PRODUCTION OF POROUS ELECTRODES FOR FUEL CELLS SUPPORTS

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by

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Abstract

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The production of electrodes with three dimensional open pore structure has been pursued as a possible alternative to the frequently used Carbon black-based anode supports. Three different fabrication methods were explored, namely through the use of a High Internal Phase Emulsion (HIPE) template, use of Polystyrene microspheres, as well as Photolithographic methods. The HIPE template proved difficult to control, due to the high sensitivity of the emulsion structure to the voltage during electroplating, which resulted in disruption in the aqueous paths through which the dissolved Ni was supposed to deposit on the substrate (Copper foil). Fabrication of a porous catalyst support (made out of Ni) by photolithography methods was successful. However, problems remain with the removal of the backing supporting the Ni structure and the fragility of the glass support used. This will require further refinement of the method.
Formation of highly porous Ni supports by electroplating through a microspheres template proved to be feasible. However, some problems remain in this case. First is the incomplete elimination of microspheres from the structure following dissolution with tetrahydrofuran (THF). Scanning Electron Microscopy (SEM), Thermal Gravimetric Analysis (TGA), and Differential Scanning Calorimetry (DSC) were used to characterize the morphology of the porous structure. Cracks in the spongiform Ni layer were observed to form following spheres thermal sintering. This resulted in overplating Ni through the cracks, leading to an undesired deposit on the back of the Toray paper as well. Both these phenomena influenced the performance of the samples during the electrochemical testing in a fuel cell-type configuration.

The catalyst was deposited on the porous Ni support by both pulse plating and electrospray methods. The structure of the Pt particles obtained by electroplating depended on the charge transfer during the electrodeposition process. For a charge transfer higher than 10 C the Ni craters became occluded by Pt particles. Pt and PtRu electrosprayed on the Ni sponge were found to be more active towards methanol oxidation than both standard anodes using PtRu deposited on a Carbon layer and the most active samples consisting of Pt pulse plated on the sponge.
DEDICATION:

The research efforts described here dedicated to three very important persons in my life: First of all my beloved parents that have always been unconditional supporters of my endeavors and to whom I owe everything I am. Second but not least my uncle Michalis Kolybakis, a person of much importance to me that always inspired and believed in me.

Σα βγεις στον πηγαινό για την Ιθάκη,
να εύχεσαι νάναι μακρύς ο δρόμος,
γεμάτος περιπέτειες, γεμάτος γνώσεις.

……..μη προσδοκώντας πλούτη να σε δώσει η Ιθάκη.

Η Ιθάκη σ’έδωσε τ’ωραίο ταξείδι.

Χωρίς αυτήν δεν θά βγαίνεις στον δρόμο…

Κι αν πτωχική την βρεις, η Ιθάκη δε σε γέλασε.

Έτσι σοφός που έγινες, με τόση πείρα,

ηδή θα το κατάλαβες οι Ιθάκες τι σημαίνουν.

(Ithaca, by K.P. Kavafys)

«Νυν ευπλόηκα, ότε νεναυάγηκα» (Ζηνών ο Κίτιευς)
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CHAPTER 1:
INTRODUCTION

1.1 Fuel Cells

1.1.1 Motivation

Energy is a key element of the interaction between nature and society and affects the economic development as well as the future of human existence. Concerns associated with human health and environmental risks have arisen rapidly over the last decades. Many of these issues are related to the production, transformation and use of energy, for example acid rain, ozone depletion and global climate change. Scientists focus their efforts into developing energy production processes that will be beneficial towards a sustainable development and simultaneously will satisfy society’s energy needs. Meeting the present needs without compromising the future should be achieved by using alternative sources of energy like the hydrodynamic, solar, wind, geothermal etc.

Development of new energy systems is necessary for sustaining growing economies, disengaged from oil. Fuel Cells are one of the key future technologies and are similar to batteries with the exception of the continuous replenishment of the fuel. They offer the possibility of reducing the world’s dependence on natural resources by increasing the energy conversion efficiency when compared to Carnot-cycle limited thermal engines that have been dominating for more than a century. Fuel cells promise to
reduce the ecological impact by creating environmentally friendly byproducts while using renewable fuel sources. They can be employed in a variety of applications, due to their flexible power output, ranging from a few watts to megawatts. Therefore, they can replace batteries, combustion engines, or even large power stations causing reduced emissions, increased energy efficiency, and decreased dependence on natural resources. Understanding fuel cells is thus pertinent to the advancement and sustainability of our energy demanding lifestyles.

1.1.2 Historical overview

Nowadays, the primary sources of energy are: (1) chemical, (2) gravitational, (3) nuclear, (4) solar and geothermal. Of course, solar energy is the form humans are more familiar with, sustaining life through photosynthesis, and being at the origin of other forms of energy originating from vegetation (thus coal and oil). With the passage of time energy requirements have increased. Technological development of the Western world and steady worldwide population growth increase the danger for the major energy supplier, the environment. Since the form of energy most used is electricity conversion of energy from its primary forms to this medium is desirable. The production and conversion of energy (except for hydroelectric power generation) involves at least one step where part of the heat is dissipated. Carnot cycles present limitations on the amount of heat transformed in any other form due to the second law of thermodynamics. Thus the disengagement from this source is an old quest [1].

Early in the 19th Century researchers recognized and struggled to achieve a high electrochemical energy conversion. A scientist and lawyer, Sir William Grove, was the person that created the “ancestor” of what is consider today a fuel cell (device that
directly and continuously converts chemical energy into electricity) [2, 3]. In 1839 he built what was called gaseous voltaic battery: a gas battery with 50 cells connected in series and found that 26 cells were the minimum needed to electrolyze water. Schoenbein drew attention to experiments of his own trying to prove that in Grove’s cell currents were a result of chemical action rather than the result of two contacting substances. Mond and Langer (1889) created the first real fuel cell prototype. Their initial remarks deal with the absorbent condensing power. They conceptualized the need for a porous non-conducting electrolyte (diaphragm) called matrix that contained the sulfuric acid and was covered on both sides by platinum. Jacques thought electrochemistry was the solution to the inefficient energy conversion from chemical to mechanical [2]. He used potassium hydroxide in a molten state as electrolyte along with coke and a Pt wire, to hold the coke, as the negative electrode. Each of these “pots” produced 116 mA cm$^{-2}$. A pivotal point in the sequence of fuel cell development events was the incorporation of solid oxides in the cell design due to their high conductivity at high temperatures.

However, it was not until the 1960s that government funding became available for development of these systems as a viable energy source [2]. General Electrics used porous electrolyte (instead of matrix) in the form of tubes to investigate the diffusion electrodes performance. The military and National Aeronautics and Space Administration (NASA) were attracted to fuel cells due to the possibility of overcoming Carnot-cycle limitations to which all heat engines are subjected. Pratt and Whitney Aircraft developed the fuel cell power plant for Apollo (1965) used to supply the electricity for life support, guidance and communications.
A comparison between the thermodynamic efficiency of a fuel cell system (χ) (Eqn. 1.1) and that of a Carnot-cycle engine (η) (Eqn. 1.2) is shown in Figure 1.1.1 [3] and explains the preference to Fuel Cells. For a fuel cell the efficiency is obtained as:

\[
\chi_{FC} = \frac{\Delta g_f(T, P)}{\Delta h_f(T, P)} \cdot 100
\]  

(1.1)

where \( \Delta g_f \) and \( \Delta h_f \) are the Gibb’s free energy and the standard enthalpy of formation for the overall reaction, respectively. On the other hand, the percent Carnot efficiency, η, of a thermal engine working between temperatures T1 and T2, with T1 > T2, is given by the following Equation:

\[
\eta = \frac{T_1 - T_2}{T_1} \cdot 100
\]  

(1.2)

Figure 1.1.1, Comparison between the efficiency limit of a hydrogen fuel cell and the Carnot cycle limit [3].
The key feature observable in Figure 1.2.1 is that at low temperatures the reversible fuel cell efficiency is higher than that of a heat engine that follows the Carnot Cycle. In reality, there are significant power losses when operating fuel cells at lower temperatures, because thermodynamics does not account for irreversibilities stemming from reaction kinetics, mass transfer limitations, and electrical losses [3, 4].

The need for sealing and circulating a liquid alkaline electrolyte in the 1960’s led General Electrics to the development of a solid polymer electrolyte. This system (0.06 cm thick ion exchange membrane made out of cross linked polystyrene [2]) did not perform reliably in the space fuel cell projects. By 1968, NASA had replaced the proton exchange membrane fuel cell (PEMFC) with the Bacon Cell [2, 5]. This promising alkaline electrolyte fuel cell enjoyed significant development during the 1970’s; however there were still problems with high cost, reliability, ruggedness, and safety that could not be solved with the technology available. Due to their efficiency and the possibility of converting the residual heat in a high temperature power plant, molten carbonate fuel cells were popular in the 1980’s and solid oxide fuel cells were developed in the 1990’s. However, some life expectancy problems still remain to be solved [6].

An uprising turn in PEM fuel cell technology occurred in the 1990’s as a result of 20 years of optimization. New formulations by Grot in 1972 improved membrane performance and together with development of electrode fabrication (Raistrick, 1986) revealed promises for applications in road vehicles (Prater, 1990) [3-5]. Grot (working at DuPont) introduced a polymer known as XR, chemically and thermally stable (able to withstand sulfuric acid and operate even at 200°C). It was derived from
Polytetrafluoroethylene (PTFE) and had an equivalent mass between 1.150-1.2 kg eq\(^{-1}\).

This polymer consists of a Teflon backbone with pendent sulfonic acid functional groups, allowing for the transport of H\(^+\) ions from the anode to the cathode [7]. It became known as Nafion®, and since then has seen much development due to concentrated funding on fuel cell technology by the U.S. Department of Energy [8]. It was used in fuel cells in the 1980’s and started becoming popular as a membrane material (Ballard first test in 1987) [4].

In recent years improved performance has been achieved by incorporating Nafion ionomer into the catalyst layer to establish continuity between the catalyst and the electrolyte. Also, carbon supports (developed for phosphoric acid cells) boosted the conductivity of the assembly. The DOE has refocused its efforts toward the commercialization of fuel cell units and systems by developing collaborations between the academic community and the private sector. This has spurred a tremendous amount of work on fuel cells, ultimately leading to their commercial viability as efficient energy conversion devices [8, 9].

The major types of fuel cells are classified according to the type of electrolyte or fuel used (listed in Table 1.1.1.), but in all cases oxidation reactions occur at the anode and reduction reactions occur at the cathode.
### TABLE 1.1.1:
FUEL CELL TYPES

<table>
<thead>
<tr>
<th>Fuel Cell Type</th>
<th>Electrolyte Used</th>
<th>Year developed</th>
<th>Operating Temperature (°C)</th>
<th>Reactions</th>
</tr>
</thead>
</table>
| Proton Exchange Membrane (PEMFC) | Ion conductive Polymer   | 1960 (General Electric) | ~80                        | Anode: $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$  
Cathode: $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ |
| Direct Methanol (DMFC)        | Ion conductive Polymer   | 1965 (Shell, ESSO)   | 50-120                     | Anode: $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 6\text{H}^+ + \text{CO}_2 + 6\text{e}^-$  
Cathode: $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ |
| Alkaline (AFC)                | Aqueous solution of KOH  | 1946 (Davtyan)      | 23-70                      | Anode: $2\text{H}_2 + 4\text{OH}^- \rightarrow 4\text{H}_2\text{O} + 4\text{e}^-$  
Cathode: $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$ |
| Solid Oxide (SOFC)            | Zirconium Oxide with Yttria | 1937 (Bauer & Preis) | 700-1000                   | Anode: $2\text{H}_2 + \text{O}^2- \rightarrow 2\text{H}_2\text{O} + 2\text{e}^-$  
Cathode: $\text{O}_2 + 4\text{e}^- \rightarrow \text{O}^2-$ |
| Phosphoric Acid (PAFC)        | Phosphoric Acid          | 1967 (Pratt & Whitney) | 150-200                   | Anode: $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$  
Cathode: $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ |
| Molten Carbonate (MCFC)       | Potassium Carbonates     | 1946 (Davtyan)      | 600-650                    | Anode: $2\text{H}_2 + 2\text{CO}_2^2- \rightarrow 2\text{H}_2\text{O} + 2\text{CO}_2 + 4\text{e}^-$  
Cathode: $\text{O}_2 + 2\text{CO}_2 + 4\text{e}^- \rightarrow \text{CO}_3^{2-}$ |

### 1.1.3 Polymer Electrolyte Membrane systems

Each membrane supplier has developed individual proprietary versions of membrane with slight alterations in structure. A common feature however is the use of a sulphonated fluoropolymers, usually fluoroethylene. Thus Nafion® has become an industrial standard.

The key component of the fuel cell are the anode (where fuel oxidation occurs on the catalyst), the cathode (reduction), and the electrolyte assembled in a very compact configuration called the Membrane Electrode Assembly (MEA). A typical MEA can be several hundred microns thick [10].
For polymer electrolyte membrane fuel cells (PEMFCs), hydrogen is typically supplied to the anode and oxygen to the cathode side. The electrolyte, usually Nafion 117, permits the transport of proton from the anode to the cathode while limiting electron transfer and fuel crossover. The structure of a PEMFC is shown in Figure 1.1.2.

![Figure 1.1.2, Membrane fuel cell components: The anode, cathode and polymer membrane are denoted as A, B and C respectively.](image)

The major components of the PEMFC are: (a) the anode that consists of a support, a diffusion layer (denoted with A) and the catalyst where the oxidation reaction produces electrons that flow through the external load towards the cathode; (b) the Nafion® membrane whose aqueous pockets provide a path for the protons to diffuse and reach the cathode side; (c) the cathode where the protons react with oxygen to produce water on the hosted catalyst/diffusion layer (denoted as C). Thus, the transport of reactants towards the reaction sites is crucial and can result in significant inefficiencies [5]. Efficient diffusion through the support (usually carbon paper or cloth) is crucial for the transport of reactants and products towards and away from the catalyst in the reaction zone.
The latter constitutes the “heart” of the fuel cell, for it is the place where the reactions happen, although successful operation of the cell strongly depends also on good contact between the membrane and the catalysts to allow proton transfer from the anode to the cathode side. In order to ensure good contact of the catalyst with the Nafion® membrane, the MEA assembly is usually subjected to intense pressure [11].

In direct methanol fuel cells though, where the fuel consists a water and methanol mixture, the water is necessary to allow solvation of protons which allows their transfer to the membrane. The conduction region (outer loop on Figure 1.1.2) acts as a circuit for electron motion towards the cathode. The outermost flow channels on both the anode and cathode side of the cell permit delivery of fuel and oxidant and also allow removal of the byproducts. As noted in table 1.1.1, in both direct methanol fuel cell (DMFC) and H₂ fuel cells the cathode side can be flooded with water. Such phenomena combined with sluggish reaction rates can strongly limit the overall rate of electrical power generation and are the predominant factors for overpotential losses [4]. Other detrimental factors can be the fuel crossover through the membrane, catalyst poisoning when using Pt, catalyst loss by corrosion, catalyst particles sintering, and Ru crossover when using PtRu on the anode side. For the case of DMFCs studied here, efficient carbon dioxide removal from the reaction zone is essential to permit cell functioning. Yet CO₂ mass transfer on the anode side has not received much attention since the development of these cells [3]. As it will be discussed in Chapter 4 the concentration of CO₂ in the reaction zone depends on the transport characteristics of the diffusion layer.
1.1.4 Electrochemical Characterization of Fuel Cells

The typical experiments used to characterize the activity of fuel cells are called polarization scans. As shown in Figure 1.1.2 the load on a fuel cell can be simulated by using a resistor connected in parallel with it. During polarization scans, the resistance (also called load) is changed and the resulting potential difference and current are recorded.

Figure 1.1.3 shows a typical polarization scan for a DMFC. Operating under reversible conditions (no losses) then all the Gibbs free energy is converted into electrical energy. In such an occasion the reversible cell potential (theoretical) is given by the following Equation [3, 12]:

\[ E = \frac{-\Delta g_f}{n \cdot F} \]  

(1.3)

where \( n \) is the number of electrons transferred for each molecule of fuel, \( F \) is the Faraday’s constant \( (9.65 \times 10^4 \text{ C mol}^{-1}) \) and \( \Delta g_f \) is the Gibbs free energy released from the overall reaction occurring in the cell. However, in practice irreversibilities arise as shown in Figure 1.1.3. The reversible potential can be determined using the standard electrode potential tables [13] that report the standard state reversible voltages of electrochemical half cell reactions (also called electromotive force, emf) to the hydrogen reduction reaction which is taken as the reference, thus giving 0.0 Volts potential.
Figure 1.1.3, Profile developed during a fuel cell polarization scan.

The characteristic shape of the plot on Figure 1.1.3 stems from four major irreversibilities; namely activation losses, fuel crossover, Ohmic losses, and mass transport limitation. Each of these factors contributes to the reduction of the cell voltage.

The reversible voltage, denoted by the horizontal line on the top of Figure 1.1.3, can be calculated at a specific temperature using the Nernst Equation [5]:

\[ E = E_{\text{std}}^0 + \frac{R_g T}{n \cdot F} \sum_i z_i \ln a_i + \frac{\Delta \tilde{s}}{n \cdot F} \cdot (T - T_o) \]  

(1.4)

where \( z_i \) is the stoichiometric coefficient of the participant species \( i \) (positive for the species undergoing reduction), \( a_i \) is the standard activity of that species, \( E_{\text{std}}^0 \) is the reversible cell potential based on the emf series, \( E \) is the reversible potential, \( R_g \) is the ideal gas constant, \( T \) and \( T_o \) are the absolute and reference temperatures respectively and \( \Delta \tilde{s} \) is the overall change in entropy. The emf values can be found from tables [13] and are specific to the particular electrochemical reactions occurring in the cell [12]. Equation
1.4 can be used for half reactions by employing as a reference the standard hydrogen electrode (SHE) usually denoted as Pt/H₂ (α=1)/H⁺(α=1, aqueous). For SHE, a Pt wire is immersed in a solution that contains an electrolyte with hydrogen cations (at unit activity). The solution is also bubbled with 1atm hydrogen. For the case of a cell, Equation 1.4 is used to provide the actual potential in the cell by subtracting the anodic value from the cathodic. The rightmost entropic term in Equation 1.4 is usually neglected since its contribution to the total voltage is small at ordinary temperatures (T < 1000 °K).

