CHAPTER 9
Carbon Supported Pt Electrode for the Development of Membraneless Methanol Fuel Cells

Abstract

This study reports on the characterization and optimization of membraneless methanol fuel cell (MLMFC) for both performance and fuel utilization. The impact of different operating conditions in terms of volumetric flow rate, variation of fuel and oxidant concentration and of different cell dimensions (electrode-to-electrode distances) on the performance (both power density and fuel utilization) of individual MLMFCs is investigated. In this study, the media flexibility of MLMFC by working in acidic and alkaline media, as well under “mixed-media” conditions in which the anode is in acidic media while the cathode is in alkali, or vice versa. Operating a fuel cell under alkaline conditions has positive effects on the reaction kinetics, both at the anode and cathode, while the cell performance under “mixed media” conditions offers an opportunity to increase the maximum achievable open cell potential (OCP). The lack of media-related constraints and the simplicity of the MLMFC design allow for these experiments to be performed consecutively in a single MLMFC without changing the system, except for altering the composition/pH of the fuel and oxidant stream. The performance of MLMFC operated with different media is described and compared.

9.1 Introduction

A membraneless fuel cell is a novel device without a membrane that converts chemical energy generated from a fuel and an oxidant into electric energy by means of oxidoreduction reactions. In membraneless micro fuel cells, liquid reactants (fuel and
oxidant) flow side by side in a laminar fashion in a single channel, not requiring a membrane for reactant flow. An additional advantage is that structures of membraneless micro fuel cells are very simple and easy to miniaturise (Jayashree et al. 2005, Jayashree et al. 2010), so that light and stackable fuel cells can be fabricated with simple microelectromechanical systems (MEMS) (Cohen et al. 2005, Bazylak et al. 2005). The implications of flexibility and the performance of operating membraneless methanol fuel cell (MLMFC) in alkaline-acidic media, in which one electrode is alkaline and the other are acidic. Another advantage of using MLMFC is the simple structure of the cell in the absence of membrane electrode assemblies in addition to a reduction in the cost of materials. Using a bipolar electrolyte increases fuel utilization and produces a higher potential when compared to the acid and alkaline fuel cell, and also there has been a considerable focus on the alkaline-acidic fuel cell in the recent past (Arun et al. 2014, Ponmani et al. 2014). In this study, new forms of simplified architectures, unique from those that have been reported in literature, have been developed by eliminating and integrating the key components of a conventional MEA. With these advantages, we believe membraneless methanol fuel cells (MLMFC) can be used as an alternative for portable power applications.

9.2 Experimental

9.2.1 Materials

All experiments were conducted at room temperature using methanol (98%, Merck) in de-ionized water as the fuel, and sodium percarbonate (99%, Riedel) dissolved in 1M sulfuric acid (98%, Merck) or 1M potassium hydroxide (98%, Merck) in de-ionized water as the oxidant.
9.2.2. Fabrication of Membraneless Methanol Fuel Cell

In the present study, we fabricated the membraneless methanol fuel cell (MLMFC) by using a laminar flow-based fuel cell configuration (Choban et al. 2004, Ponmani et al. 2014, Arun et al. 2013). In this MLMFC, methanol was used as a fuel, sodium percarbonate as an oxidant, and sulphuric acid as an electrolyte. In the crystalline state, sodium percarbonate existed as a dimeric peroxo-salt with water of hydration, but in the aqueous solution, it involved hydrogen peroxide (Cotton et al. 1988, Karunakaran et al. 1995, Karunakarana et al. 2000, McKillop et al. 2000), as shown in Eq. (9.1):

\[
2\text{Na}_2\text{CO}_3.3\text{H}_2\text{O}_2 \rightarrow 2\text{Na}_2\text{CO}_3 + 3\text{H}_2\text{O}_2 \quad (9.1)
\]

The byproduct is completely innocuous and this stable and easily handled crystalline substance is used as oxidant in MLMFC.

