CHAPTER 5

MESOPOROUS Pt-Ru BIMETALLIC CATALYST
USING HARD TEMPLATE ASSISTED
METHOD - ELECTROCHEMICAL PERFORMANCE

5.1 INTRODUCTION

Platinum nanoparticles have long been regarded as the best catalyst in fuel cells. However, the high cost, durability together with the limited reserves of platinum in nature, has been shown to be the major bottleneck to fuel cells for commercial applications (Yu & Ye 2007; Winter & Brodd 2004; Gong et al 2009). It is generally accepted that pure Pt electrocatalyst are prone to poisoning by CO since CO molecules can chemically adsorb onto the Pt surface and block the active sites (Liu et al 2004; Nagle et al 2008). To evade these limitations, Pt-based alloys are frequently synthesized as alternatives, relying on the fine tuning of Pt electronic properties to substantially improve its catalytic performance and thus reduce the amount of noble metal needed (Mukerjee et al 1995; Greeley & Mavrikakis 2004).

To date, the development of bimetallic catalysts usually consists of a primary metal that has a high catalytic activity and a secondary metal that can enhance the catalytic activity or prevent poisoning issues. The appearances of the second metal gives notable improvement in the CO tolerance, electrochemical activity and contribute to decrease of costs associated with Pt to some extent. There has been considerable improvement
on the search for Pt-based bimetallic electrocatalysts, such as Pt-Pd composites, (Peng & Yang 2009; Lim et al 2009) or Pt monolayer on a second metal, (Adzic et al 2007) or alloying platinum with less expensive 3d-transition metals (Stamenkovic et al 2006; Stamenkovic et al 2007).

Another important factor is the dependence of electrocatalytic properties on alloy composition. The ratio between alloying components plays an important role in defining the physical and chemical properties of alloy materials. In addition to the recent reports on bimetallic catalysts, the development of advanced synthetic routes are still demanded in order to provide fine control over critical parameters such as particle size and composition profile for bimetallic catalysts. One important issue relating to the application of platinum and its alloys as catalysts is the reduction of the amount used. It is essential that the consumption of platinum should be kept as low as possible without sacrificing the catalytic performance. One strategy is to create mesoporous platinum bimetallic catalyst morphology. Besides the reduction of Pt usage, the interconnected structure could have additional benefits in improving the catalytic activities that involve two or more reactants, due to their high surface area, and also to have enough absorption sites for all absorbed molecules. Compared to the solid counterparts, porous or network structured metals and alloys show improved physical and chemical performance due to their high surface area, low density and high gas permeability (Yamauchi et al 2008; Peng et al 2004; Ramanath et al 2004; Cui et al 2012).

Among the bimetallic catalyst Pt-Ru system is very interesting because it has more advantageous catalytic properties compared to Pt or Ru (Jian & Kucernak 2003; Attard et al 2001; Yamauchi et al 2007; Takai et al 2009; Esfahani et al 2012; Guo et al 2010). The Pt-Ru alloy shows outstanding electrocatalytic performance for electrocatalytic reaction in fuel
cells with respect to fuels of alcohol based (Li et al 2012; Lu et al 2012). The Ru atoms provide nucleation sites for the adsorption of oxygen containing species that initiates the further electro-oxidation of the CO adsorbed on the Pt sites. The electronic property of Ru reduces the bond energy between the catalyst and CO and thus improves the activity of methanol oxidation.

In this chapter, simple direct synthesis of mesoporous Pt-Ru bimetallic catalyst of various compositions of Pt and Ru using mesoporous silica SBA-15 (p6mm) and KIT-6 (Ia3d) as hard template with ascorbic acid as reducing agent is reported. The unique mesoporous architecture providing high surface area favours the electrocatalytic activity towards electrocatalytic reactions in fuel cells.