For a DMFC the following set of reactions occur in the cell:

\[ \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 6\text{H}^+ + \text{CO}_2 + 6\text{e}^- \text{, } E^\circ = 0.02 \text{ V vs. SHE} \]  \hspace{1cm} (1.5)

\[ \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \text{, } E^\circ = 1.129 \text{ V vs. SHE} \]  \hspace{1cm} (1.6)

As in ordinary reactions, electrochemical reactions exhibit Arrhenius dependence of the reaction rate on temperature, reflecting the existence of some activation barrier. The probability the reactant species can overcome the energy barrier determines the rate of reaction. From statistical mechanics this probability (P_{ac}) is related to the temperature as:

\[ P_{ac} = e^{-\Delta G / R_g T} \]  \hspace{1cm} (1.7)

where R_g is the gas constant, T is the temperature and ΔG is the Gibbs free energy difference between the reactant and the activated state.

For an electrochemical reaction, the Gibbs free energy is related to the cell’s overpotential by the following Equation:

\[ \Delta G = -nF \eta \]  \hspace{1cm} (1.8)
Thus the reaction rate depends on the probability of finding the species in the activated state, the concentration of the reacting species and the frequency at which the activated species are transformed to products:

\[ r = c_o^* \cdot v \cdot P_{ac} \]  

\( c_o^* \) is concentration the reactive species (the oxidative species, the one that is reduced) concentration on the electrode surface, \( v \) is the collision rate and \( P_{ac} \) is given by Equation (1.7) [5, 12].

The reaction rate and the current density are finally connected through the following important relation:

\[ i = n \cdot F \cdot r \]  

where \( n \) is the number of electrons transferred in the reaction of interest (for Equation 1.5 \( n=6 \)), \( F \) the Faraday number, \( r \) is given by Equation (1.9) and \( i \) is the current density. Upon taking into account the activation energy barrier by introducing the electron transfer coefficients (\( \alpha \)) the Butler-Volmer Equation [12] specifying the relationship between current and activation overpotential (\( \eta \)) is obtained:

\[ i = i_0 \left[ \frac{C_o^*(0,t)}{C_o^{ref}} e^{-\eta \alpha \eta} - \frac{C_R^*(0,t)}{C_R^{ref}} e^{(1-\alpha \eta)\eta} \right] \]  

where \( n \) is the number of electrons participating in the reaction, \( i \) is the observed current density, \( i_o \) is the exchange current density (value of current density when the anodic and cathodic reactions occur at the same rate, \( i_{cath}=i_{an}=i_0 \)), \( C_o(x,t) \) is the concentration of the oxidative species on the catalyst layer as a function of time and distance, \( (C_o^{ref}) \) is the reference concentration at the anode side, \( C_R(x,t) \) is the concentration of the reductive species on the catalyst (located at \( x=0 \)) as a function of time and distance, \( (C_R^{ref}) \) is the
reference concentration at the cathode side, and $f = \frac{F}{R_0 T}$. The Butler-Volmer Equation predicts that the current produced by an electrochemical reaction will eventually increase exponentially with the activation overvoltage ($\eta$). It is crucial to state that this voltage is sacrificed to drive the system (cell) from the equilibrium (where $j_{an} = j_{cat} = j_0$) to a state where a net current is flowing. This overvoltage overcomes a barrier called activation barrier and is reflected as a voltage loss in Figure 1.1.3 by the precipitous drop shown on the left hand side of the plot. Activation overvoltages, occur on both electrodes, however the one on the cathode side is typically the dominant one [3, 5].

At large overpotentials Equation (1.11) simplifies to a relationship known as Tafel’s Law [12],

$$\eta = \frac{f}{n\alpha} \ln i_0 - \frac{f}{n\alpha} \ln i$$  (1.12)

Thus a plot of $\eta$ vs. $\ln(i)$ can be used to determine the exchange current density ($i_0$) and the transfer coefficient ($\alpha$). The higher $i_0$ the smaller the activation overpotential (or activation loss) required to achieve a specific current density, so the more energy will be transformed to electricity (high reaction rate).

Equation 1.12 is valid subject to the following conditions: a) the reduction reaction gives a positive current while the anode reaction a negative one when considering the overall process, b) the reference concentration (in the present case in the bulk of the electrolyte) is equal to the concentration on the electrode’s surface.

Other factors known to impact the overpotential in the activation region are fuel crossover across the membrane, and the catalyst surface area. Potential losses due to electron conduction across the membrane are typically negligible. Permeation of fuel through the membrane i.e. fuel cross over, can produce a back emf across the cell.
Crossover losses with hydrogen as a fuel are less significant than those with methanol due to the much higher permeability of methanol in the hydrated membrane. Other losses that are specific to methanol as a fuel relate to the slow oxidation kinetics and the production of CO$_2$ on the catalyst surface which can result in bubble formation (see section 4.1.1).

The intermediate region in Figure 1.1.3 arises from Ohmic losses associated to the intrinsic resistance of the fuel cell conductors. For methanol fuel cells, protons and electrons are released on the anode and consumed on the cathode. Any accumulation/depletion at the two electrodes creates a voltage gradient capable of driving transport of electrons from the anode to the cathode. In the electrolyte, any accumulation or depletion of ions (H$^+$) creates voltage and concentration differences that drive the transport of protons. In most situations the electrical driving force dominates fuel cell ion transport. Ion conductivity in electrolytes solution is usually found to be four to eight orders of magnitude lower than electron conductivity in metals [5, 14].

Because the total resistance is the sum of all the individual resistances (interconnects, anode, cathode, membrane, though the physics governing each and the individual magnitudes are different) we can write:

$$\eta_{\text{ohmic}} = i \cdot R$$  \hspace{1cm} (1.13)

where $i$ is the current density, $\eta_{\text{ohmic}}$ is overpotential loss due to resistance (resistance polarization) and $R$ is total cell resistance combining electronic, ionic, and contact contributions.

$R$ is proportional to the thickness and inversely proportional to the cross sectional area of the conductor [5]. Although reducing the thickness can improve Ohmic losses,
there are some limitations stemming from: a) the existence of pin holes, b) electrical shorting when the roughness of the electrolyte is close to its thickness, c) fuel cross over, that leads to voltage drop, and d) high contact resistance at the interface between electrolyte and electrode.

The mechanism of ion conduction is different from electron conduction due to the different natures of these species. In the case of a metal, the valence electrons become detached, leave the lattice and are free to move (they constitute a sea of charges able to move under a field). Yet, the metal’s cations remain intact and immobile within the lattice. In a solid ion conductor the crystalline lattice consists of both positive and negative ions “seating” on specific positions. Charge transport is accomplished by motion to places of missing atoms (vacancies) or to interstitials.

For polymer electrolytes (i.e. Nafion® membrane), a backbone based on polytetraflouroethylene provides the mechanical support, while the sulfonic acid (SO$_3^-$ H$^+$) groups provide charge sites for proton transfer. Figure 1.1.4 illustrates the structure of a Nafion® membrane.
As shown in Figure 1.1.4 part of the membrane volume (a region of relatively large void volume containing some side chains, water, and sulfonic or carboxylic groups and counter ions which are not in clusters) is filled with sulfonic groups [5, 15]. These regions are hydrophilic. Clusters of sulphonated chains can lead to the adsorption of large amounts of water. Within these regions the $\text{H}^+$ ions are weakly attracted to the $\text{SO}_3^-$ group and are able to move. Although the hydrated regions are somewhat separate, it is still possible for the protons to move through, especially upon water intake. The conduction properties of Nafion® are similar to liquid electrolytes and researchers report conductivities of the order of 0.10 S cm$^{-1}$. 

Figure 1.1.4, The structure of Nafion® membrane. Long chain molecules contain hydrated regions around the sulphonated side chains, allowing proton transfer.
If allowed to swell completely, Nafion® can accommodate so much water that its volume can increase by up to 88% [5]. Water management has become one of the most studied topics in PEM fuel cells [2-5].

The right region in Figure 1.1.3 represents mass transfer limitations, otherwise known as concentration polarization. In this region the reaction rate is faster than the diffusion of reactants and products; thus there is always an upper current limit defined by mass transport. What determines the performance is the fuel concentration near the catalyst. The electrochemical reaction leads to reactant (CH₃OH) depletion and product (CO₂) accumulation, affecting the reversible fuel cell voltage. The limited mobility of the ionic species in the electrolyte can account for some of the losses associated with the concentration overpotential, \( \eta_{\text{conc}} \).

High current densities imply high reaction rates, which in turn require high reactant fluxes. The flux is governed by Fick’s Law,

\[
N_A = -D_A \nabla C_A
\]

(1.14)

where \( N_A \) is the diffusive flux (mole s\(^{-1}\) cm\(^{-2}\)) of species A to the catalyst, \( D_A \) is the diffusion coefficient (cm\(^2\) sec\(^{-1}\)), and \( \nabla C_A \) is the molar concentration gradient (mole cm\(^{-4}\)). The limiting current density \( (i_L) \) corresponds to the maximum rate of reactant transport to the catalyst, which occurs when the reactant’s concentration at the electrode surface vanishes. Combining Fick’s Law [12] and Faraday’s Law we have then Equation 1.15:

\[
i_L = -n F D_A \nabla C_A
\]

(1.15)
where \( i_L \) is the limiting current density. Using equation 1.11 as well as the limiting current condition the following expression is obtained for the concentration polarization overpotential:

\[
\eta_{conc} = \frac{f}{n} \ln\left( \frac{i_L}{i_L - i} \right)
\]  

(1.16)

1.1.5 Electrode testing methods

As shown by Equations 1.10-11 the current obtained from an electrochemical reaction strongly depends on the polarization effects (deviation from equilibrium). Thus the electrochemical behavior can be characterized by testing the system’s response under a variety of potential transients.

A potentiostat is a device that allows one to control and measure the potential in an electrochemical cell that contains 2 or 3 electrodes. The instrument applies the potential necessary to force a desired current flow through the cell (a closed circuit is formed by using electrodes immersed in the electrolyte) and vice versa. That current is the flow of electrons needed to support the active electrochemical processes. Usually, the electrode’s area is small and the solution volume is large so that current passage does not significantly alter the bulk concentrations of species.

A typical electrochemical cell is shown in Figure 1.1.5:
The cell consists of three electrodes: the working electrode (WE) (where the reaction of interest occurs), the reference electrode (RE) with a stable and known potential based on a redox system [12] with constant composition, and the counter electrode (CE) that helps to balance the reaction occurring in the working electrode and closes the loop by attracting electrolyte ions (wet electrochemical cell). Typically, the active area of the WE is fixed and is 3-4 times smaller than that of the CE. The CE can be made of any convenient material compatible with the electrolyte because its electrochemical properties do not affect the behavior of the working electrode. A significant number of ions must be present in the electrolyte to promote diffusion from the WE to the CE and vice versa.

Cyclic Voltammetry (CV), chronoamperometry (CA) and Linear Sweep Voltammetry (LSV) are the most reliable testing methods [12].
CV can give information about the electrodes activity through potential scans at both oxidative and reductive conditions. During CV, the voltage is scanned at a predefined rate between a minimum and a maximum value and the observed current is plotted against the potential, as in Figure 1.1.6.

Figure 1.1.6, Sample cyclic voltammetry curve (the onset potential and the baseline are denoted). Figure on the right gives a voltage-time plot.

The shape and reproducibility of CV scans provides information about the system’s reversibility. Examination of the above curve reveals that the anodic part of the plot (region where potential is scanned from the minimum to the maximum value) is symmetric with respect to the cathodic part (potential scanned from the maximum value towards the minimum) and the higher current densities for both regions have the same absolute value. Here a distinction has to be made between the CV scans shown above and the polarization scan depicted in Figure 1.1.3. In the CV case the potential is imposed from an outside power unit and thus the system’s “rest state” is affected. The external voltage has to be greater than the potential given by the Nernst Equation (1.4) and the cell
is called an electrolytic cell. Examples of this are the electrolytic syntheses (the production of chlorine), electroplating [12]. Conversely, during the polarization scan the reactions occur spontaneously. These are called galvanic cells and convert chemical to electrical energy [4, 5, 12].

In the anodic region of the CV scan, the potential applied on the working electrode increases, thus the overpotential increases. Considering only the anodic scan (reduction is supposed to be negligible) and combining Equation 1.7-1.10 it becomes obvious that the current increase in the anodic scan results from a high reaction rate constant and reduced species concentration at the electrode which increase the flux [5, 12]).

Catalyst oxide formation in highly oxidative conditions may contribute to the current decrease. If the amplitudes of the oxidation/reduction peaks are different or change during subsequent scans then it can be inferred that the rate at which the reaction is taking place is changing during the analysis and the scan is not reversible. The peak current value has been found to be proportional to the square root of the product of the diffusion coefficient times the scan rate and proportional to species bulk concentration. As a result CV scans are frequently used to find diffusion coefficients [12].

Another important method that helps characterize a couple of electrochemical reactions in a cell is the Tafel method. As noted by Equation 1.12, the overpotential is proportional to the logarithm of the currents. Plotting these in Figure 1.1.7 helps find the actual exchange current density (a high value is favorable since it leads to low activation overpotential).
Figure 1.1.7, Typical polarization curve for an alloy. The exchange current density \( i_0 \) calculation is shown and is related to the anodic (lower) and the cathodic (upper) Tafel regions.

It is important to note here that the Tafel relation as expressed in Equation 1.11 represents only the cathodic polarization of Figure 1.1.7. The lower branch (anodic) comes after considering Equation 1.11 for large negative values and working in the same way as before (in the x-axis are plotted the values of the absolute current). The Tafel method is popular not only in electrochemistry but in corrosion science as well. Tafel slope is the measure of the intrinsic rate of corrosion in a material. High Tafel slope corresponds to high exchange current density \( i_0 \) thus small corrosion [16].

1.1.6 Direct Methanol Fuel Cells

An attractive fuel for a cell would be a commercially available liquid (thus no need for compression and gas pumps) that can be easily transported and has high energy density. Often desirable requirements are small fuel cell size, low operational
temperatures, simple humidification and heating system [6]. Methanol possesses all of these properties.

In DMFCs, dilute methanol is supplied on the anode side and reacts with water to form carbon dioxide and protons (see Table 1.1.1). These kinds of fuel cells are called direct because the fuel is used directly. Major obstacles here are the high activation overvoltage on the anode and cathode and the fuel cross over through Nafion® which is more intense than when using hydrogen as a fuel [5]. Additionally, water produced on the cathode can flood the electrode thus reducing the oxidant flux. Slow oxygen-reduction kinetics at the cathode and anodic catalyst poisoning (Pt is the most popular) are widely encountered problems in DMFCs [2, 3, 5, 6, 14, 17].

Methanol oxidation proceeds through several intermediate steps [5, 18-20] during which undesired intermediate CO is formed. The CO poisoning problem can be reduced by alloying the catalyst with Ru, Ni, Mo, Sn, W. Ru is considered the most effective alloying partner for Pt, and a model called “bifunctional mechanism” has been developed to describe its contribution in the reaction. According to this mechanism, Pt sites are center for CO adsorption and dehydrogenation, while on the Ru sites the OHads species react with the bound CO to produce CO₂, thus removing the poison from the catalyst [5, 21]. There is still debate concerning the optimum concentration of Ru in the PtRu alloy. Some researchers have reported that ternary alloys can be superior to Pt/Ru [19]. Current DMFCs exhibit power densities of at most 100 mW cm⁻² which is by a factor of 10 smaller than hydrogen burning PEMs.

The need for highly dispersed catalysts on both anode and cathode requires catalyst deposition methods appropriate for filling porous, 3-D structures with high
surface area. Efficient catalyst utilization in fuel cells requires its confinement to the immediate proximity of the proton exchange membrane. As mentioned before, a catalyst particle embedded inside the Nafion® membrane will have many contact points thus, if well wetted by water, the Nafion® will be able to conduct the protons. As a result the reaction benefits from an increase catalyst surface area by dispersion of tiny catalyst particles. However, as it will be explained in Chapters 2 & 3 transport reactions like CO₂ evolution and methanol passage render the use of porous electrodes desirable.

1.2 Electrochemical deposition

1.2.1 Background information

Methods such as sputtering [22], ion exchange [23], evaporation, colloidal reduction techniques, photo-deposition [24-26], electrochemical deposition (ED) can be used to form coatings of metals and organic materials [27-29]. Usually, metals are plated onto metallic substrates, but by appropriate pretreatment of the substrate they can also be plated onto plastics and inorganics such as glass.

Until the middle of the 19th century electrodeposition (ED) was mainly used for decoration purposes, but the emphasis has gradually shifted to functional coatings. A pivotal point in the development of efficient ED processes was the discovery of the Tafel Equation (1905) [12]. The first recorded observation of electrodeposition was made by Picton and Linder in 1905 [29]. However, it took many years to develop quantitative models to explain in detail the various mechanisms contributing to this process [30, 31].
The power of ED lies in its ability to transform a substrate material that is not appropriate for a given task with a metal coating that is. An important function of deposition coatings is corrosion protection of metals. The total losses from corrosion amount to 2-4% of the annual Gross National Product of industrialized countries. ED finds applications in many technologies among which the most important ones are: a) micro-fabrication, b) magnetic recording devices, c) plating of protective-decorative layers to enhance appearance, d) protection from environmental conditions, and e) the formation of high surface area catalysts [28, 32].

The metals are deposited from a liquid medium (electrolyte) either by utilizing a current (electrolysis) or through autocatalysis (electrolessly) [33]. For deposition through an electrolyte, the deposit’s host is used as a cathode (where reduction occurs) in an electrical close circuit. In the electroless case no close circuit is formed, as the reaction of the metal ions occurs due to chemical reducing agents present in the solution. The electrolytic method is more popular as it constitutes almost 95% of the ED industry. The reasons for this are the greater range of metals that can be electrolytically deposited, the low cost and the relative simplicity of the process. Electroless deposition is of industrial importance for Nickel, Copper, and Nickel-based alloys i.e. NiP, NiB [28, 29, 33]. Less important are the cobalt, tin, silver and gold. The cost of the chemicals used is 10 times larger for electroless than for the corresponding electrolytic.

