CHAPTER 4

Evaluation of the Stability and Durability of Pt-Ru/ CNF and Pt-Ru/C Catalysts for Membraneless Methanol Fuel Cells

Abstract

In the present work, Pt–Ru catalysts were synthesized on carbon nanofiber and their electrocatalytic activity for methanol oxidation in membraneless fuel cell was investigated and compared with Vulcan XC-72R carbon supports. The prepared nanocatalysts were characterized by TEM, EDX, and XRD techniques. Energy dispersive X-Ray spectroscopy and X-Ray diffractometry confirmed the metal catalyst having typical Pt crystalline structure and the formation of Pt–Ru alloy. Electrochemical analyses obtained at room temperature by cyclic voltammetry and chronoamperometry showed that carbon nanofiber supported Pt-Ru catalysts gives higher current density compared to that of carbon supported Pt-Ru catalysts. The power density obtained using Pt-Ru/CNF (37.1 mW cm$^{-2}$) as anode catalyst in MLMFC was higher than that for Pt-Ru/C at room temperature. The better performance of carbon nanofiber-supported catalysts may be due to the significant increase of electrochemical active surface area and the smaller particle size. In this work, Pt-Ru/CNF and Pt-Ru/C 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 in the presence of 0.5 M H$_2$SO$_4$ as the electrolyte at room temperature. Based on the experimental results, we conclude that the CNF supported Pt-Ru nanocatalyst shows superior methanol electrooxidation than Pt-Ru/C.
4.1 Introduction

Fuel cells are considered to be alternatives to our present power sources because of their high operational efficiencies and environment-friendly working characteristics (Carrette et al., (2000); Narayanan et al., (2003)). Of various fuel cell systems, the microfluidic fuel cells have been recognized as one of the most promising candidates for small-scale portable power generation (De jong et al., (2006); Kjeang et al., (2009); Mousavi et al., (2011); Flipsen et al., (2006); Choban et al., (2003)). Microfluidic fuel cells are a novel fuel cell design that uses laminar flow to operate without a solid barrier separating fuel and oxidant. This makes it possible to have an efficient fuel cell that can provide cheap and effective power for small electronic devices. Platinum nanostuctures have been extensively investigated as electrocatalysts for methanol oxidation in fuel cells. However, the pure platinum electrode can easily adsorb CO during methanol oxidation, which poisons the electrochemical active surfaces and decreases performances (Parsons et al., (1988)). The activity of platinum toward methanol oxidation can be improved by alloying platinum with one or more other elements such as Ru, Sn, Mo, and Re (Watanabe et al., (1975); Mukerjee et al., (1999); Rauhe et al., (1995); Bockris et al., (1964); Ross et al., (1992)). This enhancement effect of alloying has been explained by models, such as the bi-functional mechanism (Freelink et al., (1994)), and/or by the electronic effect (Freelink et al., (1995)) which indicates a promotion effect of the alloyed metal on Pt, particularly Pt-Ru has been the most investigated binary system and has shown the best catalytic activity (Bockris et al., (1964); Petry et al., (1965); Gasteiger et al.,(1993); Gasteiger et al., (1994); Chrzanowski et al., (1998); Chrzanowski et al., (1998); Iwasita et al., (2000)).
The catalytic activity of Pt based catalysts may be influenced by many factors, among which the catalysts supporting material, such as a carbon particle, plays an important role in promoting catalyst activity. Carbon black particles are widely used as catalyst supports because of their relative stability in both acidic and basic media, good electric conductivity, and high surface area, however, the mesopores on carbon particles can result in part of the Pt nanoparticles getting buried deeply inside the pores and hence becoming inaccessible for the electrochemical reaction at the triple phase boundary. Further, the carbon particle can undergo corrosion, resulting in the aggregation and dissolution as well as isolation of Pt nanoparticles (Liu et al., (2006)). To overcome these challenges in carbon support, many efforts have been made to search for new catalyst supports (Borup et al., (2007)).

