**DATA ENTERED IN ZR FORMAT TO BE USED IN ZR FIT:**

**CIRCUIT MODEL : K**

---

**INITIAL PARAMETER GUESSES AND FIXED (0) OR FREE (1 OR 2) STATUS**

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**WEIGHTS INVOLVE THE MAGNITUDES OF DATA OR FUNCTION VALUES RAISED TO THE POWER 0.0000000E+00**

**-NO TRANSFORMATION MADE: DATA IN ZR FORMAT**

**ALGORITHM TERMINATES HAVING ESTIMATED THAT THE RELATIVE ERROR IN THE SUM OF SQUARES IS AT MOST FTOL**

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**PDAY= 8.5806D-03**

**PDRMS= 9.5802D-03**

---

**END MAIN FIT **
Key to Table 4.2.7(a):

1 Brief title/description of experimental data to be fitted

2 Describes the format of raw data used. Here, ZR refers to a three column data set comprising Frequency (Hz), Real Part Impedance (Ω) and Imaginary Part Impedance (Ω).

3 Indicates the circuit model to which the data is to be fitted.

4 Gives the number of data points used in the fitting process.

5 Indicates the number of components in the fitting circuit which have not been assigned fixed numerical values.

6 Shows the maximum number of iterations carried out by the fitting programme before it displays its results.

7 Gives the initial guesses/estimates of the non-fixed components of the fitting circuit (input by the user). A number 1 or 2 following the initial guess indicates that this component value will be a variable used in the fitting process, whilst the presence of a zero denotes that the component value is fixed (if entered) or of zero magnitude and therefore does not play an active part in the fitting process. All zero magnitude components are removed from the initial circuit model by their conversion (within the model) to series connected resistors with zero magnitude resistance. Thus the programme uses just eleven circuit models which may be tailored (by selective removal of components) to give vast array of equivalent circuits to which experimental data may be fitted.

8 Gives the values of equivalent circuit components as estimated by the LEVM 6 fitting programme. Row one refers to the component numbers as outlined in the circuit model and in section 7 of the output file, row two gives the fitted component values and rows three and four, respectively, provide estimates to the standard deviation and relative standard deviation of these values.
Table 4.2.7(b): Equivalent Circuit Fitting Results at 12.5 %RH, Run 1

**LEVM :** COMPLEX NON-LINEAR LEAST SQUARES IMPEDANCE DATA FITTING PROGRAM
**VERSIO N 6.0 - 2/18/93**

Impedance spectrum at 12.5 %RH (film 1, batch 1)
DATA ENTERED IN ZR FORMAT TO BE USED IN ZR FIT; CIRCUIT MODEL : K

********** FIT OF COMPLEX DATA **********
- # OF DATA POINTS = 60
- WEIGHT: IRCH = 2
- # OF FREE PARAMETERS = 5
- PRINTS EVERY -1 ITERATIONS
- MAX # ITERATIONS=100
- MAIN WT USES: DATA

WEIGHTS INVOLVE THE MAGNITUDES OF DATA OR FUNCTION VALUES RAISED TO THE POWER 0.000000D+00

**INITIAL PARAMETER GUESSES AND FIXED (0) OR FREE (1 OR 2) STATUS**

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NO TRANSFORMATION MADE: DATA IN ZR FORMAT

ALGORITHM TERMINATES HAVING ESTIMATED THAT THE RELATIVE ERROR IN THE SUM OF SQUARES IS AT MOST FTOL

FINAL L2 NORM OF THE RESIDUALS .14142132D+07
NUMBER OF FUNCTION EVALUATIONS 44
NUMBER OF JACOBIAN EVALUATIONS 38

WEIGHTED SUM OF SQUARES, S: 2.0093077717211D+12
SIGNIF SQUARES ESTIMATE, XS: 1.7393980623662D-10
SIGNIF ESTIMATE: 3.409D-03
NO. DEGREES OF FREEDOM: 115

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PARAMETER ESTIMATES
ESTIMATED STD DEV OF PARAMETERS
ESTIMATED RELATIVE STD DEV OF PARAMETERS

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ESTIMATED PARAMETER CORRELATION MATRIX

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|-----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
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********** END MAIN FIT **********
Table 4.2.7(c): Equivalent Circuit Fitting Results at 31.2 %RH, Run 1

LEVNI: COMPLEX NON-LINEAR LEAST SQUARES INMITTANCE DATA FITTING PROGRAM
VERSION 6.0 - 2/18/93

Impedance spectrum at 31.2 %RH (film 1, batch 1)
DATA ENTERED IN ZR FORMAT TO BE USED IN ZR FIT: CIRCUIT MODEL: X
********** FIT OF COMPLEX DATA **********
- # OF DATA POINTS = 60 WEIGHT: INCH = 2 # OF FREE PARAMETERS = 5
- PRINTS EVERY -1 ITERATIONS MAX # ITERATIONS=100 MAIN WT USES: DATA

WEIGHTS INVOLVE THE MAGNITUDES OF DATA OR FUNCTION VALUES RAISED TO THE POWER 0.000000+00

INITIAL PARAMETER GUESSES AND FIXED (0) OR FREE (1 OR 2) STATUS
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P( 3) = 1.000000D+07 1 P(19) = 0.000000D-00 0
P( 4) = 1.000000D+07 1 P(20) = 0.000000D-00 0
P( 5) = 1.000000D+07 1 P(21) = 0.000000D-00 0
P( 6) = 0.000000D+00 0 P(22) = 0.000000D+00 0
P( 7) = 0.000000D+00 0 P(23) = 0.000000D+00 0
P( 8) = 0.000000D+00 0 P(24) = 0.000000D+00 0
P( 9) = 0.000000D+00 0 P(25) = 0.000000D+00 0
P(10) = 0.000000D+00 0 P(26) = 0.000000D+00 0
P(11) = 0.000000D+00 0 P(27) = 0.000000D+00 0
P(12) = 0.000000D+00 0 P(28) = 0.000000D+00 0
P(13) = 0.000000D+00 0 P(29) = 0.000000D+00 0
P(14) = 0.000000D+00 0 P(30) = 0.000000D+00 0
P(15) = 0.000000D+00 0 P(31) = 0.000000D+00 0
P(16) = 0.000000D+00 0 P(32) = 0.000000D+00 0

THE FOLLOWING PARAMETERS ARE ALWAYS FIXED
P(33) = 0.000000D+00 P(37) = 0.000000D-00
P(34) = 0.000000D+00 P(38) = 0.000000D-00
P(35) = 0.000000D+00 P(39) = 0.000000D-00
P(36) = 0.000000D+00 P(40) = 0.000000D-00

-NONE TRANSFORMATION MADE: DATA IN ZR FORMAT

ALGORITHM TERMINATES HAVING ESTIMATED THAT THE RELATIVE ERROR
IN THE SUM OF SQUARES IS AT MOST FTOL

FINAL L2 NORM OF THE RESIDUALS .13953970+07
NUMBER OF FUNCTION EVALUATIONS 44
NUMBER OF JACOBIAN EVALUATIONS 38

WEIGHTED SUM OF SQUARES, S: 1.94713272930840+12
SIGMA SQUARED ESTIMATE, XS: 1.69315889505080+10
SIGMA ESTIMATE: 1.30121439242380+05
FIT QUALITY FACTOR: 3.4068-03
NO. DEGREES OF FREEDOM: 115

ORIGINAL PARAMETER NUMBERS
PARAMETER ESTIMATES
ESTIMATED STD DEV OF PARAMETERS
ESTIMATED RELATIVE STD DEV OF PARAMETERS

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PDAV= 8.5147D-03 PDMS= 9.5131D-03

ESTIMATED PARAMETER CORRELATION MATRIX

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************** END MAIN FIT **************
Table 4.2.7(d): Equivalent Circuit Fitting Results at 48.2 % RH, Run 1

| LEVM : COMPLEX NON-LINEAR LEAST SQUARES IMMITTANCE DATA FITTING PROGRAM |
| VERSION 6.0 - 2/18/93 |

Impedance spectrum at 48.2 % RH (film 1, batch 1)

DATA ENTERED IN ZR FORMAT TO BE USED IN ZR FIT;
CIRCUIT MODEL: K

********** FIT OF COMPLEX DATA **********

- # OF DATA POINTS = 60  WEIGHT: IRCH = 2  # OF FREE PARAMETERS = 5
- PRINTS EVERY 1 ITERATIONS  MAX # ITERATIONS=100  MAIN WT USES: DATA

WEIGHTS INVOLVE THE MAGNITUDES OF DATA OR FUNCTION VALUES RAISED TO THE POWER 0.000000+00

INITIAL PARAMETER GUESSES AND FIXED (0) OR FREE (1 OR 2) STATUS

| P(1) = 1.000000D-04  | P(17) = 0.000000D-00  |
| P(2) = 1.000000D-07  | P(18) = 0.000000D-00  |
| P(3) = 1.000000D-04  | P(19) = 0.000000D-00  |
| P(4) = 1.000000D-07  | P(20) = 0.000000D-00  |
| P(5) = 1.000000D-03  | P(21) = 0.000000D-00  |
| P(6) = 0.000000D-00  | P(22) = 0.000000D-00  |
| P(7) = 0.000000D-00  | P(23) = 0.000000D-00  |
| P(8) = 0.000000D-00  | P(24) = 0.000000D-00  |
| P(9) = 0.000000D-00  | P(25) = 0.000000D-00  |
| P(10) = 0.000000D-00 | P(26) = 0.000000D-00 |
| P(11) = 0.000000D-00 | P(27) = 0.000000D-00 |
| P(12) = 0.000000D-00 | P(28) = 0.000000D-00 |
| P(13) = 0.000000D-00 | P(29) = 0.000000D-00 |
| P(14) = 0.000000D-00 | P(30) = 0.000000D-00 |
| P(15) = 0.000000D-00 | P(31) = 0.000000D-00 |
| P(16) = 0.000000D-00 | P(32) = 0.000000D-00 |
| P(33) = 0.000000D-00 | P(37) = 0.000000D-00 |
| P(34) = 0.000000D-00 | P(38) = 0.000000D-00 |
| P(35) = 0.000000D-00 | P(39) = 0.000000D-00 |
| P(36) = 0.000000D-00 | P(40) = 0.000000D-00 |
|                 | P(33) = 0.000000D-00 |

THE FOLLOWING PARAMETERS ARE ALWAYS FIXED

1. 6.48700+06  2. 6.28100-08  3. 1.57900+07  4. 1.79830-11  5. 3.18060+06

FAV 2.6360-02  PRMS= 1.5684D-02

ESTIMATED PARAMETER CORRELATION MATRIX

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PDAv= 1.4005D-02  PDv= 1.5684D-02

ESTIMATED PARAMETER CORRELATION MATRIX

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AV WR 1.120D+04  SD WR 1.461D+05  SD WR 2.092D+05  # OPIT 1.120D+04  0

AV RR 2.632D-02  SD RR 1.440D-01  SD RC 6.118D-01  # OPIT 1.120D+04  0

************** END MAIN FIT **************
Table 4.2.7(e): Equivalent Circuit Fitting Results at 69.8 %RH, Run 1

LEV = COMPLEX NON-LINEAR LEAST SQUARES IMPEDANCE DATA FITTING PROGRAM
VERSION 6.0 - 2/18/93

Impedance spectrum at 69.8 %RH (film 1, batch 1, run 1)
DATA ENTERED IN ZR FORMAT TO BE USED IN ZR FIT: CIRCUIT MODEL: K

********** FIT OF COMPLEX DATA **********
- # OF DATA POINTS = 60  WEIGHT: INCN = 2  # OF FREE PARAMETERS = 5
- PRINTS EVERY -1 ITERATIONS  MAX # ITERATIONS = 100  MAIN WT USES: DATA
WEIGHTS INVOLVE THE MAGNITUDES OF DATA OR FUNCTION VALUES RAISED TO THE POWER 0.000000D+00

INITIAL PARAMETER GUESSES AND FIXED (0) OR FREE (1 OR 2) STATUS
P(1) = 1.000000D+04  1  P(17) = 0.000000D-00  0
P(2) = 1.000000D-07  1  P(18) = 0.000000D-00  0
P(3) = 1.000000D-04  1  P(19) = 0.000000D-00  0
P(4) = 1.000000D-07  1  P(20) = 0.000000D-00  0
P(5) = 1.000000D-03  1  P(21) = 0.000000D-00  0
P(6) = 0.000000D+00  0  P(22) = 0.000000D-00  0
P(7) = 0.000000D+00  0  P(23) = 0.000000D-00  0
P(8) = 0.000000D+00  0  P(24) = 0.000000D-00  0
P(9) = 0.000000D+00  0  P(25) = 0.000000D-00  0
P(10) = 0.000000D+00  0  P(26) = 0.000000D-00  0
P(11) = 0.000000D+00  0  P(27) = 0.000000D-00  0
P(12) = 0.000000D+00  0  P(28) = 0.000000D-00  0
P(13) = 0.000000D+00  0  P(29) = 0.000000D-00  0
P(14) = 0.000000D+00  0  P(30) = 0.000000D-00  0
P(15) = 0.000000D+00  0  P(31) = 0.000000D-00  0
P(16) = 0.000000D+00  0  P(32) = 0.000000D-00  0
P(33) = 0.000000D-00  0  P(37) = 0.000000D-00  0
P(34) = 0.000000D-00  0  P(38) = 0.000000D-00  0
P(35) = 0.000000D-00  0  P(39) = 0.000000D-00  0
P(36) = 0.000000D-00  0  P(40) = 0.000000D-00  0

THE FOLLOWING PARAMETERS ARE ALWAYS FIXED
P(33) = 0.000000D-00  P(37) = 0.000000D-00
P(34) = 0.000000D-00  P(38) = 0.000000D-00
P(35) = 0.000000D-00  P(39) = 0.000000D-00
P(36) = 0.000000D-00  P(40) = 0.000000D-00

-NO TRANSFORMATION MADE: DATA IN ZR FORMAT

ALGORITHM TERMINATES HAVING ESTIMATED THAT THE RELATIVE ERROR
IN THE SUM OF SQUARES IS AT MOST 1.0E-05

FINAL L2 NORM OF THE RESIDUALS  .5631243D+07
NUMBER OF FUNCTION EVALUATIONS  42
NUMBER OF JACOBIAN EVALUATIONS  36

WEIGHTED SUM OF SQUARES, S:  3.17109014949480D+13
SIGMAF SQUARED ESTIMATE, XS:  2.75746969521290D+11
SIGMAF ESTIMATE:  5.25116148600750D+05
FIT QUALITY FACTOR:  3.741D+03
NO. DEGREES OF FREEDOM:  115

ORIGINAL PARAMETER NUMBERS
PARAMETER ESTIMATES
ESTIMATED STD DEV OF PARAMETERS
ESTIMATED RELATIVE STD DEV OF PARAMETERS

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PDAV = 4.0026D+02  FDRMS = 4.2452D-02

ESTIMATED PARAMETER CORRELATION MATRIX

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********** END MAIN FIT **********
Table 4.2.7(f): Equivalent Circuit Fitting Results at 9.9 %RH, Run 2

LEVY : COMPLEX NON-LINEAR LEAST SQUARES IMMITTANCE DATA FITTING PROGRAM
VERSION 6.0 - 2/18/93

Impedance spectrum at 9.9 %RH (film 1, batch 2)
DATA ENTERED IN ZR FORMAT TO BE USED IN ZR FIT:
CIRCUIT MODEL : K

************ FIT OF COMPLEX DATA ************
- # OF DATA POINTS = 60
- WEIGHT: IRCH = 2
- # OF FREE PARAMETERS = 5
- PRINTS EVERY 1 ITERATIONS MAX # ITERATIONS=100
- MAIN WT USES: DATA

WEIGHTS INVOLVE THE MAGNITUDES OF DATA OR FUNCTION VALUES RAISED TO THE POWER 0.000000+00

INITIAL PARAMETER GUESSES AND FIXED (0) OR FREE (1 OR 2) STATUS

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THE FOLLOWING PARAMETERS ARE ALWAYS FIXED

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- NO TRANSFORMATION MADE: DATA IN ZR FORMAT

ALGORITHM TERMINATES HAVING ESTIMATED THAT THE RELATIVE ERROR IN THE SUM OF SQUARES IS AT MOST FPOL

FINAL L2 NORM OF THE RESIDUALS .11170270E+07
NUMBER OF FUNCTION EVALUATIONS 43
NUMBER OF JACOBIAN EVALUATIONS 37

WEIGHTED SUM OF SQUARES, S: 1.24774877915880E+12
SIGMAF SQUARED ESTIMATE, XS: 1.08499893839900E+10
SIGMAF ESTIMATE: 1.04163282321510E+05
FIT QUALITY FACTOR: 3.3520E+03
NO. DEGREES OF FREEDOM: 115

