Introduction

1.1 Fuel Cells

It is becoming a more accepted fact that fuel cells are one of the most fascinating and interesting aspects of today’s technology. The interest in fuel cells has intensified over the past decade because the use of fossil fuels for power generation has resulted in several negative consequences, including severe pollutions, exhaustive exploitation of the global resources, and imbalance in the political power caused by the uneven distribution of natural resources. Such problems highlight the need for a new power source—fuel cell, which is energy efficient, environment friendly and renewable.

A fuel cell is an electrochemical device that converts chemical energy into electrical energy. It produces electricity using fuel and an oxidant, in the presence of an electrolyte. Fuel cells can operate almost continuously, as long as they are supplied with the fuel. As they are effective and environmentally friendly, they are increasingly gaining wide popularity. Fuel cells are now closer to commercialization than ever before. They have the potential to help fulfill the world’s demand for power and at the same time satisfy the requirement and meet the expectations regarding environmental protection. Presently, fuel cells have found use in automobiles and space shuttles, even in cell phones, lap tops and Global Positioning Systems (GPS). (Carette et al., 2000; Perry et al., 2002; Jacoby et al., 2003; Kundu et al., 2007; Dyer et al., 2002).

Fuel cells are classified, either based on their fuel or their operating temperature, under seven categories (Acres et al., 2001). The Alkaline Fuel Cell (AFC) which utilizes hydroxide ions and operates between 50°C and 200°C are still used in space vehicles. The Phosphoric Acid Fuel Cells (PAFC) also use protons but operate at higher temperatures (~220°C) than the PEMFC or DMFC. Typical PAFC units are large stationary power
generators which preprocess natural gas into hydrogen, which is consumed by the cell. The Molten Carbonate Fuel Cell (MCFC) and the Solid Oxide Fuel Cell (SOFC) operate at temperatures above 500°C and use CO$_3^{2-}$ and O$_2^-$, respectively. The Proton Exchange Membrane (PEM) fuel cell, also termed the Polymer Electrolyte Membrane Fuel cell (PEMFC), uses the ion-exchange membrane as the electrolyte that conducts the protons. Due to the critical water management in this membrane, the operating temperature of the PEMFCs is limited, usually below 100°C. Most often, the platinum catalysts which are used for both the anode and cathode react with a hydrogen-rich fuel and the oxygen that are fed into the anode and the cathode, respectively. The PEMFCs have been employed in a wide range of applications, from a few watts for portable electronic devices to hundreds of kilowatts for combined heat and power systems (Bacon et al., 1973; Mc Nicol et al., 1981). Nevertheless, the PEMFC revealed problems associated with its operation. High temperatures can enhance the efficiency of the fuel cells due to fast kinetics, although they tend to dry out the PEM, thereby reducing the effectiveness of proton conduction. Thus, water management becomes crucial in keeping the PEM hydrated at all times in order to facilitate proton transport. Another significant problem encountered with the PEMFC is fuel crossover via the membrane, which produces a mixed potential at the cathode, thereby lowering the cell performance. In spite of the extensive efforts, these problems continue to be the major obstacles which prevent the PEMFC from being used in wide-scale portable applications (Choban et al., 2004).

Despite the advantages that fuel cells offer, this field has greater scope for development. Influenced by the boom in Micro-Electromechanical Systems (MEMS) technology, the fabrication of micro-scale devices has recorded considerable growth. Therefore, the demands for energy resources used in portable devices are under continual pressure to decrease both the power consumed and weight. However, both demands can be
fully met by employing a miniaturized power resource, such as a microfluidic fuel cell. This thesis focuses on the microfluidic membraneless fuel cells.

1.2 Microfluidic Fuel Cells

Microfluidic fuel cells, otherwise termed laminar flow-based fuel cells or membraneless fuel cells, includes those cells capable of operating within the framework of a microfluidic chip. Defined as a fuel cell with fluid delivery and removal, reaction sites and electrode structures all confined to a microfluidic channel (Kjeang et al. 2009), the microfluidic fuel cell operates without a physical barrier, such as a membrane, separating the anode and the cathode, and can use both metallic and biological catalysts. In the most common configuration, a microfluidic fuel cell utilizes the laminar flow characteristics of the microfluidic flows at low Reynolds numbers to delay the convective mixing of fuel and oxidant. Two aqueous streams, one containing the fuel (anolyte) and the other containing the oxidant (catholyte), are allowed to flow side-by-side down a single microfluidic channel as shown in Fig. 1.1. The anolyte and catholyte also contain a supporting electrolyte that facilitates the ionic transport within the streams, thereby eliminating the need for a separate electrolyte. The mixing of the two streams occurs solely by transverse diffusion and is restricted to an interfacial width in the channel center. The mixing width can be controlled by modification of the channel dimensions and flow rate (Ismagilov et al., 2000). Here, the electrodes are integrated on the walls of the manifold with sufficient distance from the co-laminar inter-diffusion zone, in order to prevent fuel crossover. The position and orientation of the electrodes also influences fuel utilization as well as ohmic resistance in the channel.
The microfluidic fuel cell design avoids several issues encountered in polymer electrolyte membrane-based fuel cells, for example humidification, membrane degradation, and fuel crossover. The co-laminar configuration also permits the composition of the anolyte and catholyte streams to be chosen independently, thus enhancing the reaction rates and cell voltage. Besides compactness, fuel cell miniaturization offers a further advantage: As electrochemical reactions are surface-based, the performance of the fuel cell benefits from a high surface-to-volume ratio, which scales as the inverse of the characteristic length (Kjeang et al., 2008). The most prominent benefit that the microfluidic fuel cells afford, however, is the economical advantage. These cells can be manufactured using inexpensive, well-established micromachining and microfabrication methods eliminating membrane costs associated with most other fuel cells. Additionally, as the microfluidic fuel cells are normally operated at room temperature they do not require auxiliary humidification, water management or cooling systems. However, significant advancements are necessary in terms of energy density and fuel utilization before we can capitalize on the advantages of the microfluidic fuel cells (Fig. 1.2).
1.2.1 Microfluidic Fuel Cell Developments