In this regard, Carbon nanostructures like, carbon nanotubes (CNTs), Nanodiamonds, Carbon nanofibers (CNF) and Graphene (Liu et al., (2002); Wang et al., (2004); Wang et al., (2007); Hsin et al., (2007); Maiyalagan et al., (2009); Song et al., (2010); Honda et al., (2001); Montilla et al., (2003); Spataru et al., (2008)) have been explored as support materials for catalysts, in particular for fuel cell catalysts, in the last few years. These nanostructured allotropes of carbon boast of essential fuel cell support properties like high surface area, high electrical conductivity and relatively good stability in acid alkaline media (Yu et al., (2007)). Catalyst supports that consist of carbon nanomaterials with high graphitic nature (CNT and CNF) are reported to be more stable (Antolini et al., (2009)). For example, a large amount of studies have shown that Pt (Pt alloys) supported on CNTs and CNFs could exhibit better performance for electrooxidation of methanol (Bessel et al., (2001)) than that on Vulcan-XC 72 R carbon particles (Yu et al.,
CNFs have lengths on the order of micrometer while their diameter varies between some tens of nanometers up to several hundreds of nanometers. The mechanical strength and electrical properties of CNFs are similar to that of CNTs while their size and graphite ordering can be well controlled. The primary distinguishing characteristic of CNFs from CNTs is the stacking of graphene sheets of varying shapes, producing more edge sites on the outer wall of CNTs than CNFs (Vasiliev et al., 2007). Compared to the traditional carbon black and CNT catalyst supports, carbon nanofiber (CNF) shows superior thermal stability and corrosion resistance in the low temperature fuel cell environment. This is because fibers offer flexibility, which does not apply to the usual powdery or granular materials.

Carbon nanofibers have an excellent combination of chemical and physical properties due to their unique structure, and blend two properties that rarely coexist in materials: high surface area and high electrical conductivity which make them suitable support for the catalysts. Studies indicated that CNF can be applied as catalyst support in PEM successfully which caused less need for Pt catalyst. (Sebastian et al., 2009; Leo et al., 2006). CNF are provided to appropriate catalyst support in fuel cell because of their graphitic structure which improve their corrosion resistance, their textural properties, which might provide benefits for mass and electron transport, as well as, the strong interaction with the metal nanoparticles which increases the catalytic activity and durability. In addition CNF fictionalization influences the amount and dispersion of the deposited nanoparticles (Li et al., 2002). These characteristics makes carbon nanofiber a promising catalyst carrier in the next generation of carbon based support materials.
In the present study, we evaluated the catalytic activity for the MOR reaction by dispersing a Pt-Ru catalyst on carbon nanofiber (CNF) and carbon (Vulcan XC 72R) support in membraneless methanol fuel cell (MLMFC). The performance of the Pt-Ru/CNF catalyst was compared with that of the Pt–Ru/C catalysts obtained by ultrasonic assisted chemical reduction method in which ethylene glycol (EG) is used as solvent and reducing agent at the same time. The synthesized nanocatalysts were characterized by scanning electron microscope (SEM), transmission electron microscope (TEM), energy dispersive X-Ray (EDX) and X-Ray diffraction (XRD) analyses. The electrochemically active surface area (ECASA) of the Pt–Ru/CNFs and Pt–Ru/C was determined using CO stripping voltammetry in 0.5 M H₂SO₄ solution. 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.

4.2 Experimental

4.2.1 Chemicals and Materials

The metal precursors used for the preparation of electrocatalysts were hexachloroplatinic acid (H₂PtCl₆.6H₂O) (from Aldrich), and ruthenium(III) chloride hydrate (RuCl₃.3H₂O) (from Merck). CNFs (Sigma-Aldrich) and Vulcan Carbon XC-72R (from Cabot Corp.,) was used as a support for the catalysts. Ethylene glycol (EG) (from Merck) was used as the solvent and reduction agent. Nafion® (DE 521, DuPont USA) dispersion was used to make the catalyst ink. Methanol (from Merck),
sodium perborate (from Riedel) and H$_2$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.

