CHAPTER 1

Introduction

1.1 Energy: A Grand Challenge in the 21st Century

Energy is the vital component of today’s society and economy. The growing concerns about global warming, climate change, environmental pollution, as well as global energy crisis have urged human beings to develop environmentally friendly technologies for renewable energy storage and conversion. Traditional energy generation methods such as combustion of fossil fuels, oil, coal, and gas are problematic as these resources are limited and there is a growing gap between their increasing demand and shrinking supply. The glory of these “Modern Times” will be gone in the next 40 years! Although we can use coal and natural gas to cover the gap left behind by the reduced supply of oil, it is only a matter of time by when all the fossil resources would be exhausted (The CIA World Factbook, 2014). The technologies employed, despite their advanced development, are inefficient, which has significantly contributed to acid rain and greenhouse gas emissions. Although inadequate, these technologies have been continued to be used for the simple reason of absence of any alternative suitable in terms of cost, scale, and availability, without collapsing the ecosystems. Because we depend on our ecosystem for sustenance, this has become a major concern for the government, industry, and even individuals. This concern has brought about the development of a range of “alternative” clean, renewable energy technologies such as solar, photovoltaic, and wind energy sources. However, these sources alone are not sufficient due to their inherently variable output, remoteness of prime locations, and the difficulty in operation and high cost incurred in their storage and transportation. The need of the hour is a technology or a combination of technologies that allow the supply of clean and cost-effective energy on a large scale, at the location of choice. One emerging and promising technology
that can meet this demand is the fuel cell, which is an electrochemical device that converts hydrogen and oxygen into electricity without combustion (Ndungu et al., 2008).

1.2 Fuel Cells: A Clean Electrical Energy Technology

Fuel cell is considered as one of the most promising products of the 21st Century, as it can compete (in terms of efficiency) with batteries, internal combustion engines, and power grids. Besides being efficient, clean, and compatible with future energy sources, fuel cell also offers several additional advantages for both mobile and stationary applications. Fuel cell is an electrochemical device with no moving components, except for the peripheral compressors and motors. As a result, its operation is extremely smooth and essentially without vibration and noise, which makes it an attractive device that can be installed at the client’s premises to eliminate power transmission lines. Its inherent modularity allows for simple construction and operation, with possible applications for distributed and portable power generation, as it can be made in variable sizes ranging from a few-watts to megawatt-scale plant with equal efficiency. Its high efficiency represents less chemical, thermal, and carbon dioxide gas emissions for the same amount of energy conversion and power generation as with the traditional energy sources.

Presently, more than 2500 fuel cells have been installed across the world for stationary applications such as hospitals, hotels, schools, telecommunication offices, utility power plants, as well as for portable applications such as mobile phones and laptops. There exists a variety of fuel cells that can be classified based on the choice of electrolyte and fuel (Kirubakaran et al., 2009). Presently, the following six major fuel cell technologies exist at varying stages of development and commercialization:

i) Proton exchange membrane fuel cells (PEMFC)
   a) Direct formic acid fuel cells (DFAFC)
b) Direct ethanol fuel cells (DEFC)

c) Direct methanol fuel cells (DMFC)

ii) Alkaline fuel cells (AFC)

a) Proton ceramic fuel cells (PCFC)

b) Direct borohydride fuel cells (DBFC)

iii) Phosphoric acid fuel cells (PAFC)

iv) Molten carbonate fuel cells (MCFC)

v) Solid oxide fuel cells (SOFC)

vi) Microfluidic membraneless fuel cells (MLFC)

These fuel cells are further classified on the basis of their operating temperature. The low operating temperature is in the range of 50–250°C for PEMFC, AFC, and PAFC and high operating temperature in the range of 650–1000°C for MCFC and SOFC.