In MLMFC, the aqueous fuel and oxidant streams flow in parallel in a single microchannel with the anode and cathode on the opposing sidewalls (Fig 9.1). Graphite plates of 1-mm thickness served as the current collectors and catalyst support structures. The Pt/C with catalyst loading 2 mg/cm\(^2\) was used as anode and cathode 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), a 3 cm length, and a 0.1 cm height. The anolyte (fuel and electrolyte) and catholyte (oxidant and electrolyte) streams flow in a laminar fashion over the anode and cathode, respectively. The electrode area along a microchannel wall between the inlets and the outlet (3 cm long and 0.1 cm wide) was used as the geometric surface area of the electrodes in this study (0.3 cm\(^2\)). The design has been described in detail elsewhere (Choban et al. 2004, Jayashree et al. 2010). The anolyte used in the anode side was 1.0 M methanol + 0.5 M H\(_2\)SO\(_4\) and the catholyte used in the cathode side was 0.1 M percarbonate +
0.5 M H$_2$SO$_4$. The flow rate of each of the streams was 0.3 mL min$^{-1}$ (total flow rate of 0.6 mL min$^{-1}$). The MLMFC was operated at the room temperature. The current-voltage characteristics of MLMFC were measured on an electrochemical workstation and the data was verified by using a multi-meter (MASTECH® MAS830L).

Fig 9.1 Schematic of the E-shaped membraneless laminar flow-based fuel cell with graphite plates molded with poly(dimethylsiloxane) (PDMS) and sealed with poly(methylmethacrylate) (PMMA)

9.3 Results and Discussion

9.3.1 Media Flexibility of MLMFC

9.3.1.1 All-Acidic and All-Alkaline Media

The pH of the electrolyte influences reaction kinetics at the individual electrodes, as well as the electrode potential at which oxidation or reduction occurs (Spendelow et al. 2004, McLean et al. 2002, Iwasita et al. 2002, Lide et al. 2004, Yu et al. 2004). Eqs. (9.2) and (9.3) represent the half-cell reactions and standard electrode potentials of ethanol oxidation and peroxide reduction in acidic media and the Eqs. (9.5) and (9.6) represent the alkaline media. Eqs. (9.4) and (9.7) represent the overall cell reaction, in all-acid or all-alkaline media. Both
the alkaline–alkaline media and the acidic–acidic media have a maximum theoretical open circuit potential (OCP) of 1.796 V. On the other hand, we use alkaline-acidic media to force reactions (9.3) and (9.5) to proceed with the aim of improving fuel cell performance.

Methanol / percarbonate in acidic media:

<table>
<thead>
<tr>
<th>Reactions</th>
<th>$E^\circ$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode: CH$_3$OH + H$_2$O $\rightarrow$ 6H$^+$ + 6e$^-$ + CO$_2$</td>
<td>$E^\circ$ = 0.016 V</td>
<td>(9.2)</td>
</tr>
<tr>
<td>Cathode: 3H$_2$O$_2$ + 6H$^+$ + 6e$^-$ $\rightarrow$ 6H$_2$O</td>
<td>$E^\circ$ = 1.78 V</td>
<td>(9.3)</td>
</tr>
<tr>
<td>Overall: CH$_3$OH + 3H$_2$O$_2$ $\rightarrow$ CO$_2$ + 5H$_2$O</td>
<td>$\Delta E$ = 1.796 V</td>
<td>(9.4)</td>
</tr>
</tbody>
</table>

Methanol / percarbonate in alkaline media:

<table>
<thead>
<tr>
<th>Reactions</th>
<th>$E^\circ$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode: CH$_3$OH + 6OH$^-$ $\rightarrow$ CO$_2$ + 5H$_2$O + 6e$^-$</td>
<td>$E^\circ$ = −0.81 V</td>
<td>(9.5)</td>
</tr>
<tr>
<td>Cathode: 3H$_2$O$_2$ + 6e$^-$ $\rightarrow$ 6OH$^-$</td>
<td>$E^\circ$ = 0.986 V</td>
<td>(9.6)</td>
</tr>
<tr>
<td>Overall: CH$_3$OH + 3H$_2$O$_2$ $\rightarrow$ CO$_2$ + 5H$_2$O</td>
<td>$\Delta E$ = 1.796 V</td>
<td>(9.7)</td>
</tr>
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</table>

