CHAPTER 5
CHAPTER 5
The Structural and Electrochemical Characterization of Pt–Ru–Ir/C Electrocatalysts
for Electro-oxidation of Methanol in Membraneless Fuel Cells

Abstract

This study presents the influence of operating systems on the performance of Pt–Ru–Ir/C electrocatalysts synthesized by ultrasonic-assisted microwave-irradiated polyol process for electrooxidation of methanol. 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 (1:1:1) was more active in methanol electrooxidation than other catalysts. The 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 (1:1:1) catalyst gave a higher current than the binary Pt–Ru/C (1:1) and Pt–Ir/C (1:1) catalysts at steady condition. The performances of Pt–Ru–Ir/C (1:1:1), Pt–Ru/C (1:1) and Pt–Ir/C (1:1) anode catalysts were evaluated in single membraneless methanol fuel cell at room temperature. Among the catalysts investigated, the Pt–Ru–Ir/C (1:1:1) exhibited the highest methanol electrooxidation reaction activity, followed by the Pt–Ru/C (1:1) and Pt–
Ir/C (1:1). 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 membraneless methanol fuel cell.

5.1 Introduction

Development of highly active anode catalysts is necessary for commercialization of membraneless methanol fuel cells (MLMFC). The binary PtRu alloy is one of the most promising electrocatalysts for methanol electro-oxidation. The promotion effect of Ru has mainly been discussed based on the so-called bifunctional mechanism or electronic effect or a mixture of both. Despite the promising activity of the PtRu alloy, further improvement in activity and durability is necessary for practical application. The alloying of the third metal to PtRu alloy should result in a change in the electronic effects. Chen et al., (2001) identified that the ternary electrocatalysts Pt_{4.5}Ru_{4}Ir_{0.5} is the most efficient and stable electrocatalyst for the oxygen electrode in a unitized regenerative fuel cell system after to combine five elements (Pt, Ru, Os, Rh and Ir) using combinatorial technique. He also showed that the addition of Ru in the Pt–Ir electrode increase the reaction rate by stabilizing the surface atom/oxygen bonds (Pettersson et al. 2006). Pt–Ru–Ir supported in carbon black and Vulcan has been used for electrooxidation of methanol system (Sivakumar et al., 2006, Pasupathi et al., 2007). In the present study, we evaluated the catalytic activity for the MOR reaction by incorporating a third metal Ir to the Pt–Ru catalyst on a carbon support in MLMFC. In the present study, the performance of the Pt–Ru–Ir/C catalyst was compared with that of the Pt–Ru/C and Pt–Ir/C catalysts obtained by the microwave-irradiated polyol process. The prepared electrocatalysts are characterized using transmission electron microscope (TEM), energy dispersive X-ray (EDX) and X-ray diffraction (XRD) analysis. Methanol electro-oxidation in the presence of above catalysts was studied using cyclic voltammetry (CV) and
chronoamperometry (CA). Finally, the catalysts were tested as the anode in microfluidic membraneless fuel cell.

5.2 Experimental

5.2.1 Materials

The metal precursors used for the preparation of electrocatalysts were H\textsubscript{2}PtCl\textsubscript{6}.6H\textsubscript{2}O (from Aldrich), RuCl\textsubscript{3}.3H\textsubscript{2}O (from Alfa Aesar), and H\textsubscript{2}IrCl\textsubscript{6}.xH\textsubscript{2}O (Alfa Aesar). Vulcan XC-72R carbon black (from Cabot Corp.,) was used as a support for the catalysts. Graphite plates (3-cm long and 0.1-cm wide from E-TEK) were used as substrates for the catalyst to prepare the electrodes. Polytetrafluoroethylene (PTFE) (6%; Aldrich) dispersion was used to prepare the catalyst slurry. Ethylene glycol (Merck) was used as the solvent and reduction agent. Methanol (Merck), sodium percarbonate (Riedel), and sulphuric acid (Merck) were used as the fuel, oxidant, and electrolyte for electrochemical analysis, respectively. All the chemicals were of analytical grade. Pt/C (40-wt%; E-TEK) was used as the cathode catalyst.