4.2.2 Catalyst Preparation

4.2.2.1 Synthesis of Pt-Ru Nanocatalysts

CNFs are commercially available purchased from Sigma-Aldrich. An oxidative pretreatment of the CNFs was performed by ultrasonic dispersion in a mixed acid aqueous solution of concentrated H$_2$SO$_4$ and HNO$_3$ in 1:3 ratios under magnetic stirrer for 2 hour. Then, the CNFs were filtered and washed by deionized (DI) water until the pH of the filtrate became 7 and consequently dried in an vacuum oven at 90°C for 5 h. The CNF supported Pt-Ru and carbon supported Pt-Ru nanocatalysts were synthesized by ultrasonic-assisted chemical reduction method. The Pt–Ru content in each samples was 40 wt.% and Pt:Ru atomic ratios were 1:1 respectively. Generally, 2.67 ml 0.038 M H$_2$PtCl$_6$ in ethylene glycol and 2.78 ml 0.036 M RuCl$_3$ in ethylene glycol were mixed with 50 ml ethylene glycol in a two-necked flask. About 70 mg CNFs were added to the mixture and the pH value of the mixture was adjusted to 9 by adding 0.5 M NaOH in ethylene glycol. The mixture was ultrasonicated for 30 min and placed in a microwave oven and heated for 3 min. The mixture was then filtered and washed with ethanol and DI water, and the filtration was repeated for several times. Finally, the Pt–Ru/CNFs catalyst was dried in a vacuum oven at 80°C for 5 h. For a comparison, Pt–Ru/C (Vulcan XC-72R) catalysts were also prepared in the same manner. The nominal loading of metals in the electrocatalysts was 40 wt.%.
4.2.3 Structural Catalyst 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 nanocatalysts 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 (Radmilovic et al., 1995)). Pt (2 2 0) diffraction peak was selected to calculate crystallite size and lattice parameter of platinum. The atomic ratio of the catalysts was determined by an energy dispersive X-Ray (EDX) analyzer, which was integrated with the TEM instrument.

4.2.4 Electrochemical Measurements and Electrode Preparation

All electrochemical measurements were carried out using an electrochemical workstation (CHI-6650; CH Instruments, USA) in a conventional three electrode cell assembly consisting of the glassy carbon disk as a working electrode, Pt foil as a counter electrode and Ag/AgCl as a reference electrode. The working glassy carbon electrode was prepared by the following steps: first, 10 mg of Pt–Ru/CNFs catalyst was suspended separately in a mixed solvent (iso-propyl alcohol (500 µL), water (500 µL) and 5 wt.% Nafion_ solution (100 µL, Aldrich)) with ultrasonication for 20 min. 10 µL of ultrasonically homogenized ink was drop-coated onto a freshly polished glassy-carbon electrode (A = 0.125 cm\(^2\)) and the
solvent was then evaporated in open air at room temperature. Similar procedure was used for Pt–Ru/C catalyst. The loading of metal on the working electrode was 0.28 mg$_{\text{metal}}$ cm$^{-2}$. The electrochemically active surface area (ECASA) of the Pt–Ru/CNFs and Pt–Ru/C was determined using CO stripping voltammetry in 0.5 M H$_2$SO$_4$ solution. CO adsorption was achieved at 0.1 V versus Ag/AgCl in a CO saturated solution for 10 min and the electrolyte was purged with nitrogen for 10 min to remove CO on the surface. The electrochemical activity of the methanol oxidation reaction was measured by cyclic voltammetry in a half cell at a scan rate of 50 mV s$^{-1}$ at room temperature in a 1 M CH$_3$OH and 0.5 M H$_2$SO$_4$ solution. All potentials in this paper were scaled versus Ag/AgCl.