A comparison of the performance of an MLMFC in all-alkaline and all-acidic media is shown in Fig. 9.2. Initially at low current densities, both the polarisation curves are identical and thus it is clear that the performance of MLMFC is independent of the medium. The mass transport limitation region is around 6 mA cm$^{-2}$ in the MLMFC in both alkaline and acidic media and was in good agreement with the previous study (Choban et al. 2005). The MLMFC worked for several days without any drop in its performance in a vast array of test conditions. No issues with carbonate formation were encountered in this MLMFC at room temperature, as any carbonate that does form is immediately removed from the system by the flowing streams.
9.3.1.2 Mixed-Media – I: Acidic Anode and Alkaline Cathode

The performance of MLMFC using a fuel stream of 1 M methanol in 1 M H₂SO₄ and an oxidant stream of 0.1 M percarbonate in 1 M KOH was investigated. The measurements were carried out at room temperature for two configurations: (i) acidic-alkaline media: acidic anode, alkaline cathode and (ii) alkaline-acidic media: alkaline anode, acidic cathode. In alkaline-acidic media of this kind, the neutralisation reaction of OH⁻ and H⁺ to form water occurs at the liquid–liquid interface between the fuel and the oxidant streams. In the first configuration, the overall cell reaction, Eq. (9.8), can be obtained from Eqs. (9.2) and (9.6):

Mixed Media 1: Acidic Anode and Alkaline Cathode:

Anode: CH₃OH + H₂O → 6H⁺ + 6e⁻+ CO₂ \hspace{1cm} E' = 0.016 V \hspace{1cm} (9.2)
Cathode: 3H₂O₂ + 6e⁻ → 6OH⁻ \hspace{1cm} E'' = 0.986 V \hspace{1cm} (9.6)
Overall: CH₃OH + 3H₂O₂ + H₂O → CO₂ + 6H⁺ + 6OH⁻ \hspace{1cm} ΔE = 0.970 V \hspace{1cm} (9.8)

In this alkaline-acidic media, the maximum theoretical OCP that can be obtained is 0.902 V. The energy liberated in methanol oxidation and peroxide reduction reactions is mostly consumed for ionisation of water. In this configuration, the coexistence of the galvanic and methanol electrolytic reactions has been found to be the reason for a very low yield of energy, and therefore they were not studied any further.

9.3.1.3 Mixed-Media – II: Alkaline Anode and Acidic Cathode

In alkaline-acidic media, the MLMFC functions using a fuel stream of an alkaline anode and an acidic cathode, which allows energy to be obtained both from the methanol oxidation/peroxide reduction reactions and from the acid/alkali electrochemical neutralisation reactions, as evident from the overall cell reaction Eq. (9.9):
Mixed Media 2: Alkaline Anode & Acidic Cathode:

Anode: \( \text{CH}_3\text{OH} + 6\text{OH}^- \rightarrow \text{CO}_2 + 5\text{H}_2\text{O} + 6\text{e}^- \) \( E^o = -0.81 \text{ V} \) (9.5)

Cathode: \( 3\text{H}_2\text{O}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 6\text{H}_2\text{O} \) \( E^o = 1.78 \text{ V} \) (9.3)

Overall: \( \text{CH}_3\text{OH} + 3\text{H}_2\text{O}_2 + 6\text{H}^+ + 6\text{OH}^- \rightarrow \text{CO}_2 + 11\text{H}_2\text{O} \) \( \Delta E = 2.59 \text{ V} \) (9.9)

In this alkaline-acidic media, the combination of two galvanic reactions yields a desirable high theoretical OCP of 2.52 V. Note that the inherent value of the electromotive force of the MLMFC is higher than that of the HFC (1.23 V) and the PEMFC or DMFC (1.21 V). However, because of the overpotentials resulting from the slow kinetics of peroxide reduction and methanol oxidation, the OCP gets reduced to a measured value of 1.62 V as shown in Fig. 9.2, which was in good agreement with the previous reported value of 1.4 V (Choban et al. 2005). In alkaline-acidic media, both \( \text{OH}^- \) and \( \text{H}^+ \) are consumed at the anode and cathode, respectively, at a rate of six ions for each molecule of methanol.

