CHAPTER 4
The Performance of Pt–Ru–W/C Ternary Electrocatalysts on Methanol Oxidation Reaction in Membraneless Fuel Cells*

Abstract

This work presents the performance of Pt–Ru–W/C ternary electrocatalysts on methanol oxidation reaction in membraneless fuel cells prepared by thermal reduction method. A systematic investigation of methanol adsorption and oxidation on binary and ternary electrocatalysts in acid medium was performed in membraneless methanol fuel cells. The different nominal compositions of binary Pt–Ru/C, Pt–W/C, and ternary Pt–Ru–W/C electrocatalysts were characterized by XRD, EDX, and TEM techniques. XRD and EDX confirmed the formation of Pt–Ru–W/C, Pt–Ru/C, and Pt–W/C metal catalyst with a typical Pt crystalline structure and the formation of Pt–Ru alloy. Electrochemical analyses obtained at room temperature by cyclic voltammetry and chronoamperometry showed that Pt50Ru50W10/C gives a greater current density in comparison to that of Pt50Ru30W20/C, Pt50Ru25W25/C, Pt50Ru50/C, and Pt50W50/C. The power density obtained using Pt50Ru40W10/C (41.2 mW cm\(^{-2}\)) as an anode catalyst in membraneless methanol fuel cell was higher than that using Pt50Ru30W20/C, Pt50Ru25W25/C, Pt50Ru50/C, and Pt50W50/C at the room temperature. CO poisoning can be reduced as a result of enhanced cell performance by the addition of W on the anode electrocatalysts. In this study, the carbon-supported binary Pt–Ru, Pt–W, and ternary Pt–Ru–W anode catalysts were successfully tested in a single membraneless fuel cell.

using 1.0 M methanol as the fuel and 0.1 M sodium perborate as the oxidant with 0.5 M $H_2SO_4$ as the electrolyte.

4.1 Introduction

The membraneless microfluidic fuel cell has been widely studied for applications in portable power electronic devices. The use of methanol as a fuel in membraneless methanol fuel cell (MLMFC) has several advantages compared to that of hydrogen such as transport and storage, ease of handling and low operating temperature, and a high energy density (Ren et al., 2000; Choi et al., 2004; Yamaguchi et al., 2005).

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. However, the use of platinum is limited due to the CO poisoning effect; therefore, the use of binary electrocatalysts, where a new metal is added onto the Pt-base, has been studied (Xu et al., 2006; Luo et al., 2006; Shobha et al., 2003). It is well known that the addition of Ru to Pt-based electrocatalysts lowers the overpotential for the methanol electro-oxidation reaction via a so-called bifunctional mechanism (Gasteiger et al., 1993; Markovic et al., 1995; (Yajima et al., 2004).

To further increase the catalytic activity of the anode, the introduction of a third metal to Pt–Ru/C binary catalyst was found to be the best electrocatalyst, because of its more tolerance to CO poisoning. Therefore, new alternative materials for electrocatalysts are required to minimize the noble metal loading and to optimum the catalytic performance. In this regard, many authors have intensively investigated Pt-based binary and ternary compounds to improve the performance of the electrocatalysts for the electrooxidation of methanol (Sivakumar et al., 2006; Neto et al., 2007; Wang et al., 2009; Kang et al., 2010; Chen et al., 2014). Hence, we prepared Pt–Ru–W/C ternary alloy electrocatalysts by using thermal reduction method.
The enhanced activity of the ternary catalyst is due to the promoting effect of the second or third elements added to Pt. In the present study, we evaluated the catalytic activity for methanol oxidation reaction (MOR) by incorporating W to Pt–Ru/C catalysts in MLMFC.

