CHAPTER 3
An Improvement in the Electro-oxidation of Methanol at Pt–Ru–Ni/C Electro catalysts in Membraneless Fuel Cells

Abstract

Carbon supported well-dispersed Pt_{100}, Pt_{60}Ru_{40}, Pt_{60}Ni_{40} and Pt_{60}Ru_{30}Ni_{10} electrocatalysts were synthesized by ultrasonic-assisted alcohol-reduction method. The particle size, lattice parameter, composition, and micro-morphology of metals in the electrocatalysts were determined by XRD, EDX, and TEM techniques respectively. X-ray diffraction analysis showed that catalysts have the Pt face centred cubic (fcc) structure, and their crystallite size were in the range 2–6 nm. Regarding the ternary Pt_{60}Ru_{30}Ni_{10}/C electrocatalyst, its lattice parameter was larger than that of Pt_{60}Ni_{40}/C and smaller than that of Pt_{60}Ru_{40}/C and Pt/C. The EDX results of the binary Pt–Ru/C and Pt–Ni/C and the ternary Pt–Ru–Ni/C catalysts are very close to the nominal values, which indicate that the metals were loaded onto the carbon support without obvious loss. The size of catalyst nanoparticles was observed via transmission electron microscopy and showed an average diameter of 3 nm. The electrocatalytic activities of Pt_{100}/C, Pt_{60}Ru_{40}/C, Pt_{60}Ni_{40}/C and Pt_{60}Ru_{30}Ni_{10}/C catalysts were investigated in terms of cyclic voltammetry (CV) and chronoamperometry (CA). The onset potentials for methanol oxidation on Pt_{60}Ru_{30}Ni_{10}/C and Pt_{60}Ru_{40}/C catalysts were significantly lower than that of Pt_{100}/C and Pt_{60}Ni_{40}/C. This clearly indicates that the performance of the ternary Pt_{60}Ru_{30}Ni_{10}/C electrocatalyst, for methanol electrooxidation is better than that of the binary Pt_{60}Ru_{40}/C and Pt_{60}Ni_{40}/C electrocatalysts due to the promoting function of Ni. The high activity of Pt_{60}Ru_{30}Ni_{10}/C electrocatalyst was also observed on membraneless methanol fuel cell, which was consistent with the half-cell measurements.
3.1 Introduction

Increasing the electrocatalytic activity and stability of Pt-based catalysts has been the focus of much recent research (Peng et al. 2009, Zhang et al. 2012, Rabis et al. 2012) and remains a critical requirement for the future implementation of membraneless fuel cells (MLMFC). The anodic current from methanol electrooxidation on Pt is very sluggish, especially at low temperatures. There is a need to improve the activity of catalysts for methanol electrooxidation. The number of possible metals which are able to activate water at a lower potential with a sufficient stability in acid is rather limited. Among the various Pt-based binary catalysts, the PtRu alloy has been reported as the most effective for methanol electro-oxidation (Datta et al. 2009). The development of a novel catalyst or the addition of a third element to Pt–Ru can be significant. It is expected that the new catalyst will be more active toward dehydrogenation, giving C–O bond cleavages during methanol oxidation (Jiang et al. 2005). The addition of Ni as the second or third element is claimed to increase the activity of Pt electrocatalysts. Current studies indicate that Pt–Ru–Ni/C electrocatalysts prepared by different methodologies were more active than the corresponding Pt–Ru electrocatalyst (Wang et al. 2006, Choi et al. 2003, Jeon et al. 2008). Martinez-Huerta et al. (Martinez-Huertal et al. 2006) prepared Pt–Ru–Ni/C electrocatalyst by the colloidal and microemulsion routes and observed that the electrocatalytic behavior of Pt–Ru/C was modified by the addition of Ni, and concluded that the presence of Ni along with Ru in the right proportion was probably responsible for enhancing methanol oxidation. Wang et al. (Wang et al. 2006) also observed that Pt–Ru–Ni/C electrocatalyst prepared by alcohol reduction method was more active for methanol oxidation than a commercial Pt–Ru/C electrocatalyst. In the present study, Pt\textsubscript{100}/C, Pt\textsubscript{60}Ni\textsubscript{40}/C, Pt\textsubscript{60}Ru\textsubscript{40}/C and Pt\textsubscript{60}Ru\textsubscript{30}Ni\textsubscript{10}/C catalysts were prepared by alcohol-reduction method from their precursors to study methanol electro-oxidation. The prepared electrocatalysts are characterized using scanning electron
microscope (SEM), 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.