5.2.2 Catalyst Preparation

The synthesis was carried out with the aid of a LG WD700 microwave oven (700W, 2450 MHz). The catalyst having 40 wt% metal and Pt:Ru:Ir atomic ratio of 1:1:1 was typically prepared as follows: 200 mg of Vulcan XC-72R carbon black was added in 120 mL of ethylene glycol and stirred vigorously to obtain a slurry. Then solutions of 2.48 mL of 0.1517 M hexachloroplatinic acid in ethylene glycol, 10.27 mL of 0.0366 M ruthenium(III) chloride in ethylene glycol, and 1.5 mL of 0.1821 M chloroiridic acid in ethylene glycol were mixed and subsequently added to the slurry. The suspension was stirred for 30 min and ultrasonicated for another 30 min, followed by the addition of a 2.5 M ethylene glycol solution of sodium hydroxide to increase the pH to >10. The suspension was exposed to
microwave irradiation in a 90 s on–10 s off–60 s on heating strategy, and then cooled to room temperature. Hydrochloric acid (3 M) was added to lower the pH to <1, to induce sedimentation of the as-synthesized Pt–Ru–Ir electrocatalyst. The product was recovered by centrifugation and washing with methanol for several times and dried in a vacuum oven at 80 °C for 8 h (Liang et al. 2006). The catalyst thus obtained is denoted as Pt₁Ru₁Ir₁/C. For comparison, Vulcan XC-72R supported Pt–Ru and Pt–Ir electrocatalysts with 40 wt% metal and an atomic ratio of 1:1 were also prepared in the same way and are denoted as Pt₁Ru₁/C and Pt₁Ir₁/C, respectively.

5.2.3 Physical Characterization

The morphology of the dispersed catalysts was examined using SEM (ZEISS EVO 50 Scanning Electron Microscope) and TEM (Philips CM 12 Transmission Electron Microscope). The particle size distribution and mean particle size were also evaluated using TEM. The crystal structure of the synthesized electrocatalysts was characterized by powder X-ray diffraction (XRD) using a Rigaku multiflex diffractometer (model RU-200 B) with Cu-Kα₁ radiation source (λ_Kα₁ = 1.5406 Å) operating at room temperature. The tube current was 40 mA with a tube voltage of 40 kV. The 2θ angular regions between 20° and 90° were recorded at a scan rate of 5° min⁻¹. The mean particle size analyzed from TEM is verified by determining the crystallite size from XRD pattern using Scherrer formula. Pt (2 2 0) diffraction peak was selected to calculate crystallite size and lattice parameter of platinum. According to Scherrer’s Eq. 5.1 (Radmilovic et al. 1995)

\[
D = \frac{0.9\lambda_{Kα₁}}{β_{2θ} \cosθ_{max}}
\]  
(5.1)
where $D$ is the average crystallite size, $\theta_{\text{max}}$ is the angle at the position of the peak maximum, $\beta_{2\theta}$ is the width of the peak (in radians), 0.9 is the shape factor for spherical crystallite and $\lambda_{K\alpha 1}$ is the wavelength of X-rays used. The lattice parameters of the catalysts were estimated according to Eq. 5.2 (Seden Beyhan et al. 2013):

$$
a = \frac{\sqrt{2} \lambda_{K\alpha 1}}{\sin \theta_{\text{max}}} \quad (5.2)
$$

where $a_0$ is the lattice parameter (nm) and all the other symbols have the same meanings as in Eq. 5.1 (Seden Beyhan et al. 2013). The atomic ratio of the catalysts was determined by an energy dispersive X-ray (EDX) analyzer, which was integrated with the TEM instrument.