The PEMFC uses a solid polymer electrolyte (Teflon-like membrane) to exchange the ions between two porous electrodes, which is an excellent conductor of protons and an insulator for electrons. In DFAFC, formic acid does not crossover the polymer; as a result, the efficiency of the concentration is higher (20–40%) than that for methanol (6%). However, this technology was not considered formerly due to the high electrochemical over voltage required under the loading conditions by the use of platinum as a catalyst. The DEFC comes under the sub-category of PEMFC due to the use of Nafion catalyst-like PEMFC. The chemical reaction involved in DEFC is the same as that in PEMFC, except that it uses ethanol instead of hydrogen as a fuel.

AFC has the capability to reach 60–70% of efficiency. It uses an aqueous solution of potassium hydroxide (KOH) as an electrolyte, and transports negative charged ions from anode to cathode and releases water as its byproduct. The major disadvantage involved in
AFC is that it is extremely sensitive to CO₂ as it takes more time to react and consumes the alkaline in the electrolyte, thereby reducing the concentration of hydroxide ion during the chemical reaction (Farooque et al., 2001; Fuel cell handbook 2004). PCFC is a relatively new fuel cell type that is developed basically with the ceramic electrolyte material. In addition, it has solid electrolyte, so the membrane does not dry out (as with PEMFCs) and its liquid does not leak (as with PAFCs). However, its major drawback is its low current density that can be increased by reducing the electrolyte thickness, improved conductivity, and optimized use of electrodes. The DBFC has major advantages such as higher power density, no need of expensive platinum catalyst, and high open circuit cell voltage (approximately 1.64 V). However, the efficiency is low as 35%; therefore, the research was focused on increased efficiency with minimized borohydride hydrolysis reaction with different catalysts such as Au, Ni, or Pd instead of Pt (Jamard et al., 2009).

PAFC is extremely tolerant to impurities in the reformed hydrocarbon fuels. The chemical reaction involved in this fuel cell is the same as that involved in PEMFC, where pure hydrogen is used as fuel (Farooque et al., 2001). The drawback of PAFC is the same as that of PEMFC; its cost also increases due to the use of platinum as a catalyst.

MCFC has the major advantages of higher efficiency of 50–60%, with no need of metal catalyst and a separate reformer due to its high operating temperature (Farooque et al., 2001). The main drawback of MCFC is its intolerance to sulfur and a slow start-up.

SOFC also has the major advantages of higher efficiency as 50–60%; moreover, a separate reformer is not required to extract hydrogen from the fuel due to its internal reforming capability. The slow start-up, high cost, and intolerance to sulfur content of the fuel cell are some of its drawbacks.

The DMFC technology is relatively new as compared to the rest of the fuel cells. Similar to PEMFC, the DMFC also uses polymer electrolyte, except that it uses liquid
methanol or alcohol instead of reformed hydrogen fuel as fuel. During chemical reactions, the anode draws hydrogen by dissolving liquid methanol (CH₃OH) in water in order to eliminate the need for an external reformer. At the cathode, the recombination of positive ions and negative ions occurs, which are supplied from the anode through the external circuit and then combined with oxidized air to produce water as the byproduct. One of the main advantages of this cell is that the anode catalyst itself draws the hydrogen from the methanol and reduces the overall cost due to the absence of reformer. However, their performance is limited by two important factors including crossover of methanol from the anode to cathode, which lowers the system efficiency and the slow kinetics of the electrochemical oxidation of methanol at the anode (Garcia et al., 2004).

The optimal selection of the size of the fuel cell is important to locate the fuel cell in a distributed system in order to meet the peak load demands for different applications of utilities (Canha et al., 2002). Thus, recently, there has been a rapidly growing demand for miniaturized power sources for portable electronic telecommunication and computing devices such as mobile phones, personal digital assistants, and laptops. Among the existing fuel cell types, one class of miniaturized power supply is that of microfluidic fuel cells, which are also known as laminar flow-based fuel cells or membraneless fuel cells. Hence, in this thesis, we have focused on the microfluidic membraneless fuel cells.

