CHAPTER 10
Summary and Recommendations for Future Work

The primary objective of this research was to develop a novel fuel cell architecture addressing the key technical challenges associated with the conventional design as well as to evaluate the fuel cells developed with sodium perborate as an oxidant for the first time in the fuel cell history. The following sections provide a summary of the outcomes of research discussed in each chapter and the recommendations for future work.

10.1 Summary

In this dissertation, an overview of the background and the motivation to develop a novel membraneless fuel cell that can overcome the technical challenges associated with conventional fuel cell suitable for portable power applications were presented in Chapter 1. The operational principles and the performance of the microfluidic fuel cells were described, with consideration of the choice of methanol as a fuel and sodium perborate as an oxidant in developing miniaturized fuel cells. In addition, different experimental procedures involved in the synthesis of Pt-based electrocatalysts and the physicochemical characterization techniques in terms of composition, morphology, and crystal structure were presented by using energy dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), X-ray diffractometry (XRD), the electrochemical analyses of cyclic voltammetry (CV), and chronoa) to evaluate the performance of electrocatalysts on methanol electro-oxidation.

In Chapter 2, the carbon-supported Pt–Ru, Pt–Ni, and Pt–Ru–Ni electrocatalysts with different atomic ratios were synthesized by the NaBH₄-reduction method.
The XRD patterns of the prepared Pt$_{50}$Ru$_{40}$Ni$_{10}$/C, Pt$_{50}$Ru$_{50}$/C, Pt$_{50}$Ni$_{50}$/C, and Pt$_{100}$/C catalysts revealed the characteristics of face-centered-cubic (fcc) crystalline Pt at 2$\theta$ values of 39, 47, 67, and 82° indexed with planes (1 1 1), (2 0 0), (2 2 0), and (3 1 1), respectively. The decrease in the lattice parameters of the alloy catalysts reflects the progressive increase in the incorporation of Ru and Ni into the alloyed state. The Pt$_{50}$Ru$_{40}$Ni$_{10}$/C alloy nanoparticles were well-dispersed on the surface of the support, with an extremely narrow size distribution.

TEM image shows the obtained mean particle diameter was approximately 3–5 nm, which is in fairly good agreement with the data calculated from XRD pattern.

The EDX results of the binary Pt–Ru/C and Pt–Ni/C and the ternary Pt–Ru–Ni/C catalysts were extremely close to the nominal values, which indicate that the metals could be loaded onto the carbon support without any obvious loss.

In cyclic voltammetry, the peak current densities of Pt$_{50}$Ru$_{40}$Ni$_{10}$/C, Pt$_{50}$Ru$_{50}$/C, Pt$_{50}$Ni$_{50}$/C, and Pt$_{100}$/C catalysts at 50 mV s$^{-1}$ were 122.2, 110.3, 85.7, and 34.2 mA/cm$^2$, respectively, demonstrating that the activity of the ternary Pt$_{50}$Ru$_{40}$Ni$_{10}$/C catalyst is a factor of approximately 4-times greater than the Pt/C catalyst. The ternary composition (Pt$_{50}$Ru$_{40}$Ni$_{10}$/C) presented much higher current density than the binary Pt$_{50}$Ru$_{50}$/C and Pt$_{50}$Ni$_{50}$/C catalysts, indicating that the activity of the ternary electrocatalysts toward MOR was much better than that of the binary compositions.
During the experiments performed on single membraneless fuel cells, Pt_{30}Ru_{40}Ni_{10}/C performed better among all the catalysts prepared with a power density of 38.2 mW cm\(^{-2}\).

Chapter 3 revealed the details of the activity and stability of the carbon-supported Pt–Ru–Os ternary electrocatalysts synthesized by microwave-irradiated polyol process for electro-oxidation of methanol in membraneless fuel cells.

- The results of XRD and EDX confirmed the formation of Pt–Ru–Os/C metal catalyst since the diffraction peaks of Os were very weak; it is therefore likely that some Os was alloyed with Pt–Ru.

- The atom ratio of Pt, Ru, and Os from EDX analyses is also in close agreement with the original precursor concentration.

- The onset potentials for the oxidation of methanol on Pt_{65}Ru_{25}Os_{10}/C (0.25 V) and Pt_{80}Ru_{10}Os_{10}/C (0.28 V) electrocatalysts was slightly lower those on the Pt_{80}Ru_{20}/C (0.32 V), Pt_{80}Os_{20}/C (0.38 V), and Pt_{100}/C (0.40 V) catalysts.