4.2 Experimental

4.2.1 Materials

The metal precursors used for the preparation of electrocatalysts were H₂PtCl₆.6H₂O (from Sigma Aldrich), RuCl₃.3H₂O (from Sigma Aldrich) and WCl₆ (from Sigma Aldrich). Vulcan XC-72R carbon black (from Cabot Corp.,) was used as a support for the catalysts. Graphite plates (from E-TEK) were used as substrates for the catalyst to prepare the electrodes. Nafion® (DE 521, DuPont USA) dispersion was used to make the catalyst slurry. Isopropyl alcohol (from Merck) was used as a solvent and NaBH₄ (from Merck) was used as the reduction agent. Methanol (from Merck), sodium perborate (from Riedel) and H₂SO₄ (from Merck) were used as the fuel, the oxidant and as the electrolyte for electrochemical analysis, respectively. All the chemicals were of analytical grade. Pt/C (40-wt%, from E-TEK) was used as the cathode catalyst.

4.2.2 Catalyst Preparation

Carbon supported ternary Pt–Ru–W catalysts with different atomic ratios were synthesized by thermal reduction method (Wang et al., 2009). 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 H₂PtCl₆.6H₂O, RuCl₃.3H₂O, WCl₆ 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. For comparison, the monometallic Pt/C, bimetallic Pt–Ru/C and Pt–W/C catalysts were synthesized under the same conditions. The electrocatalytic mixtures and atomic ratios were Pt50Ru40W10/C, Pt50Ru30W20/C, Pt50Ru25W25/C, Pt50Ru50/C, Pt50W50/C and Pt100/C. The nominal loading of metals in the electrocatalysts was 40 %wt and rest 60 %wt was carbon.

4.3 Results and Discussions

4.3.1 Physical Characterization

4.3.1.1 X-ray Diffraction (XRD)

The XRD patterns of the prepared Pt50Ru40W10/C, Pt50Ru30W20/C, Pt50Ru25W25/C, Pt50Ru50/C, Pt50W50/C and Pt100/C catalysts are shown in Fig. 4.1. The first peak located at around 25° in all the XRD patterns is attributable to the Vulcan XC-72R carbon support.

Fig. 4.1 X-ray diffraction patterns of Pt50Ru40W10/C, Pt50Ru30W20/C, Pt50Ru25W25/C, Pt50Ru50/C, Pt50W50/C, and Pt100/C catalysts
The 2θ of the (2 2 0) peak for Pt50Ru40W10/C, Pt50Ru30W20/C, Pt50Ru25W25/C, Pt50Ru50/C and Pt50W50/C, shows a higher angle shift than the characteristics of face-centered cubic (fcc) crystalline Pt at 2θ values of 39°, 47°, 67° and 82° and are indexed with planes (1 1 1), (2 0 0), (2 2 0) and (3 1 1), respectively, indicating that the electrocatalysts have good alloy formations and suggesting the effect of a different atomic rate of W in the ternary catalyst. No diffraction peaks were attributed to pure ruthenium and tungsten metals or ruthenium rich hexagonal close packed (hcp) phase, appear in the XRD patterns, suggesting that ruthenium and tungsten atoms either form an alloy with platinum or exist as amorphous oxide phases (Wang et al., 2009). The Pt–W/C electrocatalyst also showed the same characteristic peak as that of the Pt–Ru/C electrocatalysts.

The fcc lattice parameters were evaluated from the angular position of the (2 2 0) peaks, which reflect the formation of a solid solution (Table 4.1).

Table 4.1 The EDX composition, lattice parameters, and the particle size obtained for different atomic ratios of electrocatalysts