1.3 Microfluidic Fuel Cells: A Prospective Power Source for Portable Devices

With the success of laptop computers, mobile phones, and other portable devices, the demand for portable power sources have also increased. Battery technology cannot seem to keep pace with the development and the power demands of new devices. The size and growth rate of the portable power market has inspired research into newer power sources. Toward this, a promising approach is to scale down the microfluidic fuel cell technology (Carrette et
A membraneless microfluidic fuel cell is a device in which two aqueous streams flow laminarly in the absence of a physical membrane without turbulent mixing (Choban et al., 2005). Some microfluidic fuel cells are 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 confined to a microfluidic channel (Kjeang et al., 2009), the microfluidic fuel cell operates without any physical barrier such as a membrane separating the anode and the cathode, and it 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 alongside and down a single microfluidic channel (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 two streams occurs solely by transverse diffusion and is restricted to an interfacial width at the channel center. The mixing width can be controlled by modification of the channel dimensions and the flow rate (Ismagilov et al., 2000). Here, the electrodes were integrated on the walls of the manifold at 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.

Use of membraneless microfuel cell eliminates several technical issues related to the use of PEMFCs such as fuel crossover (Carrette et al., 2000), membrane degradation, a longer startup time, ohmic losses, size, fabrication, and limited durability of catalysts in water management (Eikerling et al., 2001). Moreover, the microfluidic fuel cell apparently demonstrates several advantages over PEMFC: it eliminates fouling problems due to the membrane, offers easier fabrication, and allows significant reduction in the size of the fuel cell. However, the practical applications of a microfluidic fuel cell is mainly dependent on the diffusion across the interface between the liquid streams (also called formation of depletion boundary layers) (Fig. 1.2) as well as poor fuel utilization. However, the most prominent benefit of the microfluidic fuel cells is the significant economic advantage associated with its use.
These fuel cells can be manufactured using inexpensive, well-established micromachining and microfabrication methods that would eliminate the membrane costs associated with most other fuel cells. In addition, as the microfluidic fuel cells are normally operated at the room temperature, they do not require auxiliary humidification 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.

1.3.1 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 exhibit higher volumetric and gravimetric energy densities than batteries.

Table 1.1 Summary of the theoretical energy densities for different fuels

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Gravimetric Energy Density (Wh kg(^{-1}))</th>
<th>Volumetric Energy Density (Wh L(^{-1}))</th>
</tr>
</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>
</table>

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 the 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 to measure the ohmic resistance 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 approximately 0.2 mW cm\(^{-2}\) (Choban et al., 2004; Cohen et al., 2005), which were primarily constrained by the low solubility of oxygen in the aqueous electrolyte (2–4 mM). Similar power densities were...
obtained with the use of dissolved hydrogen as fuel (Cohen et al., 2005). The combination of gaseous reactants and poly(dimethylsiloxane) (PDMS) material presents an interesting opportunity for microfluidic fuel cell fabrication and design, due to the relatively high gas permeability of PDMS. This advantageous 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 permeation rate of hydrogen through the polymer and oxygen crossover restricted the power output of the device (0.7 mW cm$^{-2}$).

