CHAPTER 10

Summary and Suggestions for Future Work

The major conclusions of the present research and suggestions for future research activities have been presented in this chapter.

10.1 Summary

In this dissertation, an overview of the fundamentals of the fuel cell technology, as well as the motivation behind the development of microfluidic membraneless fuel cells and the challenges associated with assessing membraneless fuel cells’ suitability for portable power applications were presented in chapter 1. The operational principles of a microfluidic fuel cell based on co-laminar flow were described, and the performance and viability of current microfluidic fuel cell devices were compared, with consideration of choice of reactants, electrochemical reactions, transport characteristics, and cell architectures. In addition, the experimental procedures involved in the synthesis of platinum-based electrocatalysts and the physicochemical characterization techniques in terms of composition, morphology, and crystal structure by using energy dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffractometry (XRD) and the electrochemical analyses of cyclic voltammetry (CV), and chronoamperometry (CA) to evaluate the performance of electrocatalysts on methanol electro-oxidation also demonstrated in this chapter.

The effect of addition of Ru on the structural characteristics and the electrochemical activity for methanol oxidation of carbon-supported Pt–Sn alloy catalysts in membraneless fuel cells has been described in chapter 2. The carbon-supported Pt–Sn, Pt–Ru, and Pt–Ru–Sn electrocatalysts with different atomic ratios (Pt–Sn/C (50:50), Pt–Ru/C (50:50), Pt–Ru–Sn/C (70:10:20), Pt–Ru–Sn/C (70:15:15) and Pt–Ru–Sn/C (70:20:10)) were synthesized by
ultrasonic-assisted alcohol-reduction method. The synthesized electrocatalysts were characterized by SEM, TEM, EDX and XRD analyses. The Pt metal was the predominant material in all the samples, with peaks attributed to the face-centered cubic (fcc) crystalline structure. The SEM and TEM analysis indicated that the prepared catalysts had similar particle morphology, and their particle sizes were 2–4 nm. The electrocatalytic activities were characterized by cyclic voltammetry (CV) and chronoamperometry (CA). During the experiments performed on single membraneless fuel cells, Pt–Ru–Sn/C (70:10:20) performed better among all the catalysts prepared with power density of 36.5 mW/cm². The enhanced methanol oxidation activity by the ternary Pt–Ru–Sn/C catalyst is mainly ascribed to the synergistic effect between Sn and Ru, and to the smaller particle size. In this work, for the first-time carbon-supported binary Pt–Sn/C, Pt–Ru/C and ternary Pt–Ru–Sn/C anode catalysts were successfully tested in a single membraneless fuel cell using 1.0 M methanol as the fuel and 0.1 M sodium percarbonate as the oxidant in the presence of 0.5 M H₂SO₄ as the electrolyte at room temperature. In situ reflectance infrared spectroscopy measurements showed that the oxidation of methanol produced CO₂ at low potentials indicating that the materials synthesized could be used as efficient anodes in the fuel-cell applications.

