# PtRu/C-Au/TiO$_2$ electrocatalyst for a direct methanol fuel cell

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## Abstract

Au/TiO$_2$ is added to a PtRu/C electrode to improve the performance of a direct methanol fuel cell (DMFC). A high-throughput-screening test is performed for the fast screening of the loading of Au/TiO$_2$ on PtRu/C. The electrochemically-active surface area of PtRu/C-Au/TiO$_2$ and PtRu/C is determined from cyclic voltammetry. In CO-stripping and methanol oxidation voltammetry, PtRu/C-Au/TiO$_2$ exhibits better activity for CO and methanol oxidation than PtRu/C. The performance of the DMFC is also improved by addition of Au/TiO$_2$ to the PtRu/C electrode. The CO adsorbed on Pt may move to the surface of the Au/TiO$_2$ by the interaction between PtRu/C and Au/TiO$_2$. The improved performance of the PtRu/C-Au/TiO$_2$ catalyst is explained in terms of preferential oxidation of CO or CO-like poisoning species that are generated during the oxidation of methanol on PtRu/C.
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## 1. Introduction

The direct methanol fuel cell (DMFC) is being widely investigated and considered as a prospective power source for small-power distributed generation and portable applications. Despite some progress, the DMFC has been plagued by low power density, which has been attributed to the low-activity of the available anode catalysts. Platinum is a suitable electrocatalyst for the electro-oxidation of methanol. At room or moderate temperature, however, pure platinum is a poor anode catalyst for methanol electro-oxidation. This is because CO and various intermediates are generated and act as poisons that adsorb on the active sites of the platinum catalyst [1,5]. Making alloys with a second or a third metal is a convenient way to modify the electrocatalytic properties of platinum in order to overcome the poisoning [3]. Pt-Ru alloy is considered to be the best available anodic material for DMFCs [4]. Ruthenium forms oxygenated

species at lower potentials than Pt and its presence in the catalyst promotes the oxidation of CO to CO$_2$ by a bifunctional mechanism [2]. Nevertheless, there have been many attempts to reduce the poisoning of Pt and/or Pt-Ru catalysts so as to improve the performance of DMFCs.

The oxide-supported Au catalysts have been demonstrated to be very promising candidates for the selective oxidation of CO in a gas phase reaction. Okumura et al. [6] reported that Au displayed surprisingly high activity for CO oxidation at low temperature when it was deposited on transition metal oxide. The most intensively studied system is Au supported on TiO$_2$. Whereas neither Au nor TiO$_2$ alone is active for CO oxidation, their combination generates high catalytic activity [7]. Moreover, the supported gold catalysts was able to combust the methanol decomposed derivatives at low temperature. And, it also exhibited very high catalytic activities for the water-gas shift reaction [8].

In spite of these characteristics of Au/TiO$_2$, its application for the anode catalyst of DMFC has not been reported to our knowledge. Au/TiO$_2$ could help a PtRu catalyst to electro-oxidize the methanol by removal of the methanol decomposed intermediates including CO which decrease the catalytic activity of PtRu/C.

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In this study, Au/TiO$_2$ is used with a PtRu/C catalyst for the electro-oxidation of methanol. For the fast screening of Au/TiO$_2$ loading on PtRu/C, a high-throughput-screening test was carried out. In our previous work [9], the active composition of catalyst for methanol electro-oxidation was successfully determined by high-throughput-screening test [9]. Cyclic voltammometry and operation of DMFC with the PtRu/C-Au Au/TiO$_2$ catalyst were performed to understand the effect of Au/TiO$_2$ on the electrochemical properties of PtRu/C.

## 2. Experimental

### 2.1. Preparation of Au/TiO$_2$ nanoparticles

Titanium *tert*-isopropoxide (TTIP, Aldrich), nitric acid (70%, Yakuri), iso-propyl alcohol (IPA, Duksan) and HAuCl$_4$·3.7H$_2$O (Kojima) were used without further purification. To obtain TiO$_2$ nanoparticles, a mixture of TTIP (25 ml) and IPA (4 ml) was introduced to 0.15 M nitric acid solution (150 ml) with stirring. The solution was agitated at 75 °C for 6 h. The resulting solution was centrifuged to remove the remaining organics and re-dispersed in de-ionized water to prepare a colloidal TiO$_2$ solution. HAuCl$_4$·3.7H$_2$O was dissolved in water and added to the colloidal TiO$_2$ solution. The solution was stirred at 80 °C for 15 h. The resulting solution was centrifuged and washed repeatedly with de-ionized water to remove the remaining chloride. The content of gold was fixed at 1 wt.% on TiO$_2$. The particle size of Au/TiO$_2$ was determined by means of a light scattering (DLS) method using light scattering measuring apparatus (Brookhaven Particle Sizer, Zetaplus).

