Development of Au Promoted Pd/C Electrocatalysts for Methanol, Ethanol and Isopropanol Oxidation in Alkaline Medium

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This research is aimed to investigate the Pt-free catalysts for alcohol electrooxidation in alkaline media. The results show that Pd is a good electrocatalyst for ethanol and isopropanol oxidation. The E-TEK Pt/C shows a much higher activity for methanol electrooxidation than Pd/C and PdAu/C electrocatalysts. The methanol shows a very bad activity of electrooxidation on the Pd/C and PdAu/C electrodes. Ethanol and isopropanol have higher oxidation activity on Pd/C than methanol in alkaline media. Gold can increase the palladium catalytic activity for methanol, ethanol and isopropanol oxidation. PdAu/C has higher catalytic activity and better steady-state electrolysis for ethanol and isopropanol oxidation than Pd/C and E-TEK Pt/C, however Au can’t enhance the stability and poisoning tolerance of Pd electrocatalysts for methanol oxidation.

Keywords: Ethanol; Isopropanol; Fuel cells; Palladium; Gold

1. INTRODUCTION

Much effort has been devoted to the development of direct alcohol fuel cells (DAFCs) [1,2]. Among the different possible alcohols, methanol is the most promising fuel because its use as a fuel has several advantages in aqueous electrolytes, liquid fuel available at low cost, easily handled, transported and stored, high theoretical density of energy comparable to that of gasoline [3-6]. However, the development of DAFCs based on methanol fuel is facing serious difficulties: [7,8] (i) slow electro-kinetic of methanol oxidation, (ii) high methanol crossover and (iii) high toxicity. Therefore, other alcohols were considered as alternative fuels. Among various liquid fuels, ethanol is
particularly attractive due to its much less toxicity as compared to methanol and abundant availability in great quantities via the fermentation of bio-mass crops such as cereals, sugar beet and maize [9,10]. On the other hand, isopropanol is the smallest secondary alcohol and its electrochemical oxidation is of great interest due to its particular molecular structure [11]. The direct alcohol fuel cells using isopropanol as fuel show much higher performance than direct methanol fuel cells and a much lower crossover current [12,13]. Pt and Pt-based nanoparticles have been extensively investigated as the electrocatalysts for the electrooxidation of liquid fuels such as methanol, ethanol and isopropanol [14-19]. However, the high price and limited supply of Pt constitute a major barrier to the development of DAFCs. Our previous work on the development of Pt-free electrocatalysts for alcohol oxidation has focused on Pd –based electrocatalysts and the results revealed that Pd is a good electrocatalyst for ethanol oxidation in alkaline media [20-23]. The other groups have reported the same results [24-28].

However, there is little information on the electrocatalytic properties of isopropanol oxidation on Pd catalysts [29-32]. Pd-based electrocatalysts are attractive as Pd is at least fifty times more abundant than Pt. However, the price of Pd also is expensive, so Pd loading must be decreased. One effective approach to cost reduction is to reduce the usage of the Pd catalysts with other metal to modify the Pd such as Ru. The methanol electrooxidation on Pd-Ru/C catalyst is explained as a bi-functional mechanism [33]. Pd acts as main catalyst for catalysing the dehydrogenation of alcohol during the oxidation reaction and oxygen-containing species (OH$_{ad}$) can form on the Ru surface at lower potentials. Here, Pd/C promoted by gold will be investigated as electrocatalyst for methanol, ethanol and isopropanol oxidation in alkaline media. The other metal modified Pd for alcohol electrooxidation have been reported [34-44].

