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ELECTRODEPOSITED METAL NANOCOMPOSITE CATALYSTS UTILIZING THE HEXAGONALLY ORDERED TWO-DIMENSIONAL NANOC什ANNEL ARRAYS OF ANODIC ALUMINA

By

Darcy M.J. Brewer

A Thesis submitted in conformity with the requirements
For the degree of Master of Science
School of Graduate Studies
Department of Chemistry
University of Toronto

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ABSTRACT

ELECTRODEPOSITED METAL NANOCOMPOSITE CATALYSTS UTILIZING THE HEXAGONALLY ORDERED TWO-DIMENSIONAL NANOCHANNEL ARRAYS OF ANODIC ALUMINA

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The generation of compositionally controlled metal catalysts is shown. Utilizing the extraordinary assembly of the nanochannel alumina template, monometallic and multimetallic nanowires were formed. The chemistry and electrodeposition processes of nanowire formation in the nanochannel alumina template is discussed. Methanol synthesis and the reverse water-gas shift reaction illustrate the use of controlled catalyst preparation on the product selectivity of these nanocomposites. Further studies are suggested to enhance activity of the catalyst and complete control of nanocomposite formation.
ACKNOWLEDGEMENTS

I cannot convey in mere words the patience and understanding of my supervisor Prof. Charles Mims. His support and guidance simply cannot be given enough acknowledgement within this manuscript.

What has been often coined as "left of center" research, has been both encouraged and facilitated by both Prof. Mims and Prof. Martin Moskovits. It is their understanding of the "map making" possibilities of fundamental and exploratory studies such as this work, which enthralls and excites students in the progress of chemistry.

The many researchers and peers that I have conversed with during my residency, know of their contributions to this study, and I thank them once again.

Without any one of these supporters, I truly would not have come to the understanding of the nanocomposite electrochemistry necessary for the completion of this work.

I would also like to acknowledge the support of NSERC for its extensive funding of this work.
To my mother and father, for my family, and to my friends.

For all of their support, love, and understanding.

When you have eliminated the impossible,
Whatever remains, however improbable,
Must be the truth.

Sir Arthur Conan Doyle, 1859-1930
The Sign of Four

O Captain! my Captain! our fearful trip is done,
The ship has weather’d every rack, the prize we sought is won,
The port is near, the bells I hear, the people all exulting.

Walt Whitman, 1819-1892
O Captain! My Captain!

Carpe diem, quam minimum credula postero

Quintus Horatius Flaccus Horace, 65-8 B.C.
Odes, 1, 11, 8
TABLE OF CONTENTS

ABSTRACT .................................................................................................................. ii
LIST OF FIGURES ....................................................................................................... vii

1.0 INTRODUCTION ..................................................................................................... 1

1.1 Background ........................................................................................................... 1
1.2 Motivation ............................................................................................................ 4

2.0 ANODIZATION OF ALUMINUM ........................................................................... 5

2.1 Introduction ......................................................................................................... 5

2.2 Theoretical Background ...................................................................................... 12

2.3 Experimental Results ........................................................................................ 24
2.3.1 Oxalic Acid PAAO films ........................................................................... 26

3.0 PREPARATION & CHARACTERIZATION OF AAO NANOCOMPOSITES ....... 34
3.0.1 Mechanistic Considerations upon Electrodeposition ................................... 39

3.1 Single Metal Experimental Results .................................................................... 58
3.1.1 Copper Nanocomposites ........................................................................... 59
3.1.2 Rhodium Nanocomposites ......................................................................... 63

3.2 Multimetallic Nanocomposites .......................................................................... 67
3.2.1 Gold & Iron Bimetallic Bilayered Nanocomposites .................................... 72
3.2.2 Copper & Palladium Bimetallic Nanocomposites ....................................... 76
3.2.3 Copper & Rhodium Alloy Nanocomposites ............................................... 79

3.3 Discussion .......................................................................................................... 80

3.4 References ......................................................................................................... 81

4.0 CATALYTIC STUDIES ......................................................................................... 82

4.1 Introduction ......................................................................................................... 82

4.2 Reactor Design ................................................................................................... 84

4.3 Experimental Results ......................................................................................... 85

4.4 Discussion .......................................................................................................... 87
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Nanowire formation, modulation, and etching exposure.</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>Current behaviour under potentiostatic anodization.</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>The Keller model of porous AAO.</td>
<td>9</td>
</tr>
<tr>
<td>4</td>
<td>The Murphy model of porous AAO.</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>Wood's model of porous AAO.</td>
<td>11</td>
</tr>
<tr>
<td>6</td>
<td>Anion incorporation into porous AAO.</td>
<td>18</td>
</tr>
<tr>
<td>7</td>
<td>Potential curve during anodization.</td>
<td>20</td>
</tr>
<tr>
<td>8</td>
<td>Schematic of anodization apparatus.</td>
<td>26</td>
</tr>
<tr>
<td>9</td>
<td>Anodization procedure variations.</td>
<td>28</td>
</tr>
<tr>
<td>10</td>
<td>Growth of porous AAO in 0.23M Oxalic Acid.</td>
<td>29</td>
</tr>
<tr>
<td>11</td>
<td>Example of porous AAO formed in 0.23M Oxalic Acid.</td>
<td>30</td>
</tr>
<tr>
<td>12</td>
<td>Close-up of regularity found in oxalic porous AAO.</td>
<td>30</td>
</tr>
<tr>
<td>13</td>
<td>Effect of channel-widening on oxalic porous AAO.</td>
<td>31</td>
</tr>
<tr>
<td>14</td>
<td>Side view of channel-widened porous AAO.</td>
<td>32</td>
</tr>
<tr>
<td>15</td>
<td>Top view of channel-widened porous AAO.</td>
<td>32</td>
</tr>
<tr>
<td>16</td>
<td>Gerischer's model of electrodeposition.</td>
<td>34</td>
</tr>
<tr>
<td>17</td>
<td>Potential-current curve for a single ionic solution.</td>
<td>36</td>
</tr>
<tr>
<td>18</td>
<td>Cathodic reduction of both metal and hydrogen ions.</td>
<td>36</td>
</tr>
<tr>
<td>19</td>
<td>Cathodic polarization curve of AAO during electrodeposition.</td>
<td>37</td>
</tr>
<tr>
<td>20</td>
<td>Electrodeposition of copper ions.</td>
<td>41</td>
</tr>
<tr>
<td>21</td>
<td>Bi-polarization of AAO during electrodeposition.</td>
<td>42</td>
</tr>
<tr>
<td>22</td>
<td>Flaw theory of electrodeposition.</td>
<td>42</td>
</tr>
<tr>
<td>23</td>
<td>Impurity metal theory for electrodeposition.</td>
<td>43</td>
</tr>
<tr>
<td>24</td>
<td>Voltage drop across electrodes in the bath.</td>
<td>45</td>
</tr>
<tr>
<td>25</td>
<td>Voltage drop across cathode.</td>
<td>46</td>
</tr>
<tr>
<td>26</td>
<td>Thickness of barrier layer and voltage drop of barrier layer.</td>
<td>47</td>
</tr>
<tr>
<td>27</td>
<td>Application of anodic voltage during AC electrodeposition.</td>
<td>47</td>
</tr>
<tr>
<td>28</td>
<td>Diffusion of ions into the channels during electrodeposition.</td>
<td>52</td>
</tr>
<tr>
<td>29</td>
<td>Equivalent circuit for electrodeposition.</td>
<td>52</td>
</tr>
<tr>
<td>30</td>
<td>Al (OH)3 colloids forming in the channels during electrodeposition.</td>
<td>54</td>
</tr>
<tr>
<td>31</td>
<td>Schematic for electrodeposition into porous AAO.</td>
<td>58</td>
</tr>
<tr>
<td>32</td>
<td>Rate of copper growth.</td>
<td>60</td>
</tr>
<tr>
<td>33</td>
<td>Copper Nanowires in PAAO.</td>
<td>61</td>
</tr>
<tr>
<td>34</td>
<td>Exposed copper nanowires after PAAO template has been removed.</td>
<td>61</td>
</tr>
<tr>
<td>35</td>
<td>Copper nanowires.</td>
<td>62</td>
</tr>
<tr>
<td>36</td>
<td>Close-up of liberated copper nanowires.</td>
<td>62</td>
</tr>
<tr>
<td>37</td>
<td>Rate of rhodium growth.</td>
<td>64</td>
</tr>
<tr>
<td>38</td>
<td>Example of PAAO filled with Rh nanowires.</td>
<td>65</td>
</tr>
<tr>
<td>39</td>
<td>Exposed Rh nanowires.</td>
<td>65</td>
</tr>
<tr>
<td>40</td>
<td>Rh nanowires.</td>
<td>66</td>
</tr>
<tr>
<td>41</td>
<td>Rh nanowires.</td>
<td>66</td>
</tr>
<tr>
<td>42</td>
<td>Single-bath electrodeposition of multilayers.</td>
<td>69</td>
</tr>
</tbody>
</table>
Figure 43. Dual-bath electrolytic deposition of multilayers. ........................................ 70
Figure 44. CuNi nanowires showing Ni on surface...................................................... 71
Figure 45. Exposed CuNi nanowires. ................................................................. 71
Figure 46. ARXPS results of Au/Fe nanowires. ....................................................... 72
Figure 47. Au XPS results for Au/Fe wires produced after short period etching ....... 73
Figure 48. Fe XPS results for Au/Fe wires produced after short period etching ....... 73
Figure 49. Au XPS results for Au/Fe wires produced after long period etching ....... 74
Figure 50. Fe XPS results for Au/Fe wires produced after long period etching ....... 74
Figure 51. Exposed AuFe bilayer nanowires ......................................................... 75
Figure 52. Partially etched AuFe nanocomposite showing the Au layer ................. 75
Figure 53. Pd displacement of Cu on pure Cu foil ................................................ 76
Figure 54. Pd displacement of Cu to create bilayer ............................................... 76
Figure 55. Pd aggregation during electrolytic deposition ........................................ 77
Figure 56. Pd aggregation during electrolytic deposition ........................................ 77
Figure 57. Exposed CuPd alloy aggregates with high Pd content ....................... 78
Figure 58. Exposed CuPd alloy nanowires with low Pd content ....................... 78
Figure 59. Exposed CuRh alloy nanowires with high Rh content ....................... 79
Figure 60. Exposed CuRh alloy nanowires with low Rh content ....................... 79
Figure 61. Schematic for catalytic experiments ..................................................... 84
Figure 62. Methanol synthesis results using CuPd nanowires ......................... 85
Figure 63. CO synthesis using CuPd nanowires .................................................. 86
1.0 INTRODUCTION

1.1 Background

The production of heterogeneous catalysts with a well-defined structure has been the aim of many research groups. Control of the support parameters, metal loading, and dispersion is difficult in the preparation of supported catalysts. The application of electrochemical methods in catalyst development has enabled one to control the physical and chemical characteristics of a supported catalyst to a high degree.

