Stabilization of the palladium electrocatalyst with alloyed gold for ethanol oxidation

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1. Introduction

Recently, with the emergence of alkaline membranes that conduct hydroxide ions (OH\(^-\)), alkaline direct alcohol fuel cells (DAFCs) have received increasing attention [1–5]. The most significant advantage associated with the change in the electrolyte membrane from acid to base is that the reaction kinetics of both the alcohol anodic oxidation and oxygen cathodic reduction in alkaline media become faster than in acidic media, making it possible to use Pt-free metal catalysts and to reduce the catalyst loading [6–8]. In this regard, Pd and Pd-based catalysts are emerging as an alternative to Pt-based catalysts for the alcohol oxidation reaction, especially for the ethanol oxidation reaction (EOR) in alkaline direct ethanol fuel cells (DEFCs) [6,7,9,10].

Unlike ethanol oxidation in acid media, in alkaline media the EOR activity of Pd is remarkably higher than that of Pt [11]. Xu et al. [12] compared the EOR activity on Pt and Pd in alkaline media by cyclic voltammetry with the catalysts supported on carbon Vulcan and carbon microspheres, respectively. The onset potential for ethanol oxidation on Pd shifted to lower potentials with respect to that on Pt. The current density peak on Pd was also found to be higher than on Pt. These results suggest that the activity for ethanol oxidation is higher on Pd than on Pt, regardless of the type of support used. Shen et al. [13,14] prepared a series of metal oxides (CeO\(_2\), NiO, Co\(_3\)O\(_4\), and Mn\(_3\)O\(_4\)) promoted Pd catalysts with the intermittent microwave heating method by using these metal oxides coated the carbon powder as supports. These catalysts exhibited higher activity toward the EOR in alkaline media than did Pt. In addition, the catalytic behavior of bimetallic Pd–M (M = Ru, Au, Sn and Cu) catalysts for the ethanol oxidation in alkaline media were also reported [15–17]. Relatively, the study of the stability problems of the Pd-based catalysts is scarce.

Motivated by the idea that a monometal catalyst can become more stabilized with the incorporation of gold due to its unique electron-withdrawing effect to neighboring primary metal atoms, in this work we prepare Pd–Au alloy electrocatalysts for the ethanol oxidation reaction in an alkaline medium with the dimethylformamide co-reduction method under an ultrasonic process. The atomic ratio of Pd to Au is varied from 7:1 to 3:1 and 1:1 on the basis of a crystal cell of the face-centered cubic. Electrochemical characterizations indicate that in terms of the peak current density, the prepared catalyst samples are sequenced in Pd/C > Pd\(_3\)Au/C > Pd\(_7\)Au/C > PdAu/C, but the stability tests demonstrate that the catalyst samples are sequenced in PdAu/C > Pd\(_3\)Au/C > Pd\(_7\)Au/C > Pd/C. On the compromise between the activity and stability, it turns out that the PdAu/C can exhibit an enhanced catalytic stability while maintain the comparable catalytic activity for the ethanol oxidation reaction as compared with the monometallic Pd/C catalyst.

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The objective of this work was investigated the stabilizing effect of gold on palladium in Pd–Au alloy electrocatalysts for the EOR in an alkaline medium. The idea of the incorporation of Au to Pd arises from the following point. Since Au is the most electronegative metal, and can result in the electron-withdrawing effect to the neighboring metal atoms in the Au-based nanoparticles, the incorporation of Au to Pd can increase the onset potential of the surface oxide formation during the fuel cell operation, and reduce the total quantity of metal dissolution in the Pd–Au alloy catalysts, and hence stabilize the Pd–Au catalyst. With this idea, a series of carbon supported Pd–Au nanoparticles with different Pd to Au ratios were prepared by the dimethylformamide (DMF) co-reduction method under an ultrasonic process. The results indicated that the use of the Pd3Au/C catalyst in the alkaline DEFC anode not only enhanced the catalytic stability, but also could maintain fairly good catalytic activity toward the EOR.