5.2 EXPERIMENTAL

5.2.1 Preparation of Mesoporous Pt–Ru Particles

The silica templates (KIT-6 or SBA-15) were prepared according to the method given in Section 4.2.1 and 4.2.2. The preparation method of mesoporous bimetallic catalyst is shown in Figure 5.1 in which aqueous metal precursor solutions, $K_2PtCl_4$ as Pt precursor and $RuCl_3$ as Ru precursor were mixed. In both metal precursor solutions, the concentration of metal sources was kept constant at 25wt%. The Pt and Ru precursor solutions were mixed with four different ratios. The synthesis procedure of mesoporous Pt-Ru is same as that of mesoporous Pt (refer chapter 4; section 4.2.3). The samples prepared from SBA-15 powder were denoted as $S_{Pt_xRu_y}$, while the samples prepared from KIT-6 powder were denoted as $K_{Pt_xRu_y}$ (x and y are compositional ratios of Pt and Ru in the products, respectively). The relationship between the precursor compositions and the product compositions are summarized in Table 5.1. Ru$^{3+}$ ions have a lower tendency
toward reduction than $[\text{PtCl}_4]^{2-}$ ions according the standard reduction potential. Henceforth, the reduction of $[\text{PtCl}_4]^{2-}$ ions easily occurs but $\text{Ru}^{3+}$ ions could not be simultaneously reduced at the same rate. However the Ru content of the materials increased with increase in the amount of Ru precursor.

Figure 5.1 Schematic representation of synthesis procedure of mesoporous Pt bimetallic catalyst using hard template assisted method
Table 5.1 Relationship between precursor composition and product composition of Pt-Ru bimetallic catalyst prepared using KIT-6 and SBA-15 silica templates

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Template used</th>
<th>Precursor composition (molar ratio)</th>
<th>Product composition as obtained from EDX analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>K_{Pt_{95}Ru_{5}}</td>
<td>KIT-6</td>
<td>95 5</td>
<td>95 5</td>
</tr>
<tr>
<td>K_{Pt_{93}Ru_{7}}</td>
<td>KIT-6</td>
<td>87 13</td>
<td>93 7</td>
</tr>
<tr>
<td>K_{Pt_{90}Ru_{10}}</td>
<td>KIT-6</td>
<td>74 26</td>
<td>90 10</td>
</tr>
<tr>
<td>K_{Pt_{85}Ru_{15}}</td>
<td>KIT-6</td>
<td>50 50</td>
<td>85 15</td>
</tr>
<tr>
<td>S_{Pt_{95}Ru_{5}}</td>
<td>SBA-15</td>
<td>95 5</td>
<td>95 5</td>
</tr>
<tr>
<td>S_{Pt_{93}Ru_{7}}</td>
<td>SBA-15</td>
<td>87 13</td>
<td>93 7</td>
</tr>
<tr>
<td>S_{Pt_{90}Ru_{10}}</td>
<td>SBA-15</td>
<td>74 26</td>
<td>90 10</td>
</tr>
<tr>
<td>S_{Pt_{85}Ru_{15}}</td>
<td>SBA-15</td>
<td>50 50</td>
<td>85 15</td>
</tr>
</tbody>
</table>

5.3 RESULTS AND DISCUSSION

5.3.1 Physical Characterization

5.3.1.1 SEM characterization

Figure 5.2 shows the morphology of the obtained mesoporous K_{Pt_{95}Ru_{5}} and S_{Pt_{95}Ru_{5}} after removal of the silica template synthesised using KIT-6 and SBA-15 template respectively. The low magnification SEM image shows that the mesoporous particles were isolated from each other and had narrow particle size distribution ranging from 200 to 250nm. Inspite of the increased Ru content in the precursor solutions, the porous structures was not disturbed. On the particle surface of S_{Pt_{95}Ru_{5}}, periodically arranged nanowires replicated from SBA-15 were seen. In the case of the KIT-6 system, Pt nanowires replicated from both sides of pores of a double gyroid mesostructure were clearly observed in S_{Pt_{95}Ru_{5}} sample which was also
confirmed from Small Angle X-ray Scattering (SAXS) (Section 5.3.1.3) measurements. The obtained Pt-Ru bimetallic catalyst exhibited well defined mesoporous structure and uniform shape.