Proof-of-concept microfluidic fuel cells have been demonstrated based on hydrogen (Cohen et al., 2005; Mitrovski et al., 2004; Mitrovski et al., 2006), methanol (Choban et al., 2005; Choban et al., 2005; Jayashree et al., 2006), formic acid (Sun et al., 2007; Li et al., 2007; Choban et al., 2004; Cohen et al., 2005, Jayashree et al., 2005), hydrogen peroxide (Hasegawa et al., 2005), sodium perborate (Ponmani et al., 2014), sodium percarbonate (Ponmani et al., 2014) and vanadium redox species (Ferrigno et al., 2002) as fuel.

Table 1.1 provides relevant data on alternative fuels and their theoretical energy densities. These fuels are known to exhibit higher volumetric and gravimetric energy densities than batteries.
<table>
<thead>
<tr>
<th>Fuel</th>
<th>Gravimetric energy density (Wh Kg(^{-1}))</th>
<th>Volumetric energy density (WhL(^{-1}))</th>
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</thead>
<tbody>
<tr>
<td>Formic acid</td>
<td>2086</td>
<td>1710</td>
</tr>
<tr>
<td>Sodium borohydride</td>
<td>2925</td>
<td>2840</td>
</tr>
<tr>
<td>Methanol</td>
<td>4690</td>
<td>6400</td>
</tr>
<tr>
<td>Ethanol</td>
<td>6100</td>
<td>7850</td>
</tr>
</tbody>
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Most of these devices included a Y- or T-shaped microfluidic channel design featuring two aqueous co-laminar streams with the fuel and oxidant dissolved in a supporting electrolyte and electrodes on opposite channel walls, parallel to the inter diffusion zone. The power density of these fuel cells was predominantly restricted by the rate of mass transport to the active sites, typically in the cathodic half-cell, and the overall system performance suffered from low fuel utilization. The all-liquid feature of most microfluidic fuel cells enables the use of an external reference electrode to characterize the individual half-cells and measure the ohmic resistance \textit{in situ} during fuel cell operation. Using this experimental approach, the overall cathodic mass transport limitation of dissolved oxygen-based systems was unambiguously verified (Choban et al., 2005). For early devices involving the use of formic acid in the anodic stream and dissolved oxygen in the cathodic stream, the maximum power density levels achieved were limited to only about 0.2 mW cm\(^{-2}\) (Choban et al., 2004; Cohen et al., 2005), primarily constrained by the low solubility of oxygen in the aqueous electrolyte (2-4 mM). Similar power densities were obtained using dissolved hydrogen as fuel (Cohen et al., 2005). The combination of gaseous reactants and poly(dimethylsiloxane) (PDMS) material opens up an interesting opportunity for microfluidic fuel cell fabrication and design, due to the relatively high gas permeability of PDMS. This feature facilitates the gaseous reactant supply through thin layers of PDMS to a pair of electrodes separated by an
electrolyte channel (Mitrovski et al., 2004; Mitrovski et al., 2006). The power output of the
device (0.7 mW cm\(^{-2}\)) was restricted by the permeation rate of hydrogen through the polymer
and oxygen crossover.

Cohen et al., (2005) demonstrated that the open circuit potential of a hydrogen/oxygen
fuel cell could be raised well beyond the standard cell potential of 1.23 V by implementing an
alkaline dissolved hydrogen stream and an acidic dissolved oxygen stream in a co-laminar
microfluidic fuel cell. The media flexibility was also explored by Kenis’ group by operating a
methanol/oxygen fuel cell under all-acidic, all-alkaline, and mixed-media conditions (Choban
et al., 2005). Compared with the membrane-based fuel cells, the microfluidic fuel cell design
eliminated the problem of membrane clogging by the carbonates formed in the alkaline
media. The methanol/oxygen fuel cell produced a room-temperature peak power density of 5
mW cm\(^{-2}\) at 1.0 V cell voltage under mixed-media conditions (alkaline anolyte and acidic
catholyte), compared with 2.4 and 2.0 mW cm\(^{-2}\) for the all-acidic and all-alkaline conditions,
respectively. Operation under mixed-media conditions, however, caused exothermic
neutralization of OH\(^-\) and H\(^+\) at the co-laminar flow interface and a resultant reduction in
ionic strength. Hasegawa et al., (2005) used the mixed-media approach to operate a
microfluidic fuel cell on the hydrogen peroxide as both fuel and oxidant, in alkaline and
acidic media, respectively. This fuel cell produced relatively high power densities, but the
electrochemical reactions required net consumption of the supporting electrolyte, which
negatively affected both the overall energy density and cell resistance via reduced ionic
conductivity. An acidic hydrogen peroxide solution was also employed as the oxidant in a
laser-micromachined microfluidic fuel cell device (Li et al., 2007) with power densities up to
2 mW cm\(^{-2}\), partially restricted by instabilities caused by oxygen evolution from hydrogen
peroxide decomposition. Two methods have recently been proposed to stabilize the co-
laminar liquid-liquid interface; a liquid-liquid interface less susceptible to mixing was
provided by the magnetic techniques (Aogaki et al., 2007) or by adding a third stream containing a blank electrolyte to further separate the anolyte and catholyte streams (Sun et al., 2007).