- Among the catalysts investigated in the single cell test, the power density obtained for Pt_{65}Ru_{25}Os_{10}/C (37.1 mW cm\(^{-2}\)) catalyst was greater than that for Pt_{60}Ru_{10}Os_{10}/C (29.8 mW/cm\(^2\)), Pt_{60}Ru_{20}/C (24.2 mW cm\(^{-2}\)), and Pt_{60}Os_{20}/C (20.6 mW cm\(^{-2}\)).

- The significantly enhanced catalytic activity for methanol oxidation can be attributed to the high dispersion of ternary catalysts and to Os as its promotion agent.
Chapter 4 describes the synthesis, characterization, and electrocatalytic properties of Pt\textsubscript{50}Ru\textsubscript{40}W\textsubscript{10}/C, Pt\textsubscript{50}Ru\textsubscript{30}W\textsubscript{20}/C, and Pt\textsubscript{50}Ru\textsubscript{25}W\textsubscript{25}/C, Pt\textsubscript{50}Ru\textsubscript{50}/C, Pt\textsubscript{50}W\textsubscript{50}/C and Pt\textsubscript{100}/C catalysts prepared by thermal reduction method.

- The composition of ternary electrocatalysts can be conveniently controlled by adjusting the initial metal salt solution and preparation conditions. XRD results show the homogenous alloy structure of Pt, Ru, and W.

- The TEM images indicated an average size of Pt\textsubscript{50}Ru\textsubscript{40}W\textsubscript{10}/C, Pt\textsubscript{50}Ru\textsubscript{30}W\textsubscript{20}/C, and Pt\textsubscript{50}Ru\textsubscript{25}W\textsubscript{25}/C nanoparticles of size 3–3.5 nm.

- The electrochemical experiments showed the maximum catalytic activity for methanol oxidation for Pt\textsubscript{50}Ru\textsubscript{40}W\textsubscript{10}/C than for the Pt\textsubscript{50}Ru\textsubscript{30}W\textsubscript{20}/C, Pt\textsubscript{50}Ru\textsubscript{25}W\textsubscript{25}/C, Pt\textsubscript{50}Ru\textsubscript{50}/C, Pt\textsubscript{50}W\textsubscript{50}/C, and Pt\textsubscript{100}/C. An important aspect of the catalyst activity is the real surface area, which was determined by the CO adsorption method. The real surface area estimated by this method is in good agreement with the enhancement in the electrocatalytic activity. It was shown that W-modified Pt–Ru/C surfaces offer energetically different sites for adsorption and oxidative desorption, which can be selectively populated by CO species, either via the direct adsorption of CO dissolved in the electrolyte or via the adsorption and decomposition reaction of methanol.

- A considerable increase in the voltammetric charge of ternary Pt\textsubscript{50}Ru\textsubscript{40}W\textsubscript{10}/C catalyst was observed in the double-layer region, indicating that the addition of W into binary Pt–Ru/C leads to an enhanced activity for the oxidation reactions.
The promoting effect of Rh on Pt–Ru/C catalyst for methanol oxidation is presented in Chapter 5.

- The Pt_{50}Ru_{25}Rh_{25}/C, Pt_{50}Ru_{50}/C, Pt_{50}Rh_{50}/C, and Pt_{100}/C catalysts were prepared by co-impregnation reduction method.

- For Pt–Rh/C, the diffraction peaks were slightly shifted to higher angles of 2θ with respect to those of Pt/C electrocatalyst, indicating a lattice contraction and alloy formation. On the other hand, results for the Pt–Ru/C and Pt–Ru–Rh/C electrocatalysts showed no shift in the diffraction angles with some segregation of metallic Ru; this was evidenced by the diffraction peaks originating from the hexagonal structure of Ru atoms. The average particle size for Pt–Ru/C, Pt–Rh/C, and Pt–Ru–Rh/C electrocatalysts were in the range of 3–5 nm, which was in good agreement with the result of TEM images.

- The peak current densities of Pt_{50}Ru_{25}Rh_{25}/C, Pt_{50}Ru_{50}/C, Pt_{50}Rh_{50}/C, and Pt_{100}/C catalysts were 80.2, 49.7, 44.3, and 40.1 mA/cm², respectively.