2. Experimental

2.1. Materials

All of the chemicals used were of analytical grade. Palladium nitrate dihydrate and hydrogen tetrachloroaurate trihydrate were purchased from Aldrich. N,N-dimethylformamide (DMF), ethanol, potassium hydroxide and perchloric acid (all from Merck KGaA) were used as received. Carbon cloth and vulcan XC-72 carbon powder (particle size 20–40 nm) were procured from E-TEK Company. 5 wt.% A3-solution was received from Tokuyama and used as received.

2.2. Preparation of the carbon supported metal nanoparticles

The carbon powder supported Pd–Au alloy nanoparticles were prepared as follows: 40 mL of 5 mM Pd(NO3)2 DMF aqueous (1:1 v/v) solution was mixed with 142 mg of carbon powder in a beaker and stirred for 40 min, during which 10 mL of HAuCl4 DMF solution (20 mM) was added drop-wise. The mixture was then sonicated for 1 h by means of an ultrasonic homogenizer (SonicVCX500, Freq 20 kHz) with an input power of 150 W. The precipitate formed was thus collected by centrifugation, washed several times with ethanol and water and dried at 70 °C in an oven. (Pd–Au loading: 30 wt.%, with palladium to gold mole ratio of 1). The carbon powder supported 30 wt.% Pd, Au and Pd–Au alloy (with palladium to gold mole ratio of 7 and 3) samples were prepared with the same procedure. The Pd to Au ratio adopted in this work was optimized on the basis of a crystal cell of the face-centered cubic with the proposed structures shown in Fig. 1.

2.3. Characterization methods

Transmission electron microscopy (TEM) images were obtained by using a high-resolution JEOL 2010F TEM system operating with a LaB6 filament at 200 kV. The samples were dispersed in ethanol under sonication and dropped on the carbon-coated grid and then imaged. The X-ray diffraction (XRD) patterns of the carbon supported Pd, Au and Pd–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. The bulk composition of the prepared nanocomposites was evaluated by inductively coupled plasma atomic emission spectroscopy (ICP–AES).

2.4. Electrochemical measurements

Electrochemical measurements were carried out by cyclic voltammetry (CV) using a potentiostat (EG&G Princeton, model 273A). A conventional, three-electrode cell consisting of glassy carbon electrode (GCE) with an area of 0.125 cm² as the working electrode, Pt foil as the counter electrode and a Hg/HgO/KOH (1.0 mol L⁻¹) (MMO, 0.098 V vs. SHE) 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

Fig. 1 – Structure of proposed Pd₃Au (a), Pd₇Au (b), and PdAu (c) crystal cell with the blue representing Pd and the yellow representing Au. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
GCE. The catalyst ink was prepared by ultrasonically dispersing 10 mg of the carbon supported catalysts in 1.9 mL of ethanol, to which 0.1 mL of 5 wt.% A3-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. Solutions were prepared from analytical grade reagents and DI water. CV experiments were done at room temperature in 1.0 M KOH solution containing 1.0 M ethanol at 50 mV s⁻¹. For all of the experiments, stable voltammogram curves were recorded after scanning for 40 cycles in the potential region from −0.926 to 0.274 V in 1.0 M KOH solution. Normalized currents are given in terms of geometric (mA cm⁻²).

2.5. Cell performance test

The in-house fabricated alkaline DEFC consisted of a membrane electrode assembly (MEA) with an active area of 1.0 cm x 1.0 cm, sandwiched between a pair of current collectors. The MEA was comprised of an anion-exchange membrane (A201, Tokuyama) and two electrodes. The cathode electrode was a single-side electrode consisting of a non-platinum HYPERMECTM catalyst (Acta) with a loading of 1.0 mg cm⁻², which was attached to a backing layer made of carbon cloth (E-TEK). To fabricate anode, the catalyst inks were prepared by mixing in-house-made carbon supported Pd and Pt–Au catalysts with 5 wt.% A3-solution in ethanol. The prepared catalyst inks were uniformly brushed on the carbon cloth with an approximate metal loading of 3.0 mg cm⁻² on the anode. The DEFC 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 carbon supported Pd–Au samples was characterized by XRD; the result is shown in Fig. 2a, along with the diffraction pattern of the Pd/C catalyst for comparison. For all the samples, the broad peak centered at about 25° corresponds to the amorphous nature of the Vulcan XC-72 carbon [18]. For the