The electrolytic ED technique can be continuous (DC) or non (AC). DC electro-deposition is most popular and uses a constant overpotential on the cathode side. This can be achieved by either controlling the current (galvanostatic deposition) or the potential (potentiostatic deposition) through a potentiostat. In the galvanostatic mode, the current
passing through the cell is regulated by a power unit and the cell’s impedance determines the potential. This method is used for continuous strip plating where precise current control is required [34]. In the potentiostatic mode the potential is controlled and predefined by the power unit and the current is defined by the cell impedance. Electrical impedances and slow responses of the instrumentation prevent the surface from attaining the desired voltages instantaneously. The method is used when the cathode’s surface area is constantly changing i.e. barrel plating [34]. Each of the aforementioned methods can be accomplished by either using three electrodes (working, auxiliary and the reference) or two (working and auxiliary). The two electrode mode is most popular in industrial scale processes (here the AE serves both as the cathode and as a RE).

Depending on the deposition conditions the applied potential can be scanned over a wide range of values. According to the Pourbaix diagrams [35] side reactions may occur (hydrogen reduction, oxygen evolution) during the course of deposition and can consume part of the supplied charge [35, 36]. The mass of the deposited metal species depends on the amount of electrons actually used for the reduction reaction of interest and is given by the Faraday Equation [28]:

$$m_r = \frac{MW \cdot \epsilon \cdot I_m \cdot t}{n \cdot F} \quad (1.17)$$

where \(m_r\) is the real mass of the deposit on the cathode (g), \(I_m\) the average cathodic current applied (A), \(t\) the total deposition time (s), \(MW\) the molecular weight of the deposited metal (g mol\(^{-1}\)), and \(\epsilon\) the current efficiency defined as the fraction of the total charge \(Q_{total}\) actually used for metal deposition:

$$\epsilon = \frac{Q_{depos}}{Q_{total}} \quad (1.18)$$
\(Q_{\text{depos}}\) is the amount of charge described by the deposition of interest (C). The total charge supplied is equal to:

\[
Q_{\text{total}} = I_m \cdot t
\]  

(1.19)

In many electrodeposition processes hydrogen is produced on the cathode side [35, 36]. Depending on the potential and the pH, oxygen can be reduced, water decomposed, and other reactions may occur [28, 34, 36].

1.2.2 Deposition phenomena

During DC galvanostatic/potentiostatic deposition a concentration gradient begins to develop near the substrate and propagates towards the bulk of the electrolyte. Figure 1.2.1 shows a schematic representation of the concentration in the vicinity of the deposited electrode.
Figure 1.2.1. Concentration profile development in the vicinity of an electrode during the application of potential. A denotes the profile for no deposition, B shows the profile for short term deposition and C denotes the profile for long term deposition.

Figure 1.2.1 shows that for prolonged deposition times the concentration of the reactants on the surface becomes negligible and the diffusion rate on the surface decreases [12]. Techniques such as periodically interrupting the cathodic potential or stirring can be used to decrease the diffusion layer thickness.

By interrupting the applied potential (or current), the deposition reaction is stopped thus the bulk ions in the electrolyte can diffuse back to the cathode and reduce the concentration gradient. Upon application of the next pulse a higher initial concentration exists on the electrode. At these conditions the rate of deposition depends more on the kinetics and is less affected by diffusion since the deposition time is slow relative to relaxation. [34, 37].
In galvanostatic pulse plating a sequence of short, high current, square-wave pulses are introduced on the cathode with the goal of nucleating small catalyst particles finely dispersed on a support. The theory of heterogeneous nucleation has been well described in literature [28, 38-40]. Figure 1.2.2 depicts a cluster or particle formed on a substrate after electrodeposition.

![Figure 1.2.2 Spherical model of a nucleus covering a substrate. Θ is the contact angle between the nucleus and the substrate](image)

According to the heterogeneous nucleation theory, the Gibbs free energy of a spherical particle formed on a substrate is given by the following relationship:

\[
\Delta G = \alpha_3 r^3 \Delta G_v + \alpha_1 r^2 \gamma_1 + \alpha_2 r^2 (\gamma_3 - \gamma_2)
\]

(1.20)

where \(\alpha_1\), \(\alpha_2\) and \(\alpha_3\) are geometrical factors related to the curved surface area, the projected area and the nucleus volume [39, 40], \(\gamma_1\), \(\gamma_2\) and \(\gamma_3\) are the interfacial tensions between deposit and electrolyte, substrate and electrolyte and substrate and deposit, respectively, and \(\Delta G_v\) is the Gibbs free energy change upon solidification.

The nucleus size \(r_0\) at which the Gibbs free energy achieves a maximum \(\Delta G_0\) can be found by differentiating Equation 1.20 and setting the derivative equal to zero:
\[
    r_o = \frac{-2(\alpha_1\gamma_1 + \alpha_2\gamma_2 - \alpha_2\gamma_2)}{3\alpha_2\Delta G_v}  \quad (1.21)
\]

\[
    \Delta G_o = \frac{4(\alpha_1\gamma_1 + \alpha_2\gamma_2 - \alpha_2\gamma_2)^2}{27 \alpha_1^2\Delta G_v^2}  \quad (1.22)
\]

Figure 1.2.3 shows the overall Gibbs free energy change with radius according to the heterogeneous nucleation theory for the formation of a spherical cluster on a substrate. This plot is applicable to particle formation during electrodeposition, with \( \Delta G \) now controlled by the applied voltage.

---

Figure 1.2.3, Gibbs free energy change as a function of cluster size. Line 1 (solid) shows the energy distribution at small overpotentials while line 2 (dotted) shows the energy distribution at high applied overpotentials. \( r_o \) is the critical nucleation size and \( \Delta G_o \) is the energy barrier for nucleation.
Figure 1.2.3 shows that there is a maximum free energy barrier that a nucleus needs to overcome in order to be stable. Nuclei with radius $r_o$ or bigger will grow during electrodeposition. Equation 1.8 states that the Gibbs free energy is proportional to the applied overpotential. Thus when large overpotentials are applied the free energy peak shifts to the left, which is consistent with the energy profile change shown on Figure 1.2.2. The radius of the nuclei decreases for high overpotentials in agreement with Equation 1.21. By applying short, intense pulses one should thus be able to induce the formation of a large number of small nuclei.

The ability of pulse plating to reduce concentration gradients has proven beneficial in cases where 3-D porous structures are used as deposits. Filling topologically complex structures with metals can pose non-trivial challenges, as the uniformity of the product depends sensibly on the geometry of the host and the processing method [41]. Electrochemical, chemical or physical vapor deposition inside porous constructs require great care to prevent premature occlusion of the external pores, which can lead to incomplete filling. For a bed of insulating, non-reactive microspheres resting on a conductive backing, electro-plating can be effective because deposition initiates deep within the structure and then proceeds towards the exterior boundary of the template in immediate contact with fresh electrolyte. During pulse plating the deposition inside pores relaxes thus reducing mass transfer problems. The term throwing power (TP) is often used to describe the uniformity of pulse plated samples in recessed regions of the substrate.
Efficient catalyst utilization in fuel cells requires its confinement to the immediate proximity of the proton exchange membrane (thereby decreasing the proton transfer distance). With porous electrode films this can be accomplished by electroplating the catalyst, since the electric field enhancement at the exposed ridges favors local deposition with high selectivity.

Another advantage of using ED is that the deposits can be handled immediately after the process without excessive post treatment. Also the use of volatile organic solvents necessary for the formulation of coatings is minimal. This contributes to safety, personnel health and environmental protection. In an industrial environment, ED is amenable to automation and the operation cost is 30% less than spray, electrostatic and dip coating [29]. Its great weakness remains the inability to plate on non-conductive substrates.

1.2.3 Theoretical background of pulse plating

As mentioned in section 1.2.2, during pulse plating short current (or voltage) pulses are followed by inactive intervals. The duration of the cathodic pulse is defined as on-time \( t_{on} \) and the respective current as the on-time current. The same terminology applies to the off time \( t_{off} \) period leading to the definition of duty factor:

\[
DF = \frac{t_{on}}{t_{on} + t_{off}}
\]  

(1.23)

where during the \( t_{off} \) the power unit is interacting with the cell in such a way as to not drive any current through the circuit. This is schematically illustrated in Figure 1.2.4.
Figure 1.2.4, Current-time profile indicative of pulse electrodeposition.

As noted in the Figure 1.2.4 during the $t_{\text{off}}$ the electrolyte ions are free to relax the concentration gradient. Short, intense potential pulses enhance the nucleation rate (see section 1.2.2) thus increasing the specific surface area of the deposit. Due to relaxation in the off time the diffusion layer is comparable in size to the roughness of the support, the peaks and recesses are equally accessible for diffusion and the asperities are not amplified as in DC plating [41]. The average deposition current $I_m$ (A) is given by Equation 1.24:

$$I_m = DF \cdot i_c$$  \hspace{1cm} (1.24)

where $i_c$ is the on time current.

1.3 Microfabrication techniques for electrode production

Lately scientific efforts have been directed at exploring the use of microsystems techniques such as thin film deposition, photolithography printing, and silicon
microfabrication for the production of micro fuel cells. Since reaction conditions in a micro environment differ from what happens in normal fuel cell environment e.g. transport issues), scaling down these systems poses challenges.

As current micro Fuel Cells do not give more that 5W of power the commercial viability of these systems require improvement of both the materials and the fabrication techniques [42]. Full integration of all components into a single unit is perhaps the biggest challenge, as each component must be designed to take advantage of miniaturization techniques.

Nafion®, which is the electrolyte used in DMFCs and PEMs, is not very compatible with silicon microfabrication methods because the membrane can swell or shrink leading to dimensional stability problems. Researchers have focused on producing alternative gas diffusion layers based on silicon as well as novel catalyst supports [43]. Both of these components have to be porous in order to allow diffusion of reactants and products. The great advantage of microfabrication lies in the ability to produce nanometer thick layers, thus reducing transport resistances. These layers can be made porous by employing photolithographic techniques. Microfabrication of flow microchannels (fuel and oxidant flow field) has proven feasible whereas membrane development studies has experienced slow progress [10].

Problems such as methanol crossover, catalyst dissolution and activation are still present in microsystems. New ideas on the use of microscale phenomena have led researchers to the fabrication of microfuel cells with membraneless, laminar flow MEAs [42].
Micro size fuel cells require altering the characteristics of the diffusion layer as well as the fuel and oxidant flow fields. Diffusion layers are typically made of carbon based materials, (i.e. carbon paper, fibers, cloth), that are electrically conductive but thick and sometimes hydrophobic. Novel designs of such supports will be presented in Chapter 4 of this dissertation. The main focus here is on producing thin, highly porous supports.

High platinum cost necessitates the formation of small and highly dispersed catalyst particles on a conductive support. Some researchers have focused on optimizing the reaction zone close to the catalyst. In another approach, new flow fields were designed by fabricating the trenches on alternative media (silicon wafers, PMMA [42]) using integrated fabrication techniques (parallel, serpentine, spiral and interdigitated). Issues related to high fuel consumption at the entrance and non uniform current density distribution in the electrodes have led to the incorporation of parallel / serpentine flow fields into the micro fuel cells.

1.3.1 Introduction to lithography

The invention of p-n junctions 30 years ago was an important step in the development of semiconductor materials. As a result photolithography and silicon microfabrication techniques have enjoyed significant development, allowing the production of very large scale integrated circuits with nanometer size features. In the 70’s the smaller produced feature was 8 μm in size while nowadays 50 nm structure are common [32].

Lithography is a two step method that is based on the pattern transfer to a silicon wafer (can also be glass, PMMA or even metal layers) through a mask. Initially, the mask
pattern is delineated on a photosensitive layer called photoresist (PR) and then is transferred onto the underlying substrate through selective PR dissolution.

The pattern is designed on a computer and is transferred on a photoplate after exposing it through a UV light source. On the top of the photoplate lies an emulsion layer seating over a glass. The light beam is controlled by a set of lenses and is mechanically routed over the emulsion layer. Quite often the photomask is used as a master mask (MM) though it can also be used as a reticle to a further reduction process. Usually the reduction proceeds with a 5x or 10x decrease in dimensions.

Photomasks are also used to expose Cr bearing glass plates. These have a PR layer covering a thick Cr coating on glass. The chrome layer can be etched in a mild acidic environment thus rendering the mask transparent in the regions where PR has removed. This final product is known as the master mask (MM) [32].

Before the projection of light through the MM, the PR is applied on the wafer by spin coating. The PR can be estimated using the following Equation 1.25:

\[ t \approx \frac{k \cdot s^2}{\sqrt{rpm}} \]  

(1.25)

where k is a PR-specific constant, s is the % of solids in the PR and rpm is the spin speed. What makes the PRs sensitive are chemical reactions caused by light. Some PRs crosslink when subjected to light and are called negative. As a result of the crosslinking, the exposed regions become insoluble and remain on the substrate after immersion in a solvent (developer). The unexposed areas of the negative PRs dissolve thus they reveal the underlying substrate. Positive PRs are those that do not crosslink when exposed to UV light so the projected area is soluble. Generally, they are more expensive, give good
resolution and are soluble in aqueous developers. They contain a resin, a solvent and a photoactive dissolution inhibitor that dissolves in basic environments [44].

In integrated circuit fabrication (ICF) several layers (i.e. metals, alloys, semiconductors etc) are successively deposited on silicon wafers. Alignment is a major concern and is achieved through fiducials present on the MM. These have to overlap after its new layer is deposited. Another important parameter is the resolution. The chemistry of the developing process as well as equipment used for the exposure characterize the level of detail during pattern projection. The most popular projection methods are the contact, the proximity and the projection printing.

During the contacting printing, the PR / substrate assembly is flood exposed with ultraviolet light after bringing the MM into contact with the host. It is a cheap, and easy and gives high resolutions since it can transfer the pattern with almost 100% accuracy. However, mask damage, photoresist swelling, debris formation after the contact, particles deposition on the plates, lack of flatness and light diffraction can affect the resolution [32, 44]. During proximity method, a small and constant space is present between the mask and the wafer. Defect problems mentioned before are avoided though now the light diffraction is bigger and planarity plays a crucial role. Projection printing is described in literature as the remedy to the other two (previously mentioned) methods. The distance between the mask and the substrate is big and the light comes through a complex set of lenses. Mask damage is avoidable however, the cost is high. The resolution is affected by light diffraction problems and is given by Equation 1.26:

\[
\sigma = \frac{k \cdot \lambda}{NA}
\]  

(1.26)
where \( k \) is a constant, \( \lambda \) is the wavelength and \( NA \) the numerical aperture (measure of the light gathering).

Currently, lithographic trends are based on non-optical techniques such as extreme ultra violet projection (EUV), e-beam, x-ray and immersion lithography. In the EUV method a light with frequency close to the low end of the x-ray spectrum (\( \lambda = 10 \) to 14 nm) is collected by a system of mirrors and lenses on the wafer after passing through a EUV reflection reticle [32, 44]. The depth of focus is good, the resolution is around 10 nm but the cost is high. The X-ray lithography method uses an electron gun pointing on a rotating target. X-rays are emitted and after passing through a beryllium window hit on the mask-wafer assembly. The resolution is high though the mask technology is special and difficult.

The most advanced lithography technique is the e-beam lithography. An electron beam is concentrated on a wafer (no mask is necessary) through a set of condenser and projector lenses. The resolution is high but the method is slow. In immersion lithography a liquid medium, with refractive index close to 2 separates the lens from the substrate. Transparency is important since the light passes through the medium. Bubble formation, cleanliness and topography affect the resolution.

1.3.2 Resist development and thin film deposition

Soon after the PR is printed and developed, trenches, usually exposing underlying metal layers, are revealed. Photoresist development depends on the exposure conditions (i.e. light diffraction) as well as the ability of the solvent to produce high aspect ratio features. Light scattering problems are always present and the development is strongly
unisotropic. Trenches developed in an exposed PR on a conducting substrate can be used as templated through which metal substrates can be grown.

Thin film deposition methods can be physical (evaporation, sputtering) or chemical (chemical vapor deposition, low pressure and plasma enhanced chemical vapor deposition). Epitaxy (derived from the Greek words epi=on and taxis=order) implies the deposition of substances in an ordered manner and is a special case of chemical deposition. The choice of the deposition method depends on the host characteristics (i.e. topography), on the desired surface chemistry, the purity of the deposits etc.[29, 33, 36, 38, 44].

E-beam evaporation is the most popular thin film deposition technique. A crucible bearing the metal or alloy is exposed to an electron beam (~10 keV energy) in a high vacuum environment (~ 10^{-6} Torr). The low pressure assures low contamination levels. However, the need for high vacuum conditions leads to complicated pumping systems (use of ion, diffusion, and turbo pumps). The metal source is heated by the electron beam and quite frequently it blasts spitting metal residues on the chamber walls as well onto the target sample [32, 44].

Another popular deposition method is sputtering. It can provide uniform deposits and thus good step coverage due to the big metal crucible used as a target. Its disadvantage is the high cost and the presence of impurities (low vacuum environment).

In chemical vapor deposition (CVD) a reaction in the gas phase is responsible for the substrate’s coating. The reactive species have to diffuse in a chamber, adsorb on the wafer’s surface and react. The reaction species diffusivity can be high at low pressures however non uniform concentrations produced by local depletion can lead to
irregularities (wafers seating near the exit are less exposed to the gas reactants). High temperature and low reaction rates are drawbacks [44].

Metal layers seating below the PR can be often etched in an effort to form porous domains within the wafer/sample. The two basic types of etch processes used in semiconductor fabrication are the wet and dry etching. A number of parameters characterize the effectiveness of the process such as: the rate, the uniformity (isotropic or not), the selectivity.