In the present work, catalyst production via electrochemical methods consists of two major steps. The first step involves anodization of aluminum to generate a porous aluminum oxide layer on top of the aluminum substrate. The second step involves electrodeposition of one or more metals into the channels of the aluminum oxide film, and the subsequent etching to yield the nanowire catalyst.

AC electrodeposition of a metal into a porous anodic oxide film yields a heterogeneous catalyst with relatively fine, pure metal formed from a well-defined, regularly structured support. Facile control of the loading of a wide range of metals is clearly an attractive feature of the AC electrodeposition technique. The versatility of the electrodeposition method combined with that of the anodization process facilitates the tailoring of heterogeneous catalysts for a wide range of applications. The electrodeposition
technique is readily applied to the development of bimetallic catalysts and catalysts with specific promoters or poisons for particular industrial applications.

The overall procedure which was used to generate nanochannel alumina template nanowire catalysts is schematically shown in Figure 1.

![Diagram](image)

Figure 1. Nanowire formation, modulation, and etching exposure.
It is well known that a porous anodized film is formed on the surface of aluminum by anodization in acid or alkaline solutions. Recently, many investigations have been made on new applications of these films by studying the porous microstructure of the films, e.g. high density recording media and "quantum size effects". The properties of these structures, which differ significantly from those of the corresponding bulk material, can be modified significantly by varying the size and the shape of the nanocomposite. Dramatic "quantum size effects" should occur for structures typically less than 10 nm in dimension which confine the electronic charge carriers in more than one dimension. One well-known effect is bandgap widening, caused by carriers acquiring a significant quantum energy of localization. Likewise, solids formed by electrodeposition of small crystallites may have mechanical, electrical, and thermal properties quite different from their bulk counterparts. The remarkable properties of the nanochannel alumina template that are pertinent to this work are:

(1) the channels, and hence the nanowires, are uniform in diameter and length,

(2) the density of channels is very large compared to other nanotemplates,

(3) the channel density and diameter can be controlled easily by varying the electrochemical or chemical parameters.
1.2 Motivation

Firstly, to controllably create a nanocomposite template using the nanochannel alumina template. This was accomplished using oxalic acid as the anodizing electrolyte.

Secondly, to controllably create monometallic nanowires which have catalytic properties.

Thirdly, to controllably create bimetallic metal alloy nanowires with known, determined composition and morphology, and that are of catalytic interest.

Fourthly, to use these metal nanocomposites for industrially and/or environmentally relevant heterogeneous catalytic studies.

Finally, to extend this to controllably create multilayered multimetallic nanowires using the same basic techniques as for the alloy wires.
2.0 Anodization of Aluminum

2.1 Introduction

Anodization involves the electrochemical oxidation of a metal, leaving a metal oxide layer deposited on top of the metal substrate. Metals commonly anodized are Zn, Sn, W, Al, Ta, Li, and Mg. The oxide layer generated via anodization is either macroscopically smooth, or is porous, depending upon the nature of the electrolyte and the anodizing conditions. The "smooth" oxide films are known as barrier-type films, where the oxide is completely insoluble in the electrolyte. Barrier layer oxide films are formed on metals upon anodization in solutions in which these oxide films are insoluble, e.g. neutral boric acid solutions, aqueous ammonium borate or tartrate solutions (pH 5-7), ammonium tetraborate in ethylene glycol, and several organic electrolytes including citric, malic, and glycollic acids. The barrier layer oxide films are usually thin, compact and hard. The thickness of these films is proportional to the applied voltage, 1.4 nm/V up to the oxide breakdown voltage of 500-700V, which corresponds to 700 – 1,000 nm. According to Keller et al. the thickness of the barrier layer oxide film grown on the metal surface varies from 1.0 nm to 1.5 nm/V, depending upon the dissolving power of the electrolyte. The resulting film shows rectifying properties which have proven to be useful.
Porous films are generated in solutions in which the oxide formed is slightly soluble. Electrolytes producing porous films are phosphoric, sulphuric, oxalic, and chromic acids over a wide range of concentrations.

Even though there is a large excess of incipient channels, with respect to the number of substrate flaws (a typical barrier-type film contains approximately $2.4 \times 10^{12}$ flaws/m$^2$), it appears that the metal substructure influences channel development as the main channels and cells develop most rapidly along the metal subgrain boundaries. It is for this reason that electropolishing should be performed prior to anodization, as will be shown later.

Both types of anodic oxide films have numerous commercial applications. The barrier type films are employed as dielectric capacitors, and in the protection of vacuum deposited aluminum. The porous films when sealed offer excellent corrosion resistance, and are used extensively in applications where corrosion resistance and material weight is vital.

The porous oxides of many of the metals can be electrolytically "coloured" to yield materials which are very useful. Some applications include: optoelectronic devices, hardcoating and decoration, as well as many architectural and aeronautical applications.

Prior to formation of the porous oxide, a barrier type film must be generated. The porosity then develops from a competition between field-assisted dissolution and film growth, as will be described in a subsequent section.
Abd-Rabbo et al.\textsuperscript{2}, and Thompson et al.\textsuperscript{3}, have proposed that there are two simultaneous processes which contribute to film growth. The oxide film grows via ionic migration through the existing film, with \( \text{OH}^- \), \( \text{O}^{2-} \), the acid anion, and \( \text{Al}^{3+} \) as the mobile species. The aluminum oxide layer is formed at the metal/film interface during the ionic migration process.

The formation of a porous anodic oxide on the aluminum substrate involves conversion of a barrier-type film to a porous film. This conversion is thought to be a thermally enhanced, field-assisted dissolution process, with the acid anion having a significant influence on the formation rate, structure, dimensions, and substructure of the porous oxide film.

Electrolytes in which the anodic oxide films are slightly soluble are those which will produce porous anodic oxide films. Porous anodic oxide films always have a thin, compact barrier layer film intervening between the porous film and the aluminum metal, but the distinguishing feature of these porous films is a high density of deep, narrow and fairly-uniform channels which are normal to the aluminum surface.

Porous oxide films can be generated in acidic, neutral, and alkaline solutions. Acidic solutions are exclusively employed in the formation of porous oxide films. Acidic electrolytes commonly employed are sulphuric, oxalic, chromic, and phosphoric acid. The dimensions of the porous film depend mainly on the type of electrolyte used and to a lesser extent, the anodizing voltage.
If aluminum is electrolyzed at constant voltage in a sulphuric acid bath, the current-time curve will be as shown in Fig. 2. 

![Log i vs Log t graph]

**Figure 2.** Current behaviour under potentiostatic anodization.

The physical chemistry aspects of the curve of Fig. 2 may be explained by dividing the curve into four zones A, B, C and D. In zone A, a thin and homogeneous barrier layer is formed on the aluminum surface. In zone B, the surface of the oxide film becomes irregular
because of the expansion in the volume of the barrier layer. When the surface becomes irregular, the current density becomes non-uniform.

The current density increases in the hollows and decreases in the high spots. Nanochannels are generated in the hollows with large current density because of the action of the electric field and the electrolytic action of the bath. Channel growth stops in some of the micro-channels while it continues in other channels. This reaction stage is the zone C in the current-time curve. In zone D, the number of channels is constant, but the depth of the channel increases rapidly. Nanochannels are formed in the oxide film during the reaction stages in this way.

Two models have been proposed to represent the structure of the oxide film – the "Keller Model" and the "Murphy Model".

Keller\textsuperscript{1}, after observing the oxide film (phosphoric acid bath at 120 V) using an electron

![Image of Keller model of porous AAO](image_url)

**Figure 3. The Keller model of porous AAO.**
Figure 4. The Murphy model of porous AAO.

The surface of the oxide film has colloids with high water content and the inner layer of aluminum compounds as shown in Fig. 4.

Murphy has reported the structure of oxide film as an aggregate of colloidal particles of hexagonal column. On the other hand, the Keller model is also called the "Hexagonal Column Model."
Considering the validity of the two models, the Keller Model is an "established model", but the Murphy Model is sometimes more appropriate for explaining certain phenomena. Therefore, the Murphy Model is a model that is difficult to discard.

Wood\(^6\) of the University of Manchester has proposed a new structural model for oxide film, shown in Fig. 5.