![Figure 2](image-url)

Fig. 2 – XRD analysis of the monometallic Pd and bimetallic Pd–Au particles in (a) and regional comparison between 36 and 42° in (b).
Pd/C, PdAu/C and PdAu/C samples, all reflections expected for a face-centered cubic (fcc) lattice, corresponding to the structure of the pure bulk metals, are observed [19,20]. In contrast, the reflections of the Pd7Au/C sample presented the single peaks in the (111) and (200) crystalline phases, while the splitting peaks in (220) and (311) crystalline phases, it is obvious that a slight phase separation occurred. Similar results were observed by Schmidt and Juszczyk [19,21]. The segregation of Pd and Au in Pd–Au alloys during preparing procedures, which can be considered as the initial stage of phase separation, was also observed in UHV measurements by Auger electron spectroscopy [22,23] and low-energy ion scattering [24], consistent with theoretical predictions [25].

For the sake of comparison, the XRD patterns between the range of 36 and 42° of the carbon supported metal particles are enlarged in Fig. 2b. Careful comparisons of the (111) peak values with that of the Pd/C, Pd-(111) = 39.60°, suggest that Pd and Au are alloyed well in Pd7Au/C (111 and 200 phases), Pd3Au/C and PdAu/C samples and hence a single crystalline phase is observed. To underline this in Fig. 2b, the positions of the (111) reflections are projected onto the horizontal axis. The character peaks shifted to a lower peak value for the Pd–Au alloy samples as compared to the position displayed by the Pd/C sample. The minimum magnitude of the shift is ca. 0.1°, and the trend is observed throughout the series. Compared to that of the Pd/C \(d_{111} = 2.274 \text{ Å}\), the shift of the (111) peaks of the Pd7Au/C alloy to a lower 2θ angle by about 1.2° could be indexed to a higher \(d\) space \(d_{111} = 2.342 \text{ Å}\) crystal structure of Pd due to incorporation of the Au atoms, while the \(d_{111}\) value of Pd3Au/C is 2.314 Å, which is in the middle of the Pd/C and PdAu/C. As compared with the Pd/C, the Pd3Au/C shows a more “Pd like” structure with the \(d_{111}\) value of 2.280 Å. The refined peak value and \(d_{111}\) space parameters of all samples are presented in Table 1.

Typical TEM images of the Pd/C, Pd7Au/C, Pd3Au/C and PdAu/C samples are shown in Fig. 3(a–d), respectively. It can be observed from Fig. 3 that all the carbon supported metal nanoparticles, roughly in the spherical shape, are well dispersed with negligible agglomerations on the carbon

<table>
<thead>
<tr>
<th>Sample</th>
<th>2θ value (°)</th>
<th>(d_{111}) space (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/C</td>
<td>39.60</td>
<td>2.274</td>
</tr>
<tr>
<td>Pd7Au/C</td>
<td>39.49</td>
<td>2.280</td>
</tr>
<tr>
<td>Pd3Au/C</td>
<td>38.88</td>
<td>2.314</td>
</tr>
<tr>
<td>PdAu/C</td>
<td>38.40</td>
<td>2.342</td>
</tr>
</tbody>
</table>

Fig. 3 — TEM images of the Pd/C (a), Pd7Au/C (b), Pd3Au/C (c) and PdAu/C (d).
powder. The evaluation of the characteristic diameter of the carbon supported metal nanoparticles from an ensemble of 100 particles results in a particle size distribution of 3.6–8.4 nm with an average diameter of 5.6 nm for the carbon supported Pd particles. For the Pt7Au/C, Pd3Au/C and PdAu/C samples, the particle size distribution are 2.8–10.0 nm, 1.6–6.2 nm and 2.0–7.6 nm, the average diameter are 4.8 nm, 4.2 nm and 4.4 nm, respectively. It can be observed from Fig. 3 that the incidental aggregation accrued for the entire carbon supported metal nanoparticles. This phenomenon was also reported in Yamazaki’s work [26]. It was found that these aggregations are independent of solvents, which may result from the ultrasonic process.