Figure 5.2  Low and high-magnification SEM images of (a) K_Pt_{95}Ru_{5} particles prepared with mesoporous silica KIT-6 and (b) S_Pt_{95}Ru_{5} prepared with mesoporous silica SBA-15
5.3.1.2 TEM, SAED pattern and EDX

Figure 5.3(a) shows the TEM image of the as synthesized mesoporous $\text{K}_9\text{Pt}_{95}\text{Ru}_5$ bimetallic catalyst and Figure 5.3(c) shows the HR-TEM image of a single particle taken along the edges. The observed lattice fringes correspond to the (111) plane of Pt-Ru and the d-spacing was found to be 0.23nm. The Pt-Ru bimetallic catalyst possessed well developed crystallinity as observed from the lattice fringes the HR-TEM image with homogeneously distributed Pt and Ru contents. The observed SAED pattern had diffused rings and intense points located on the rings. The ring patterns, each of which was assignable to the (111), (200), or (220) lattice plane of the fcc structure and are shown in Figure 5.3(b).

![Figure 5.3](image_url)

**Figure 5.3** (a) TEM image of $\text{K}_9\text{Pt}_{95}\text{Ru}_5$ with (b) SAED pattern and (c) HR-TEM image $\text{K}_9\text{Pt}_{95}\text{Ru}_5$ with inset indicating atomic steps on the Pt surface
Figure 5.4  (a) DF-TEM image of K$_{95}$Pt$_{5}$Ru$_{5}$ and (b) corresponding energy-dispersive spectroscopy elemental mapping images (Pt - Ru, Pt (red color) and Ru (green color))

The nature of the product was further clearly visualized in dark-field (DF-TEM) image and is shown in Figure 5.4(a). Nanoscale elemental mapping revealed that both Pt and Ru were distributed evenly over the entire area as observed from Figure 5.4(b). The mesoporous Pt particle prepared from KIT-6 and SBA-15 possessed mostly single-crystalline structure and is shown in Figure 4.3(b) in Section 4.3.5. However the co-deposition of two metal species, in this case Pt and Ru, with different standard electrode potentials may have affected the reduction of the domain size relative to the single element case.
5.3.1.3 Small-angle X-ray scattering

Figure 5.5 shows small-angle XRD profiles of the original mesoporous silica particles and the obtained mesoporous Pt–Ru bimetallic particles. All the mesoporous Pt-Ru bimetallic materials showed notable peak with $2\theta=0.9^\circ$ (d=9.2nm), that is the distance between the centres of two adjacent pores. The main peak positions of the obtained samples were exactly the same as those of the original mesoporous silica. This shows that the replication of Pt retained the original mesostructural symmetry.

![SAXS profile of (a) K_Pt_xRu_y and (b) S_Pt_xRu_y particles. The patterns of the original mesoporous silica templates (KIT-6 and SBA-15) are also shown as references.](image)

5.3.1.4 Wide-angle X-ray diffraction

To confirm the formation of mesoporous Pt-Ru bimetallic catalyst the wide angle X-ray diffraction (WAXRD) patterns were measured (Figure 5.6a and 5.6b). All the peaks corresponding to various hkl planes viz., (111), (200), (220), (311) and (222) are observed revealing the fcc Pt crystal structure. In addition, these peaks showed a shift of 1° towards higher angles, indicating that the Pt–Ru was formed as a single-phase alloy and confirming successful incorporation of Ru atoms into the fcc crystal structure. The X-ray diffraction profile of the nanostructures showed face centered cubic (fcc)
structure, and is consistent with the SAED pattern in Figure 5.3(b), Section 5.3.1.2.

Figure 5.6  Wide-angle XRD patterns of Pt-Ru samples prepared with (a) mesoporous silica KIT-6 and (b) SBA-15
5.3.1.5 Surface area and pore size analysis

From N$_2$ gas adsorption desorption isotherms, the surface areas of S$_{\text{Pt95Ru5}}$ and K$_{\text{Pt95Ru5}}$ were calculated and was found be around 42 and 40 m$^2$.g$^{-1}$ respectively with the average pore sizes around 3.0 and 2.8 nm. The data are given in Table 5.2. In the case of S$_{\text{Pt95Ru5}}$, the pore size of 3.0 nm indicates void space between Pt nanowires. This pore size value is almost the same as the wall thickness of the original mesoporous silica SBA-15. In the case of K$_{\text{Pt95Ru5}}$, the mesopore size of 2.8 nm indicates void space enclosed by four Pt nanowires and is in good agreement with the wall thickness of the original KIT-6. The surface area of all the mesoporous Pt-Ru alloy catalyst falls in the range of 34 to 42 m$^2$.g$^{-1}$ with a pore size ranging between 2.13 and 2.94nm and is given in Table 5.2.

