Effect of surface composition of Pt-Au alloy cathode catalyst on the performance of direct methanol fuel cells

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Abstract

A pure Pt cathode catalyst in direct methanol fuel cells is not only favored for oxygen reduction but also for the unwanted oxidation of methanol that permeates from the anode. Based on the idea that alloying another metal can alter the surface structure of Pt and hence reduce the active sites for methanol adsorption, in this work we prepare carbon supported Pt-Au nanoparticles with different surface compositions with the dimethylformamide co-reduction method by adjusting the pH value from 14 to 12. The electrochemical characterizations indicate that the alloyed Pt-Au catalyst prepared under pH = 13 exhibits lower catalytic activity to methanol oxidation but retains the oxygen-reduction activity similar to that of the Pt/C. The cell performance tests show that the PtAu/C can almost double the peak power density of the cell with the Pt/C cathode, although the Pt loading in the PtAu/C cathode is only half of that in the Pt/C cathode.

1. Introduction

Direct methanol fuel cells (DMFCs) have been recognized as one of the most promising power sources for powering portable electronic devices because liquid methanol has high specific energy and this type of fuel cell has a simple and compact structure [1–5]. Since platinum has the highest catalytic activity for the oxygen reduction reaction (ORR), the carbon-supported platinum (Pt/C) is the state-of-the-art electro-catalyst for the DMFC cathode [4–6]. However, as this type of catalyst is also active to methanol oxidation, methanol that crosses over from the anode to the cathode can be oxidized at the Pt cathode, creating the so-called mixed potential, which reduces the cathode potential. Moreover, the added methanol oxidation reaction (MOR) at the cathode can significantly reduce the active sites designated for the ORR, further lowering the cathode potential. One of the methods to reduce the adverse impacts of methanol crossover has been to develop so-called methanol-tolerant catalysts that are active to the ORR but inactive to the MOR.

Recently, Pt-based alloys, including Pt-Cr, Pt-Fe, Pt-Co, Pt-Ni and Pt-Au, have been investigated as methanol-tolerant cathode catalysts [7–11]. Among all these alloys tested, the Pt-Au catalyst has been the most promising one in terms of both the catalytic activity and stability [12,13]. Studies indicate that the methanol-tolerant mechanism of the Pt-based alloys can be attributed to the diluted Pt sites for methanol dehydrogenation as compared with the pure Pt catalyst [7]. In line with this idea, efforts have been made to synthesize methanol-tolerant cathode catalysts by attempting to dilute Pt sites. However, the dilution of Pt sites will lead to a reduction in the Pt sites available for the ORR, which will significantly lower the overall Pt utilization.

Because of the ORR is a surface-structure sensitive reaction on electrodes, the utilization of Pt in electro-catalysts can be defined as the dispersion or exposed percentage of Pt atoms in...
the catalyst [14]. To enhance the Pt utilization as the cathode catalyst in DMFCs, an effective approach is to control the neighboring Pt sites that are unfavorable for the MOR while available for the ORR. This approach has not, however, been well attempted in previous studies. In the present work, a series of carbon supported Pt-Au nanoparticles were prepared by the dimethylformamide co-reduction method [15]. The exposed Pt sites on the alloy surfaces were controlled by changing the preparing condition. As a result, the use of the as-prepared Pt-Au alloy catalysts in the DMFC cathode showed a strong methanol-tolerant behavior, but could still maintain fairly good catalytic activity for the cathode ORR.

2. Experimental

All of the chemicals used were of analytical grade. Hexachloroplatinic acid and hydrogen tetrachloraurate trihydrate were purchased from Aldrich. N,N-dimethylformamide (DMF), ethanol, methanol, perchloric acid, sodium hydroxide and potassium chloride (all from Merck KGaA) were used as received. 80 wt.% PtRu/C, carbon paper and Vulcan XC-72 carbon powder (particle size 20–40 nm) were procured from E-TEK Company. 5 wt.% Nafion solution was received from Dupont and used as received.