### 2.2. High-throughput-screening test

The procedure for the high-throughput-screening test has been described previously [9]. To prepare the electrode arrays, commercial PtRu/C (Pt:Ru:C = 40:20:40, wt.%) received from E-Tek was mixed with Au/TiO$_2$ colloid and deposited on a Teflon-coated Toray carbon sheet, as shown in Fig. 1. The array was dried at 80 °C and reduced at 350 °C in a hydrogen environment.

The electrolyte solution was composed of 6 M methanol and a small amount of H$_2$SO$_4$; the pH was adjusted to 7 [9]. Finally, a quinine solution (100 μM) was added to the electrolyte solu-

tion as a proton indicator. To elucidate the effect of CO in the electro-oxidation of methanol, CO gas was purged into the electrolyte solution for 2 h to make a CO-saturated methanol solution. The array was used as the working electrode and a platinum wire as the counter electrode. A potential sweep between −0.3 and 0.8 V at a rate of 20 mV s$^{-1}$ was carried out with a potentiostat/galvanostat (Autolab Co.). When fluorescence emission was obtained by the illumination of 254 nm UV on the array, the brightest spot in the array was selected as the most active composition of PtRu/C and Au/TiO$_2$. The array underpotential sweep was recorded by a Nikon digital camera.

### 2.3. Cyclic voltammetry of PtRu-Au/TiO$_2$ catalysts

Cyclic voltammetry was conducted in a three-compartment electrochemical cell, that contained freshly prepared, oxygen-free (purged and blanked with nitrogen) 0.2 M H$_2$SO$_4$. An Ag/AgCl electrode saved as the reference electrode, and a platinum wire was used as a counter electrode. The working electrode was prepared by spraying the catalysts dispersed in iso-propyl alcohol on to carbon paper at 4 mg cm$^{-2}$. Cyclic voltammograms were obtained between +1.0 and −0.3 V at a scan rate of 20 mV s$^{-1}$ with a potentiostat/galvanostat (Autolab Co.). All potentials are reported with respect to the reversible hydrogen electrode. The CO-stripping voltammetry curves were obtained after adsorption of CO on catalysts at −0.2 V. The cell was flushed for 30 min with nitrogen to remove the remaining CO in the electrolyte. The CO-stripping voltammetry was also performed at a scan rate of 20 mV s$^{-1}$. To observe methanol electro-oxidation, 0.5 M methanol solution in 0.5 M H$_2$SO$_4$ solution was used as the electrolyte.

### 2.4. Operation of direct methanol fuel cell

Tests were conducted on a small-scale laboratory DMFC with an external electrode area of 0.5 cm × 0.5 cm. The anode catalysts were PtRu/C (Pt:Ru:C = 40:20:40, E-Tek) and Au/TiO$_2$ with PtRu:Au/TiO$_2$ = 10:0 and 7:3. For the cathode, Pt/C (Pt:C = 60:40, E-Tek) was used. The required amount of each catalyst was 4.0 mg cm$^{-2}$ on carbon paper. The membrane-electrode assembly (MEA) was fabricated by a hot pressing method for 6 min at 125 °C, 2.5 t (2000 psi). The anode fuel
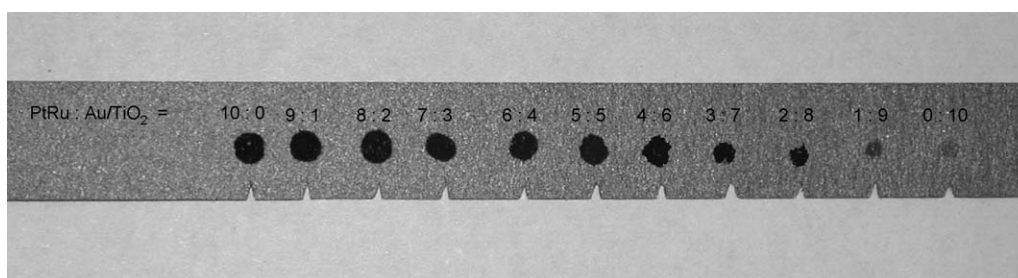