One way to address the limitation of oxygen solubility is to integrate an air-breathing porous cathode structure that enables gaseous oxygen transport from the ambient air, a source of oxygen that has a significantly higher diffusivity and concentration than dissolved oxygen. Jayashree et al., (2005) introduced the first microfluidic fuel cell with an integrated air-breathing cathode, using a graphite plate anode covered with palladium black nanoparticles and a porous carbon paper cathode covered with platinum black nanoparticles. The air-breathing cell architecture required a blank cathodic electrolyte stream (without the dissolved oxidant) to provide sufficient separation between the interdiffusion zone and the cathode, and to facilitate ionic transport to the cathodic reaction sites. A peak power density of 26 mW cm$^{-2}$ was achieved with 1 M formic acid in a 0.5 M sulfuric acid anolyte and a blank 0.5 M sulfuric acid catholyte flowing at 0.3 mL min$^{-1}$ per stream. The air-breathing cell architecture was also evaluated using methanol (Jayashree et al., 2006), a fuel that facilitates higher overall energy density than formic acid. Despite the modest power densities obtained with 1 M methanol fuel (17 mW cm$^{-2}$), this study demonstrated significantly improved reaction kinetics for both methanol oxidation and oxygen reduction by switching from an acidic to an alkaline supporting electrolyte. The air-breathing cells also enabled significantly higher coulombic fuel utilization than the cells based on dissolved oxygen, up to a maximum 33% per single pass at 0.1 mL min$^{-1}$ (Jayashree et al., 2005). However, in the context of microfluidic fuel cells, the air-breathing feature reduces the flexibility of the scale-up by three-dimensional stacking of the individual cells, and requires a recirculation scheme to achieve practical fuel utilization and overall energy conversion efficiency.
The use of alternative oxidants with solubility at higher concentrations than the dissolved oxygen opens up another avenue towards improving the performance of typically mass-transfer limited microfluidic fuel cells. An all-vanadium microfluidic fuel cell design based on soluble vanadium redox species was introduced (Ferrigno et al., 2002). Vanadium redox fuel cells utilize two different aqueous vanadium redox couples, \( \text{V}_2^+/\text{V}_3^+ \) and \( \text{VO}_2^+/\text{VO}_2^+ \), as fuel and oxidant, respectively, dissolved in dilute sulfuric acid. This combination of redox pairs offers several advantages for microfluidic fuel cell operation: they provide well-balanced electrochemical half-cells in terms of reaction rates and transport characteristics; they have high solubility and enable relatively high redox concentrations; they have a large difference in formal redox potentials, resulting in a high open-circuit voltage (up to \( \sim 1.7 \text{ V at uniform pH} \)); and the reactions are facilitated by bare carbon electrodes without precious metal catalysts. Apart from the works presented in this thesis, the highest power density of the microfluidic fuel cells reported to date was 38 mW cm\(^{-2}\). This performance was achieved using the vanadium redox system at 1.5 mL min\(^{-1}\) flow rate (Ferrigno et al., 2002). The fuel utilization at this flow rate was, however, limited to \( \sim 0.1\% \), and the energy density of such a fuel cell system would ultimately be limited by the solubility of the vanadium redox species.

Mathematical and computational modeling is an important tool in the analysis of the transport phenomena and electrochemical reactions occurring inside a microfluidic fuel cell. This was first demonstrated by Bazylak et al. (2005) by using computational modeling to analyze microfluidic fuel cells having different cross-sectional channel geometries and electrode configurations. It was found that high aspect ratio (width/height) channel geometry with the electrodes placed orthogonally to the co-laminar flow interface on the top and bottom walls would significantly improve the fuel utilization and reduce the inter-diffusional mixing width. A similar computational model was developed by Chang et al. (2006); Chen et
al., (2007), extended with the Butler-Volmer electrochemical reaction kinetics, with the capacity to predict complete polarization curves. The results obtained for a dissolved oxygen-based cell confirmed the cathodic mass transport limitation and they recommended high aspect ratio channels or a thicker cathode catalyst layer to improve the performance. This work was complemented by an in-depth theoretical study of the cathode kinetics of the same fuel cell (Chen et al., 2006), and a Butler-Volmer model of the hydrogen peroxide fuel cell (Chen et al., 2007). No modeling efforts to date have been applied to the air-breathing microfluidic fuel cell architecture or the vanadium redox system.

Overall, the development of co-laminar microfluidic fuel cells to date has been remarkable, given that it is a relatively new invention. Research thus far has resulted in operational devices giving promising performances in terms of power density and open circuit voltage, but little has been done in order to design practical, efficient and competitive devices with high energy density and high fuel utilization. The most prominent constraint identified for the current microfluidic fuel cells is their low energy density, defined as the energy output per system volume or mass. The core physics of the co-laminar flow configuration requires that both streams are liquid and that they contain an electrolyte.

Although reactants may be added to the system in high concentrations, the energy density of all the devices presented thus far has been low compared with the other microstructured fuel cells due to the impractical single-pass use of the liquid electrolyte without any type of recirculation or recycling. Incorporation of a recirculation system for the electrolyte becomes a challenge due to space constraints and the inevitable mixing/contamination issues. Moreover, although fuel utilization data (excluding the present work) up to 33% per single pass have been presented, the fuel utilization at practical flow rates and useful cell voltages has generally fallen below 10%. Besides, there is a paucity of engineering solutions for important functions such as the integration of fuel and oxidant
storage, waste handling, and low-power microfluidics based fluid delivery (normally driven by a syringe pump via external tubing) using integrated micropumps and microvalves.