3.2 Experimental

3.2.1 Materials

The metal precursors used for the preparation of electrocatalysts were $\text{H}_2\text{PtCl}_6.6\text{H}_2\text{O}$ (from Aldrich), $\text{RuCl}_3.3\text{H}_2\text{O}$ (from Alfa Aesar), and $\text{NiCl}_2.6\text{H}_2\text{O}$ (from Aldrich). Vulcan XC-72R carbon black (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% from Aldrich) dispersion was used to make the catalyst slurry. Ethylene glycol (from Merck) was used as the solvent and reduction agent. Methanol (from Merck), sodium percarbonate (from Riedel) and $\text{H}_2\text{SO}_4$ (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.

3.2.2 Catalyst Preparation

Carbon supported ternary Pt–Ru–Ni catalysts with different atomic ratios were synthesized by the ultrasonic-assisted alcohol-reduction process (Ribandenenira et al. 2010). Initially, the precursors were suspended in ethylene glycol and water (75/25 v/v), followed by the addition of carbon support. The resulting mixtures were treated in an ultrasound bath and were refluxed for 3 h under the open atmosphere. Then the solution was made alkaline (about pH 12) and heated at 140 °C for 3 h under agitation to enable the metal’s reduction. Finally,
the precipitate was collected by filtration, washed with deionized (DI) water, and dried at 70 °C for 2 h. For comparison, the monometallic Pt/C, bimetallic Pt–Ru/C and Pt–Ni/C catalysts were synthesized under the same conditions. The electrocatalytic mixtures and atomic ratios were Pt\(_{100}/C\), Pt\(_{60}\)Ru\(_{40}/C\), Pt\(_{60}\)Ni\(_{40}/C\) and Pt\(_{60}\)Ru\(_{30}\)Ni\(_{10}/C\). The nominal loading of metals in the electrocatalysts was 40 %wt and rest 60 %wt was carbon.

3.2.3 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-K\(_{\alpha1}\) radiation source (\(\lambda_{K\alpha1} = 1.5406\) Å) operating at room temperature. The tube current was 40 mA with a tube voltage of 40 kV. The 2\(\theta\) 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 Scherer formula. Pt (2 2 0) diffraction peak was selected to calculate crystallite size and lattice parameter of platinum. According to Scherrer’s Eq. 3.1 (Radmilovic et al. 1995)

\[
D = \frac{0.9\lambda_{K\alpha1}}{\beta_{2\theta} \cos \theta_{\text{max}}} \quad (3.1)
\]

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
\( \lambda_{\text{K}\alpha 1} \) is the wavelength of X-rays used. The lattice parameters of the catalysts were estimated according to Eq. 2.2 (Seden Beyhan et al. 2013):

\[
a = \frac{\sqrt{2} \lambda_{\text{K}\alpha 1}}{\sin \theta_{\text{max}}} \quad (3.2)
\]

where \( a \) is the lattice parameter (nm) and all the other symbols have the same meanings as in Eq. 2.1 (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.

### 3.2.4 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 (RHE). 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.

3.2.5 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 sulfuric 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 (2Na\(_2\)CO\(_3\).3H\(_2\)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. (3.3):

\[
2\text{Na}_2\text{CO}_3.3\text{H}_2\text{O}_2 \rightarrow 2\text{Na}_2\text{CO}_3 + 3\text{H}_2\text{O}_2
\] (3.3)

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. 3.1). 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 ºC for 30 min to obtain anode and cathode electrodes. The catalysts tested on the anode side were Pt\textsubscript{100}/C, Pt\textsubscript{60}Ru\textsubscript{40}/C, Pt\textsubscript{60}Ni\textsubscript{40}/C and Pt\textsubscript{60}Ru\textsubscript{30}Ni\textsubscript{10}/C with catalyst loading 2 mg/cm\textsuperscript{2}. On the cathode side, Pt\textsubscript{100}/C with catalyst loading 2 mg/cm\textsuperscript{2} was used in all 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\textsuperscript{2}). The design is 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\textsubscript{2}SO\textsubscript{4} and the catholyte used in the cathode side was 0.1 M percarbonate + 0.5 M H\textsubscript{2}SO\textsubscript{4}. The flow rate of each of the streams was 0.3 mL min\textsuperscript{-1} (total flow rate of 0.6 mL min\textsuperscript{-1}). The MLMFC was operated at room temperature. The current-voltage characteristics of MLMFC were measured using an electrochemical workstation (CH Instruments, model CHI6650, USA) and the data was verified using a multi-meter (MASTECH\textsuperscript{®} MAS830L).
3.3 Results and Discussions