<table>
<thead>
<tr>
<th>Electrocatalyst</th>
<th>Nominal Atomic ratio</th>
<th>EDX Atomic ratio</th>
<th>Lattice parameter (nm)</th>
<th>Crystallite size (nm)</th>
<th>Particle size from TEM (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C</td>
<td>Pt 100 - Ru - W 99</td>
<td></td>
<td>0.3915</td>
<td>4.5</td>
<td>4.1</td>
</tr>
<tr>
<td>Pt–W/C</td>
<td>Pt 50 - Ru 50 W 51</td>
<td></td>
<td>0.3886</td>
<td>4.0</td>
<td>3.8</td>
</tr>
<tr>
<td>Pt–Ru/C</td>
<td>Pt 50 - Ru 50 W 52</td>
<td></td>
<td>0.3903</td>
<td>3.5</td>
<td>3.3</td>
</tr>
<tr>
<td>Pt–Ru–W/C</td>
<td>Pt 50 - Ru 25 W 52</td>
<td></td>
<td>0.3901</td>
<td>3.4</td>
<td>3.2</td>
</tr>
<tr>
<td>Pt–Ru–W/C</td>
<td>Pt 50 - Ru 30 W 52</td>
<td></td>
<td>0.3898</td>
<td>3.3</td>
<td>3.1</td>
</tr>
<tr>
<td>Pt–Ru–W/C</td>
<td>Pt 50 - Ru 40 W 52</td>
<td></td>
<td>0.3896</td>
<td>3.1</td>
<td>3.0</td>
</tr>
</tbody>
</table>

The decrease in lattice parameters of the alloy catalysts reflects the progressive increase in the incorporation of Ru and W into the alloyed state. The difference of lattice
parameters and the shift of (2 2 0) plane indicate interactions between Pt, Ru and W. The average particle size for Pt–Ru/C, Pt–W/C, and Pt–Ru–W/C electrocatalysts were in the range of 3–4.5 nm was estimated using the Scherrer equation.

### 4.3.1.2 Transmission Electron Microscopy (TEM)

TEM image of the Pt50Ru40W10/C, Pt50Ru30W20/C and Pt50Ru25W25/C alloy catalysts and the corresponding particle size distribution histogram are presented in Fig. 4.2. From the TEM images, the average particle diameter was found to be approximately 3-3.5 nm, which is in fairly good agreement with the data calculated from XRD. The particle size distribution of these catalysts is shown in Table 4.1 in accordance to the TEM images.
Fig. 4.2 TEM image and particle size distribution of a) Pt50Ru40W10/C, b) Pt50Ru30W20/C and c) Pt50Ru25W25/C catalyst
4.3.1.3 Energy Dispersive X-ray Spectroscopy (EDX)

Energy dispersive X-ray spectroscopy is conducted by focusing the electron beam on several different selected regions of the carbon supported Pt–Ru–W nanoparticles. An EDX spectrum of Pt–Ru–W/C nanoparticle is shown in Fig. 4.3. The average composition of the sample was in atom ratio of Pt:Ru:W = 5:4:1.

![EDX spectra of Pt/C, Pt–Ru/C, and Pt–Ru–W/C catalysts](image)

**Fig. 4.3 EDX spectra of a) Pt/C, b) Pt–Ru/C and c) Pt–Ru–W/C catalysts**

The EDX results of the Pt/C, binary Pt–Ru/C and ternary Pt–Ru–W/C catalysts are very close to the nominal values, which indicate that the metals were loaded onto the carbon support without obvious loss.
4.3.2 Electrochemical Characterization

4.3.2.1 Cyclic Voltammetry

Fig. 4.4a shows the cyclic voltammogram (CV) on the Pt50Ru40W10/C, Pt50Ru30W20/C, Pt50Ru25W25/C, Pt50Ru50/C, Pt50W50/C and Pt100/C catalysts for CO oxidation in a solution of 0.5 M H2SO4. Due to the strong adsorption of CO onto the Pt surface, the hydrogen adsorption-desorption of the Pt was completely blocked in the hydrogen region; indicating the presence of a saturated CO adlayer (Choi et al., 2003).