The power output of a single planar microfluidic fuel cell is inadequate for most practical applications. The feasibility of enlarging a single planar cell, i.e. increasing the geometrical area of the electrodes and microchannel, is limited by structural constraints, increased crossover, and increased ohmic losses if the average distance between the anodic and cathodic active sites becomes great. In order to produce adequate power, multiple independent planar cells could be accommodated on a single plane and stacked, as done in the typical PEM fuel cells. The volumetric power density of such devices would, however, be limited by the volume of the sealing and structural elements separating the cells. In traditional PEM fuel cell stacks, which are limited by similar issues (Chen et al., 2007), the bi-polar plates serve as structural and electrical components. The intrinsic advantage of non-planar electrode–electrolyte interfaces has been recognized and demonstrated for such cells using, for example, waved membrane-electrode assemblies (Chen et al., 2007). In contrast, the microfluidic fuel cells presented to date contain mostly nonparticipating structural material such as glass or PDMS. The scale-up of microfluidic fuel cell technology in a volumetrically efficient manner continues to remain a challenge.

1.3 Membraneless Methanol Fuel Cell (MLMFC)

In the present study, the fabrication and performance of MLMFC was evaluated using laminar flow-based configuration that fulfills the aforementioned requirements. In this type of membraneless fuel cell, methanol is used as the fuel, sodium perborate as the oxidant, and sulfuric acid as the electrolyte. Sodium percarbonate ($2\text{Na}_2\text{CO}_3\cdot3\text{H}_2\text{O}_2$) is a cheap, environment friendly, nontoxic, and large-scale industrial chemical, primarily used as a source of “active oxygen” in detergents and as a mild antiseptic. In the crystalline state,
sodium percarbonate exists as a dimeric peroxo-salt with the water of hydration; but, in an aqueous solution, it affords hydrogen peroxide (Cotton et al., 1988; Karunakaran et al., 1991; 1995; 2000; McKillop et al., 2000; Karunakaran et al., 2002; Ponmani et al., 2014; Arun et al., 2014; Gowdhamamoorthi et al., 2014), commercially, industrially, as well as in the laboratory, as demonstrated in Eq. (1.1) below:

\[
2\text{Na}_2\text{CO}_3.3\text{H}_2\text{O}_2 \rightarrow 2\text{Na}_2\text{CO}_3 + 3\text{H}_2\text{O}_2 \quad (1.1)
\]

The byproduct was completely innocuous, and this stable and easily handled crystalline substance was used as an oxidant in our MLMFC.

Methanol is considered as one of the most promising combustible materials used in fuel cells, because of its high-energy storage (5,019 A h Kg\(^{-1}\)), low toxicity, large-scale production from biomass, easy storage and transportation, and facile electro-oxidation on Pt catalyst. Methanol is renewable, and its complete oxidation to CO\(_2\) and H\(_2\)O produces a high yield of 6 electrons per molecule in acid electrolyte, as shown in Eq. (1.2) below:

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \quad (1.2)
\]

However, methanol electro-oxidation on pure platinum encounters several problems such as the difficulties in adsorption and dehydrogenation of the methanol molecule and the formation of CO-intermediates that poisons the Pt anode catalysts. The slow kinetics of the methanol electro-oxidation reaction (MOR) on Pt anode diminishes the overall performance of the MLMFC system.
1.4 Methanol Electro-Oxidation on Pt and Pt-Based Alloy Catalysts

Platinum was initially used as an electrocatalyst in the anode, as it was known to be the best electrocatalyst for the electro-oxidation of methanol. A detailed mechanism was proposed for oxidation of methanol at Pt electrodes, where M represents an alloying component or promoter metal (Beden et al., 1992; Freelink et al., 1995; Ley et al., 1997; Gurau et al., 1998; Kua et al., 1999), as in the following equations:

\[
\text{Pt} + \text{CH}_3\text{OH} \rightarrow \text{Pt}-(\text{CH}_3\text{OH})_{\text{ads}} \quad (1.3)
\]

\[
\text{Pt}-(\text{CH}_3\text{OH})_{\text{ads}} \rightarrow \text{Pt}-(\text{CH}_3\text{O})_{\text{ads}} + \text{H}^+ + e^- \quad (1.4a)
\]

\[
\text{Pt}-(\text{CH}_3\text{O})_{\text{ads}} \rightarrow \text{Pt}-(\text{CHO})_{\text{ads}} + \text{H}^+ + e^- \quad (1.4b)
\]

\[
\text{Pt}-(\text{CHO})_{\text{ads}} \rightarrow \text{Pt}-(\text{CO})_{\text{ads}} + \text{H}^+ + e^- \quad (1.4c)
\]

\[
\text{Pt}-(\text{CO})_{\text{ads}} \rightarrow \text{Pt}-(\text{H}_2\text{O})_{\text{ads}} + \text{M} + \text{CO}_2 + \text{H}^+ + e^- \quad (1.7)
\]

However, methanol electro-oxidation on pure Pt is limited due to the carbon monoxide (CO) poisoning effect, which results in a substantial decrease in its activity.
Therefore, alloying of platinum with other metals such as Ru, Pd, Mo, Sn, Co, Cu, W, Os, and Ni (Xiong et al., 2002; Chan et al., 2004; Rivera et al., 2004) have been studied as a convenient method of modifying the electrocatalytic properties of platinum in order to reduce or avoid the poisoning effect. Among all the catalyst systems, Pt–Ru/C catalysts have received more attention due to its high CO tolerance, which can be achieved via its electronic effects and bifunctional mechanisms (Gasteiger et al., 1993; Yajima et al., 2004) that improves the catalytic activities of electrochemical reactions. Nevertheless, efforts are being made to improve the performance of Pt–Ru/C anode catalysts to a suitable level for successful commercialization.