ORIGINAL PARAMETER NUMBERS
PARAMETER ESTIMATES
ESTIMATED STD DEV OF PARAMETERS
ESTIMATED RELATIVE STD DEV OF PARAMETERS

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ESTIMATED PARAMETER CORRELATION MATRIX

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<td>.1416D-00</td>
<td>.1718D-00</td>
<td>.2035D-00</td>
<td>.2357D-00</td>
</tr>
<tr>
<td>PDMS</td>
<td>.1000D-01</td>
<td>.1416D-00</td>
<td>.1718D-00</td>
<td>.2035D-00</td>
<td>.2357D-00</td>
</tr>
</tbody>
</table>

AV WR  SD WR  SD WI  SD WC  AV FR
1.442D+04 1.213D+05 8.928D-04 1.042D-05 -1.442D+04 0

AV RR  SD RR  SD RI  SD RC  SSE
2.452D-02 1.153D-02 1.432D-01 9.939D-02 5.433D-01 0

************** END MAIN FIT **************

144
Table 4.2.7(g): Equivalent Circuit Fitting Results at 30.4 %RH, Run 2

LEVM : COMPLEX NON-LINEAR LEAST SQUARES IMMITTANCE DATA FITTING PROGRAM
VERSION 6.0 - 2/18/93

Impedance spectrum at 30.4 %RH (film 1, batch 2)
DATA ENTERED IN ZR FORMAT TO BE USED IN ZR FIT;
CIRCUIT MODEL : K

********** FIT OF COMPLEX DATA **********
- # OF DATA POINTS = 60    WEIGHT: IRCH = 2
- PRINTS EVERY -1 ITERATIONS MAX # ITERATIONS=100    MAIN WT USES: DATA
- WEIGHTS INVOLVE THE MAGNITUDES OF DATA OR FUNCTION VALUES RAISED TO THE POWER 0.000000+00

INITIAL PARAMETER GUESSES AND FIXED (0) OR FREE (1 OR 2) STATUS
P( 1) = 1.000000D+04 1     P(17) = 0.000000D+00 0
P( 2) = 1.000000D+07 1     P( 8) = 0.000000D+00 0
P( 3) = 1.000000D+04 1     P(19) = 0.000000D+00 0
P( 4) = 1.000000D-07 1     P(20) = 0.000000D+00 0
P( 5) = 1.000000D-03 1     P(21) = 0.000000D+00 0
P( 6) = 0.000000D+00 0     P(22) = 0.000000D+00 0
P( 7) = 0.000000D+00 0     P(23) = 0.000000D+00 0
P( 8) = 0.000000D-04 0     P(24) = 0.000000D+00 0
P( 9) = 0.000000D-00 0     P(25) = 0.000000D+00 0
P(10) = 0.000000D-00 0     P(26) = 0.000000D+00 0
P(11) = 0.000000D+00 0     P(27) = 0.000000D+00 0
P(12) = 0.000000D+00 0     P(28) = 0.000000D+00 0
P(13) = 0.000000D+00 0     P(29) = 0.000000D+00 0
P(14) = 0.000000D+00 0     P(30) = 0.000000D+00 0
P(15) = 0.000000D+00 0     P(31) = 0.000000D+00 0
P(16) = 0.000000D+00 0     P(32) = 0.000000D+00 0

THE FOLLOWING PARAMETERS ARE ALWAYS FIXED
P(33) = 0.000000D+00 0     P(37) = 0.000000D+00 0
P(34) = 0.000000D+00 0     P(38) = 0.000000D+00 0
P(35) = 0.000000D+00 0     P(39) = 0.000000D+00 0
P(36) = 0.000000D+00 0     P(40) = 0.000000D+00 0

-NO TRANSFORMATION MADE: DATA IN ZR FORMAT

ALGORITHM TERRMINATES HAVING ESTIMATED THAT THE RELATIVE ERROR IN THE SUM OF SQUARES IS AT MOST FTOL

FINAL L2 NORM OF THE RESIDUALS .14675270+07
NUMBER OF FUNCTION EVALUATIONS 46
WEIGHTED SUM OF SQUARES, S: 2.15362416410110+12
WEIGHTED SQUARED ESTIMATE, XS: 1.87275534356620+10
FIT QUALITY FACTOR: 3.416D+03
NO. DEGREES OF FREEDOM: 115

ORIGINAL PARAMETER NUMBERS
PARAMETER ESTIMATES ESTIMATED STD DEV OF PARAMETERS
ESTIMATED RELATIVE STD DEV OF PARAMETERS

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<tr>
<th>Parameter</th>
<th>Estimate</th>
<th>Std Dev</th>
<th>Rel Std Dev</th>
</tr>
</thead>
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<td>0.000000D+00</td>
</tr>
<tr>
<td>P(2)</td>
<td>1.000000D+07</td>
<td>0.000000D+00</td>
<td>0.000000D+00</td>
</tr>
<tr>
<td>P(3)</td>
<td>1.000000D+04</td>
<td>0.000000D+00</td>
<td>0.000000D+00</td>
</tr>
<tr>
<td>P(4)</td>
<td>1.000000D-07</td>
<td>0.000000D+00</td>
<td>0.000000D+00</td>
</tr>
<tr>
<td>P(5)</td>
<td>1.000000D-03</td>
<td>0.000000D+00</td>
<td>0.000000D+00</td>
</tr>
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<td>P(6)</td>
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<td>0.000000D+00</td>
<td>0.000000D+00</td>
</tr>
<tr>
<td>P(7)</td>
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<td>0.000000D+00</td>
<td>0.000000D+00</td>
</tr>
<tr>
<td>P(8)</td>
<td>0.000000D-04</td>
<td>0.000000D+00</td>
<td>0.000000D+00</td>
</tr>
<tr>
<td>P(9)</td>
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<td>P(11)</td>
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<tr>
<td>P(13)</td>
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<td>0.000000D+00</td>
<td>0.000000D+00</td>
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<tr>
<td>P(14)</td>
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<td>0.000000D+00</td>
<td>0.000000D+00</td>
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<tr>
<td>P(15)</td>
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<td>0.000000D+00</td>
<td>0.000000D+00</td>
</tr>
<tr>
<td>P(16)</td>
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<td>0.000000D+00</td>
<td>0.000000D+00</td>
</tr>
</tbody>
</table>

PARAMETER CORRELATION MATRIX

AV WR SD WR SD WI SD WC AV FR # IT
7.3131D+03 1.7660D+05 8.9310D+04 1.3680D+05
AV RR SD RR SD RI SD RC SSE # OPIT
2.102D-02 1.207D-02 1.3990D-01 9.710D-02

*********** END MAIN FIT ***********
Table 4.2.7(h): Equivalent Circuit Fitting Results at 45.8% RH, Run 2

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Estimate</th>
<th>Std Dev</th>
<th>RelStd</th>
<th>Correlation Matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>1.000000D+04</td>
<td>6.79240+06</td>
<td>8.19690+04</td>
<td>1.0000+01 -1.3910+00</td>
</tr>
<tr>
<td>P2</td>
<td>1.000000D+00</td>
<td>5.44930-08</td>
<td>1.18580-09</td>
<td>-1.5910+04 2.4200+05</td>
</tr>
<tr>
<td>P3</td>
<td>1.000000D+04</td>
<td>1.57730+07</td>
<td>5.40430+04</td>
<td>1.8670+05 6.9640-01</td>
</tr>
<tr>
<td>P4</td>
<td>1.000000D+00</td>
<td>1.65520-11</td>
<td>1.61290-13</td>
<td>1.0000+01 2.8570-02</td>
</tr>
<tr>
<td>P5</td>
<td>1.000000D+00</td>
<td>3.55320+06</td>
<td>4.34850+04</td>
<td>2.8570+05 1.4800-02</td>
</tr>
</tbody>
</table>

1. LEVM : COMPLEX NON-LINEAR LEAST SQUARES IMPEDANCE DATA FITTING PROGRAM
2. VERSION 6.0 - 2/18/93
3. Impedance spectrum at 45.8% RH (film 1, batch 2)
4. DATA ENTERED IN ZR FORMAT TO BE USED IN ZR FIT;
5. CIRCUIT MODEL : K
6. FIT QUALITY FACTOR: 3.4920+03
7. NO. DEGREES OF FREEDOM: 115
Table 4.2.7(i): Equivalent Circuit Fitting Results at 66.4 %RH, Run 2

LEVM : COMPLEX NON-LINEAR LEAST SQUARES IMMITTANCE DATA FITTING PROGRAM
VERSION 6.0 - 2/18/93

Impedance spectrum at 66.4 %RH (film 1, batch 2)
DATA ENTERED IN ZR FORMAT TO BE USED IN ZR FIT; CIRCUIT MODEL : K

********** FIT OF COMPLEX DATA **********
- # OF DATA POINTS = 60
- WEIGHT; IRCH = 2
- # OF FREE PARAMETERS = 5
- PRINTS EVERY -1 ITERATIONS
- MAX # ITERATIONS=100
- MAIN WT USES: DATA
WEIGHTS INVOLVE THE MAGNITUDES OF DATA OR FUNCTION VALUES RAISED TO THE POWER 0.000000+00

INITIAL PARAMETER GUESSES AND FIXED (0) OR FREE (1 OR 2) STATUS
P( 1) = 1.000000D+04 1 P(17) = 0.000000D+00 0
P( 2) = 1.000000D-07 1 P(18) = 0.000000D+00 0
P( 3) = 1.000000D+04 1 P(19) = 0.000000D+00 0
P( 4) = 1.000000D-07 1 P(20) = 0.000000D+00 0
P( 5) = 1.000000D-03 1 P(21) = 0.000000D+00 0
P( 6) = 0.000000D+00 0 P(22) = 0.000000D+00 0
P( 7) = 0.000000D+00 0 P(23) = 0.000000D+00 0
P( 8) = 0.000000D+00 0 P(24) = 0.000000D+00 0
P( 9) = 0.000000D+00 0 P(25) = 0.000000D+00 0
P(10) = 0.000000D+00 0 P(26) = 0.000000D+00 0
P(11) = 0.000000D+00 0 P(27) = 0.000000D+00 0
P(12) = 0.000000D+00 0 P(28) = 0.000000D+00 0
P(13) = 0.000000D+00 0 P(29) = 0.000000D+00 0
P(14) = 0.000000D+00 0 P(30) = 0.000000D+00 0
P(15) = 0.000000D+00 0 P(31) = 0.000000D+00 0
P(16) = 0.000000D+00 0 P(32) = 0.000000D+00 0

THE FOLLOWING PARAMETERS ARE ALWAYS FIXED
P(33) = 0.000000D+00 P(37) = 0.000000D+00
P(34) = 0.000000D+00 P(38) = 0.000000D+00
P(35) = 0.000000D+00 P(39) = 0.000000D+00
P(36) = 0.000000D+00 P(40) = 0.000000D+00

NO TRANSFORMATION MADE: DATA IN ZR FORMAT

ALGORITHM TERMINATES HAVING ESTIMATED THAT THE RELATIVE ERROR IN THE SUM OF SQUARES IS AT MOST FTOL
FINAL L2 NORM OF THE RESIDUALS .2277113D+07
NUMBER OF FUNCTION EVALUATIONS 43
NUMBER OF JACOBIAN EVALUATIONS 37
WEIGHTED SUM OF SQUARES, S: 5.18524230535560+12
SIGMAF SQUARED ESTIMATE, XS: 4.5089063524831D+10
SIGMAF ESTIMATE: 2.1234185127963D+05
FIT QUALITY FACTOR: 3.5230+03
NO. DEGREES OF FREEDOM: 115

ORIGINAL PARAMETER NUMBERS
PARAMETER ESTIMATES
ESTIMATED STD DEV OF PARAMETERS
ESTIMATED RELATIVE STD DEV OF PARAMETERS

1 2 3 4 5
1.5233D+07 1.7659D-11 6.2324D-06 7.9719D-08 3.2576D-06
6.0949D-04 2.0243D-13 1.0313D-05 2.1446D-09 4.9281D-06
4.0012D-03 1.1463D-02 1.6548D-02 2.7020D-02 1.5128D-02

PDAV= 1.4832D-02 FORMS= 1.6614D-02

ESTIMATED PARAMETER CORRELATION MATRIX
1.000D+00 0.000D+00 0.000D+00 0.000D+00 0.000D+00
-0.428D+00 1.000D+00 0.000D+00 0.000D+00 0.000D+00
-0.842D+00 0.000D+00 1.000D+00 0.000D+00 0.000D+00
-0.742D+00 0.000D+00 0.000D+00 1.000D+00 0.000D+00
0.842D+00 0.000D+00 0.000D+00 0.000D+00 1.000D+00

AV WR SD WR SD WI SD WC AV FR # IT
8.843D+03 2.056D+05 2.281D+05 2.123D+05 8.843D+03 0

AV RR SD RR SD RI SD RC SSE # OPIT
2.686D-02 1.504D-02 1.880D-01 1.304D-01 3.734D-01 0

************* END MAIN FIT. *************
Table 4.2.8: Equivalent Circuit Component Values Obtained From Complex Non-linear Least Squares Fitting of Impedance Data Using the LEVM 6.0 Programme

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Relative Humidity /%RH</th>
<th>R₁ /ΜΩ</th>
<th>C₁ /nF</th>
<th>R₂ /ΜΩ</th>
<th>C₂ /nF</th>
<th>R₃ /ΜΩ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.5</td>
<td>16.1</td>
<td>0.0181</td>
<td>6.78</td>
<td>54.2</td>
<td>3.08</td>
</tr>
<tr>
<td></td>
<td>31.2</td>
<td>16.4</td>
<td>0.0191</td>
<td>6.83</td>
<td>54.1</td>
<td>2.90</td>
</tr>
<tr>
<td></td>
<td>48.2</td>
<td>15.8</td>
<td>0.0180</td>
<td>6.49</td>
<td>62.8</td>
<td>3.18</td>
</tr>
<tr>
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<td>69.8</td>
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<td>6.99</td>
<td>82.2</td>
<td>3.32</td>
</tr>
<tr>
<td>2</td>
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<td>6.84</td>
<td>52.8</td>
<td>3.26</td>
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<td>30.4</td>
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<td>6.79</td>
<td>54.0</td>
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<td>6.79</td>
<td>54.5</td>
<td>3.55</td>
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<td></td>
<td>66.4</td>
<td>15.2</td>
<td>0.0177</td>
<td>6.23</td>
<td>79.4</td>
<td>3.26</td>
</tr>
</tbody>
</table>

From the results of the LEVM fit (Table 4.2.8) it is clear that several trends occur with increasing relative humidity. On average, the bulk capacitance, C₁, of the sensor increases and the corresponding bulk resistance, R₁, decreases. This is as expected since on exposure to an increasing level of humidity, the sensor takes up an increasing amount of water. At 0 %RH the dielectric will consist predominantly of aluminium hydroxide and air. On exposure to a humidified atmosphere, surface adsorbed water, which has a greater dielectric constant than air, will replace air from the sensor pores and thereby increase the overall dielectric constant of the device. Since capacitance is directly proportional to the dielectric constant, C₁ will increase with %RH. The decrease in R₁ occurs because of the greater surface conductivity (via protons and solvated ions within the adsorbed water layers at the sensor surface) at higher relative humidity. C₂, the capacitance of the coherent surface hydroxide layer, increases with
%RH because, again, adsorbed water will increase the dielectric constant of this layer. However, its more compact nature (as compared to the porous bulk material) should mean that less water is taken up by this component of the device. On the other hand, with increased water adsorption the dissolution of residual electrolyte ions (Al$^{3+}$, SO$_4^{2-}$) in addition to free hydroxyl species should facilitate the build-up of surface charge at both palladium/aluminium hydroxide interfaces. Hence, the quantity of (double layer) charge at these interfaces will be greater at higher relative humidity, and since capacitance is equal to the ratio of charge over potential, at the constant (sinusoidal) potential employed here, the double layer capacitance must also be greater. It is noted that $C_2$ is always larger than $C_1$ since the charge separation in $C_2$ (the thickness of the coherent surface layer) is smaller than that of the bulk porous film; smaller charge separation equates to larger capacitance. In the case of $R_2$, the resistance of the coherent surface layer, it is unclear whether increasing humidity is marked by its overall increase or decrease. Run 1 appears to show an overall increase in $R_2$, while the opposite is true of run 2. Decreasing resistance would be expected as a consequence of increasing surface conduction from adsorbed water and ion dissolution. However, as already discussed, the more compact nature of the surface layer will mean that less water is adsorbed per unit volume here than in the bulk hydroxide deposit, giving rise to a less pronounced change in $R_2$ as compared to $R_1$. Finally, $R_3$, the resistance along the pore walls, appears to remain approximately constant throughout since its magnitude relates to the inherent resistance of the aluminium hydroxide substrate and should therefore be independent of water content.