![Cyclic Voltammogram](image)

**Fig. 4.4a** CVs of Pt50Ru40W10/C, Pt50Ru30W20/C, Pt50Ru25W25/C, Pt50Ru50/C, Pt50W50/C and Pt100/C electrocatalysts in 0.5 M H2SO4

The electrochemically active surface areas (SEAS) of the electrocatalysts were calculated by using Eq. (4.1) (Zhou et al., 2003; Bonesi et al., 2010; Beyhan et al., 2013). SEAS values were estimated using CO adsorption (SEAS/CO) and roughness of electrodes.
Where $Q_{CO}$ is the charge corresponding to CO on the Pt surface, $[Pt]$ (mg/cm$^2$) is the Pt loading on the electrode surface, 420 $\mu$C/real cm$^2$ is the charge required to oxidize a monolayer of CO on the Pt surface. The roughness of each electrode is calculated by dividing $S_{EAS}$ obtained with the apparent surface area. Estimation of the electrode roughness and $S_{EAS}$ values are shown in Table 4.2. Based on these values, the highest electrochemically active area is achieved for the ternary electrocatalysts. The real surface area estimated by this method is in good agreement with the enhancement in electrocatalytic activity. It is 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.

\[
S_{EAS, CO} (m^2/g) = \frac{Q_{CO}(\mu C/cm^2)}{420(\mu C/cm^2) \times [Pt]} \tag{4.1}
\]

Table 4.2 Comparison of hydrogen desorption charge and carbon monoxide desorption charge, and its electrochemical active surface area ($S_{EAS}$) and electrode roughness

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$Q_{CO}/\mu$C</th>
<th>Electrode real Surface area (cm$^2$)</th>
<th>$S_{EAS/CO}$ ($m^2gPt^{-1}$)</th>
<th>Roughness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt$_{100}$/C</td>
<td>1260</td>
<td>3.0</td>
<td>30</td>
<td>84.0</td>
</tr>
<tr>
<td>Pt$<em>{50}$W$</em>{50}$/C</td>
<td>672</td>
<td>1.6</td>
<td>32</td>
<td>44.8</td>
</tr>
<tr>
<td>Pt$<em>{50}$Ru$</em>{50}$/C</td>
<td>735</td>
<td>1.7</td>
<td>35</td>
<td>49.0</td>
</tr>
<tr>
<td>Pt$<em>{50}$Ru$</em>{25}$W$_{25}$/C</td>
<td>840</td>
<td>2.0</td>
<td>40</td>
<td>56.0</td>
</tr>
<tr>
<td>Pt$<em>{50}$Ru$</em>{30}$W$_{20}$/C</td>
<td>966</td>
<td>2.3</td>
<td>46</td>
<td>64.4</td>
</tr>
<tr>
<td>Pt$<em>{50}$Ru$</em>{40}$W$_{10}$/C</td>
<td>1029</td>
<td>2.4</td>
<td>49</td>
<td>68.6</td>
</tr>
</tbody>
</table>

The CV curves were obtained in a half cell between 0.05 and 1.2 V (vs. Ag/AgCl) in the absence of methanol. The characteristic features of polycrystalline Pt, i.e. hydrogen adsorption/desorption peaks in low potential region, oxide formation/stripping wave/peak in high potential region and a flat double layer in between, are observed for all the synthesized catalysts. The voltammograms of the electrocatalysts did not display a well-defined hydrogen region between 0.05 and 0.35 V, as the catalyst’s features in this region are influenced by their surface composition. Taking the Pt$_{100}$/C composition as a reference, the binary Pt$_{50}$Ru$_{50}$/C and Pt$_{50}$W$_{50}$/C catalysts showed a voltammetric charge similar to that of the pure Pt catalyst. However, a considerable increase in the voltammetric charge of ternary Pt$_{50}$Ru$_{40}$W$_{10}$/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.