XPS was employed to analyze the valence state and surface composition of the carbon supported metals. Fig. 4a shows the regional Au4f spectra of the Au/C, Pd7Au/C, Pd3Au/C and PdAu/C samples. The Au4f spectra show a doublet containing a low-energy band (Au4f7/2) and a high energy band (Au4f5/2) at 84.1 and 87.7 eV for Au/C, the positions of the peaks are consistent with the results reported elsewhere [27], indicating the existence of Au0. The binding energies (B.E.) of the 4f7/2 signal for Au component in the carbon supported bimetallic Pd–Au samples are given in Table 2. The results indicated Au0 dominant in all the bimetallic Pd–Au samples. From Fig. 4a, it can be observed that the Au 4f binding energies of the Au0 species is slightly shifted to a lower peak value for the bimetallic Pd–Au samples as compared to the positions displayed by the Au0 species of Au/C. The decrease in the Au binding energy for the bimetallic Pd–Au samples relative to the Au/C suggests electron transfer from Pd to Au, which can be related to the perturbed electronic interaction between Pd and Au atomic orbit and in turn to their alloy formation. The same situation was observed for the bimetallic Pt–Au and Pt–Ag particles reported elsewhere [27,28].

The XPS spectra of the Pd in Pd/C, Pd7Au/C, Pd3Au/C and PdAu/C samples are shown in Fig. 4b. The Pd3d spectra show a doublet containing a low-energy band (Pd3d5/2) and a high energy band (Pd3d3/2) at 335.4 and 340.7 eV for Pd/C sample, indicating the existence of Pd0 [29]. The binding energies of the 3d5/2 signals for the Pd component in the Pd7Au/C, Pd3Au/C and PdAu/C samples are given in Table 2, indicating Pd0 dominant in all the bimetallic Pd–Au samples [29]. As compared with the Pd/C, it can be observed that no clearly shift happened for the Pd3d binding energies for the bimetallic Pd–Au samples, however, the shape of the XPS spectra were changed, indicating the composition changed of the different

Fig. 4 – XPS of Au4f (a), And Pd3d (b) spectra in carbon supported Au, Pd and Pd–Au samples.
chemical states. To identify different chemical states of Pd, the spectrum can be fitted by three pairs of overlapping Lorentzian curves. Fig. 5a shows the Pd3d spectrum of Pd/C, which was deconvoluted into three components, as labeled by 1, 2 and 3 with respective binding energies of 335.4, 336.5 and 337.8 eV for the Pd 3d5/2 band. These three pairs of peaks indicated that Pd is present in three different chemical states. The most intense peaks with Pd 3d5/2 signal at 335.4 eV were due to metallic Pd. The second set of doublets, observed at binding energy of 336.5 eV, could be attributed to the chemical state on PdOads. The third pair of curves was corresponding to the PdO species [29,30]. The amount of Pd species was calculated from the relative intensities of these three peaks and the results are summarized in Table 3. Here again, the Pd3d spectra of the Pd7Au/C, Pd3Au/C and PdAu/C samples could also be deconvoluted into three components, as labeled by 1, 2 and 3 in Fig. 5(b–d). Akin to the XPS spectrum of the Pd/C sample, the components 1, 2 and 3 are ascribed to Pd0, PdOads and PdO signals, respectively; The binding energies of the Pd 3d5/2 signal and the respective relative intensities of these components in the samples are given in Table 3. From which, it can be observed that Pd0 predominates in the entire samples, indicating that DMF is an effective reagent for Pd2+ reduction under an ultrasonic process presented in this work. The incorporation of Au resulted in a relatively lower amount of Pd0 species present in the bimetallic Pd–Au samples (and the Pd0 species decreased with the increased Au concentration) than that of the Pd/C, indicating the electron transfer from Pd to Au and hence reducing Pd dissolution in electrochemical testing. Furthermore, on the basis of the intensities of the XPS peaks, the surface composition of the Pd and Au components in the bimetallic samples could be obtained. The surface atomic ratio of Pd: Au is 7:1.73, 3:0.92 and 1:0.94 for the