The performance and stability of Pt–Ru–Ni/C nano-alloy electrocatalysts in membraneless methanol fuel cells has been comprised in Chapter 3. Carbon supported well-dispersed Pt₁₀₀, Pt₆₀Ru₄₀, Pt₆₀Ni₄₀ and Pt₆₀Ru₃₀Ni₁₀ electrocatalysts were synthesized by ultrasonic-assisted alcohol-reduction method. The particle size, lattice parameter, composition, and micro-morphology of metals in the electrocatalysts were determined by XRD, EDX, and TEM techniques respectively. X-ray diffraction analysis showed that catalysts have the Pt face centred cubic (fcc) structure, and their crystallite size were in the range 2–6 nm. Regarding the ternary Pt₆₀Ru₃₀Ni₁₀/C electrocatalyst, its lattice parameter was
larger than that of Pt_{60}Ni_{40}/C and smaller than that of Pt_{60}Ru_{40}/C and Pt/C. The EDX results of the binary Pt–Ru/C and Pt–Ni/C and the ternary Pt–Ru–Ni/C catalysts are very close to the nominal values, which indicate that the metals were loaded onto the carbon support without obvious loss. The size of catalyst nanoparticles was observed via transmission electron microscopy and showed an average diameter of 3 nm. The electrocatalytic activities of Pt_{100}/C, Pt_{60}Ru_{40}/C, Pt_{60}Ni_{40}/C and Pt_{60}Ru_{30}Ni_{10}/C catalysts were investigated in terms of cyclic voltammetry (CV) and chronoamperometry (CA). The onset potentials for methanol oxidation on Pt_{60}Ru_{30}Ni_{10}/C and Pt_{60}Ru_{40}/C catalysts were significantly lower than that of Pt_{100}/C and Pt_{60}Ni_{40}/C. The electrochemical results showed that the catalytic activity in 1.0 M CH_{3}OH + 0.5 M H_{2}SO_{4} solution at 0.5 V vs. RHE increased in the following sequence: Pt_{60}Ru_{30}Ni_{10}/C > Pt_{60}Ru_{40}/C > Pt/C > Pt_{60}Ni_{40}/C. This clearly indicates that the performance of the ternary Pt_{60}Ru_{30}Ni_{10}/C electrocatalyst, for methanol electrooxidation is better than that of the binary Pt_{60}Ru_{40}/C and Pt_{60}Ni_{40}/C electrocatalysts due to the promoting function of Ni. In addition, its CO-tolerance is better than that of the Pt_{60}Ru_{40}/C and Pt_{60}Ni_{40}/C catalysts. The effect of Ni in the Pt_{60}Ru_{30}Ni_{10}/C catalyst can be illustrated by the hydrogen spillover effect of Ni hydroxides and electron effect of metallic Ni. The high activity of Pt_{60}Ru_{30}Ni_{10}/C electrocatalyst was also observed on membraneless methanol fuel cell, which was consistent with the half-cell measurements.

The study on the investigation of high surface area carbon-supported Pt_{100}, Pt_{80}Sn_{20}, Pt_{80}Ni_{20} and Pt_{80}Sn_{10}Ni_{10} electrocatalysts in a membraneless fuel cell for the methanol electro-oxidation reaction at room temperature has been presented in chapter 4. The carbon-supported electrocatalysts were synthesized by ultrasonic-assisted ethylene glycol-reduction method. The electrocatalysts were characterized in terms of structure, morphology and composition by using XRD, TEM and EDX techniques. Energy dispersive X-ray
spectroscopy and X-ray diffractometry results confirmed the formation of Pt–Sn/C, Pt–Ni/C, Pt–Sn–Ni/C metal catalyst having typical Pt crystalline structure and the formation of Pt–Sn alloy. Transmission electron microscopy measurements revealed a decrease in the mean particle size of the catalysts for the ternary compositions. The structural change is beneficial for the catalytic activity of the compositions. The electrocatalytic activities of Pt_{100}/C, Pt_{80}Sn_{20}/C, Pt_{80}Ni_{20}/C and Pt_{80}Sn_{10}Ni_{10}/C catalysts for methanol oxidation in an acid medium were investigated by cyclic voltammetry (CV) and chronoamperometry (CA). The electrochemical results showed that addition of Ni to Pt/C and Pt–Sn/C catalysts significantly shifted the onset of methanol and CO oxidations toward lower potentials. The shift is due to the electronic effect exerted by Ni along with the bifunctional mechanism, thus enhancing the catalytic activity, especially in the case of the ternary Pt–Sn–Ni/C composition. Chronoamperometry results showed that Pt_{80}Sn_{10}Ni_{10}/C gives a high current at steady condition. The single membraneless methanol fuel cell performances of the Pt_{80}Sn_{10}Ni_{10}/C, Pt_{80}Sn_{20}/C and Pt_{80}Ni_{20}/C anode catalysts were evaluated at room temperature. Among the catalysts investigated, the power density obtained for Pt_{80}Sn_{10}Ni_{10}/C (38 mW/cm$^2$) catalyst was higher than that of Pt_{80}Sn_{20}/C (25.7 mW/cm$^2$) and Pt_{80}Ni_{20}/C (18.6 mW/ cm$^2$), using 1.0 M methanol + 0.5 M H$_2$SO$_4$ as anode feed and 0.1 M sodium percarbonate + 0.5 M H$_2$SO$_4$ as cathode feed.