Fig. 4.4b corresponds to representative CVs of methanol oxidation under acidic conditions (1.0 M CH$_3$OH and 0.5 M H$_2$SO$_4$) catalyzed by Pt$_{50}$Ru$_{40}$W$_{10}$/C, Pt$_{50}$Ru$_{30}$W$_{20}$/C, Pt$_{50}$Ru$_{25}$W$_{25}$/C, Pt$_{50}$Ru$_{50}$/C, Pt$_{50}$W$_{50}$/C and Pt$_{100}$/C catalysts. The onset potential for the oxidation of methanol in a positive scan was a key factor for evaluating the catalyst activity (Cao et al., (2007)). The onset potentials for the oxidation of methanol on the Pt$_{50}$Ru$_{40}$W$_{10}$/C
(0.30 V), Pt_{50}Ru_{30}W_{20}/C (0.34 V) and Pt_{50}Ru_{25}W_{25}/C (0.38 V) electrocatalysts were slightly lower than that on the Pt_{50}Ru_{50}/C (0.40 V), Pt_{50}W_{50}/C (0.42 V) and Pt_{100}/C (0.45 V) catalysts.

![CV curves of different electrocatalysts](image)

**Fig. 4.4b CVs of Pt_{50}Ru_{40}W_{10}/C, Pt_{50}Ru_{30}W_{20}/C, Pt_{50}Ru_{25}W_{25}/C, Pt_{50}Ru_{50}/C, Pt_{50}W_{50}/C and Pt_{100}/C electrocatalysts in 1.0 M methanol + 0.5 M H_{2}SO_{4}**

All the current values were normalized by the geometric surface area of the electrode used. The CV curves depict the presence of a peak in the potential range of the positive sweep and another peak in the negative sweep. The peak in the positive sweep is associated with the methanol oxidation, and the peak in the negative sweep is related to the oxidation of carbonaceous intermediate products from incomplete methanol oxidation. The peak current densities of Pt_{50}Ru_{40}W_{10}/C, Pt_{50}Ru_{30}W_{20}/C, Pt_{50}Ru_{25}W_{25}/C, Pt_{50}Ru_{50}/C, Pt_{50}W_{50}/C and Pt_{100}/C catalysts are 48.4, 43.2, 41.8, 25.3, 24.7 and 4.9 mA/cm², respectively, showing that the activity of the ternary Pt_{50}Ru_{40}W_{10}/C catalyst is a factor of ~9 times higher than that of the Pt/C catalyst. Table 4.3 summarizes the CV results of Pt_{50}Ru_{40}W_{10}/C, Pt_{50}Ru_{30}W_{20}/C, Pt_{50}Ru_{25}W_{25}/C, Pt_{50}Ru_{50}/C, Pt_{50}W_{50}/C and Pt_{100}/C electrocatalysts including the positive peak potentials and the corresponding peak current densities of MOR.
Table 4.3 CV results of Pt50Ru40W10/C, Pt50Ru30W20/C, Pt50Ru25W25/C, Pt50Ru50/C, Pt50W50/C and Pt100/C electrocatalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Positive peak potential (mV vs. Ag/AgCl)</th>
<th>Peak current density (mA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt100/C</td>
<td>898</td>
<td>4.9</td>
</tr>
<tr>
<td>Pt50W50/C</td>
<td>880</td>
<td>24.7</td>
</tr>
<tr>
<td>Pt50Ru50/C</td>
<td>892</td>
<td>25.3</td>
</tr>
<tr>
<td>Pt50Ru25W25/C</td>
<td>895</td>
<td>41.8</td>
</tr>
<tr>
<td>Pt50Ru25W25/C</td>
<td>898</td>
<td>43.2</td>
</tr>
<tr>
<td>Pt50Ru40W10/C</td>
<td>900</td>
<td>48.4</td>
</tr>
</tbody>
</table>

The CV results show that pure Pt100/C catalysts do not behave as an appropriate anode for MOR due to its poisoning by strongly adsorbed intermediates such as CO. However, the introduction of Ru and W promotes the electrocatalytic activity.