In an ideal etch process the sidewalls revealed after etching should be planar and the edge profile vertical without any lateral etching. When etching is isotropic it proceeds uniformly in each direction so that lateral etching is significant and the so called undercut is produced [44]. In wet etching a solution is used in order to dissolve solids by mild agitation. Wet etching works well for thin films on substrates, and can also be used to etch the substrate itself. Problems arise from undercutting since the etching process is not dimensionally controllable. For very small features i.e. 0.50 – 1.0 μm wide the etchant can remove the material entirely. Popular liquid etchants are the hydrofluoric acid (HF) used for etching glass, potassium hydroxide for Si, a dilute mixture of phosphoric and nitric acid used for Aluminum etc [44]. It has been found that some wet etchants etch crystalline materials at very different rates depending upon which crystal face is exposed.

The dry etching technology can split in three separate classes called reactive ion etching (RIE), sputter etching, and vapor phase etching. In RIE, the substrate is placed inside a reactor in which several gases are introduced. A plasma is struck in the gas mixture using an RF power source, breaking the gas molecules into ions. The ions are accelerated towards the surface of the material being etched and give a gas product.
Sputter etching is essentially RIE without reactive ions. The only difference is that the substrate is now subjected to the ion bombardment instead of the material target used in sputter deposition [44]. In vapor phase etching the wafer to be etched is placed inside a chamber, in which one or more gases are introduced. The material is dissolved at the surface after a reaction with the gas molecules. Generally speaking dry etching technologies have almost two orders of magnitude higher cost than wet methods and are used when features resolution or vertical side walls are a necessity [44, 45].

1.4 Scope of the present study

The prevailing design of commercially available direct methanol fuel cells (DMFC) electrodes currently involves a Pt-based catalyst deposited on a carbon black film supported by some type of Carbon backing (carbon paper, carbon cloth etc) [46]. The carbon black incorporates Nafion ionomer that functions both as a binder and as a proton/electrical conductor. While necessary to ensure mechanical integrity of the assembly under operating conditions, use of the ionomer has the undesired effect of reducing the porosity and increasing the tortuosity of the carbon black layer, so that additional mass transfer resistances are introduced to hinder the transport of reactants (methanol) and products (carbon dioxide) towards and away from the reaction zone. Foreseeable progress in the development of improved catalysts is bound to exacerbate this problem, especially with regard to CO₂ management, which is a major performance-limiting factor in current DMFC systems [47].

The search for novel electrode configurations with improved mass transfer characteristics thus remains a significant technological issue. This is the theme of the
present dissertation, where we explore the use of micro- porous nickel for potential replacement of carbon black layers in DMFC anodes. Figure 1.4.1 schematically compares the design of a typical DMFC anode with the alternative configuration with the carbon black (CB) replaced by a porous Ni (or Ni-P) layer.

Nickel Electrodes with high surface area have been produced by ceramic foil cast technologies (mixing Ni powders with organic binders, sintering and thermal decomposition) [48], cold rolling, plasma spraying [49], after powder pressing, electrodeposition [50], chemical or physical vapor deposition on polymer templates [51], cathodic codeposition of the Raney Nickel precursor alloys, through deposition from a
poly HIPE template [52-54], etc. Such Nickel structures have been used as hydrogen evolution cathodes, as biological cell hosts [55], as capacitors [56], for the electroorganic synthesis of Cu, for water purification, as reduction media in electro organic synthesis [52], as cathodes in water electrolysis [14, 57].

In the following Chapters three possible methods (use of an emulsion template, microspheres template, and microfabrication techniques) to produce microporous metals are considered. The most successful samples were then used as catalyst supports. The formed electrodes are tested for methanol oxidation and their activity is related to the deposition conditions.
CHAPTER 2:  
DEVELOPMENT OF HIGH INTERNAL PHASE EMULSION

2.1 Introduction

The present chapter focuses on the following topics: 1) production of a high internal phase emulsion (HIPE), 2) study of its stability, 3) plating of Ni through the formed aqueous phase channels in the HIPE, and 4) imaging of the deposited materials on a Cu foil.

Emulsions are homogeneous mixtures of two or more immiscible phases. Usually the dispersed phase is an organic i.e. oil (o), and the medium is an aqueous (w) solution (denoted as o/w emulsion). According to Lissant [58] emulsions with a dispersed phase occupying more than 70% of the volume are called High Internal Phase Emulsions (HIPE). Strictly speaking HIPEs have an internal phase volume equal to or greater than 74.05% (maximum volume occupied by uniform spheres closely packed). In such an occasion the internal phase takes the shape of deformed polyhedral droplets [59] with relative big contact areas surrounded by the dispersion medium although bicontinuous microstructures of interpenetrating phases is also possible.

To stabilize the emulsion structure a surfactant is necessary to decrease the surface tension between the phases. Surfactants consist of two parts: a hydrophobic (repelled by water) and a hydrophilic (attracted to water part). Such molecules sit at the interface between oil and aqueous media and lower the interfacial energy. The
hydrophilic part attaches to the aqueous solution and the hydrophobic to the oil phase. It is the nature of the employed surfactant that facilitates the HIPE formation. The more hydrophilic an oil-phase is the more hydrophobic surfactant requires to form a stable HIPE and the opposite.

The local structure of a typical oil-in-water (o/w) emulsion is displayed in Figure 2.1.1

![Structure of a microemulsion](image)

Figure 2.1.1, Structure of a microemulsion. The spheres are 100μm drops of oil and they constitute the dispersed phase (Micropore Technologies, Loughborough, UK)

In Figure 2.1.1 it is seen that the majority of the droplets are in direct contact with their neighbors. Their contact angle $\theta$ is related to the deformation of the droplets and is affected by the chemistry of the system (i.e. removal of continuous phase will deform the drops into polyhedrals). Emulsions that have been sheared (i.e. stirring during production) are found to display a relative monodispersity. A popular emulsion example is the mayonnaise sauce, formed by finely dispersed oil droplets in lemon juice stabilized by lecithin surfactant from egg yolks.
Porous materials with pore sizes in the range of 0.3-10 nm have been prepared by templating against organized assemblies of small molecules, surfactants, and copolymers[60].

HIPEs have been used as templates for the synthesis of porous polymeric materials. Polymerization of the monomer (oil phase) is achieved by heating the emulsion in a sealed glass container. The concentration of the surfactant in the monomer phase is found to be critical for the formation of a stable porous polymeric structure [61]. Polymeric structures of this type (named PolyHIPEs (PHIPEs)) have found use in the safe transportation of hazardous and flammable liquids as well as supports for conducting polymers. The variety of monomers that can be employed is largely dictated by the physical chemistry of the emulsion system. Most studied is the copolymer of styrene/divinylbenzene (DVB).

Formation of porous metals is another application of HIPEs. Attempts to form microporous metals by depositing through the aqueous phase of HIPEs have been made [53, 54, 59]. The first attempts to use emulsions as templates to produce high surface area materials began in earnest during the late 1980’s [62]. Many of these involved the formation of polyHIPEs through the polymerization of the organic phase (continuous medium) and the subsequent sublimation of the aqueous phase. Ni is a good candidate for deposition through the aqueous domains of an emulsion since: a) it is easily plated, b) forms one phase with other metals, c) it can be catalytically active, d) large variety of plating baths available and e) has been well studied due to its use as a plating agent, in stainless steel, and in the microfabrication industry [63].
Brown et al. [54] were able to produce a porous polymer phase and reported the structure of the precursor emulsion to be similar to that of cured PHIPE. To form the emulsion they used a Nickel salt in water with potassium persulphate as the aqueous phase, Sorbitan monooleate as the surfactant, an oil phase consisting of styrene, divinyl benzene, 2-ethyl-hexyl acrylate and potassium persulphate as the initiator. After polymerizing the oil phase they were able to plate through the formed interconnected pores structure. Figure 2.1.2 is a micrograph of the porous polymer structure obtained [54].

![Micrograph of porous polymer structure](image)

Figure 2.1.2, Porous polymer structures produced from the polymerization of styrene, 2-ethyl-hexyl-acrylate, divinyl benzene and sorbitan monooelate in an emulsion. Magnification 0.35 kX (Brown et.al. 2001 [54]).

Here a distinction must be drawn between a high surface area structure and an ordered structure. Much of the research about emulsion plating has been able to show improvement in surface area over conventional metal samples [59] but these have not
been ordered and porous (see Figure 2.1.3) [54, 56]. Brown et al. [54] attempted to do the opposite and plate through the an w/o emulsion containing Ni sulphamate in the aqueous phase. The resulted deposits had an irregular structure with a variety of features. They attribute these to high local current densities and Ni ion depletion in the aqueous domains close to the electrode. Their ability to plate indicated the interconnection of the aqueous pockets during electroplating.

Figure 2.1.3, Images A) and B) are FESEM micrographs of Ni electrodeposits using a (Ni sulphamate, Nickel chloride, Boric Acid)-(styrene, 2-ethyl-hexyl-acrylate, divinylbenzene)-sorbitan monooeleate emulsion as the template under 5mAcm\(^{-2}\) current density for 0.04 and 0.70kX magnification respectively [53, 54].

Replicating the 3-D porous structure of the HIPE requires the formation of stable oil droplets in the emulsion arranged in a crystal-like fashion. If the “crystalline” order is disturbed by any means (increased temperature, pH changes, strong electrical fields) rough porous patterns will be formed. Actually the authors found that for o/w HIPE the bulk conductivity was low even when salts were used.

When an emulsion is places in an electric field, charge polarization effects produce Maxwell stresses on the emulsion droplets causing disruption of the equilibrium
structure. In order to retain the structure of the emulsion template the plating conditions must involve a sufficiently slow deposition rate, to minimize droplet distortion and coalescence events. Pulse plating (see section 1.2.2) could prove useful for this task since it provides the ability to control the deposition time and the applied potential (potentiostatic mode) or current (galvanostatic mode) thus minimizing distortion. However, electrical impedances prevent the surface from attaining the desired potential instantaneously, and create an unstable current upon the onset of the applied overpotential. This makes the potentiostatic deposition process difficult to control. On the other hand galvanostatically controlled plating can be beneficial, since the current transients are controllable. When interrupting the applied current, or pulsing, the driving force toward deposition is removed, therefore the bulk metal in the electrolyte is given time to diffuse to the cathode through the interstitial water channels. Upon reestablishment of the applied current, nucleation of new particles at the cathode’s surface is induced.

The University of Notre Dame Electrochemistry research group was one of the first to examine the use of a High Internal Phase Emulsion (HIPE) as a template for patterning a porous structure. The incorporation of metal salts inside the aqueous phase of an emulsion renders it a potential candidate for the deposition of metals through this soft template.
2.2 Experimental system

Copper was chosen as the substrate for the deposition of Ni through the HIPE template. Copper can be easily cleaned in dilute ammonium persulfate and organics are easily removed from its surface using ethanol. Copper foil, 0.01 inch thick (Alfa Aesar), was cut into 9/16 inch diameter disks which were thoroughly cleaned by immersion in ethanol for 5 min. Further steps involved drying the samples, immersing them in a 2.5% v/v. ammonium persulfate solution for 10 min and immediately rinsing with DI water to stop the etching.

Electroplating Ni on Cu through the HIPE was accomplished using the set up schematically illustrated on Figure 2.2.1.
Immediately before mounting the copper in the plating cell, the samples were immersed in 5% v/v HCl in order to remove oxides and activate the surface. The plating cell arrangement included the use of a metal disk contact between the sample and the stainless steel rod (9/16”) to support the whole assembly. This cylindrical-shape piece had a hole on the bottom side that bore a host for the power unit wire. Teflon was formulated around the stainless steel rod in order to be able to screw part A (see Figure 2.2.2). Teflon rings were placed on top of the samples to minimize leakages.
Microemulsion drops were added on the host (through the hole on top of A) and the plating cell was connected to a Dynatronix Pro Series Power Supply (Amery, WI), having the anodic-Cu side connected with the negative wire and the 1.5 inch carbon rod (counter electrode) connected to the positive side. The viscous emulsion was added on the copper using a pipette.

![Figure 2.2.2, The microemulsion plating cell. The sample was placed on the metal contact on the top of B and then part A was screwed around B. Teflon o- rings were put on top of sample to minimize leakages and provide some space for the emulsion.](image)

Since emulsion stability is important for the replication of its structure through electroplating, it was necessary to determine whether the texture of the electrodeposited Ni was a replica of the equilibrium structure of the microemulsion, or the result of a dynamic process involving thermally-, chemically-, or electrically-induced evolution of the microemulsion structure during electrodeposition. Three major factors can contribute...
to the stability of the surfactant/electrolyte mixture: 1) the salt concentration, 2) the temperature and 3) the pH [64].

The selection of the microemulsion components was based on the following considerations: dodecane was chosen as the oil phase because of its low volatility (high flash point), which would make it safer to use in an industrial setting (as opposed to octane for example, which is highly flammable). Cheaply available Triton X-100 (Sigma Aldrich) was used as the surfactant. Its non-ionic nature was specifically sought to minimize problems related to charge redistribution (e.g. from depletion of Ni) around the hydrophilic part of the surfactant molecule, which may have caused collapse of the emulsion during electroplating. Non-ionic surfactants have no ionizable hydrophilic groups, and are thus less sensitive to changes in the ionic strength of the surrounding aqueous environment. The aqueous medium used was the Ni based Watts solution (600 g l⁻¹ NiSO₄, 40 g l⁻¹ NiCl and 10 g l⁻¹ HBO₃ [65]) which is widely used for Ni depositions.

Several mixtures with different mass fractions of oil phase (dodecane), surfactant (Triton X-100) and Ni plating solution (Watts bath [65]) were produced in sealed test tubes in order to identify the compositions giving stable microemulsions. The sealed tubes were stirred using a vortex mixer and allowed to equilibrate for 3 days. After plating, the samples were washed with DI water, removed from the cell and then air dried under a heat lamp.

To produce an oxide free Cu mandrel a mild etching recipe was adopted. Four etching solutions, containing NH₄⁺, were tested along with a strong acid etching solution and an electrolytic etch. The solutions were: 1) 0.1 M FeCl₃ and 0.1 M HCl, 2) 0.1 M
FeCl$_3$, 0.1 M HCl and 10 g per 100 ml (NH$_4$)$_2$S$_2$O$_8$, 3) aqua regia (20 ml HNO$_3$ and 60 ml HCl), 4) 2.5% wt (NH$_4$)$_2$S$_2$O$_8$:NH$_4$OH:H$_2$O in ratio 1:1:1, 5) 10 g per 100 ml NH$_4$SCN, and 6) NH$_4$SCN:NaOH:H$_2$O in ratio 1:1:1. Eighteen 18 Cu samples were tested in total. The Aqua Regia completely etched away the mandrel in less than 8 mins. The meekest etchant proved to be the ammonium persulphate solution thus all the Cu samples, prior to their use, were immersed in it.

2.3 Results

2.3.1 Emulsion structure

Two separate evaluations of Triton were conducted to determine if a single stable emulsion phase could be produced for plating studies. The first study was performed on a binary system of Ni plating solution and Triton X-100. This system was of interest because of the presumed ability to form worm like micelles, which would have allowed us to produce porous metal deposits with nanometer size features. The second evaluation concerned a pseudo-ternary system of Ni plating solution / Triton X-100 / dodecane (oil phase). This system was of interest because of the ability to control the size of the internal phases thereby allowing us to produce metal deposit with controllable porosity. The relative abundance of the phases in emulsions controls the structure, leading to either a water phase embedding oil rich micelles or an inverted structure with an outer oil phase. [64].

Initially twenty test tubes were filled with a 10 ml mixture of Triton X-100 and the Ni plating solution in increments of 5% vol. ranging from 0-100% Ni plating solution.
The components were corked, mixed with a vortex mixer, and then immersed in a water bath at 25 °C for one week. After that, the only sample that exhibited one phase contained 40% Ni plating solution and 60% Triton X-100. This phase appeared to be stable in the form of an emulsion. After placing it in a centrifuge to remove the bubbles a translucent green single phase remained. The solution was used to electroplate through the formed templates, but the resulting Ni film did not exhibit any visible porosity.

The number of phases was recorded, and digital images were taken of the test tubes in order to determine the relative abundance and color of the phases. Figure 2.3.1 shows some of the samples/concentrations collected for the Triton X-100 / nickel plating solution system.

![Figure 2.3.1](image.png)

Figure 2.3.1, A) to C) Digital Camera images obtained after the production and the subsequent mixing of Triton X-100 with the Ni solution components. For A) 9.534 gr of Triton X-100 and 0.511 gr of Ni solution were used, for B) 4.019 gr of Triton X-100 and 6.077 gr of Ni solution were used, and for C) were used 0.527 gr of Triton X-100 and 9.567 gr of Ni solution (courtesy of Simone Arvin, [66]).

Images A to C show some of the possible configurations of mixtures of different compositions. The sample in image A consisted primarily of Triton X-100 dominating over the Ni solution. Image B corresponds to roughly similar weights of Triton and Ni
plating solution. The bubbles were caused by stirring and were subsequently eliminated by centrifugation. The sample in image C, containing as a prevalent component Nickel plating solution, exhibits two clearly distinguishable phases, the top opaque one consisting of a microemulsion, and the bottom one consisting primarily of nickel plating solution with some dissolved Triton.

The phase behavior of multi-component systems at fixed temperature and pressure is best represented using a phase diagram [64]. The phase rule dictates the maximum number of phases that can be formed at equilibrium and is written as:

$$p + f = N + 2$$

(2.1)

where $p$ is the number of phases, $N$ the constituents and $f$ the degrees of freedom.

As the phase rule indicates, a mixture consisting of 5 components (Nickel sulphamate, Nickel Chloride, Boric acid, Triton and water) can present at most 4 coexisting liquid phases when temperature and pressure are held constant. Analysis of the digital images was done using the tools in Adobe Photoshop and allowed the determination of both the relative abundance of the phases as well as the approximate nickel content of each phase from colorimetric analysis. A color calibration was performed using plain deionized water of same volume with the Ni plating solution in the emulsion (for several concentrations) and then several different kinds of concentration of the aqueous phase and the surfactant were tested. Digital images were captured by the use of a FinePix A 310 camera and the analysis was performed based on three major colors (red, green and blue). The concentration values found were then averaged.