Cohen et al. (2005) demonstrated that the open circuit potential of a hydrogen/oxygen fuel cell can 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. Kenis’ group explored the media flexibility by operating a methanol/oxygen fuel cell under all acidic, all alkaline, and mixed media configurations (Choban et al., 2005). Compared with the membrane-based fuel cells, the microfluidic fuel cell design does not have 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) in comparison 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 the 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 a 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 due to 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 of up to 2 mW cm$^{-2}$, which were partially restricted by instabilities caused by oxygen evolution from hydrogen peroxide decomposition. Two methods were recently 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 of 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, which is a source of oxygen with significantly higher diffusivity and concentration than dissolved oxygen. Jayashree et al. (2005) introduced the first-ever microfluidic fuel cell with an integrated air-breathing cathode by 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 dissolved oxidant) to provide sufficient separation between the interdiffusion zone and the cathode and to facilitate ionic transport to the cathodic reaction sites. As a result, 1 M formic acid in a 0.5 M sulfuric acid anolyte achieved a peak power density of 26 mW cm$^{-2}$ 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 with methanol (Jayashree et al., 2006), which 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 showed significantly higher coulombic fuel utilization than the cells based on dissolved oxygen, up to a maximum of 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 presents another avenue toward improving the performance of typically mass-transfer limited microfluidic fuel cells. Accordingly, 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, $V_2^+/V_3^{2+}$ and $VO_2^{+/VO_2^{+}}$, as fuel and oxidant, respectively, dissolved in dilute sulfuric acid. This combination of redox pairs offers several advantages for microfluidic fuel cell operations. Thus, 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, which results in a high open-circuit voltage (up to approximately 1.7 V at uniform pH); and the reactions were facilitated by bare carbon electrodes without precious metal catalysts. Moreover, the highest power density of the microfluidic fuel cells reported until date is 38 mW cm$^{-2}$. Vanadium redox system performed similarly at 1.5 mL min$^{-1}$ flow rate (Ferrigno et al., 2002). The fuel utilization at this flow rate was, however, limited to approximately 0.1%, and the solubility of the vanadium redox species may ultimately limit the energy density of such a fuel cell system.

Mathematical and computational modeling is an important tool in the analysis of the transport phenomena and electrochemical reactions occurring inside a microfluidic fuel cell. Bazylak et al. (2005) first demonstrated the computational modeling to analyze microfluidic fuel cells with different cross-sectional channel geometries and electrode configurations. High aspect ratio (width/height) channel geometry with the electrodes placed orthogonally to
the co-laminar flow interface on the top and bottom walls were found to significantly improve the fuel utilization and reduce the inter-diffusional mixing width. A similar computational model developed by Chang et al. (2006) and Chen et al. (2007) was 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, recommending high aspect ratio channels or a thicker cathode catalyst layer to improve the performance. The results of the present 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). The air-breathing microfluidic fuel cell architecture or the vanadium redox system developed until date involves no modeling efforts.

Overall, the development of co-laminar microfluidic fuel cells has been remarkable, considering that it is a relatively new invention. Research thus far has resulted in the development of operational devices with promising performances in terms of power density and open circuit voltage, but little efforts has been made to design practical, efficient, and competitive devices with high-energy density and greater fuel utilization efficiency. 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 the streams be liquid and 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 as compared with the other microstructured fuel cells, owing 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 is challenging due to the space constraints and the inevitable mixing/contamination issues. Moreover, although fuel utilization data (excluding those in the
present work) exhibits up to 33% per single pass, the fuel utilization at practical flow rates and useful cell voltages has generally declined to <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) by using integrated micropumps and microvalves.

The power output of a single planar microfluidic fuel cell is inadequate for most practical applications. The structural constraints, increased crossover, and increased ohmic losses when the average distance between the anodic and cathodic active sites increases are the limits of the feasibility of enlarging a single planar cell, that is, increasing the geometrical area of the electrodes and microchannel. In order to produce adequate power, multiple independent planar cells could be accommodated on a single plane and stacked, as 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 until date contain mostly nonparticipating structural material such as glass or PDMS. Thus, the scale-up of microfluidic fuel cell technology in a volumetrically efficient manner continues to remain a challenge.

1.4 Membraneless Methanol Fuel Cell (MLMFC): A Promising Liquid Fuel Cell

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 perborate (NaBO$_3$.4H$_2$O) 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. It is a peroxo-salt with an anionic formula of B$_2$(O$_2$)$_3$(OH)$_2$$. In the crystalline state, sodium perborate 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:

\[
[B(OH)_3(O_2H)]^+ + H^+ \rightarrow [B(OH)_3] + H_2O_2
\]  

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:

\[
CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-
\]  

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.