3.3.1 Physical Characterization

3.3.1.1 X-Ray Diffraction (XRD)

XRD patterns reveal the bulk structure of the catalyst and its support. Fig. 3.2 shows the XRD patterns of the Pt$_{100}$/C, Pt$_{60}$Ru$_{40}$/C, Pt$_{60}$Ni$_{40}$/C and Pt$_{60}$Ru$_{30}$Ni$_{10}$/C catalysts. It can be seen that the first peak located at a 2$\theta$ value of about 25$^\circ$ in the XRD pattern is referred to Vulcan XC-72R carbon support. The other four peaks are characteristic of face centered cubic (fcc) crystalline Pt, corresponding to the planes (1 1 1), (2 0 0), (2 2 0) and (3 1 1) at 2$\theta$ values of about 40$^\circ$, 47$^\circ$, 68$^\circ$ and 82$^\circ$, respectively, indicating that the alloy catalysts have principally single-phase disordered structures (i.e. solid solutions). Comparing with the reflections of pure Pt, the diffraction peaks for the Pt–Ru, Pt–Ni, and Pt–Ru–Ni catalysts are shifted slightly to a higher 2$\theta$ values. The slight shifts of the diffraction peaks reveal the formation of an alloy involving the incorporation of Ru and Ni atoms into the fcc structure of Pt. It is important to note that no diffraction peaks, indicating the presence of either pure Ru and Ni or Ru-rich hexagonal close packed (hcp) phase, and Ni oxide, appear.
Fig. 3.2 X-Ray diffraction patterns of Pt\textsubscript{100}/C, Pt\textsubscript{60}Ru\textsubscript{40}/C, Pt\textsubscript{60}Ni\textsubscript{40}/C and Pt\textsubscript{60}Ru\textsubscript{30}Ni\textsubscript{10}/C catalysts

The lattice parameters of Pt–Ru/C, Pt–Ni/C, and Pt–Ru–Ni/C catalysts, which reflect the formation of a solid solution and be calculated by using the Pt (2 2 0) crystal faces, are given in Table 3.1. The lattice parameters obtained for the Pt–Ru/C, Pt–Ni/C, and Pt–Ru–Ni/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 Ni into the alloy state. Among four catalysts, the lattice parameter for Pt–Ru–Ni/C is the smallest, while that for Pt/C is the biggest. The average particle size $d$ may be estimated from full width at half-maximum (FWHM) of Pt (2 2 0) according to Debye–Scherrer formula (Wang et al., 2006, Wang et al., 2005, He et al., 1997, Giorgi et al., 2001).
Table 3.1 The lattice parameters and the particle size obtained for different atomic ratios of electrocatalysts

<table>
<thead>
<tr>
<th>Electrocatalyst</th>
<th>(2 2 0) Diffraction peak position ($2\theta$)</th>
<th>Lattice parameter (Å)</th>
<th>Average crystallite size from XRD (D) (nm)</th>
<th>Average Particle size from TEM (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt$_{100}$/C</td>
<td>67.54</td>
<td>3.919</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pt$<em>{60}$Ni$</em>{40}$/C</td>
<td>67.96</td>
<td>3.898</td>
<td>4.3</td>
<td>3.7</td>
</tr>
<tr>
<td>Pt$<em>{60}$Ru$</em>{40}$/C</td>
<td>67.94</td>
<td>3.899</td>
<td>4.5</td>
<td>3.7</td>
</tr>
<tr>
<td>Pt$<em>{60}$Ru$</em>{30}$Ni$_{10}$/C</td>
<td>68.02</td>
<td>3.896</td>
<td>4.0</td>
<td>3.6</td>
</tr>
</tbody>
</table>

3.3.1.2 Scanning Electron Microscopy (SEM)

SEM images of Pt$_{60}$Ru$_{40}$/C, Pt$_{60}$Ni$_{40}$/C and Pt$_{60}$Ru$_{30}$Ni$_{10}$/C catalysts prepared are shown in Fig. 3.3a–c. SEM image clearly shows that the nanoparticles of the catalysts are uniformly dispersed on the carbon support. The SEM images confirm the porous structure of the catalysts prepared.