<table>
<thead>
<tr>
<th>Sample</th>
<th>B.E. (Pd5/2, eV)</th>
<th>B.E. (Au7/2, eV)</th>
<th>at.% (Pd/Au) from XPS</th>
<th>at.% (Pd/Au) from ICP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/C</td>
<td>335.4</td>
<td>–</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Pd7Au/C</td>
<td>335.6</td>
<td>83.9</td>
<td>80/20</td>
<td>88/12</td>
</tr>
<tr>
<td>Pd3Au/C</td>
<td>335.5</td>
<td>84.0</td>
<td>76/24</td>
<td>74/26</td>
</tr>
<tr>
<td>PdAu/C</td>
<td>335.4</td>
<td>83.9</td>
<td>51/49</td>
<td>47/53</td>
</tr>
</tbody>
</table>

Table 2 — Binding energies and relative intensities of palladium and gold species (normalized to the total metal) of the carbon supported Pd and Pd–Au samples.

Fig. 5 — Pd3d XPS spectra of the Pd/C (a), Pd7Au/C (b), Pd3Au/C (c) and PdAu/C (d) fitted by three pairs of overlapping Lorentzian curves labeled by 1, 2 and 3.
Pd$_7$Au/C, Pd$_3$Au/C and PdAu/C samples, respectively. The bulk composition of the prepared nanocomposites was evaluated by ICP, the ICP analysis shows that the respective Pd to Au ratios for the three samples is 7:0.96, 3:1.06 and 1:1.12, which is close to the Pd:Au ratios of the starting materials. The relative intensities of the Pd and Au species from XPS and ICP results are presented in Table 2.

### 3.2. Electrochemical characterizations

It has been reported that the electro-catalytic properties of the Pd-based catalyst depends on the type of the Pd crystallite phases present on the carbon supporting materials [19,29,31]. Thus, to understand the nature of the Pd crystallite phases present in the carbon supported Pd and bimetallic Pd–Au catalysts, which can be roughly characterized by the hydrogen adsorption/desorption (H$_{ads/des}$) profiles of the CV [31–34]. We conducted the CV studies for the Pd/C, Pd$_7$Au/C, Pd$_3$Au/C and PdAu/C electrodes in the potential range between $-0.2$ and $1.0$ V in 0.5 M HClO$_4$. The CV curves after 40 times cycling are presented in Fig. 6a. As can be seen in Fig. 6a, the voltammetric features of the bimetallic Pd–Au electrodes are similar to the polycrystalline Pd electrode (the black line): the adsorption and desorption of hydrogen within the potential range of $-0.20$ to $0.10$ V, the double-layer capacitance region between $0.10$ and $0.45$ V, the formation of surface oxide at potentials more positive than $0.45$ V, and the reduction of the surface oxide in the cathodic potential scan [32]. However, the clear shifts of the peak positions for the H$_{des}$ can be observed in the bimetallic Pd–Au catalysts, indicating the arrangement transformation of Pd atoms as compared with Pd/C [31,33,34]. Furthermore, in the cathodic sweep, a monolayer oxide (PdO$_x$) reduction peak potential difference of over 20 mV has been noted between the supported Pd–Au and Pd catalysts. This result indicates the potential difference in the formation of the monolayer oxide during the anodic sweep for the four distinct Pd crystallite phases present in the Pd–Au alloy and monometallic Pd catalysts [34]. From the potential range of the surface oxide formation region shown in Fig. 6b, it can be observed that the value of the potential of surface oxide formation on Pd–Au electrodes is higher than on pure Pd and increases with a decrease in Pd concentration in the alloy phase, suggesting that the electrode becomes more stable [32–35]. It should be noticed that the peak positions for the H$_{des}$ of the Pd$_7$Au/C catalyst show opposite shift as compared with the Pd$_3$Au/C and PdAu/C catalysts, which indicated different arrangement transformation of Pd atoms in the Pd$_7$Au/C catalyst. This difference may result from the surface alloy effect between the segregated Au and Pd phases, since the phase separation occurred in the Pd$_7$Au/C catalyst, which can be seen from the XRD result. From the integrated area of the hydrogen desorption peaks shown in Fig. 6a, it can be evaluated that the exposed surface areas (ESA) of Pd in the carbon supported Pd and Pd–Au catalysts is in sequence of Pd/C > Pd$_7$Au/C > Pd$_3$Au/C > PdAu/C.