- The activity change for methanol oxidation decreased in the order of Pt_{50}Ru_{25}Rh_{25}/C>Pt_{50}Ru_{50}/C>Pt_{50}Rh_{50}/C>Pt_{100}/C, which was in fairly good agreement with our CV results.

- The OCV of Pt_{50}Ru_{25}Rh_{25}/C was the highest value of 0.83 V, which is approximately 0.31 V higher than that of Pt_{100}/C.

The investigation of Pt_{50}Ru_{10}Sn_{10}/C electrocatalysts synthesized by ethylene glycol reduction method is presented in Chapter 6.
The diffraction peaks of Pt₈₀Ru₂₀/C were shifted toward higher 2θ values relative to those of Pt₁₀₀/C, whereas the peaks of Pt₈₀Sn₂₀/C were shifted toward lower angles, revealing the formation of a solid solution, due to the incorporation of Sn into the fcc structure of Pt. Notably, the ternary Pt₈₀Ru₁₀Sn₁₀/C electrocatalysts showed intermediate 2θ values as compared to those of Pt₈₀Ru₂₀/C and Pt₈₀Sn₂₀/C catalysts.

The EDX results of the ternary Pt–Ru–Sn/C catalysts indicate that the metals were loaded onto the carbon support without any obvious loss.

Addition of Sn to Pt/C and Pt–Ru/C catalysts significantly shifted the onset potential of methanol and CO oxidations toward lower potentials, thus enhancing the catalytic activity, especially in the case of ternary Pt–Ru–Sn/C composition.

CA results showed that the ternary Pt₈₀Ru₁₀Sn₁₀/C catalysts gave a higher current than the binary Pt₈₀Ru₂₀/C, Pt₈₀Sn₂₀/C catalysts under steady condition.

The maximum power densities obtained for Pt₈₀Ru₁₀Sn₁₀/C, Pt₈₀Sn₂₀/C, Pt₆₀Ru₂₀/C, and Pt₁₀₀/C were 39.7, 35.1, 29.2, and 6.8 mW cm⁻², respectively.

Chapter 7 describes the carbon-supported, well-dispersed Pt₁₀₀, Pt₅₀Ru₅₀, Pt₅₀Co₅₀, Pt₆₀Ru₃₀Co₁₀, Pt₆₀Ru₂₀Co₂₀, and Pt₆₀Ru₁₀Co₃₀ electrocatalysts synthesized by the Pechini method.

XRD analysis showed that the catalysts have a Pt fcc structure with a crystallite size of 3–4.5 nm. No diffraction peaks were attributed to pure ruthenium and cobalt or ruthenium rich hexagonal close-packed (hcp) phase,
which appear in the XRD patterns, suggesting that ruthenium and cobalt atoms either form an alloy with platinum or exist in the amorphous oxide phases.

- The EDX values of the binary Pt–Ru/C and Pt–Co/C and the ternary Pt–Ru–Co/C catalysts were extremely close to the nominal values, indicating that the metals were loaded onto the carbon support without any obvious loss.

- In comparison to pure Pt, the oxidation of CH3OH_ads at Co containing Pt–Ru/C surfaces exhibited a shift in the peak potential to lower potentials. At a low potential, higher current efficiencies for CO2 were observed on Pt–Ru–Co/C electrodes than on pure Pt surfaces, suggesting that, in the presence of Co, Ru ad-atoms promote the reaction path via CO_ads in the low potential region.

- The performance of the ternary Pt60Ru30Co10/C electrocatalysts for methanol electro-oxidation was better than that of the binary Pt50Ru50/C and Pt50Co50/C electrocatalysts due to the promoting function of Co. In addition, its CO-tolerance was better than that of the Pt50Ru50/C and Pt50Co50/C catalysts. Thus, the onset potentials for the oxidation of methanol on the Pt60Ru30Co10/C (0.24 V), Pt60Ru20Co20/C (0.29 V), and Pt60Ru10Co30/C (0.31 V) electrocatalysts were slightly lower than those on the Pt50Ru50/C (0.35 V), Pt50Co50/C (0.36 V), and Pt100/C (0.42 V) catalysts.