The carbon powder supported platinum nanoparticles were prepared as follows: 80 mL of 5 mM H2PtCl6, DMF aqueous (1:1 v/v) solution was mixed with 182 mg of carbon powder and ultrasonicated for 40 min. After a homogeneous suspension was formed, the mixture was introduced into a microwave oven (800 W, 2.45 GHz) and heated for 2 min at a specified fraction of the maximum microwave power [16]. The precipitate thus formed was collected by centrifugation, washed several times with ethanol and water and dried at 70 °C in oven. (Pt loading: 30 wt.% named 30Pt/C). The carbon powder supported Pt-Au alloy catalysts were prepared with the co-reduction method as described in the reference [17]. Briefly, 20 mL of 10 mM H2PtCl6 and HAuCl4 DMF solution were mixed and illuminated with UV light for 3 h. The carbon powder of 182 mg was suspended into the resulting solution under vigorous stirring. After a homogeneous suspension was formed, 40 mL NaOH solution with pH value of 14/13/12 was added into the precursor’s solutions, respectively. The prepared catalysts were named with 30PtAu14/C, 30PtAu13/C and 30PtAu12/C, respectively (Pt-Au loading: 30 wt.%, with platinum to gold mole ratio of 1). For comparison, the 30Au14/C sample was also prepared with the same method.

The X-ray diffraction (XRD) patterns of the carbon supported Pt and Pt-Au catalysts were obtained with a Philips powder diffraction system (model PW 1830) using a Cu Kα source operating at 40 keV at a scan rate of 0.025 s⁻¹. The valence state and the surface composition of the prepared samples were carried out by the X-ray photoelectron spectroscopy (XPS) technique, which is equipped with a Physical Electronics PHI 5600 multi-technique system using Al monochromatic X-ray at a power of 350 W. The survey and regional spectra were obtained by passing energy of 187.85 and 23.5 eV, respectively.

Electrochemical measurements were carried out by cyclic voltammetry (CV) using a potentiostat (EG&G Princeton, model 273A). A conventional, three-electrode cell consisting of GCE with an area of 0.125 cm² as the working electrode, Pt foil as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode was used. The reference electrode was placed in a separate chamber, which is located near the working electrode through a Luggin capillary tube. The working electrode was modified with the catalyst layer achieved by dropping a suitable amount of catalyst ink on the GCE. The catalyst ink was prepared by ultrasonically dispersing 10 mg of the carbon supported Pt or Pt-Au catalyst in 1.9 mL of ethanol, to which 0.1 mL of 5 wt.% Nafion solution was added, and the dispersion was ultrasonicated for 30 min to obtain a homogeneous solution. A quantity of 9 μL of the dispersion was pipetted out on the top of the GCE and dried in air to yield a metal loading of 108 μg cm⁻². The CV experiments were performed in 0.5 M HClO₄ solution with/without 1.0 M CH₃OH at a scan rate of 50 mV s⁻¹. Polarization curves for the oxygen reduction reaction (ORR) were obtained in 0.5 M HClO₄ solution using rotating disk electrode (RDE) with the speed controlled by a Metrohm 628-10 unit. Before the RDE study, the electrodes were cycled at 50 mV s⁻¹ between −0.2 and 1.0 V until reproducible cyclic voltammograms were obtained. Normalized currents are given in terms of geometric (mA cm⁻²).