4.3.2.2 Chronoamperometry

Fig. 4.5 shows the current densities measured at a constant potential jumping from 0.05 to 1.2 V in 1.0 M methanol+0.5 M H2SO4. The currents decay with time in a parabolic style and reach an apparent steady state within 80s. It can be seen that the current density of methanol electrooxidation on the Pt50Ru40W10/C catalyst is higher than that on the Pt50Ru30W20/C, Pt50Ru25W25/C, Pt50Ru50/C, Pt50W50/C and Pt100/C catalyst at the same potentials. The activity change for methanol oxidation decreases in the order of Pt50Ru40W10/C > Pt50Ru30W20/C > Pt50Ru25W25/C > Pt50Ru50/C > Pt50W50/C > Pt100/C, which is in fairly good agreement with our CV results.
For the durability test, the chronoamperometric experiments were carried out at 0.05 to 1.2 V for 25 min in the same conditions. Before each measurement, the solution was purged with high-purity nitrogen gas for at least 30 min to ensure oxygen-free measurements.

4.3.3 Single Cell Performance

The microfluidic architecture of laminar flow-based membraneless 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 and composition). Here we focused on maximizing cell performance, in terms of power density, by tailoring various structural characteristics and catalytic activity of carbon supported ternary Pt–Ru–W catalysts. A single cell performance was tested using Pt_{50}Ru_{40}W_{10}/C, Pt_{50}Ru_{30}W_{20}/C, Pt_{50}Ru_{25}W_{25}/C, Pt_{50}Ru_{50}/C, Pt_{50}W_{50}/C and Pt_{100}/C electrocatalysts as the anode. Polarization curves and power densities are shown in Fig. 4.6. For each catalyst, the open-circuit voltages (OCV) were different, as would be expected in
onset potentials. The OCVs of Pt$_{50}$Ru$_{40}$W$_{10}$/C, Pt$_{50}$Ru$_{30}$W$_{20}$/C, Pt$_{50}$Ru$_{25}$W$_{25}$/C, Pt$_{50}$Ru$_{50}$/C, Pt$_{50}$W$_{50}$/C, are higher than that of Pt$_{100}$/C, 0.54 V, and the order of OCV is exactly same as the onset potentials.

The OCV of Pt$_{50}$Ru$_{40}$W$_{10}$/C is the highest value of 0.90 V, which is approximately 0.36 V higher than that of Pt$_{100}$/C. This indicates that Pt$_{100}$/C is more rapidly poisoned by CO than any other alloy catalyst and that the oxidation of adsorbed CO is enhanced by the second or third metal. In the case of Pt$_{50}$Ru$_{40}$W$_{10}$/C the overall performance is superior to that of the bimetallic electrocatalysts. The maximum power densities obtained for Pt$_{50}$Ru$_{40}$W$_{10}$/C, Pt$_{50}$Ru$_{30}$W$_{20}$/C, Pt$_{50}$Ru$_{25}$W$_{25}$/C, Pt$_{50}$Ru$_{50}$/C, Pt$_{50}$W$_{50}$/C and Pt$_{100}$/C are 41.2, 37.4, 30.8, 29.1, 20.6 and 6.8 mW cm$^{-2}$, respectively (Table 4.4). We conclude that the substitution of a small amount of W for Ru aids in cleaning surfaces poisoned by CO and provides additional reaction sites for methanol oxidation.

Fig. 4.6 Polarization and power density curves of Pt$_{50}$Ru$_{40}$W$_{10}$/C, Pt$_{50}$Ru$_{30}$W$_{20}$/C, Pt$_{50}$Ru$_{25}$W$_{25}$/C, Pt$_{50}$Ru$_{50}$/C, Pt$_{50}$W$_{50}$/C and Pt$_{100}$/C electrocatalysts
Table 4.4 Summary of performance of single fuel cell tests using (2 mg cm\(^{-2}\) catalyst loading, 40 wt\% catalyst on carbon)