Impedance data obtained at high relative humidity (91.7 %RH and 88.1 %RH on runs 1 and 2 respectively) proved too complicated to model on any standard equivalent circuit. It is not clear why a high frequency inductive loop (with negative -$Z''$ values) should be present in the impedance spectrum of device which is essentially a capacitor.
with a mixed aluminium hydroxide, air and water dielectric. Inductive semicircles in the impedance spectra of electrochemical systems have been related to corrosion and electrocrystallisation processes [54]. It is thought that the sensor's high water content at high relative humidity, coupled with the large amplitude of the applied potential, may cause dissolution/recrystallisation of the hydroxide film by pH cycling (hydrogen generation and oxidation) at the palladium contact electrode surfaces. This could explain the inductance observed in the impedance data. On partial dissolution (or pitting) of the coherent hydroxide layer, adsorbed water within the sensor's pores would gain access to the bare palladium surface. Thus the impedance of the device would fall dramatically, as is observed. The maximum real part impedance at this level of humidity is approximately 7 MΩ compared to over 20 MΩ at lower relative humidities. In addition to the decreased impedance, electrolyte access to the palladium surfaces would allow water electrolysis to occur. The large amplitude potential to which these electrodes are subjected would then give rise to excessive rates of gas evolution at overpotentials not normally employed in impedance analyses. Hence the impedance spectrum would relate to a complex hybrid of electrochemical processes, hydroxide dissolution and recrystallisation and surface proton conduction: virtually impossible to fit to any equivalent circuit model.

The break-up of the coherent surface hydroxide layer at high relative humidity appears to be entirely reversible; the sensor response to low humidity levels is restored on drying of the device as illustrated by the near identical spectra obtained from the two consecutive runs. However, it is advised that this type of sensor not be exposed to relative humidities as high as 90 %RH, since the uncertain nature of physical and electrochemical processes occurring here will lead to a largely unstable sensor reading. Thus the effective "window" of operation for this device appears to lie between 40 and 90 %RH.
4.3 : Conclusions

It has been successfully demonstrated that cathodic precipitation, via a pulsed potential regime, is a suitable process for the manufacture of humidity sensing devices. An aluminium hydroxide based sensor, generated by such a process, was shown to have good sensitivity to changes in relative humidity over the range 40 to 90 %RH when compared to a commercially available sensor. Furthermore, the sensing device does not appear to suffer substantially from hysteresis problems on exposure to changing levels of atmospheric humidity. Impedance analysis of the sensing film at a range of relative humidities below 70 %RH and subsequent modelling of the acquired data indicate an equivalent circuit model similar to that proposed for a dry-film alumina device. It is therefore reasoned that both employ the same humidity sensing mechanisms. Unfortunately, the sensor response to high relative humidity (90 %RH) did not appear to fit any standard equivalent circuit model.

Improved sensitivity to low levels of relative humidity (< 40 %RH) is expected on calcination of the hydroxide deposit (converting it to a form of alumina) and investigation into the effect of salt doping should eventually yield a device with excellent response characteristics over the entire humidity spectrum.
Chapter 5

Thick Film Generation
Chapter 5 : Thick Film Generation

5.1 : Non-gassing Cathodes

Having established routes to thin films of controllable porosity and having looked briefly at a possible application of such films, it was decided that means of generating thicker deposits of the alumina precursor should be investigated. It was evident that in order to achieve this aim, the cathode substrate onto which the deposits would be precipitated should not be allowed to become saturated with hydrogen. Saturation would eventually lead to outgassing of hydrogen from the cathode which would ultimately dislodge the growing film from the electrode surface. Initial investigations into non-gassing deposition surfaces concentrated on the use of a vacuum chamber (Figure 5.1.1) attached to the rear face of a palladium sheet cathode. Such an arrangement should allow excessive build-up of hydrogen in the palladium lattice to be prevented by its continual removal under decreased pressure. However, an electrochemical solution proved to be more practicable. By employing a palladium sheet in aqueous aluminium sulphate electrolyte between a working anode and counter cathode a bipolar electrode was generated (Figure 5.1.2). This electrode was made to generate hydrogen at its cathodic face, which was subsequently absorbed by the palladium, diffused through the bulk metal substrate, and was then oxidised at the anodic face. The result was a non-gassing cathode at which thick film ceramic precursor could be precipitated.
Figure 5.1.1: Vacuum Chamber for Removal of Hydrogen from a Palladium Plate Cathode Under Reduced Pressure
For the purpose of this investigation, the experimental set-up employed was as follows. Both the working anode and counter cathode, used to drive the bipolar electrode, consisted of 10 mm by 40 mm lengths of high surface area platinum gauze (Johnson Matthey plc.). These were coiled to give cylinders of length 10 mm and diameter 5 mm, and were then tacked onto 1 mm diameter platinum wire (Johnson Matthey plc.) - the wires being set into glass (ca. 10 mm exposed length, with copper contacts silver soldered onto the unexposed ends). The bipolar electrode consisted of a sheet of palladium foil (50x50 mm, 0.125 mm thick, 99.95% pure, Goodfellow). The foil was degreased with acetone, washed with HPLC grade water (Rathburn), dried, and sealed (with silicone rubber sealant) into the cell (Figure 5.1.3), exposing an electrode area of approximately 7 cm$^2$ (30 mm diameter) to both anolyte and catholyte, prior to use. No further pre-treatment was carried out. All potentials were
measured (and are quoted) with respect to a mercury, mercurous sulphate reference electrode \( (E^o = 0.615 \text{ V @ 25°C}) \). Solutions were prepared using HPLC grade water (Rathburn) and high purity (Analar grade) chemicals (BDH and Fisons). Voltammetric control was carried out using a Schlumberger Solartron 1286 Electrochemical Interface.

**Figure 5.1.3: Schematic Diagram of the Bipolar Cell Employed in Thick Film Generation at a Non-gassing Cathode**
With 1.0 M sulphuric acid in the cathode compartment of the cell (to avoid hydroxide precipitation at this electrode) and 0.01 M aluminium sulphate in the anode compartment, a series of 100 (linear ramp) potential cycles, with limits of +0.300 V to +1.500 V (initial scan positive from +0.300 V, open circuit potential, OCP = +0.326 V) and scan rate 100 mVs⁻¹, were applied to the cell’s controlling anode. Thus a cathode was generated at the palladium sheet surface opposite this electrode, and an anode on the reverse side of the sheet. In order to avoid confusion between the two sets of electrodes, the anode and cathode faces of the bipolar plate are, in future, referred to as the “virtual” anode and “virtual” cathode respectively.

During potential cycling, it was noted that the onset of oxygen evolution from the virtual anode face occurred at around +1.3 V applied potential. This would indicate that at this cell potential the rate of supply of hydrogen to the virtual anode (or its rate of oxidation there) is not sufficient to sustain the current demanded by the cell’s driving reaction (oxygen evolution from the working anode). Hence, in order to sustain the cell current the virtual anode seeks another reaction; oxygen evolution. The optimum working region for hydrogen oxidation at the virtual anode under these conditions thus appears to be below +1.3 V applied potential.

Throughout the 100 potential cycles, the growth of a thin white deposit was observed at the virtual cathode surface. The deposit gave extensive coverage of the 30 mm diameter exposed palladium surface as the cycle number approached 100, proving that the bipolar arrangement was indeed suitable for the generation of surface films of ceramic precursor.

In order to produce a thicker deposit, a potential of +1.200 V was applied to the cell (following completion of cycle 100) for a period of 30 minutes. It was reasoned that
the chosen potential should lie in the region of hydrogen oxidation at the virtual anode with little or no oxygen evolution occurring. Indeed, no gas evolution was observed from the virtual anode during polarisation. On inspection of the virtual cathode throughout this 30 minute period, a continual growth of deposit towards the working electrode was observed. The deposit reached a thickness of approximately 1 mm, whereupon small fragments were dislodged from the bulk film and fell to the bottom of the cell. However, the bulk of the film remained intact and continued to increase in thickness.

5.2: Conclusions

The experiment described thus proves that thick (ca. 1 mm) films of aluminium hydroxide can be manufactured using the non-gassing virtual cathode of the bipolar cell. The fragmentation of the film towards the end of the deposition period may indicate a lack of structural integrity in deposits generated by this method. It should, however, be possible (as shown in Chapter 2 for smaller scale deposits) to employ a tailored potential regime in order to generate deposits of controlled thickness, density and structural integrity. In addition, by employing a contoured bipolar electrode, the deposition method described above may offer a simple electrochemical route to preshaped ceramic bodies: a technique explored by Mitchell and Wilcox [30] for the manufacture of ceramic tubes at a palladium wire cathode.
Chapter 6

Self-feeding Hydrogen Anodes
Chapter 6: Self-feeding Hydrogen Anodes

6.1: Proof of Concept

6.1.1: Experimental Set-up

In the bipolar cell described in Chapter 5, the transport of hydrogen through the palladium plate, and its oxidation at the positive face, results in a self-feeding hydrogen anode (a hydrogen anode requiring no external hydrogen source) at this surface [55,56] (see Appendix 4). The characteristics of this anode were investigated, paying particular attention to optimisation of the operating potential “window” for hydrogen oxidation. Sulphuric acid was chosen as the electrolyte for both cell compartments since it acts as an excellent source and sink for protons, it does not readily attack the cell’s electrodes and because its only gaseous electrolysis products are hydrogen and oxygen. For the purpose of experiments carried out, the following set-up was employed:

The cell illustrated in Figure 5.1.3 was used throughout. However, the working electrode was employed as a cathode, in order to facilitate the monitoring of potentials at the adjacent virtual anode (see Figure 6.1.1). Voltammetric data (cyclic voltammograms) were recorded using a Schlumberger Solartron 1286 Electrochemical Interface and a Bryans A3 26000 X-Y chart recorder. Additional V/V plots were recorded on an Advance Bryans X-Y chart recorder. A Beckmann 3050 multimeter was employed in the measurement of certain electrode potentials. A Fylde 255DA buffer amplifier was also used to allow simultaneous measurement of the reference to working and reference to bipolar (anodic face) electrodes, without drawing current from the circuit incorporating the latter (see circuit diagram, Figure 6.1.2). 1.0 M sulphuric acid was used throughout as electrolyte; prepared from
the 98% acid (Fisons) and HPLC grade water (Rathburn). Temperature control was achieved with a Tecam TE-7 Tempette and water bath.

Figure 6.1.1: Schematic Diagram of the Bipolar Cell as Used in Investigation of Self-feeding Hydrogen Anodes
6.1.2: Hydrogen Degassing

In order to ensure that each new experiment began with the same initial conditions, it was essential to remove any residual hydrogen from the bipolar palladium plate prior to each run. This was achieved by electrochemical oxidation, in the acid electrolyte, with the palladium sheet as working electrode. Before degassing was attempted, a suitable potential was selected by firstly introducing hydrogen into the palladium lattice, and then using cyclic voltammetry to determine the potential at which the maximum rate of hydrogen oxidation occurred. With the cell connected as in Figure 6.1.2, a series of 10 (linear ramp) potential cycles were applied to the cell (Pt working electrode), sweep limits being set at 0.000 V and -1.000 V and scan rate 10 mVs\(^{-1}\) (initial scan negative from 0.000 V). This potential regime was chosen, instead of a constant potential, in order introduce hydrogen into the palladium lattice under similar conditions to the intended experimental runs. The open circuit potential
(reference to palladium virtual anode potential) was recorded as being +0.167 V prior to the onset of the 10 cycles. It was reasoned that successful degassing should result in the reattainment of an OCP close to this value. Following completion of the 10 cycles, the cell connections were changed to make the palladium sheet the working electrode (see Figure 6.1.3). Having recorded the new OCP (reference to palladium working electrode) as being -0.588 V, a cyclic potential scan was carried out; scan rate 10 mVs⁻¹ with sweep limits -0.600 V and +1.000 V (the forward scan was initiated from -0.600 V in the positive direction). The recorded cyclic voltammogram (Figure 6.1.4) showed a current peak for hydrogen oxidation at around -0.4 V. The only other electrochemical processes being oxygen evolution (onset at +0.9 V) and reduction (0.0 V on the reverse half cycle).

**Figure 6.1.3: Degassing Circuit Employed in the Removal of Hydrogen from the Palladium Plate**
Figure 6.1.4: Cyclic Voltammogram Showing Peak Hydrogen Oxidation Current at the Hydrogen-rich Palladium Plate Electrode
From these findings, a degassing potential of -0.4 V was chosen. It was decided that an elevated temperature of 40°C should be used in order to accelerate the oxidation reaction. Hence, the degassing procedure was carried out as follows. The cell, connected to the 1286 Electrochemical Interface (as in Figure 6.1.3) was placed in the water bath at 40°C and allowed to equilibrate for 20 minutes. A potential of -0.400 V was applied until zero current was recorded. The new OCP was then noted and compared to the original (pre-experiment) value. Following this first degassing process, the final OCP was found to be +0.147 V. Since this value was close to the initial OCP, the degassing was considered successful. For all subsequent experiments the above degassing procedure was followed, with temperature set to 40°C unless otherwise stated. All initial open circuit potentials were close to +0.160 V and are therefore not noted for individual experiments.

6.1.3: Initial Investigation of the Electrochemistry Occurring at the Bipolar Electrode’s Anodic Face

A series of 10 linear ramp potential cycles were applied to the Pt working electrode, each having sweep limits of 0.000 V and -1.000 V and scan rate 10 mVs⁻¹. The temperature throughout was maintained at room temperature, 20.5°C. The first cycle was initiated from 0.000 V in the negative direction. Throughout cycling, the change in both current (through the cell’s external circuit) and the reference to virtual anode potential with applied (reference to working electrode) potential, were recorded by the two chart recorders. The resulting plots can be seen in Figure 6.1.5. Here, plots with potential on both axes are used as a means of monitoring the electrochemistry occurring at the virtual anode. The change in potential at the virtual anode relates directly to the process occurring at this face, whereas, the current is governed
primarily by the reaction taking place at the driving cathode. All plots employing two potential axes will be referred to as "voltvoltograms".

Figure 6.1.5: Cyclic Voltvoltograms and Cyclic Voltammograms Recorded During Potential Cycling of the Bipolar Cell

(a) Cycle 1 Voltvoltogram
(b) Cycle 2 Voltvoltogram

RE/WE potential /V

1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
-1.0

-0.8
-0.6
-0.4
-0.2
0.0
0.2
0.4
0.6
0.8
1.0

(c) Cycles 1 and 2 Voltammograms

RE/WE potential /V

-100
-90
-80
-70
-60
-50
-40
-30
-20
-10
0

10
20
30
40
50

Current /mA
(d) Cycle 4 Voltvoltogram

(e) Cycle 4 Voltammogram
(f) Cycle 6 Voltvoltogram

(g) Cycle 6 Voltammogram
(h) Cycle 8 Voltvoltogram

![Volts CEL Cycle 8](image)

(i) Cycle 8 Voltammogram

![Current Amplitude Cycle 8](image)
(j) Cycle 10 Voltvoltogram

(k) Cycle 10 Voltammogram
A proposed explanation of the electrochemical phenomena occurring during the first cycle (Figure 6.1.5(a)) is as follows:

1. At 0.000 V applied RE/Pt WE potential, the RE/Pd virtual anode potential is approximately +0.17 V vs Hg/Hg\(_2\)SO\(_4\) reference electrode (or approx. +0.79 V vs SHE). At this potential, a surface oxide layer is present on the palladium surface. Reasons for this assumption will become apparent as the remainder of the cycle is discussed.

2. Onset of oxygen evolution - no (or very little) hydrogen is present at the virtual anode surface because sufficient time has not elapsed for it to diffuse through the palladium sheet (following its generation at the cathodic face, during ramping of the applied potential, and subsequent transport through the metal). Hence there is no linear increase observed in the RE/virtual anode potential, corresponding to the overpotential for hydrogen oxidation (as seen on later cycles).

3. A potential has been reached at which oxygen evolution occurs from the virtual anode face of the bipolar electrode. The gassing is visible to the naked eye.


5. Oxygen evolution ceases to occur and the potential of the virtual anode returns (roughly) to its original value, corresponding to the anode face being coated with a surface oxide layer. An oxide layer must be present, since the electrode face in question was driven to oxygen evolution and hence, surface oxidation must have occurred. Therefore, a surface oxide film is probably present on the virtual anode.
face prior to the potential cycling, since the measured open circuit potential is close to the RE/Pd virtual anode potential at point 5 on the plot.

6. The bipolar electrode's anodic face remains a palladium oxide electrode.

7. At this point of the cycle it is believed that hydrogen, generated and absorbed at the cathodic face of the palladium, has diffused through the bulk palladium metal to the anodic face. Here, it chemically reduces the surface oxide film back to bare palladium. It then accumulates at the surface as an adsorbed layer of hydrogen atoms, thus explaining the observed potential change; the potential (RE/Pd virtual anode) now being \(-0.481\) V vs Hg/Hg\(_2\)SO\(_4\) reference or \(+0.134\) V vs SHE which is approaching the potential expected at an \(\alpha\)-phase palladium-hydrogen surface in the same electrolyte [57].