The in-house fabricated DMFC consisted of a membrane electrode assembly (MEA), with an active area of 1.0 cm x 1.0 cm, sandwiched between two bipolar plates, which were fixed by two fixture plates. The MEA consisted of a Nafion 115 membrane and two electrodes. For fabrication of the cathode, commercial-grade 30 wt.% Teflon treated carbon paper (E-TEK) was employed as the backlayering. The gas diffusion layer (GDL) was fabricated on one side of the carbon paper comprising Vulcan XC-72 carbon and 30 wt.% Teflon. To fabricate cathode catalyst layers, the cathode inks were prepared by mixing in-house-made carbon supported Pt and Pt-Au catalysts with 10 wt.% Nafion solution in ethanol. The prepared cathode inks were uniformly brushed on the GDL in a 1.0 cm² area to give an approximate metal loading of 1.0 mg cm⁻² on the cathode. Finally, 0.5 mg cm⁻² of Nafion was uniformly coated on the cathode catalyst layers and dried at 80 °C in oven. The commercial 80% PtRu/C (4 mg cm⁻²) catalyst was used as the anode. The MEA was formed by sandwiching the Nafion 115 membrane between the anode and the cathode and by hot pressing it at 135 °C under a pressure of 4 MPa for 3 min.

The MEAs fabricated by using the carbon supported Pt and Pt-Au catalysts at the cathode were tested in a single cell fixture (with an active area of 1.0 cm²) having serpentine flow channels with both widths and depths of 0.7 mm. The MEAs were initially activated at 80 °C for 24 h by feeding 1.0 M methanol at a flow rate of 0.5 mL min⁻¹ to the anode and dry oxygen gas at a flow rate of 50 sccm to the cathode. After the activation process, the DMFC performance curves were recorded by fixing the load current, which was controlled with an electric load system (BT2000, Arbin Instrument, Inc.).

3. Results and discussion

3.1. Physicochemical characterizations

The XPS spectra of the prepared samples in the Pt 4f and Au 4f region are shown in Fig. 1. The binding energies (B.E.) of the
4f\textsubscript{7/2} signal for Pt and Au components in the samples are given in Table 1. As can be seen in Fig. 1, the positions of the peaks are consistent with the results reported elsewhere [18], i.e., displaying the 4f\textsubscript{7/2} core level of the Pt\textsuperscript{0} species in 30Pt/C samples at about 71.4 eV. From the XPS result, it can be observed that the Pt 4f binding energies of the Pt\textsuperscript{0} species is shifted to a higher peak value for the Pt-Au bimetallic samples as compared to the positions displayed by the Pt\textsuperscript{0} species of 30Pt/C. The minimum magnitude of the shift is ca. 0.16 eV, and the trend is observed throughout the series. The increase in the Pt binding energy for the bimetallic Pt-Au samples relative to the 30Pt/C suggests electron transfer from Pt to Au, which can be related to the perturbed electronic interaction between Pt and Au atomic orbit and in turn to their alloy formation. The same situation was observed for the bimetallic Pt-Au metal reported elsewhere [19]. The increased binding energy of the Pt atoms gives a potential increase in the durability of the Pt-Au alloy electro-catalyst. The relative abundances of the different species detected by the XPS analysis and the surface atomic ratios are summarized in Table 1. It can be observed that the surface composition depends on the samples, which in some cases arise from the different preparative conditions. The surface atomic ratio of Pt:Au is 1.17:1 for the 30PtAu14/C sample. However, the surface of the 30PtAu13/C sample shows more Pt-rich with the relative atomic ratio of the metal phase being Pt:Au = 1.11:1. Further reducing the pH value to 12 led to a substantial increase in Pt on the surface, as shown by the Pt to Au atomic ratio of 12.5:1 of the 30PtAu12/C sample, indicating an Au–Pt core–shell-like structure formation in 30PtAu12/C sample. Nevertheless, the zero state Au metal was obtained for all the Au-based samples with the Au 4f binding energies of the Au\textsuperscript{0} species shifting to a lower binding energy as compared to the position displayed by the Au\textsuperscript{0} species of 30Au14/C with the binding energy peaks of Au 4f region at 84.2, 87.8 eV [20]. The XPS result indicated that the bimetallic Pt-Au samples with controlled surface composition can be obtained by adjusting the preparing conditions.