1.4.1 Bifunctional Mechanism

The bifunctional mechanism was first postulated by Watanabe et al. (Watanabe et al. (1973; 1975), which involves facile water activation at the second metal (Ru or Sn) sites, thereby promoting the oxidation of CO\(_{\text{ads}}\) to CO\(_2\) by supplying oxygen-containing species at lower potentials. According to the bifunctional mechanism, methanol is dissociatively adsorbed on the Pt sites giving adsorbed CO\(_{\text{ads}}\) and/or formyl-like species—CHO\(_{\text{ads}}\); the ruthenium in Pt–Ru catalyst dissociates water into Ru–OH\(_{\text{ads}}\) and H on the surface of the catalyst and, then, the species adsorbed onto Pt and Ru sites combine to form CO\(_2\) (Watanabe et al., 1975; Swathirajan et al., 1991; Markovic et al., 2001; Gojkovic et al., 2003), as shown below:

\[
\text{Pt} + \text{CH}_3\text{OH}_{\text{solution}} \rightarrow \text{Pt–CH}_3\text{OH}_{\text{ads}} \rightarrow \text{Pt–COH}_{\text{ads}} + 3\text{H}^+ + 3e^- \quad (1.8a)
\]

\[
\text{Pt–COH}_{\text{ads}} + 3\text{H}^+ + 3e^- \rightarrow \text{Pt–CO}_{\text{ads}} + \text{H}^+ + e^- \quad (1.8b)
\]
Ru + H₂O → Ru–OH_ads + H⁺ + e⁻ \hspace{1cm} (1.9)

Pt–COH_ads + Ru–OH_ads → Pt + Ru + CO₂ + 2H⁺ + 2e⁻ \hspace{1cm} (1.10)

Pt–CO_ads + Ru–OH_ads → Pt + Ru + CO₂ + H⁺ + e⁻ \hspace{1cm} (1.11)

This bifunctional mechanism successfully explains several aspects of methanol and CO oxidation reactions on Pt–Ru.

1.4.2 Electronic (Ligand) Effect

According to the electronic effect, the presence of ruthenium changes the electronic structure of platinum such that it weakens the Pt–CO bond (Goodenough et al., 1988; Krausa et al., 1994; Lu et al., 2001). The weakening of the CO binding is assumed to promote easy CO removal. To explain this mechanism, Freelink et al. (1995; 1996) showed that the stretching frequency of the linearly bonded CO shifts to a higher value due to the changes in the CO binding strength to the surface that is induced by Ru through an electronic effect on Pt. The authors also showed that the Ru-oxide film is removed by reaction with methanol during its electro-oxidation, which confirms the bifunctional mechanism. So far, the experimental confirmation of these mechanisms has been indirect. There are no direct measurements either the influence of ruthenium on the binding energy of CO on platinum or about water activated on the Pt–Ru surface. Although the electronic effect in Pt–Ru appears to be less prominent (Frelink et al., 1995; Iwasita et al., 2000), the contribution of both the bifunctional and electronic effects of Pt–Ru on methanol oxidation reaction (MOR) has been postulated.
The Pt–Sn/C and Pt–Ru/C electrocatalysts’ performance also depends on the preparation procedures and their atomic ratios. Jiang et al., (2005) prepared the Pt–SnO₂ alloy by the polyol method, which inhibited the hydrogen adsorption/desorption process. Lamy et al., (2004) investigated ethanol oxidation using the carbon-supported Pt–Sn catalysts prepared by a co-impregnation reduction method and a modified polyol process. Bonnemann et al., (1994) developed a colloidal method to prepare unsupported and supported metals, which are then used to prepare carbon supported fully non-alloyed Pt–Sn catalysts. Cunha et al., synthesized the Pt–Ru–Sn/C trimetallic electrocatalysts for ethanol oxidation by the Pechini method (Cunha et al., 2011). Recently, Jarupuk Thepkaew et al., (2013) prepared the catalysts by co-reduction of the metal precursors in an aqueous domain of the lyotropic liquid crystalline phase of a nonionic surfactant. They studied the role of Ru and Sn in the mesoporous Pt–Ru and Pt–Ru–Sn alloys for the ethanol electro-oxidation reaction.

To further improve the Pt–Sn/C and Pt–Ru/C electrocatalyst activity, a third metal was introduced into their composition, which enhanced the dehydrogenation reaction and CO bond breakage during methanol oxidation. The main advantage of the introduction of the third metal is the reduction of the oxidation potential of the small organic molecules, coupled with the rise in current density. The enhanced activity of the ternary catalyst is due to the promoting effect of the second or third elements added to the Pt. Among the several ternary compositions tested, Pt–Sn–M and Pt–Ru–M (M = Ni; Ir and Rh) have repeatedly been reported to enhance the catalytic activity for MOR in Direct Methanol Fuel Cells (DMFCs) (Colmati et al., 2007). Following that, Pt–Sn–M and Pt–Ru–M have also been used in the Membraneless Methanol Fuel Cell (MLMFC) system, and were found to improve the catalytic activity for MOR. Therefore, this thesis focused on the enhancement of the catalytic activity for MOR by incorporating a third metal M (M = Ni, Ir and Rh) to the Pt–Sn/C and Pt–Ru/C catalysts under the MLMFC operating conditions. The steps involved in the