![Figure 5. Wood's model of porous AAO.](image)

The bold black-line part of the Wood Model is a fine oxide layer that does not contain electrolytic anions, and the aggregate of black circles shown in the figure is an oxidized aluminum colloidal layer containing a large number of electrolytic anions. Wood has proposed the Wood Model based on observations of oxide film using an electron microscope and results of tests of instrumental analysis. The Wood Model is said to be a compromise between the Keller Model and the Murphy Model.
2.2 Theoretical Background

There is a concentration gradient of OH⁻ and oxyanions through the oxide layer, with enrichment of the anions at the outer layer. There is also a buildup of cations (Al³⁺) near the metal/oxide interface. The proportions of OH⁻, O²⁻, and oxyanions migrating under the field depends upon the relative ease of discharge under local conditions existing at the oxide/electrolyte interface. The O²⁻ and acid anions do not undergo reactions once they enter the film, but the OH⁻ is converted to O²⁻ with the release of a proton. The proton migrates quickly out of the field and does not contribute to oxide formation. The OH⁻ ions (0.153 nm) are only slightly larger than the O²⁻ ions (0.140 nm), thus OH⁻ can penetrate easily into the oxide layer. The oxyanions tend to remain in the outer layer, and in fact may be incorporated via a deposition mechanism, rather than by ionic migration. The OH⁻ in the film leads to a hydrogen-bonded oxide layer, with the degree of hydrogen bonding increased at high pH as there is an increase in the number of OH⁻ available for adsorption, competing with oxyanions, water, and O²⁻ for entry into the film.

The other process leading to oxide film growth occurs at the film/solution interface. A solid state growth mechanism, coupled with a dissolution/precipitation, or dissolution/deposition mechanism leads to further oxide film growth on an aluminum substrate.

Markedly different films are formed by one or a combination of these mechanisms, with the differences depending on the fate of the Al³⁺ ions not consumed in the ionic
migration mechanism. The Al\(^{3+}\) is ejected from the oxide layer at the film/solution interface, and the fate of the Al\(^{3+}\) rests with the efficiency in the deposition/precipitation process at the film/solution interface.

The nature of the incorporated acid anion strongly influences the size distribution of the pure and contaminated microcrystalline alumina, and the hydrogen-bonding characteristics of the intercrystalline region. The steady-state anodizing behaviour of porous anodic films is related to the distribution of acid anions in the oxide cell and the effective strength across the pure alumina region. Oxide films possessing a high level of acid anions and a thin oxide cell boundary region exhibit higher growth rates. Enhanced ionic migration through the oxide film, due to the presence of a thicker contaminated alumina region, coupled with the generation of larger voltage drops across the cell boundary region leads to the enhanced film growth rates in highly contaminated films.

The structure, composition, and dimensions of porous oxide films are highly dependent upon the anodizing conditions. The type of electrolyte employed, temperature of the anodizing conditions, the applied voltage or current density, and the electrolyte concentration all markedly influence the oxide film characteristics. With judicious selection of anodizing conditions, a highly tailored porous oxide film can be developed for use in specific applications.

The relationship between the channel diameter and channel length of oxide film is analogous to a cave of height 2 m and depth 1 km. The situation of a dog or a cat entering
this cave is similar to that of an ion or a molecule entering the channel in the film. To give an idea of the number of channels in an oxide film - if each channel of the anodized aluminum is occupied by one person, only about 10% of the total channels in a 1 cm² area of oxide film would be occupied by the entire population of the earth, with more than 90% of the channels still unoccupied.

Various causes may be attributed to the differences in properties of the nanochannel alumina template, but there are four main ones: differences in the film structure, differences in the crystallographic composition, differences in the electrolyte inclusion in the film, and differences in the water content. The differences in the oxide film structure because of the differences in the conditions of anodizing of aluminum have already been described.

The points mentioned below, explaining the changes in the crystallographic composition of oxide film because of the differences in the conditions of anodizing of aluminum, have already been confirmed. The main component of the oxide film is said to be alumina (Al₂O₃), but depending on the arrangement of aluminum atoms and oxygen atoms, there are various types of alumina, such as alpha-alumina, gamma-alumina, and beta-alumina. However, it has been reported that the oxide film does not contain a pure aluminum compound, but contains an amorphous aluminum compound. According to research on barrier-type films, the alumina in this film has been reported as gamma-prime-alumina. Gamma-prime-alumina has properties that lie between amorphous alumina and crystalline alumina. It has also been reported that crystalline gamma-alumina is dispersed in amorphous alumina, and that gamma-alumina and hydrated alumina are included in
amorphous alumina. H atoms and H₂O are connected to a part of the cyclic compound consisting of aluminum atoms and oxygen atoms, forming cyclic aluminic acid trihydrate. According to other research reports¹⁰, the structure is similar to the crystalline structure of Al₂O₆, similar to the spinel structure of Fe₃O₄.

These researchers have explained experimental results considering the barrier-type film to be a homogeneous layer. Others⁹ have considered this film to be a non-homogeneous layer. Researchers who consider the film to be a non-homogeneous layer, follow the concept that crystalline gamma-alumina is dispersed in amorphous alumina. There are research results claiming that the outer surface of the barrier layer is amorphous and the inner surface is crystalline. Since the electrolyte is in contact with the outer surface of the layer, hydration probably progresses, and dehydration occurs on the inner surface of the layer probably due to the action of an electric field such as in electro-osmosis. Consequently, it is more correct to consider the barrier layer to consist of a multi-layer structure rather than a homogeneous layer.¹¹

Oxide film formed in an electrolytic bath at ambient temperature is randomly-formed amorphous alumina but in high temperature baths, the crystallinity increases. If the film thickness increases, or anodizing has been carried out at a high voltage, or in an electrolytic bath of dilute electrolyte, or by alternating current electrolysis, there is a relative improvement in crystallinity. For instance, a barrier-type film anodized at a voltage of less than 100 V contains amorphous alumina only, but if the oxide film is formed at a voltage greater than 100 V, gamma-alumina has been verified in addition to amorphous alumina. A
barrier-type film is formed by cyclic macromolecule alumina, but researchers have reported formation of chain macromolecule alumina in case of a porous film.\textsuperscript{10}

The points mentioned below have been verified with respect to inclusion of anions in the electrolyte. This is important with respect to the poisoning of the nanocomposite catalyst by anion incorporation into the electrodeposited nanowires. There is little inclusion of anions of the electrolyte in barrier-type oxide films. In a bath containing boric acid mixed with sodium borate or in a bath containing ethylene glycol mixed with ammonium borate, the quantity of boric acid in the anodized barrier-type film is 1%.

The quantity of anions contained in a porous oxidized film is about 10 to 19%. It has been reported\textsuperscript{8} that a porous oxidized film formed in a sulphuric acid bath contains sulfate anions in excess of 17% and SO\textsubscript{3} anions amounting to 13%. The anion content also varies depending on the conditions of electrolysis. If the bath temperature is low, and current density is high, the content of sulfate anions increases. The reasons for the high sulfate anion content in oxide film formed by anodizing in a low temperature bath by proposing the equation given below.

\[ \text{SO}_4^{2-} \rightarrow \text{SO}_3 + \text{O}_2^{2-} \]

(Film surface) \hspace{1cm} (in solution) \hspace{1cm} (in film)

In a high temperature bath, the content of sulfate anions in the oxide film reduces according to the above reaction.
Research has also been carried out on the bonding condition of sulfate anions in the oxide film.\textsuperscript{12} An oxide film containing 13% of SO\textsubscript{3} when washed for a long period, showed that the SO\textsubscript{3} content became 8% after analysis. This study showed that the SO\textsubscript{3} content in the oxide film was 8%, and the difference of 13% and 8%, that is, 5% was SO\textsubscript{3} weakly adsorbed in the oxide film surface, with sulfate remaining in the channels of the porous layer. The former is called "bonded anion" and the latter is called "free anion".

If the thickness of the oxide film is greater than 6 microns, the SO\textsubscript{3} anion content remains constant at 13%, but for a film thickness greater than 60 microns, the SO\textsubscript{3} content is 8%.

The phosphate anion content or the oxalate anion content in a porous film anodized in a phosphoric acid or an oxalic acid bath is of the order of 5% to 15%, similar to the film formed in the sulphuric acid bath. However, as S is a catalyst poison in this work, oxalic acid is preferable for template development.

Experimental results that show almost similar anion content in these types of porous films suggest that: (1) the ease of mobility is almost the same for sulfate anions, phosphate anions and oxalate anions in the oxide film and (2) the transition of the barrier layer to porous layer because of these electrolytic baths is due to an almost similar mechanism.
In recent years, there have been several research reports showing that the anion content in oxide film is not uniform but has a concentrated distribution as shown in Fig. 6. In other words, electrolytic anions are distributed densely at the center of the barrier layer and the channel wall.13

The facts mentioned below regarding water content in anodized films have been confirmed by research. There is considerable difference in the water content in aluminum oxide film and the water content in barrier-type film and porous film. Barrier-type films are generally said to be anhydrous oxides but it is reported that a water content of 2.5% is included in the form of boehmite (AlO(OH)).

It has also been reported that 15% of water by volume is included in a porous film formed in a sulphuric acid bath or an oxalic acid bath, 1 to 6% water is included in films formed in a sulphuric acid bath, and the water content required for formation of $2\text{Al}_2\text{O}_3\cdot\text{H}_2\text{O}$ is included in the film formed in the oxalic acid bath. A film formed in chromic acid bath is
almost in the same state as anhydrous alumina. Recent research has also shown that the water content in anodized films formed in AC sulphuric acid baths is more than the water content in films formed in DC sulphuric acid baths.¹⁴

Values of water content are conflicting, but in all cases, the water in the oxide film is not adsorbed water but is included in the form of hydroxides of hydrated oxides. Since film structure, crystalline structure, electrolyte inclusion, and water content described above, vary depending on the conditions of anodizing of aluminum, the properties of oxide film also vary.⁸

Electroplating is possible at a small negative voltage but the formation of oxide film requires a voltage of about 10 to 30 V. The current during anodizing of aluminum is of two types: ionic current and electronic current, and each of these types must be distinguished correctly and considered.