Table 5.2 Variation of surface area and porosity of the mesoporous Pt-Ru alloy of different compositions of Pt and Ru content employing KIT-6 and SBA-15 silica template methods

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Surface area (m$^2$.g$^{-1}$)</th>
<th>Pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$_{\text{Pt95Ru5}}$</td>
<td>40</td>
<td>2.82</td>
</tr>
<tr>
<td>K$_{\text{Pt93Ru7}}$</td>
<td>38</td>
<td>2.13</td>
</tr>
<tr>
<td>K$_{\text{Pt90Ru10}}$</td>
<td>36</td>
<td>2.23</td>
</tr>
<tr>
<td>K$_{\text{Pt85Ru15}}$</td>
<td>34</td>
<td>2.76</td>
</tr>
<tr>
<td>S$_{\text{Pt95Ru5}}$</td>
<td>42</td>
<td>2.94</td>
</tr>
<tr>
<td>S$_{\text{Pt93Ru7}}$</td>
<td>41</td>
<td>2.24</td>
</tr>
<tr>
<td>S$_{\text{Pt90Ru10}}$</td>
<td>38</td>
<td>2.53</td>
</tr>
<tr>
<td>S$_{\text{Pt85Ru15}}$</td>
<td>35</td>
<td>2.42</td>
</tr>
</tbody>
</table>
5.3.2 Electrochemical Characterization- Hydrogen Oxidation Reaction

5.3.2.1 Cyclic voltammetry

Electrochemical measurements were done for the obtained \( K_{\text{Pt}_{95}\text{Ru}_{5}} \) and \( S_{\text{Pt}_{95}\text{Ru}_{5}} \) bimetallic alloy catalysts to investigate the potential use as electrocatalyst. The electrocatalytic performance toward hydrogen oxidation reaction (HOR) is recorded in aqueous solution of sulphuric acid of 0.5M at room temperature. Figure 5.7a and 5.7c shows a typical cyclic voltammogram of the adsorption/desorption reaction of mesoporous Pt-Ru at a scan rate of 50mV.s\(^{-1}\). The ECSA of mesoporous Pt-Ru was found to be 87 m\(^2\).g\(^{-1}\) while Pt black showed 38 m\(^2\).g\(^{-1}\) and mesoporous Pt showed ECSA of 61 m\(^2\).g\(^{-1}\). The high ECSA of Pt-M is the effectiveness of a mesoporous structure. The durability of the electrodes was tested for 4,000 cycles and the ECSA of the electrodes before and after accelerated durability test was shown in Figure 5.7b and 5.7d. Porous Pt-Ru (10% ECSA loss) are found to be more durable than Pt black (45% loss), suggesting that the unique geometry of these pores facilitates the durability of the catalyst.

![Figure 5.7 (Continued)](image-url)
Figure 5.7  (a,c) Cyclic voltammetry curves towards hydrogen oxidation reaction and (b,d) ADT of Pt-Ru bimetallic catalyst prepared with mesoporous silica KIT-6 and SBA-15. Pt black is taken for comparison
5.3.3  Electrochemical Measurements-Methanol Oxidation Reaction

5.3.3.1  Cyclic voltammetry

As shown in the cyclic voltammogram Figure 5.8a, the methanol oxidation process was seen from the two anodic peaks occurring on both forward and reverse sweeps. The magnitude of the peak in the forward scan indicates the electrocatalytic activity of the catalyst towards methanol oxidation reaction. Both S_Pt95Ru5 and K_Pt95Ru5 bimetallic catalysts exhibited better electrocatalytic performance than mesoporous Pt or commercially available Pt black as observed from Figure 5.8(b).