1.5 General Experimental Procedures

Prior research on the aspects of catalyst and electrode preparation in the membraneless fuel cells have focused mainly on the attempts to lower the catalyst loading, and improve catalyst utilization, identify the substitutes for platinum, and improve the diffusion of the reactants both in the diffusion layer of the electrode backing and in the layer of catalysts. All the research studies were aimed at improving the fuel cell performance. The performance of the fuel cell is determined by the voltage and current density that it produces. Different methods have been developed to prepare the Pt based electrocatalysts for fuel cell applications including chemical and physical methods (Lamy et al., 2012; Liu et al., 2006; Petrii et al., 2008; Bagkar et al., 2009). The chemical methods are regarded as the most suitable methods for the synthesis of the Pt based electrocatalysts due to their simplicity and ease of application on a large scale for the preparation of large quantities of catalysts. The objective of the current research in electrocatalyst preparation is the development of new methods for the cost-effective preparation of the highly active catalysts to overcome the cost effect imposed by the use of noble catalysts in the fuel cells and to enhance their commercialization. In this study, the most important and recent chemical methods utilized for the carbon supported electrocatalysts will be summarized with special emphasis on the catalysts for methanol electro-oxidation in membraneless fuel cells.
1.5.1 Alcohol Reduction Method

The alcohol reduction process is a very efficient means of preparing the electrocatalysts for membraneless ethanol fuel cells. Initially, the metal precursors are suspended in ethylene glycol and water (1/1 v/v), followed by the addition of the carbon support. Then the solution is made alkaline (about pH 12) and heated at 140°C for 3 h under agitation to enable the reduction of the metal. The chemical reduction is performed using the common reducing agents such as methanol, ethylene glycol and propanol.

1.5.2 Co-Impregnation Method

The co-impregnation method is the simplest and most straightforward approach; it is the most widely used method for catalyst preparation due to the simplicity of the steps involved and the utilization of relatively inexpensive reagents. It includes just two major steps – impregnation and reduction. The impregnation step involves dispersing the dissolved metal precursor onto the high-surface-area carbon in an aqueous solution to form homogeneous slurry. The chemical reduction is then performed using common reducing agents such as hydrazine and sodium borohydride.
1.5.3 Pechini Method

The Pechini method is based on the polymerization between ethylene glycol and citric acid (CA) in the presence of soluble metal – CA complexes. The essential steps involved in the Pechini method are as follows. Suitable metal precursors are introduced into the ethylene glycol after dissolution in citric acid, which is added in a great excess to form a metal-citrate complex. Then the temperature is increased to 60 – 120°C to speed up the polyester formation due to the reaction between the free citric acid and ethylene glycol. After the formation of the plastic-like gel, the temperature is further increased to remove the excess ethylene glycol. The resulting mixture is then treated at 400 – 450°C to oxidize the organic compounds. The resulting mixture thus obtained contains a mixture of homogeneously distributed metallic ions with appropriate stoichiometry.

1.5.4 Polyol Method

The polyol process is a technique in which a polyalcohol such as ethylene glycol is used both as solvent and reducing agent. In this method, the metal precursors are dissolved in ethylene glycol containing NaOH. The suspension is then exposed to microwave irradiation. The resulting mixture is treated with hydrochloric acid to induce the sedimentation of the as-synthesized electrocatalysts. A distinctive property of the polyol process is that it does not require any type of polymer stabilizer. Microwaves are electromagnetic waves. Dielectric materials in a microwave field will be heated by the amount proportional to the dielectric loss tangent, which defines the ability of a material to convert the electromagnetic energy into heat energy at a given frequency. The greatest advantage of microwave irradiation is that it can heat a substance uniformly through a glass or plastic reaction container, leading to a more homogeneous nucleation and shorter crystallization time compared with those for conventional heating. This ensures the formation of uniform metal colloids.
1.6 Analysis Techniques used for the Characterization

The characterization and manipulation of individual nanostructures require not only extreme sensitivity and accuracy, but also an atomic-level resolution. This leads to various microscopies that play a central role in the characterization and measurements of nanostructured materials. Although the techniques used depend upon the material type, and the information required, one is normally interested in first knowing the size, crystalline type, morphology, and composition. The different characterization techniques used for the electrocatalysts synthesized are described in detail below.

1.6.1 Physical Characterization

1.6.1.1 Powder X-Ray Diffraction Analysis

Powder X-ray Diffraction (XRD) analysis has been widely used as a primary characterization technique in nanomaterial research, for obtaining features like crystal structure, crystallite size, lattice constants, and strain. Information regarding the particle size distribution and mechanical stress can be inferred from an analysis of the width of the diffraction lines. Two main factors help to determine the powder XRD patterns, namely, (a) the size and shape of the unit cell and (b) the atomic number and position of the various atoms in the cell, because every crystalline material has its own characteristic powder pattern. In fact, this method is often otherwise referred to as the powder ‘fingerprint’ method. For diffraction, only short wavelength X-rays in the range of a few angstroms to 0.1 angstrom (1 KeV - 120 KeV) are used. As the wavelength of the X-rays is comparable to the size of atoms, they are ideally suited for probing the structural arrangement of the atoms and molecules in a wide range of materials. The XRD offers unparalleled accuracy in the measurement of atomic spacing, and is the technique of choice for determining the strain states in particles; however, monochromatic X-rays needed for diffraction must be produced.
XRD is based on the constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed towards the sample. Moreover, copper (Cu) is the most common target material for diffraction, with CuKα radiation = 1.5418Å (8 KeV). As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. Powder diffraction patterns are typically plotted as the intensity of the diffracted X-rays versus the angle 2θ. Peaks will appear in the diffraction pattern at 2θ values, when constructive interference is at the maximum, that is, when Bragg’s Law (2dsinθ = nλ) is satisfied. Experimentally obtained diffraction patterns of the sample are compared with the standard powder diffraction files published by the International Centre for Diffraction Data, Joint Committee Powder Diffraction Standards (Connolly et al., 2007).