Growth of oxide film occurs due to the flow of ionic current. Ionic conduction under weak and strong electric fields needs to be considered for understanding the mechanism by which ionic conduction takes place. The motion of ions opposite to the direction of the electric field cannot be ignored in ionic conduction in weak electric fields. However, ions do not move in a direction opposite to the electric field in a strong electric field. In the anodizing of aluminum, a barrier layer of 10 angstrom is formed at 1 V; therefore, the strength of the electric field is as high as 10⁷ V cm⁻¹. Consequently, ionic conduction may
be considered only in the anodizing of aluminum under strong electric fields. The ionic current for cations or anions under a strong electric field is given by:

$$I = Ae^{BE}$$ (1)

Here, $i$ is the ionic current density, $E$ is the voltage strength, and $A$ and $B$ are constants. This equation shows that when the voltage applied on an oxide film, the ionic current increases exponentially. If voltage is applied on the wires, the current increases

![Diagram of anodization process](image)

**Figure 7. Potential curve during anodization.**
directly in proportion to the voltage applied — this is well known as Ohm's Law. Ionic
conduction does not obey Ohm (Ω)'s Law. It has been suggested, see below, that the above
equation shows that the strength of the potential barrier in ionic conduction decides the ionic
current density.

Potential barriers to ion mobility in aluminum-aluminum oxide-water solution
systems are known to exist at three locations: (1) at the interface of aluminum-aluminum
oxide interface, (2) in the aluminum oxide layer (oxide bulk), and (3) at the interface of
aluminum oxide-water solution. The largest potential barrier from the barriers at these three
locations will become the rate-determining step for determining the rate of ionic conduction.
For instance, Fig. 6 shows that ion mobility is at the rate-determining step in the oxide
film.15

The main theories that deal with ionic conduction in an oxide film are the Cabrera-
Mott theory16, the Verwey theory,17 the Dewald theory18 and the Dignam theory.19

On the other hand, in practice, electron conduction during anodizing of aluminum
may be ignored; however, under certain experimental conditions, electron conduction has
considerable importance. For instance, it has been pointed out that when the "burning" of an
oxide film occurs when a metal is anodized, the light-emitting phenomenon is due to
electronic current. It is important to investigate electron conduction to know more about the
properties of oxide films.
The band gap for pure aluminum oxide, said to be a few eV to 10 eV, acts as an insulating barrier to electron conduction. However, anodized aluminum is not pure aluminum oxide. Moreover, the inclusion of electrolytic cations in the film is high; therefore, it may be called a semiconductor with a high degree of impurities. Consequently, there are various concepts explaining electron conduction in anodized aluminum by semiconductor conduction mechanisms. There is a problem; however, in applying the conduction mechanism of single-crystal semiconductors directly to amorphous anodized films. It is more important to relate electron conduction to amorphous semiconductor theories, which are being systematically formulated in physics.

Vermilyea's theory\textsuperscript{20} related to electron currents in anodized films is a very important theory. This theory states that the rectifying action of oxide film occurs because of the existence of weak spots on the oxide film. Oxide films of uniform thickness are not always formed even on high-purity aluminum and there are weak spots. These weak spots are called "flaws". The diameter of the flaw is of the same order as the thickness of the barrier layer of the oxide film. The thickness of the barrier layer in parts of the flaw does not exceed half the thickness of the normal barrier layer. Electron conduction improves in such parts of the flaw. Wood has shown that electrodeposition of metal ions in the channels of oxide film during Asada's electrolytic deposition method is based on the "flaw concept" proposed by Vermilyea.

Sasaki\textsuperscript{21} has proposed the n-i-p junction type film model from measurements of photoelectric effects and electrode capacitance for the oxide film formed on tantalum.
other words, the inner layer of 20 to 50 angstroms in contact with the metal phase consists of n-type oxides of excess metal ions (donor - excess metal ion), the middle layer consists of genuine semiconducting oxides with stoichiometric composition which grows in thickness, and the outer layer of 20 to 50 angstroms of p type oxides (acceptor - excess oxygen ion or surface-adsorbed oxygen). The existence of excess \( \text{Al}^{3+} \) ions or deficient oxygen ions in the barrier layer during formation of the film has been experimentally verified. The outer p-type oxide layer is also formed by protons that penetrate from the electrolyte.

An anodic oxide film may exhibit rectification as an electrode or a diode in the metal/film/electrolyte system. The rectification of the anodic oxide film diode can be predicted from the Sasaki theory also. In other words, the part in contact with the substrate metal is an n-type semiconductor with excess metal ions or deficient oxygen ions; the surface of the film is a p-type semiconductor consisting of deficient metal ions, excess oxygen ions or protons that have penetrated from the electrolyte, therefore, the diode functions as an n-p junction or an n-i-p junction. Consequently, if the contact with the counter electrode metal is an ohmic contact, the current flows easily toward the cathode. Even in a metal/film/electrolyte system, rectification can be observed, which converts the flow toward the cathode in the positive direction, and this is called "electrolytic rectification". Electrolytic rectification differs from diode rectification in that the electrode reactions corresponding to constant current proceed at the film/electrolyte interface. In metal/film/electrolyte systems, if film growth or film dissolution occurs by anodic polarization, and if proton penetration into the film or reduction of film occurs by cathodic polarization, the mechanism becomes complex.
2.3 Experimental Results

Anodic aluminum oxide (AAO) films otherwise know as nanochannel alumina templates grown in strong acid electrolytes possess very regular and highly anisotropic porous structures with pore diameters ranging from below 10 to 200 nm, pore lengths from 1 to 100 μm, and pore densities in the range \(10^8 - 10^{11}\) cm\(^{-2}\). The pores have been found to be uniform and nearly parallel, making nanochannel alumina templates ideal for the electrochemical deposition of fairly monodispersed nanometer-scale particles. Other porous films such as polymeric membranes, manufactured by etching nuclear tracks, have also been used.

In using templates to produce nanostructures, one must take into account the template's chemical stability, its insulating properties, the minimal diameter and uniformity of the pores, and the pore density. Pore sizes small enough to ensure the observation of quantum size effects in the deposited structures are not readily available with commercial anodic aluminum oxide membrane filters such as those produced by Anopore. The Anopore filters also contain only wide nanochannels, with some filters tapering to give a small region of 20nm channels.

The smallest mean pore diameter in nuclear track polycarbonate membranes used for the fabrication of nanowires has been reported to be 18 nm. Recently, membranes with
nominal 10 nm diameter pores have become available from Poretics and from other sources. These have been used to fabricate nanoelectrode assemblies. However, direct measurement of the diameter distribution function for metallic wires deposited into these pores determined that the mean pore diameters of nominal 10 nm and the nominal 30 nm membranes were respectively 36 ± 3 and 57 ± 3 nm. The nominal size specified for these membranes corresponds, in fact, to the value of the smallest pores in the distribution, rather than to the mean. Additionally, the nuclear track pores are not parallel, and the pore density \(6 \times 10^8 \text{ cm}^{-2}\) is substantially lower than in the nanochannel alumina templates.

The pore diameters and densities of anodic aluminum oxide films such as those described in this paper can be easily varied by changing anodization parameters such as the electrolyte used, its concentration, and the anodizing voltage. The main constraint in using porous alumina films directly after anodization is the insulating, dense oxide barrier layer separating the Al substrate and the porous portion of the aluminum oxide. The thickness of the barrier layer is a function of the anodizing voltage (10-14 Å/V). This imposes a limitation on the use of dc electrodeposition to fill the pores. However, the inherent rectifying properties of the barrier layer allow the pores to be filled uniformly by ac electrolysis without simultaneously depositing material on the surface or into the macroscopic defects of the film.
2.3.1 Oxalic Acid PAAO films

Oxalic anodic oxide films were grown on 0.15 mm thick 99.999% aluminum foil, which was sectioned in 10 cm x 4 cm slats to create uniform films for catalysis. Samples were degreased ultrasonically in trichloroethylene for 20 min, electropolished to a mirror finish in a 5:1 v/v solution of CH₃CH₂OH (95%)/HClO₄ (70%) at 60V and 10°C for 30 sec., etched in 0.24M Na₂CO₃ at 80-85°C for 2 min. To remove the native oxide layer, and then anodized in oxalic acid electrolyte with graphite counter electrodes. The anodization was carried out as schematically shown in Fig. 8.

Figure 8. Schematic of anodization apparatus.
Post-anodization procedures were sometimes implemented to generate a better template for electrodeposition, as shown in Fig. 9. The anodizing voltage could be stepwise decreased in 2V intervals over a period of 7 min. In order to reduce the thickness of the barrier layer. This thinning of the barrier layer was found to improve electrodeposition, although the true reason why this works has not been shown. The channel diameter could also be increased, controllably, by widening the channels in 0.1M H$_3$PO$_4$ at 313K for varying times producing channel diameters from 17 nm up to the cell size ~60 nm. Channel diameters and oxide thickness were determined by SEM (Hitachi S-4500 field emission instrument operated at 20 kV and equipped with energy dispersive X-ray (EDX) fluorescence analysis).

Increasing the concentration of H$_2$C$_2$O$_4$ (aq.) gave no apparent change in morphology of the film, although the rate of film growth was increased. This supports the theory that composite dimensions are primarily determined by acid anion. The electropolishing made quite a difference in the regularity of the film.
Figure 9. Anodization procedure variations.
Figure 10. Growth of porous AAO in 0.23M Oxalic Acid.

Thickness (nm) = 42 x Anodization Time (min)
Figure 11. Example of porous AAO formed in 0.23M Oxalic Acid.

Figure 12. Close-up of regularity found in oxalic porous AAO.
Figure 13. Effect of channel-widening on oxalic porous AAO.
Figure 14. Side view of channel-widened porous AAO.