The density of each phase was estimated using the following procedure: each test tube was placed on an analytical balance. The top phase was removed using a disposable
pipette and placed in a second test tube that had already been tared on a second analytical balance. Both test tubes were reweighed on their respective analytical balance and the new weights were recorded. The phase that had been removed was then centrifuged. The test tube that had been centrifuged was placed next to an empty test tube of equal size. A volume of water was then titrated into the empty test tube until the volume of liquid was equivalent to the phase that had been centrifuged. This volume was then recorded and the process was repeated for the second phase. In total, nearly 250 phases were recovered from the original 90 test tubes and their densities calculated.

Figure 2.3.2 A shows the calibration of Ni concentration using Ni sulfamate standard solutions and determined from the red light intensity. Similar calibration plots were done for the blue and green colors in order to have a better estimate of the Ni concentration present in each of the 250 tubes tested.

Figure 2.3.2, A) Red light Intensity calibration of aqueous Ni sulfate in respect to the ratio of Ni concentration to 600 gL⁻¹, B) Ni concentration vs. the Ni solution concentration in the Ni sulfate-Triton mixture for each of the phases observed through the optical microscope.
Figure 2.3.2 B displays the nickel concentration obtained from the phase in the Triton X-100 / Nickel plating solution mixture as function of the ratio of nickel plating solution mass to total mass. It is seen that for a fixed composition up to 3 different phases were detected, as shown by the three different points on the ordinate for a set value of the abscissa. For low nickel solution to total mass ratios there was always one phase visible with zero nickel concentration. For low Ni concentration and high Triton loads a solid residue was formed on the bottom of the test tubes. This was caused by osmotic forces which pumped out water from the Ni plating solution into the abundant Triton phase causing supersaturation and crystallization of the nickel salts. As the percentage of Ni plating solution increased, the amount of water coexisting with the Triton X-100 became sufficiently large to allow incorporation of Nickel into the Triton X-100 water mixture, leading to the formation of multiple green-colored phases.

Unfortunately a homogeneous microemulsion phase obtained from this pseudo binary system failed to produce porous electrodeposited nickel. For this reason it was deemed appropriate to explore a pseudo ternary system consisting of Triton X-100 / Nickel plating solution / dodecane. In order to produce the samples the constituents were added to 18x150mm test tubes with a micropipette in the following order: 1) Dodecane, 2) Ni plating solution, 3) Triton X-100. This was necessary because of the high viscosity of the Triton X-100 which made it hard to mix with the rest of the components. A set of 90 test tubes were filled with 10 gr mixtures of Triton X-100, dodecane and Ni plating solution. The amounts chosen were based on the middle section of the diagram in Figure 2.3.2 B. An analytical balance was set up with a test tube holder on the scale to secure the test tube while on the pan. The scale was tared before each addition. After adding the
components the samples were immediately corked, mixed on a vortex mixer and placed in a water bath set at 25 °C.

Only one sample mixture out of the ninety tested exhibited a single emulsion phase which was stable for at least three days after the initial mixing. The mixture was composed of 1 gr Triton X-100, 6 gr dodecane and 3 gr Ni plating solution, and it exhibited an opaque texture with a light green color with a few air bubbles, which were subsequently eliminated by centrifugation. This sample was used for electroplating Ni onto a copper substrate. Figure 2.3.3 displays optical microscope images (Nikon) of the microemulsion sample placed between glass slides. The images were captured using a Nikon microscope equipped with an HP camera using 20 X objective lens. In image A the large dark objects are tiny gas bubbles. Image B is a microemulsion after centrifugation. From the image it is not clear, whether the structure is of dispersed droplets or of the bicontinuous kind.
Figure 2.3.3, Microemulsion structure observed under an optical microscope before (A) and after centrifugion (B). The composition of the mixture was 1 gr Triton, 6 gr dodecane and 3 gr Ni plating solution. Image C shows the Ni morphology after deposition through the aqueous pockets of the emulsion at 2V using the Dynatronix unit.

The overall goal in using this system was to plate the Ni ions residing in the aqueous phase without affecting the texture of the emulsion. When an electric field is applied to a high internal phase emulsion, the structure reacts to the field and continuous aqueous channels can be destroyed. It is the structure of these channels that are hopefully replicated on the electrode surface [56]. An effective HIPE template would be one where: 1) the template is only slightly affected by the electric field during pulse plating and 2) the template relaxes nearly back to its original state during the off-cycle. Brown and others have examined this problem for the system of sorbitan monooleate / styrene /
Ni plating solution and found that their HIPE behaved as a dielectric during deposition exhibiting charging and discharging. Since the systems had a decay time, there was a limit of how short the off-time could be.

To define the optimal plating conditions we did tests for the sorbitan monooleate / styrene / Ni plating solution system and observed a typical charge / discharge cycle with a decay time of 2.5 ms (PID quarter-like wave response) and for the Triton X-100 / dodecane / Ni plating solution system found a decay time of 0.3 ms. In both cases the currents used were on the order of a few mA in an attempt not to distort the microemulsion structure. Image 2.3.3 C shows the deposited Ni structure on the Cu substrate obtained with a duty factor (DF) of 0.5 and the on-time (OT) of 0.5 ms after plating through the Triton X-100/dodecane/Ni plating solution based emulsion. The current density during the on-time cycle was 1 mA cm\(^{-2}\). Several features should be noted about these structures: 1) the high surface area of dendritic type pattern as at 100,000 X., 2) the broad range of pores at various length scales, and 3) patchy coverage over the entire surface of the substrate. The pores formed did not replicate the expected aqueous phase structure, possibly due to disruption of the emulsion structure during the course of the experiment. Thus a set of mild plating conditions were further pursued.

Figure 2.3.4 (A) displays another type of morphology of plated nickel obtained under the conditions DF=0.6, t\(_{on}\)=1 msec, 33 kcycles at 2.5 V, whereas Figure 2.3.4 (B) displays a typical potential versus time pattern during pulse electrodeposition through the HIPE. It is seen that the potential is not constant during each pulse but exhibits a significant relaxation. This was later found to be caused by interaction of the circuitry of the Dynatronix plating unit with the impedance characteristics of the microemulsion. To
solve this problem, a new electroplating circuit was built by James Kirskey, laboratory Electronics Technician at the University of Notre Dame. Figure 2.3.5 displays a diagram of the circuit which was assembled on a circuit board. A Tektronix TDS 2002 oscilloscope (Richardson, TX), of infinite resistance, was connected in parallel to the cell and used to monitor the response for each square current pulse introduced by the Dynatronix and the new circuitry on the cell.

Figure 2.3.4, (A) FESEM image of the Ni deposited through the HIPE bearing the optimum concentration (1 gr Triton X-100, 3 gr Ni solution and 6 gr dodecane) onto the Copper paper foil under: DF=0.6, t_{on}=1 msec, for 33k cycles at 2.5 V. (B) electrochemical cell voltage vs. time for DF=0.6, t_{on}=1 msec and 33 kcycles.
Figure 2.3.5, Draft of the alternative circuit developed under the helpful guidance of Mr. James Kirskey. A direct negative bias is applied on the negative side of the cell while an oscillatory voltage is introduced on the positive side.

Figure 2.3.6 shows a voltage versus time profile recorded during pulse electrodeposition through the HIPE using the new circuitry is displayed in Figure 2.3.6. It is seen that now the potential during each pulse is relatively stable exhibiting no significant relaxation. However, we should note that the amplitude of the voltage pulse tended to decrease over time so that manual adjustment was necessary to keep a fixed potential pulse amplitude.
Figure 2.3.6, Cell voltage vs. time at (DF/CT/N) of (0.5/0.9 msec/2.4 Megacycles), during Pulse Plating of Ni from the HIPE using the alternative circuit.

Several samples were produced under nominally identical conditions, but the resulting morphologies of the nickel deposits varied from sample to sample, possibly due to variability in the wetting characteristics of the copper substrate. In three of those samples however, these plating conditions resulted in the production of porous metal deposits. Figure 2.3.7 displays the morphology of one of such samples.
Figure 2.3.7, A), B) and C) are FESEM images showing the morphology of the material plated on a Cu substrate resulting from the experiments using the circuit described on Figure 2.3.5. Prior to FESEM imaging the sample was washed with copious amounts of distilled water and then dried (magnification is 0.6, 3 and 10 kX).

The microstructure of the deposits in Figure 2.3.7 is consistent with the expected replica of a bi-continuous microemulsion structure of interpenetrating dodecane and aqueous (Ni plating solution) phases. The ratio of void-to-solid phase volumes estimated from Figure 2.3.7 is congruent with the ratio of dodecane-to-Ni plating solution volumes in the precursor HIPE.

The spongy deposit was characterized to determine its chemical composition and crystallographic structure. The plated structures were most likely made of Ni, since they were insoluble in water (thereby excluding the possibility of soluble salts) and suffered
no damage from electron beam irradiation under the SEM, as would be expected for some sort of organic- or polymer-based material. The samples were also immersed in Tetrahydrofuran (THF) for 5 min and suffered no dissolution excluding the possibility of an organic deposit. Such samples were characterized using X-Ray Diffractometry (XRD) and X-Ray Photoelectron Spectroscopy (XPS) to determine their crystal structure and composition. The XRD pattern did not reveal any crystalline structures at the surface, except for metallic Cu (200 and 111 planes), which was the substrate material. XPS analysis, on the other hand, showed an atomic surface composition of 35% Cu, 29% Ni, 1% S, and 35% O$_2$, indicating a substantial presence of Ni. The ratio of the areas covered by the spongy layer to the total area of the sample determined from the SEM images is about 0.30, and therefore, consistent with the XPS measurements. We believe the sponge to be made of amorphous Ni. This unusual finding warrants further investigation. Unfortunately, although the spongy structure was replicated three times in the previous runs, subsequent experiments gave irreproducible results in terms of the deposit’s morphological homogeneity over the entire surface of the sample. Because of such poor reproducibility, this avenue of work was not further pursued.

2.4 Conclusions

Several formulations of binary mixtures of Triton X-100, Ni plating solution as well as ternary mixtures of Triton X-100, Ni plating solution and dodecane were investigated in order to determine the conditions for the formation of a homogeneous HIPE. In the case of pseudo binary systems, where the emulsion would have presumably
consisted a worm like micelles, no templating effect was observed on the nickel deposits obtained by electroplating on a Cu substrate. For the ternary system however, the use of an improved electronic circuit capable of providing stable voltage pulses resulted in the formation of a porous nickel deposit in three out of twenty samples. The microstructure in this case appeared to replicate the expected bicontinuous microstructure of the HIPE. When characterized by XRD and XPS the porous deposits were found to consist of amorphous nickel. Because of the poor reproducibility of these samples, this research was not further pursued as a possible avenue for the production of porous anode supports for fuel cells
CHAPTER 3:
PRODUCTION OF POLYMER TEMPLATE AND USE FOR THE FABRICATION OF
FUEL CELL ELECTRODE SUPPORTS

3.1 Introduction

The present chapter focuses on the following topics: 1) production of polymeric microspheres, 2) the use of microsphere templates to form porous three dimensional metal structures, 3) identification of suitable catalysts and their deposition methods onto porous Ni supports and 4) testing of anodes based on porous-Ni supported catalyst for methanol oxidation.

3.1.1 Methods of Polymer production

Polymeric microspheres can be obtained by emulsion polymerization methods whereby microscopic droplets of monomer dispersed in a suitable medium are polymerized using a suitable initiator. The term polymer denotes a macro molecule made up by the repetition of some simpler unit, the monomer [67]. The polymer chain can be linear, branched or cross-linked. The number of repeating monomer units is referred to as the degree of polymerization.

There are basically two approaches to polymer formation: chain growth and step growth polymerization. Chain growth polymerization involves combining monomers starting from a single reactive site and growing the polymer from that site (this can be an
ion or a radical). On the other hand, step polymerization involves combination of units with other complementary functions. The methodologies discussed in the present chapter involved chain radical polymerization.

Three stages are essential in chain polymerization: a) initiation by creation of an active center such as a free radical, b) propagation by the addition of monomers to the growing chain, and c) termination as shown in the following reaction scheme:

\[ I \xrightarrow{k_i} 2R \bullet \]  
(3.1)

or \[ R \bullet + M \xrightarrow{k_p} RM \bullet \]

\[ RM_n \bullet + M \xrightarrow{k_p} RM_{n+1} \bullet \]  
(3.2)

\[ RM_n \bullet + RM_m \xrightarrow{k_i} R_{n+m} M_{n+m} \]  
(3.3)

where \( R \bullet \) represents the initiating radical and \( M \) the monomer.

For industrial production issues such as the physical properties of the reactants (e.g., viscosity), temperature control, toxicity of byproducts, and flammability of the reactants must be carefully considered. Polymerization can be carried out with monomer alone (bulk) or dispersed in a solvent (solution), in emulsions (emulsion) or as suspended droplets (suspension polymerization).

In bulk polymerization monomer and initiator are the only components. The mixture can be stirred or left quiescent. Because of the large heat of reaction, this method is difficult to control, and, in fact, often dangerous, and as such is seldom employed on an industrial scale. Heat removal is hampered by low thermal conductivity and high viscosity.
These limitations can be overcome by employing the emulsion polymerization scheme whereby the monomer is finely dispersed in the form of micrometer size droplets in an inert suspending medium which acts as a thermal buffer.

Emulsion polymerization has many features in common with suspension polymerization, except for the size of the polymer particles obtained [67, 68]. Emulsions typically comprise small particles 0.05-5 μm in diameter whereas suspensions typically produce particles 100-1000 μm in size. In both cases water soluble initiators are used (rather than monomer soluble) and the end product is an emulsion or suspension of polymer beads. The essential reactants for emulsion polymerization are the monomer, a dispersing medium, a surfactant, and an initiator. The surfactant is necessary to stabilize the micelles that incorporate the monomer [67, 69]. Because of their small size, micelles have higher surface area per unit volume than drops. Consequently, when free radicals are generated in the aqueous phase the micelles capture most of them. After this initiation step, the solution will consist of stabilized monomer-swollen polymer particles and monomer droplets that may either start to react or may function as reservoirs that supply the swollen particles with monomer. Typically, each particle can not tolerate more than a few radicals at a time because otherwise a termination reaction would occur between the growing chain radicals due to the high probability of their reactive ends meeting in the small volume offered by the drop. These mechanisms as well as some degree of coalescence are typically responsible for the polydispersity in particle sizes obtained by emulsion polymerization [67].
3.1.2 Formation of spheres

Template directed synthesis is a low cost and high-throughput procedure that allows the formation of objects with complex topology. Polymeric microspheres can be used as templates to produce porous metals and ceramics.

The production of monodisperse spheres has been a subject of interest from the beginning of the 20th century [60]. The best established methods are emulsion polymerization for polymer latexes and controlled precipitation for inorganic hydrous oxides.

Polymethylmethacrylate (PMMA) and polystyrene (PS) microspheres can be produced by emulsion polymerization in aqueous suspending media. Almog et al. [70], however, found that the size of the latex particles can be controlled by varying the amount of monomer used as well as by substitution of the suspending medium (water) with a suitable organic non solvent. They also found that the solubility parameter of the medium affects the diameter of the microspheres, whereas the surfactant primarily controls the polydispersity.

Almog et. al. [70] therefore demonstrated the possibility of producing nearly monodisperse, micrometer size polystyrene microspheres using n-butanol as the suspending medium. The microsphere synthesis method considered in the present chapter is entirely based on that work.

3.1.3 Production of porous Nickel structures using microsphere templates

Microporous structures have been considered for potential use as cells hosts [55] and are commercially used in rechargeable batteries (Inco Limited, Ontario Canada), as catalyst supports, noise reduction media, filtration media etc (Recemat International, The
Netherlands and Ultramet Advanced Materials, CA). They are also promising for application in biosensors, separations systems, adsorption, photonics, catalysis, magnetic storage media etc [60, 71, 72]. Porous metals have been produced by powder pressing, chemical or physical vapor deposition on polymeric scaffolds, and even through the use of templates consisting of self-assembled colloidal crystals. Layer-by-layer deposition and Langmuir-Blodgett vertical lift are some of the methods permitting deposition of organized layers of micro-particles [60, 73]. These techniques permit attaining good control of the thickness and uniformity of the final construct, but are impractical for industrial implementation. Also templates consisting of monodisperse silica spheres self-assembled into colloidal crystals have been employed for the synthesis of nano- and meso-porous carbons. The method involved partially sintering the organized spheres and then filling the remaining voids with a monomer that was polymerized in situ [74]. Etching away the silica beads with hydrofluoric acid produced a spongiform structure that replicated the negative of the precursor template.

Polymeric microspheres are similarly useable as templates for the synthesis of micro-porous materials. After the spheres are organized on a substrate and then lightly sintered to establish connectivity, the interstitial voids should be filled with a precursor, which upon solidification, followed by either simultaneous degradation or subsequent dissolution of the template, yields a spongy structure with percolating voids. With polymeric spheres, sintering can be realized by thermal treatment near the glass transition temperature (Figure 3.1.1).
In consideration of potential industrial uses, ease of fabrication and availability of precursor materials are of paramount importance. The Ni-sponge fabrication method considered in the present work involved DC electroplating from a standard electrolyte solution (Watts Bath, [65]) through a template of polystyrene microspheres that were produced in-house by a method similar to that employed in industrial production of latexes. The Watts solution originally contained 3 components (nickel chloride, nickel sulphate and bromic acid) and represents the base for all versions of nickel plating solutions that are popular nowadays [75].

Monodisperse polymeric spheres of the kind considered in most previous works [55] are readily available commercially, but at a cost that would be prohibitive for large-scale use. In-house synthesis was thus deemed necessary in order not only to reduce costs but also explore potential processing hurdles. Particles with diameters varying by a factor of two were found to be easily producible in significant amounts. Polydisperse spheres
can also attain a higher packing density than uniform-sized ones, so that spongiform Ni films obtained from them should exhibit a higher porosity than those from “monodisperse” templates.

Filling topologically complex structures with metals can pose non-trivial challenges, as the uniformity of the product depends sensibly on the geometry of the host and the processing method [41]. Queheillalt et al. [50] produced open-cell metal foams by e-beam evaporation of Ni alloys around a thermally-degradable polymeric scaffold. Chemical or physical vapor deposition inside porous constructs requires great care to prevent premature occlusion of the external pores, which can lead to incomplete filling. For a bed of microspheres resting on a conducting backing electro-plating can be effective, because deposition initiates deep within the structure and then proceeds towards the exterior boundary of the template in immediate contact with fresh electrolyte [41].