2. EXPERIMENTAL

All chemical reagents in this work were of analytical grade purity. All the solutions were freshly prepared with deionized water. Noble metal supported on carbon black (Vulcan XC-72R, Cabot Corp., USA) was synthesized at room temperature by chemical reduction using NaBH$_4$. Excess 0.01 M NaBH$_4$ solution was mixed with the 0.005 M PdCl$_2$ solution with HCl solution and 0.005 M HAuCl$_4$ containing carbon black and 0.01 M citrate acid under stirring. The resulted material was washed with deionized water and dried at 60°C in vacuum. The working electrodes were fabricated by casting Nafion-impregnated catalyst ink onto a 0.50 cm$^2$ carbon rod electrode. The Nafion, noble metal loading on electrode was 0.10 mg cm$^{-2}$. The noble metal percentage loading was controlled as 20 wt% in the electrocatalysts. The experiments were carried out at 30°C controlled by water-bath thermostat. All electrochemical measurements were carried out in a three-electrode cell using Solarton 1255B frequency response analyzer (UK, Solarton). A platinum foil (3.0 cm$^2$) and saturated calomel electrode (SCE, 0.241 V versus SHE) were used as counter and reference electrodes. One salt bridge was existed between the solution and the reference. X-ray diffraction (XRD) was carried out on a diffractometer (EDS, Oxford) and transmission electron microscopy (TEM) was performed with a morphology of the noble metal particles was examined by HRTEM (JEM-2010FEF).
3. RESULTS AND DISCUSSION

The electrocatalysts of PdAu41(4:1 by weight)/C, PdAu21(2:1 by weight)/C, PdAu11(1:1 by weight)/C all exhibit an XRD pattern of a typical face-centered-cubic (fcc) lattice structure as shown in Fig. 1.

![Figure 1. XRD pattern of catalysts.](image)

All of the diffraction peaks of palladium and gold can be observed indicating the coexistence of Pd and Au in the electrocatalysts. The strong diffraction peaks at the Bragg angles of 40.0°, 46.4° and 67.6° correspond to the (111), (200) and (220) facets of palladium crystal, and the diffraction peaks at the Bragg angles of 38.1°, 44.3°, 64.6° and 78.0° correspond to the (111), (200), (220) and (311) facets of gold crystal.
Fig. 2 shows the typical TEM images of Pd/C, Au/C, PdAu21/C, PdAu41/C electrocatalysts. The PdAu particles of PdAu41 are well dispersed on carbon supports and average particle sizes is about 5 nm. The distribution of PdAu nanoparticles of PdAu41 appears to be uniform. Both XRD and TEM results indicate that the PdAu41/C electrocatalysts were successfully prepared by the chemical reduction method used in this study.

Fig. 3 shows the typical cyclic voltammograms (CVs) for the electrooxidation reactions of methanol, ethanol and isopropanol on Pd/C electrode (Pd loading: 0.10 mg cm$^{-2}$) in 1.0 M KOH solution. The CV was carried out at a scan rate of 50 mV s$^{-1}$ in the potential range from -0.9 to 0.2 V. An alcohol oxidation peak can be clearly observed. The electrooxidation of alcohols on Pd/C electrode
was characterized by two well-defined current peaks on the forward and reverse scans. The magnitude of the peak current on the forward scan indicates the electrocatalytic activity of the Pd/C for the oxidation reaction of the alcohols. The values onset potential ($E_s$) for alcohol electrooxidation are -0.55 V for methanol, -0.66 V for ethanol and isopropanol. The lower value of $E_s$ shows more easily electrochemically oxidized for alcohol. Methanol has a very high value of $E_s$, so it’s difficult to be electrochemically oxidized on Pd. The currents for ethanol and isopropanol oxidation begin to rise much more sharply at more negative potential, which will directly improve the fuel cells efficiency. The peak current densities ($j_p$) are 30 mA cm\(^{-2}\) (-0.22 V) for methanol, 83 mA cm\(^{-2}\) (-0.21 V) for ethanol, 22 mA cm\(^{-2}\) (-0.32 V) for isopropanol. The current density at -0.4 V ($j_{-0.4V}$) are 4.5 mA cm\(^{-2}\) for methanol, 29.7 mA cm\(^{-2}\) for ethanol, 15.8 mA cm\(^{-2}\) for isopropanol. The results show that ethanol and isopropanol has higher activity on Pd/C than that of methanol. This indicates that Pd is not a good electrocatalyst for methanol oxidation in alkaline media, which is same as the previous literatures [45-47].