Fig. 3.3 SEM images of a) Pt$_{60}$Ru$_{40}$/C, b) Pt$_{60}$Ni$_{40}$/C and c) Pt$_{60}$Ru$_{30}$Ni$_{10}$/C catalysts
3.3.1.3 Transmission Electron Microscopy (TEM)

The TEM images of the Pt\textsubscript{60}Ru\textsubscript{40}/C, Pt\textsubscript{60}Ni\textsubscript{40}/C and Pt\textsubscript{60}Ru\textsubscript{30}Ni\textsubscript{10}/C catalysts are shown in Fig.3.4 a-f, together with the obtained averaged value of the particle diameter distribution histograms. The micrographs of the electrocatalysts show that all catalysts have a good dispersion on Vulcan XC-72R with a size in the same range and follow a log-normal size distribution (Granqvist et al. 1976, Granqvist et al. 1976, Ehrburger et al. 1978).

Fig. 3.4 TEM image and histograms of a and d) Pt\textsubscript{60}Ru\textsubscript{40}/C, b and e) Pt\textsubscript{60}Ni\textsubscript{40}/C and c and f) Pt\textsubscript{60}Ru\textsubscript{30}Ni\textsubscript{10}/C catalysts
From the particle distribution of 1 to 7 nm, the average particle size for Pt$_{60}$Ru$_{40}$/C, Pt$_{60}$Ni$_{40}$/C and Pt$_{60}$Ru$_{30}$Ni$_{10}$/C catalysts were between 3 and 4 nm. In comparison to Pt$_{60}$Ru$_{40}$/C and Pt$_{60}$Ni$_{40}$/C the mean particle size of Pt$_{60}$Ru$_{30}$Ni$_{10}$/C was smaller. The variations of the mean particle size for these catalysts are quite similar in both cases (TEM and XRD), indicating good particle dispersion without the formation of large particle aggregates (Table 3.1).

### 3.3.1.4 Energy Dispersive X-ray (EDX) Analysis

The EDX analyses of all the Pt$_{60}$Ru$_{40}$/C, Pt$_{60}$Ni$_{40}$/C and Pt$_{60}$Ru$_{30}$Ni$_{10}$/C catalysts are shown in Fig. 3.5. Fig. 3.5a-c indicates the presence of Pt, Ru and carbon; Pt, Ni and carbon; and both the combinations of Pt, Ru, Ni, and carbon, respectively. The EDX results are shown in Table 3.2. The catalysts prepared had the desired elements with some variation in composition. The EDX results of the binary Pt$_{60}$Ru$_{40}$/C and Pt$_{60}$Ni$_{40}$/C and the ternary Pt$_{60}$Ru$_{30}$Ni$_{10}$/C catalysts are very close to the nominal values, which indicate that the metals were loaded onto the carbon support without obvious loss.

**Table 3.2 EDX composition of synthesized electrocatalysts in at %**

<table>
<thead>
<tr>
<th>Electro catalyst</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–Ni/C</td>
<td>60</td>
<td>-</td>
</tr>
<tr>
<td>Pt–Ru/C</td>
<td>60</td>
<td>40</td>
</tr>
<tr>
<td>Pt–Ru–Ni/C</td>
<td>60</td>
<td>30</td>
</tr>
</tbody>
</table>
3.3.2 Electrochemical Characterization

3.3.2.1 Cyclic Voltammetry

Fig. 3.6a shows representative cyclic voltammograms (CV) obtained for the Pt$_{60}$Ru$_{30}$Ni$_{10}$/C electrocatalysts. The hydrogen adsorption/desorption region (0.0–0.4 V vs. Ag/AgCl) is poorly defined, and the current in the double layer region (0.4–0.8 V vs. Ag/AgCl) is higher compared with pure Pt-catalyst. This behavior is characteristic of supported carbon electrocatalysts containing transition metals. Taking the Pt$_{100}$/C composition as reference, the binary Pt-catalyst incorporated with Ru or Ni has a voltammetric charge similar to that of the pure Pt catalyst. However, when both metals are simultaneously added to Pt to form ternary catalysts (Pt–Ru–Ni/C), a considerable increase in the voltammetric charge is observed.
Fig. 3.6a Cyclic voltammetry of Pt$_{100}$/C, Pt$_{60}$Ni$_{40}$/C, Pt$_{60}$Ru$_{40}$/C and Pt$_{60}$Ru$_{30}$Ni$_{10}$/C electrocatalysts in 0.5 M H$_2$SO$_4$ at room temperature with a scan rate of 50 mV/s