### 5.2.4 Electrochemical Measurement

Electrochemical studies of the electrocatalysts were carried out using the thin porous coating technique (Colmati et al. 2007). All electrochemical measurements were performed on an electrochemical workstation (CH Instruments, model CHI6650, USA) interfaced with a personal computer using the CHI software, at room temperature. A common three-electrode electrochemical cell using cyclic voltammetry (CV) and chronoamperometry (CA) techniques was used for the measurements. Catalyst coated glassy carbon electrode (GCE, 3 mm diameter and 0.071 cm$^2$ of electrode area, from CHI, USA) was used as the working electrode and platinum foil was used as the counter electrode. Ag/AgCl in saturated KCl was used as the reference electrode. The working electrode was prepared by applying catalyst ink made of 20 mg of electrocatalyst in a solution of 50 mL of water containing three drops of
6% PTFE suspension. The resulting mixture was treated in an ultrasound bath for 10 min to obtain a uniform dispersion. The catalyst slurry was then drop-cast on to a glassy carbon electrode and allowed to dry at 100 °C for 30 min. For assessing the electrocatalytic activity of the working electrode, cyclic voltammetry was obtained in 1.0 M methanol and 0.5 M sulfuric acid solution with a scan rate of 50 mV s\(^{-1}\). For the durability test, the chronoamperometric experiments were carried out at 0.1 V for 3000 s in the same electrolyte. Before each measurement, the solution was purged with high-purity nitrogen gas for at least 30 min to ensure oxygen-free measurements.

5.2.5 Single Cell Test

In the present study, we fabricated the membraneless methanol fuel cell (MLMFC) by using a laminar flow-based fuel cell configuration (Narayanan et al., 2003, 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. Methanol is considered as one of the most promising combustible materials used in microfluidic fuel cells, because of its high-energy density, low toxicity, large scale production from biomass, easy storage and transportation. Sodium percarbonate (\(2\text{Na}_2\text{CO}_3\cdot3\text{H}_2\text{O}_2\)) is a cheap, environment friendly, nontoxic, and large-scale industrial chemical, primarily used as a source of ‘active oxygen’ in detergents and as a mild antiseptic. 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. (5.3):

\[
2\text{Na}_2\text{CO}_3\cdot3\text{H}_2\text{O}_2 \rightarrow 2\text{Na}_2\text{CO}_3 + 3\text{H}_2\text{O}_2
\] (5.3)
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 opposing sidewalls (Fig. 5.1). Graphite plates of one mm thickness served as current collectors and catalyst support structures. The different anode and cathode catalysts were coated onto the graphite plates. For single cell, the anode catalysts with different atomic ratios were prepared as follows: The catalyst ink was prepared by mixing required quantity of catalyst with a solution of 50 mL of water containing three drops of 6% PTFE dispersion in an ultrasonic bath for 10 min to obtain a uniform dispersion. The catalyst slurry was then spread on the graphite plate by brush and dried at 100 °C for 30 min to obtain anode and cathode electrodes. The catalysts tested on the anode side were Pt–Ru–Ir/C (1:1:1), Pt–Ru/C (1:1), Pt–Ir/C (1:1), and Pt/C with a catalyst loading 2 mg/cm². On the cathode side, Pt₃/C with catalyst loading 2 mg/cm² was used 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), at 3-cm length, and 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 the 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 cm²). 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 H₂SO₄ and the catholyte used in the cathode side was 0.1 M percarbonate + 0.5 M H₂SO₄. 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. 5.1 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)

5.3 Results and Discussions

5.3.1 Physical Characterization

5.3.1.1 X-Ray Diffraction (XRD)

XRD analyses were performed to obtain structural information of the catalysts. Fig. 5.2 shows the XRD patterns of the Pt–Ru–Ir/C (1:1:1), Pt–Ru/C (1:1), Pt–Ir/C (1:1) and Pt/C catalysts. The peak at 25–30° observed in all diffraction patterns of the carbon-supported catalysts is attributed to the (0 0 2) plane of the hexagonal structure of the Vulcan XC-72R carbon support (Tayal et al. 2011). The diffraction peaks at around 40°, 47°, 68°, and 82° are attributed to the Pt (1 1 1), (2 0 0), (2 2 0), and (3 1 1) crystalline planes, respectively, which represents the typical character of crystalline Pt with face-centered cubic (FCC) crystalline structure (Radmilovic et al. 1995, Yang et al. 2003, Li et al. 2005). Comparing with the reflections of pure Pt, the diffraction peaks for the Pt–Ru/C, Pt–Ir/C, and Pt–Ru–Ir/C catalysts are shifted slightly to a higher 2θ values. The slight shifts of the diffraction peaks reveal the formation of an alloy involving the incorporation of Ru and Ir atoms into the fcc
structure of Pt. No diffraction peaks related to pure Ru and Ir or their oxides/hydroxides were observed in the XRD patterns (Wang et al. 2014). The average crystallite sizes for the Pt–Ru–Ir/C (1:1:1), Pt–Ru/C (1:1) and Pt–Ir/C (1:1) catalysts, calculated by Scherrer’s formula (R admilovic et al. 1995, Liu et al. 2005), are 3.2, 3.5 and 3.8 nm, respectively, which are very close to those obtained by TEM. Bragg’s equation (R admilovic et al. 1995) is used to obtain the lattice parameters of 3.864 Å, 3.905 Å, 3.891 Å and 3.919 Å for the Pt–Ru–Ir/C (1:1:1), Pt–Ru/C (1:1), Pt–Ir/C (1:1) and Pt/C catalysts respectively.