![Figure 4](image)

**Figure 4.** CVs of methanol, ethanol and isopropanol oxidation reaction on Au/C electrode in 1.0 M KOH solution containing 1.0 M alcohol at a sweep rate of 50 mV s\(^{-1}\) with a Au loading of 0.10 mg cm\(^{-2}\), 298 K.

Fig. 4 shows the typical CVs for the electrooxidation reactions of methanol, ethanol and isopropanol on Au/C electrode (Au loading: 0.10 mg cm\(^{-2}\)) in 1.0 M KOH solution. An alcohol oxidation peak can be clearly observed for ethanol and isopropanol, however no oxidation peak can be observed for methanol indicating that Au has no activity for methanol electrooxidation with the potential lower than 0.2 V. Some researchers have reported the activity of methanol electrooxidation on Au in alkaline medium [48, 49]. However the onset potential is high, no oxidation peak can be observed for methanol with the potential lower than 0.2 V.
The values of $E_s$ for alcohol electrooxidation on Au/C are -0.34 V for ethanol, -0.20 V for isopropanol. The ethanol and isopropanol on Au/C have much higher values of $E_s$ than that on Pd/C, showing that they are more difficult to be electrochemically oxidized than that on Pd/C.

![Figure 5. CVs of methanol oxidation on Pd/C (Pd loading: 0.10 mg cm$^{-2}$), PdAu41/C (Pd loading: 0.075 mg cm$^{-2}$) and E-TEK Pt/C (Pt loading: 0.10 mg cm$^{-2}$) electrodes in 1.0 M KOH solution containing 1.0 M methanol with a sweep rate of 50 mV s$^{-1}$, 298 K.](image)

Fig. 5 shows the CVs of methanol oxidation on Pd/C (Pd loading: 0.10 mg cm$^{-2}$), PdAu41/C (Pd loading: 0.075 mg cm$^{-2}$), PdAu21/C (Pd loading: 0.067 mg cm$^{-2}$), PdAu11/C (Pd loading: 0.05 mg cm$^{-2}$) and E-TEK Pt/C (Pt loading: 0.10 mg cm$^{-2}$) electrodes in 1.0 M KOH solution containing 1.0 M methanol with a sweep rate of 50 mV s$^{-1}$. The electrochemical performance of methanol oxidation on these three different electrocatalysts was given in Table 1. The E-TEK Pt/C shows a much higher activity for methanol electrooxidation than Pd/C and PdAu/C electrocatalysts.

**Table 1.** Comparison of performances of methanol oxidation on Pd/C (Pd loading: 0.10 mg cm$^{-2}$), PdAu41/C (Pd loading: 0.075 mg cm$^{-2}$), PdAu21/C (Pd loading: 0.067 mg cm$^{-2}$), PdAu11/C (Pd loading: 0.05 mg cm$^{-2}$) and E-TEK Pt/C (Pt loading: 0.10 mg cm$^{-2}$) electrodes in 1.0 M KOH solution containing 1.0 M methanol with a sweep rate of 50 mV s$^{-1}$, 298 K

<table>
<thead>
<tr>
<th>Electrocatalyst</th>
<th>$E_s$/ V</th>
<th>$E_p$/ V</th>
<th>$j_p$/ mA cm$^{-2}$</th>
<th>$j$-0.4V / mA cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/C</td>
<td>-0.55</td>
<td>-0.22</td>
<td>30</td>
<td>4.5</td>
</tr>
<tr>
<td>PdAu41/C</td>
<td>-0.58</td>
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<td>41</td>
<td>5.1</td>
</tr>
<tr>
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<td>-0.22</td>
<td>37</td>
<td>4.4</td>
</tr>
<tr>
<td>PdAu11/C</td>
<td>-0.55</td>
<td>-0.22</td>
<td>32</td>
<td>3.8</td>
</tr>
<tr>
<td>E-TEK Pt/C</td>
<td>-0.71</td>
<td>-0.26</td>
<td>57</td>
<td>23.7</td>
</tr>
</tbody>
</table>
The methanol shows a very bad activity of electrooxidation on the Pd/C and PdAu/C electrodes. The current density at peak potential and at the potential of -0.4 V on PdAu/C is higher than that on Pd/C. The results show that PdAu/C has higher catalytic activity for methanol electrooxidation than Pd/C in alkaline media. The effect of the gold loading on the PdAu/C catalysts was conducted by fixing the whole loading of palladium and gold of 0.1 mg cm$^{-2}$ and recording the peak current density at peak potential during methanol electrooxidation. The activity for methanol oxidation increases by addition of gold and reducing palladium and the results is shown in Table 1. It can be seen that peak current increases with the increasing the gold loading in the catalysts. The oxidation current decreases with the further increase the gold loading.