Fig. 1. Array of PtRu and Au/TiO$_2$ for high-throughput-screening test.
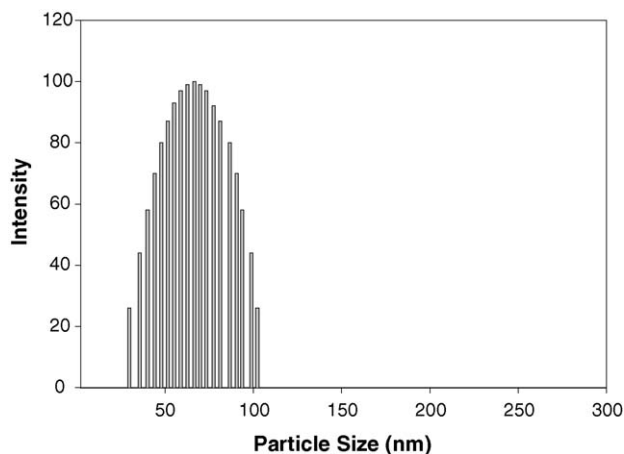
Fig. 2. Particle-size distribution of Au/TiO$_2$ nanoparticles.

was 2 M methanol solution and oxygen was fed at atmospheric pressure. Current–voltage curves were obtained from 40 to 80 °C.

## 3. Results and discussion

### 3.1. High-throughput-screening test of PtRu/C-Au/TiO$_2$ catalysts

The Au/TiO$_2$ nanoparticles were prepared in the range of 60–70 nm, as shown in Fig. 2. The Au/TiO$_2$ colloids were well-mixed with PtRu/C in various ratios. The mixture was deposited and reduced on carbon paper to prepare the electrode array. The fluorescence images of the PtRu/C-Au/TiO$_2$ array for electro-oxidation of methanol at various potentials are shown in Fig. 3. The fluorescence of the PtRu/C-Au/TiO$_2$

spot is distinguishable above 0.3 V. While the first spot (only PtRu) does not emit any light, PtRu:Au/TiO$_2$ = 9:1, 8:2 and 7:3 mixtures are active for the electro-oxidation of methanol. At 0.4 V, the spots of PtRu:Au/TiO$_2$ = 9:1, 8:2 and 7:3 are brighter than the others. Thus, addition of Au/TiO$_2$ assists methanol electro-oxidation on platinum. It is well known [5,10–13] that the CO or CO-like substances produced on the Pt surface act as self-poisons during the electrochemical oxidation of methanol. Au/TiO$_2$ may be effective for the decomposition of these deactivating species at room temperature and thereby improve the activity for the electro-oxidation of methanol. The Au/TiO$_2$-only-catalyst (the last spot) does emit any fluorescence, which indicates that acidic protons are not formed in the Au/TiO$_2$-only-system. Since the methanol is generally decomposed to acetic acid and/or formic acid at low temperature [8], no detection of acidic protons means that Au/TiO$_2$ does not have any activity for the oxidation of methanol under the present experimental conditions. This proves that Au/TiO$_2$ might selectively remove the CO or CO-like poisoning species that are produced during the electro-oxidation of methanol over the PtRu catalyst.