**Second Potential Cycle**

The following is a summary of the electrochemical processes occurring during cycle 2 (Figure 6.1.5(b)):

1. Continued from cycle 1; at this point adsorbed hydrogen is present on the palladium surface (anodic face). The potential is \(-0.551\) V (\(+0.064\) V vs SHE), corresponding to an \(\alpha\)-phase palladium-hydrogen surface [57].

2. The potential remains constant at the virtual anode face, since only hydrogen is present at its surface.
3. Onset of hydrogen oxidation. Absorbed hydrogen atoms on the electrode's surface are oxidised back to protons. The positive slope marks the increase in overpotential of this process with increasing current.

4. Transition from hydrogen oxidation to oxygen evolution (water oxidation). As the applied RE/Pt WE potential becomes more negative, there is an increased rate of hydrogen generation at the bipolar's virtual cathode face. Consequently, there is also an increased quantity of hydrogen being transported through the palladium, to be oxidised at the anodic face. However, this increase is accompanied by a rise in current passing through the cell's external circuit - due to ramping of the applied RE/Pt WE potential. This increased current demands that the rate of hydrogen generation and oxidation at opposite faces of the bipolar electrode rise in accordance to the increasing current. Whilst it is expected that the hydrogen generation reaction is capable of sustaining the current demanded of it, the oxidation process is limited by the rate of diffusion of hydrogen through the palladium. The oxidation can only occur as fast as the resupply of hydrogen, via diffusion, to the virtual anode. Hence, at some point during the cycle, the current required of the hydrogen oxidation reaction cannot be sustained by the virtual anode, since the required rate of oxidation exceeds the rate of hydrogen resupply by diffusion. At this point the virtual anode seeks an alternative reaction to sustain the current, this reaction being water oxidation (oxygen evolution) - hence the reason for the observed potential (RE/Pd virtual anode potential) rise, and the inferred transition.

5. Transition complete - oxygen evolves from the palladium virtual anode.

6. Continued oxygen evolution.
7. Oxygen evolution has ceased in this potential region, and the palladium virtual anode again adopts the potential of a palladium oxide electrode.

8. Hydrogen again diffuses through the Pd sheet to the virtual anode face, where it chemically reduces the oxide layer on the surface to the bare metal, and generates a palladium-hydrogen electrode (again having a potential of +0.064 V vs the SHE).

The palladium sheet will contain more hydrogen on the return sweep of cycle 2 than on the return sweep of cycle 1. Hence, chemical oxide reduction due to the presence of hydrogen at the anodic face will occur earlier (at a more negative applied RE/Pt WE potential) on this second return sweep. This is observed by the potential (RE/Pd) drop occurring closer to the more negative limit of the applied RE/Pt WE potential cycle.

**Observed Trends: Cycles 1 to 10**

Examination of the voltvoltograms (Figures 6.1.5(a), (b), (d), (f), (h) and (j)) of the 10 cycles reveal three distinct electrochemical trends:

1. With each successive cycle, there is a marked decrease in the time the palladium anode spends as a palladium oxide electrode before sufficient hydrogen diffuses through the metal and affects its reduction. This is noted by the decrease in width of the potential window corresponding to the presence of a palladium oxide electrode surface. On the return of cycle 1 the palladium surface remains oxidised for around 0.45 V before reduction begins and the RE/Pd anode potential commences its return to around +0.06 V vs SHE. However, by cycle 10, this
window has decreased to just \( \sim 0.15 \) V, indicating the chemical reduction process is accelerated with each cycle.

2. There is also a broadening of the hydrogen oxidation potential region (at the virtual anode) with increasing cycle number. This region spans 0.13 V on the forward sweep of cycle 2, and increases to 0.27 V by cycle 10.

3. Consequently, the need for oxygen evolution from the anode to sustain the cell current is pushed to more cathodic applied (RE/Pt WE) potentials.

Another point worthy of note is the gradual decrease in potential adopted by the virtual anode on attainment of a palladium-hydrogen surface during the latter part of cycles 2 to 10. For cycle 2, the potential is +0.064 V vs SHE which is reduced to +0.009 V by cycle 10. The final potential is in the region expected for a \( \beta \)-phase palladium-hydrogen sample close to the hydrogen saturation limit [57] (see Appendix 1). This clearly demonstrates increased hydrogen retention with each successive cycle. It was found that all three trends could be accounted for by this progressive hydrogen saturation. As the cycle number rises:

- The palladium takes up an increasing quantity of hydrogen

- Following surface oxide generation, it takes less time for hydrogen to reach the oxide and reduce it since more hydrogen is stored in the palladium lattice than on the previous cycle. Hence, reduction occurs at more negative applied (RE/Pt WE) potentials.
• Oxide reduction is completed over shorter periods of time, since larger quantities of hydrogen are accessible. Thus, the oxide’s potential window narrows.

• During the forward sweeps, hydrogen oxidation at the anode surface is sustained for longer periods, since more hydrogen is available to be oxidised. Hence, the hydrogen oxidation window broadens, and the necessity for oxygen evolution occurs at increasingly more negative applied potentials.

6.1.4: Evidence for the Chemical Nature of the Oxide Reduction Step

Employing the same cell as with the previous experiment but with a 0.047 mm thick palladium plate as bipolar electrode, a potential of -1.000 V was applied to the cell’s working electrode (cell connected as in Figure 6.1.2). This drove the virtual anode to an initial potential of +1.34 V (vs mercury, mercurous sulphate reference) at which oxygen was continually generated at its surface. It was reasoned that during the observed oxygen evolution, the bipolar plate would still be capable of generating hydrogen at its cathodic face, and oxidising it at the anodic face. Hence, if sufficient time was allowed, the concentration of hydrogen in the palladium substrate during oxygen gassing should facilitate chemical reduction of the anode’s oxide layer on termination of polarisation. This was indeed observed. Polarisation was stopped after a period of 87 minutes following which, the potential at the virtual anode fell rapidly to -0.35 V where it remained for 4 seconds, eventually falling to a final value of -0.60 V (see Figure 6.1.6). The fact that the final potential is around -0.60 V (+0.02 V vs SHE) would indicate that hydrogen is present at the virtual anode surface, and that reduction of the oxide layer (present at -0.35 V) has been achieved. No current was flowing during the observed potential drop, and therefore, the processes causing these
potential changes are not electrochemical. Another conclusion which can be drawn from the data is that the rate of oxide reduction is limited by non-electrochemical processes, and therefore by the rate of diffusion of hydrogen through the palladium plate.
Figure 6.1.6: Potential-Time Profile Showing Evidence of the Chemical Nature of Surface Oxide Reduction
6.2: Prolonged Potential Cycling

It was reasoned that prolonged potential cycling of this bipolar system, in the 0.000 V to -1.000 V applied potential region would result in continued hydrogen saturation of the bipolar electrode, affecting prolonged hydrogen oxidation on the forward sweeps. Thus, eventually, the necessity for the anode to evolve oxygen at the extreme cathodic applied RE/Pt WE potentials should be removed. Overall, the transition from hydrogen oxidation to oxygen evolution at the virtual anode should be suppressed.

Prior to evaluation of the effects of continued potential cycling, the bipolar system was degassed as before, ensuring that the experiment began with a hydrogen-free bipolar electrode.

*Hydrogen Oxidation to Oxygen Evolution Transition Suppression*

A series of 100 plus 0.000 V to -1.000 V potential cycles (scan rate 10 mVs⁻¹) were applied to the system’s platinum working electrode. The cell temperature was held at room temperature (20.0°C) throughout. Selected cyclic voltvolttograms and voltammograms recorded during cycling, can be seen in Figure 6.2.1.
Figure 6.2.1: Selected Cyclic Voltvoltograms and Voltammograms from a Series of 100+ Consecutive Potential Scans

(a) Cycles 2 to 6

(b) Cycle 2 Voltammogram
(c) Cycles 7 to 11

(d) Cycles 12 to 16
(e) Cycles 46 to 50

(f) Cycle 83
(g) Cycle 110

(h) Cycle 110 Voltammogram
Here, all three trends previously described are, as expected, observed throughout potential cycling. The potential window, in which the palladium’s anodic face has an oxide surface layer, narrows with each cycle, hydrogen oxidation is sustained for longer, but most notably, the onset of oxygen evolution is pushed to increasingly cathodic applied potentials with each cycle. In the extreme, at around cycle 110, the transition from hydrogen oxidation to oxygen evolution is no longer observed in the 0.000 V to -1.000 V potential window. Consequently, the anode sustains hydrogen oxidation for approximately one third of each cycle. From the cyclic voltammograms of cycles 2 and 110 (Figures 6.2.1(b) and (h)) and the corresponding cyclic voltamograms (Figures 6.2.1(a) and (g)) it is evident that the maximum hydrogen oxidation current increases from 30 mA to 60 mA throughout the prolonged potential cycling, again illustrating the increasing availability of hydrogen for oxidation. It was also noted that the potential at the virtual anode following oxide reduction, and the consequent attainment of a palladium-hydrogen surface, decreased from -0.557 V on cycle 2 to -0.612 V (+0.003 V vs SHE) by cycle 110. The final potential is very close to 0.000 V, the expected value for hydrogen saturated $\beta$-phase palladium hydride. The palladium plate has therefore almost attained its hydrogen saturation limit and will readily give up hydrogen for oxidation at the virtual anode. This level of saturation almost certainly explains the observed changes in electrochemistry at the anode face with increasing cycle number.

6.3 : Operating Temperature Effects on the Bipolar System

The electrochemical processes occurring at the virtual anode in 1.0 M sulphuric acid electrolyte, within the 0.000 V to -1.000 V window, were probed at a series of temperatures in the range 20-70°C. The experiments were carried out as follows: beginning with the cell at approximately 70°C, a series of three 0.000 V to -1.000 V
(scan rate 10 mVs\(^{-1}\)) cycles were applied to the system’s working electrode. 5 minutes after the termination of cycle 3, degassing was carried out at -0.40 V and (approx.) 70°C in the acid electrolyte. Following degassing, a 20 minute equilibration period was allowed for the virtual anode to attain a nominal open circuit potential of around +0.160 V. During this period, the cell temperature was thermostatted to 60°C in preparation for the next temperature run. Three potential cycles were applied to the system, using the above parameters, at temperature intervals of roughly 10°C, the final run being carried out at 20°C. Degassing was carried out between runs at the cell temperature until 30°C, whereupon the degassing temperature was elevated to 40°C following each run in order to accelerate the process. Electrochemical data recorded at each temperature can be seen in Figure 6.3.1 in the form of cyclic voltvolttograms and cyclic voltammograms.

Because of the temperature dependence of the mercury, mercurous sulphate electrode’s reference potential,

\[ E^0/V = 0.63495 - 781.44 \times 10^{-6}T - 426.89 \times 10^{-9}T^2 \]

all potentials at elevated temperature have been corrected to room temperature (25°C). Thus 0.000 V (the start potential for each run) at all temperatures refers to an absolute potential of +0.615 V vs SHE (or 0.000 V vs mercury, mercurous sulphate reference at 25°C). The variation of reference potential with temperature at 30, 40, 50, 60 and 70°C and the corresponding start potential are given, as a guide, in Table 6.3.1.
Table 6.3.1: Variation of Reference and Start Potentials with Temperature

<table>
<thead>
<tr>
<th>Cell Temperature (°C)</th>
<th>Reference Potential /V</th>
<th>Start Potential vs New Reference /V</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>+0.611</td>
<td>+0.004</td>
</tr>
<tr>
<td>40</td>
<td>+0.603</td>
<td>+0.012</td>
</tr>
<tr>
<td>50</td>
<td>+0.595</td>
<td>+0.020</td>
</tr>
<tr>
<td>60</td>
<td>+0.587</td>
<td>+0.028</td>
</tr>
<tr>
<td>70</td>
<td>+0.578</td>
<td>+0.037</td>
</tr>
</tbody>
</table>
Figure 6.3.1: Cyclic Voltvoltograms and Cyclic Voltammograms Recorded During Potential Cycling at Temperatures in the Range 20-70°C

(a) 64.2°C Voltvoltograms

(b) 64.2°C Voltammograms
(c) 59.6°C Voltvoltograms

(d) 59.6°C Voltammograms
(e) 48.9°C Voltvoltograms

![Voltvoltograms Graph](image)

(f) 48.9°C Voltammograms

![Voltammograms Graph](image)
(g) 38.9°C Voltvoltograms

(h) 38.9°C Voltammograms
(i) 29.1°C Voltvoltograms

(j) 29.1°C Voltammograms
(k) 20.3°C Voltvoltograms

(l) 20.3°C Voltammograms
Table 6.3.2 lists the important parameters obtained from cyclic voltammograms and voltvoltagrams recorded during each of the six temperature runs. Examination of plots and the data reveals the following electrochemical trends occurring at the bipolar electrode’s anodic face:

1. There is a continual rise in the cell’s maximum current with increasing temperature from 20.3°C to 59.6°C. This is as expected, since the current is driven by the electrochemical reaction taking place at the working platinum electrode, namely hydrogen generation. Increasing the temperature at which this reaction is forced to occur results in an increase in reaction rate and consequently in the current driven through the cell. However, from 59.6°C to 64.2°C there is a slight decrease in the maximum current. This may be due to excess evolution of hydrogen from the platinum working electrode at elevated temperature. The presence of excess gaseous hydrogen at this electrode’s surface may impede electrolyte access to its surface and thereby restrict further hydrogen generation and consequently the flow of current through the cell. Outgassing of hydrogen from the palladium, which will become more prominent at elevated temperature, may also contribute to the fall in current by impeding the current-carrying process through the bipolar plate.

2. The onset of oxygen evolution during forward sweeps (cycles 2 and 3) is pushed to more negative applied potentials at higher temperatures. As with the negative shift of onset of gassing experienced on continual potential cycling, this phenomenon can be explained in terms of hydrogen saturation. At higher operating temperatures, the rate of hydrogen generation at the bipolar electrode’s cathodic face increases as does the rate at which the palladium substrate absorbs hydrogen. Hence, the palladium electrode substrate absorbs more of the gas as the temperature rises. Coupled with an increased diffusion rate of hydrogen through
the metal, the result is a much more dynamic process for hydrogen resupply to the oxidising anode. Overall, the rate of hydrogen resupply will increase with increasing temperature, meaning that hydrogen oxidation at the bipolar’s anodic face is sustained for longer, and the need for oxygen evolution is moved to higher cathodic applied potentials.

3. The width of the hydrogen oxidation region increases as the operating temperature is raised. The explanation for this observation is the same as in the case of the shift in oxygen evolution onset.

4. The maximum hydrogen oxidation current increase with temperature up to 59.6°C is as expected, since hydrogen will be supplied to the virtual anode at an increasing rate at a higher temperature. The decrease in current from 59.6°C to 64.2°C can be explained in terms of reduced cell current and physical desorption of hydrogen from the palladium plate which will be more prominent at higher temperatures. Any physically desorbed hydrogen will not take part in electrochemical hydrogen oxidation and will therefore decrease the current relating to this process.

5. The potential window pertaining to a palladium oxide electrode surface decreases with increasing temperature. Explanation can again be taken from increased hydrogen generation and diffusion rates within the bipolar system, supplying hydrogen to the virtual anode at a faster rate and thereby allowing it to carry out the oxide reduction over shorter periods.
Table 6.3.2: Data Obtained from Cyclic Voltammograms and Voltvoltograms Recorded During Potential Cycling in the Range 20-70°C (All Values Relate to Cycle 3 of 3)

<table>
<thead>
<tr>
<th>Average Temp. °C</th>
<th>Width of PdO region /V</th>
<th>Width of H₂ oxidation region /V</th>
<th>Onset of Oxygen evolution /V (RE/WE) vs SHE</th>
<th>Maximum H₂ oxidation current / mA</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.3</td>
<td>0.55</td>
<td>0.15</td>
<td>-0.19</td>
<td>49</td>
</tr>
<tr>
<td>29.1</td>
<td>0.39</td>
<td>0.18</td>
<td>-0.21</td>
<td>70</td>
</tr>
<tr>
<td>38.9</td>
<td>0.20</td>
<td>0.21</td>
<td>-0.24</td>
<td>105</td>
</tr>
<tr>
<td>48.9</td>
<td>0.13</td>
<td>0.21</td>
<td>-0.25</td>
<td>125</td>
</tr>
<tr>
<td>59.6</td>
<td>0.11</td>
<td>0.23</td>
<td>-0.28</td>
<td>153</td>
</tr>
<tr>
<td>64.2</td>
<td>0.09</td>
<td>0.23</td>
<td>-0.28</td>
<td>147</td>
</tr>
</tbody>
</table>

The overall conclusion which can be drawn from data obtained so far for the bipolar system is that hydrogen diffusion through the palladium plate is the rate limiting process affecting the maximum hydrogen oxidation current. Increasing the hydrogen diffusion rate by employing an elevated temperature was found to improve the anode’s oxidation performance. It was therefore reasoned that increasing the flux of hydrogen through the plate by decreasing its thickness should yield a similar result.