4.3 Results and Discussion
4.3.1 Physical Characterization
4.3.1.1 X-Ray Diffraction (XRD)

Structural features such as average crystallite size and lattice parameter were investigated by X-Ray diffraction. Fig 4.1 shows the XRD patterns of Pt–Ru/CNFs, and Pt-Ru/C catalysts. The broad diffraction peak at around 26° is associated with the (0 0 2) plane of CNF. The strong diffraction peak at 20 of ~40° and the other three peaks at ~46°, 67°, and 81° are attributed to the Pt–Ru (1 1 1), (2 0 0), (2 2 0), and (3 1 1) planes respectively, which represents the typical character of crystalline Pt with face-centered cubic (fcc) crystalline structure. Compared to pure Pt, the Pt–Ru diffraction peaks are shifted slightly to higher 2θ values, which suggest that the Ru atoms are embedded into the crystalline lattice of Pt to produce the Pt–Ru alloy (Zhao et al., (2009); Ma et al., (2009)). This shift can be explained by the lattice constant reduction which is caused by Ru incorporation.
No diffraction peaks related to pure Ru and their oxides/hydroxides were observed in the XRD patterns. The absence of diffraction peaks typical for Ru can be due to a number of reasons such as Ru not being dissolved in the Pt lattice, that is, forming a Pt-Ru alloy and/or the Ru being present in the amorphous form (Wang et al., 2007; Guo et al., 2007). Moreover, the relatively sharp and narrow diffraction peaks of the Pt–Ru/CNF catalyst showed a higher crystalline structure compared with the Pt–Ru/C catalyst. The fcc lattice parameters were evaluated from the angular position of the (2 2 0) peaks and the calculated value for Pt–Ru/CNF catalysts were smaller than that of Pt-Ru/C catalysts, indicating a lattice contraction caused by the incorporation of Ru into the fcc structure of platinum after alloying. The average crystallite size was estimated using the Scherrer equation. The lattice parameters and the average crystallite size of the catalysts obtained from the XRD patterns are listed under Table 4.1.
Table 4.1 Characterization parameters for the Pt–Ru/CNF, and Pt–Ru/C nanocatalysts

<table>
<thead>
<tr>
<th>Electrocatalysts</th>
<th>Nominal</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(2 2 0) Diffraction peak position (20°)</td>
<td>Lattice parameter (nm)</td>
</tr>
<tr>
<td>Pt_{50}–Ru_{50}/CNF</td>
<td>Pt_{51}–Ru_{49}/CNF</td>
<td>68.02</td>
</tr>
<tr>
<td>Pt_{50}–Ru_{50}/C</td>
<td>Pt_{49}–Ru_{51}/C</td>
<td>67.84</td>
</tr>
</tbody>
</table>

4.3.1.2 Scanning Electron Microscopy (SEM)

SEM images of Pt-Ru/CNFs, as well as Pt-Ru/C catalysts prepared are shown in Fig. 4.2a–b. SEM image clearly shows that the nanoparticles of the catalysts are uniformly dispersed on the support. The SEM images confirm the porous structure of the catalysts prepared.

![Fig. 4.2 SEM images of a) Pt-Ru/CNF and b) Pt-Ru/C nanocatalysts](image)
4.3.1.3 Transmission Electron Microscopy (TEM)

The TEM images of the Pt-Ru/CNF, as well as Pt-Ru/C catalysts are presented in Fig. 4.3a–d, respectively. As shown in Fig. 4.3, Pt–Ru nanoparticles were uniformly dispersed on carbon nanofiber with an average particle size of 2.8 nm, which is slightly smaller than Pt–Ru/C with an average particle size of about 3.5 nm respectively. However, the small spherical shape Pt–Ru nanoparticles were more uniformly dispersed on the carbon nanofiber than on the carbon supports. The uniform dispersion of metal nanoparticles on CNF is clearly due to the high surface area of carbon nanofiber, which offers large active sites for anchoring metal ions and metal nanoparticles. The particle size distribution of these catalysts is shown in Table 4.1 in accordance to the TEM images. The mean particle size found by TEM image and XRD analysis were similar.

Fig. 4.3 TEM images and histograms of (a, c) Pt-Ru/CNF, (b, d) Pt–Ru/C, nanocatalysts
4.3.1.4 Energy Dispersive X-Ray (EDX) Analysis

Energy dispersive X-Ray (EDX) analysis was used to check the presence of metal particles. The catalysts prepared had the desired elements with some variation in composition. The EDX analyses of the Pt-Ru/CNFs, and Pt-Ru/C, catalysts are shown in Fig. 4.4a-b. The Pt and Ru signals identified on all the figures indicate the successful deposition of these atoms on both CNF and carbon supports. The results of EDX analysis further confirm that the Pt:Ru atomic ratio are closely 1:1, which was in agreement with the concentration ratio in the precursor solutions, and is conceded to be the most active composition for the methanol electro-oxidation reaction.
Fig. 4.4 EDX spectra of (a), Pt-Ru/CNF (b) Pt–Ru/C nanocatalysts