The effect of CO on the electro-oxidation of methanol over PtRu/C-Au/TiO$_2$ was observed by using a CO-saturated methanol electrolyte. CO gas was purged into 6 M methanol electrolyte for 2 h. The initial oxidation potential is 0.4 V, i.e., about 0.1 V different from that for the catalyst arrays without CO (Fig. 3). This might be due to the inhibition of methanol electro-oxidation by CO in methanol. The fluorescence is detected from 0.5 V at PtRu:Au/TiO$_2$ = 9:1, 8:2 and 7:3 as shown in Fig. 4. The active regions are same as those for pure methanol in Fig. 3. The initial oxidation potential of PtRu/C-Au/TiO$_2$ is also lower than that of the PtRu/C catalyst. This means that the catalytic activity for methanol electro-oxidation and CO tolerance of PtRu/C is improved by the addition of Au/TiO$_2$.
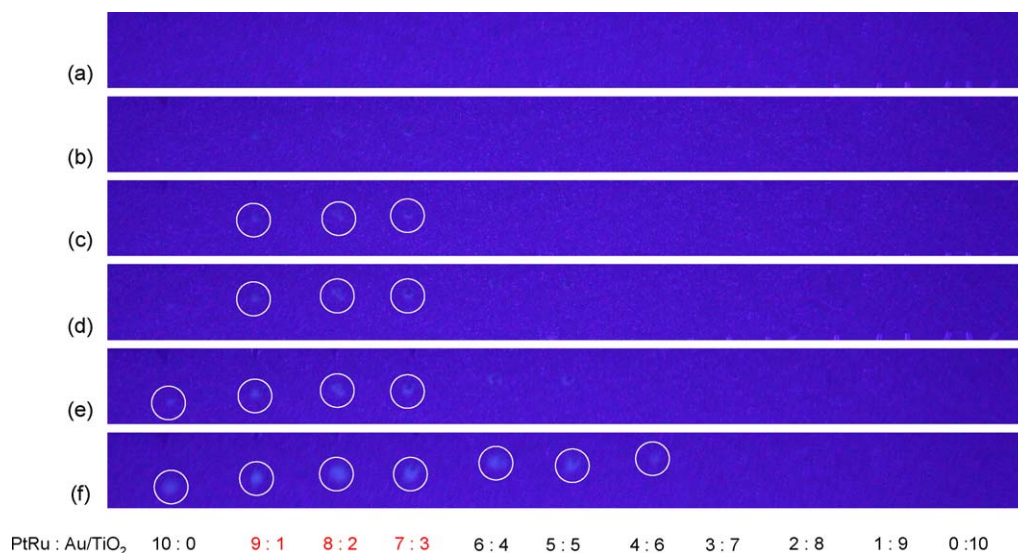


Fig. 3. Fluorescence images of PtRu/C-Au/TiO$_2$ electrocatalyst array for potential scan in 6 M methanol solution. (a) 0 V; (b) 0.2 V; (c) 0.3 V; (d) 0.4 V; (e) 0.5 V; (f) 0.7 V.
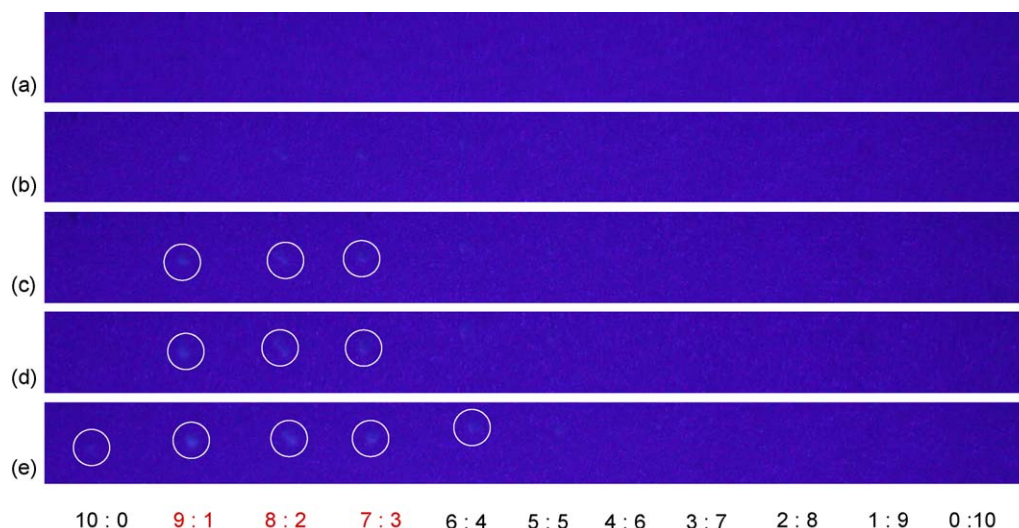
Fig. 4. Fluorescence images of PtRu/C-Au/TiO₂ electrocatalyst array for potential scan in CO-saturated methanol solution. (a) 0 V; (b) 0.3 V; (c) 0.4 V; (d) 0.5 V; (e) 0.7 V.