![Fig. 5.2 X-Ray diffraction patterns of Pt/C, Pt–Ru/C (1:1), Pt–Ir/C (1:1), and Pt–Ru–Ir/C (1:1:1) catalysts](image)

The lattice parameters and the average crystallite size of the catalysts obtained from the XRD patterns are listed under Table 5.1. The lattice parameters obtained for the Pt–Ru/C, Pt–Ir/C, and Pt–Ru–Ir/C catalysts are smaller than those for Pt/C. In fact, the decrease in lattice parameters of the alloy catalysts reflects the progressive increase in the incorporation
of Ru and Ir into the alloy state. Among four catalysts, the lattice parameter for Pt–Ru–Ir/C is the smallest, while that for Pt/C is the biggest.

Table 5.1 Characterization parameters for the Pt/C, Pt–Ir/C (1:1), Pt–Ru/C (1:1) and Pt–Ru–Ir/C (1:1:1) catalysts

<table>
<thead>
<tr>
<th>Electrocatalysts</th>
<th>(2 2 0) Diffraction peak position (2θ)</th>
<th>Lattice parameter (Å)</th>
<th>Average crystallite size D from XRD (nm)</th>
<th>Average Particle size from TEM (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C</td>
<td>67.55</td>
<td>3.919</td>
<td>3.9</td>
<td>-</td>
</tr>
<tr>
<td>Pt–Ir/C (1:1)</td>
<td>68.16</td>
<td>3.891</td>
<td>3.8</td>
<td>3.4</td>
</tr>
<tr>
<td>Pt–Ru/C (1:1)</td>
<td>67.82</td>
<td>3.905</td>
<td>3.8</td>
<td>3.2</td>
</tr>
<tr>
<td>Pt–Ru–Ir/C (1:1:1)</td>
<td>68.64</td>
<td>3.864</td>
<td>3.2</td>
<td>2.9</td>
</tr>
</tbody>
</table>

5.3.1.2 Transmission Electron Microscopy (TEM)

The particle size, morphology, and size distribution have significant effect on the performance of electrocatalysts (Li et al. 2005). With this in mind, TEM was carried out to investigate the particle size and distribution of Pt–Ru–Ir nanoparticles on the surface of carbon support. The TEM images of Pt–Ru–Ir/C (1:1:1), Pt–Ru/C (1:1) and Pt–Ir/C (1:1) catalysts are shown in Fig.5.3, together with the obtained averaged value of the particle diameter distribution histograms. It can be seen that the spherical metal particles of the catalysts are uniformly dispersed on Vulcan XC–72R, with some aggregates observed in Pt–Ru/C. The average particle size for Pt–Ru–Ir/C (1:1:1), Pt–Ru/C (1:1) and Pt–Ir/C (1:1) catalysts were between 2 and 4 nm. The small particle size and the homogeneous size distribution of the catalysts are ascribed to the rapid reduction of the metal salts and easy nucleation of the metal particles in ethylene glycol facilitated by microwave irradiation (Verde et al. 2005, Seden Beyhan et al. 2013, Ribeiro et al. 2007).
In comparison to Pt–Ru/C (1:1) and Pt–Ir/C (1:1), the mean particle size of Pt–Ru–Ir/C (1:1:1) was smaller. The variation in the mean particle size for these catalysts was quite similar in both the cases (TEM and XRD), indicating good particle dispersion without formation of large particle aggregates (Table 5.1).

5.3.1.3. Energy dispersive X-ray (EDX) Analysis

The EDX analyses of all the Pt–Ru/C (1:1), Pt–Ir/C (1:1), and Pt–Ru–Ir/C (1:1:1) catalysts are shown in Fig. 5.4. The catalysts prepared had the desired elements with some
variation in composition. Fig. 5.4 a-c indicates the presence of Pt, Ir, Ru and C, respectively.