Fig. 3.6b corresponds to representative cyclic voltammograms registered in the presence of methanol. All the current values were normalized by the geometric surface area of the electrode used. There were three oxidation peaks when methanol CV was carried out on the Pt/C catalyst (vs. Ag/AgCl), two during the forward scan and one during the reverse scan. The first one appears at around 0.77 V and the second one appears at higher potential during the forward scan. Only the first oxidation peak is reported in the present work and the second oxidation peak appears at higher potential, where bimetallic and tri-metallic catalysts are not so stable, is not reported. The main results of CV test of Pt$_{60}$Ru$_{40}$/C, Pt$_{60}$Ni$_{40}$/C and Pt$_{60}$Ru$_{30}$Ni$_{10}$/C catalysts are listed in Table 3.3 including the positive peak potentials and corresponding peak current densities of methanol electrooxidation. It can be seen from Fig. 3.6b that the onset potential of a current rise for methanol electro oxidation on the Pt$_{60}$Ru$_{30}$Ni$_{10}$/C catalyst corresponds to that on the Pt$_{60}$Ru$_{40}$/C and Pt$_{60}$Ni$_{40}$/C catalyst, i.e. about 0.45 V vs. Ag/AgCl. The potential for methanol electrooxidation, at which the peak current occurs is 0.961 V (vs. Ag/AgCl), and the peak current density is 32.6 mA/cm$^2$ during
positive potential scanning on the Pt$_{60}$Ru$_{30}$Ni$_{10}$/C catalyst. The peak potential and the peak current density on the Pt$_{60}$Ru$_{30}$Ni$_{10}$/C catalyst are about 0.72V (vs. Ag/AgCl) and 16.4 mA/cm$^2$, respectively during its reverse scanning. The peak potential for methanol electrooxidation and the peak current density on the Pt$_{60}$Ru$_{40}$/C and Pt$_{60}$Ni$_{40}$/C catalysts are about 0.981 V & 0.959 V (vs. Ag/AgCl) and 22.4 & 19.9 mA/cm$^2$, respectively, during positive potential scanning. The peak potential for methanol electrooxidation and the peak current density on the Pt$_{60}$Ru$_{40}$/C and Pt$_{60}$Ni$_{40}$/C catalysts are about 0.73 V & 0.72 V (vs. Ag/AgCl) and 7.8 & 6.7 mA/cm$^2$, respectively, during its reverse scanning. The peak potential on the Pt$_{60}$Ru$_{30}$Ni$_{10}$/C catalyst during positive potential scanning is ~20 mV lower than that for the Pt$_{60}$Ru$_{40}$/C and Pt$_{60}$Ni$_{40}$/C catalysts. But the peak current density for the Pt$_{60}$Ru$_{30}$Ni$_{10}$/C catalyst is 10.2 and 12.6 mA/cm$^2$ higher than that for the Pt$_{60}$Ru$_{40}$/C and Pt$_{60}$Ni$_{40}$/C catalysts respectively. So, the performance of Pt–Ru–Ni/C catalyst for methanol electrooxidation is much better than that for the Pt–Ru/C and Pt–Ni/C catalysts.

![Graph](image)

**Fig. 3.6b** Cyclic voltammetry of Pt$_{100}$/C, Pt$_{60}$Ni$_{40}$/C, Pt$_{60}$Ru$_{40}$/C and Pt$_{60}$Ru$_{30}$Ni$_{10}$/C electrocatalysts in 0.5 M H$_2$SO$_4$ and 1.0 M methanol at room temperature with a scan rate of 50 mV/s
Table 5.3 CV results of Pt$_{100}$/C, Pt$_{60}$Ru$_{40}$/C, Pt$_{60}$Ni$_{40}$/C and Pt$_{60}$Ru$_{30}$Ni$_{10}$/C electrocatalysts at room temperature