**Figure 6.** Current-time curves for methanol oxidation on Pd/C(Pd loading: 0.10 mg cm$^{-2}$), PdAu41/C(Pd loading: 0.075 mg cm$^{-2}$) and E-TEK Pt/C(Pt loading: 0.10 mg cm$^{-2}$) electrodes in 1.0 M KOH solution containing 1.0 M ethanol at -0.4 V, 298 K.

The stability of methanol oxidation on Pd/C, PdAu41/C and E-TEK Pt/C electrodes in 1.0 M KOH solution containing 1.0 M ethanol was investigated in 1.0 M KOH containing 1.0 M methanol at a potential of -0.4 V. The results are shown in Fig. 6. The rapid current decay shows the poisoning for the electrocatalysts. Nevertheless, at the end of the test, the oxidation current is much larger on E-TEK Pt/C than that on Pd/C and PdAu41/C. This indicates that Pd is not a good electrocatalyst for methanol oxidation in alkaline media. In the same time, the oxidation current is larger on PdAu41/C than that on Pd/C after electrochemical polarization, however the oxidation current on PdAu41/C rapidly decays showing a poisoning for the electrocatalysts. Au can’t enhance the stability and poisoning tolerance of Pd electrocatalysts for methanol oxidation.

Fig. 7 shows the CVs of ethanol oxidation on Pd/C, PdAu41/C, PdAu21/C, PdAu11/C and E-TEK Pt/C electrodes in 1.0 M KOH solution containing 1.0 M ethanol with a sweep rate of 50 mV s$^{-1}$. The electrochemical performance of ethanol oxidation on these electrodes was given in Table 2. The current density at peak potential and at the potential of -0.4 V on PdAu/C is higher than that on Pd/C.
and E-TEK Pt/C. The results show that PdAu/C has higher catalytic activity for ethanol electrooxidation than Pd/C and E-TEK Pt/C in alkaline media.

The effect of the gold loading on the PdAu/C catalysts was conducted by fixing the whole loading of palladium and gold of 0.1 mg cm\(^{-2}\) and recording the peak current density at peak potential during ethanol electrooxidation. The activity for ethanol oxidation increased by addition of gold and reducing palladium and the results is shown in Table 2. It can be seen that peak current increases with the increasing the gold loading in the catalysts. The oxidation current decreases with the further increase the gold loading.

**Table 2.** Comparison of performances of ethanol oxidation on Pd/C(Pd loading: 0.10 mg cm\(^{-2}\)), PdAu41/C(Pd loading: 0.075 mg cm\(^{-2}\)), PdAu21/C(Pd loading: 0.067 mg cm\(^{-2}\)), PdAu11/C(Pd loading: 0.05 mg cm\(^{-2}\)) and E-TEK Pt/C(Pt loading: 0.10 mg cm\(^{-2}\)) electrodes in 1.0 M KOH solution containing 1.0 M ethanol with a sweep rate of 50 mV s\(^{-1}\), 298 K.