1.5 Methanol Electro-Oxidation on Pt and Pt-Based Alloy Catalysts: A Novel Mechanism

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:

\[
\begin{align*}
\text{Pt} + \text{CH}_3\text{OH} & \rightarrow \text{Pt}-(\text{CH}_3\text{OH})_{\text{ads}} \quad (1.3) \\
\text{Pt}-(\text{CH}_3\text{OH})_{\text{ads}} & \rightarrow \text{Pt}-(\text{CH}_3\text{O})_{\text{ads}} + \text{H}^+ + \text{e}^- \quad (1.4a) \\
\text{Pt}-(\text{CH}_3\text{O})_{\text{ads}} & \rightarrow \text{Pt}-(\text{CH}_2\text{O})_{\text{ads}} + \text{H}^+ + \text{e}^- \quad (1.4b) \\
\text{Pt}-(\text{CH}_2\text{O})_{\text{ads}} & \rightarrow \text{Pt}-(\text{CHO})_{\text{ads}} + \text{H}^+ + \text{e}^- \quad (1.4c) \\
\text{Pt}-(\text{CHO})_{\text{ads}} & \rightarrow \text{Pt}-(\text{CO})_{\text{ads}} + \text{H}^+ + \text{e}^- \quad (1.4d) \\
\text{M} + \text{H}_2\text{O} & \rightarrow \text{M}-(\text{H}_2\text{O})_{\text{ads}} \quad (1.5) \\
\text{M}-(\text{H}_2\text{O})_{\text{ads}} & \rightarrow \text{M}-(\text{OH})_{\text{ads}} + \text{H}^+ + \text{e}^- \quad (1.6)
\end{align*}
\]
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.

1.5.1 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:

$$\text{Pt}-(\text{CO})_{\text{ads}} + M-(\text{OH})_{\text{ads}} \rightarrow \text{Pt} + M + \text{CO}_2 + H^+ + e^- \quad (1.7)$$
\[
\text{Pt} + \text{CH}_3\text{OH}_{\text{solution}} \rightarrow \text{Pt–CH}_3\text{OH}_{\text{ads}} \rightarrow \text{Pt–COH}_{\text{ads}} + 3\text{H}^+ + 3e^- \quad (1.8a)
\]

\[
\text{Pt–COH}_{\text{ads}} + 3\text{H}^+ + 3e^- \rightarrow \text{Pt–CO}_{\text{ads}} + \text{H}^+ + e^- \quad (1.8b)
\]

\[
\text{Ru} + \text{H}_2\text{O} \rightarrow \text{Ru–OH}_{\text{ads}} + \text{H}^+ + e^- \quad (1.9)
\]

\[
\text{Pt–COH}_{\text{ads}} + \text{Ru–OH}_{\text{ads}} \rightarrow \text{Pt} + \text{Ru} + \text{CO}_2 + 2\text{H}^+ + 2e^- \quad (1.10)
\]

\[
\text{Pt–CO}_{\text{ads}} + \text{Ru–OH}_{\text{ads}} \rightarrow \text{Pt} + \text{Ru} + \text{CO}_2 + \text{H}^+ + e^- \quad (1.11)
\]

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

### 1.5.2 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 performance of Pt–Ru/C electrocatalysts also depends on the preparation procedures and their atomic ratios. Bonnemann et al. (1994) developed a colloidal method to prepare unsupported and supported metals, which were then used to prepare carbon-supported fully non-alloyed, Pt–Sn catalysts. Salazar-Banda et al. (2006) prepared boron-doped diamond surfaces for methanol and ethanol electro-oxidation in an acidic medium by the Sol-gel method. Neto et al. (2007) investigated the electro-oxidation of methanol and ethanol with Pt–Ru ternary alloy catalysts prepared via an alcohol-reduction process using ethylene glycol as the solvent and reduction agent. Recently, Chen et al. (2014) prepared a Pt–Ru ternary alloy by the sodium borohydride (NaBH₄)-reduction method to compare the study of tungsten-modified Pt–Ru electrocatalysts for methanol oxidation.