## 3.2. Cyclic voltammetry of PtRu/C-Au/TiO₂ catalysts

Results from the high-throughput-screening test, show that the catalysts with the compositions of PtRu:Au/TiO₂ = 9:1, 8:2 and 7:3 are most active for the electro-oxidation of methanol. Cyclic voltammetry was performed for these catalysts as well as PtRu/C; the voltammograms obtained in 0.2 M H₂SO₄ are given in Fig. 5. Between 0 and 0.4 V, hydrogen atoms are adsorbed on the cathodic sweep and desorbed on the anodic sweep. The electrochemically-active surface area of the catalysts is calculated from the charge associated with the cathodic deposition of hydrogen atoms as described in [14]. The active surface area of the catalysts was calculated form the measured charges assuming 210 $\mu$C Pt$^{-1}$ cm$^{-2}$ [15], i.e.,

Electrochemically active surface area

$$= \frac{\text{Measured } H \text{ charge } (\mu C\,cm^{-2})}{\text{Pt loading} \times 210\,\mu C\,cm^{-2}\,Pt^{-1}} \qquad (1)$$
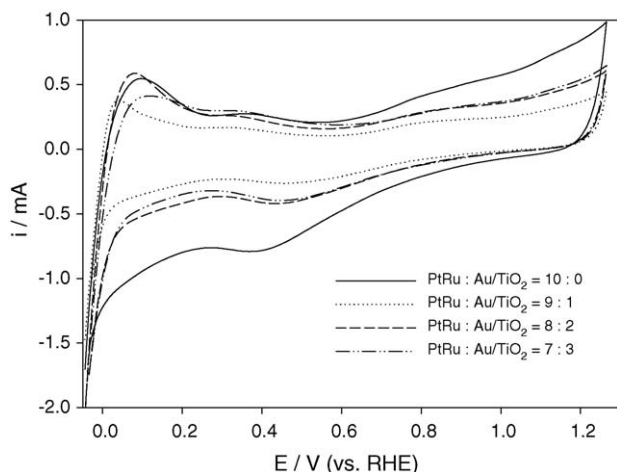


Fig. 5. Cyclic voltammograms for PtRu/C-Au/TiO₂ electrode in 0.25 M H₂SO₄ at scan rate of 20 mV s$^{-1}$.

The active surface areas of the PtRu/C and PtRu/C-Au/TiO₂ electrodes are listed in Table 1. The electrochemically-active surface area of Pt is enhanced with increasing content of Au/TiO₂. Since Au/TiO₂ has no, or very low, activity compared with pure platinum, the enhanced surface area of Pt might be attributed to interaction between PtRu/C and Au/TiO₂. Shim et al. [16] have reported an increase in the electrochemically-active surface area after the addition of WO₃ and TiO₂ to a Pt/C electrode [16]. This behaviour was considered to be due to the formation of new sites at the interface between the platinum and the oxide materials. With a PtRu/C-Au/TiO₂ electrode, PtRu could interact with Au/TiO₂ during the thermal reduction at 350 °C. This interaction could enhance the electrochemically-active surface area of the electrocatalyst, which should be beneficial to the electro-oxidation of methanol over the PtRu/C-Au/TiO₂ catalyst. Thus, enhanced active area would compensate for the decreased amount of PtRu/C in the PtRu/C-Au/TiO₂ electrode.

The CO stripping voltammograms of PtRu/C-Au/TiO₂ catalysts are presented in Fig. 6. It is well known that CO is stripped from the Pt surface at about 0.7 V [20]. The onset of CO oxidation for PtRu/C catalyst started at 0.40 V. This indicates that PtRu/C has a higher activity for the oxidation of CO than pure platinum a finding that is consistent with many other studies [17–20]. According to the bifunctional mechanism of electrooxidation [17], the synergistic effect of PtRu arises from the fact that Ru activates water molecules to form the active oxidant, i.e., a surface hydroxyl intermediate (Ru-OH). Abundant –OH