The EDX results are shown in Table 5.2.

![EDX spectra of Pt-Ru/C (1:1), Pt-Ir/C (1:1), and Pt-Ru-Ir/C (1:1:1) catalysts](image)

**Fig. 5.4 EDX spectra of a) Pt–Ru/C (1:1), b) Pt–Ir/C (1:1), and c) Pt–Ru–Ir/C (1:1:1) catalysts**

The EDX results of the binary and the ternary catalysts are very close to the nominal values, which indicate that the metals were loaded onto the carbon support without obvious loss.
Table 5.2 EDX composition of synthesized electrocatalysts in at %.

<table>
<thead>
<tr>
<th>Electrocatalyst</th>
<th>Nominal atomic ratio</th>
<th>Atomic ratio – EDX</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pt</td>
<td>Ru</td>
</tr>
<tr>
<td>Pt–Ir/C (1:1)</td>
<td>50</td>
<td>-</td>
</tr>
<tr>
<td>Pt–Ru/C (1:1)</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Pt–Ru–Ir/C (1:1:1)</td>
<td>34</td>
<td>33</td>
</tr>
</tbody>
</table>

5.3.2 Electrochemical Characterization

5.3.2.1 Cyclic Voltammetry

Typical cyclic voltammograms (CVs) of Pt–Ru–Ir/C (1:1:1), Pt–Ru/C (1:1), Pt–Ir/C (1:1) and Pt/C catalysts in 0.5 M H₂SO₄ solution are shown in Fig. 5.5a. The cyclic voltammetry curves were obtained in a half cell at a scan rate of 50 mV s⁻¹ between −0.1 and +1.0 V (vs. Ag/AgCl) in the absence of ethanol and at room temperature. 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 0.0 and 0.4 V, as the catalyst’s features in this region are influenced by their surface composition (Wang et al. 2014, Seden Beyhan et al. 2013). Taking the Pt₁₀₀/C composition as a reference, the binary Pt–Ru/C (1:1) and Pt–Ir/C (1:1) catalysts showed a voltammetric charge similar to that of the pure Pt catalyst. However, a considerable increase in the voltammetric charge of ternary Pt–Ru–Ir/C (1:1:1) catalyst was observed in the double-layer region between 0.4 and 0.8 V, indicating that the addition of Ir into binary Pt–Ru/C leads to an enhanced activity for the oxidation reactions. This behavior can be explained by a better material dispersion on carbon.
and the formation of ultrafine particles (Ribeiro et al. 2007). The latter phenomenon was being confirmed by XRD data, which give a $D$ value close to 3.5 nm.

Fig. 5.5a Cyclic voltammetry of Pt/C, Pt–Ru/C (1:1), Pt–Ir/C (1:1), and Pt–Ru–Ir/C (1:1:1) electrocatalysts in 0.5 M H$_2$SO$_4$ at room temperature with a scan rate of 50 mV/s.

Fig. 7.5b corresponds to representative cyclic voltammograms (CV) of methanol oxidation under acidic conditions (1.0 M CH$_3$OH and 0.5 M H$_2$SO$_4$) catalyzed by Pt–Ru–Ir/C (1:1:1), Pt–Ru/C (1:1), Pt–Ir/C (1:1) and Pt/C catalysts. All the current values were normalized by the geometric surface area of the electrode used. The CV curves (Fig. 5.5b) 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–Ru–Ir/C (1:1:1), Pt–Ru/C (1:1), Pt–Ir/C (1:1) and Pt/C catalysts at 50 mV s$^{-1}$ are 82.3, 42.2, 39.9, and 20.5 mA/cm$^2$, respectively, showing that the activity of the ternary Pt–Ru–Ir/C (1:1:1) catalyst is a factor of ~4 times higher than that of the Pt/C catalyst and ~2 times higher than
that of the binary Pt–Ru/C (1:1) and Pt–Ir/C (1:1) catalysts. Almost no activity variation was observed, even after 6 h of uninterrupted cycling of the potential between 0 and 0.8 V, indicating the facile removal of adsorbed CO intermediates.