In order to determine the average particle size and the Pt-Au alloy effect, the carbon supported Pt and Pt-Au samples were characterized by XRD and the results are shown in Fig. 2a. For the sake of comparison, the range between 36 and 42° is enlarged in Fig. 2b. For all the samples, the broad peak centered at about 25° corresponds to the amorphous nature of the Vulcan XC-72 carbon [21]. For the 30Pt/C, 30PtAu14/C and 30PtAu13/C samples, all reflections expected for a face-centered cubic (fcc) lattice, corresponding to the structure of the pure bulk metals, are observed [15]. In contrast, the diffraction patterns of the 30PtAu12/C sample shows two sets of such reflections, which indicates the condensation of two different crystalline phases, although both correspond to the

<table>
<thead>
<tr>
<th>Sample</th>
<th>B.E. (Pt\textsubscript{7/2}, eV)</th>
<th>B.E. (Au\textsubscript{7/2}, eV)</th>
<th>At.% (Pt)</th>
<th>At.% (Au)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30Pt/C</td>
<td>71.3</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30PtAu14/C</td>
<td>71.8</td>
<td>83.9</td>
<td>46.08</td>
<td>53.92</td>
</tr>
<tr>
<td>30PtAu13/C</td>
<td>71.5</td>
<td>84.1</td>
<td>52.61</td>
<td>47.39</td>
</tr>
<tr>
<td>30PtAu12/C</td>
<td>71.5</td>
<td>84.1</td>
<td>92.60</td>
<td>7.40</td>
</tr>
</tbody>
</table>

Table 1 – Binding energies and relative intensities of platinum and gold species (normalized to the total metal) of Pt/C and PtAu/C samples.
same crystal structure type. The refined peak value and \(d_{111}\) space parameters of all samples are presented in Table 2.

Careful comparisons of the (111) peak values with that of the 30Pt/C and 30Au14/C, Pt-(111) = 39.85°, Au-(111) = 38.17° [20], suggest that Pt and Au are alloyed well in the 30PtAu14/C and 30PtAu13/C samples and hence a single crystalline phase is observed, while phase separation occurs in the 30PtAu12/C sample [12]. To underline this in Fig. 2b, the positions of the (111) reflections are projected onto the horizontal axis. The reflections for the 30PtAu12/C sample appear at the positions fairly close to those expected for the bulk metals: 39.71° for Pt, and 38.27° for Au. Accordingly, the two different phases in this sample seem to correspond to a situation where the metallic constituents condense independently without atomic level alloying. Compared to that of the 30Pt/C, the shift of the (111) peak of the 30PtAu14/C to a lower \(2\theta\) angle by about 1.35 degree could be indexed to a higher \(d\) space (\(d_{111} = 2.336 \text{ Å}\)) crystal structure of Pt due to incorporation of the Au atoms, while the \(d_{111}\) value of 30PtAu13/C is 2.314 Å, which is in the middle of the 30Pt/C and 30PtAu14/C. As compared with 30PtAu14/C, the 30PtAu13/C shows a more “Pt like” structure, which makes the 30PtAu13/C more attractive as the Pt-based electro-catalyst for both the MOR and ORR [5].

The average particle size of the carbon supported Pt and Pt-Au alloy samples were calculated from the broadening of the (111) diffraction peaks using Scherrer’s equation [22]:

\[
d = \frac{0.9 \lambda}{B_{2\theta} \cos \theta_{\text{max}}}
\]

where \(\lambda\) is the wavelength of the X-ray (1.54056 Å), \(\theta\) is the angle at the maximum of the peak, and \(B_{2\theta}\) is the width of the peak at half-height. It turns out that the mean particle size of 30Pt/C, 30PtAu14/C and 30PtAu13/C are 3.0, 3.6 and 2.8 nm, respectively.