The simplest and most widely used method for estimating crystallite size is from the Full Width at Half Maximum (FWHM, in radians) of a diffraction peak using the Debye-Scherrer Eq. 1.12 (Cullity et al., 1978; Radmilovic et al., 1995),

\[
d = \frac{0.9\lambda_{Kα}}{b_{2θ} \cos \theta_{max}}
\]  

(1.12)

where d is the average crystallite size, \( \theta_{max} \) is the angle at the position of the peak maximum, \( b_{2θ} \) is the FWHM (in radians), 0.9 is the shape factor for spherical crystallite, and \( \lambda_{Kα} \) is the wavelength of X-rays used. The lattice parameters of the catalysts were estimated according to Eq. 1.13 (Radmilovic et al., 1995),

\[
a = \frac{\sqrt{2} \lambda_{Kα}}{\sin \theta_{max}}
\]  

(1.13)
Where \( a \) is the lattice parameter (nm), and all the other symbols have the same meanings as in Eq. 1.12 (Beyhan et al., 2013). The size obtained from Scherrer’s formula yields the apparent or average particle size for a material. The crystal structure of the synthesized electrocatalysts was characterized by powder XRD using a Rigaku multiflex diffractometer (model RU-200 B), with a Cu-K\(_{\text{al}}\) radiation source (\( \lambda_{\text{K\text{al}}} = 1.5406 \text{ Å} \)) operating at room temperature, at IIT Madras, Chennai, India.

### 1.6.1.2 Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) is one of the most widely used techniques for the characterization of nanostructures. It provides information regarding the surface morphology and nanostructures of the materials. When the electron beam impinges on the samples, many types of signals are generated, and any of these can be displayed as an image. The two signals most often used to generate the SEM images are the Secondary Electrons (SE) and the Backscattered Electrons (BSE). The secondary electrons which are responsible for the topological contrast provide information mainly on the surface morphology. The backscattered electrons which are responsible for the atomic number contrast carry information on the composition of the samples (Oura et al., 2003). The electrons interact with the atoms that constitute the sample producing signals that contain information regarding the sample’s surface topography, composition and other properties such as electrical conductivity (Watt et al., 1997). This has many advantages such as, a large depth of field and higher resolution, which allows more of a particular sample to be in focus at one time, and hence can be magnified at much higher levels.

SEM studies of the electrocatalysts prepared in the present work have been conducted, using the SEM (ZEISS EVO 50 Scanning Electron Microscope), IIT, Chennai and
1.6.1.3 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) is one of the commonest techniques used to determine the actual size and shape of nanomaterials. The advantages of the TEM technique allow for the direct visualization of the sample and easily provide a direct measure of the morphology of the nanocrystals, including the size and shape of the particles, size distribution, self-assembly, as well as their crystal lattice spacing. From the image, the particle sizes can be determined by comparison with the scale bar; and the size distribution can be evaluated from a statistical measurement of hundreds of particles. During the preparation of the TEM specimen, a small amount of the prepared powder was dispersed in a few milliliters of solvent (ethanol or acetone) in an ultrasonic bath and ultrasonically treated for 30 minutes. Using an eye dropper, one drop of the resulting suspension was placed onto a carbon-coated copper grid. The samples were then oven dried in vacuum at ambient temperature before examination. The sample was then bombarded with a uniform electron beam, with an acceleration voltage ranging from 100 kV to 3 MV; based on the density of the material present, some of the electrons were scattered and disappeared from the beam. Samples with high density, such as metal and metal oxide, often generated images with a high degree of resolution and contrast (Okeefe et al., 1978). The compositional elements of the samples were performed by the Energy Dispersive X-ray spectrometer (EDX), mostly associated with the TEM analysis. The EDX was mainly used to accurately determine the composition of the sample under investigation. Upon exposing the samples to high energy electron beams the various atoms present in the samples emitted characteristic X-rays, observed as several distinct peaks on an energy scale, relative to the amounts of each atomic
species, from which an accurate composition of the sample could be determined (Lin et al., 1996).

TEM and EDX studies of the electrocatalysts prepared have been performed, using a Philips CM 12 Transmission Electron Microscope IIT, Chennai.

1.6.2 Electrochemical Characterization Methods

Electrochemical studies on the electrocatalysts were then conducted using the thin porous coating technique [8]. All the electrochemical measurements were performed on an electrochemical workstation (CH Instruments, model CHI6650, USA) interfaced with a personal computer using the CHI software, at room temperature. A common three-electrode electrochemical cell applying cyclic voltammetry (CV) and chronoamperometry (CA) techniques was used for the measurements.

1.6.2.1 Cyclic Voltammetry

Cyclic Voltammetry (CV) is an electrochemical technique used to study the basic characteristics of an electrochemical system, including the mechanism of electrode reactions and their kinetic behavior. In CV measurements, a three-electrode electrochemical cell setup is needed, in which three electrodes, namely the Working Electrode (WE), Reference Electrode (RE) and Counter Electrode (CE) are used. The WE is the electrode where the main electrochemical reaction occurs. The WE potential is controlled in reference to the RE and the current produced at the WE flows between the WE and CE, which is used as the indicator for the current. During the CV measurements, the working electrode potential is swept from an initial potential limit to a final potential limit and back to the initial potential while recording the current. The sweeping of the potential is performed linearly and the sweep rate can be controlled in a wide range. By plotting the current thus measured against the potential
applied, a voltammogram is obtained [94]. In electrocatalyst characterization, the CV is used for the determination of the Electrochemical Surface Area (ECSA) from the voltammogram of the catalyst in acid solution where the hydrogen adsorption and desorption regions are utilized for this purpose.