Table 5.3 summarizes the CV results of Pt–Ru–Ir/C (1:1:1), Pt–Ru/C (1:1), Pt–Ir/C (1:1) and Pt/C electrocatalysts including the positive peak potentials and the corresponding peak current densities of methanol electro-oxidation (MOR). The CV results show that pure Pt\textsubscript{100}/C catalysts (Fig. 5.5b) do not behave as an appropriate anode for MOR due to its poisoning by strongly adsorbed intermediates such as CO (Vigier et al. 2004). However, the introduction of Ru and Ir promotes the electrocatalytic activity. Fig. 5.5b shows that the onset potentials of methanol electro oxidation for binary Pt–Ru/C (1:1), and Pt–Ir/C (1:1) catalysts are at about 0.4 V vs. Ag/AgCl. While for ternary Pt–Ru–Ir/C (1:1:1) catalyst onset potential for methanol electro-oxidation is earlier at about 0.3 V vs. Ag/AgCl, i.e. shifted to negative
potential by 0.1 V. This observation can be explained by the more pronounced oxophilic character of Ru at low potentials in comparison with Ir (Wang et al. 2014, Liang et al. 2006, Hui Wang et al. 2014). The superior activity of the Pt–Ru–Ir/C (1:1:1) electrocatalyst can be attributed to the combination of electronic effect and bifunctional mechanism (Choi et al. 2000, Park et al. 2002, Park et al. 2004). Again, the ternary compositions (Pt–Ru–Ir/C) presented much higher current densities than the binary Pt–Ru/C, and Pt–Ir/C catalysts, indicating that the activity of the ternary electrocatalysts toward MOR was much better than that of the binary compositions.

Table 5.3 CV results of Pt/C, Pt–Ru/C (1:1), Pt–Ir/C (1:1), and Pt–Ru–Ir/C (1:1:1) electrocatalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Scan rate 50 mV/s</th>
<th>Positive peak potential (mV vs. Ag/AgCl)</th>
<th>Peak current density (mA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C</td>
<td>0.82</td>
<td>20.3</td>
<td></td>
</tr>
<tr>
<td>Pt–Ir/C (1:1)</td>
<td>0.84</td>
<td>39.7</td>
<td></td>
</tr>
<tr>
<td>Pt–Ru/C (1:1)</td>
<td>0.85</td>
<td>42.5</td>
<td></td>
</tr>
<tr>
<td>Pt–Ru–Ir/C (1:1:1)</td>
<td>0.77</td>
<td>82.5</td>
<td></td>
</tr>
</tbody>
</table>

5.3.2.2 Chronoamperometry (CA)

Fig. 5.6 shows the chronoamperometric curves of Pt–Ru–Ir/C (1:1:1), Pt–Ru/C (1:1), Pt–Ir/C (1:1) and Pt/C catalysts for the methanol oxidation at a constant potential of 0.5 V versus Ag/AgCl and at room temperature. During the first 5 min, a sharp decrease in the current density. Followed by relative stabilization was noted. This occurs because the active sites were initially free from the adsorbed/oxidized methanol molecules. However, as the reaction proceeds, the adsorption rate of a new methanol molecule depends on the availability of the catalyst active site. On the other hand, the reason for the decay of current value is due
to poisoning of surface active sites by intermediates and instability of catalyst particles. This reaction is metal-dependent and proceeds faster (high current density) in the case of metals with a good ability to oxidize the intermediate species responsible for poisoning of the catalytic sites (CO) (Ribeiro et al. 2008). Thus, the surface becomes unstable, and the phenomena such as crystallization, segregation of the metal surface, and agglomeration of particles may occur to create new catalytic sites. The latter are quickly poisoned, thereby contributing to the continuous decrease in the current (Radmilovic et al. 1995). The compositions Pt–Ru/C (1:1), Pt–Ir/C (1:1) and Pt/C gave rise to extremely rapid rates of poisoning of the catalytic sites, resulting in a very low activity. However, ternary material Pt–Ru–Ir/C (1:1:1) had good ability to overcome catalyst poisoning, thus furnishing a high current density (Wang et al. 2014). Chronoamperometric analysis usually indicates the rate of decay of the current density with time, which is directly linked with anti-poisoning ability. The long term poisoning rates of Pt–Ru–Ir/C (1:1:1), Pt–Ru/C (1:1), Pt–Ir/C (1:1) and Pt/C catalysts were calculated by measuring the ratio of the current at 1,000 s ($I_{1,000}$) and 100 s ($I_{100}$). The ratios of $I_{1,000}/I_{100}$ for the binary Pt–Ru/C (1:1), Pt–Ir/C (1:1) and the ternary Pt–Ru–Ir/C (1:1:1) catalysts were found to be 27.3, 28.2 and 51.1%, respectively, indicating that the ternary Pt–Ru–Ir/C (1:1:1) catalyst has superior anti-poisoning ability to the binary Pt–Ru/C (1:1) and Pt–Ir/C (1:1) catalysts. The ternary Pt–Ru–Ir/C (1:1:1) catalysts demonstrated higher current than the binary Pt–Ru/C (1:1) and Pt–Ir/C (1:1) catalysts. Higher current obtained for the ternary electrocatalysts may be explained by the operation of a beneficial synergistic effect between Ru and Ir, which may indicate an increase in the structural defects or roughness, making the ternary electrocatalysts better candidates for MOR.
5.3.3 Single Cell Performance