Figure 15. Top view of channel-widened porous AAO.
2.4 References

3.0 Preparation & characterization of AAO nanocomposites

In this work, electrodeposition involves metallic ion deposition reactions in the channels of anodic oxide film. These are electrochemical reactions given by the equation below.

\[ \text{M}^{n+} + n\text{e}^- \rightarrow \text{M}^0 \]  \hspace{1cm} (2)

The reaction (2) is similar to the electroplating reaction equation. Therefore, it is important to understand the theory of electroplating when studying electrolytic nanowire formation in the nanochannel alumina template. Gerischer's Electrodeposition Theory\(^1\) is an important electroplating theory as it considers complexed cations in solution; something which is very relevant for electrodeposition into porous AAO. This theory is explained below.

![Gerischer's model of electrodeposition](image)

**Figure 16.** Gerischer's model of electrodeposition.
Figure 16 shows Gerischer's electrodeposition model. Metallic ions in aqueous solution are not bare ions (for instance, Cu$^{2+}$). These ions are either surrounded by water molecules (Cu(OH)$_2$) or they are in chain/anion complex form. Metallic ions surrounded by such ligands either disperse or migrate to the solid phase surface, and cause detachment of the ligands in the electric double layer, and become bare metallic ions. These metallic ions accept electrons from the metallic surface and are thereby reduced. Metallic atoms diffuse over the surface of the metallic surface and crystallize at the kinks.

During the electrolytic deposition into the anodic oxide film, the phenomenon mentioned in Gerischer's electrodeposition model occurs, most relevantly when there is metal already in the channels. Deposition of metal on the bare anodic oxide film, however, is very complex, as there are many deposition pathways. It is the existence of a barrier layer or a porous layer in conjunction with the use of AC electrolytic deposition which makes the entire nanowire formation much more complex.

Due to this convoluted nature of electrodeposition into porous AAO, some theoretical discussion is necessary. When the voltage is low, a linear relationship exists between voltage and current. When the voltage increases, an exponential curve is obtained. If the voltage is increased further, the current value becomes constant because the rate of supply of ions to the electrode reaches its limit. This constant current density is called the limiting current density. The higher the metallic salt concentration, the higher the limiting current density. If the bath
is agitated, the limiting current density increases but the bath temperature does not change appreciably.

![Diagram of potential-current curve for a single ionic solution.](image)

**Figure 17.** Potential-current curve for a single ionic solution.

Fig. 17 is said to be a virtual condition because together with the reduction reaction of metallic ions in normal aqueous solutions, reduction reactions of existing hydrogen ions or oxygen occur in the bath.

![Diagram of cathodic reduction of both metal and hydrogen ions.](image)

**Figure 18.** Cathodic reduction of both metal and hydrogen ions.
The solid line in Fig. 18 is the voltage-current curve of reduction of metallic ions in an acidic solution. This curve may be considered a composite curve formed by the two dotted-line curves. For instance, the solid-line curve of Fig. 18 is obtained as the sum of the reduction current \( (i_H) \) of hydrogen ions and the reduction current \( (i_M) \) of metallic ions.

![Diagram of voltage-current curve](image)

**Figure 19.** Cathodic polarization curve of AAO during electrodeposition.

The solid-line voltage-time curve of Fig. 19 is the curve obtained when negative voltage is applied stepwise to anodic oxide film in a mixed solution of metal sulfate and acid. This solid-line curve may be considered to be formed by three curves as shown in the figure. The dotted line generated at low voltage is the reduction current of hydrogen ions, and the dotted line generated at high voltage is the reduction current of metal ions. However, the assignment of the dotted line generated at an intermediate voltage is not clear.\(^2\)

Cathodic electrolysis of oxide film is different from electroplating in that the thickness of the porous layer of oxide film also affects cathodic reactions. The deposition
solutions were acidified metal sulphates, with pH in the range 1-3. Low pH levels should be employed in the deposition of metals with high E° values such as Sn, Ag, Au, Cu, Pd, Pt, etc., whereas less noble metals Fe, Co, Ni, etc. are deposited from relatively neutral solutions pH=3.5-7. For metals with E° less than 0.0 V (vs. hydrogen), hydrogen evolution competes with metal reduction at low pH levels. The neutral electrodeposition solutions also contain additives to effect buffering, enhance electrolyte conductivity, and to prevent accumulation of aluminum ions and contaminants in the electrolysis bath. Surfactant additives, for example, were needed in nanowire formation to ensure relatively compact deposits. The reason for this will be illustrated later.

The modifications of the porous anodic aluminum oxide films as well as the barrier layer between the porous films and the aluminum base may occur during the electrodeposition depending on the electrodeposition conditions applied to the porous films.

The AC conditions were employed to take advantage of the rectifying properties of the anodic film; however the AC voltage also serves to activate a much larger population density of flaws in the barrier layer than the $10^8$-$10^{10}$ flaws/m² expected under DC deposition conditions. Under AC conditions essentially all of the channels in the film are filled, corresponding to a channel density of $10^{13}$ m⁻².
3.0.1 Mechanistic Considerations upon Electrodeposition

The types of reactions during secondary electrolysis vary depending on the thickness of anodic oxide film, type of bath used for secondary electrolysis, and applied voltage.

The possible anodic reactions that occur during secondary electrolysis of anodic oxide film are:

1. Formation of thick barrier layer
2. Occurrence of "flaws"
3. Anodic decomposition of water
4. Acidification in the channels of the film
5. Neutralization reactions due to $\text{H}^+$ ions in the channels
6. Chemical dissolution and field-assisted dissolution of anodic oxide film
7. Formation of new porous layers
8. Current recovery phenomena

On the other hand, the reactions during cathodic electrolysis of anodic oxide film are:

1. Cathodic reduction reactions of $\text{H}^+$ ions
2. Cathodic reduction reactions of oxygen in the bath
3. Cathodic reduction reactions of metallic ions
4. Alkalization in the channels of the film
5. Formation of metallic hydroxides in the channels of the film
6. Breakdown of barrier layer and "spalling" of the film
When anodic oxide film is AC-electrolyzed, various reactions occur depending on the pH and composition of the AC electrolytic bath. If the bath is strongly acidic, both anodic reactions and cathodic reactions mentioned above occur. If the bath is weakly acidic or neutral, cathodic reactions occur but almost no anodic reactions occur. AC electrolysis is not only a combination of anodic electrolysis and cathodic electrolysis, but also has its own reactions, such as:

1. Faradaic and non-Faradaic currents.
2. Changes with time of anodic peak current, cathodic peak current, as well as the total quantity of current.
4. AC recovery phenomena.

Finally, precautions necessary for either type of secondary electrolysis are:

2. Differences in ionic current and electronic current

A major component of the anodic oxide film is aluminum. Pure aluminum oxide is an insulating material and does not conduct electricity. Anodic oxide film is not pure aluminum oxide, but it is close to an insulating material; it is a semiconductor. For metallic ions to be deposit in the channels of anodic oxide film, the electrons must move to
the barrier layer surface, as shown in Fig. 20. Does the movement of electrons shown in Figure 20 actually occur? There is no definite answer to this question; various deposition mechanisms have been proposed to enhance our understanding of this electrodeposition process.

![Diagram of electrodeposition process]

**Figure 20. Electrodeposition of copper ions.**

One of the concepts proposed is that since anodic oxide film does not conduct electricity easily, if voltage is applied on the film, dielectric polarization occurs, as shown in Fig. 21, and metal is deposited on the negative electrode. Dielectric polarization is similar to the phenomenon of static electricity that occurs when plastic is rubbed with cloth. This model could possibly be used to account for the Pd and Ni electrodeposition results, as will be shown later.
Figure 21. Bi-polarization of AAO during electrodeposition.

Barrier layers have flawed parts, as shown in Fig. 22 and electrons can flow through these flawed parts. If these flaws occur to a great extent, the rapid deposition of metal during the cathodic cycle could cause total surface deposition. This results in blocked nanochannels and a subsequent cessation of nanowire formation.

Figure 22. Flaw theory of electrodeposition.
As mentioned above, the barrier layer has metallic impurities that have not been oxidized, and electrons flow through these impurities. (See Fig. 23.) This concept is unlikely, as there is not an overly excessive amount of Al metal found only in the barrier layer.

![Figure 23. Impurity metal theory for electrodeposition.](image)

If the anodic oxide film is considered a semiconductor, electrons could move through the barrier layer via the quantum tunneling effect. A corollary to the semiconductor concept is that the barrier layer consists of several layers of semiconducting material, and electrons flow because of the n-i-p bond of the semiconducting material.

Few, if any, of the theories mentioned above have been empirically validated, therefore, all should be considered and not neglected.
A primary consideration with respect to metal deposition in the channels of the film is the excessive cathodic voltage. The electrolytic deposition method is similar to the electroplating process, in principle, as metal is reduced and deposited in the channels of the anodic oxide film in the form of nanowires. The bath voltage necessary for metal deposition in standard DC electroplating is of the order of a few volts. During electrolytic deposition, into the nanochannel alumina template however, a higher voltage of about 6 to 14 V is used. This difference is due to the existence of the barrier layer of anodic oxide film. It is difficult to pass current through the barrier layer, and high voltages are necessary for depositing metal. As shown previously, explanations up to this point are quite easy to conceptualize. Before proceeding with further explanations, however, the concept of bath voltage should be made clear. The applied bath voltage ($V_{cell}$) is distributed as shown in Fig. 23. Consider the instant of application of AC voltage when the anodic oxide film is the negative electrode, and the counter electrode is the positive electrode.
A voltage drop \( (V_a) \) occurs at the anodic oxide film electrode, and also at the counter electrode \( (V_{c}) \). The voltage drop \( (iR) \) occurs due to the bath resistance \( (R) \). Thus, the composition of bath voltage \( (V_{cell}) \) can be expressed by (3).

\[
V_{cell} = V_c + V_a + iR
\]  

(3)
This equation shows that the entire bath voltage is not impressed on the anodic oxide film electrode. For instance, if the bath voltage is 15 V, only 5 to 10V may be impressed on the anodic oxide film electrode, depending on the barrier layer thickness, as shown below.