### 3.2. Electrochemical characterizations

#### 3.2.1. CV test in the base electrolyte

It has been reported that the electro-catalytic properties of the Pt-based catalyst depends on the type of the Pt crystallite phases present on the carbon supporting materials [23,24]. Thus, to understand the nature of the Pt crystallite phases present in the 30Pt/C, 30PtAu14/C and 30PtAu13/C catalysts, which can be roughly characterized by the hydrogen adsorption/desorption (Hads/desor) profiles of the CV [25], we conducted the CV studies for the 30Pt/C, 30PtAu14/C and 30PtAu13/C electrodes in the potential range between −0.2 and 1.0 V in 0.5 M HClO4 at a sweep rate of 50 mV s\(^{-1}\). As can be seen in Fig. 3, the voltammetric features of the 30PtAu14/C (the blue line) and 30PtAu13/C (the red line) are similar to the polycrystalline Pt electrode (the black line): the adsorption and desorption of hydrogen within the potential range of −0.20 to 0.08 V, the double-layer capacitance region between 0.08 and 0.56 V, the formation of Pt oxides at potentials more positive than 0.56 V, and the reduction of Pt oxides in the cathodic potential scan [26,27]. However, the clear shifts of the peak positions for the Hads/desor can be observed in the 30PtAu14/C and 30PtAu13/C catalysts, indicating the arrangement transformation of Pt atoms as compared with 30Pt/C [28]. Furthermore, in the cathodic sweep, a monolayer oxide (PtOx) reduction peak potential difference of over 20 mV has been noted between the supported Pt-Au and Pt catalysts. This result indicates the potential difference in the formation of the monolayer oxide during the anodic sweep for the two distinct Pt crystallite phases present in the Pt-Au alloy and monometallic Pt catalysts. From the integrated area of the hydrogen desorption peaks (\(Q_H\)) shown in Fig. 3, it can be seen that the exposed surface areas of Pt in the three catalysts is in sequence of 30Pt/C > 30PtAu13/C > 30PtAu14/C.

The data of CV measurements allow us to count the number of surface exposed Pt atoms (\(N_{\text{Pt}}\)) as the number of adsorbed H atoms (\(N_{\text{H}}\)) on the electrode catalyst [14,29]:

\[
N_{\text{Pt}} = N_{\text{H}} = \frac{Q_{\text{H}}}{Q_{e}}
\]

where \(Q_{e}\) is the elementary charge or charge of an electron (\(Q_{e} = 1.602 \times 10^{-19} \text{ C}\)). Thus, the ratio of \(N_{\text{Pt}}\) or \(N_{\text{H}}\) to the total number of Pt atoms (\(N_{\text{Pt}}\)) in the electrode catalyst gives the utilization percentage of Pt.

\[
U_{\text{Pt}} = \frac{N_{\text{Pt}}}{N_{\text{Pt}}}
\]

The calculation results are shown in Table 3. It can be seen that the 30PtAu13/C catalyst shows the highest Pt utilization, which made it possible to reduce Pt utilization by this technique.

#### 3.2.2. MOR catalytic activity measurements

The electro-oxidation of methanol on the carbon supported Pt and Pt-Au alloy catalysts were evaluated in the potential range between −0.2 and 1.0 V in 0.5 M HClO4 + 1.0 M CH3OH at the sweep rate of 50 mV s\(^{-1}\). The CV curves after 40 times cycling