The electro-catalytic properties of the carbon supported Pd and Pd–Au catalysts were evaluated by the CV measurements in 1.0 M KOH + 1.0 M CH$_3$CH$_2$OH solution at room temperature. As can be seen in Fig. 7 (the 40th circle, the forward scans), during the positive-going scan the current increases rapidly until a current peak is seen for all the catalyst coated electrodes with the same total metal loading. Even though the general features of the voltammetric curves are somewhat similar, it is evident that the electrode composition has a significant influence on the behavior toward ethanol oxidation. The large ethanol oxidation peak is about 2.3 mV for Pd/C, but $-70.4$, $-17.3$ and $-12.2$ mV for the Pd$_7$Au/C, Pd$_3$Au/C and PdAu/C samples, respectively. The bulk composition of the prepared nanocomposites was evaluated by ICP, the ICP analysis shows that the respective Pd to Au ratios for the three samples is 7:0.96, 3:1.06 and 1:1.12, which is close to the Pd:Au ratios of the starting materials. The relative intensities of the Pd and Au species from XPS and ICP results are presented in Table 2.

### Table 3 - Binding energies and relative intensities of different palladium species of the carbon supported Pd and Pd–Au samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Species</th>
<th>Binding energy (3d$_{5/2}$, eV)</th>
<th>Relative intensity (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/C</td>
<td>Pd$<em>0$/PdO$</em>{ads}$/PdO</td>
<td>335.4/336.5/337.8</td>
<td>64.89/24.79/10.32</td>
</tr>
<tr>
<td>Pd$_7$Au/C</td>
<td>Pd$<em>0$/PdO$</em>{ads}$/PdO</td>
<td>335.6/337.0/338.9</td>
<td>64.71/20.84/14.44</td>
</tr>
<tr>
<td>Pd$_3$Au/C</td>
<td>Pd$<em>0$/PdO$</em>{ads}$/PdO</td>
<td>335.4/336.5/338.0</td>
<td>64.66/25.71/9.63</td>
</tr>
<tr>
<td>PtAu/C</td>
<td>Pd$<em>0$/PdO$</em>{ads}$/PdO</td>
<td>335.3/336.7/338.1</td>
<td>51.06/38.09/10.85</td>
</tr>
</tbody>
</table>

Fig. 6 – CV curves in 0.5 M HClO$_4$ solution at the sweep rate of 50 mV s$^{-1}$. 

Fig. 7 – CV curves in 1.0 M KOH + 1.0 M CH$_3$CH$_2$OH solution at room temperature.

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**Table 3** - Binding energies and relative intensities of different palladium species of the carbon supported Pd and Pd–Au samples.
PdAu/C and PdAu/C catalysts, respectively, which shifted to a lower potential. The negative shift of the peak potential indicates that the gold in the bimetallic Pd–Au catalysts shows the improved catalytic activity for the EOR [36,37]. However, the current densities of the EOR on the bimetallic Pd–Au catalysts are lower than that on the Pd/C catalyst. The monotonic increase in the peak current density during the ethanol oxidation indicates that the number of Pd active sites is determinant on the peak current, which is consistent with the ESA value of Pd.