The influence of operating systems on the performance of Pt–Ru–Ir/C electrocatalysts synthesized by ultrasonic-assisted microwave-irradiated polyol process for electro-oxidation of methanol has been presented in chapter 5. X-ray diffractometry (XRD) results revealed a face-centered cubic structure for platinum, and there was evidence that Ru and Ir atoms were incorporated into the Pt structure. Transmission electron microscopy (TEM) analysis showed that the very small Pt–Ru–Ir nanoparticles possessing amorphous structure were well
dispersed on the surface of this carbon support. The electrochemical investigation was carried out in acidic medium (0.5 M H₂SO₄) both in the absence and in the presence of methanol. Energy dispersive X-ray (EDX) spectroscopy analysis indicated that the experimental composition was in agreement with the nominal composition of the catalysts. Cyclic voltammetry (CV) results showed that Pt–Ru–Ir/C (70:20:10) was more active in methanol electro-oxidation than other catalysts. Addition of Ir to Pt/C and Pt–Ru/C catalysts significantly shifted the onset of methanol and CO oxidations toward lower potentials, thus enhancing the catalytic activity, especially in the case of the ternary Pt–Ru–Ir/C composition. Chronoamperometry (CA) results showed that the ternary Pt–Ru–Ir/C (70:20:10) and Pt–Ru–Ir/C (70:10:20) catalysts gave a higher current than the binary Pt–Ru/C (70:30) and Pt–Ir/C (70:30) catalysts at steady condition. Based on the exploration of the structure–performance relationship, a speculative mechanism for the superior performance of the Pt–Ru–Ir/C catalyst was proposed: the enhanced performance is due to the interaction between RuO₂ and IrO₂, leading to facile oxidation of COads on active metal sites at a lower potential relative to the Pt–Ru/C analogue. The performances of Pt–Ru–Ir/C (70:20:10), Pt–Ru–Ir/C (70:10:20), Pt–Ru/C (70:30) and Pt–Ir/C (70:30) anode catalysts were evaluated in single membraneless methanol fuel cell (MLMFC) at room temperature. Among the catalysts investigated, the Pt–Ru–Ir/C (70:20:10) exhibited the highest methanol electro-oxidation reaction activity, followed by the Pt–Ru–Ir/C (70:10:20), Pt–Ru/C (70:30) and Pt–Ir/C (70:30). From the electrochemical tests and single cell test, the carbon-supported Pt–Ru–Ir/C catalysts offer the potential to be considered as an alternative anode catalyst for MLMFC.

The promoting effect of iridium on Pt–Sn/C catalyst for methanol oxidation has been dwelt in chapter 6. The combination of bi-metallic Pt–Sn/C, Pt–Ir/C and tri-metallic Pt–Sn–Ir/C electrocatalysts were prepared by the ultrasonic-assisted Pechini method on carbon
Vulcan XC-72R. The nominal loading of metals in the electrocatalysts was 40 wt.% and rest 60 wt.% was carbon. SEM image clearly shows that the nanoparticles of the catalysts are uniformly dispersed on the carbon support. The particles showing high contrast are of Sn, charged by the electron beam. Transmission electron microscopy and X-ray diffractometry analyses revealed that the size of the prepared catalysts were in the range 3–5 nm. Pt lattice parameter decreased with the addition of Ir, and increased with the addition of Sn in Pt–Sn–Ir/C catalyst. The electrochemical investigation of these different electrode materials was carried out as a function of the electrocatalyst composition, in a 0.5 M H₂SO₄ solution, with either the presence or the absence of methanol. Cyclic voltammetric measurements and Chronoamperometric results obtained at room temperature showed that ternary Pt–Sn–Ir/C catalysts displayed better electrocatalytic activity towards methanol electrooxidation compared to Pt–Sn/C, Pt–Ir/C and Pt/C, mainly at low potentials. The single membraneless methanol fuel cell (MLMFC) test with catalyst loading of 2 mg/cm² and 1.0 M methanol + 0.5 M H₂SO₄ as anolyte and 0.1 M percarbonate + 0.5 M H₂SO₄ as catholyte, showed an enhancement of catalytic activity in the following order: Pt–Sn–Ir/C (70:10:20) > Pt–Sn–Ir/C (70:20:10) > Pt–Sn/C (70:30) > Pt–Ir/C (70:30) > Pt/C (100). Detection of larger quantity of CO₂ in the product of MLMFC with the Pt–Sn–Ir/C (70:20:10) anode further indicates efficiency of the catalyst.