The study of carbon-supported Pt–Ru–Mo electrocatalyst synthesized by Bonnemann’s method and characterized in terms of their structure, morphology, and composition by using XRD, TEM, and EDX techniques has been presented in Chapter 8.
The lattice parameters obtained for the Pt–Mo/C (0.3889 nm), Pt–Ru/C (0.3902 nm), and Pt–Ru–Mo/C (0.3898 nm) catalysts were smaller than those for Pt/C electrocatalyst (0.3915 nm), indicating that, the decrease in the lattice parameters of the alloy catalysts results from the progressive increase in the incorporation of Ru and Mo into the alloyed state. Narrower particle size distribution was observed with an average particle diameter of 1.5 nm, which was in fairly good agreement with the data calculated from XRD.

The average composition of the sample was in the atom ratio of Pt:Ru:Mo = 1:1:1.

CV for methanol oxidation reactions showed that the CO poisoning effect was largely inhibited by Pt34Ru33Mo33/C electrocatalysts, indicating the ability of Mo to promote either the CO to CO₂ oxidation or a weaker adsorption of CO on the Pt34Ru33Mo33/C catalysts.

Among the catalysts investigated, the power density obtained for Pt34Ru33Mo33/C (36.5 mW cm⁻²) catalyst was higher than that for Pt50Ru50/C (24.2 mW cm⁻²) and Pt50Mo50/C (21.4 mW cm⁻²) with 1.0 M methanol+0.5 M H₂SO₄ as the anode feed and 0.1 M sodium perborate+0.5 M H₂SO₄ as the cathode feed.

Chapter 9 presents the continuous flow operation of membraneless methanol fuel cell (MLMFC) using acid/alkaline bipolar electrolyte.

A microscale MLMFC was fabricated, and its performance was evaluated under different operating conditions. In this MLMFC, sodium perborate was used as an oxidant for the first time under “multi-media” configuration. Our
experiments revealed that MLMFC are media flexible and that they can be operated in all-acidic, all-alkaline, or even multi-media configurations.

- Sodium perborate affords hydrogen peroxide in an aqueous medium. At room temperature, the laminar flow-based microfluidic fuel cell produced a maximum power density of 22.25 mW cm\(^{-2}\) under alkaline anode/acidic cathode multi-media configurations. We concluded that multi-media MLMFC may outperform the all-acidic and all-alkaline MLMFCs.

- The effects of flow rates of the fuel and oxidant and variations in the concentrations of methanol, perborate, and electrolytes were evaluated under multi-media configurations. The performance was characterized by V–I curves and anode polarization plots.

- The MLMFC offers the advantages of miniature size, simplicity of fabrication, use of aqueous fuel, and good cost efficiency. Furthermore, perborate is a cheap, nontoxic, stable, easy to handle, environment friendly, large-scale industrial chemical, which is also a convenient source of hydrogen peroxide. We expect that the MLMFC may be a promising candidate for practical fuel cell applications in order to establish a clean and sustainable energy future.

10.2 Recommendations for Future Work

The result of the present work hints at the several opportunities for future work in this domain. Some of these opportunities are outlined below:

In this research, a novel architecture to eliminate the Proton Exchange Membrane (PEM) was successfully demonstrated. In addition, the flexibility of the MLMFC was
evaluated under all acidic, all alkaline, and “mixed media” configurations. The experimental results showed that the influence of methanol is little as the cell performance is primarily cathode-limited. On the contrary, the variation of perborate concentration can particularly affect the cell performance; hence, elevation in the concentration of perborate can significantly improve the cell performance.

The MLMFC was not limited to the use of a specific type of catalyst, fuel, oxidant, or liquid electrolytes. Therefore, other combinations can be easily interchanged with this configuration, which allows for the direct application of the advancements in other types of fuel cells into this design without any large modifications.

In this study, methanol oxidation at various Pt-based surfaces were studied, albeit to obtain more power density. Furthermore, variations in the electrocatalysts need to be tested to put MLMFC into practical applications. Since the catalyst layer has been always considered as one of the most significant aspects of cell performance improvement, selecting different catalyst materials and modifying the layer configuration could be investigated to further enhance the electrochemical reactions.

The fuel cell tests performed in this work were based on a single cell performance; however, future work would include fuel cell tests with multiple cells connected in series, parallel, or in combination of both. Furthermore, due to its structural simplicity, a large scale cell-to-cell connection seems feasible for improving the extractable power density.

A membraneless structure is one of the unique aspects of this fuel cell. Due to the simple structure of the developed fuel cells, the anode and cathode can be arranged on the same plane without a PEM, which enables flexible adjustment of the fuel cell dimensions in order to meet the specific design needs for the applications of microfluidic systems and portable power sources.