The performance of a real fuel cell is of ultimate importance for practical application. Fig. 5.7 shows the performance of membraneless methanol fuel cell (MLMFC) with Pt/C, Pt–Ir/C (1:1), Pt–Ru/C (1:1) and Pt–Ru–Ir/C (1:1:1) as anode catalysts. When Pt/C was used as the anode catalyst, the performance of single cell was poor. The open-circuit potential (OCP) was 0.53 V, far less than the reversible OCP (1.145 V) (Cunha et al. 2011), which was mainly attributed to poor catalytic activity towards ethanol electro-oxidation. The maximum output power density for Pt/C is 4.42 mW/cm$^2$. The results of MLMFC adapting to different catalysts are summarized in Table 5.4. When the current was normalized to the geometric area of single cell, it was observed that the cell performance of Pt–Ru–Ir/C (1:1:1) catalyst was better than other catalysts. In the low current discharging region, the power drawn from single cell was almost the same for all catalysts except Pt/C. However, as the voltage reach around 0.3 V Pt–Ru–Ir/C (1:1:1) started drawing more current in comparison to others.
Table 5.4 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/C</td>
<td>0.52</td>
<td>4.42</td>
<td>45.11</td>
</tr>
<tr>
<td>Pt–Ir/C (1:1)</td>
<td>0.59</td>
<td>18.16</td>
<td>108.05</td>
</tr>
<tr>
<td>Pt–Ru/C (1:1)</td>
<td>0.66</td>
<td>25.13</td>
<td>123.81</td>
</tr>
<tr>
<td>Pt–Ru–Ir/C (1:1:1)</td>
<td>0.72</td>
<td>34.81</td>
<td>213.12</td>
</tr>
</tbody>
</table>

![Graph showing polarization and power density curves](image)

**Fig. 5.7** Polarization and power density curves of different catalyst at 2 mg cm\(^{-2}\) catalyst loading on anode and cathode at room temperature

The open-circuit potential for Pt–Ir/C (1:1) and Pt–Ru/C (1:1) catalysts was (0.59 V and 0.66 V respectively) lower than for Pt–Ru–Ir/C (1:1:1) (0.72 V). In addition, there was a rapid initial fall in cell voltage for all catalysts, which was due to the slow initial ethanol electro-oxidation reaction at the electrode surface. After an initial drop of 50 mV the change in slope of the polarization curve for Pt–Ru–Ir/C (1:1:1) decreased, and it started drawing...
more current. This is attributed to the more effective catalytic ability of Pt–Ru–Ir/C (1:1:1), once the methanol electro-oxidation reaction being initiated. Based on peak power density drawn from single cell, Pt–Ru–Ir/C (1:1:1) is the best anode catalyst with peak power density value of 34.81 mW/cm$^2$. In agreement with the cyclic voltammetry and chronoamperometry data, the Pt–Ru–Ir/C (1:1:1) anode catalyst exhibits higher single cell performance than Pt–Ir/C (1:1) and Pt–Ru/C (1:1) in the MLMFC tests.

References