![Figure 25. Voltage drop across cathode.](image)

In the electroplating process, the entire voltage drop ($V_c$) at the negative electrode can be used for deposition of metal, but in the AC electrolytic deposition process, as shown in Fig. 25, only a part of $V_c$ can be used for deposition of metal.

The voltage drop at the anodic oxide film electrode is the sum of voltage drop ($\eta_{oxide}$) due to barrier layer and voltage drop ($\eta_{HL}$) for metal deposition. This is expressed by the following equation:

$$V_c = \eta_{oxide} + \eta_{HL}$$

The value of $\eta_{oxide}$ is quite high; therefore, the voltage of bath for AC electrolytic deposition becomes high. $\eta_{oxide}$ does not drop linearly, as shown in Fig. 26, but drops as a
curve. This is because the barrier layer does not have uniform electrical characteristics. Since the voltage drop in the barrier layer is non-linear, if the barrier layer's thickness is half, the electrolytic deposition bath voltage will not be half. This can be clearly understood from Fig. 25.

![Image of a diagram showing voltage distribution](image)

**Figure 26.** Thickness of barrier layer and voltage drop of barrier layer.

To add to this, when the barrier layer is being AC electrolyzed, its properties do not remain constant. During the electrodeposition, the anodic voltage affects metal deposition in the channels of the oxide film.

![Image of a diagram showing anodic voltage application](image)

**Figure 27.** Application of anodic voltage during AC electrodeposition.
In principle, only the negative voltage (cathodic voltage) is adequate for metal deposition in the channels of anodic oxide film. However, during AC electrolysis, both cathodic voltage and anodic voltage are applied. (See Figure 27.) The cathodic voltage is higher due to rectification, thus enabling nanowire formation.

The AC electrolytic deposition process reports that "the effect of anodic voltage in the electrolytic deposition process is to re-form the barrier layer." However, this seems to be a conclusion arrived at by inspiration rather than based on experiments. In addition, it has been reported that anodic voltage has the effect of allowing the hydrogen gas generated in the anodic oxide film to escape. Hydrogen gas escapes quickly, therefore, spalling (peeling off fragments of the oxide film) can be prevented, but this explanation is also based on hypothesis. Chemical interpretation on the effect of anodic voltage is still not fully understood to this day.

It can be easily understood that the condition of the barrier layer surface at the base of the channels of anodic oxide film dramatically affects metal deposition in the channels of the film. This has not yet been given the attention with which this concept deserves. For instance, electrodepositing metal from an acid sulfate electrolyte, into a nanochannel alumina template anodized in oxalic acid doesn’t seem to concern most researchers in the field. Some researchers, however, have realized this dilemma, and have tried to place the metal cation into the same solution as the anodization. No one, however, has tried electrodeposition from an oxalic acid electrolyte.
If the oxide film after anodization is placed in tap water or distilled water for half a day or longer, and then electrodeposition is carried out, no deposition will occur. If the anodic oxide film that has been placed in water, is returned to the sulphuric acid bath, immersed in this solution for a few minutes, rinsed and then electrodeposition is carried out, deposition proceeds as usual. The reason for no electrodeposition after placing it in water is likely that the surface of the oxide film is subjected to hydration reactions when placed in water, and the porous AAO becomes inactive. When this film is placed in the sulphuric acid bath, the hydrate formed on the film when placed in water is dissolved in sulphuric acid, and the anodic oxide film becomes active again.

The nanochannel alumina template film thickness could also affect the electrodeposition process. If the porous film layer is thin, the supply of hydrogen ions from the bulk solution is immediate, therefore, the rise of pH in the channels of the oxide film cannot occur easily and only hydrogen gas is generated. This creates an incredible problem for small pore nanochannel alumina templates.

On the other hand, if the thickness of porous layer film is large, the supply of hydrogen ions from the channels of the oxide film is slow; therefore, the pH in the channels of the oxide film rises. This rise of pH will dramatically affect many of the electrolytic processes occurring in the nanochannels, either beneficially or detrimentally.
If an anodic oxide film is subjected to cathodic polarization, metallic ions are discharged and deposited on the surface when the applied voltage overcomes the resistance of the barrier layer. Electrons are supplied by the aluminum metal through the barrier layer in the form of electronic current. On the other hand, in case of an anodic oxide film, the passage of H⁺ ions and SO₄²⁻ ions has been measured. In cathodic polarization, a current of H⁺ ions flows initially, but after the limit is reached, this current changes over to electronic current, reduces, and deposits the metal.

The limiting current is reported as approximately 0.67 mA/cm². This value is relatively high. Ionic current accompanies transfer of material. If metal is deposited on the barrier layer in the nanochannels, the ionic current can be considered to be cut off. Therefore, the initial stage of electrolysis may also be considered as the stage where the electronic current and the ionic current are superimposed.

During electrolysis, all ions in the electrolyte become currents according to the transport number of each ion. Metallic ions are discharged and deposited on the cathodic surface, therefore, the ionic concentration far from the surface decreases. That is, the discharge of metallic ions becomes proportional to the transport rate according to the diffusion. If other conducting salts exist, the dissociated ions divide the transport number; therefore, the arrival of the metallic ions is further restricted.
If the quantities of active metallic ions on the exposed surface of the electrolyte and the surface of the electrode are taken as $a_0$ and $a$ respectively, the diffusion coefficient as $D$, and the thickness of the diffusion layer as $d$, then the diffusion current $i$ is given by:

$$i = \frac{-F D Z (a_0 - a)}{d}$$  \hspace{1cm} (5)

Here, if $D = 10^{-5} \text{ cm}^2/\text{sec}$, $a=0$, $a_0 = 10^{-4} \text{ mol/cm}^3$, $i = 5 \text{ mA/cm}^2$, then for a metal with $Z = 2$, $d$ is 0.05 cm or 500 $\mu$m.

In practice, even if the thickness of the anodic oxide film is assumed as 10 microns, this value is well within the thickness of the diffusion layer. Since the diameter of the channel is 10-50 nm, electrolysis could be thought of as being carried out in very small, and thin electrolytic cells, i.e. nanoporous electrolysis is being carried out. Supply of metallic ions by stirring or by convection is difficult; therefore, ions are supplied only by diffusion. Thus, the electrolysis in a nanochannel can be considered to be diffusion controlled. This condition is shown in Fig. 28.
Figure 28. Diffusion of ions into the channels during electrodeposition.

The frequency of AC voltage can be varied during AC electrodeposition. It was found that if the AC voltage frequency is less than 100 Hz, the electrodeposition usually occurs well. If the frequency is >200 Hz, the deposit is very poor, or there is no deposition at all. This is probably due to the fact that as the frequency increases, only charge and discharge from the oxide film occurs; the deposition current due to metal ions does not flow. This point is shown by the equivalent circuit of Fig. 29. At low frequencies, current flows in both paths, but at high frequencies, the impedance of the oxide film becomes smaller.

Figure 29. Equivalent circuit for electrodeposition.
During electrodeposition of Cu from a copper sulfate bath, the deposit is satisfactory even at an AC frequency of >200 Hz. Why is the frequency dependence of most metal sulfate and copper sulfate baths different? Referring to the equivalent circuit of Fig. 28, the reactive impedance of the copper sulfate bath is very small. Even if the AC frequency is high, considering that the reactive impedance and the oxide film impedance are almost the same, the anodic oxide film will be colored at the voltage frequency.

Electrodeposition of nanowires is also temperature dependent. If the temperature is below 10°C, poor films will be obtained. At low temperatures, ion mobility is suppressed and the deposition rate is slow, therefore, the deposit is very colloidal and/or poor. At temperatures in the range of 10°C to 60°C, the electrodeposit is good, as the throwing power is satisfactory. At bath temperatures above 60°C, again poor to no deposit is obtained. At this temperature, due to the sealing effect of the oxide film, the surface of the channel becomes inactive; therefore, electrolytic reactions are delayed.

The current during the AC electrolytic deposition of the oxide film decreases gradually over a prolonged period because the electric resistance (impedance) of the oxide film increases gradually. There are two reasons for the increase in electric resistance of oxide film.

They are:

1. electric resistance of the barrier layer increases
2. electric resistance increases due to material electrodeposited in the channels of the film.
The total electric resistance (total impedance) during electrodeposition can be measured, although this wasn’t done in the present work, but the electric resistance of the barrier layer alone cannot be measured during electrodeposition. It might be possible to gain some insight into this characteristic via impedance spectroscopy.

The electric resistance material formed in the channels of the oxide film during the electrodeposition is metallic oxide. In addition to \( \text{Cu}^{2+}, \text{Mg}^{2+}, \text{H}^+, \text{OH}^- \) ions, \( \text{Al}^{3+} \) ions also exist in the nanochannels of the film immersed in the electrolyte. \( \text{Cu}^{2+} \), and \( \text{H}^+ \) ions are subjected to cathodic reduction, but not \( \text{Al}^{3+} \) ions. Due to cathodic reduction, the \( \text{H}^+ \) ions in the channels of the film become alkaline. The result is that \( \text{Al} \text{(OH)}_3 \) is formed in the channels of the film. These \( \text{Al} \text{(OH)}_3 \) colloids reduce the electrolytic current.

Figure 30. \( \text{Al} \text{(OH)}_3 \) colloids forming in the channels during electrodeposition.
If the Al\(^{3+}\) content in the electrolyte increases, electrodeposition will not occur any more; that is, the reason for the pale color of poor electrodeposition is the formation of Al (OH)\(_3\) in the channels of the oxide film. Fig. 30 shows the process of formation of Al (OH)\(_3\) colloids in the channels of the film. Even if Mg\(^{2+}\) ions are added to the electrolyte, Mg (OH)\(_2\) is formed in the channels of the oxide film, resulting in poor metal deposition; albeit, Mg\(^{2+}\) is not as susceptible to hydroxylation as Al\(^{3+}\) thereby aiding in deposition. It was found that after only 25-30 uses, the electrolyte solution gives visibly poorer results, due to Al contamination.