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Positive peak potential (V vs. Ag/AgCl)</th>
<th>Peak current density (mA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt$<em>{60}$Ni$</em>{40}$/C</td>
<td>0.959</td>
<td>19.9</td>
</tr>
<tr>
<td>Pt$<em>{60}$Ru$</em>{40}$/C</td>
<td>0.981</td>
<td>22.4</td>
</tr>
<tr>
<td>Pt$<em>{60}$Ru$</em>{30}$Ni$_{10}$/C</td>
<td>0.961</td>
<td>32.6</td>
</tr>
</tbody>
</table>

Pure Pt$_{100}$/C catalyst (Fig. 3.6b) does not behave as a very good anode for methanol electrooxidation due to its poisoning by strongly adsorbed intermediates such as CO$_{ads}$ (Vigier et al. 2004). However, the binary and ternary electrocatalysts performed better than Pt$_{100}$/C for methanol oxidation. Moreover, when the binary electrocatalysts were compared to the ternary ones in terms of oxidation wave onset potential and achieved current densities, the latter catalysts gave the best electrical performances. A lot of work has been focused on the methanol electro-oxidation with Pt–Ru/C and Pt–Ni/C electrocatalysts (Wang et al. 2006, Wang et al. 2005, He et al. 1997). When Ru–OH is generated by dissociative adsorption of water on catalyst surface, methanol oxidation proceeds. However, the strong adsorption of OH on the catalyst surface at higher potentials inhibits further methanol oxidation, thus methanol oxidation peaks are observed during positive potential scanning. When the potential scanning is reversed, the strongly adsorbed OH is reduced with the potential lowering. Then methanol oxidation occurs again, thus its oxidation peaks are observed during negative potential scanning as shown in Fig. 3.6b. On the other hand, addition of Ni to Pt (Pt–Ni/C) had a little effect, whereas addition of Ni to Pt–Ru greatly enhanced the electrocatalytic activity. It can be seen from the above results that the performance of the Pt$_{60}$Ru$_{30}$Ni$_{10}$/C catalyst is better than that of the Pt$_{60}$Ru$_{40}$/C catalyst, mainly due to the improving effect of Ni in Pt–Ru/C catalyst for methanol electro-oxidation.
3.3.2.2 Chronoamperometry

The Pt$_{60}$Ru$_{40}$/C, Pt$_{60}$Ni$_{40}$/C and Pt$_{60}$Ru$_{30}$Ni$_{10}$/C electrocatalysts performances for methanol oxidation were studied by chronoamperometry (CA) at 0.4 V for 2 h, to evaluate both the electrocatalytic activity of the catalysts and the poisoning of the active surface under continuous operation conditions. Fig. 3.7 shows representative chronoamperograms obtained for the different electrocatalysts whose current densities were normalized by Pt mass. During the first five minutes, there was a sharp decrease in the current density and after some time, it becomes relatively stable. This behavior can be explained assuming that initially the active sites are free from adsorbed methanol molecules, but a new adsorption of methanol molecules is a function of the liberation of the active sites by methanol oxidation and intermediate species (CO, CH$_x$, CH$_3$CHO and CH$_3$COOH) formed during the first minutes, which are responsible for poisoning of the catalytic sites (Ribeiro et al. 2007).

![Fig. 3.7 Chronoamperometry of Pt$_{100}$/C, Pt$_{60}$Ru$_{40}$/C, Pt$_{60}$Ni$_{40}$/C and Pt$_{60}$Ru$_{30}$Ni$_{10}$/C electrocatalysts at room temperature](image)