6.4: Effect of Decreased Plate Thickness

It was decided that investigation should be carried out into the effect of decreased bipolar electrode plate thickness on the performance of the self-feeding hydrogen anode. For this purpose, the experimental set-up described in section 6.1 was
retained, however, two new cells were prepared to the same specifications as before but with bipolar plates of thickness 0.047 mm and 0.030 mm (99.95 % palladium, Goodfellow). Both plates were degreased with acetone and washed with HPLC grade water prior to being sealed into the cell with silicone rubber sealant. Each cell's two driving electrodes, reference electrode and electrolyte were as previously used. The cell containing the 0.047 mm plate was also employed for the experiment described in section 6.1.4.

As with all previous experiments outlined in this chapter, a Schlumberger Solartron 1286 Electrochemical Interface was employed in control of the applied potential regime, and an Advance Bryans X-Y chart recorder was used to record all cyclic voltamograms. A Fylde 255DA buffer amplifier was also employed for reasons explained in section 6.1.1. The cell circuit for elevated temperature experiments carried out with the 0.047 mm plate was as shown in Figure 6.1.2. However, in the case of the 0.030 mm plate and for extended cycling of the 0.047 mm system, one alteration to the circuit was made; cyclic voltammetric data was logged, as a text file, by a personal computer connected via serial ports to the 1286 Electrochemical Interface. This eliminated the need for a second chart recorder. Data was handled by Microsoft Windows Terminal Version 3.1 and plotted with the aid of Microsoft Excel 5.0.

Degassing between experiments was carried out at -0.400 V and 40°C as described in section 6.1.2 unless stated otherwise.
6.4.1 : 0.047 mm Plate - Effect of Continuous Potential Cycling

With the cell containing 1.0 M sulphuric acid electrolyte at room temperature (20.8°C) a series of linear ramp potential cycles were applied to the platinum mesh working electrode. Sweep limits were set to 0.000 V and -1.000 V with a scan rate of 10 mVs⁻¹. The initial scan was negative from 0.000 V. The experiment was terminated on completion of cycle 20, the point at which the desired changes in the cell’s electrochemical behaviour were observed. Throughout cycling, electrochemical data was recorded as cyclic voltvoltagrams and voltamnograms, a selection of which can be seen in Figure 6.4.1.

The data clearly shows similar electrochemistry occurring at the 0.047 mm thick palladium bipolar electrode as with the 0.125 mm plate. Potentials at the virtual anode on the forward scan of cycle 1 indicate the initial presence of a surface oxide film and the increase in potential at around -0.60 V (applied RE/Pt WE potential) marks the onset of oxygen evolution from the palladium surface. Differences arise on the return sweep where the sharp drop in potential at -0.82 V (applied), marking the end of oxygen evolution, is followed by a very narrow palladium oxide region (ca. 0.02 V compared to approximately 0.55 V for the 0.125 mm plate during cycle 1). Oxide reduction is then followed by a region of hydrogen oxidation (-0.76 V to -0.66 V) after which the palladium sample adopts a potential of -0.586 V (+0.029 V vs SHE) indicating the presence of β-phase palladium hydride.
Figure 6.4.1: Cyclic Voltvoltograms and Voltammograms Recorded During Extended Potential Cycling of the 0.047 mm Bipolar System

(a) Cycle 1

(b) Cycle 1 Voltammogram
(c) Cycle 4

(d) Cycle 6
(e) Cycle 8

(f) Cycle 10
(g) Cycle 12

(h) Cycle 14
(i) Cycle 16

(j) Cycle 18
(k) Cycle 20

(i) Cycle 20 Voltammogram
On continued cycling, as expected from the findings in section 6.2 for the thicker palladium electrode, the hydrogen oxidation region broadens, the onset of oxygen evolution is pushed to increasingly more negative applied (RE/Pt WE) potentials, and the palladium oxide region diminishes. These observations are again explained in terms of gradual hydrogen saturation with increasing cycle number, making hydrogen more readily available for oxidation at the virtual anode. By cycle 20, the virtual anode sustains hydrogen oxidation at the lower sweep limit (-1.000 V applied potential) and the transition to oxygen evolution is no longer observed. The maximum hydrogen oxidation current remains roughly constant at 120 mA throughout cycling. This compares favourably to the 60 mA attained following prolonged potential cycling of the 0.125 mm plate. By cycle 20, the palladium-hydrogen potential at the virtual anode is -0.615 V (+0.000 vs SHE) indicating a hydrogen saturated β-phase palladium hydride. Under similar conditions, the 0.125 mm plate requires a further 90 cycles to attain this level of hydrogen saturation and the accompanying hydrogen oxidation characteristics. Since both palladium samples originate from the same source and have undergone similar surface preparation, it is evident that differences observed in their performance are almost certainly due to increased flux of hydrogen through the thinner palladium plate and not hydrogen redox kinetics at its surface. A thinner plate would transport more hydrogen through it per unit area in a given time, allowing quicker saturation and prolonged hydrogen oxidation to occur.

6.4.2 : 0.047 mm Plate - Effect of Increased Temperature

Beginning with the degassed 0.047 mm bipolar plate and a fresh 1.0 M H₂SO₄ electrolyte solution, the cell was thermostatted to 70°C by immersion in a water bath for a period of 20 minutes. A series of three linear ramp potential cycles were then applied to the cell’s Pt working electrode with sweep limits 0.000 V and -1.000 V and
scan rate 10 mVs\(^{-1}\) (initial scan negative from 0.000 V). The palladium was then degassed and the temperature lowered to 60°C where a further 3 cycles were initiated. Three cycle runs were also carried out at approximately 50, 40, 30 and 20°C and the degassing programme outlined in section 6.3 was followed between runs. Cyclic voltvoltoograms and voltammograms, recorded at each temperature, are shown in Figure 6.4.2. Table 6.4.1 gives details of hydrogen oxidation potentials and currents in addition to potentials for the onset of oxygen evolution and the lifetime of the palladium oxide surface film at each temperature.

Here, there appear to be certain differences in the overall system trends observed with increasing temperature as compared to results obtained with the 0.125 mm plate. The width of the hydrogen oxidation region on the forward scans is seen to decrease with increasing temperature and as a consequence, the onset of oxygen evolution from the virtual anode occurs at more positive applied (RE/Pt WE) potentials. This can be explained in terms of the increased hydrogen flux through the thinner palladium plate, and faster hydrogen diffusion rates encountered at higher temperature. Both will aid the natural outgassing of hydrogen from the palladium plate, during parts of the cycles where little or no current flows, as the temperature is raised. Thus, any outgassed hydrogen will no longer be available for oxidation and will therefore impede the hydrogen oxidation current, allowing oxygen evolution to take over as the preferred anodic process.

Looking at cycles 2 and 3 at 68°C (Figure 6.4.2(a)), during the first half of each forward scan, where very little current flows through the cell, hydrogen will be physically outgassed from the bipolar palladium substrate. The hydrogen oxidation window is therefore narrower than expected since less hydrogen is available for oxidation than is expected. During oxygen evolution at the virtual anode, hydrogen
will continue to be generated and absorbed at the virtual cathode. Eventually, the hydrogen concentration in the palladium plate reaches a critical value where its oxidation can replace the generation of oxygen as the preferred anodic reaction. This occurs at \(-0.94\) V (applied RE/Pt WE potential) on the return scan of both cycle 2 and 3. The anode now sustains hydrogen oxidation for a longer period than on the forward scan because more hydrogen is available. During the latter part of the reverse scan, outgassing will again occur, allowing the observed sequence of events to be repeated on subsequent cycles.

As the temperature is decreased, hydrogen outgassing becomes less prominent, and a similar behaviour to that observed with the 0.125 mm plate is seen; by 29.9°C less hydrogen is oxidised on the reverse scan than on the forward one and the onset of oxygen evolution occurs at more a negative applied (RE/Pt WE) potential than the oxygen cut-off.

It is worth noting that although the hydrogen oxidation “window” on the forward scan narrows with increasing temperature, the maximum hydrogen oxidation current (taken from the forward or reverse scan as appropriate) exhibits an overall increase. This occurs because as current flows and hydrogen is allowed to build up, the increased diffusion rate at higher temperatures will ensure that the flux of hydrogen through the plate to the anodic face also increases, thereby allowing a higher current to flow. This also explains why a slight decrease in width of the palladium oxide region is observed at higher temperature; chemical reduction of this layer directly follows the hydrogen build-up and therefore occurs over a shorter period of time with increased hydrogen flux.
Figure 6.4.2: Cyclic Voltvoltograms and Voltammograms Recorded for the 0.047 mm System at Temperatures in the Range 20-70°C

(a) 68.0°C Voltvoltograms

(b) 68.0°C Voltammograms
(c) 57.0°C Voltvoltograms

(d) 57.0°C Voltammograms
(e) 47.8°C Voltoltograms

(f) 47.8°C Voltammograms
(g) 38.1°C Voltammograms

(h) 38.1°C Voltammograms
(i) 29.9°C Voltvoltagrams

(ii) 29.9°C Voltammograms
(k) 20.0°C Voltvoltograms

(l) 20.0°C Voltammograms
Table 6.4.1: Data Obtained from Cyclic Voltammograms and Voltvoltoagrams Recorded During Potential Cycling in the Range 20-70°C (All Values Relate to Cycle 3 of 3)

<table>
<thead>
<tr>
<th>Average Temp. ℃</th>
<th>Width of PdO region /V</th>
<th>Width of H₂ oxidation region /V</th>
<th>Onset of Oxygen evolution /V (RE/WE) vs SHE</th>
<th>Maximum H₂ oxidation current /mA</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.0</td>
<td>0.03</td>
<td>0.25</td>
<td>-0.31</td>
<td>88 f</td>
</tr>
<tr>
<td>29.9</td>
<td>0.03</td>
<td>0.25</td>
<td>-0.29</td>
<td>98 f</td>
</tr>
<tr>
<td>38.1</td>
<td>0.02</td>
<td>0.25</td>
<td>-0.29</td>
<td>105 f</td>
</tr>
<tr>
<td>47.8</td>
<td>0.02</td>
<td>0.25</td>
<td>-0.29</td>
<td>148 f</td>
</tr>
<tr>
<td>57.0</td>
<td>0.02</td>
<td>0.24</td>
<td>-0.28</td>
<td>148 r</td>
</tr>
<tr>
<td>68.0</td>
<td>0.02</td>
<td>0.23</td>
<td>-0.26</td>
<td>170 r</td>
</tr>
</tbody>
</table>

In the table above, the width of the hydrogen oxidation region refers the forward sweep of cycle 3 at each temperature, whereas the maximum hydrogen oxidation current relates to the larger of the forward (f) or reverse (r) currents.

6.4.3 : 0.030 mm Plate - Effect of Continuous Potential Cycling

A series of continuous potential cycles (sweep limits 0.000 V and -1.000 V and scan rate 10 mVVs⁻¹) were applied to the platinum working electrode of the cell containing a 0.030 mm thick palladium plate and 1.0 M H₂SO₄ electrolyte. The temperature was held at room temperature (25.3°C) throughout. Following cycle 20, on observation of suppression of oxygen evolution at the virtual anode, the experiment was terminated. A selection of cyclic voltvoltoagrams and voltammograms, recorded during cycling, are shown in Figure 6.4.3.
Figure 6.4.3: Cyclic Voltvoltograms and Voltammograms Recorded During Extended Potential Cycling of the 0.030 mm Bipolar System

(a) Cycle 1

(b) Cycle 1 Voltammogram
(c) Cycle 2

(d) Cycle 4
(e) Cycle 6

(f) Cycle 10
(g) Cycle 12

(h) Cycle 14
(i) Cycle 15

(j) Cycle 17
(k) Cycle 20

![Graph showing RE/WE potential vs. cycle number.]

(l) Cycle 20 Voltammogram

![Graph showing current density vs. potential.]

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During cycling, the transition from hydrogen oxidation to oxygen evolution was gradually pushed out of the working potential window as with the 0.125 mm and 0.047 mm plates. In addition to this, the potential corresponding to a palladium-hydrogen electrode surface decreased from -0.582 V (+0.033 V vs SHE) on cycle 1 to -0.615 V (0.000 V vs SHE) by cycle 20 indicating that continual hydrogen saturation of the palladium substrate had occurred. However, from results obtained at the two larger bipolar plate thicknesses, it should be expected that the smaller volume of palladium employed here would become hydrogen saturated in less than 20 cycles (the number required for the 0.047 mm plate). Explanation can again be given in terms of the physical outgassing of hydrogen which results in the anode oxidising more hydrogen on the reverse scans of cycles 1 to 6 than on the forward scans as seen in Figures 6.4.3(a), (c), (d) and (e). The smaller volume of the 0.030 mm plate and the higher cell currents sustained than with the two thicker plates mean that the hydrogen concentration inside this plate must be greater. This will increase the hydrogen flux through the thinner plate, thereby facilitating the loss of hydrogen via diffusion and physical desorption. However, by cycle 10, hydrogen outgassing appears to be less prominent and, once again, the anode oxidises more hydrogen on the forward scan than on the reverse. It is not clear why this phenomenon should occur midway through cycling.

On continued cycling, the voltage profile follows that observed for the two thinner plates until eventually, the hydrogen oxidation to oxygen evolution transition is no longer observed in the working potential window. It is noted that the maximum hydrogen oxidation current increases from 93 mA on cycle 2 to 132 mA by cycle 20 which is slightly higher than the maximum of 120 mA attained on continued potential cycling of the 0.047 mm plate. This is as expected from a thinner electrode with greater scope for hydrogen flux.
6.4.4: 0.030 mm Plate - Effect of Increased Temperature

The effect of elevated temperature on the electrochemistry occurring at the 0.030 mm thick bipolar electrode’s virtual anode face was investigated over the range 20-70°C. Experimental details are as outlined in sections 6.3 and 6.4.2 for the 0.125 mm and 0.047 mm plates respectively. Cyclic voltvoltoagrams and voltammograms recorded at each temperature are shown in Figure 6.4.4 and electrochemical data are summarised in Table 6.4.2.

Looking at the cyclic voltvoltoagrams recorded at 69°C (Figure 6.4.4(a)) it is evident that physical outgassing of hydrogen occurs here during potential cycling to an even greater extent than with the 0.047 mm plate. The width of the hydrogen oxidation region for cycle 3 is only 0.16 V compared to 0.23 V for the thicker plate, indicating that the 0.030 mm plate, with comparable hydrogen uptake on cycling but contained in a smaller volume, physically desorbs hydrogen faster (as expected) from the increased hydrogen flux from the thinner palladium sample. From the maximum hydrogen oxidation currents on the reverse scan for each sample (170 mA for the 0.047 mm plate at 68.0°C and 142 mA for the 0.030 mm plate at 69.7°C) and the wider palladium oxide region with the 0.030 mm sample it is again observed that hydrogen leakage from the thinner plate decreases its performance at elevated temperature.
Figure 6.4.4: Cyclic Voltvoltograms and Voltammograms Recorded for the 0.047 mm System at Temperatures in the Range 20-70°C

(a) 69.7°C Voltvoltograms

(b) 69.7°C Voltammograms
(c) 59.7°C Voltvoltograms

(d) 59.7°C Voltammograms
(e) 50.0°C Voltvoltograms

![Voltvoltograms](image)

(f) 50.0°C Voltammograms

![Voltammograms](image)
(g) 40.9°C Voltvoltograms

(h) 40.9°C Voltammograms
(i) 30.1°C Voltvoltagrams

(j) 30.1°C Voltammograms
(k) 24.7°C Voltvoltograms

![Voltvoltogram](image)

(l) 24.7°C Voltammograms

![Voltammogram](image)
Table 6.4.2: Data Obtained from Cyclic Voltammograms and Voltvoltograms Recorded During Potential Cycling in the Range 20-70°C (All Values Relate to Cycle 3 of 3)

<table>
<thead>
<tr>
<th>Average Temp. /°C</th>
<th>Width of PdO region /V</th>
<th>Width of H₂ oxidation region /V</th>
<th>Onset of Oxygen evolution /V (RE/WE) vs SHE</th>
<th>Maximum H₂ oxidation current / mA</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.7</td>
<td>0.03</td>
<td>0.20</td>
<td>-0.28</td>
<td>107 f</td>
</tr>
<tr>
<td>30.1</td>
<td>0.03</td>
<td>0.22</td>
<td>-0.28</td>
<td>118 f</td>
</tr>
<tr>
<td>40.9</td>
<td>0.03</td>
<td>0.20</td>
<td>-0.27</td>
<td>145 r</td>
</tr>
<tr>
<td>50.0</td>
<td>0.04</td>
<td>0.19</td>
<td>-0.22</td>
<td>148 r</td>
</tr>
<tr>
<td>59.7</td>
<td>0.04</td>
<td>0.25</td>
<td>-0.30</td>
<td>175 r</td>
</tr>
<tr>
<td>69.7</td>
<td>0.06</td>
<td>0.16</td>
<td>-0.19</td>
<td>142 r</td>
</tr>
</tbody>
</table>

In the above table, as with data from the 0.047 mm plate, the width of the hydrogen oxidation window refers to the forward scan, whereas, the maximum oxidation current is taken from the forward (f) or reverse (r) scan as appropriate.