Table 1
Electrochemically-active surface area of PtRu/C-Au/TiO₂ electrode

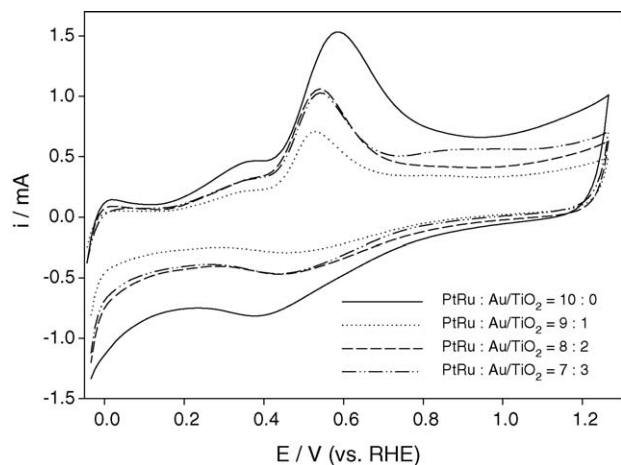| PtRu:Au/TiO₂ | Active surface area (m² g$^{-1}$ Pt) |
| --- | --- |
| 10:0 | 73.959 |
| 9:1 | 65.633 |
| 8:2 | 110.145 |
| 7:3 | 127.277 |

Fig. 6. CO-stripping voltammograms for PtRu/C-Au/TiO$_2$ electrode in 0.25 M H$_2$SO$_4$ at scan rate of 20 mV s$^{-1}$.
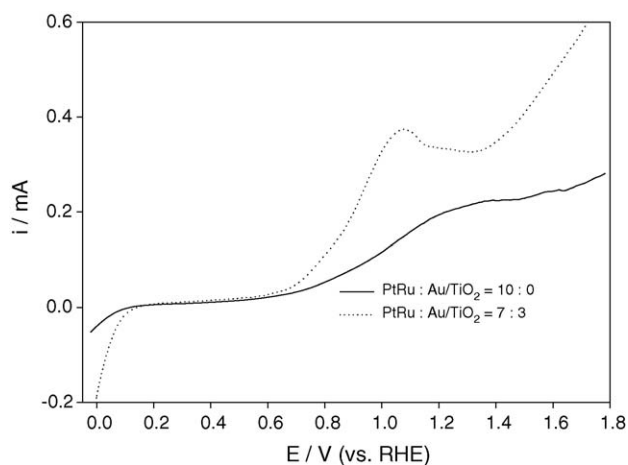


Fig. 7. Cyclic voltammograms for PtRu/C-Au/TiO$_2$ electrode in 0.5 M methanol + 0.5 M H$_2$SO$_4$ solution during positive-going sweep. (Scan rate: 20 mV s$^{-1}$.)

species subsequently oxidize the CO bound to a neighbouring Pt site [18]. The bifunctional mechanism is commonly written as:

$$Ru + H_2O \rightarrow Ru\text{-}OH + H^+ + e^- \tag{2}$$

$$Pt\text{-}CO + Ru\text{-}OH \rightarrow CO_2 + H^+ + e^- + Pt + Ru \tag{3}$$
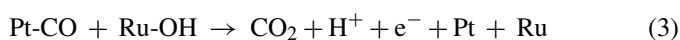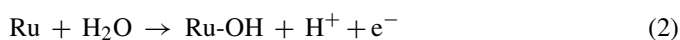
This oxidation of CO takes place at about 0.4 V, i.e., about 0.2–0.3 V more negative compared with Pt.

The addition of Au/TiO$_2$ to a PtRu/C electrode lowers the potential for CO oxidation by 20 mV, see Fig. 6 and Table 2. The potential of the CO-stripping peak also shifts to more negative values. This means that the addition of Au/TiO$_2$ to a PtRu/C catalyst can improve the activity for CO oxidation. In addition, an Au/TiO$_2$ electrode without PtRu/C does not show any CO-oxidation peaks in during CO-stripping experiments. Therefore, if it is possible that the adsorbed CO on platinum could be moved to Au/TiO$_2$, it could be more easily oxidized to CO$_2$ by following reactions [7].