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak (111)</th>
<th>(2\theta) value (°)</th>
<th>(d) space (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30Pt/C</td>
<td>Pt</td>
<td>39.85</td>
<td>2.260</td>
</tr>
<tr>
<td>30PtAu14/C</td>
<td>Pt-Au</td>
<td>38.50</td>
<td>2.336</td>
</tr>
<tr>
<td>30PtAu13/C</td>
<td>Pt-Au</td>
<td>38.89</td>
<td>2.314</td>
</tr>
<tr>
<td>30PtAu12/C</td>
<td>Pt</td>
<td>39.71</td>
<td>2.268</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>38.27</td>
<td>2.350</td>
</tr>
</tbody>
</table>
are presented in Fig. 4. It can be seen that the current densities of the methanol oxidation reaction on the Pt-Au alloy catalysts are much lower than that on the Pt/C catalyst. The monotonic increase in the peak current density during the methanol oxidation indicates that the number of Pt sites determines the peak current, which is consistent with the sequence of the Qs, shown in Fig. 3. It is well understood that at least three adjacent Pt sites in the proper crystallographic arrangement are necessary to activate the chemisorption of methanol during the methanol oxidation [8]. For the Pt-Au alloy catalysts with a disordered structure, the probability of finding three neighboring Pt atoms on the surface is lower if no Pt enrichment on the surface takes place. In this work, the carbon supported Pt-Au catalysts were prepared from the DMF co-ordinated Pt-Au complex precursors. It has been demonstrated that the Pt-Au precursor involving the Pt-Au interaction presented in solution, which offers the possible nucleation of Pt-Au alloy with the atomic-level mixing during the co-reduction process [15]. This explains the behavior that the bimetallic Pt-Au alloy catalysts prepared with this method result in a lower peak current density for the MOR due to the composition effect (especially the surface composition effect) in terms of their disordered surface structure in the Pt-Au alloy catalysts. And the same situation was also observed for the bimetallic Pt-Cr alloy catalyst [8]. Although the addition of Au does not increase the peak current, the peak potential is shifted, as shown in Fig. 4. The large methanol oxidation peak potential is approximately 0.76 V for 30Pt/C catalyst, but 0.65 and 0.73 V for 30PtAu14/C and 30PtAu13/C catalysts, respectively, which shifted to a lower potential. It has been reported that Ru is the most promising component in Pt based binary catalysts for methanol oxidation, by virtue of either a bifunctional mechanism or an electronic effect [4,5]. In contrast, it is generally understood that alloyed Pt with Au does not fulfill a bifunctional mechanism because Au does not exist in an oxide form and cannot easily adsorb OH to provide an oxygen source for the removal of adsorbed CO. A possibility for the improvement in peak potential for the MOR of the Pt-Au alloy is the accelerated rate of HCOOH electro-oxidation [29]. This indicates that Au in Pt-Au alloy aids in increasing the probability of inducing a major reaction pathway for methanol oxidation to avoid the formation of adsorbed CO. This conclusion is supported by Choi’s work [29] and our previous works [15,17]. For the MOR electro-catalyst, another important factor for evaluating the catalytic activity is its resistance to carbonaceous species accumulation. In methanol electro-oxidation, the anodic peak during the reverse scan is usually attributed to the removal of intermediate carbonaceous residues formed on the catalyst during the forward scan. Therefore, the ratio of two anodic current densities, I/Ib, is commonly used to describe catalyst susceptibility to poisoning [30]. For the 30Pt/C, this value is 0.55, which indicates that a significant number of methanol molecules are only partially oxidized in the forward scan. However, for the Pt-Au samples, we observed a larger I/Ib ratio of 1.34 and 0.73 for 30PtAu14/C and 30PtAu13/C, respectively. This can be explained by the third body effect for Pt-Au catalyst by decreasing the formation of COads [31–35]. This result indicates that optimizing the Pt to Au ratio with three adjacent Pt sites available in the bimetallic catalyst can lead to a high catalytic and high CO tolerance catalyst for the MOR. Based on the Pt-Au alloy with the cluster of Pt3Au3, they may display six different isomers as shown in Fig. 5 (adapted from reference [34]). It can be seen that the Fig. 5 (a, c, e, f and g) may offer the three adjacent Pt sites for methanol adsorption. It is reported [34] that Fig. 5a, the planar structure, is the most stable structure within the five Pt3Au3 isomers. The Pt-Au alloy based on this structure may serve as the electro-catalyst for the MOR. This hypothesis has been proved by Park’s work [35] that the Pt-modified Au nanoparticles can enhance the electro-catalytic for the MOR. Although the catalytic activity of the Pt-Au alloy catalyst is higher than that of the Pt catalyst, it is far below than the archetypal Pt-Ru catalyst [4,5]. For this reason, the Pt-Au alloy cannot be used as the DMFC anode catalyst. On the contrary, by adjusting the surface structure of the bimetallic Pt-Au alloy to avoid the three adjacent Pt sites, the Pt-Au