At lower temperatures, hydrogen outgassing becomes less prominent. This is seen in the gradual move towards oxidation of equal quantities of hydrogen on both forward and reverse scans, until at 20°C (Figure 6.4.4(k)) the width of the hydrogen oxidation region on the forward scan is greater than on the reverse and the bipolar plate begins to retain more hydrogen than it loses to desorption.
A certain degree of confusion is apparent in the overall trends occurring on increasing temperature. The maximum hydrogen oxidation current shows an overall increase (except between 59.7°C and 69.7°C) which is to be expected from the increased hydrogen generation and diffusion rates sustained at elevated temperature. However, the width of the palladium oxide region appears to increase with temperature and trends in the width of the hydrogen oxidation region and onset of oxygen evolution are unclear. It must be assumed that hydrogen loss via diffusion and physical desorption during low current areas of each cycle have an increasingly substantial effect on the performance reduction of the 0.030 mm bipolar plate. Thus the electrode’s hydrogen oxidation performance at a given applied (RE/Pt WE) potential on a forward scan would appear to be better at lower temperature where hydrogen loss is less of a problem. It is only at the cathodic extreme of the working potential window, where hydrogen is generated in increasingly large quantities at the palladium cathode face, that hydrogen loss is suppressed and the hydrogen anode delivers the higher currents expected from the thinner plate.

6.5 : Relative Hydrogen Oxidation Performance at Varying Bipolar Plate Thickness

Tables 6.5.1 and 6.5.2 show comparison of the maximum hydrogen oxidation currents attained on extended potential cycling and elevated temperature at each of the three palladium bipolar plate thicknesses. From the data displayed in Table 6.5.1 it is clear that at room temperature, on extended potential cycling, the hydrogen oxidation performance of the bipolar palladium electrode is enhanced at decreased plate thickness. This is as expected, since a thinner plate will allow a greater flux of hydrogen through to the anode face at a given rate of hydrogen generation (at the cathode face) thereby allowing larger hydrogen oxidation currents to flow. The
decreased hydrogen storage volume with smaller plate thickness will give rise to steeper hydrogen concentration gradients across the bipolar plate, thus facilitating the hydrogen transport process through the palladium sample.

Table 6.5.1: Maximum Hydrogen Oxidation Currents Attained on Extended Potential Cycling of the Bipolar System

<table>
<thead>
<tr>
<th>Plate Thickness /mm</th>
<th>Cycle Number</th>
<th>Max. Hydrogen Oxidation Current /mA</th>
<th>Max. Current Density for Hydrogen Oxidation /mA cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.125</td>
<td>2</td>
<td>30</td>
<td>4.2</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>60</td>
<td>8.5</td>
</tr>
<tr>
<td>0.047</td>
<td>2</td>
<td>118</td>
<td>17.7</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>116</td>
<td>16.4</td>
</tr>
<tr>
<td>0.030</td>
<td>2</td>
<td>93</td>
<td>13.2</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>132</td>
<td>18.7</td>
</tr>
</tbody>
</table>

Interesting behaviour is observed from the data obtained at elevated temperature (Table 6.5.2). Although there is a general trend towards increasing maximum hydrogen oxidation current with increasing temperature for each plate, decreasing the plate thickness does not appear to have much effect on the relative maximum oxidation current reached. Below 50°C, the oxidation currents attained at each temperature show a marked increase with reduced thickness as would be expected.
from the greater hydrogen flux and concentration gradients associated with thinner palladium samples. However, above 50°C, there appears to be very little change in maximum current on reduction of plate thickness. This is particularly the case with the 0.047 mm and 0.030 mm samples where the maximum current densities attained are 24.1 mA cm\(^{-2}\) and 24.8 mA cm\(^{-2}\) respectively.

The explanation for the observed current limitations at elevated temperature may lie with increased rate of hydrogen loss, through physical processes, with decreased plate thickness. As previously discussed, assuming comparable amounts of hydrogen are generated at the cathodic face of each bipolar plate, a thinner plate, having less volume, will sustain a steeper hydrogen concentration gradient from cathode face to anode face. This will give rise to increased flux of hydrogen through the thinner plate, facilitating its loss from the palladium substrate by diffusion and physical desorption at elevated temperature. Hydrogen thus removed from the plate will not be available for electrochemical oxidation and therefore the oxidation current will be decreased accordingly. At each plate thickness a dynamic equilibrium may be reached where the rate of hydrogen supply to the anode reaches a maximum because of the increased competition between the quantity hydrogen retained and transported to the anode and that lost by physical desorption. It is conceivable that the rate plateau may correspond to the same hydrogen oxidation current for all three samples assuming the same equilibrium conditions are reached at each plate thickness.

From the investigation undertaken here, it would appear that the maximum current density for hydrogen oxidation under the conditions employed is 24.8 mA cm\(^{-2}\) (for the 0.030 mm thick bipolar plate at 59.7°C).
Table 6.5.2: Maximum Hydrogen Oxidation Currents Attained at Elevated Temperature

<table>
<thead>
<tr>
<th>Plate Thickness /mm</th>
<th>Temperature /°C</th>
<th>Max. Hydrogen Oxidation Current /mA</th>
<th>Max. Current Density for Hydrogen Oxidation /mA cm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.125</td>
<td>20.3</td>
<td>49</td>
<td>6.9</td>
</tr>
<tr>
<td></td>
<td>29.1</td>
<td>70</td>
<td>9.9</td>
</tr>
<tr>
<td></td>
<td>38.9</td>
<td>105</td>
<td>14.9</td>
</tr>
<tr>
<td></td>
<td>48.9</td>
<td>125</td>
<td>17.7</td>
</tr>
<tr>
<td></td>
<td>59.6</td>
<td>153</td>
<td>21.6</td>
</tr>
<tr>
<td></td>
<td>64.2</td>
<td>147</td>
<td>20.8</td>
</tr>
<tr>
<td>0.047</td>
<td>20.0</td>
<td>88</td>
<td>12.4</td>
</tr>
<tr>
<td></td>
<td>29.9</td>
<td>98</td>
<td>13.9</td>
</tr>
<tr>
<td></td>
<td>38.1</td>
<td>105</td>
<td>14.9</td>
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<tr>
<td></td>
<td>47.8</td>
<td>148</td>
<td>20.9</td>
</tr>
<tr>
<td></td>
<td>57.0</td>
<td>148</td>
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<td></td>
<td>68.0</td>
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<td>24.1</td>
</tr>
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<td>0.030</td>
<td>24.7</td>
<td>107</td>
<td>15.1</td>
</tr>
<tr>
<td></td>
<td>30.1</td>
<td>118</td>
<td>16.7</td>
</tr>
<tr>
<td></td>
<td>40.9</td>
<td>145</td>
<td>20.5</td>
</tr>
<tr>
<td></td>
<td>50.0</td>
<td>148</td>
<td>20.9</td>
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<td></td>
<td>59.7</td>
<td>175</td>
<td>24.8</td>
</tr>
<tr>
<td></td>
<td>69.7</td>
<td>142</td>
<td>20.1</td>
</tr>
</tbody>
</table>
6.6: Conclusions

It has been demonstrated that a self-feeding hydrogen anode can be created at the positive face of a hydrogen-sorbing bipolar electrode. The effect on the hydrogen oxidation performance of this anode with extended potential cycling, elevated temperature and reduced bipolar plate thickness was investigated. It was shown that for a given plate thickness, extended cycling and elevated temperature both served to facilitate the hydrogen supply mechanism to the anode and thereby increase the maximum oxidation current attained within the operating potential window. However, problems of hydrogen loss through physical desorption at increased temperature and increased flux through a thinner palladium plate lead to restrictions on the achievable current density. The highest performance, 24.8 mAcm\(^2\) at 59.7°C, was attained with the 0.030 mm plate. Further investigation needs to be carried out in order to determine the optimum working temperature, plate thickness and sustainable current density if the device is to be commercially exploited. Particularly, minimisation of the physical outgassing process needs to be addressed, since this is seen as a major contributor to the restriction of the maximum sustainable hydrogen oxidation current.

Although palladium was used here as the bipolar electrode substrate, it should be possible to successfully employ other cheaper hydrogen sorbing materials (alloys, composites etc.) for this application. An increasing number of such materials are becoming available for hydrogen storage applications. Of particular note are the lanthanum-nickel alloys [39,40] (of AB\(_3\) stoichiometry).

Employed as a single bipolar cell, the system described here does not offer energy savings as a hydrogen anode; an oxygen evolving anode is still required as a counter electrode to drive the bipolar plate. A stacked array of self-feeding hydrogen anodes,
however, could substantially decreased the energy consumption of processes dependent on non-interfering counter anodes or the proton pump action of this bipolar electrode. Application is seen in the electrosynthesis of compounds which are readily oxidised at the potentials sustained at an oxygen evolving anode but which remain stable at hydrogen oxidation potentials. The bipolar electrode as described also offers the possibility of being used, in conjunction with ion-conducting membranes, in industrial salt splitting [58-60] for example, the generation of sulphuric acid and sodium hydroxide from aqueous sodium sulphate electrolytes. In addition to this, the non-gassing nature of the electrode’s cathodic face makes it an excellent choice as a substrate electrode for cathodic precipitation as outlined in Chapter 5. A stacked array of flow through cells incorporating this bipolar plate design may also be used in a number of purification processes including dialysis, decontamination of water and recovery of metals from electrolyte waste where the contaminants (or recoverable metals) have insoluble hydroxide salts. For such application, metal hydroxide deposits, accumulated at the non-gassing cathode, would have to be periodically removed in order to avoid current degradation through excessive build-up of the resistive cathode film.
Chapter 7

Overall Conclusions and Recommendations
Chapter 7: Overall Conclusions and Recommendations

It has been successfully demonstrated that cathodic precipitation is a useful technique for the generation of precursors to alumina. Furthermore, it was shown that by manipulation of the deposition potential regime, control over the porosity and macro morphology of the deposited film was achievable. Films generated by a constant applied potential proved to be bulky, porous and structurally weak. Continued growth at the deposit/electrolyte interface, during polarisation, lead to extremely hydrated deposits of aluminium hydroxide which fragmented extensively on drying. On the other hand, pH cycling at the palladium electrode surface and the growth of material within the deposit pores, occurring with pulsed or cycled potential programmes, facilitated the generation of thinner, less porous and denser deposits of the alumina precursor. Mechanisms proposed for pore-size reduction and densification were later substantiated by a series of in-situ optical studies of film growth at a palladium strip working electrode.

Although the research described here deals solely with the generation of precursors to alumina, cathodic precipitation may be employed in the deposition of any ceramic precursor containing metal ions which have insoluble hydroxides. Indeed, by employing a series of deposition electrolytes or a single mixed salt electrolyte, cathodic precipitation should prove a simple, inexpensive route to the generation of laminated and mixed oxide ceramics respectively. The addition of colloidal suspensions of micro-fibres or particulates to the deposition medium also should facilitate the manufacture of ceramic composite materials. When employing electrochemical cathodic precipitation in the generation of protective ceramic surface coatings, the material to be coated will, in most cases, be incapable of hydrogen absorption and consequently, hydrogen gassing from its surface will disrupt the film
growth process. In such cases, it should be possible to precoat the material to be protected with a thin layer of palladium metal (by either electrochemical plating or physical vapour deposition). Thus, the material's surface will become hydrogen absorbing and will therefore support the film growth mechanisms required for successful cathodic precipitation. The application of a surface coating of palladium should therefore allow the deposition of ceramic precursor material (for use in surface coatings for heat and corrosion protection) at almost any surface including that of non-conducting glass and plastic.

Future research should concentrate on tailoring the applied potential regime and electrolyte composition to the manufacture of deposits with predetermined stoichiometry and physical morphology. It is anticipated that further investigation into control of deposit growth morphology should eventually lead to an electrochemical technique for the manufacture of electrical, engineering and sensing ceramics to rival most chemical and physical processes.

In order to demonstrate the potential of cathodic precipitation as a versatile ceramic fabrication technique, it was applied to the generation of humidity sensing films. A device generated by a pulsed potential programme was shown to exhibit good sensitivity to changes in atmospheric humidity in the range 40 to 90 %RH when compared to the response of a commercially available sensor. AC impedance analysis of this aluminium hydroxide based device indicated a similar equivalent circuit model, and therefore similar conduction characteristics, to that predicted for a dry alumina device. Further investigation into the effect of salt doping and calcination of the cathodically generated sensing material is required in order to improve the low humidity response of the device.
Finally, it was demonstrated that thick films of ceramic precursor could be generated at the non-gassing cathodic face of a bipolar palladium plate. Investigation into the properties of this cathode lead to the realisation of a self-feeding hydrogen anode at the opposite face of the bipolar plate. It was found that continual potential cycling, elevated temperature and reduced plate thickness all served to improve the hydrogen oxidation performance of the anode by facilitating the hydrogen transport process through the palladium substrate. However, loss of hydrogen by physical desorption proved to be a problem at elevated temperature as the plate thickness was decreased. Optimum performance, 24.8 mA cm\(^{-2}\) for hydrogen oxidation under the employed experimental conditions, was attained at 59.7°C for a 0.030 mm thick bipolar plate. It is anticipated that further investigation into the extent of physical hydrogen desorption with increasing temperature and decreasing plate thickness should lead to improved hydrogen oxidation performance. Future research should therefore concentrate on minimisation of hydrogen loss from the bipolar substrate and optimisation of plate thickness and operating temperature allowing optimum performance to be attained. Substitution of palladium with less expensive hydrogen-sorbing materials should also be carried out in order to reduce the capital cost of the device. It is expected that the self-feeding hydrogen anode described here should make an attractive alternative to currently available anodes which are based on gas diffusion electrode technology. Applications are seen in a number of electrochemical processes including salt splitting, water treatment, recovery of metals from waste electrolyte and the generation of oxidation sensitive materials, where benefits will be gained from the ability to employ a bipolar array of cells thereby dramatically reducing operating costs.

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Appendix 1

The Palladium/Hydrogen System
Appendix 1 : The Palladium/Hydrogen System

First reported in 1866 by T. Graham [61,62], the bulk absorption of hydrogen by palladium has been the subject of much fundamental research [63-65]. Graham discovered that on cooling from red heat, palladium could absorb up to 935 times its own volume of hydrogen. This amounted to an approximate palladium hydride composition of Pd₄H₅, which inferred a hydrogen concentration approaching that in liquid H₂. Reheating the alloy resulted in outgassing of absorbed hydrogen, making palladium a convenient hydrogen storage system. He found that the specific affinity of palladium for hydrogen absorption made it capable of hydrogen concentration and purification from gaseous mixtures: an application for which it is widely used today.

At room temperature (25°C) a clean specimen of palladium metal can readily absorb sufficient hydrogen to give a hydride with a H:Pd ratio of 0.5 (formula PdH₀.₅). As a result, the volume of the face centred cubic palladium lattice may expand by as much as 10%. However, under such conditions there is little or no macro-disruption to the specimen and an increase in surface roughness may be the only visible evidence that hydrogen absorption has occurred. On heating to 300°C hydrogen is outgassed and the palladium is almost completely restored to its original dimensions.

At the atomic level, small quantities of hydrogen entering the palladium lattice at room temperature cause very little change in the lattice dimensions. At around three atoms percent hydrogen (PdH₀.₀₅) the α-phase is formed. The lattice remains cubic close packed with respect to palladium and the lattice constant, a, is virtually unchanged. At this stage, the ‘hydride’ can be thought of as a solid solution of hydrogen in palladium. Upon further absorption, volumes of the lattice take up hydrogen into the octahedral interstices giving rise to localised areas of hydride with a
structure very similar to that of sodium chloride. This configuration is known as the β-phase. Again the palladium atoms remain cubic close packed. However, insertion of hydrogen into the octahedral sites causes localised lattice expansion which in turn exerts strain on areas which are still in the α form. Thus, the strained α-phase lattice becomes more susceptible to hydrogen absorption. A two phase system exists until a hydrogen concentration of around fifty atoms percent (PdH$_{0.5}$) is attained. Here, the hydride is fully converted to the β-form; having a defect (non-stoichiometric) sodium chloride structure. Following conversion to the β-phase, minimal expansion occurs on further hydrogen up-take since the remaining octahedral sites are situated in an already expanded lattice. Overall, the lattice constant increases from 3.891 Å for palladium metal to 3.894 Å for the α-phase at PdH$_{0.03}$ and 4.026 Å for the β-phase at PdH$_{0.6}$ [66].