The stabilizing effect of gold on palladium was determined in an accelerated stability test by continuously applying CV sweeps from −0.926 to 0.274 V. We conducted the test by applying potential sweeps at the rate of 50 mV s⁻¹ in 1.0 M KOH solution at room temperature. It is worth mentioning that based on previous studies [34,35], in the above accelerated stability test, Pd dissolution is possible, but Au dissolution is unlikely as it is much more stable than Pd. For comparison, the Pd/C catalyst with the same metal loading as that in bimetallic Pd–Au samples was subjected to the same potential cycling conditions. After 3000 cycles, changes in electro-catalytic properties of the EOR were determined. Fig. 8 shows the CV curves of the 40th and 3000th cycles in the potential range between −0.926 and 0.274 V in 1.0 M KOH 1.0 M CH₃CH₂OH solution. The catalytic activity of the Pd/C catalyst, measured as the current densities of EOR obtained before and after potential cycling, showed a 48 mA cm⁻² degradation in peak current densities over the cycling period (Fig. 8a); in contrast, the corresponding change for Pd₃Au/C amounts to a loss of 23 mA cm⁻² (Fig. 8b) with enhanced stability of the Pd catalyst. The same situation was also observed for the Pd₇Au/C and the PdAu/C catalysts shown in Fig. 8(c and d). The characterization details of the peak potential (Eₚ) and peak current density (Iₚ) before and after potential cycling are summarized in Table 4. In fuel cell applications, the anode potential of the alkaline DEFCs is

Fig. 7 – CV curves in 1.0 M KOH + 1.0 M CH₃CH₂OH solution at the sweep rate of 50 mV s⁻¹.

Fig. 8 – CV curves of Pd/C (a), Pd₇Au/C (b), Pd₃Au/C (c) and PdAu/C (d) in 1.0 M KOH + 1.0 M CH₃CH₂OH solution at the sweep rate of 50 mV s⁻¹.
lower than the peak potential, so the selected current densities on $-70 \text{ mV}$ of the four catalysts were also shown in Table 4, from which, it can be observed that in terms of the current density degradation at the potential of $-70 \text{ mV}$, the catalyst samples are in sequence of $\text{Pd/C} > \text{Pd}_{3}\text{Au/C} > \text{PdAu/C} > \text{PdAu/C}$. This result confirms that the mono Pd catalyst can become more stable with alloyed Au due to the electron-withdrawing effect from Pd to Au and the intrinsic stability of Au in the alloyed Pd–Au catalysts. The same behavior was observed by Liang and Zhang’s work [38,39], who demonstrated that the Pt for the oxygen reduction reaction (ORR) and PtRu for the methanol oxidation reaction (MOR) could be stabilized against dissolution by modifying the Pt and PtRu nanoparticles with Au clusters. It should be mentioned that the incorporation of Au to the Pt or PtRu catalysts has been proved to improve the stability, but the addition of Au to the Pt or PtRu catalyst did not exhibit the increased activity for the ORR or the MOR [38,39]. However, this is not the case for the incorporation of Au to Pd. In the Pd–Au catalyst, Au can not only play a role in reducing Pd dissolution, but also can increase the activity for the EOR in alkaline media. The improved catalytic activity of Au in the Pd–Au catalysts can be evidenced from Fig. 8: after potential cycling the peak potential of the EOR with the Pd/C is 175 mV, while the value is 129, −11.0 and −33.6 mV with the Pd$_7$Au/C, Pd$_3$Au/C and PdAu/C, respectively, which shift to a lower potential; at the potential of $-70 \text{ mV}$, the catalyst samples yielded similar cell performance, with a peak power densities of $\sim 58 \text{ mW cm}^{-2}$. However, after continuous discharging for 60 times with each interval of 4 h, the Pd/C catalyst showed a peak power density of $\sim 42 \text{ mW cm}^{-2}$, which was much lower than that of the Pd$_3$Au/C catalyst with the value of 52 mW cm$^{-2}$. The characterization details of the peak power densities for the 12th and 72th discharging of the two catalysts are summarized in Table 4. It can be seen that after the initial operation for 48 h, both the Pd/C and Pd$_3$Au/C catalysts yielded similar cell performance, with a peak power densities of $\sim 58 \text{ mW cm}^{-2}$. However, after continuous discharging for 60 times with each interval of 4 h, the Pd/C catalyst showed a peak power density of $\sim 42 \text{ mW cm}^{-2}$, which was much lower than that of the Pd$_3$Au/C catalyst with the value of 52 mW cm$^{-2}$. The characterization details of the peak power densities for the 12th and 72th discharging of the two catalysts are summarized in Table 4. It can be seen from Table 4, the Pd/C catalyst showed 24% degradation in the peak power density after continuous discharging. By contrast, with the Pd$_3$Au/C catalyst, the peak power density was degraded by 8%. The result demonstrates that the Pd$_3$Au/C is a decent anode catalyst in alkaline DEFCs in terms of its activity and stability.