The pronounced synergetic effect of the nano-sized Pt–Ru–Rh/C catalyst for methanol oxidation in membraneless methanol fuel cell (MLMFC) has been reported in chapter 7. Carbon-supported Pt₅₀Ru₄₀Rh₁₀, Pt₅₀Ru₁₀Rh₄₀, Pt₅₀Ru₅₀ and Pt₅₀Rh₅₀ electrocatalysts were synthesized by ultrasonic-assisted co-impregnation reduction method. The physicochemical characterizations demonstrated that all the compositions have the Pt face-centered cubic (fcc) structure with variations in the lattice parameter, indicating the incorporation of Ru and Rh.
Transmission electron microscopy measurements revealed a decrease in the mean particle size of the catalysts for the ternary compositions. The electrochemical characterization showed that binary and ternary electrocatalysts have higher catalytic activity than Pt/C toward methanol electro-oxidation. Voltammetric data showed the addition of Rh to Pt–Ru/C significantly diminished the potential of methanol and CO oxidation, due to the electronic effect exerted by this metal along with the bifunctional mechanism. Single cell tests on a membraneless methanol fuel cell at room temperature with Pt$_{50}$Ru$_{40}$Rh$_{10}$/C showed superior performance (32.16 mW/cm$^2$) compared to Pt$_{50}$Ru$_{50}$/C, Pt$_{50}$Rh$_{50}$/C and Pt$_{100}$/C electrocatalysts. The $i$–$V$ characteristic curve indicated an enhancement in fuel cell performance with the addition of Rh and Ru to Pt-catalyst.

Chapter 8 described the electrosynthesis, characterization and electrocatalytic properties of Pt–Sn–Rh/C (50:10:40) Pt–Sn–Rh/C (50:40:10) Pt–Sn/C (50:50), Pt–Rh (50:50)/C and Pt/C (100) catalysts towards oxidation of methanol by ultrasonic-assisted co-impregnation reduction method with metal loading of 40 wt.% (and rest 60 wt.% is carbon). H$_2$PtCl$_6$·6H$_2$O, SnCl$_2$·2H$_2$O, and RhCl$_2$·XH$_2$O as metal sources and Vulcan XC-72R as support were used. A systematic investigation of alcohol adsorption and oxidation on binary and ternary electrocatalysts in acid medium was performed in membraneless methanol fuel cell (MLMFC). The different nominal compositions of binary Pt–Sn/C, Pt–Rh/C and ternary Pt–Sn–Rh/C electrocatalysts were characterized by TEM, EDX, and XRD techniques. Energy dispersive X-ray spectroscopy and X-ray diffractometry confirmed the formation of Pt–Sn–Rh/C, Pt–Sn/C, Pt–Rh/C metal catalyst having typical Pt crystalline structure and the formation of Pt–Sn alloy. For Pt–Sn/C and Pt–Sn–Rh/C, two additional peaks were observed at 34° and 52° that were identified as a SnO$_2$ phase. Electrochemical analyses obtained at room temperature by cyclic voltammetry and chronoamperometry showed that Pt–Sn–Rh/C
(50:10:40) gives higher current density compared to that of Pt–Sn–Rh/C (50:40:10), Pt–Sn/C (50:50) and Pt–Rh/C (50:50). The power density obtained using Pt–Sn–Rh/C (50:10:40) (32.94 mW cm$^{-2}$) as anode catalyst in MLMFC was higher than that for Pt–Sn–Rh/C (50:40:10), Pt–Sn/C (50:50) and Pt–Rh/C (50:50) at room temperature, with catalyst loading of 2 mg cm$^{-2}$. Addition of Rh on anode electrocatalyst enhanced the cell performance, by helping in breaking the CO bond. However, the less percentage of Rh in Pt–Sn–Rh/C (50:40:10) blocked the further oxidation of intermediates resulting in a decreased cell performance. In this work, carbon-supported binary Pt–Sn/C, Pt–Rh/C and ternary Pt–Sn–Rh/C anode catalysts were successfully tested in a single membraneless fuel cell using 1.0 M methanol as the fuel and 0.1 M sodium percarbonate as the oxidant in the presence of 0.5 M $\text{H}_2\text{SO}_4$ as the electrolyte at room temperature. Based on the experimental results, we conclude that the trimetallic combination of Pt–Sn–Rh/C (50:10:40) shows superior methanol electro-oxidation than bimetallic combinations of Pt–Sn/C (50:50) and Pt–Rh/C (50:50).