Monitoring changes in the palladium/hydrogen ratio with hydrogen pressure at different temperatures illustrates the relationship between hydrogen uptake and the resulting hydride phase composition. Figure A1.1, taken from Shaw’s “Inorganic Hydrides” [67], shows plots of isotherms for temperatures in the region of 80 to 313°C. Three distinct regions can be identified:

1. A rapid rise in the isotherm with increasing hydrogen content relating to the generation of a solid solution of hydrogen in palladium - the α-phase.

2. The plateau region. Here, two immiscible phases exist; the solid solution or α-phase, and the non-stoichiometric hydride or β-phase. The plateau region diminishes with increasing temperature until around 300°C (the critical temperature) where it disappears altogether. Increasing the hydrogen content of the palladium
along the plateau region gives rise to predominance of the β-phase at the expense of the α-phase.

3. Here, the material exists solely as the β-phase hydride. At this point a further increase in hydrogen pressure causes little change in hydrogen content. In this region, the rate of uptake of hydrogen increases with increasing temperature whereas the equilibrium concentration decreases. This is illustrated by the fact that although the final composition will be reached quicker and at much lower hydrogen pressures for the higher temperature sample, theoretically at -78°C a hydride with composition PdH (H/Pd = 1) is attained whereas at 100°C the maximum H/Pd ratio is approximately 0.6 (PdH$_{0.6}$).

From an electronic point of view, the uptake of hydrogen by palladium causes little change to the material’s properties. The electrical conductivity remains high, falling from 9.3 x 10$^4$ mhos for the metal at room temperature to 4.5 x 10$^4$ mhos on hydrogen saturation. It is thought that some of the palladium’s valency electrons are donated to the hydrogen atoms, thereby forming palladium-hydrogen bonds and that the remainder are used in bonding between palladium atoms allowing them to take part in conduction. Hydrogen is therefore predominantly present as the hydride ion (H⁻) within the palladium lattice, although some will exist as protons. Thus the bonding does not fall into any specific category and the material may be thought of as part hydride and part palladium-hydrogen solid solution. Such a model explains the material’s metallic character and its non-stoichiometry.
In addition to changes in the physical nature and conductivity of palladium on hydrogen uptake, there are marked changes in its electrochemistry corresponding to transitions between the three phase regions (α, α+β and β). On initial exposure to one atmosphere of hydrogen in sulphuric acid electrolyte, the potential of a palladium electrode (vs SHE) falls steeply from around 100 mV to 50 mV (the initial potential being dependent on the thickness and surface morphology of the sample used). On further hydrogen absorption there then follows a plateau region where the potential remains at a constant 50 mV. Finally, the potential falls gradually to zero. Aben and Burgers [57] showed (with the aid of X-ray diffraction) that the electrode’s surface layer in these three regions consisted, respectively, of the α-, coexistent α+β and β-
phase. An investigation by Schuldiner, Castellan and Hoare [68], however, failed to observe the fall in potential to zero from the plateau region. Here, a further decrease to zero volts was only attained when the palladium was cathodically charged, thereby electrochemically saturating the β-phase lattice with hydrogen. It is thought [68] that these apparently conflicting results arise because of differences in degree of surface activation of the palladium samples used by the two groups; only well activated electrodes give rise to the equilibrium potential of 0 V.

Although it has been extensively researched, the palladium-hydrogen system still remains the most complex of all the metal hydride systems. The commercial demand for pure hydrogen and new means of its safe convenient storage will ensure that further studies are carried out and that a better understanding of the interaction between palladium and hydrogen is obtained.
Appendix 2

Conduction Mechanisms in Aluminium Oxide (and Hydroxide) Humidity Sensors
Appendix 2: Conduction Mechanisms in Aluminium Oxide (and Hydroxide) Humidity Sensors

The sensing properties of alumina-based devices arise from changes in the surface conductivity of the porous material with humidity [45]. At low humidities, where relatively few surface sites have adsorbed water molecules, it is thought that a phonon-induced electron tunnelling between donor water sites is responsible for conduction. On the other hand, at high humidities, where monolayer coverage of water molecules has been attained, protonic conduction is the dominant mechanism. A phonon [69] is a quantum of vibrational energy generated within a solid’s crystal lattice as a result of the vibration of atoms therein. Because all atoms within a lattice vibrate about fixed points, their vibration throughout the lattice is correlated and therefore gives rise to oscillations, within the whole crystal, known as ‘lattice waves’. These waves may travel through the crystal at speeds of the order of the speed of sound. The quantum of vibrational energy, or phonon, is therefore analogous to the photon as related to light waves. A collision between a phonon and electron (as with a photon and electron) may result in transfer of energy to the electron allowing it to ‘tunnel’ through the energy barrier between conduction bands of donor water sites at the alumina surface. As a result, surface conduction may be achieved with minimal surface water adsorption. With increased atmospheric water content, the corresponding rise in the number of surface sites incorporating adsorbed water molecules (donor water sites) will supply more electrons to the conduction bands and thereby increase the probability of phonon-induced electron tunnelling. The smaller gap between adjacent water sites on increased humidity will lower the energy barrier between the conduction bands of the two sites, thereby making electron tunnelling easier. Anion impurities at the alumina surface will also aid conduction via electron tunnelling by injecting electrons into the alumina conduction bands. A high surface
concentration of anions will therefore increase the magnitude of the sensor’s conductivity at low surface water content. Hence, the conductivity of an alumina surface may be very sensitive to changes in atmospheric humidity even at low relative humidity where proton conduction is unfeasible.

Alumina films generated by anodisation of an aluminium surface are generally formed at potentials in the region of 10 to 100 V (with respect to a platinum cathode) in acid electrolyte. They consist of a thin (ca. 1 nm/V) coherent layer of alumina in contact with the metal, on top of which is grown porous alumina with cylindrical parallel sided pores. The porous layer typically has pores of diameter 1 nm/V at the centre of columnar cells of 2.5 to 2.8 nm/V diameter. Figure A2.1 depicts a typical Al₂O₃ humidity sensor. The sensor material is an amorphous ionic solid with some covalent character. Al=O bonds are predominant in the coherent surface layer, whereas Al-O-Al bonds appear in the porous region. The material contains impurities in the form of free or adsorbed water and acid anions (up to 20% by weight) from the electrolyte in which it was generated. It has also been established [70] that the films prepared in acid may contain Al³⁺ and OH⁻ ions as well as bound water molecules and free acid trapped in the pores. Anions are attracted to the positively charged alumina surface during film growth. They become held there by hydrogen bonding of their oxygen atoms to hydrogen atoms of surface adsorbed water molecules. The result is a sensor surface comprised of microcrystals of amorphous alumina held together by regions containing electrolyte anions, water molecules, hydroxyl ions and protons, linked by a multitude of hydrogen bonds.
Species at the sensor surface which contribute to the conductivity of the device are aluminium and oxygen ions with unsatisfied valency (Lewis-acid and Lewis-base sites respectively) and adsorbed anions which introduce donor surface states at low humidities along with sites to hydrogen bond water, and provide mobile ions for conduction at high humidities. On introduction of the dry oxide surface to a humidified atmosphere chemisorption of water takes place. For every water molecule, two surface hydroxyls are formed. The OH\(^-\) group adsorbs onto an Al\(^{3+}\) ion and the remaining proton uses an adjacent O\(^2-\) site to form the second hydroxyl:

\[
\text{Al}^{3+} + \text{OH}^- = [\text{Al}:\text{OH}]^{2+} \quad \text{and} \quad \text{O}^{2-} + \text{H}^+ = \text{O}:\text{H}^- 
\]

Chemisorption continues until the oxide surface is covered in hydroxyl groups (around 19 OH per 100 Å\(^2\)) [45]. At relatively low humidities, once the chemisorption
process is complete, the first physisorbed layer of water molecules begins to form. Water molecules from the humidified atmosphere each hydrogen bond to two hydroxyl groups [71]. As water condensation continues, randomly distributed water sites on the alumina surface are formed. These then grow into clusters or islands of molecules which eventually coalesce to form a continuous physisorbed layer of water. The attainment of this monolayer of water molecules is complete when the atmospheric humidity reaches around 40 %RH [49]. Prior to this point, phonon-induced electron tunnelling is thought to be the major contributor to conduction. The double hydrogen bonding of water molecules in the first physisorbed layer restricts free rotation in an applied electric field and thereby inhibits proton conduction.

At high relative humidities (in excess of 40 %RH) a second physisorbed layer of water molecules builds up. It is thought [72] that the water molecules in this layer are, in general, singly hydrogen bonded making them more mobile and more readily available to provide protons for proton conduction via the Gröthuss chain reaction [50] ('proton hopping'). Surface anions and the hydroxylated alumina surface also provide mobile protons. As the humidity increases further, additional water layers form. Dissolution of anions and cations (residual electrolyte from sensor fabrication) into the increasing volume of physisorbed water now aids the conduction process by introducing an ionic conduction path. Eventually, maximum surface conductivity is attained and the sensor is no longer sensitive to further rises in atmospheric humidity.

In general, devices fabricated from dry alumina are more sensitive to low relative humidity (0 to 40 %RH) and their performance is often enhanced by the introduction of high surface concentrations of anion impurities. Conversely, high humidity sensitivity may be improved by decreasing the anion concentration or introduction of salt dopants into the alumina substrate.
Although the humidity sensor described in Chapter 4 is based on aluminium hydroxide and not anodised aluminium, it is thought that similar conduction mechanisms should be involved with both devices since it is surface conduction which determines the sensor's response to humidity and the alumina surface needs first to be hydroxylated before sensing can occur. However, it is evident that the aluminium hydroxide sensor shows a better response to the high end of the humidity spectrum (40 to 100 %RH). This may be due to the greater degree of water retention in the dry hydroxide substrate allowing the first physisorbed water layer to form prior to attainment of a 40 %RH atmosphere, thereby giving rise to a conductivity plateau from 0 to 40 %RH. Above 40 %RH, the second physisorbed layer builds up and proton conductivity then accounts for the sensitivity of the device to high relative humidity.
Appendix 3

Impedance, Impedance Spectra and Equivalent Circuit Modelling
Appendix 3: Impedance, Impedance Spectra and Equivalent Circuit Modelling

By applying a known potential across an unknown electrical resistance and measuring the resulting current, we can accurately calculate, by application of Ohms law, the value of that resistance. Given an unknown capacitance, we are faced with a slightly more complicated solution. Firstly, the capacitor is charged to various known potentials using a direct current (DC) polarisation. Then, for each potential, the capacitor is discharged through a ballistic galvanometer giving a deflection, the magnitude of which is directly proportional to the charge passed. Thus, knowing the galvanometer's ballistic constant, the charge passed at each potential can be calculated. Finally, the ratio of charge passed (Q in coulombs) over potential across the capacitor (V in volts) will be constant and numerically equal to the capacitance (C in farads).

\[ \frac{Q}{V} = C \]

However, given a series or parallel combination of resistor and capacitor (or more involved circuitry) things become a lot more complicated. In this situation, DC polarisation is of little use in resolving the individual component values, and therefore, alternating current (AC) techniques must be employed.

The total resistance to current flow of a circuit under AC polarisation is known as the circuit’s impedance. The relationship between a circuit’s impedance and the frequency of the applied AC signal, which will be unique to that particular circuit, allows us to determine the values of its individual components. This is of particular use in probing conducting materials and electrochemical cells. Here, breaking the material or device
down into a circuit of discrete electronic components which mimic its conduction characteristics, may provide us with a better understanding of the device and allow us to improve on its design. The process of fitting an electronic circuit to the impedance characteristics of a non-electronic device is known as equivalent circuit modelling, a technique now widely used in the electrochemical community.

Resistance to the flow of an alternating current must, by its very nature, be a vector quantity. Thus a circuit under AC polarisation has both a real part and an imaginary part to its total impedance, which is quantified by the complex representation:

\[ Z = Z' + jZ'' \]

where \( Z \) is the total impedance (vector sum)

\( Z' \) is the real part impedance

\( Z'' \) is the imaginary part impedance

and \( j \) is the square root of minus one

Complex impedance can be represented diagramatically on Cartesian axes as an Argand diagram as depicted in Figure A3.1.

Here, the real part impedance is plotted along the abscissa and the imaginary part along the ordinate axis. This gives a point with co-ordinates \((Z',Z'')\) whose distance from the origin is equal to the magnitude of the impedance, \( Z \). The angle \( \phi \) is referred to as the phase angle and is a measure of the lag between current and potential under AC conditions.
For the system under investigation, taking values of $Z'$ and $Z''$ at various frequencies leads to the attainment of a data set which is recognised as the impedance spectrum of that system. Impedance spectra are commonly expressed in one of two graphical representations. The complex plane plot (Figure A3.2) has the impedance data plotted in Argand diagram form with negative values of $Z''$ up and positive values down. A Bode plot (Figure A3.3) displays both phase angle, $\phi$, and log(modulus of $Z$) vs log(frequency/Hz). The Bode representation is useful for displaying high frequency features of the impedance spectrum which may be hidden in a complex plane plot (where the high frequency points are often very close together). On a Bode plot, a pure resistance is represented by a horizontal line (log $Z$ vs log (frequency)) and a constant phase angle of $0^\circ$ while pure capacitance is shown as a straight line with slope -1 and a constant phase angle of $90^\circ$. 

Figure A3.1: Argand Diagram Representation of a Complex Number
Figure A3.2: Complex Plane Plot of Impedance Data from a Parallel RC Circuit

Figure A3.3: Bode Plot of Impedance Data from a Parallel RC Circuit
Obtaining An Equivalent Circuit Model From Impedance Data

For the purpose of fitting the data to an idealised equivalent circuit it is convenient to employ the complex plane representation. It is possible to determine, with varying degrees of accuracy, the value of equivalent resistive, capacitive, inductive, etc. components of the system under test, by manipulation of its impedance spectrum data in complex plane form. For ideal one or two component systems (rarely observed for real electrolytes), equivalent circuit modelling is relatively straightforward [73]. Typical impedance responses to several simple combinations of resistance, capacitance and inductance are as shown in Figure A3.4. An explanation of each response is also given.

Figure A3.4: Impedance Responses Of Simple Series And Parallel Circuits

(a) Pure R

(b) Pure C

where \( \omega_{\text{max}} \) is the frequency at the peak \( Z'' \) value \( (Z''_{\text{max}}) \)
(c) Pure L

\[ L = \frac{Z''_{\text{max}}}{\omega_{\text{max}}} \]

(d) Constant Phase Element

\[ -Z'' \]

\[ Z' \]

(e) R and C in Series

\[ C = \frac{1}{-Z''_{\text{max}}, \omega_{\text{max}}} \]

\[ Z' = R \]

\[ -Z'' \]

\[ Z' \]

(f) R and C in Parallel

\[ C \text{ obtained from } Z''_{\text{max}} = \frac{-\omega_{\text{max}} CR^2}{1 + (\omega_{\text{max}} CR)^2} \]

\[ Z' = R \]

\[ -Z'' \]

\[ Z' \]

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(g) R and L in Series

\[ L = \frac{Z''_{\text{max}}}{\omega_{\text{max}}} \]

(h) R and L in Parallel

\[ Z' = R \]

L obtained from \[ Z''_{\text{max}} = \frac{R'\omega_{\text{max}}L}{R'(\omega_{\text{max}}L)^2} \]

(i) R and cpe in Series

(j) R and cpe in Parallel

[Diagram showing R and cpe in Series]

[Diagram showing R and cpe in Parallel]

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Explanation of Figure A.3.4:

(a) Pure Resistance

\[ Z = R \]

The impedance has a real value and no imaginary value at all frequencies (i.e. \( Z = R \) and \( Z = Z' + jZ'' \) imply that \( Z' = R \) and \( jZ'' = 0 \), so \( Z'' = 0 \)). Thus, as the applied frequency is swept, the response is always \( Z' = R, Z'' = 0 \), giving rise to a single point at \( (R,0) \) on the complex plane plot.