It is technically very difficult to obtain uniform deposition over the entire film surface. The cause of this unevenness varies depending on the case; the two main causes are:

1. unevenness due to the unevenness in the oxide film itself
2. unevenness due to the non-uniform distribution of current during electrodeposition.

When oxide film is formed in a electrolytic bath, the porous layers and barrier layers in the vicinity and at the central part of the aluminum specimen may differ. In addition, the film thickness may vary in the hollows and raised portions of uneven aluminum sections. Such films will give unevenly deposited metal in spite of care and precautions in electrolyte formulation.

The metal deposition conditions will also vary depending on whether a sine wave AC voltage or distorted AC voltage is applied. It was found that square wave pulses, for
instance, gave little to no deposit at all. Differences in voltage waveforms are likely to change the rate of deposition reaction or reaction mechanism, therefore, the particle size distribution of metallic colloids will change.

During electrodeposition, if the variation in barrier layer thickness is excessive, or if the porous layer is excessively thin, satisfactory deposition will not be obtained.

If $V_{AC}$ is greater than the originally applied anodization voltage ($V_{DC}$), which is almost always the case, there is an initial surge in current density in the aluminum oxide film during which electrodeposition of metals into the channels occurs immediately. The barrier layer simultaneously thickens to a value approximate to the anodization conditions at this higher voltage. In addition, the channel propagation continues in a reanodization process once the new barrier overlayer has been established.

If $V_{AC}$ is less than $V_{DC}$ the barrier layer will become thinner and new narrower channels will begin propagating at the base of the channels of the original porous aluminum oxide film. Once this new equilibrium barrier layer is achieved, the metal will be electrodeposited into the new channels first, then the channels formed during the original anodization process. The existence and extent of reanodization depends upon the relative aggressiveness of the acid used in the electrodeposition electrolyte compared to that of the original anodization electrolyte. This should concern those using sulphuric acid electrolytes, such as the present work, in an oxalic acid nanochannel alumina template. Tachihara et al.\textsuperscript{3} found that electrodeposition in neutral electrolyte resulted in thicker barrier layers regardless
of the difference in magnitude between $V_{DC}$ and $V_{AC}$. The metal deposits in the channels of
the porous films are metallic with little or no oxide present. Moskovits et al.\textsuperscript{4} found that the
metals were present as a colloid with the aid of specular reflectance spectra. Other groups
proposed that the metals were electrodeposited as solid metal columns. Also, Furneaux et
al.\textsuperscript{5}, investigated the sample using electron microscopy and postulated that the metal deposits
were relatively loose, sponge-like material. Electron microscopy indicates that the metal
column is not necessarily compact. This has phenomenal ramifications when trying to
construct multimetallic multilayered nanomaterials.
3.1 Single Metal Experimental Results

The experimental procedure for nanowire formation is shown in Fig. 31.

Figure 31. Schematic for electrodeposition into porous AAO.
3.1.1 Copper Nanocomposites

Copper electrodeposition was carried out in a solution containing

\[
\begin{align*}
0.5 \text{M } & \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \\
0.05 \text{M } & \text{MgSO}_4 \cdot 7\text{H}_2\text{O} \\
0.05 \text{M } & \text{H}_2\text{SO}_4 \\
0.001 \text{M } & \text{NaOSO}_3 (\text{CH}_2)_{11}\text{CH}_3
\end{align*}
\]

The electrodeposition potential was varied to obtain optimum deposition conditions including rate and quality of the nanowires. The AC frequency was varied but only gave satisfactory results below 100 Hz.

In order to create the proper complex for electrodeposition, recalling Gerischer's theory, the acid must be added prior to the addition of the metal salt. If not, a hexa-aqua complex forms which is very difficult, or even impossible to electrodeposit.

Surfactant addition gave a far better deposit, most likely due to the H₂ removal during electrodeposition. The surfactant will also aid in keeping the pH of the electrolyte in the nanochannels low, inhibiting the detrimental metal hydroxide formation.

The copper deposition rate is graphically shown in Fig. 32. A low voltage (5-7 VAC) and low frequency (60-100 Hz) gave optimum results.
Fig. 32. Rate of copper growth.

Fig. 33 shows Cu deposition into a non-electropolished template. Severe flaws, as shown, will occur if no electropolishing is performed prior to anodization, but is not seen in electropolished films.

To liberate the nanowires, the oxide template was etched away in 0.1M NaOH. It was found the 0.5M Na₂CO₃ gave a slower, more even etch, for the purpose of nanowire exposure, as well as less of a chance of nanowire reduction to metal hydroxide. (See Figs. 34-36)
Figure 33. Copper Nanowires in PAAO.

Figure 34. Exposed copper nanowires after PAAO template has been removed.
Figure 35. Copper nanowires.

Figure 36. Close-up of liberated copper nanowires.
3.1.2 Rhodium Nanocomposites

Rhodium electrodeposition was carried out in a solution containing

\[ 0.3 \text{ M} \text{Rh}_2(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O} \]
\[ 0.05\text{ M} \text{MgSO}_4 \cdot 7\text{H}_2\text{O} \]
\[ 0.05\text{ M} \text{H}_2\text{SO}_4 \]
\[ 0.001\text{ M} \text{NaOSO}_3(\text{CH}_2)_{11}\text{CH}_3 \]

Again, the electrodeposition voltage was varied to obtain optimum deposition conditions including rate and quality of the nanowires. The AC frequency was varied but only gave satisfactory results at 60 Hz.

The rate of rhodium deposition is shown in Figure 37. XPS and EDX both show that the nanowires are pure rhodium with little oxide present.

The electrodeposition and subsequent etching was carried out as with Cu, but only 0.5M \text{Na}_2\text{CO}_3 was used for the Rh composites. Even very dilute hydroxide etching destroyed the nanowires as etching was performed. (See Figs. 38-41)
Figure 37. Rate of rhodium growth.
Figure 38. Example of PAAO filled with Rh nanowires.

Figure 39. Exposed Rh nanowires.
Figure 40. Rh nanowires.

Figure 41. Rh nanowires.
3.2 Multimetallic Nanocomposites

There were a number of innovative methods used to create multimetallic nanowires with the nanochannel alumina template.

Single bath with both metals in high concentration.

This method was used in the making of alloy nanowires of set composition. A typical electrolyte composition was 0.2M CuSO$_4$ · 5H$_2$O, 0.2M Rh$_2$ (SO$_4$)$_3$ · 2H$_2$O, 0.05M MgSO$_4$ · 7H$_2$O, 0.05M H$_2$SO$_4$, and 0.001M NaOSO$_3$ (CH$_2$)$_{11}$CH$_3$

Each metal’s concentration in the electrolyte could be varied, resulting in a controlled alloy ratio.

Single bath with one metal in high concentration and low concentration of the other.

This method was used in the attempt to make multilayered nanowires of set composition. A typical electrolyte composition was 0.5M CuSO$_4$ · 5H$_2$O, 0.005M PdSO$_4$ · 2H$_2$O, 0.05M MgSO$_4$ · 7H$_2$O, 0.05M H$_2$SO$_4$, and 0.001M NaOSO$_3$ (CH$_2$)$_{11}$CH$_3$.

The motivation and reasoning behind the utilization of this method was based on the work by other researchers in the giantmagnetoresistance field. The object was to electrodeposit the low concentration, high reduction potential metal at low voltage. The voltage would then be increased, above the reduction potential for the high concentration of the other metal.
species. Both metals would deposit, but the layer would consist of almost completely, the high concentration metal. The voltage would then be lowered below the latter metal's reduction potential, and again, only the low concentration metal would be deposited.

Due to the necessity for AC electrodeposition into the nanochannels, this method proved problematic and relatively non-quantifiable.

**Single bath with both metals in high concentration with displacement.**

This method was used in the attempt to make multilayered nanowires. A typical electrolyte composition was 0.2M CuSO\(_4\) \cdot 5H\(_2\)O, 0.2M Rh\(_2\) (SO\(_4\))\(_3\) \cdot 2H\(_2\)O, 0.05M MgSO\(_4\) \cdot 7H\(_2\)O, 0.05M H\(_2\)SO\(_4\), and 0.001MNaOSO\(_3\)(CH\(_2\))\(_{11}\)CH\(_3\)

The difference in reduction potential for the two metals, if sufficiently large, can be used to create multilayers. The higher reduction potential metal, when oxidized in solution, will be reduced by the lower reduction potential metal, and the latter will oxidize and return to solution. The overall reaction,

\[
Pd^{2+} + Cu^0 = Pd^0 + Cu^{2+}
\]

This is schematically shown for CuPd in Fig. 42.
Figure 42. Single-bath electrodeposition of multilayers.
Dual bath with electrolytic deposition in both baths

This method was employed to make CuNi, (See Figs. 44-45) and CuRh nanowires. A bilayered metal nanowire composite of AuFe was created using this dual bath electrolytic deposition (See Figs. 46-52). This result began to illustrate, again, the dilemma of having anodic electrolysis during metal deposition.

Dual bath with electrolytic deposition in one bath and electroless displacement in the other

This method was employed to make CuPd nanowires. (See Figs. 53-54). When the concentration of Pd was in large in the electroless bath, metallic Pd was deposited on the surface of the template as shown in Figs. 55 and 56.

Figure 43. Dual-bath electrolytic deposition of multilayers.
Figure 44. CuNi nanowires showing Ni on surface.

Figure 45. Exposed CuNi nanowires.
3.2.1 Gold & Iron Bimetallic Bilayered Nanocomposites

Figure 46. ARXPS results of Au/Fe nanowires.
Figure 47. Au XPS results for Au/Fe wires produced after short period etching.

Figure 48. Fe XPS results for Au/Fe wires produced after short period etching.
XPS Results for Au/Fe wires produced after long period etching

Figure 49. Au XPS results for Au/Fe wires produced after long period etching.