<table>
<thead>
<tr>
<th>Electrocatalyst</th>
<th>Es / V</th>
<th>Ep / V</th>
<th>jp / mA cm(^{-2})</th>
<th>j-0.4V / mA cm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/C</td>
<td>-0.66</td>
<td>-0.21</td>
<td>83</td>
<td>29.7</td>
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<tr>
<td>PdAu41/C</td>
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<td>-0.22</td>
<td>108</td>
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<tr>
<td>PdAu21/C</td>
<td>-0.68</td>
<td>-0.24</td>
<td>89</td>
<td>36.9</td>
</tr>
<tr>
<td>PdAu11/C</td>
<td>-0.67</td>
<td>-0.22</td>
<td>77</td>
<td>33.2</td>
</tr>
<tr>
<td>E-TEK Pt/C</td>
<td>-0.72</td>
<td>-0.27</td>
<td>44</td>
<td>33.4</td>
</tr>
</tbody>
</table>

**Figure 7.** CVs of ethanol oxidation on Pd/C(Pd loading: 0.10 mg cm\(^{-2}\)), PdAu41/C(Pd loading: 0.075 mg cm\(^{-2}\)) and E-TEK Pt/C(Pt loading: 0.10 mg cm\(^{-2}\)) electrodes in 1.0 M KOH solution containing 1.0 M ethanol with a sweep rate of 50 mV s\(^{-1}\), 298 K.
The stability of ethanol oxidation on Pd/C, PdAu41/C and E-TEK Pt/C electrodes in 1.0 M KOH solution containing 1.0 M ethanol was investigated in 1.0 M KOH containing 1.0 M ethanol at a potential of -0.4 V. The results are shown in Fig. 8.

**Figure 8.** Current-time curves for ethanol oxidation on Pd/C (Pd loading: 0.10 mg cm$^{-2}$), PdAu41/C (Pd loading: 0.075 mg cm$^{-2}$) and E-TEK Pt/C (Pt loading: 0.10 mg cm$^{-2}$) electrodes in 1.0 M KOH solution containing 1.0 M ethanol at -0.4 V, 298 K.

**Figure 9.** CVs of isopropanol oxidation on Pd/C (Pd loading: 0.10 mg cm$^{-2}$), PdAu41/C (Pd loading: 0.075 mg cm$^{-2}$) and E-TEK Pt/C (Pt loading: 0.10 mg cm$^{-2}$) electrodes in 1.0 M KOH solution containing 1.0 M isopropanol with a sweep rate of 50 mV s$^{-1}$, 298 K.
Nevertheless, at the end of the test, the oxidation current is larger on PdAu41/C than that on Pd/C and E-TEK Pt/C. In the same time, the oxidation current is larger on Pd/C than that on E-TEK Pt/C. This indicates that Pd is a good electrocatalyst for ethanol oxidation in alkaline media and Au enhances the stability and poisoning tolerance of Pd electrocatalyst.

Fig. 9 shows the CVs of isopropanol oxidation on Pd/C, PdAu41/C, PdAu21/C, PdAu11/C and E-TEK Pt/C electrodes in 1.0 M KOH solution containing 1.0 M isopropanol with a sweep rate of 50 mV s⁻¹. The electrochemical performance of isopropanol oxidation on these electrodes was given in Table 3.

<table>
<thead>
<tr>
<th>Electrocatalyst</th>
<th>$E_s$ / V</th>
<th>$E_p$ / V</th>
<th>$j_p$ / mA cm⁻²</th>
<th>$j_{0.4V}$ / mA cm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/C</td>
<td>-0.66</td>
<td>-0.32</td>
<td>22</td>
<td>15.8</td>
</tr>
<tr>
<td>PdAu41/C</td>
<td>-0.68</td>
<td>-0.32</td>
<td>34</td>
<td>23.6</td>
</tr>
<tr>
<td>PdAu21/C</td>
<td>-0.69</td>
<td>-0.31</td>
<td>32</td>
<td>20.1</td>
</tr>
<tr>
<td>PdAu21/C</td>
<td>-0.68</td>
<td>-0.31</td>
<td>24</td>
<td>16.3</td>
</tr>
<tr>
<td>E-TEK Pt/C</td>
<td>-0.75</td>
<td>-0.32</td>
<td>9</td>
<td>7.6</td>
</tr>
</tbody>
</table>