Removal of the polystyrene template after metal deposition can be effectively accomplished by dissolution in a suitable solvent. (Thermal degradation is another method, but it was found to be unsuitable for the present purpose, as it produced significant damage in the spongy metal deposit.) The suitability of a solvent in terms of its capability to dissolve a given polymer is quantified by thermodynamic parameters related to the intermolecular forces between polymer chains and solvent. The strength of such intermolecular forces is quantified by the cohesive energy density (CED) defined as the ratio of the molar internal energy of evaporation to the molar volume of the liquid. The square root of the CED is called the solubility parameter (SP), $\delta$:

$$\delta = \sqrt{CED} \quad (3.4)$$
Based on molecular arguments, Flory and Huggins demonstrated that maximum compatibility between a polymer and a solvent will correspond to nearly identical values of their solubility parameters [67]. Based on this argument, for polystyrene the best matching solvent proves to be tetrahydrofuran (THF).

Ni has been used as a reduction catalyst both in pure form or as an alloy with other metals (Pt, Ru etc) [19, 21]. Electrode supports based on Ni foam have been recently investigated by Skowronski and Wazny [75] for possible use in alkaline direct methanol fuel cells. The Ni foam pore sizes ranged from 200-500 µm in diameter, and was produced by sintering a fine Ni powder within the voids of a degradable template. Use of such sintered-metal foams as electrode supports may present problems, however, because the metal ligaments point towards the interior of the structure, so that only a small fraction of the total area remains available to support the catalyst in the immediate proximity of the proton exchange membrane. In conventional electrodes the latter goal is attained by occluding the pores in the carbon paper backing with a carbon black/ionomer mixture to yield a support that is impervious to the fine catalyst particles.

On the other hand, spongiform metal (or metal alloy) films obtained by electroplating through a microsphere template exhibit a uniformly flat boundary, so that both the desired catalyst confinement and a significant open porosity can simultaneously be achieved. The use of Ni for non-alkaline fuel cells would generally not be advisable, based on the expected susceptibility of the metal to corrosion. This choice, however was deemed reasonable here as a first step towards establishing the feasibility of the fabrication methods. Stability concerns can be addressed in the future through the use of
Ni-P alloys, which are renowned for their good electrical properties and good corrosion resistance at high P contents (around 10%) [33].

3.1.4 Catalyst choice and deposition methods

The high activity of Pt makes it the catalyst of choice for the oxidation of organic compounds such as methanol, carbon monoxide, formaldehyde, formic acid etc [3, 76-80]. Despite its high cost, Pt is widely employed in DMFCs in both pure form and as an alloy [17]. Specifically, pure Pt is employed on the cathode side of the DMFC, where oxygen reduction occurs. The use of pure Pt as the anodic catalyst in DMFCs presents problems, however, because the metal is susceptible to gradual poisoning by adsorbed CO at low temperatures [75, 76, 81, 82]. The remedy has been to alloy Pt with other metals (e.g., Ruthenium) to increase tolerance to poisoning while retaining acceptable activity [75, 82]. The use of pure Pt as the anodic catalyst for some of the samples considered here was deemed pertinent for two reasons. First, evaluation of the impact on cell performance of the new supports was performed over relatively short time scales, so that poisoning was not an issue. Second, the high activity of Pt versus any of its alloys was specifically sought to amplify the influence of mass transfer resistances on cell performance, thereby permitting a more sensitive evaluation of the transport characteristics of the support.

Efficient catalyst utilization in fuel cells requires its confinement to the immediate proximity of the proton exchange membrane. With spongy Ni films this can be accomplished by either electro-spraying (ES) or electroplating the catalyst, since, in both cases, electric field enhancement at the exposed ridges in the metal scaffold favors local deposition with high selectivity. In the present work both methods were considered.
Specifically, commercial Pt and PtRu catalysts were delivered by electro-spray, whereas deposits of Pt nanoparticles were obtained by pulse plating. General principles of electrodeposition by pulse plating have been described earlier (see section 1.2.2).

Electrospraying, often referred to as electrohydrodynamic atomization, is a technique in which the meniscus of a conducting liquid is subjected to a strong electric field generated by high voltage applied between the liquid and an opposing electrode. In a suitable range of voltages the meniscus acquires a conical shape causing a thin jet of fine, micrometer size droplets to issue from its apex [83, 84].

Ni foam–supported Pt has been used as a catalyst for carbon monoxide oxidation as well as oxygen reduction [75, 76]. Skowronski and Wazny [75] considered catalyst systems like Pt, Pt/polyaniline, Pt/C supported on Ni foams. These composite systems were tested in alkaline media for methanol oxidation and both Ni and Pt were found to be active. Liu et al. [17] reported the deposition of Pt and segmented Pt-Ru-Ni nanorods inside the pores of aluminum oxide membranes. They observed that the Pt-Ru-Ni pair sites had the lower potential for water dissociation and were more active than Pt alone. CO poisoning tolerance has been investigated and PtRuNi alloys proved to be promising candidates [69].

3.2 Experimental

3.2.1 Microspheres production

Polystyrene microspheres were produced following the procedure of Almog et al. [70], whereby 50 g of styrene (monomer) were intimately mixed with 0.50 g
Azobisisobutironitrile (AIBN) (initiator), and then 2 gr of Aliquat 336 ($C_{25}H_{54}ClN$, surfactant), 400 ml of tert-butanol (suspending medium) and 7 gr of polyacrylic acid (interfacial stabilizer) were added to the mixture. All reagents were purchased from Sigma-Aldrich in their highest available purity, and used as received. The reaction was carried out in a spherical three-neck glass flask equipped with a loading port, a total-reflux condenser, a thermometer, and a magnetic stirrer. After loading the reactants, the flask was flushed with nitrogen and then all openings were sealed. The vessel was kept in a water bath at 70 °C, and the reaction was allowed to proceed for 15 hrs, following which two phases were distinguishable in the flask, namely, a top, clear rich in tert-butanol and a white one at the bottom embedding microspheres and a small amount of residual tert-butanol. The top liquid was discarded, and the bottom, gelatinous residue was placed in a Petri dish and kept under a heat lamp in air for 3 days (atmospheric oxygen binds with radicals, producing inactive species, and inhibiting further reaction). During this time the product gradually exuded most of the residual ter-butanol, which was periodically withdrawn, to finally yield a dry, powdery residue. The powder was dispersed in methanol by mild sonication to yield a 2% suspension by weight, which was stored at room temperature in sealed containers until further use. The particles obtained using this procedure gave templates that were easy to sinter and fully permeable by the Ni plating solution.

An alternative treatment, whereby the reaction products were subjected to three washing cycles in fresh methanol, was also considered in order to eliminate any residual ter-butanol, but the resulting templates turned out to be not easily permeable by the Ni plating solution (hydrophilicity decreased).
Differential Scanning Calorimetry (2920 Modulated DSC, TA instruments) and intrinsic viscosity measurements were employed to estimate the glass transition temperature and average molecular weight of the polystyrene in the spheres, respectively. DSC scans were run from 80 to 135 °C at a rate of 3 °C min⁻¹ and gave a glass transition temperature of 107 °C which is consisted with the reported value of 110 °C [85, 86].

Intrinsic viscosity data in THF at 23 °C were obtained using a standard Ubbelhode viscometer. A series of polystyrene spheres solutions in THF were produced starting from a high concentration stock solution which was then diluted to produce samples with logarithmically-spaced concentration decreasing by a factor of 2 each time. The stock solution contained 10.0 g of spheres dissolved in 109.5 ml THF, to give a concentration of Co=0.091 g ml⁻¹. The viscosities of solutions with increasing polymer concentration were sequentially measured.

The viscosity-average molecular weight of the polymer was estimated using the Mark-Houwink correlation [67],

\[ [\eta] = kM^a \]  

(3.5) 
with the reported values of k = 1.1x10⁻³ (ml g⁻¹.725 mol⁰.725) and a = 0.725 for polystyrene in THF at 23 °C. The detailed results of these measurements are given in Appendix A.

The microspheres were deposited on Toray carbon paper (CP) disks 1.6 cm diameter (E-Tek, TGH0 060, 0.17 mm thick) sandwiched between a bottom Teflon holder and a top, flat silicone ring both bearing a central opening 0.95 cm in diameter to define the deposition area and permit draining of the residual methanol through the porous CP support. The template was assembled by repeated delivery of 30 drops of the
sonicated (30 min) methanol suspension of spheres onto the disk, followed by drying under a heat lamp, until complete coverage of the top layer of carbon fibers by a uniform bed of spheres.

3.2.2 Microspheres sintering

Upon completion of the sphere deposition process the top of the CP disk displayed a white, uniform shade, reflecting a preponderance of spheres organized in multi-layer fashion, whereas the back retained the original appearance of the bare CP with only a slightly lighter tone. The spheres were sintered by placing the disk with their bare side onto a hot plate kept at a temperature of 110 °C. Optimal sintering conditions were sought to promote the formation of only a small neck between neighboring particles. This was accomplished by setting the hot plate temperature at 110 °C, varying the sintering time between 2 and 3 minutes in increments of 5 seconds, and then examining the samples by FE-SEM to determine the extent of the contact region. Satisfactory results were obtained for a baking time of 135 s. Solubility tests in tetrahydrofuran (THF) at room temperature were run on as-produced spheres as well as after sintering, and in both cases they were found to be completely soluble. Figure 3.2.1 shows a FESEM image of a typical sample of microspheres following sintering.
3.2.3 Deposition of Ni and removal of the template.

Ni was plated through the microspheres template by galvanostatic deposition under a direct current (DC) of 20 mA from an unstirred solution consisting of 600 g lt⁻¹ NiSO₄·6H₂O, 10 g lt⁻¹ NiCl₂·6H₂O, and 40 g lt⁻¹ H₃BO₃ (q)[65]. Prior to use, the solution was stirred for 3-5 days and then filtered through fresh activated carbon to remove organic impurities. The plating time was tuned to fill the template up to or below the top layer of spheres immediately facing the plating solution. A Dynatronix Pro Series Power Supply (Dynatronix, Amery, WI) was employed with a two-electrode configuration involving the CP disk as the cathode and a glassy carbon rod as the auxiliary electrode. The CP disks were housed within a cylindrical cavity with a
narrower, 1.1 cm in diameter, opening at the end bored through a Teflon holder and pressed in the back by a spring-loaded carbon disk against a flat silicone gasket with a circular opening 0.95 cm in diameter (defining the plating area) and with the top side of the microspheres bed directly exposed to the electrolyte solution. The 0.6 cm diameter auxiliary electrode (carbon rod) was placed 4 cm away from the sample, and a 1 liter beaker housed the assembly and the electrolyte. Figure 3.2.2 shows the holder for the working electrode that also incorporated the o-rings, spring, and graphite support mentioned earlier.

Figure 3.2.2, Sample holder (C) used for Ni and Pt electrodeposition. A: Silicon backing piece to hold the spring (B) in place.

Plating conditions for Ni were initially estimated using Equation 1.16 assuming 100% efficiency. However, ICP analysis (see section 3.2.5) of representative samples indicated a true efficiency of about 80%. To determine the optimal deposition conditions
experiments were run under DC and pulse plating mode (at duty factors from 0.1 to 0.9 in 0.1 increments). Small differences in the amounts of Ni deposited were found, although pulse plating tended to yield slightly rougher deposits than DC deposition. Therefore, in order to minimize experimental times all subsequent depositions were run under DC conditions. Electrodeposition tests at currents in the range -1 to -100 mA indicated -20 mA as the optimal current to obtain acceptable deposits within a total deposition time of about 5 min. The average mass of Ni deposited per sample was equivalent to a uniform, dense, 2.5 µm thick layer over the 3/8” diameter deposition area. This corresponded to an actual thickness of the Ni sponge of about 20 µm (see section 3.3.2).

After plating, the samples were washed with distilled water and allowed to dry. Removal of the microspheres was accomplished by dissolution in THF. The selection of the solvent was based on its solubility parameter (18.6 Mpa$^{0.5}$) which is close to that of polystyrene (18.5 Mpa$^{0.5}$) [70]. Towards this end, each sample was subjected to 2 wash cycles at room temperature involving immersion in 20 ml of THF followed by agitation on a variable-speed shaker for 30 min, and replacement of the liquid by an equal amount of fresh THF. The samples were then allowed to dry under a heat lamp for 30 min, and stored at reduced pressure in a dessicator until further use. Figure 3.1.1 schematically illustrates the sequence of steps employed to produce the Ni sponge supports.

3.2.4 Catalyst delivery

The catalyst delivery methods considered were pulse electrodeposition, electrospray, and air spray. The traditional air-spray method was only used for standard anodes and for the cathode (both based on carbon black diffusion layers), as it gave poor results for spongiform Ni samples, because the large, mm-size droplets did not distribute
evenly over the small sample area (0.71 cm\(^2\)) and also penetrated deep inside the pores by capillarity, absorbing the catalyst-ionomer mixture, and resulting in significant occlusion.

Electrodeposition of Pt was accomplished by pulse plating using square-wave galvanostatic pulses at duty factors of 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, on-time currents of –0.01, -0.1, and -0.25 A, (off time current=0 A) and a sufficient number of cycles to deliver a specified total charge from an unstirred Pt 5Q bath consisting of 26 mM Pt(NH\(_3\))\(_4\)HPO\(_4\) (Alfa Aesar) and 30 mM Na\(_2\)HPO\(_4\) (Fisher) as a pH=10 buffer [87, 88]. A Voltalab electrochemical station (PGZ 402, Hach Company, Loveland, CO) was employed with a three-electrode configuration involving the Ni sponge as the cathode, a coiled Pt wire as the anode, and a standard calomel electrode (SCE) as the reference. The electrodes and the electrolyte were housed in a 250 ml beaker. After plating, the samples were removed from the bath and immediately washed with distilled water.

Commercial Pt and Pt-Ru nano-particle catalysts (Johnson Matthey) were delivered by DC electrospray using the simple apparatus schematically illustrated in Figure 3.2.3.
The setup consisted of a syringe pump driving the piston of a 5 ml syringe housing the catalyst-ionomer dispersion in methanol (ink), and connected with a short segment of Tygon tubing to a 0.34 mm ID needle that served as the negative electrode. The sample to be electrosprayed served as the positive electrode and was positioned 4 cm away from the tip of the negatively-biased needle. A DC power supply was used to establish a 5 kV voltage difference between the two electrodes. The pumping rate was tuned to deliver a flow rate of ~0.5 ml hr$^{-1}$ sufficient to sustain a steady jet of micrometer-size liquid droplets through the needle, visible by the naked eye as a fine mist. The catalyst inks contained 0.08 g PtRu, 0.223 mg Nafion® ionomer, and 0.6 ml MeOH for the PtRu case and 0.105 gr Pt, 0.024 mgr Nafion ionomer and 10 ml MeOH for Pt. Each ink was sprayed for 10 min.
The actual masses of Ni and catalyst deposited were determined by digestion of representative samples in aqua regia and analysis of the residual liquid by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES).

3.2.5 Determination of mass by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

Nominally identical samples to those tested by CV in the Nuvant system and were immersed in 5 ml of aqua regia (consisting of 2 ml HNO$_3$ and 3 ml HCl) and heated on a hot plate at ~ 100 °C for 12 hrs. After dissolution the sample bottles were opened and the aqua regia was completely evaporated at 150 °C for 5-6 hrs to yield a dry and solid precipitate. This precipitate was then re-dissolved in 5 ml of 12.1 N HCl at 100 °C for 12 hrs, followed by dilution with millipore water to a final mass of 100 gr. Finally, the diluted liquid was analyzed by ICP-OES to determine Pt, Ru, and Ni concentration. For each metal and each experiment the concentrations were determined using freshly obtained calibration data from standards. The assay permitted measurement of metal masses down to 10 µg within 10%.

3.2.6 Electrochemical characterization

Methanol oxidation tests were conducted using a Gamry Multi-Potentiostat Unit (Gamry Instrument, Warminster, PA) with a three-electrode configuration involving the sample bearing the catalyst as the anode (WE), a graphitic rod as the auxiliary electrode (AE) and a Standard Calomel Electrode (SCE) as a reference. The distance between the WE and the SCE was about 3 cm, while the AE did not interfere in the field between the WE and the SCE (see Figure 1.1.5).
Cyclic voltammetry scans from 0.0 to 1.0 V vs. SCE at a rate of 20.0 mV sec\(^{-1}\) at ambient temperatures were performed in a neutral solution containing 0.5 M MeOH and 0.1 M Na\(_2\)SO\(_4\) titrated to neutral pH using a 0.01 M NaOH (Fisher) and also in an acidic solution (pH=0.5) containing 1.0 M H\(_2\)SO\(_4\) and 0.5 M MeOH. The neutral solution was chosen to mimic an environment similar to that expected to prevail in a methanol fuel cell, whereas the acidic solution was selected to test the stability of the Ni sponge in a highly corrosive environment. In the neutral system CV scans were run until attainment of a steady cycle, but in acidic solution the upper Ni sponge layers did not survive the forward scan of the first cycle. Standard anodes with (Johnson Matthey) Pt or PtRu catalysts air-sprayed on carbon black were also tested in both electrolytes, in order to establish a basis for comparison (nominal loadings were 1.0 and 4.0 mg cm\(^{-2}\) respectively). From the CV diagram the onset potential and the amplitude of the oxidation peak were determined in order to characterize the activity of each sample.