Figure 50. Fe XPS results for Au/Fe wires produced after long period etching.
Figure 51. Exposed AuFe bilayer nanowires.

Figure 52. Partially etched AuFe nanocomposite showing the Au layer.
3.2.2 Copper & Palladium Bimetallic Nanocomposites

Figure 53. Pd displacement of Cu on pure Cu foil.

Figure 54. Pd displacement of Cu to create bilayer.
Figure 55. Pd aggregation during electrolytic deposition.

Figure 56. Pd aggregation during electrolytic deposition.
Figure 57. Exposed CuPd alloy aggregates with high Pd content.

Figure 58. Exposed CuPd alloy nanowires with low Pd content.
3.2.3 Copper & Rhodium Alloy Nanocomposites

Figure 59. Exposed CuRh alloy nanowires with high Rh content.

Figure 60. Exposed CuRh alloy nanowires with low Rh content.
3.3 Discussion

Through correct metal complexation and control, Cu and Rh nanowires can be made relatively reproducibly. The formulations, as well as the complexation chemistry, is now known to create these and a few other monometallic nanocomposites controllably.

Using varied concentrations of reagents, in single and dual bath methods, metal alloy nanowires have been created in a controlled fashion for CuRh, CuPd, and CuNi. The latter two alloys were shown to be unstable at high Pd or Ni concentrations. The lack of proper complexation as well as having anodic electrolysis during electrodeposition are likely the main reasons for this result.

A dual electrolytic method could not be extended to the catalytically active metal nanocomposites of CuPd or CuNi. The creation of CuRh multilayers was never completely affirmed by SEM, but further work with this system “should” be able to generate multilayers. However, the need for complete coulometric control is of utmost importance for this. The etching conditions might also be playing a role in that all bimetallic multilayers were destroyed by NaOH, whereas CuRh nanowires, made in a multilayered fashion, were stable when etched in Na$_2$CO$_3$. Even under ideal conditions, the control of alloying (interstitial), composition, and morphology, will likely be very difficult under aqueous conditions. This is a result of the complex aqueous chemistry occurring during electrodeposition, due to anodic electrolysis.
3.4 References


4.0 CATALYTIC STUDIES

4.1 Introduction

One of the objectives of nanoscale catalyst research is to produce a material with exceedingly high selectivity at high yield in the reaction product or product slate, that is, chemicals by design, with the option of altering the product by changing the surface functionality or composition at the nanoscale. For instance, new catalysts with increasing specificity are now being fabricated in which only one or two spatial dimensions are of nanometer size.

A second objective is to discover nanoscale materials or structures with exceedingly high storage capacity per unit volume and weight for gases such as H₂ or CH₄, which would then be more economic for use either as a combustion fuel or as the means to power fuel cells for ultralow-emission vehicles or for electric power generation.

A third objective is to fabricate molecular sieving membranes using inorganic crystalline materials such as zeolites. For molecular sieving membranes, one critical challenge rests on discovering ways to create large-scale, thin, nearly defect-free membranes.

In nanoscale catalyst materials the critical chemical selectivity is likely to be intimately associated with the local environment around what may be called the active site. This suggests that the size, type, and geometry of the atoms making up the active site will
play a critical role in defining the conditions under which this active site will be able to carry out its designed function. Fabrication of materials with exactly the same structure and composition at each active site has been and will continue to be a major challenge to materials and catalytic scientists.

Another challenge is to control the thermal and chemical stability of the fabricated nanostructure. It is generally accepted that the smaller the nanostructure (active site), the more likely the structure is to move, aggregate, decompose, or in some way change its shape, composition, or morphology upon exposure to thermal and/or chemical cycling. Identifying windows of stable operation in which the specific structure or material will be able to retain the desired (and designed) behavior is critical for commercial applications. On the other hand, the driving force for investigating nanostructured materials is the fact that they typically exhibit unique properties that are expected to open windows of opportunity previously inaccessible with existing materials. It is with this impetus that a controlled and "assembled" structure was used. By "putting up the fences" to aggregation, resulting in the generation of an ordered array of metal nanowires, it was hoped to generate an ideal model catalyst.
4.2 Reactor Design

Figure 61. Schematic for catalytic experiments.
4.3 Experimental Results

The catalytic reactions investigated involved the synthesis of methanol from carbon dioxide and hydrogen and the reverse water-gas shift reaction. Although only very preliminary results were obtained, Figs. 62 and 63. The catalytic results were obtained over non-reduced nanowires, therefore showing little activity. It should be noted though that the variation in selectivity is a fulfillment of a key objective of the research.

![Graph](image)

Figure 62. Methanol synthesis results using CuPd nanowires.
Figure 63. CO synthesis using CuPd nanowires.
4.4 Discussion

The ability to control composition and morphology has given preliminary results for selectivity control in the hydrogenation of CO$_2$. The results indicate that the Pd metal facilitated the reaction by dissociating the hydrogen faster than Cu would do this dissociation. This gives at least an indication that through diligent control of nanowire composition, product control can be achieved in the catalysis.

A proper catalytic reactor with analysis system for studying this catalysis, under industrially relevant conditions, should be devised with the ability for high pressure reaction and UHV characterization. Above and beyond this fact, only fully characterized nanochannel alumina template nanowire catalysts will generate the necessary results to support modifications and improvements in the catalyst. Optimum activity and selectivity studies, as well as kinetic and mechanistic work, can be achieved if this electrochemical control is performed.
5.0 CONCLUSIONS

The objectives of the present work were fivefold. Firstly, to controllably create a nanocomposite template using porous AAO. This has been accomplished using oxalic acid as the anodizing electrolyte. The degree of control is not yet up to standard as to reproducibly generate a template of known morphology. Electropolishing, temperature control, as well as low noise voltage electrolysis has been shown to be essential in achieving reproducibility and control.

Secondly, to controllably create monometallic nanowires which have catalytic properties. Through correct metal complexation and control, Cu and Rh nanowires can be made reproducibly. The formulations, as well as the complexation chemistry, is now known to create these and a few other monometallic nanocomposites controllably.

Thirdly, to controllably create bimetallic metal nanowires with known, determined composition and morphology, and that are of catalytic interest. Using varied concentrations of reagents, in single and dual bath methods, metal alloy nanowires have been created in a controlled fashion for CuRh, CuPd, and CuNi. The latter two alloys were shown to be unstable at high Pd or Ni concentrations. The lack of proper complexation as well as having anodic electrolysis during electrodeposition are likely the main reasons for this result.

Fourthly, to controllably create multilayered multimetallic nanowires using the same basic techniques as for the alloy wires. A bilayered metal nanowire composite of AuFe was
created using dual bath electrolytic deposition. This result began to illustrate, again, the dilemma of having anodic electrolysis during metal deposition. This method could not be extended to the catalytically active metal nanocomposites of CuPd or CuNi. The creation of CuRh multilayers was never completely affirmed by SEM, but further work with this system “should” be able to generate multilayers. However, the need for complete amperometric control is of utmost importance for this. The etching conditions might also be playing a role in that all bimetallic multilayers were destroyed by NaOH, whereas CuRh nanowires, made in a multilayered fashion, were stable when etched in Na₂CO₃. Even under ideal conditions, the control of alloying (interstitial), composition, and morphology, will likely be very difficult under aqueous conditions. This is a result of the complex aqueous chemistry occurring during electrodeposition, due to anodic electrolysis.

Finally, to use these metal nanocomposites for heterogeneous catalytic studies. The ability, albeit not perfect, to control composition and morphology has given preliminary results for selectivity control in the hydrogenation of CO₂. A proper catalytic reactor with analysis system for studying this catalysis, under industrially relevant conditions, must be devised with the ability for high pressure reaction and UHV characterization.
6.0 RECOMMENDATIONS

To create a controlled metal nanowire catalyst, the first and foremost an in-depth study utilizing all published results must be done on the porous AAO template made in oxalic acid itself. Only in the last 3-5 years has porous AAO began to be used extensively for high-tech nanocomposite formation, under controlled conditions. The anodic formation and "colouring" of various AAO films has been performed for decades, but little of this work can be extended into the development of leading edge technology for nanocomposition using the nanochannel alumina template. In order to accomplish this, there are fundamental studies, using oxalic acid, which must be done. Complete studies on how varying temperature, voltage, current, concentration, etc., affect porous AAO must be performed. These studies will only be meaningful if they are done if they are performed in a rigorously controlled fashion. The procedure for investigation must be done in close relation to the procedures that will be followed in this lab to make the materials. How does the anodic electrolysis during non-aqueous electrodeposition affect the template morphology? This question is one of many which must be answered in complete nanocomposite control is to be achieved. The establishment of a meticulous protocol of investigation to completely describe template formation in oxalic acid is of fundamental importance. The investigation, which in empirical form, will validate many of the descriptions already in the literature.

Once the template is made reproducibly and with complete control, suitable electrolytes must be found, whether aqueous or non-aqueous, for any metal of interest that
will be used for nanocomposition. The success for generating monometallic nanowires, of many metals, has been aptly demonstrated in this lab, but not in a controlled meticulous way. The same ideology that will have perfected the template, will have to be extended into the formation of controlled nanowires.

Many multimetallic composite nanowires is the greatest challenge, especially when considering multilayered structures. The most promising future in this direction seems to lie with metal colloids/clusters. Albeit, the likelihood of creating multilayered nanowires in very wide nanochannels would have a higher probability of success. Adequate control of multilayer composition and morphology under aqueous conditions, using porous AAO, is problematic at best. Only using DC electrodeposition, under coulombetric control, has anyone made multilayered layered nanowires this fashion. Even the latter work has not utilized the nanochannel alumina template, but the only the polycarbonate membranes.

Once a reproducible a completely characterized material is made, the catalytic studies will give great insight into the mechanistic nature of the chemistry occurring during reaction.