Nevertheless, the performance of Pt–Ru anode catalysts of fuel cells needs to be optimized to enhance the catalytic activity, which can be achieved by the introduction of a third element into the Pt–Ru bimetallic nanocatalysts. The enhanced activity of these catalysts can be attributed to the promoting effect of the second or third elements added to Pt. Among the numbers of ternary compositions tested, Pt–Ru–M/C ternary catalysts play a vital role in the electro-oxidation of methanol. Therefore, this thesis was focused on the enhancement of the catalytic activity for MOR by incorporating a third metal M (M = Ni, Os, W, Rh, Sn, Co, Mo) into the Pt–Ru/C catalysts. The steps of synthesis and characterization of the electrocatalysts (Pt–Ru–Ni/C, Pt–Ru–Os/C, Pt–Ru–W/C, Pt–Ru–Rh/C, Pt–Ru–Sn/C, Pt–Ru–Co/C, and Pt–Ru–Mo/C) as well as the effect of the third metal M on the enhanced catalytic activity of Pt–Ru/C have been presented in this study.
The present thesis comprises of 10 chapters that have been briefly summarized below. Here, we have focused on maximizing the cell performance in terms of power density and fuel utilization by tailoring various structural and operational parameters in the presence of electrocatalysts, including absolute flow rate, electrode-to-electrode distance, and the concentration effect of fuel and oxidant along with the mode of delivery.

1.6 Nanostructured Electro-catalysts: Great Opportunities to Improve Fuel Cell Performance

Efficient electro-catalytic reactions are essential for a fuel cell. In the electro-catalytic reaction, the surface of the electro-catalyst plays a crucial role, as it is the place where all the chemical reactions occur, including adsorption, dissociation, electron and atom transportation, and chemical bond cleavage and formation. All of these steps are directly related to the efficiency and power generation capability of the fuel cell. In early years, the investigation of electro-catalytic reaction was mainly focused on the model surfaces, usually atomically clean single crystals (Markovic et al., 1995; 1996; 2001; 2002; Savinova et al., 1997; Jerkiewicz et al., 1998; Chen et al., 1999; Climent et al., 2000; Tripkovic et al., 2001). However, due to the low specific surface area of single crystals, large gap between ultra-vacuum and ambient pressure, and the huge differences between single crystals and real-world polycrystals, these studies have remained mostly theoretical with little practical application of fuel cells.

Recently, the advancement in nanoscience and nanotechnology, especially the precise morphology-controlled nano-material preparations, has heralded the electro-catalysis into the new world at the “bottom” of substances. The specific surface area greatly increases as the catalyst size shrinks into the nanoscale. For example, for a round-shaped catalyst, the specific surface area increases 100 times when its diameter reduces from 1 μm to 10 nm. Considering
the high prices of precious metals, the use of nanoscaled catalyst can greatly reduce the cost of precious metal catalysts.

Nano-catalysts are more attractive due to their unique electronic and physical properties, which are totally different from the bulk-scaled materials. Electro-catalysis is a catalytic process, in which the charge (electrons) is transferred through the catalyst surface. In this process, the dangling bonds on the catalyst surface are more active and are of unique importance in the activation of the electro-chemical reactions. When the size of the catalysts shrink to the nanoscale level, the abundance of surface defects and the large surface curvature leads to an increase in the number of dangling bonds on the surface, which in turn results in higher catalytic activity.

In order to further improve the catalytic functions, the nanostructured catalyst can be further manipulated by employing a second or even a third element. In nanoscales, the local electronic structure can be modified by the addition of some foreign elements, which affects the adsorption-desorption energy of certain species at the active sites. Based on this so-called electronic effect theory, different bimetallic and trimetallic catalysts have been prepared and used widely in ORR (Markovic et al., 2001; Schmidt et al., 2002; Gonzalez et al., 2006; Yano et al., 2007; Wang et al., 2009; Jayasayee et al., 2012), alcohols (Zhou et al., 2003; 2004; Kowal et al., 2009), or organic acids oxidation (Kang et al., 2012; Lee et al., 2008; Chen et al., 2006; Choi et al., 2006; Chen et al., 2007; Winjobi et al., 2010).