The second type of electrochemical characterization involved tests in the NuVant system. This apparatus permits the simultaneous analysis of a 5”x5” array of 0.71 cm\(^2\) anodes against a single 4”x4” H\(_2\) cathode, separated by a Nafion 117 membrane. Figure 3.2.4 displays the essential components of the NuVant cell and Figure 3.2.5 displays an image of the anode side flow field embedding the 25 positions housing the current collectors. An advantage of this setup over a single-fuel-cell testing system is that all samples share a common cathode, so that their currents can be reliably compared independent of the variability in cathode characteristics. The system is operated in half-cell mode against a dynamic hydrogen electrode (DHE) as the reference, exploiting the following anodic and cathodic reactions:
\[ \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \quad \text{(anode)} \quad (3.6) \]

\[ 6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2 \quad \text{(cathode)} \quad (3.7) \]

Figure 3.2.4, Nuvant cell design. Components A and G denote the top and bottom block of the assembly, components B and F define the flow fields on the cathode and anode side respectively. C and E correspond to gaskets and component D is the MEA embedding the cathode (on the left hand side) and the 25 sample anodes on the right hand side, separated by the Nafion® membrane.
Half-cell tests permit eliminating effects related to the slow kinetics of the oxygen reduction reaction and possible flooding at the cathode in a real fuel cell. The proton reduction reaction in Equation 3.8 is not kinetically limited and does not yield water, so that flooding is eliminated and variations in the cathode’s characteristics are less crucial. Because all 25 samples in the Nuvant cell share the same membrane, cathode, and potential, half-cell tests yield direct information on the anodes’ performance. The Nuvant system has been successfully employed to characterize novel catalysts, and is known to provide rankings that conform to real fuel cell behavior [46, 89].

Membrane-electrode assemblies (MEA) for Nuvant tests were produced as follows: The Nafion® 117 membrane (DuPont, DE) was purified and swelled by a multiple cleaning procedure in a solution of 3% H₂O₂ (30%, Fisher Scientific) and then 1 M H₂SO₄ (36N, Fisher Scientific) for at least three cycles at 90 °C, and finally stored in
distilled water. The Nafion® was then pressed flat at ~120 °C and ~700 lb in⁻² for 3 min. Then the cathodic side was pressed against the membrane at ~1600 lb in⁻² and 120 °C for 3 min. The cathode and the standards were prepared by spraying the Carbon Black (CB) ink (containing 3.5% wt. carbon black, 8% wt. Nafion® ionomer and methanol) onto the Toray carbon paper and then depositing the catalyst by air spray of an ink consisting of 8% wt. Pt, 15% wt. Nafion® ionomer and methanol. Prior to deposition, the inks were stirred for 3-4 days. The Pt and CB loading on the cathode were both 1 mg cm⁻².

The final step involved placing the anodes in the pre-configured slots and then pressing them against the Nafion/Cathode assembly at ~1600 lb in⁻² and ~120 °C for 3 min. The individual pressing steps were repeated 4 times, each involving a sequential 90° rotation of the assembly to ensure a uniformly flat MEA.

Samples of Ni sponge bearing pulse plated and electrosprayed Pt, Ni sponges with electrosprayed PtRu, Ni sponge alone, and standards obtained by air spraying (Johnson Matthey) PtRu on carbon black were simultaneously tested by CV and LSV scans in half-cell mode to evaluate their overall performance toward methanol oxidation. The tests were run under half-cell conditions, flowing a 0.5 M methanol solution in the serpentine pattern (shown in Figure 3.2.5) across each 0.71 cm² anode at 8 ml min⁻¹. Fully humidified hydrogen was supplied to the cathode at ~180 ml min⁻¹ (STP). The entire system was operated at atmospheric pressure. Tests were run at temperatures of 60 and 80 °C. Some of the 25 anode slots were occupied with standards bearing 1.2 mg cm⁻² PtRu.
3.3 Results

3.3.1 Support Morphology

FESEM images of the top of the spongiform Ni deposits on CP at different magnifications are shown in Figure 3.3.1.

![Figure 3.3.1](image)

Figure 3.3.1, SEM images of the Ni sponge developed on the Toray CP after spheres addition, sintering, Ni deposition and dissolution in THF (Image A corresponds to 0.4 kX, image B to 1 kX and images C and D to 5 kX magnification respectively).

The average thickness of the spongiform Ni layer could not be measured, but was estimated to range from 15 to 20 µm, based on the relation:

\[
H = \frac{m_{\text{Ni}}}{A \cdot \rho_{\text{Ni}} \cdot \varepsilon_{\text{CP}} \cdot (1 - \varepsilon_{\text{sp}})}
\]  (3.8)
where H is the average thickness, A and \( \rho_{\text{Ni}} \) are the known sample area (0.71 cm\(^2\)) and density of Ni (8.9 g cm\(^{-3}\)), respectively, \( m_{\text{Ni}} \) is the mass of Ni measured by ICP-OES, \( \varepsilon_{\text{cp}} \) (~0.71) the known void fraction in the carbon paper, and \( \varepsilon_{\text{sp}} \) the estimated void fraction in the sponge (0.62 \( \leq \varepsilon_{\text{cp}} \leq 0.74 \)). The average thickness of the carbon black/ionomer diffusion layer in the standard anodes, estimated using the same equation, was found to be comparable to that of the Ni sponge, ranging from 20 to 30 \( \mu \)m.

In Figure 3.3.1 C and D it is seen that the pores communicate and penetrate into the construct. In all cases, no residual spheres were visible on the top surface of the Ni sponge, but in the back some residual particles were visible decorating the fibers of the CP support. The as-sintered spheres exhibited gradual charging under prolonged exposure to the electron beam in the SEM, but the residual particles did not, indicating that they were encased in Ni. Figures 3.3.1 A and B reveal significant cracking in the sponge caused by shrinkage of the microspheres bed upon thermal sintering. The presence of such cracks and regions of low packing density in the template, that would have permitted easy passage of plating solution across the structure, can explain the Ni plating in the back of the sample.

To estimate the amount of residual spheres, samples were tested by Thermal Gravimetric Analysis (TGA) in \( \text{N}_2 \) from 150 °C to 1500 °C at a rate of 10 °C min\(^{-1}\). Typical TGA data for as-deposited microspheres and Ni sponge after dissolution of the spheres are shown on Figure 3.3.2 (bottom and top curves, respectively). Polystyrene undergoes significant decomposition between 400 and 500 °C in \( \text{N}_2 \), to yield predominantly styrene and other volatile compounds [67, 90]. The mass of residual polymer estimated from the TGA data and the known masses of carbon paper and plated
Ni (the latter obtained from ICP-OES analysis, as discussed in section 3.2.5) amounted to about 11% of the total mass of spheres in the original template.

Figure 3.3.2, Remaining weight (%) versus temperature (°C) for Ni sponge and Carbon Paper (with sintered spheres) during Thermal Gravimetric Analysis (TGA) at a heating rate of 10 °C min⁻¹. Sample was preheated at 100 °C for 10 min and the analysis was run in an Argon flow of 100 sccm.

Whereas no spheres were visible in the exposed side of the Ni sponge, some occupancy of the bulk pore volume by residual particles could not be ruled out. Efforts to fracture the samples to permit cross-sectional FESEM imaging were unsuccessful, because Ni is not brittle so that the sample did not fracture cleanly, but tended to tear. A reduced porosity would clearly have a negative impact on the transport characteristics of the support and needs to be examined in future work.
3.3.2 Catalyst deposition on Ni sponge

Figures 3.3.3 B, C and D display the top surfaces of spongiform Ni samples with pulse plated Pt for charge transfers of 1, 5, and 10 C respectively at 0.1 DF and -0.1A on time current (OTC), while Figure 3.3.3 A shows the top of the bare sponge prior to catalyst deposition.

Figure 3.3.3, FESEM images of: A) the Ni sponge at 30 kX, B), C), and D) Pt deposited on the Ni sponge at 0.1 duty factor (DF) and on-time currents of –0.1A. The charge transfer during deposition was 1, 5 and 10 C respectively. The measuring bars mark half a micron (magnification is 50kX), measure bar for A is 1 μm.

The ridges of the craters are decorated with Pt particles that increase in size and number with increasing total plating time. At low levels of charge transfer (1 C, actual Pt mass=0.27 mg cm\(^{-2}\)) the Pt particles appear to be isolated and of spherical shape with
dimensions ranging from 50-100 nm, whereas for higher amounts of charge transfer (10 C, with 0.61 mg cm$^{-2}$ of Pt) larger particles are formed (~150 nm) and they cluster around the craters in the sponge. For charge transfers of 15 C or higher the Pt particles become even larger (d>150 nm) and they begin occluding the pores in the Ni, resulting in a significant reduction in the area available for mass transfer across the structure. Pt electrodeposition experiments were run at duty factors of 0.05, 0.1, 0.25 and 0.5, and (for each duty factor) at on-time currents of -0.05, -0.1A, and -0.25A to identify the parameters that would yield the best performing electrodes. Those samples were then selected for NuVant analysis. Only results for the best performing samples are presented here.

Spongiform Ni samples were electrosprayed with the same Pt and PtRu inks that were used for the cathode and standards preparation. Figures 3.3.4 A, B and C show FESEM images of samples that were electrosprayed with methanol/ionomer dispersion of Johnson Matthey Pt nanoparticles. The nominal size of the catalyst particles ranged from 5-10 nm as reported by the manufacturer. The final deposits shown in Figure 3.3.4 B are seen to consist of clusters ranging from 0.1 to 1.0 µm in size sparsely distributed on the surface of the sponge.
Figure 3.3.4, FESEM images of: A), B) and C) electrosprayed Pt on Ni sponge at 1, 15 and 15 Kx respectively. Images A and B represent the same sample while C is a nominal identical site (measure bar for A is 20 μm and for B, C is 2 μm).

The actual catalyst loadings were smaller than those estimated from the ink Pt concentration, flow rate, and electrospray time (0.2 mg cm\(^{-2}\) vs. an expected 0.95 mg cm\(^{-2}\) Pt). This was a result of settling of the dispersion in the syringe during the electrospray process. The cluster size and coverage in Figure 3.3.4 B are similar to those of samples electrosprayed with Johnson Matthey PtRu. In the latter case, however, the use of substantially higher amounts of ionomer in the solution was found to be necessary in order to prevent significant settling of the particles during electrospray. Thus, as opposed to the electrosprayed Pt case where no ionomer is clearly identifiable on the surface of the sponge (except perhaps from the charging in Figure 3.3.4 B), the FESEM images of
the samples electrosprayed with PtRu revealed substantial coverage of the sponge by a uniform ionomer film.

3.3.3 Analysis of methanol oxidation activity

It has been reported that Nickel or its hydroxides can act as catalysts in weakly acidic and alkaline methanol solutions [82]. Kowal et al. [91] inferred the formation of a multilayer NiOOH film from electrochemical analysis in alkaline environments. Nakashima et al. [92] argued for the existence of Ni hydroxide after a short CV scan for a PtNi electrode in acid media. Prior to testing samples with deposited catalysts for methanol oxidation activity, the activity of the Ni sponge alone was tested in alkaline, neutral, and acidic solutions. CV scans were recorded in neutral electrolytes consisting of 1.0 M Na$_2$SO$_4$, 0.5 M CH$_3$OH (titrated to pH=7 with 0.01 M NaOH), alkaline media (1.0 M NaOH, 0.5 M CH$_3$OH, pH=14), and a strongly acid electrolyte (0.5M H$_2$SO$_4$, 1M CH$_3$OH). The Ni sponge appeared to be slightly active in alkaline media (with a peak MeOH oxidation current of ~14 mAcm$^{-2}$ for a 20 mV s$^{-1}$ scan rate) and practically inactive in the neutral medium. In the case of acidic electrolyte (pH=0) the Ni sponge completely disintegrated at around 0.3 V vs. SCE in the first forward scan (0.0 to 1.0 V vs. SCE) of the CV test, as was expected from analysis of Pourbaix diagrams [35].

Samples characteristics and mass specific peak methanol oxidation currents are reported in Appendices B and C. The Ni plating data exhibit good reproducibility for DC conditions (current efficiency ~80-85 %). On the other hand, the Pt deposition data exhibit significant scatter, possibly as a result of hydrogen evolution during pulse plating. The highest mass specific methanol oxidation currents were obtained for samples produced under the conditions DF= 0.25, Ion= -100 mA, Q= 10 C, corresponding to a Pt
loading of 0.61 mg cm$^{-2}$. These samples were thus deemed suitable for evaluation in the NuVant system.

Figure 3.3.5 displays the cyclic voltammograms for pulse plated Pt (Q=10 C, I$_{on}$=-0.1 A, DF=0.25) and electrosprayed Pt or PtRu on Ni sponge.

![Cyclic Voltammetry Scans](image)

Figure 3.3.5, Catalysts activities by Cyclic Voltammetry scans in the neutral bulk. Plotted are the mass specific current densities calculated by Inductively Coupled Plasma Optical Emission Spectroscopy for: A) Pulse plated Pt onto Ni sponge at DF = 0.25, Ion = -0.1 A B) Pt and PtRu electrosprayed

The used was the neutral (pH=7) and scan rate was 20 mV s$^{-1}$. The contribution of the Ni sponge to the activity was found to be insignificant (the Ni was electrochemically stable during the entire course of the experiments; i.e. for over 20 CV cycles). For the pulse plated Pt an oxidation peak is evident, though small, at 0.4 V vs. SCE. The mass specific currents for electrosprayed Pt and PtRu on Ni were comparable to that of the PtRu standard. In all of these tests the catalyst was localized at the electrodes’ surface (Figures 3.3.3 and 3.3.4) directly facing the methanol solution. Hence, these tests probed the intrinsic activity of the catalyst, irrespective of the mass transfer phenomena that are expected to be relevant to fuel cell performance.
3.3.4 NuVant Analysis

The final characterization involved half-cell tests in a fuel-cell-type assembly in the NuVant System (NuVant Co., Crown Point, IN). Triplicates of nominally identical samples were incorporated in an MEA and tested for their performance as DMFC anodes (conditions are noted in the corresponding figures). Recall that, for spongiform Ni anodes with pulse plated Pt the best samples tested were obtained using a DF=0.25 and OTC=-0.1A (see section 3.3.3). These samples displayed good mass specific activity during the previous CV tests and exhibited fully open pores (unobstructed by Pt particles) upon FESEM imaging. Pt and PtRu electrospayed samples were also tested in this NuVant runs, and PtRu standards with 1.2 mg cm$^{-2}$ loading were used for comparison purpose.

The tests reported here were run at 60 °C and atmospheric pressure.

Figure 3.3.6 compares the current density traces from LSV scans obtained in the NuVant system for nominally identical samples hot pressed in the MEA assembly at 110 °C and 160 °C.
Figure 3.3.6, Mass specific current density versus voltage from a LSV run in the NuVant system (at 60 °C) with the MEAs hot pressed at two different temperatures (110 °C and 160 °C). Each curve is the average of three nominally identical samples (Pt plated at DF=0.25, I_on=-0.1A, Q=10 C).

It can be seen that both samples behaved similarly, yet, those that were hot pressed at 160 °C displayed a lower activity than those hot pressed in MEA at 110 °C. These differences were initially attributable to the occlusion of the porous nickel structure by microspheres that remained undissolved following treatment with THF, and that melted at 160 °C but not at 110 °C. Partial occlusion of the structure implies that only a fraction of the catalytic area is accessible to methanol, and such a fraction is expected to exhibit variability from sample to sample.

To explore this hypothesis an attempt was made to thermally degrade the residual polystyrene spheres. Porous Ni electrodes were heat treated at 350 °C for 20 min in a
nitrogen atmosphere, followed by further dissolution in THF, in order to promote
degradation and further removal of residual polymer believed to occlude the pores of the
spongy metal. Heat treatment at temperatures higher than 350 °C was found to be
unfeasible, owing to the nearly complete loss of spongy Ni from the carbon paper
support, as expected from thermal expansion effects. Thermo-gravimetric analysis run
after this degradation/dissolution treatment still revealed a small decrease in mass at
around 400 °C, indicative of the continued presence of residual polymer in the sponge,
although in much reduced amounts relative to the untreated case. Such samples were
electroplated with Pt, as discussed earlier, and tested in the NuVant system for activity.
Figure 3.3.7 shows LSV curves for the Pt plated Ni sponges at Q=10 C, $I_{on}$=-0.1 A and
$DF=0.1$. 
No significant difference in performance between the untreated and heat-treated samples can be seen, suggesting that the presumed reduction of open porosity primarily stems from Ni overplating within regions of low sphere packing density pervading the randomly-packed microsphere template.

Figures 3.3.8 A and B show NuVant CV scans at 20 mV sec$^{-1}$ for Ni sponge anodes with pulse plated Pt, electrosprayed Pt and PtRu (Figure 3.3.8 A), and PtRu standards (Figure 3.3.8 B).
Figure 3.3.8, Mass specific current during a NuVant test by CV at 60 °C for: A) Pt pulse plated (Q=10 C, DF=0.25, \(I_{on}=-0.1\) A), Pt and PtRu electrosprayed and B) PtRu standards.

It is apparent that the pulse plated Pt performs similar to the electrosprayed PtRu, and that the electrosprayed Pt performs better on a per catalyst mass basis than the previous two. The activation potential (where the slope of the CV scans suddenly changes due to onset of oxidation) is \(~0.6\) V vs. SCE for Pt electroplated and \(~0.3\) V vs. SCE for the Pt and PtRu electrosprayed. Figure 3.3.8 B shows that the performance of the PtRu standard is inferior (per mass basis) to the electrosprayed samples (note the different scales on the plots), as expected from reduced mass transfer limitations across the porous Ni structure as compared to the denser carbon black layer in the standard.
3.4 Conclusions

Spongiform Ni layers produced by electrodeposition through microsphere templates have been investigated as potential substitutes for carbon black diffusion layers in direct methanol fuel cell anodes. The overall performance towards methanol oxidation of the anodes incorporated in fuel cell assemblies was found to be comparable on a per catalyst mass basis with that of standard anodes using carbon black/ionomer diffusion layers although the electrosprayed samples were the most active. Such a behavior is likely to be attributable to reduced mass transfer limitations across the porous metal relative to the case where denser carbon black/ionomer films are employed. Thermal gravimetric analysis of spongiform Ni samples after polymer dissolution revealed the presence of a small amount of residual spheres. This may have possibly resulted in partial occlusion of the sponge with a concomitant reduction in mass transfer across the structure. However, Ni overplating within the sponge itself is likely to be the dominant factor for pores occlusion.