<table>
<thead>
<tr>
<th>Anode catalysts</th>
<th>Open circuit Voltage (V)</th>
<th>Maximum power density (mW cm(^{-2}))</th>
<th>Maximum current density (mA cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(_{100})/C</td>
<td>0.54</td>
<td>6.8</td>
<td>48.4</td>
</tr>
<tr>
<td>Pt(<em>{50})W(</em>{50})/C</td>
<td>0.66</td>
<td>20.6</td>
<td>100.7</td>
</tr>
<tr>
<td>Pt(<em>{50})Ru(</em>{50})/C</td>
<td>0.71</td>
<td>29.1</td>
<td>131.3</td>
</tr>
<tr>
<td>Pt(<em>{50})Ru(</em>{25})W(_{25})/C</td>
<td>0.82</td>
<td>30.8</td>
<td>199.6</td>
</tr>
<tr>
<td>Pt(<em>{50})Ru(</em>{30})W(_{20})/C</td>
<td>0.85</td>
<td>37.4</td>
<td>225.4</td>
</tr>
<tr>
<td>Pt(<em>{50})Ru(</em>{40})W(_{10})/C</td>
<td>0.90</td>
<td>41.2</td>
<td>249.3</td>
</tr>
</tbody>
</table>

In membraneless fuel cells, pure Pt/C catalyst does not behave as a very good anode for methanol electro-oxidation due to its poisoning by strongly adsorbed intermediates such as CO (Vigier et al., 2004). The binary and ternary electrocatalysts performed better than Pt/C for methanol oxidation. Moreover, when the binary electrocatalysts were compared to the ternary ones in terms of oxidation the latter catalysts gave the best electrical performances. On the other hand, addition of W to Pt (Pt–W/C) had a little effect, whereas addition of W to Pt–Ru greatly enhanced the electrocatalytic activity.

As mentioned in our earlier studies (Gowdhamamoorthi et al., 2014; Ponmani et al., 2014), these results also demonstrated that the performance of the developed membraneless fuel cell enhanced profoundly if the concentration of oxidant in cathodic stream is 10 times larger, and the current density is also increased approximately ten times.

4.4 Conclusions

In this work, the study of methanol oxidation on carbon-supported Pt–Ru–W ternary nanoparticles has revealed details concerning the activity and stability of the catalysts in membraneless fuel cells. The maximum activity for methanol oxidation was found for the
Pt$_{50}$Ru$_{40}$W$_{10}$/C than the Pt$_{50}$Ru$_{30}$W$_{20}$/C, Pt$_{50}$Ru$_{25}$W$_{25}$/C, Pt$_{50}$Ru$_{50}$/C, Pt$_{50}$W$_{50}$/C and Pt$_{100}$/C. The significantly enhanced catalytic activity for methanol oxidation can be attributed to the high dispersion of ternary catalysts and to W acting as a promotion agent. XRD results show the homogenous alloy structure of Pt, Ru and W. The TEM images indicated an average size of Pt$_{50}$Ru$_{30}$W$_{10}$/C, Pt$_{50}$Ru$_{30}$W$_{20}$/C and Pt$_{50}$Ru$_{25}$W$_{25}$/C nanoparticles of 3-3.5 nm. The atom ratio of Pt, Ru and W from EDX analyses is close agreement with the original precursor concentration. The composition of ternary Pt$_{50}$Ru$_{40}$W$_{10}$/C nanoparticles can be conveniently controlled by adjusting the initial metal salt solution and preparation conditions. The electrochemical experiments showed that the Pt$_{50}$Ru$_{40}$W$_{10}$/C nanoparticles have higher catalytic activity than that of the other catalysts. We expect that the MLMFC may be a promising candidate for practical fuel cells to establish a clean and sustainable energy future. Further work is necessary to characterize the catalysts using different surface analysis techniques and to conduct tests of these electrocatalysts in microfluidic membraneless fuel cells.

References