4.3.2 Electrocatalytic Activities of Nanocatalysts

4.3.2.1 Cyclic Voltammetry (CV)

The electrocatalytic activity of methanol oxidation on carbon nanofiber-supported Pt–Ru nanoparticles was characterized by cyclic voltammetry and compared with Pt–Ru/C in the presence and absence of methanol in an electrolyte of 0.5 M H₂SO₄ at 50 mV s⁻¹. The voltammograms of each sample became similar and stable after the tenth cycle. The resulting voltammograms from the tenth cycle are shown in Fig. 4.5.
Fig 4.5  Cyclic voltammetry of Pt-Ru/CNF, and Pt-Ru/C nanocatalysts in 0.5 M H$_2$SO$_4$ at room temperature with a scan rate of 50 mV s$^{-1}$.

The intensity of the peak current normalized by the weight of Pt in catalyst revealed the electrochemical activity of Pt–Ru nanoparticles (Gowdhamamoorthy et al., 2014). The efficiencies of the Pt–Ru nanoparticles were compared with regard to oxidation potential, forward oxidation peak current density, and the ratio of the forward peak current density to the backward peak current density; these data are summarized in Table 4.3. Fig. 4.5 shows the cyclic voltammetry of Pt–Ru/CNF as well as Pt–Ru/C electrocatalysts deposited onto glassy-carbon electrode in the absence of methanol. Typical hydrogen adsorption/desorption peaks are observed in the potential range –0.2 to 0.1 V (vs. Ag/AgCl). The hydrogen adsorption of Pt–Ru/CNF are apparently larger than those of Pt–Ru/C, suggesting that may be due to the smaller particle size of the catalysts.
It is well-known that the electrochemically active surface area (ECASA) reveals the available number of active sites on the catalyst surface for electrochemical reactions and determines the efficient transport routes for electron on the electrode surface; therefore, the larger the ECASA, the higher the electrocatalytic activity for methanol oxidation reactions (MOR) (Huai-Ping Cong et al., (2000)). The ECASA of Pt–Ru/CNF and Pt–Ru/C nanocatalysts can be calculated according to Eq. (4.1) and (4.2) (Arun et al., (2015)):

\[
S_{\text{ECASA}_H}(m^2/g) = \frac{Q_H(\mu C/cm^2)}{210 (\mu C/cm^2) \times 0.77 \times [\text{Pt}]} 
\]

\[
S_{\text{ECASA}_CO}(m^2/g) = \frac{Q_{CO}(\mu C/cm^2)}{420 (\mu C/cm^2) \times [\text{Pt}]} 
\]

Where \(Q_H\) is the charges corresponding to desorption of hydrogen on the Pt surface, \([\text{Pt}]\) (mg cm\(^{-2}\)) is the Platinum loading on the electrode surface, 210 \(\mu C\) cm\(^{-2}\) is the charge required to oxidize a monolayer of hydrogen on the Pt surface, and 0.77 is the hydrogen monolayer coverage (Biegler et al., (1971)). The ECASA of different catalysts were calculated based on Eq. (4.1) and are listed in Table 4.2. The calculated ECASA of Pt–Ru/CNF (71 m\(^2\) g\(_{\text{Pt}}\)^{-1}), were higher than that of Pt–Ru/C (37 m\(^2\) g\(_{\text{Pt}}\)^{-1}). It indicated that the smaller particle size and better dispersion of catalysts on the carbon nanofiber has a significant impact on improving the ECASA value.
Table 4.2 Comparison of hydrogen desorption charge and carbon monoxide desorption charge, and its electrochemical active surface area (ECASA) and electrode roughness