$$CO\text{-}(Au/TiO_2) + 1/2O_2 \rightarrow Au/TiO_2 + CO_2 \tag{4}$$

$$CO\text{-}(Au/TiO_2) + H_2O \rightarrow Au/TiO_2 + CO_2 + H_2 \tag{5}$$
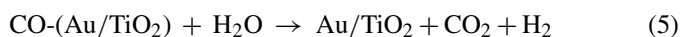
The adsorption energy of CO on Au/TiO$_2$ is 52 kJ mol$^{-1}$, as reported by Meier and Goodman [21]; while the activation energy for the reaction between adsorbed CO and Au/TiO$_2$ is nearly zero [7]. In the case of Ru-OH, the adsorption energy of CO is about 60 kJ mol$^{-1}$, as calculated by Desai and Neurock [22]. Therefore, if the CO is movable from the platinum site to the

surface of Au/TiO$_2$ and/or Ru, the oxidation of CO over Au/TiO$_2$ could energetically occur preferentially or simultaneously with that over Ru-OH. Since the PtRu/C-Au/TiO$_2$ catalysts were thermally reduced at 350 °C, the interaction between PtRu/C and Au/TiO$_2$ could make it possible to move the CO adsorbed on the Pt to the surface of Au/TiO$_2$. The oxidation of CO over Au/TiO$_2$ could reduce the coverage of CO on the PtRu surface and promote the electro-oxidation of CO. This might shift the onset and peak voltages for CO oxidation, as shown in Fig. 6.

Cyclic voltammograms for PtRu/C-Au/TiO$_2$ in 0.5 M methanol + 0.5 M H$_2$SO$_4$ solution during the positive-going sweep are shown in Fig. 7. In the case of PtRu/C, the onset of methanol oxidation begins at about 0.6 V after almost complete desorption of adsorbed hydrogen. The oxidation current increases considerably with increasing potential until a current peak is seen at about 1.3 V. By contrast, the addition of Au/TiO$_2$ results in a negative shift in both the onset methanol oxidation and peak potential. Furthermore, it is clear that PtRu/C-Au/TiO$_2$ presents a higher positive peak current density, and consequently a higher activity for methanol electro-oxidation [3]. These results indicate the Au/TiO$_2$ promotes methanol electro-oxidation. It is well known that a Pt catalyst is deactivated by adsorbed CO and by CO-like species that are formed from methanol decomposition [10]. On the other hand, Au/TiO$_2$ is not active for methanol decomposition but for the oxidation of CO and CO-like poisoning species. Thus, cyclic voltammetric data indicate that, Au/TiO$_2$ enhances the removal of CO and CO-like poisoning species from the Pt surface.

Based on the above results, the ratio of PtRu:Au/TiO$_2$ was fixed at 7:3, which shows the lowest CO and methanol oxidation voltages. Polarization curves were obtained for the single-cell DMFC that used PtRu/C or PtRu/C-Au/TiO$_2$ electrodes (Fig. 8). The performance is increased by the addition of the Au/TiO$_2$ at all operating temperatures. At 80 °C, the open-circuit voltage (OCV) increases from 0.738 V (PtRu/C) to 0.8050 V (PtRu/C-Au/TiO$_2$) and the power density is greatly improved, i.e.,