1.6.2.2 Chronoamperometry

In Chronoamperometry (CA) technique, the working electrode potential is fixed at a specific value at which an electrochemical reaction occurs. In EOR, by recording the current response versus time (I-t curve, chronoamperometric curve) at the specific potential, the catalytic activity of the catalysts at this potential can be determined. This technique is used in electrocatalyst research for EOR to check the catalyst stability at specific a potential and also to differentiate the catalytic activity of the different catalysts under identical conditions.

1.7 Single cell performance test

In MLMFC, the aqueous fuel and oxidant streams flow in parallel in a single microchannel with the anode and cathode on opposite sidewalls (Fig. 1.3). Then 0.1-cm thick graphite plates were used as the structures of current collection and catalyst support. The different anode and cathode catalysts were coated onto the graphite plates. For a single cell, the anode catalysts having different atomic ratios were prepared as follows: catalyst ink was prepared by mixing the required amount of catalyst in 50 mL of water containing three drops of 6% PTFE dispersion in an ultrasonic bath for 10 min to obtain uniform dispersion. The catalyst slurry was then spread onto the graphite plate by brushing, followed by drying at 100°C for 30 min to obtain the anode and cathode electrodes. The catalysts tested on the anode side were Pt–Sn–M and Pt–Ru–M (M = Ni, Ir and Rh) with a catalyst loading of 2 mg/cm². On the cathode side, Pt\textsubscript{100}/C with a catalyst loading of 2 mg/cm² was used in all the
experiments. The two catalyst-coated graphite plates were aligned to form a channel with 0.1 cm electrode-to-electrode distance (width), at 3-cm length and 0.1-cm height. The anolyte (fuel and electrolyte) and catholyte (oxidant and electrolyte) streams flowed in a laminar fashion over the anode and cathode, respectively. The electrode area along the microchannel wall between the inlets and the outlet (3-cm long and 0.1 cm wide) was used as the geometric surface area of the electrodes in this study (0.3 cm$^2$). The design has been described in detail elsewhere (Choban et al., 2004; Jayashree et al., 2010). The anolyte used in the anode side was 1.0 M methanol + 0.5 M H$_2$SO$_4$ and the catholyte used in the cathode side was 0.1 M percarbonate + 0.5 M H$_2$SO$_4$. The flow rate of each of the streams was 0.3 mL min$^{-1}$ (total flow rate of 0.6 mL min$^{-1}$). The MLMFC was operated at room temperature. The current-voltage characteristics of MLMFC were measured on an electrochemical workstation and the data verified using a multi-meter (MASTECH® MAS830L).

Fig. 1.4 Schematic representation of the E-shaped membraneless laminar flow-based fuel cell with graphite plates molded with poly(dimethylsiloxane) (PDMS) and sealed with poly(methylmethacrylate) (PMMA)
1.8 Scope and Objective of the Work

Due to the slow kinetics of the methanol electro-oxidation reaction (MOR) on the Pt anode, which diminishes the overall performance of the membraneless methanol fuel cell (MLMFC) system, considerable efforts have been made to develop alternative anode electrocatalysts that offer high catalytic activity for the MOR. For example, the alloying of Pt with other elements such as Sn, Ru, Mo, Pd, Rh, W, Ni and Ir has been studied, and among them, Sn and Ru have shown the best catalytic effect on MOR. The second metal of the co-catalysts reveals a bifunctional mechanism and exerts a ligand effect. To further improve the Pt–Sn/C and Pt–Ru/C electrocatalyst activity, a third metal is introduced into their composition, which helps to enhance the dehydrogenation reaction and the CO bond breakage during ethanol oxidation. The main advantage of introducing the third metal is the reduction of the oxidation potential of the small organic molecules, coupled with an increase in the current density. The enhanced activity of the ternary catalyst is due to the promoting effect of the second or third elements added to Pt. Among the number of ternary compositions tested, Pt–Sn–M and Pt–Ru–M (M = Ni, Ir and Rh) have repeatedly been reported to have enhanced catalytic activity for MOR in direct methanol fuel cells (DMFCs). Following this Pt–Sn–M and Pt–Ru–M have also been used in the membraneless methanol fuel cell (MLMFC) system, and were found to improve the catalytic activity for MOR. Therefore, the present study focused upon the enhancement of the catalytic activity for MOR by incorporating a third metal M (M = Ni, Ir and Rh) to the Pt–Sn/C and Pt–Ru/C catalysts.

The steps involved in the synthesis of the electrocatalysts (Pt–Sn–Ru/C, Pt–Sn–Ni/C, Pt–Ru–Ni/C, Pt–Sn–Ir/C, Pt–Ru–Ir/C, Pt–Sn–Rh/C, and Pt–Ru–Rh/C), and the effect of the third metal M on the enhanced catalytic activity of Pt–Sn–M and Pt–Ru–M as well as the physicochemical characterization techniques in terms of composition, morphology, and crystal structure were studied by using energy dispersive X-ray spectroscopy (EDX),
scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray
diffractometry (XRD) while the electrochemical analyses of cyclic voltammetry (CV), and
chronoamperometry (CA) were done to evaluate the performance of the electrocatalysts on
methanol electro-oxidation.

References