Future efforts should focus on improving the electrochemical stability of the electrodes through the use of Ni-P alloys as well as on exploring the effect of spheres’ size on the final microstructure of the spongiform constructs. Creating a highly dispersed Pt catalyst in such a structure remains a challenge.
CHAPTER 4:
PRODUCTION OF POROUS NICKEL ELECTRODES BY MICROFABRICATION METHODS

4.1 Introduction

4.1.1 Microfabricated Fuel Cells

In the present chapter we consider an alternative method for the fabrication of supports for fuel cell anodes. The work described in Chapters 2 and 3 addresses the production of supports through the use of removable templates, in the form of either polymeric microspheres or aqueous channels in a HIPE. These systems, however, presented problems related to controllability and reproducibility of the final microstructures in terms of both geometry and size of the features. On the other hand, well established Integrated Circuit (IC) fabrication methods permit production of features with tightly controlled geometrical characteristics as well as size.

Microfabrication techniques are now routinely used for the mass production of microchips, biosensors etc [44]. By using silicon micromachining techniques like Reactive Ion Etching (RIE), Physical Vapor Deposition (PVD), Photolithography, wet agent etching etc. a tight control of the size and geometry of the features can be achieved with resolutions down to a few micrometers.
Over the last decades considerable attention has been devoted towards the production of micro Fuel Cells for possible use in electronic devices [10, 42, 43, 73, 93, 94]. The present chapter does not attempt to address this topic directly, although the fabrication methods employed here could also be used to produce micro Fuel Cells. Rather our work aims at exploring the possibility of producing supports for DMFC anodes with well defined characteristics in an effort to allow careful study of the effects of mass transfer phenomena on DMFC performance, and specifically on CO$_2$ management, which remains a major problem in DMFCs.

This issue, as schematically illustrated in Figure 4.1.1, can be described by the following, simple steady state mass transfer problem.

![Figure 4.1.1](image_url)

Figure 4.1.1, (A) Schematic of an ordinary MEA in a DMFC, (B) representation of the CO$_2$ concentration on the vicinity of the reaction zone/nafion layer
As stated in Equation 1.5, for every mole of CO\(_2\) produced 6 electrons are formed. Therefore the flux of CO\(_2\), \(N(x,t)\), leaving the reaction zone can be related to the current yield of the cell by the following Equation:

\[
N(x,t) = -D \frac{dC}{dx} = \frac{i}{6F}
\]  

(4.1)

where \(x\) and \(t\) are the distance from the reaction zone within the diffusion layer and time, respectively, \(D\) is the effective diffusion coefficient of carbon dioxide (cm\(^2\) s\(^{-1}\)), \(i\) the current density (A cm\(^{-2}\)), \(F\) the Faraday constant (C mole\(^{-1}\)) and 6 is the number of electrons released by the methanol oxidation. At steady state \(N\) is independent of \(x\) and \(t\), so that the standard differential mass balance can be solved to yield:

\[
C_{x=0,CO_2} = \frac{i \cdot L}{6 \cdot F \cdot D}
\]  

(4.2)

where \(L\) is the thickness of the diffusion layer (cm), and \(C_{x=0,CO_2}\) is the concentration of the CO\(_2\) in the immediate vicinity of the catalyst in the reaction zone (mole cm\(^3\)). Equation 4.2 assumes a nil CO\(_2\) concentration on the flow field side of the diffusion layer, which can be achieved by insuring a sufficiently high fuel flow rate. From the above relation, for a moderate value of the current density \((i=28\) mA cm\(^{-2}\)), a typical value of the diffusion coefficient \((D=5*10^{-6}\) cm\(^2\) sec\(^{-1}\)) and with \(L=60\) μm we obtain \(C_{x=0,CO_2}= 60\) mM, which is six times larger than the solubility limit at 1 atm partial pressure [95]. This indicates that bubbles will naturally form, unless \(C_{x=0,CO_2}\) is reduced by suitably modifying the transport characteristics of the diffusion layer in terms of both thickness and permeability.
4.2 Experimental Methods

4.2.1 Description of Ni porous support fabrication

An important characteristic of the porous electrode to be produced relates to its ability to accommodate expansion and contraction of the Nafion® membrane without suffering structural damage that would compromise the electrical connectivity. Also, to exploit available microfabrication tools it is important that the pattern be comprised of the periodic replica of a fundamental unit. Simple polygonal units such as equilateral triangles, squares, rhombuses, etc. can not be stretched when connected in a periodic network pattern, however. Therefore, the pattern shown in Figure 4.2.1 C was designed to meet all of the necessary requirements.

Figure 4.2.1, A) Pattern depicting the structure of the master mask that was used for the fabrication of the Ni support-electrodes. B) Optical microscope image of the master mask, C) Major cell used for the fabrication of the mask pattern.
The above polygons are a variation on the basic equilateral triangle theme (which allows easy replication of the pattern), however, they are designed to comply without rupture under a biaxial stretch up to an extension of about 50%.

Another important aspect of the processing is the ability to handle without damaging the thin metal pattern through the several fabrication steps necessary to assemble the MEA. This is especially crucial in the final assembly step (after catalyst deposition) whereby the electrodes are hot pressed against the Nafion® membrane, thus resulting in the application of intense mechanical stresses on the various components. Towards this purpose the following fabrication strategy was conceived as illustrated in Figure 4.2.2.
The first step in the production of the Ni support involved the successive physical vapor deposition of Cr and Au on a borosilicate glass slide. The role of the glass slide was to provide support for the Ni structure during the MEA assembly and to serve as a planar support onto which to deposit the metals. To shorten the time necessary for dissolution of the glass, we used 0.08-0.13 mm thin slides (Erie Scientific, NH), with
square shape (4”x4”). The Au layer (0.2 μm) was used in order to shield the Ni from the HF during removal of the glass. The Cr layer (0.5 μm) was designed to improve adhesion between the Au and the glass and also to provide further mechanical strength to the glass itself in order to reduce the chance of cracking during HF treatment (from residual internal stresses present in the glass).

Next, a photoresist was spin coated on the Au layer at 1500 rpm for 30 sec (conditions recommended by the supplier for a 10 μm thick layer). Since our goal was to produce a thick metal layer the photoresist had to be viscous, compatible with Au, and easily dissolved in a non acidic remover. These requirement were met by the following resist SPR 220-7.0 (Rohm and Haas Electronic Materials). The remover was MF-24 A (Rohm Haas Electronic Materials) which contained 97% water, 2% Tetramethylammonium hydroxide and less than 1% Polyglycol. To promote adhesion, the Au layer was treated with hexamethyldisilazane (HMDS, Alfa Aesar) for 1 min prior to the photoresist application.

The next step involved the projection of the desired pattern (see Figure 4.2.1) on the photoresist, through a chrome mask, by using a MANN 3696 projection Stepper. The exposure times as well as the focus point on the photoresist were adjusted in order to account for an optimal pattern printing. Since the planarity of the resist depended on the flatness of the Au/Cr/glass sandwiched layers, the printed surfaces showed variability in geometrical characteristics attributable to over- or under- exposure. After carefully handling several resist-spinned samples and performing exposures at different light intensities, focus points, and times we concluded that optimal patterning occurred after a
4 s exposure under a 200 mJ cm\(^{-2}\)sec\(^{-1}\) light intensity. The focal point was manually adjusted and was found to correspond to a value equal to 42.

To remove the resist, the sandwiched layer of Au/Cr/glass was immersed in the MF-24A and the container was gently agitated for 120 sec (recipe recommended by Rohm Haas Electronic Materials). Subsequently, the Ni layer was deposited on the formed trenches from the Watt’s solution [65] under DC conditions with a 10 mA current. The deposition time was governed by the desired Ni layer thickness. As shown in Figure 4.2.2 E, the photoresist that had remained unexposed on the Au surface was removed in MF-24 A after a flood exposure with a Cobilt 2 system. The necessary light beam intensity was 18.6 mJ cm\(^{-2}\) and the exposure duration was 120 s.

Upon termination of the previous step a porous Ni structure was revealed on the top of the Au. Then we deposited the catalyst on the microfabricated multilayer assembly by electrospray of a Pt ink similar to that used for cathode preparation (see section 3.2.4). Due to the total dissolution of the photoresist after flood exposure, the Pt catalyst was deposited not only on the Ni but also on the adjacent Au area. However, the majority of the catalyst was found on the Ni, due to the high electric field intensities on the protruding edges.

Following catalyst delivery, the assembly was hot pressed against a Nafion® membrane and a standard cathode (1 mg cm\(^{-2}\) Pt) by following the same procedure for MEA assembly described on section 3.2.6. Subsequently, the MEA was placed in a special 4”x4” square shaped polyethylene bath designed to bear a few ml of the etching solution each time. The MEA served as the bottom of this bath with the cathode side on the exterior and the glass on the anode side facing the liquid in the bath. Initially a dilute
solution containing a (20:14:66) mixture of (49% HF), (70% HNO₃) and (H₂O) was dropwise added on the glass side. Dissolution of the glass by the HF was immediately followed by dissolution of the Cr layer as well. Preliminary glass-dissolution tests revealed an glass etch rate of ~2 μm min⁻¹. Following this step the HF was removed and the tank was flushed with distilled water and dried. Finally, the exposed Au shielding the Ni from the acid was removed by gently agitating a small amount of Hg.

It should be noted that in preliminary HF etching tests the glass slide fractured into several small pieces due to residual, unrelaxed stresses. In order to overcome this problem, the glass slides were annealed at 575 °C for 5 hrs prior to their use as supports of the assembly. Following this treatment the samples still fractured, but only in two or three pieces. The presence of deposited metals (Cr, Au and Ni) on the slide mitigated this problem because of the ability of the metal films to strengthen the assembly and inhibit crack propagation.

Unfortunately due to time constrains this set up could not be tested for activity. This should be the subject of future work.

4.3 Results

4.3.1 Ni support formation

Figure 4.3.1 shows the trenches filled with Ni electrodeposited on the Au/Cr/Borosilicate multilayer substrate after the second photoresist removal step. Because in the 4” x 4” assembly the bottom (glass) and top (photoresist) layers were non-
conductive a rectangular patch with dimension 0.4 cm x 0.9 cm was developed out of the resist to permit establishing electrical contact on the Au layer during electrodeposition.

Figure 4.3.1, FESEM images of the top of Ni deposits filling the trenches developed in the Megaposit 220-7.0 photoresist (A, B, C and D at 1kX, 10kX, 20kX and 5kX magnification respectively).

The Ni was DC plated under a current of -2.5 mA for 5.5 hrs (higher currents gave very thick, irregular deposits). Through profilometry we found that the metal layer thickness was ~4.2 μm. The FESEM image in Figure 4.3.1 D (image taken after 60° tilting) shows that the thickness of the Ni was indeed greater than 3.9 μm. Cross sectional imaging of the sample was not possible due to the charging of the glass substrate. Figure
4.3.1 C shows the width of the upper section of the nickel trench to be ~4 μm which was almost 2.5 times larger than the desired value (1.5 μm). This broadening was caused by light diffraction during exposure through the thick resist film resulting in an exposure of a width larger than the desired 1.5 μm. Efforts to remedy this problem by decreasing the exposure time from 4 to 3 sec, were unsuccessful as the photoresist film remained underexposed.

Figure 4.3.2 A shows the photoresist trenches filled with Ni and topped with electrosprayed Pt (using a 3.5 kV potential for 3 min).

Figure 4.3.2, A) FESEM image of the top of the Pt sprayed Ni layer covering the Au-Cr-Borosilicate glass side sandwich (magnification 5kX), B) Optical microscope image of photoresist trenches developed after exposure through contact lithography (1:1 ratio) by the use of the original chrome-master mask. The features in this pattern are almost 4 times larger than those of the pattern in A.

It can be seen in Figure 4.3.1 A-D that the pattern does not resemble closely the original design shown in Figure 4.2.1, and that in fact the porosity is much lower than the intended one. This problem could not be circumvented owing to diffraction limitations.
Therefore, a larger pattern was produced by performing a contact lithography exposure (1:1 ratio of dimensions versus the 10:1 reduction through the MANN 3696 Stepper) using the same Chrome Mask as the one employed to produce the structures in Figures 4.3.1. Figure 4.3.2 B shows the trenches developed on a 10-12 μm thick layer of the Megaposit 220-7.0 photoresist by contact lithography. The width of the trenches is now ~15 μm, and the pattern is very well resolved. The yellow area represents the unexposed (not dissolved) photoresist, revealing a porosity around ~65%.

Figure 4.3.3 shows the Ni structures resulting from filling the trenches in the substrate in Figure 4.3.2 B followed by final removal of the remaining photoresist.

Figure 4.3.3, FESEM image of the top (A) and side (B) (at 60°) respectively of Ni trapezoid-shape deposits formed after photoresist exposure through contact lithography (1:1 ratio) by the use of the original chrome master-mask. The features in this pattern are 6 times larger than those of stepper lithography (magnification 1 and 5kX respectively).
Ni electrodeposition was plated using the Watts solution [65] under a 10 mA current for 5.5 hrs. The width of the Ni walls replicates the width of the trenches in Figure 4.3.2. B and is about 15 μm. The depth of the trench was bigger than 6 μm and close to almost 10 μm.

4.4 Conclusions

The fabrication of a porous Ni layer on top of the Au/Cr/Borosilicate glass assembly was shown to be feasible. The produced layers had a trapezoidal shaped cross section when the photoresist was exposed through the MANN 3696 instrument. When using projection printing to a 10:1 reduction ratio an aspect ratio of 2.6 resulted. This broadening was caused by light diffraction and stems from some inherent limitation of the photolithography equipment when operating with thick resist films. The use of contact lithography to produce in a 1:1 size ratio with the Cr mask, successfully produced Ni structure with desired characteristics (aspect ratio of 1.4).

Unfortunately due to time limitations this project could not be carried on to completion to the final stage of MEA assembly and Fuel Cell testing.
5.1 Summary

5.1.1 Results of the HIPE

The goal of this work was to produce porous supports for fuel cell anodes, in an effort to reduce mass transfer resistances for the transport of reactants and products towards and away from the reaction zone in a DMFC.

Porous Ni structures were produced by three different methods, namely through the use of: 1) a High Internal Phase Emulsion (HIPE) template, 2) a Polystyrene microspheres template, and 3) by photolithographic methods. The present chapter states the conclusions from the fabrication studies as well as suggestions about possible future work.

The HIPE template method proved difficult to control, due to the high sensitivity of the emulsion structure to the electric field during electroplating, which resulted in disruption in the aqueous path through which the dissolved Ni was supposed to deposit on the substrate. The binary system Triton X-100 / Ni plating solution was studied and found to exhibit multiple phases.

The ternary system consisting Triton X-100 / Ni plating solution / dodecane exhibited an even greater complexity. In this case only one combination of concentrations
gave a stable microemulsion (1 g Triton X-100, 6 g dodecane and 3 g Ni plating solution). Electrodeposition through this HIPE was problematic because the microstructure was sensitive to the applied voltage, which was difficult to control using the Dynatronix power unit. However, when using a new circuit capable of supplying a steady voltage pulse porous structures embedding amorphous nickel were formed. The reproducibility of such structures was poor, however, requiring further study.

5.1.2 Conclusion for the microspheres’ template

Spongiform Ni layers produced by electrodeposition through a microspheres’ template have been investigated as potential substitute for carbon black diffusion layers in direct methanol fuel cell anodes. The formation of porous Ni supports by electroplating proved feasible. Pt and PtRu catalysts were deposited on the porous Ni support by pulse plating and electrospray methods. The size and the number density of the Pt particles obtained by electroplating depended on the charge transfer. For a charge transfer higher than 10 C the Ni craters became occluded by Pt particles. Pt and PtRu electrosprayed on Ni sponge were found to be more active towards methanol oxidation than both standard anodes using PtRu deposited on a carbon black layer and the most active samples consisting of Pt pulse plated on the sponge.

The spongiform nickel produced exhibited imperfections in terms of both cracking and residual microspheres embedded in the structure. Cracks in the spongiform Ni layer were observed to form following spheres thermal sintering. As a consequence Nickel overplated within the sponge. We believe this to be the factor causing occlusion of the porosity, leading to increased mass transfer limitations, and consequently, to reduced current densities.
5.1.3 Conclusions for the micro Fuel Cell fabrication

The fabrication of a porous Ni layer on top of the Au/Cr/Borosilicate glass assembly proved feasible. However, due to light diffraction through the thick photoresist in projection printing the final Ni layer had a trapezoidal cross section. The aspect ratio of the Ni walls was ~2.6. Projecting the pattern through contact lithography greatly improved the geometry of the final structure giving walls with an aspect ratio of ~1.4 and a ~70 % porosity of the layer.

5.2 Future work

The formation of a 3-D open structure that replicates the porosity of a High Internal Phase Emulsion (HIPE) on a support has proven difficult so far due to the sensitive nature of the emulsion. Future work should involve a careful study of the effects of plating parameters (voltage pulse shaper and intensity, and current) on the structure of the microemulsion, as reflected on the final morphology of the electroplated metal. Water-soluble fluorescent dyes could be used to optically probe the evolution of the morphology of the microemulsion during plating. These studies would help determining whether the texture of the electrodeposited metal is indeed a replica of the equilibrium structure of the microemulsion, or is the result of dynamic processes involving thermally-, chemically-, or electrically-induced effects during electrodeposition.

The stability of the Ni supports made by using the microspheres template can be further improved by substituting Ni with corrosion resistant Ni-P alloys. Future endeavors should also include the use of microspheres with larger diameter embedding polymer with lower molecular weight to enhance ordering and facilitate dissolution of the
template. Reduced cracking of the template could be achieved by sintering the spheres using solvent vapors to plasticize the polymer. Deposition a highly dispersed fine catalyst remains a challenge.

With regard to the microfabricated fuel cell electrodes, removal of the glass backing supporting the Ni structure may in the future present problems, as residual internal stresses in the glass may cause cracking during dissolution with HF. One possible solution would be to use polymeric backing layers such as PMMA which then could be removed by standard photolithographic methods.
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TABLE A.1, CONTINUED
APPENDIX B:
### TABLE B. 1
EXPERIMENTAL DATA FOR NI AND PT ELECTRODEPOSITION

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### TABLE C 1.
**EXPERIMENTAL DATA FOR PT ACTIVITY**

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