CHAPTER 7

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.

7.1 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 chronoamperometry (CA) to evaluate the performance of electrocatalysts on methanol electro-oxidation.

In chapter 2, Pt, Pt–Ru and Pt–Ru–M (M = Ni, Mo, and Ce) nanocatalysts supported on MWCNTs were successfully synthesized by ultrasonic-assisted chemical reduction. Well dispersion and size distribution were found for the synthesized nanocatalysts. The trimetallic nanocatalysts not only had a high electrochemically active surface area and improved electrocatalytic activity than that of bimetallic Pt–Ru/MWCNTs, for methanol oxidation, but also indicated a simple way to prepare such catalysts, while enhancing the electrochemical performance. The effect of the operating conditions on the performance of an MLMFC with Pt/MWCNTs, Pt–Ru/MWCNTs, Pt–Ru–Ni/MWCNTs, Pt–Ru–Mo/MWCNTs, and Pt–Ru–Ce/MWCNTs as anode catalysts was investigated. The performance of an MLMFC using Pt–Ru–Ni/MWCNTs as the anode catalyst was better than that of the other catalysts synthesized by the same method, which could be attributed to the electronic effect, the bifunctional mechanism, and the hydrogen spillover. These results indicated that MWCNTs could be good candidates for use as supporting material in high-loading metal catalysts in fuel cells.

Graphene nanosheet (GNS) and carbon supported Pt-Ru nanocatalyst for methanol oxidation is presented in chapter 3. In this study, graphene nanosheets were synthesized by the modified Hummer’s method by loading 40 wt.% Pt and Pt–Ru nanoparticles on to a graphene nanosheet, using an improved ultrasonic-assisted chemical reduction method. The synthesis results show that the Pt–Ru nanoparticles are uniformly dispersed on the graphene nanosheets compared to the Vulcan XC-
72R carbon. In comparison to Vulcan XC-72R carbon as a catalyst support, graphene nanosheets can more effectively enhance the electrocatalytic activity of Pt–Ru nanoparticles for the oxidation of methanol into CO₂, which is attributed to the special structure of the graphene nanosheets. These qualities achieve a considerably higher ECASA value and a larger catalytic current density for methanol oxidation, as well as a far higher \( I_p/I_B \) value, for GNS-supported catalysts compared to the Vulcan XC-72R carbon. Considering its facile process and superior performance for methanol oxidation, GNS is a promising support material for electrocatalysts.

The investigation of Pt-Ru/CNF and Pt-Ru/C electrocatalysts synthesized by ultrasonic assisted chemical reduction method is presented in chapter 4. In this study, Pt-Ru catalyst supported on carbon nanofiber (CNF), and Vulcan XC 72R has been characterized and tested in a membraneless methanol fuel cell operating at room temperature. The catalyst supported on the carbon nanofiber showed good stability in the CV analyses and agglomeration of particles was not observed. During the experiments performed on single membraneless fuel cells, Pt-Ru/CNF performed better than carbon supported Pt-Ru catalyst with a power density of 37.1 mW cm⁻². From single cell tests it can be concluded that the catalyst supported on CNF performed better because of the higher alloying, and high dispersion of Pt-Ru nanoparticles on CNF, which favors the promotion of water activation on the secondary metal. The higher alloying level also has an electronic effect, modifying the adsorption energy of the methanol residues and hence increasing the activity for methanol oxidation and leading to higher performance. The enhancements in activity and stability over Pt-Ru/C catalyst have been solely attributed to small particle size
and high dispersion of Pt-Ru nanoparticles on the CNF support. These findings suggest that Pt-Ru/CNF should be considered a good electrocatalyst material for methanol oxidation in fuel cells.

In Chapter 5, Pt–Ru catalysts were synthesized on carbon aerogel and their electrocatalytic activity for methanol oxidation in membraneless fuel cell was investigated and compared with Pt-Ru/C. The crystallite size, lattice parameter, composition, and particle size of metals in the catalysts were determined by XRD, EDX, and TEM techniques, respectively. The XRD patterns of the prepared Pt-Ru/CAG and Pt-Ru/C catalysts revealed the characteristics of face-centered-cubic (fcc) crystalline Pt at 2θ values of 40, 47, 67, and 81° 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 into the alloyed state. TEM images possess diameter of 2.5-3.5 nm with spherical shape and are uniformly dispersed on surface of carbon aerogels. Cyclic voltammetry results showed that the Pt-Ru/CAG was more active in methanol electro-oxidation than in Pt-Ru/C. CA results showed that the carbon aerogel supported Pt-Ru nanocatalyst gave higher current than the carbon supported Pt-Ru nanocatalysts. The power density obtained for Pt–Ru/CAG (36.5 mW cm⁻²) was higher than that of Pt-Ru/C, using 1.0 M methanol + 0.5 M H₂SO₄ as anode feed and 0.1 M sodium perborate + 0.5 M H₂SO₄ as cathode feed. The Pt-Ru/CAG catalyst showed higher catalytic activities toward the methanol oxidation reaction as compared to the Pt-Ru/C catalyst. This may be attributed to the mesopores of carbon aerogel promoting the mass transportation of methanol in catalyst layer. From the electrochemical tests and the single cell test, the carbon aerogel supported Pt-Ru nanocatalysts offer the
potential to be considered as an alternative anode catalyst for membraneless fuel cell.

Chapter 6 presents the continuous flow operation of membraneless methanol fuel cell (MLMFC) using acid/alkaline bipolar electrolyte. A microscale MLMFC was fabricated on PDMS, and its performance was evaluated under different operating conditions. In this MLMFC, sodium perborate was used as an oxidant under alkaline-acid configuration. Our experiments revealed that MLMFC are media flexible and that they can be operated in all-acidic, all-alkaline, or even alkaline-acid 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 21.9 mW cm\(^{-2}\) under alkaline anode/acidic cathode alkaline-acid media configurations. We concluded that alkaline-acid 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 alkaline-acid 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.

In conclusion, the use of nanomaterials in membraneless fuel cells may significantly improve the electrocatalytic performance for high energy density and high power density while reducing the manufacturing cost. The prominent
electrocatalytic behaviour of the nanomaterials is contributed mainly from their unique, physical-chemical properties such as sizes, shapes, pore structure distribution, surface defects, and chemical properties.

In general, the nanostructures could provide an economic and effective way to prepare precious metal catalysts for remarkably reducing the usage of the noble metals while the unique nanostructures, and as nanotubes, nanofibers, carbon aerogel and graphene nanosheets are believed to provide high surface area, superior conductivity and better mass transport as well as high intrinsic catalytic activity. An amalgamation of these novel electrocatalyst supports and improved catalytic activity could bring about revolutionary changes in the quest for high-performance, long-lasting MLMFCs.

7.2 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 medial 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.