In alkaline-acidic media, in which an alkaline anode and an acidic cathode are used, a higher overall cell potential was realized compared to that obtained for the all-acidic and all-alkaline MLMFC experiments. Fig. 9.2 shows the power density curves of the MLMFC experiments performed using different media combinations at the anode and cathode.
Fig. 9.2 Performance of media flexibility on current and power density of MLMFC at room temperature; a) All alkaline media ((Fuel): 1 M methanol + 1 M KOH. (Oxidant): 0.1 M percarbmonte + 1 M KOH), b) All acidic media ((Fuel): 1 M methanol + 1 M H$_2$SO$_4$. (Oxidant): 0.1 M percarbmonte + 1 M H$_2$SO$_4$), c) Alkaline-acidic media ((Fuel): 1 M methanol +1 M KOH. (Oxidant): 0.1 M percarbmonte + 1 M H$_2$SO$_4$)

When all-acidic and all-alkaline are used, the maximum power densities generated by the MLMFC are 2.24 and 2.68 mW cm$^{-2}$, respectively, both at a cell potential of about 0.49 V, whereas the when an alkaline-acidic media is used, it results in a power density maximum of 22.21 mW cm$^{-2}$ at a cell potential of about 0.51 V. The alkaline-acidic media fuel cell clearly outperforms both the all-acidic and all-alkaline fuel cell (Table 9.1). The higher power densities in the MLMFC using alkaline-acidic media result from higher overall cell potentials due to the unprecedented ability to operate the cathode and anode at different pH values in an MLMFC.
Table 9.1 Effect of medium on the performance of the MLEFC

<table>
<thead>
<tr>
<th></th>
<th>All-alkaline</th>
<th>All-acidic</th>
<th>Alkaline-acidic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Open circuit voltage (V)</td>
<td>0.95</td>
<td>0.92</td>
<td>1.57</td>
</tr>
<tr>
<td>Short-circuit current density (mA cm(^{-2}))</td>
<td>6.52</td>
<td>5.67</td>
<td>45.51</td>
</tr>
<tr>
<td>Peak power density (mW cm(^{-2}))</td>
<td>2.68</td>
<td>2.24</td>
<td>22.21</td>
</tr>
<tr>
<td>Cell voltage at peak power density (V)</td>
<td>0.49</td>
<td>0.49</td>
<td>0.51</td>
</tr>
<tr>
<td>Current density at peak power density (mW cm(^{-2}))</td>
<td>5.36</td>
<td>4.51</td>
<td>37.26</td>
</tr>
</tbody>
</table>

9.3.2 Influence of Fuel Composition

The effect of fuel on the performance of MLMFC was analysed by varying the concentration of methanol between 0.5 and 4 M (Fig. 9.3).

![Fig. 9.3 Effect of methanol concentration on the current and power density of the MLMFC at room temperature; (Fuel): xM methanol + 1 M KOH. (Oxidant): 0.1 M percarbonate + 1 M H\(_2\)SO\(_4\))](image-url)
The effect of methanol concentration was investigated by varying the concentration of methanol as 0.5, 1.0, 1.5, 2.0, 3.0 to 4.0 M while fixing the concentration of KOH at 1.0 M. Among these several combinations of fuel and oxidant, the fuel solution containing 1.0 M methanol and 1.0 M KOH gives the highest and most stable performance.

The experimental results show that the fuel cell performance decreases as the ethanol concentration increases. This decreasing trend in cell performance at higher ethanol concentrations can be explained as resulting from (a) creation of mixed potential at the cathode due to fuel crossover; (b) kinetic decrease in anode; (c) transport resistance increase at the anode; and (d) ohmic resistance increase.