The peak current for isopropanol is 34 mA cm⁻² on PdAu41/C and increase 55% than that on Pd/C. The peak potential for E-TEK Pt/C is also -0.32 V as the same as PdAu/C, but the peak current is less than that on Pd/C and PdAu/C electrode. The current at the potential of -0.4 V on PdAu41/C is 23.6 mA cm⁻² and three times than that on E-TEK Pt/C. The results show that Pd/C and PdAu/C has higher catalytic activity for isopropanol electrooxidation than E-TEK Pt/C in alkaline media. The effect of the gold loading on PdAu/C catalysts was conducted by fixing the whole loading of palladium and gold of 0.3 mg cm⁻² and recording the potential and current density at peak potential during isopropanol electrooxidation. The activity for isopropanol electrooxidation increases by addition of gold and reducing palladium and the results are shown in Table 3. It can be seen that current increases with the increase gold loading in the catalysts. The oxidation current decreases with the further increase gold loading.

The stability of isopropanol oxidation on Pd/C, PdAu41/C and E-TEK Pt/C electrodes in 1.0 M KOH solution containing 1.0 M isopropanol was investigated in 1.0 M KOH containing 1.0 M isopropanol at a potential of -0.4 V. The results are shown in Fig. 10. Nevertheless, at the end of the test, the oxidation current is larger on PdAu41/C than that on Pd/C and E-TEK Pt/C. In the same time, the oxidation current is larger on Pd/C than that on E-TEK Pt/C. This indicates that Pd is a good electrocatalyst for isopropanol oxidation in alkaline media and Au enhances the stability and poisoning tolerance of Pd electrocatalysts.

Pd acts as main catalyst for catalysing the dehydrogenation of alcohol during the oxidation reaction in the PdAu/C catalysts. Gold is a good catalyst for CO oxidation [50,51]. CO-like
intermediate species on the gold surface can be oxidized to produce CO\textsubscript{2} or other products which could be dissolved in water, releasing the active sites on noble metal for further electrochemical reaction.

![Graph](image)

**Figure 10.** Current-time curves for isopropanol oxidation on Pd/C (Pd loading: 0.10 mg cm\textsuperscript{-2}), PdAu41/C (Pd loading: 0.075 mg cm\textsuperscript{-2}) and E-TEK Pt/C (Pt loading: 0.10 mg cm\textsuperscript{-2}) electrodes in 1.0 M KOH solution containing 1.0 M isopropanol at -0.4 V, 298 K.

At low gold content, there are not enough gold sites to effectively assist the releasing of adsorbed CO-like poisoning specie and the oxidation current remains almost at the level obtained from pure palladium metal. When increasing the gold content, the current density increases. The decrease in the oxidation current with the further increase in the gold content can be rationalized in terms of an inhibition of ethanol adsorption, which is probably due to the diminution of palladium sites. The mechanistic study is in progress. The in situ FTIR and other methods are being used to further study the reaction mechanism.

4. CONCLUSIONS

The preliminary results in the present study show that Pd is a good electrocatalyst for ethanol and isopropanol oxidation. Ethanol has a higher activity on Pd/C than isopropanol and methanol. The addition of Au to Pd/C significantly promotes the catalytic activity and poisoning tolerance of Pd electrocatalysts for the electrooxidation of ethanol and isopropanol fuel. The Pd-based electrocatalysts show better electrocatalytic activity and stability for ethanol and isopropanol oxidation than that of
the E-TEK Pt/C catalysts. This indicates the promises of the Pd-based electrocatalysts for the development of bio-ethanol and isopropanol fuel based direct alcohol fuel cells.

The promoting mechanism of Au in Pd electrocatalysts is not clear at this stage. One hypothesis is that Pd acts as primary active sites for the catalyzing of the dehydrogenation of ethanol or isopropanol and CO-like intermediate species can be oxidized on the Au surface to produce CO$_2$ or other products which could release the active sites.

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