Fig. 3.7 Chronoamperometry of Pt$_{100}$/C, Pt$_{60}$Ru$_{40}$/C, Pt$_{60}$Ni$_{40}$/C and Pt$_{60}$Ru$_{30}$Ni$_{10}$/C electrocatalysts at room temperature
The Pt$_{60}$Ru$_{30}$Ni$_{10}$/C electro-catalysts gave higher current than the binary Pt$_{60}$Ru$_{40}$/C and Pt$_{60}$Ni$_{40}$/C electro-catalysts. Higher current obtained for the ternary electrocatalysts may be explained by the operation of a beneficial synergistic effect between Ru and Ni. This may indicate an increase in structural defects or roughness, making the ternary electrocatalysts better candidates for methanol electro-oxidation. The addition of small quantities of Ni to Pt–Ru/C electrocatalyst produced Pt$_{60}$Ru$_{30}$Ni$_{10}$/C electrocatalysts with superior performance for methanol electro-oxidation. The improvement of the catalytic activity for methanol oxidation of the Pt$_{60}$Ru$_{30}$Ni$_{10}$/C electrocatalysts has been attributed to the combination of Ru and Ni that promotes water activation leading to the formation of OH species that facilitates the oxidation of CO-like species intermediates generated from methanol decomposition releasing the sites of Pt (Martinez-Huerta et al., 2006, Zhang et al., 2007, Huang et al., 2009, Oh et al., 2008). Also, the modification of electronic structure by electron structure by electron transfer from Ni to Pt has been considered to enhance the oxidation of CO-like species on Pt Sites (Park et al. 2002). Similar results were also observed in methanol oxidation using non-supported Pt–Ru (50:50) and Pt–Ru–Ni (50:40:10) electrocatalysts. The superior activity of the Pt–Ru–Ni/C electrocatalyst was attributed to the modification of electronic properties of platinum and to the presence of nickel oxide species resulting in a combination of electronic effect and bifunctional mechanism (Oh et al. 2008, Park et al. 2002). These observations suggest that the performance of Pt–Ru–Ni/C electrocatalysts depend greatly on its atomic ratios and its preparation procedure.

### 3.3.4 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–Ni catalysts. The Pt$_{100}$/C, Pt$_{60}$Ru$_{40}$/C, Pt$_{60}$Ni$_{40}$/C and Pt$_{60}$Ru$_{30}$Ni$_{10}$/C catalysts were evaluated as anode catalysts for methanol electro-oxidation by single membraneless methanol fuel cell (MLMFC), and the data are presented in Fig. 3.8. When Pt$_{100}$/C was used as the anode catalyst, the performance of single cell was poor. The open-circuit potential (OCP) was 0.56 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$_{100}$/C is 4.45 mW/cm$^2$. The results of MLMFC adapting to different catalysts are summarized in Table 3.4. When the current was normalized to the geometric area of single cell, it was observed that the cell performance of Pt$_{60}$Ru$_{30}$Ni$_{10}$/C 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$_{100}$/C. However, as the voltage reach around 0.3 V Pt$_{60}$Ru$_{30}$Ni$_{10}$/C started drawing more current in comparison to others.

Table 3.4 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>0.56</td>
<td>4.46</td>
<td>37.5</td>
</tr>
<tr>
<td>Pt$<em>{60}$Ni$</em>{40}$/C</td>
<td>0.60</td>
<td>17.93</td>
<td>123.57</td>
</tr>
<tr>
<td>Pt$<em>{60}$Ru$</em>{40}$/C</td>
<td>0.72</td>
<td>24.11</td>
<td>133.10</td>
</tr>
<tr>
<td>Pt$<em>{60}$Ru$</em>{30}$Ni$_{10}$/C</td>
<td>0.74</td>
<td>37.51</td>
<td>237.31</td>
</tr>
</tbody>
</table>
The open-circuit potential for Pt$_{60}$Ru$_{40}$/C and Pt$_{60}$Ni$_{40}$/C catalysts was (0.72 V and 0.60 V respectively) lower than for Pt$_{60}$Ru$_{30}$Ni$_{10}$/C (0.74 V). In addition, there was a rapid initial fall in cell voltage for all catalysts, which was due to the slow initial methanol electro-oxidation reaction at the electrode surface. After an initial drop of 50 mV the change in slope of the polarization curve for Pt$_{60}$Ru$_{30}$Ni$_{10}$/C decreased, and it started drawing more current. This is attributed to the more effective catalytic ability of Pt$_{60}$Ru$_{30}$Ni$_{10}$/C, once the methanol electro-oxidation reaction being initiated. Based on peak power density drawn from single cell, Pt$_{60}$Ru$_{30}$Ni$_{10}$/C is the best anode catalyst with peak power density value of 37.51 mW/cm$^2$. The results are similar to those of cyclic voltammetric and chronoamperometric measurements.

![Fig. 3.8 Polarization and power density curves of different catalyst at 2 mg cm$^{-2}$ catalyst loading on anode and cathode at room temperature](image)

Fig. 3.8 Polarization and power density curves of different catalyst at 2 mg cm$^{-2}$ catalyst loading on anode and cathode at room temperature
As discussed previously the addition of small quantities of Ni to Pt–Ru/C catalyst produced the superior performance of Pt–Ru–Ni/C electrocatalysts for methanol electro-oxidation due to the promoting function of Ni.

References