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>( Q_{H}/\mu C )</th>
<th>( Q_{CO}/\mu C )</th>
<th>Electrode real surface area (cm(^2))</th>
<th>( \text{ECASA}/H ) (m(^2)g(_{Pt})(^{-1}))</th>
<th>( \text{ECASA}/CO ) (m(^2)g(_{Pt})(^{-1}))</th>
<th>Roughness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-Ru/CNF</td>
<td>574.03</td>
<td>1596</td>
<td>3.8</td>
<td>71</td>
<td>76</td>
<td>106.4</td>
</tr>
<tr>
<td>Pt-Ru/C</td>
<td>299.1</td>
<td>882</td>
<td>2.1</td>
<td>37</td>
<td>42</td>
<td>58.8</td>
</tr>
</tbody>
</table>

*The electrochemical active surface area (\( S_{\text{ECASA}/H} \) and \( S_{\text{ECASA}/CO} \)) were calculated from Eq. (4.1) and Eq.(4.2).*

Fig. 4.6 (a)&(b) shows the CO-stripping voltammograms of Pt–Ru/CNF and Pt–Ru/C catalysts recorded in 0.5 M H\(_2\)SO\(_4\) at a scan rate of 50 mV s\(^{-1}\) between 0.05 and 0.9 V vs Ag/AgCl. A CO\(_{ads}\) oxidation peak is observed at 0.25 and 0.32 V vs. Ag/AgCl for Pt–Ru/CNF and Pt–Ru/C respectively. For the Pt–Ru/CNF nanoparticles, there was a cathodic shift of at least 100 mV due to CO oxidation, compared with Pt–Ru/C. The peak positions in the voltammograms of Pt–Ru/CNF and Pt–Ru/C nanoparticles are similar, but the peaks of carbon supported substrates are less symmetric than those of CNF supported nanoparticles. The higher symmetry of the oxidation peak in the voltammograms of Pt–Ru/CNF suggests that effective, strong electronic interactions take place between the Pt–Ru nanoparticles and the CNF.
Fig 4.6 CO stripping voltammetry of Pt-Ru/CNF, and Pt-Ru/C nanocatalysts in 0.5 M H₂SO₄ at room temperature with a scan rate of 50 mV s⁻¹.

Fig. 4.7 shows the cyclic voltammograms (CV) of methanol electro-oxidation catalyzed by Pt–Ru/CNF as well as Pt–Ru/C catalysts in a 1.0 M CH₃OH and 0.5 M H₂SO₄ solution at room temperature. In carbon nanofiber as well as Vulcan XC-72R carbon supported Pt–Ru electrodes, two oxidation peaks can be observed on the forward scan and a single peak can be observed on the backward scan towards oxidation-reduction reactions. The peak in the forward scan is associated with the methanol oxidation, and the peak in the backward scan is at related to the oxidation of carbonaceous intermediate products formed from incomplete methanol oxidation. The ratio of the forward peak current ($I_F$) to the backward peak current ($I_B$) can be used to evaluate the tolerance of the catalysts to
the accumulation of the intermediate carbonaceous species (Mu et al., 2005). A higher $I_F/I_B$ value indicates higher tolerance of intermediate carbon species. The data obtained from Fig. 4.7 are also listed in Table 4.3.

### Table 4.3 CV results of Pt–Ru/CNF, and Pt–Ru/C nanocatalysts at room temperature

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Forward anodic peak ($I_F$) (mA cm$^{-2}$)</th>
<th>Backward anodic peak ($I_B$) (mA cm$^{-2}$)</th>
<th>$I_F/I_B$ ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-Ru/CNF</td>
<td>54.1</td>
<td>19.7</td>
<td>2.7</td>
</tr>
<tr>
<td>Pt-Ru/C</td>
<td>32.6</td>
<td>18.5</td>
<td>1.7</td>
</tr>
</tbody>
</table>

The nanocatalysts in our work, the Pt–Ru/CNF catalysts exhibited a higher $I_F/I_B$ value (2.7) than the Pt–Ru/C (1.7), indicating them much more complete oxidation of methanol in the forward scan and the effective removal of poisoning CO-like species from the surface of catalysts. Table 4.4 summarizes the CV results of the prepared electrocatalysts including the onset potentials, positive peak potentials and the corresponding peak current densities of MOR.