In a fluidic system, fuel crossover can create mixed potentials, decrease in cell efficiency, and could even deactivate the catalyst. Fortunately, the device design and operating parameters can both be controlled to prevent fuel crossover (Ismagilov et al. 2004, Chang et al. 2006) in any membraneless fuel cell; therefore the higher methanol concentration is not the cause for decrease of performance in a fuel cell. The kinetic decrease in the anode also cannot be a factor because the electro-oxidation of methanol on Pt has a positive reaction order between 0.5 and 1 M. Thus, the activity at the anode increases initially as the concentration of fuel increases. Therefore, the anode is not limited by kinetic performance at higher methanol concentrations. Taking into account these factors, the methanol concentration of 1 M seems to be the best composition for the fuel, and so this value was fixed for the remaining experiments.

9.3.4 Influence of Oxidant Composition

The effects of percarbonate concentration on the cell performance were investigated at 0.01, 0.025, 0.05, 0.075 and 0.1 M. The power density increased as sodium percarbonate concentration increases in the MLMFC system and reaches the maximum of 1.62 V at 0.1 M
sodium percarbonate. Peak power densities of 1.04, 2.79, 5.84, 14.01, 22.21 mW cm$^{-2}$ were obtained at 0.01, 0.025, 0.05, 0.075 and 0.1 M of sodium percarbonate, respectively (Fig. 9.4). A further increase in the oxidant concentration shows no improvement in the cell performance. Therefore, the value of 0.1 M has been fixed as the percarbonate concentration in the oxidant solution.

![Graph showing the effect of percarbonate concentration on the current and power density of the MLMFC at room temperature.](image)

**Fig. 9.4 Effect of percarbonate concentration on the current and power density of the MLMFC at room temperature; (Fuel): 1 M methanol + 1 M KOH. (Oxidant): x M percarbonate + 1 M H$_2$SO$_4$)

Likewise, the effect of H$_2$SO$_4$ concentration in the oxidant solution has also been analysed. The concentration of H$_2$SO$_4$ was varied between 0.1 and 1.0 M. The maximum power density (22.21 mW cm$^{-2}$) was obtained at 1 M H$_2$SO$_4$ (Fig. 9.5). A further increase in the concentration of H$_2$SO$_4$ shows no improvement in the cell performance. Therefore, the value of 1 M has been fixed as the H$_2$SO$_4$ concentration in the oxidant solution.
9.3.5 Influence of Distance Effect

In order to analyze the potential benefit arising from a reduced diffusion length of the reacting species moving between the anode and cathode, the distances were varied between 1 and 100 mm. When the distance between the anode and cathode decreased, the maximum power density was observed, as shown in Fig. 9.6. Considering the role of a charge carrier, a shorter diffusion length is believed to result in a faster electrochemical reaction because the diffusion time of reacting species would be shorter. This leads to more reactions taking place at a given time, which increases the total number of charges involving the electrochemical reactions at the anode and cathode. This finding provides a good evidence for the presence of a charge carrier moving between the anode and cathode in the fuel mixture to complete redox reactions of the fuel cell (Sung et al. 2007).
Fig. 9.6 Effect of distance between anode and cathode on the maximum power density of the MLMFC at room temperature; ((Fuel): 1 M methanol + 1 M KOH. (Oxidant): 0.1 M percarbonate + 1 M H$_2$SO$_4$)

9.3.6 Influence of Fuel Mixture Flow Rate

Since maximum power density is dependent on the transport time of the reacting species, it can be controlled by the flow rate. In this experiment, flow rates of 0.1, 0.3, 0.5, 0.7 and 1.0 mL min$^{-1}$ were tested. The cell potential and current were measured with different external loads as a function of the flow velocity of the fuel mixture. Using the flow rate applied and the cross-sectional area of the channel, a flow velocity can be calculated. In our experiments, the maximum power density was obtained at a flow rate of 0.3 mL min$^{-1}$, after which the maximum power density decreases with an increase in the flow rate as shown in (Fig. 9.7). It is believed that more electrochemical reactions would take place at a given time and a greater output current could develop in the end.
Fig. 9.7 Effect of flow rate of fuel mixture on the current and power density of the MLMFC at room temperature; (Fuel): 1 M methanol + 1 M KOH. (Oxidant): 0.1 M percarbonate + 1 M H$_2$SO$_4$)

References