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pt loading (μg cm⁻²)</th>
<th>Particle sized (nm)</th>
<th>Uₚ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30Pt/C</td>
<td>108</td>
<td>3.0</td>
<td>33.9</td>
</tr>
<tr>
<td>30PtAu14/C</td>
<td>49.8</td>
<td>3.6</td>
<td>24.5</td>
</tr>
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<td>30PtAu13/C</td>
<td>56.8</td>
<td>2.8</td>
<td>50.1</td>
</tr>
</tbody>
</table>

Table 3 – Comparison of particle size and Pt utilization in the as-prepared catalysts.

Fig. 4 – CV curves in 0.5 M HClO₄ + 1.0 M CH₃OH at the sweep rate of 50 mV s⁻¹.

Fig. 5 – Structure of Pt₃Au₃ isomers with the blue representing Pt and the green representing Au [34].
alloy can serve as the well methanol-tolerant cathode catalyst in DMFCs.

3.2.3. ORR catalytic activity measurements

Fig. 6 shows the linear sweep voltammograms (LSV) obtained from rotating disk electrode (RDE) studies in 0.5 M HClO₄ saturated with pure oxygen at the scan rate of 5 mV s⁻¹ and the rotating speed of 2000 rpm. From Fig. 6, it can be observed that the ORR on all the catalysts is diffusion controlled when the potential is less than 0.2 V and is under mixed diffusion kinetics control in the potential region between 0.2 and 0.6 V. From the linear sweep voltammograms, it can be seen that the 30PtAu14/C catalyst shows the lowest catalytic activity with an ORR current density of 2.0 mA cm⁻² at 0.49 V, and the value is 6.9 for the 30PtAu13/C and 30Pt/C. From this result, it can qualitatively be concluded that 30PtAu14/C sample is a poor catalyst for oxygen reduction in acidic solutions as compared to 30Pt/C and 30PtAu13/C. It is worth mentioning that the onset potential of the 30PtAu14/C and 30PtAu13/C catalysts in oxygen-saturated solution becomes lower than that of the 30Pt/C catalyst, suggesting the unfavorable oxygen adsorption on these catalysts surface, mainly due to the fact the addition of Au atom decreases the active sites for oxygen adsorption. For O₂ adsorption on an electrode surface, no reliable information on the sites and configuration is given. Yeager [36] proposed three plausible models for O₂ adsorbed on the metal surface, as shown in Fig. 7 (adapted from reference [37]):

i) O₂ interacting with two bonds with a single substrate atom (Griffiths model).
ii) End-on adsorption through a single bond (Pauling model).
iii) A bridge model, with two sites.

The tight-binding extended Hückel calculations indicate that the chemisorption of molecular oxygen on a Pt surface appears to be more favorable at the two-fold bridge site than on top, or three-fold sites [38]. And dual adsorption sites are likely to be involved in the dissociation of O₂ [37]. Combining the MOR and ORR mechanism on the electrode surface, the methanol-tolerant ORR catalyst may avoid the three adjacent Pt sites while make the two adjacent Pt sites available on the bimetallic Pt₂Au₂ alloy surface. Based on the Pt-Au alloy with the cluster of Pt₂Au₂, they may display four different isomers as shown in Fig. 8 (adapted from reference [34]). It can be seen that the Fig. 8 (a, b and d) may offer the two adjacent Pt sites for oxygen adsorption. And Fig. 8a has been shown as the most stable structure within the three Pt₂Au₂ isomers. The Pt-Au alloy based on this structure may show well methanol-tolerant ORR catalytic activity in DMFCs. For the ORR catalyst, the durability is also one of the key factors in determining the ORR activity. Au is the most electronegative metal, and will contribute to the electron-withdrawing effect from Au to the neighboring Pt and stabilize the bimetallic Pt-Au catalyst accordingly and this hypothesis has been confirmed by the XPS result as can be seen in Fig. 1. In addition, Zhang’s work [13] demonstrated that the platinum ORR electro-catalysts could be stabilized against dissolution by modifying Pt nanoparticles with Au clusters. Based on these studies, the bimetallic Pt-Au alloy nanoparticles will be the ideal methanol-tolerant cathode catalyst in DMFCs for contributing to both the catalytic activity and stability.