### Table 4 – Sample labeling and characterization details of carbon supported Pd and Pd–Au samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_p$ (mV)</th>
<th>$I_p$ (mA cm$^{-2}$)</th>
<th>$I_{-70 \text{ mV}}$ (mA cm$^{-2}$)</th>
<th>$d_p$ (mW cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/C</td>
<td>2.3/175</td>
<td>179/131</td>
<td>160/76.0</td>
<td>56.0/42.3</td>
</tr>
<tr>
<td>Pd$_7$Au/C</td>
<td>−70.4/129</td>
<td>123/100</td>
<td>123/61.0</td>
<td>−</td>
</tr>
<tr>
<td>Pd$_3$Au/C</td>
<td>−17.3/−11.0</td>
<td>167/123</td>
<td>150/112</td>
<td>57.5/52.8</td>
</tr>
<tr>
<td>PdAu/C</td>
<td>−12.2/−33.6</td>
<td>112/82.5</td>
<td>100/78.0</td>
<td>−</td>
</tr>
</tbody>
</table>

3.3. Direct ethanol fuel cell performance test

The electrochemical characterizations presented above have shown that the bimetallic Pd–Au catalysts with the Pd:Au of ratio 3 shows advantages over the others by giving the stabilizing effect while retaining the comparable catalytic activity with that of the Pd/C catalyst. In this section, we present the performance test results using Pd$_3$Au/C as the anode catalyst of an alkaline DEFC with its cathode consisting of a non-platinum HYPERMECTM catalyst (Acta) with a loading of 1.0 mg cm$^{-2}$ catalyst. The cell performance with the Pd$_3$Au/C anode is compared with the Pd/C anode. Fig. 9 shows the polarization and power density curves. It can be seen that after the initial operation for 48 h, both the Pd/C and Pd$_3$Au/C catalysts yielded similar cell performance, with a peak power densities of $\sim 58 \text{ mW cm}^{-2}$. However, after continuous discharging for 60 times with each interval of 4 h, the Pd/C catalyst showed a peak power density of $\sim 42 \text{ mW cm}^{-2}$, which was much lower than that of the Pd$_3$Au/C catalyst with the value of 52 mW cm$^{-2}$. The characterization details of the peak power densities for the 12th and 72th discharging of the two catalysts are summarized in Table 4. It can be seen from Table 4, the Pd/C catalyst showed 24% degradation in the peak power density after continuous discharging. By contrast, with the Pd$_3$Au/C catalyst, the peak power density was degraded by 8%. The result demonstrates that the Pd$_3$Au/C is a decent anode catalyst in alkaline DEFCs in terms of its activity and stability.

4. Conclusions

In this work, the carbon supported Pd–Au alloy electro-catalysts with the Pd to Au atomic ratio of 7:1, 3:1 and 1:1 were successfully prepared with the DMF co-reduction method under an ultrasonic process. The catalytic activity and stability of the Pd–Au alloy catalysts were characterized through the EOR in alkaline media and were compared with those of the Pd/C. The result indicated that the Pd$_3$Au/C catalyst can exhibit an enhanced catalytic stability while maintaining the comparable catalytic activity for the EOR as compared with the Pd/C catalyst. The cell performance tests demonstrated that the use of the Pd$_3$Au/C could yield almost
the same peak power density as that of the Pd/C during the initial cell operation, but the long term operation showed that the Pd/C degraded faster than the Pd3Au/C did. This result suggests that the Pd3Au/C is a potential anode catalyst in alkaline DEFCs applications.

Acknowledgments

The work described in this paper was fully supported by a grant from the Research Grants Council of the Hong Kong Special Administrative Region, China (Project No. 623008).

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