1.7 Synthesis System and Typical Catalyst Preparation 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 ethanol electro-oxidation in membraneless fuel cells.

![Fig. 1.3 Schematics of the procedure for fabricating the catalyst layer on graphite plates](image)

**1.7.1 Conventional NaBH₄ Reduction Method**

A conventional NaBH₄ reduction method was used to synthesize ternary electrocatalysts for membraneless methanol fuel cells. The carbon black was ultrasonically
dispersed in a mixture of ultrapure water (Millipore MilliQ, 18 MΩ cm), and isopropyl alcohol for 20 min. The precursors were added to the ink and then mixed thoroughly for 15 min. The pH value of the ink was adjusted by NaOH solution to 8 and then raised its temperature to 80 °C. Twenty-five milliliters of 0.2 mol L⁻¹ solution of sodium borohydride was added into the ink drop by drop, and the bath was stirred for 1 h. The mixture was cooled, dried and washed repeatedly with deionized (DI) water until no Cl⁻ ions existed. The catalyst powder was dried for 3 h at 120 °C and stored in a vacuum vessel.

1.7.2 The 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.

1.7.3 Thermal Reduction Method

In thermal reduction method the carbon black was ultrasonically dispersed in a mixture of ultrapure water (Millipore MilliQ, 18 MΩ cm), and isopropyl alcohol for 20 min.
Then the precursors were added to the ink, and then mixed thoroughly for 20 min. The ink was dried with a magnetic stirrer at 60 °C. The dried compounds with carbon were put into a tube furnace and reduced at 400 °C with a gaseous mixture of H₂ and Ar with an atomic ratio of 1:9. The catalyst powder was stored in a vacuum vessel.

1.7.4 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.

1.7.5 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.

1.7.6 The 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.

### 1.7.7 The Bonnemann’s Method

The Bonnemann method was chosen as crystallite sizes between 1.5 and 2.5 nm can
be obtained, showing enhanced electrocatalytic activities due to their favorable surface-to-
bulk ratio. First NR4X (tetraalkylammonium-X) stabilized colloidal precursors (where X is
the electrocatalyst particle) were prepared via the reduction of metal precursors dissolved in
THF tetrahydrofuran. Then a suspension of Vulcan XC-72R carbon black (from Cabot
Corp.,) in ultrapure water (Millipore MilliQ, 18 MΩ cm), was impregnated with the
appropriate amount of the colloidal solution. Finally, thermal treatments were carried out in a
H₂ reducing atmosphere at 300°C for 120 min.

### 1.8 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.

1.8.1 Physical Characterization

1.8.1.1 Powder X-Ray Diffraction Analysis

Powder X-ray Diffraction (XRD) analysis has been widely used in nanomaterial research as a primary characterization technique, 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 X-ray diffraction patterns, viz., (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. X-ray diffraction 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 vs. the angle
Peaks will appear in the diffraction pattern at \(2\theta\) values, when constructive interference is at the maximum, that is, when Bragg’s Law \((2d\sin\theta = n\lambda)\) 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 (ICDD), Joint Committee Powder Diffraction Standards (JCPDS) (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’s Eq. 1.12 (Cullity et al., 1978; Radmilovic et al., 1995),

\[
d = \frac{0.9\lambda_{K\alpha}}{\beta_2\theta_{\text{max}} \cos \theta_{\text{max}}} \tag{1.12}
\]

where \(d\) is the average crystallite size, \(\theta_{\text{max}}\) is the angle at the position of the peak maximum, \(\beta_2\) is the FWHM (in radians), 0.9 is the shape factor for spherical crystallite and \(\lambda_{K\alpha}\) is the wavelength of X-rays used. The lattice parameters of the catalysts were estimated according to Eq. 1.13 (Radmilovic et al., 1995),

\[
a = \frac{\sqrt{2} \lambda_{K\alpha}}{\sin \theta_{\text{max}}} \tag{1.13}
\]

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 X-ray diffraction (XRD) using a Rigaku multiflex diffractometer (model RU-200 B) with a Cu-K\(_{\alpha}\) radiation source (\(\lambda_{K\alpha} = 1.5406\ A\)) operating at room temperature, at IIT-M, Chennai.
1.8.1.2 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-M, Chennai.