### Table 4.4 Positive peak potential and Peak current density of Pt-Ru/CNF, and Pt-Ru/C nanocatalysts at room temperature.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Onset Potential (V)</th>
<th>Positive peak potential (V vs. Ag/AgCl)</th>
<th>Peak current density (mA cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-Ru/CNF</td>
<td>0.25</td>
<td>0.70</td>
<td>54.1</td>
</tr>
<tr>
<td>Pt-Ru/C</td>
<td>0.32</td>
<td>0.72</td>
<td>32.6</td>
</tr>
</tbody>
</table>
Fig 4.7  Cyclic voltammetry of Pt-Ru/CNF, and Pt-Ru/C nanocatalysts in 0.5 M H$_2$SO$_4$ and 1 M Methanol at room temperature with a scan rate of 50 mV s$^{-1}$.

As shown in Fig. 4.7, the onset potentials of Pt–RuCNF for methanol electro-oxidation were noted at 0.25 V, while the onset potentials on Pt–Ru/C were at 0.32 V vs. Ag/AgCl respectively. In addition, the results not only indicate that the onset potentials shift to negative direction on Pt–Ru/CNF compared with Pt–Ru/C, but also reveal that the peak current densities become much larger, indicating methanol electro-oxidation is more active on CNF based catalysts than that on carbon supported catalysts. The enhanced activity of Pt-Ru/CNF catalyst is due to higher dispersion of Pt-Ru nanoparticles and may be better oxidation of CO intermediated during methanol oxidation.
4.3.2.2  Chronoamperometry (CA)

The Pt-Ru/CNFs, and Pt-Ru/C, nanocatalyst performances for methanol oxidation were studied by chronoamperometry (CA) at 0.6 V vs Ag/AgCl for 2 h to evaluate both the electrocatalytic activity of the catalysts and the poisoning of the active surface under continuous operation conditions. Fig. 4.8 shows the representative chronoamperograms obtained for the different nanocatalysts whose current densities were normalized by Pt mass.

![Chronoamperometry of Pt-Ru/CNF, and Pt-Ru/C nanocatalysts with a scan rate of 50 mV s⁻¹.](image)

**Fig 4.8**  Chronoamperometry of Pt-Ru/CNF, and Pt-Ru/C nanocatalysts with a scan rate of 50 mV s⁻¹.
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. 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. During the throughout operation, the current density of methanol oxidation at the Pt–Ru/CNFs catalyst was substantially higher than that at the Pt–Ru/C catalyst, although the current decay with time was observed in both samples. From the results, Pt–Ru/CNFs exhibited higher catalytic activity and better stability for methanol oxidation than Pt–Ru/C.

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 nanofiber supported Pt–Ru catalysts. A single membraneless methanol fuel cell (MLMFC) was tested using the Pt–Ru/CNF and Pt–Ru/C catalysts as the anode. Polarization curves and power densities are shown in Fig. 4.9.
Table 4.5  Summary of performance of single fuel cell tests using Pt-Ru/CNF, and Pt-Ru/C nanocatalysts

<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-Ru/CNF</td>
<td>0.76</td>
<td>37.1</td>
<td>230</td>
</tr>
<tr>
<td>Pt-Ru/C</td>
<td>0.70</td>
<td>28.1</td>
<td>185</td>
</tr>
</tbody>
</table>

Fig. 4.9  Polarization and power density curves of Pt-Ru/CNF, and Pt–Ru/C nanocatalysts at room temperature
The catalyst loadings are 0.28 mg cm$^{-2}$ at both electrodes and Pt/C was used as the cathode catalyst. The OCVs of Pt–Ru/CNF are higher than that of Pt–Ru/C and the order of OCV is exactly same as the onset potentials. Although the difference between Pt–Ru/C and Pt–Ru/CNF is relatively small in the low-current-density region, the significant support effect of CNF becomes larger as the current density increases. 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–Ru/CNF decreased, and it started drawing more current. This event can be attributed to the more effective catalytic ability of Pt–Ru/CNF, once the MOR reaction is initiated. The results of MLMFC adopting to CNF and carbon supported catalysts are summarized in Table 4.5. Based on the peak power density drawn from a single cell, Pt–Ru/CNF is the best anode catalyst with a peak power density value of 37.1 mW cm$^{-2}$. 
References