(b) Pure Capacitance

\[ Z = \frac{1}{j\omega C} \]

where \( \omega \) is the angular frequency of the AC signal such that \( \omega = 2\pi f \)

(\( f \) is the frequency in Hz)

Multiplying top and bottom by \( j \) gives

\[ Z = (j/j^2\omega C) = -j/\omega C \]

Hence, the real part impedance, at all frequencies, is zero and the imaginary part is equal to \(-j/\omega C\). Therefore, \( Z'' = -1/\omega C \) such that \( Z'' \) varies with reciprocal frequency. Hence, the resulting complex plane plot is a straight line (-\( Z'' \) always positive) parallel to the -\( Z'' \) axis and beginning at the origin \( (Z' = 0) \).
(c) Pure Inductance

\[ Z = j\omega L. \]

Hence, \( Z' = 0 \) at all frequencies, and \( Z'' = \omega L \). The resulting complex plane plot being a straight line (\(-Z''\) always negative) parallel to the \(-Z''\) axis and beginning at the origin (\( Z' = 0 \)).

(d) The Constant Phase Element

An equivalent component sometimes encountered in electrochemical systems is the constant phase element (cpe). The cpe is not a discrete electronic component and no analogous electronic circuit which reproduces all its impedance characteristics can be fabricated. Constant phase elements are introduced into an equivalent circuit where conventional components fail to adequately model the impedance characteristics of the device under investigation. They are generally thought of as a 'leaky capacitor'; a hybrid between resistor and capacitor. The impedance of a cpe is given by

\[ Z_{\text{cpe}} = k(j\omega)^p \]

where \( p \) lies between 0 and 1 and \( k \) is a constant.

When \( p = 0 \), \( Z = k \) and the cpe takes the form of a pure resistance with \( R = k \).

When \( p = 1 \), \( Z = -jk/\omega \) and the cpe becomes a pure capacitance with \( C = 1/k \).
However, when \( p = \frac{1}{2} \), \( Z = k(j\omega)^{-\frac{1}{2}} \)

therefore

\[
Z = \frac{k}{\sqrt{j\omega}}
\]

and multiplying top and bottom by \((1 - j)\) gives

\[
Z = \frac{k(1 - j)}{\sqrt{j\omega - j\sqrt{j\omega}}}
\]

expanding the denominator by squaring the terms within a square root gives

\[
Z = \frac{k(1 - j)}{\sqrt{(\sqrt{j\omega - j\sqrt{j\omega}})^2}} = \frac{k(1 - j)}{\sqrt{j\omega - 2j^2\omega - j^2j\omega}} = \frac{k(1 - j)}{\sqrt{j\omega + 2\omega - j\omega}} = \frac{k(1 - j)}{\sqrt{2\omega}}
\]

therefore

\[
Z = \frac{k(1 - j)}{(2\omega)^{\frac{1}{2}}}
\]

which is known as the Warburg impedance. The equivalent component is imagined as a pair of infinitely long wires, one highly conducting and the other consisting of a series of resistors. Between each resistor there is a connection to the other wire via a capacitor.
Displayed in complex plane form, the impedance spectrum of an isolated cpe (if one were to exist) would take the form of a line, beginning at the origin and inclined at an angle of $\pi/2$ to the $Z'$ axis.

(e) Resistor and Capacitor in Series

In accordance to Kirchoff's law, resistances (and impedances) in series can be summed. Therefore, for a resistance and capacitance in series,

\[ Z = R - j\omega C \]

Hence, $Z' = R$ and $Z'' = -1/\omega C$. The real part impedance is therefore frequency independent, whilst the imaginary part varies linearly with applied frequency. Therefore, the complex plane plot is a straight line parallel to the -$Z''$ axis (with -$Z''$ always negative) and passing through $Z' = R$.

(f) Resistor And Capacitor In Parallel

Here, impedances in parallel are summed as their reciprocals:

\[ 1/Z = 1/R + j\omega C \]

Therefore:

\[ Z = \frac{1}{\frac{1}{R} + j\omega C} = \frac{1}{1 + j\omega CR} = \frac{1}{1 + j\omega CR} = \frac{R}{1 + j\omega CR} \]
and multiplying top and bottom by the complex conjugate, yields:

\[ \frac{R}{1 + j\omega CR} \cdot \frac{1 - j\omega CR}{1 - j\omega CR} = \frac{R - j\omega CR^2}{1 - j^2\omega^2 C^2 R^2} = \frac{R - j\omega CR^2}{1 + (\omega CR)^2} = \frac{R(1 - j\omega CR)}{1 + (\omega CR)^2} \]

Therefore:

\[ Z' = \frac{R}{1 + (\omega CR)^2} \]

and

\[ Z'' = \frac{-\omega CR^2}{1 + (\omega CR)^2} \]

Thus, when \( \omega = 0 \), \( Z' = R \) and \( Z'' = 0 \); when \( \omega = \infty \), \( Z' = 0 \) and \( Z'' = 0 \). And from the equation for \( Z' \),

\[ (\omega CR)^2 = \frac{R}{Z'} - 1 \]

Substituting into the equation for \( Z'' \) gives

\[ Z'' = \frac{-\omega CR^2}{1 + \left(\frac{R}{Z'} - 1\right)} = \frac{-\omega CR^2}{\frac{R}{Z'} - 1} = -Z' \omega CR \]

Squaring both side gives:

\[ Z''^2 = Z'^2 \omega^2 C^2 R^2 = Z'^2 (\omega CR)^2 \]

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Substituting again for \((\omega CR)^2 = \frac{R}{Z'} - 1\) gives

\[
Z'' = Z'^2 \left( \frac{R}{Z'} - 1 \right) = \frac{RZ'^2}{Z'} - Z'^2 = RZ' - Z'^2
\]

adding \(\frac{R^2}{4}\) to each side gives:

\[
Z'' + \frac{R^2}{4} = RZ' - Z'^2 + \frac{R^2}{4}
\]

which rearranges to

\[
\frac{R^2}{4} = \left( Z'^2 - RZ' + \frac{R^2}{4} \right) + Z''^2
\]

and this is equivalent to

\[
\frac{R^2}{4} = \left( Z' - \frac{R}{2} \right)^2 + (Z'')^2
\]

which is the equation of a circle with radius \(R/2\) and centre \((R/2, 0)\). Hence, the complex plane plot is semicircular (since negative values of \(-Z''\) do not occur).
(g) **Resistor and Inductor in Series**

\[ Z = R + j\omega L \]

Hence, \( Z' = R \) at all frequencies, and \( Z'' = \omega L \). The complex plane plot in this case is a straight line parallel to the -Z'' axis, with all -Z'' values negative. The line passes through the point \((R,0)\).

(h) **Resistor and Inductor in Parallel**

\[ \frac{1}{Z} = \frac{1}{R} + \frac{1}{j\omega L} \]

Therefore

\[ Z = \frac{1}{\frac{1}{R} + \frac{1}{j\omega L}} = \frac{1}{\frac{j\omega L + R}{Rj\omega L}} = \frac{Rj\omega L}{R + j\omega L} \]

Multiplying top and bottom by the complex conjugate \((R-j\omega L)\) gives

\[ Z = \frac{Rj\omega L}{R + j\omega L} \cdot \frac{R - j\omega L}{R - j\omega L} = \frac{R^2 j\omega L - Rj^2 \omega^2 L^2}{R^2 - Rj\omega L + Rj\omega L - j^2 \omega^2 L^2} = \frac{R^2 j\omega L + R\omega^2 L^2}{R^2 + \omega^2 L^2} \]

or further simplified

\[ Z = \frac{R(\omega L)^2 + R^2 j\omega L}{R^2 + (\omega L)^2} \]
Thus

\[ Z' = \frac{R(\omega L)^2}{R^2 + (\omega L)^2} \quad \text{and} \quad Z'' = \frac{R^2\omega L}{R^2(\omega L)^2} \]

When \( \omega = 0 \), \( Z' = 0 \) and \( Z'' = 0 \) and when \( \omega = \infty \), \( Z' = 0 \) and \( Z'' = 0 \)

From the equation for \( Z' \)

\[ Z'R^2 + Z'(\omega L)^2 = R(\omega L)^2 \]

and so

\[ Z'R^2 = R(\omega L)^2 - Z'(\omega L)^2 = (\omega L)^2(R - Z') \]

therefore

\[ (\omega L)^2 = \frac{Z'R^2}{(R - Z')} \]

Substituting for \((\omega L)^2\) into the equation for \(Z''\) gives

\[ Z'' = \frac{R^2\left(\frac{Z'R^2}{R - Z'}\right)^{1/2}}{R^2 + \left(\frac{Z'R^2}{R - Z'}\right)} = \frac{R^2\left(\frac{Z'}{R - Z'}\right)^{1/2}}{R^2 + \left(\frac{Z'R^2}{R - Z'}\right)} \]
Multiplying top and bottom by \( \frac{R - Z'}{R^2} \) gives

\[
Z'' = \frac{R^2Z'^2}{(R - Z')^2} \cdot \frac{R - Z'}{R^2} = \frac{RZ'^2}{(R - Z')^2} = Z'' \cdot \frac{(R - Z')^2}{R^2}
\]

or

\[
Z'' = \sqrt{Z(R - Z')}
\]

expanding and squaring both sides gives

\[
Z''^2 = -Z'^2 + Z'R
\]

and therefore

\[
Z''^2 + Z'^2 - Z'R = 0
\]

adding \( \frac{R^2}{4} \) to both sides gives

\[
\frac{R^2}{4} = \left( \frac{R^2}{4} + Z'^2 - Z'R \right) + Z''^2
\]

which reduces to

\[
\frac{R^2}{4} = \left( \frac{R}{2} - Z' \right)^2 + Z''^2
\]
This is the equation of a circle with centre \((R/2,0)\) and radius \(R/2\). And since positive values of \(-Z''\) do not occur for a parallel RL combination the complex plane plot is a semicircle.

(i) **Resistor and Constant Phase Element in Series**

As with an isolated cpe, the impedance spectrum of a series R/cpe combination will be represented by a line inclined at an angle of \(\pi/2\) to the \(Z'\) axis. However, in this case, the line will contact the \(Z'\) axis at \(Z' = R\).

(j) **Resistor and Constant Phase Element in Parallel**

Here, the impedance spectrum takes the form of a depressed semicircle which cuts the \(Z'\) axis at both the origin and at \(Z' = R\). The diameter of the depressed semicircle, \(d\), is related to the resistance \(R\) and parameter \(p\) as follows:

\[
d = R/\sin[\pi/2]
\]

**Impedance Data Relating to Electrochemical Systems Under DC Polarisation**

Impedance studies carried out on materials and electrochemical devices have one rather unfortunate drawback. Although used to provide impedance information about the sample material or electrolyte placed between two contact electrodes, they also inadvertently probe the conducting characteristics of the electrodes themselves, and both electrode/electrolyte interfaces. Layers of impurity at the electrode or electrolyte surfaces and poor contact areas between the two will add to the system’s contact impedance and therefore affect the impedance spectrum. In addition to this, because
the charge carriers in the electrodes are electrons and those in the electrolyte are (in most cases) ions, charge transfer at the two interfaces will impede the flow of current through the system and contribute to its observed impedance characteristics. For most electrochemical purposes, there are two classes of electrode contact; those capable of exchanging ions with the electrolyte, and those which are not. Electrodes comprising atoms which cannot be exchanged with the electrolyte via redox processes are called blocking electrodes. In such cases, the test system (which can be represented schematically as in Figure A3.5) can be thought of as having the equivalent circuit depicted in Figure A3.6.

Figure A3.5: Test System Under DC Polarisation

Figure A3.6: Equivalent Circuit For System Having Blocking Electrodes

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Here, $C_{dl}$ represents the sum of the double layer capacitances at each electrode/electrolyte interface. Under DC polarisation, initial current flows as oppositely charged ions migrate through the electrolyte to the corresponding electrode/electrolyte interface where they induce an opposite charge at the electrode surface thereby setting up a double layer of charge. The result is a build-up of each species at the corresponding (oppositely charged) electrode and a depletion at the other. Ionic motion then becomes opposed by a chemical potential gradient, and when this has increased sufficiently to counterbalance the applied electric field, migration ceases. At this point the cell is said to be concentration polarised, and the double layer ‘capacitors’ at the electrode/electrolyte interfaces are ‘fully charged’. The value of this capacitance will be greater than $C_g$, the geometric capacitance, which is due to the separation of charges between the two electrode surfaces, owing to the smaller charge separation at the interfacial double layer. Finally, $R_b$ is the bulk resistance of the system. A typical impedance spectrum of a system having blocking electrodes is shown, in complex plane form, in Figure A3.7.
On the other hand, electrodes which are capable of exchanging ions with the electrolyte are termed non-blocking electrodes. These impose a subtle but important change in the system’s impedance characteristics; the equivalent circuit now has to incorporate a charge transfer resistance, $R_{ct}$, in parallel with the double layer capacitance (Figure A3.8). This resistance arises because ions can cross the electrode/electrolyte boundary but electrons cannot and therefore charge has to be transferred to and from electrons and ions at the two interfaces. The charge transfer process is not infinitely facile, and thus resistance to current flow occurs. Consequently, charge builds up at either side of the interface giving rise to a double layer capacitance associated with the charge transfer process. A typical impedance spectrum for an electrolyte connected to two non-blocking electrodes is shown in Figure A3.9.
DC impedance measurements on systems containing either blocking of non-blocking electrodes fail to resolve individual equivalent circuit components because of their association with parallel circuits. Hence, AC techniques are invoked. With the aid of a complex non-linear least squares immitance fitting programme such as LEVM 6.0 (J. Ross MacDonald, University of North Carolina, Chapel Hill, U.S.A.) and a basic knowledge of equivalent circuit modelling, AC impedance spectra can be used to obtain detailed conduction profiles of most electrochemical devices.
The Warburg impedance is associated with the resistance to mass transfer within an electrolyte and therefore relates to diffusion and migration processes. The presence of a constant phase element (often seen as a depressed semicircle on the complex plane plot) is usually ascribed to surface roughness at the interface between electrode and electrolyte [73].
Appendix 4

Hydrogen Anodes
Appendix 4: Hydrogen anodes

Ways of increasing the cost-effectiveness of electrochemical processes continue to promote research interest in hydrogen anodes [74-77]. In cathodic processes such as electroplating and electrowinning, where oxygen evolution from the counter anode is an unimportant, or an interfering by-product, its replacement with an anode which oxidises hydrogen [74] can decrease the processes' power consumption, and consequently its running cost. Elimination of oxygen from the reaction vessel would also allow certain readily oxidisable materials to be used as electrolyte or be generated at the cathode without being destructively oxidised at the counter electrode.

Unfortunately, owing to the critical nature of the porosity and interfacing of laminates within these devices, commercially available hydrogen anodes require rather precise and elaborate fabrication techniques. In general, gas diffusion electrodes of the type used in hydrogen anodes (Figure A4.1) comprise a hydrophilic/hydrophobic composite of catalysed high surface area carbon and, in general, fluorocarbon, which is sintered onto or into a planar substrate. Preferred substrate materials include carbon cloth, carbon paper, metal mesh and expanded metal. Control of porosity is crucial to the successful operation of the electrode. The goal is to fabricate a three phase interface of very high surface area, which allows for intimate contact of feed gas, electrolyte, catalyst and catalyst support.
Figure A4.1: Schematic Diagram of a Typical Hydrogen Anode

Typical hydrogen anodes [78-81] employ a platinum-alloy catalyst, absorbed onto high surface area carbon cloth from a colloidal suspension. The fabrication process is lengthy, and the resulting anodes can have a number of imperfections. Most notably, they suffer from substantial penetration of feed gas from the gas cavity to the electrode front face. This is evident when gas pressure is maintained so as to counteract the hydrostatic head generated by an appreciable depth of electrolyte solution. This makes optimum electrochemical performance and gas economy somewhat unachievable.

The hydrogen anode design explored in Chapter 6, it is believed, overcomes some of the problems faced by more conventional designs. By employing a thin sheet of hydrogen-sorbing metal substrate (e.g. palladium) as a bipolar electrode in an aqueous
medium, the cathodic face is made to generate and absorb hydrogen, which is then transported through the electrode structure to the anodic face, where it is oxidised. The resulting anode is self-feeding, requiring no external hydrogen source. This eliminates the requirements for hydrogen storage and handling normally associated with other designs. Subramanyan [82] explains a similar arrangement employed in the electrochemical determination of hydrogen diffusion coefficients in metals. Subramanyan's technique, however, involves the use of isolated control circuits for the generation and oxidation of hydrogen at opposite faces of the metal membrane under analysis. This method does not constitute a true bipolar arrangement in the sense that the current from the source electrode does not pass directly through the bipolar plate to the sink electrode.

The utility of this type of electrode will be dictated by sustainable current density, stability and cost. It is recognised that palladium in sheet form is unlikely to satisfy all of these criteria, yet opportunities exist for the production of composite, high active area electrodes, containing one or more of the numerous hydrogen sorbing materials available today [83].
References
References


61. R. A. Smith (Editor), *The Collected Chemical and Physical Researches of Thomas Graham*, Edinburgh, 1876.


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