The performance and evaluation of membraneless methanol fuel cell under different operating conditions has been discussed in chapter 9. The experiments described in this study show that membraneless methanol fuel cells are media flexible; they can be operated in all-acidic, all-alkaline, or even mixed-media configurations. The membraneless architecture of laminar flow-based fuel cells overcomes the fuel crossover and water management issues that plague membrane-based fuel cells (i.e., PEMFC, DMFC) and enables independent control of stream characteristics (i.e., flow-rate, composition and pH). Here we focused on maximizing cell performance, in terms of power density and fuel utilization per pass, by tailoring various structural and operational parameters, including absolute flow rate, fuel-to-electrolyte flow rate ratio, electrode-to-electrode distance, and oxygen concentration and mode of delivery.
In conclusion, methanol electro-oxidation on pure platinum encounters many problems such as the difficulties in CO bond breaking at low temperature and the formation of CO-intermediates that poison 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. Considerable efforts have been taken to develop alternative anode electrocatalysts that offer high catalytic activity for MOR. For example, alloying of Pt with other elements such as Sn, Ru, Mo, Pd, Rh, W, Ni and Ir have been studied on carbon support, and among them, Sn and Ru have shown the best catalytic effect on MOR. To further improve 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 the oxidation of methanol. 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 catalysts investigated, the Pt–Sn–M exhibited the highest methanol electro-oxidation reaction activity, followed by the Pt–Ru–M (M = Ni, Ir and Rh) in membraneless methanol fuel cell (MLMFC) system. In addition, the electrocatalysts’ performance also depends on the preparation procedures and their atomic ratios.

10.2 Suggestions for Future Work

The present results provide an overview for the characteristics of this microfluidic fuel cell model and also benefit the further design work to optimize the cell performance. Some of opportunity for future work is outlined below.

The experimental results indicates that by improving the channel design in a better way the cell performance can further be significantly increased, since it has a big difference between the measured OCP and the theoretical OCP.
The oxidant concentration is considered to be an important factor, since it affects the cell performance invariably and it is difficult to dissolve the substance into solution to obtain a high concentration, hence exploration of a new liquid oxidant will be interesting for future improvements.

One of the most significant aspects of cell performance improvement is the catalyst layer hence different catalyst materials could be investigated to enhance the electrochemical reaction, as well as the electrode design.

Ultimately, since the experimental work of Choban et al. offers a better cell performance than the Y-shaped modeling work by using planar channel design, it will be very interesting to test our E-shaped channel but with vertical planner design for the specific case when there is a significant difference in density between the top flow and the bottom flow.