3.3. Direct methanol fuel cell performance test

The electrochemical characterizations presented above have shown that the 30Pt/C gives the highest catalytic activity for both the MOR and ORR, while the 30PtAu14/C shows otherwise among the three catalysts. In this section, we present the performance test results using 30Pt/C, 30PtAu14/C and 30PtAu13/C as the cathode catalyst of a DMFC with its anode consisting of the PtRu/C catalyst. Fig. 9 shows the polarization and power density curves. It can be observed that the open circuit voltage (OCV) is strongly dependent on the Pt-based cathodes. For the DMFC with the 30PtAu13/C catalyst, the OCV is about 0.64 V, which is about 60 mV higher than that with the 30Pt/C catalyst (ca. 0.58 V). As clearly shown in Fig. 6, the onset

Fig. 6 – Linear sweep (5 mV s⁻¹) recorded in 0.5 M HClO₄ solution saturated with oxygen at a rotating rate of 2000 rpm.

Fig. 7 – Models for O₂ adsorbed on metal sites, (a) Griffiths model, (b) Pauling model, (c) Bridge model. Adapted from [37].

Fig. 8 – Structure of Pt₂Au₂ isomers with the blue representing Pt and the green representing Au [34].
potential of the ORR on the 30PtAu13/C electrode is 0.64 V, which is identical to that of the 30Pt/C electrode. The higher OCV with the 30PtAu13/C catalyst may result from the relatively lower MOR catalytic activity of the 30PtAu13/C catalyst than that of the 30Pt/C on the cathode. Fig. 9 also shows that with the 30PtAu14/C catalyst, higher performance can be achieved at low current densities (including OCV), mainly due to the low MOR activity effect of the catalyst. However, at high current densities, since the rate of methanol crossover decreases, the advantage of using the 30PtAu14/C catalyst becomes insignificant. As a result, the DMFC with the 30PtAu14/C catalyst yielded a peak power density of 60 mW cm$^{-2}$, which is lower than 67 mW cm$^{-2}$ with the 30Pt/C catalyst and 96 mW cm$^{-2}$ with the 30PtAu13/C catalyst. The highest performance achieved with the 30PtAu13/C catalyst can be attributed to the two facts: i) the lower MOR activity of the 30PtAu13/C; and ii) the similar ORR activity as that of the 30Pt/C catalyst on the cathode. Finally, it is worth mentioning that the cell performance comparison was made based on the same total metal (Pt+Au) loading. For this reason, the Pt loading in the 30PtAu13/C catalyst was much lower than that in the 30Pt/C catalyst. The high performance with the low Pt loading bimetallic Pt-Au catalyst suggests an improvement in Pt utilization.

### 4. Conclusions

In this work, the carbon supported bimetallic Pt-Au nanoparticles were prepared with DMF co-reduction method, and the resulted samples were analyzed with XPS and XRD measurements. The results indicated that the bimetallic Pt-Au nanoparticles with controlled crystalline phases and surface compositions can be obtained by adjusting the preparing conditions. The catalytic activities of the prepared catalysts were characterized through the MOR and ORR in an acid solution. The studies indicated that the catalytic activity of the prepared catalysts is sensitive to the surface active sites of platinum, and these Pt active sites can be modified by Au atoms in the bimetallic Pt-Au alloy catalysts. As a result, the 30PtAu13/C catalyst exhibits a lower MOR activity while its catalytic activity for the ORR remains similar to that of the original Pt/C catalyst. The DMFC performance test results indicated the reduced Pt loading and increased Pt utilization achieved with the 30PtAu13/C as the cathode catalyst as compared with the conventional Pt/C catalyst.

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### REFERENCES