![Cyclic voltammetry curves towards methanol oxidation reaction of Pt95Ru5 samples prepared using KIT-6 and SBA-15, (b) Summary of current density for all samples.](image)

The Ru surface sites can allow facile formation of oxygenated species to oxidize the dissociative intermediates produced on nearby Pt sites, and alloying facilitates the C-H cleavage reaction in methanol decomposition at lower potential. Two mechanisms have been proposed for the superior performance of Pt–Ru alloy, Ru reduces the strength of the Pt-CO bond and subsequently dissociates water to produce adsorbed OH species, which react with CO adsorbed on the Pt surface to generate CO₂. The mass-normalized current density of S_Pt95Ru5 (598mA.mg⁻¹) was approximately 2 times higher
than that of mesoporous Pt (298 mA·mg$^{-1}$) and around 8 times higher than Pt black (72 mA·mg$^{-1}$).

5.3.3.2 Linear sweep voltammetry

The onset potential with respect to the methanol electro-oxidation on Pt sites is related to the breaking of C-H bonds and subsequent removal of intermediates such as CO$_{ad}$ by oxidation, with OH$_{ad}$ supplied by the Pt-OH sites. From the linear sweep voltammetry (LSV) curves shown in Figure 5.9, it was shown that the onset potential for methanol oxidation was lower for the mesoporous Pt–Ru bimetallic catalyst than for Pt samples. The onset potential for methanol oxidation was lower for the mesoporous Pt-Ru bimetallic catlayst as compared to Pt, may be due to better methanol accessibility as a consequence of mesoporous structure. The oxidation potential of mesoporous Pt-Ru were lower than those of mesoporous Pt and Pt black, suggesting the ease of methanol oxidation as observed from the linear sweep voltammetry curves.

![Figure 5.9 LSV curves Pt$_{92}$Ru$_5$ samples prepared with mesoporous silica KIT-6 and SBA-15](image-url)
5.3.3.3 Chronoamperometry measurements

The stability of the catalysts was examined by chronoamperometric curves recorded at 0.65 V for 3000 seconds and are shown in Figure 5.10. The current density of all the catalysts decayed rapidly at the initial stage, which might be due to the formation of intermediate species during methanol oxidation such as CO$_{ads}$ and CHO$_{ads}$. The current density of all the catalysts gradually reached a steady state after quick decay at the beginning. $S_{Pt95Ru5}$ and $K_{Pt95Ru5}$ showed good activity and stability with the ending current density of 52mA.mg$^{-1}$ at 3000 seconds.

![Figure 5.10 Chronoamperometric curves recorded at 0.65V for 3000s of Pt-Ru samples prepared with mesoporous silica KIT-6 and SBA-15](image)

The current densities of both $S_{Pt95Ru5}$ and $K_{Pt95Ru5}$ were higher than those of mesoporous Pt and Pt black over the entire time period. The performance of the mesoporous catalyst followed the order of $S_{PtRu}>K_{PtRu} >$ mesoporous Pt $>$ Pt black, which was the same trend for all the compositions. The 2D hexagonal structure with straight channels might be suitable for methanol diffusion, rather than the complicated inverse double
gyroid structure. With the increase of Ru content in the products, the current densities decreased, while the onset potentials did not change may be due to the decreased surface areas. Hence, high surface area samples like highly ordered mesoporous Pt, mesoporous Pt-Ru bimetallic catalyst significantly enhances the catalytic activity towards the electro-oxidation of methanol compared to microporous Pt back samples.

5.4 CONCLUSION

Mesoporous Pt–Ru bimetallic particles were synthesized in different compositions and uniform particle sizes by using SBA-15 and KIT-6 as hard templates. Both Pt and Ru were atomically distributed in the frameworks without any phase segregation. The electrochemical performance and stability of the mesoporous Pt–Ru alloys towards methanol oxidation was highly enhanced compared to that of Pt black and mesoporous Pt. The highly effective surface area of the mesoporous Pt–Ru alloy structure drastically enhanced the catalytic activity towards electro-oxidation of methanol. Alloying Pt with Ru substantially improves its catalytic performance by reducing the CO poisoning and required noble metal. The results revealed that our Pt–Ru alloy can serve the purpose of effective electrocatalyst in fuel cell applications together with the superiority of mesoporous structure.