Table 2
Onset potential and peak potential for electro-oxidation of CO

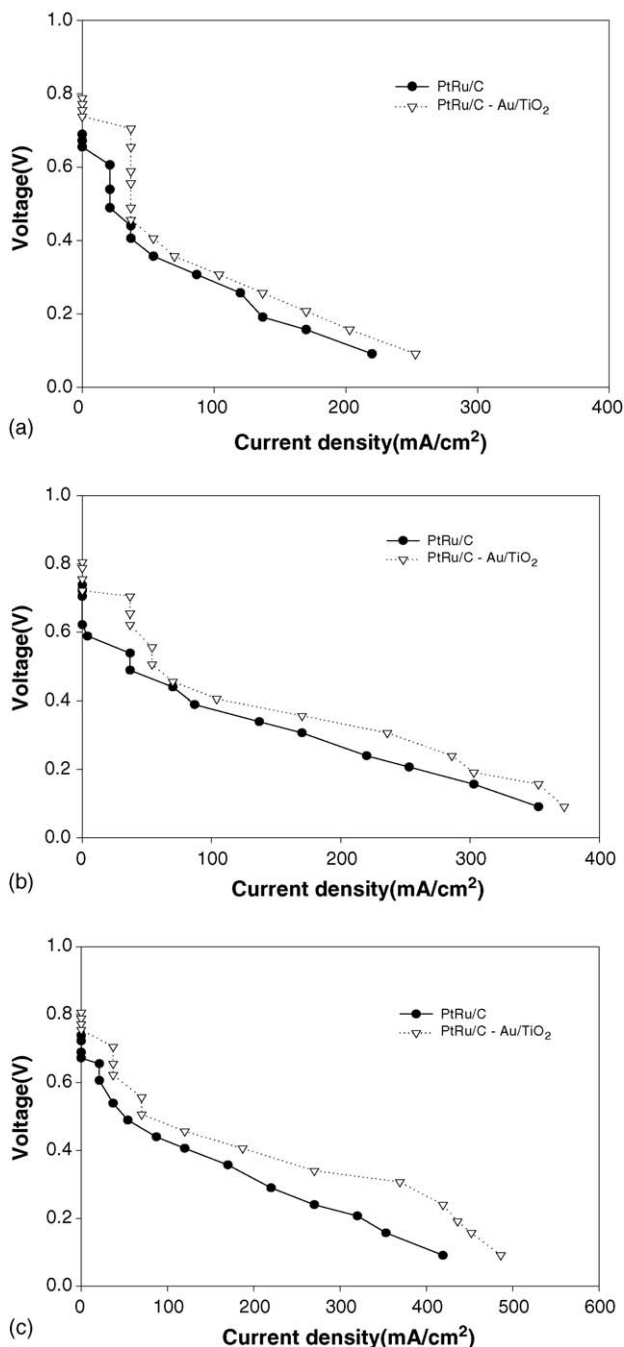| PtRu:Au/TiO$_2$ | Onset potential (V) | Peak potential (V) |
|---|---|---|
| 10:0 | 0.147 | 0.345 |
| 9:1 | 0.142 | 0.274 |
| 8:2 | 0.122 | 0.284 |
| 7:3 | 0.122 | 0.284 |

Fig. 8. DMFC performance of PtRu/C and PtRu/C-Au/TiO₂ electrodes PtRu:Au/TiO₂ = 7:3. Operation temperature: (a) 40 °C; (b) 60 °C; (c) 80 °C.

from 66.24 mW cm$^{-2}$ (PtRu/C) to 113.283 mW cm$^{-2}$ (PtRu/C-Au/TiO₂).

For the electro-oxidation of methanol, various adsorbates such as (CH$_x$OH)$_{ad}$ [10], (–COH)$_{ad}$ [10], formyl (–HCO)$_{ad}$ [11], carboxy (–COOH)$_{ad}$ [11], or (HCOO$^-$)$_{ad}$ [5] have been claimed to be the reactive intermediates. Further detailed investigations may be required to reach a precise conclusion, but it is evident that these CO or CO-like species act as self-poisons of the Pt catalyst. Haruta et al. [23] reported that Au/TiO₂ could oxidize the methanol decomposed intermediates. As shown in CO-stripping

voltammograms, Au/TiO₂ can oxidize the CO adsorbed on Pt. Under the present experimental conditions, however, methanol is not decomposed on Au/TiO₂. Rather, Au/TiO₂ preferentially oxidizes CO or CO-like poisoning species that are produced during operation of the DMFC. This may lead to an increased catalytic activity of PtRu/C with concomitant improved performance of the DMFC.

## 4. Conclusions

Au/TiO₂ has been added to a PtRu/C electrode to improve the performance of a direct methanol fuel cell. High-throughput-screening tests show that catalysts composed of PtRu:Au/TiO₂ = 9:1, 8:2 and 7:3 are the most active for the electro-oxidation of methanol. The PtRu/C-Au/TiO₂ electrode presents better activity for CO and methanol oxidation than PtRu/C. The CO adsorbed on Pt may be easily oxidized on the surface of Au/TiO₂ by interaction between PtRu/C and Au/TiO₂. Performance of the DMFC is also improved by the addition of Au/TiO₂ to the PtRu/C electrode.

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