1.8.2 Electrochemical Characterization Methods

Electrochemical studies on the electrocatalysts were then conducted using the thin porous coating technique (Colmati et al., 2007). 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.

1.8.2.1 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. Catalyst coated glassy carbon electrode (GCE, 3 mm diameter and 0.071 cm² of electrode area, from CHI, USA) was used as the working electrode and platinum foil was used as the counter electrode. Ag/AgCl in saturated KCl was used as the reference electrode. The working electrode was prepared by applying catalyst ink made of 20 mg of electrocatalyst in a solution of 50 mL of ultrapure millipore water containing 1 mL of Nafion solution (5 wt.%). The resulting mixture was treated in an ultrasound bath for 10 min to obtain a uniform dispersion and a known volume (11.3 μL) of catalyst slurry was then drop-cast on to a glassy carbon electrode and allowed to dry at 100 °C for 30 min. The loading of metal on the working electrode was 0.28 mgmetal cm⁻². 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. 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.

1.8.2.2 Chronoamperometry

In Chronoamperometry (CA) technique, the working electrode potential is fixed at a specific value at which an electrochemical reaction occurs. In MOR, 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 MOR to check the catalyst stability at specific potential and also to differentiate the catalytic activity of the different catalysts under identical conditions.

1.9 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. 1.4). 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 1 mL of Nafion solution (5 wt.%) in an ultrasonic bath for 10 min to obtain a 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–Ru–M (M = Ni, Os, W, Rh, Sn, Co, and Mo) with a catalyst loading of 2 mg cm$^{-2}$. On the cathode side, Pt$_{100}$/C with a catalyst loading of 2 mg cm$^{-2}$ 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.

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).

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 cm²). 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 H₂SO₄ and the catholyte used in the cathode side was 0.1 M perborate + 0.5 M H₂SO₄. 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).

1.10 Scope of the Work

Despite all efforts devoted to the MLMFC development, the main problem is that methanol oxidation at a platinum electrode is a self-poisoning reaction, since strongly adsorbed CO are produced by electrooxidation of methanol (Beden et al., 1981; Hamnett (1997); Burnstein et al., (1997)). It has been shown that the combination of Pt with a second or a third metal is a convenient way to modify the electrocatalytic properties of this metal (Peled et al., (2001)). Therefore, various Pt-based binary catalysts such as Ru, Sn, Mo, W, Os, Rh, Co, and Ni have been intensively investigated with the view of enhancing the catalytic activity by eliminating or inhibiting the CO poisoning effect on the basis of a bifunctional mechanism or an electronic effect (Ishikawa et al., (2000); Sung et al., (2000); Park et al., (2002)). Although it is known that Pt–Ru/C is the best catalyst for methanol electrooxidation, considerable effort continues to be focused on the development of new ternary electrocatalysts (Lima et al., (2001); Choi et al., (2003)) to further improve the Pt–Ru/C electrocatalyst activity. 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–Ru–M (M = Ni, Os, W, Rh, Sn, Co, and Mo) have repeatedly been reported to enhance the catalytic activity of MOR in direct methanol fuel cells (DMFCs). Following this 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, Os, W, Rh, Sn, Co, and Mo) to Pt–Ru/C catalysts.

The steps involved in the synthesis of the electrocatalysts (Pt–Ru–Ni/C, Pt–Ru–Os/C, Pt–Ru–W/C, Pt–Ru–Rh/C, Pt–Ru–Sn/C, Pt–Ru–Co/C, and Pt–Ru–Mo/C), and the effect of the third metal M on the enhanced catalytic activity of Pt–Ru–M/C 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), 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


