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# Pt and Pd decorated Au nanowires: Extremely high activity of ethanol oxidation in alkaline media

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#### A R T I C L E I N F O

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#### 1. Introduction

The direct alcohol fuel cell (DAFC) is a promising candidate as a portable power source for highly efficient, relatively clean electric power generation [1–7]. Ethanol, as a promising fuel in such fuel cells, has recently attracted considerable interest. It appears to be a very attractive fuel in the DAFCs due to its high energy density and the fact that it is a renewable energy resource, which can be produced in great quantities from biomass. Ethanol is also considered to be a "green" chemical as it is a less toxic than methanol. Direct ethanol fuel cells (DEFCs) can be divided into acid- and alkaline-type based on the electrolytes used [8]. With the intensive research in the area anion exchange membranes development the ethanol oxidation reaction (EOR) in alkaline medium has attracted much attention [9–11].

Pt-based electrodes are generally considered to be the best electrodes for alcohol oxidation as well as the Pd catalysts can be the alternatives in alkaline medium for EOR [9,12]. However, the exorbitant cost and CO poisoning of platinum limit its commercial applications. Platinum is often alloyed with an oxophilic metal to improve its performance [13,14]. To reduce the cost and increase the Pt utilization efficiency, high surface area supports such as carbon [15,16], foreign metal [17–19], and metal oxides [7,20], are studied. Highly ordered Pt- and Pd-based nanowire array

#### ABSTRACT

Highly ordered Pt and Pd decorated Au nanowire arrays, Pt/Au NWA and Pd/Au NWA, are prepared by anodized aluminum oxide (AAO) template based electrodeposition combined with chemical reduction. The effect of shell material on the ethanol oxidation currents is studied. The maximum current densities are several times higher on the modified electrodes than on the unmodified Pt (Pd) NWA. The most highly active electrode shows almost 4-fold increase in the ethanol peak current. Pt/Au and Pd/Au NWA electrodes show a similar dependence of the ethanol oxidation current density on the Pd or Pt deposition time, which most likely, reflects the optimal upper layer thickness. The synergistic effect between substrate and deposit materials seems to be the most important factor explaining such unusually high activity.

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(NWA) with high surface-to-volume ratios have been shown to be highly electrocatalyticaly active for alcohol oxidation [21–23]. This indicates that nanowire or nanotube array architecture can be a potential substrate to improve noble metal utilization efficiency. Besides it can act as a template, which means that no stabilizer is required, it also serves as an excellent current collector. The synergistic effect of Pd–Au bimetallic surfaces in Au-covered Pd nanowires for ethanol oxidation in alkaline media was recently shown [24].

In this work, we report on the fabrication process and electrocatalytic properties of Pt/Au and Pd/Au NWA electrodes, which are produced by the electrodeposition and the chemical reduction process. The inner part of the fabricated electrode, Au has a larger lattice constant on which the thin upper layer of Pd or Pt is expanded. It is believed that such structure would lead to *d*band up-shifting [25]. At the same time, the electron transfer may take place which results in improvement in their catalytic activity [25]. To the best of our knowledge, this is the first report on such extremely high activity of ethanol oxidation in an alkaline medium in Pt–Au and Pd–Au systems.

#### 2. Experimental

Au, Pd, and Pt NWAs were deposited within a homemade AAO template [26]. A Pt foil and either Ag/AgCl (+0.222 vs. NHE) (acidic solutions) or Hg/HgO (+0.098 V vs. NHE) (alkaline solutions) electrodes were used as the counter and reference electrodes, respectively. The deposition of the Au NWA was carried out from an IM-Gold series commercial gold electrolyte at -0.9 V for 10 min.

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Fig. 1. SEM images of (a) Au and (b) Pt<sub>30 min</sub>/Au NWAs NWAs electrodes.

The Pd NWA were deposited from the electrolyte containing 0.658 g of Pd(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>, 25 mL of Palladure<sup>®</sup>, and 30 mL of deionized water at -0.8 V for 5 min. Pt was electrodeposited potentiostatically (E = 0.1 V) for 20 min from an aqueous electrolyte containing 1 wt.% H<sub>2</sub>PtCl<sub>6</sub> and 0.6 mol dm<sup>-3</sup> HClO<sub>4</sub>. After transferring the obtained structure to a rigid glass and removing AAO [27], the decoration of Pt on the Au NWA electrodes was carried out by immersing the electrodes in 5 mL deionized water containing 40 µL of 50 mmol dm<sup>-3</sup> H<sub>2</sub>PtCl<sub>6</sub> and 160 µL of 100 mmol dm<sup>-3</sup> L-ascorbic acid for several minutes. The deposition of the Pd on Au NWA electrodes was also achieved by immersing Au into 5 mL of 0.25 mmol dm<sup>-3</sup> PdCl<sub>2</sub> and 25 µL of 100 mmol dm<sup>-3</sup> L-ascorbic acid [28].

The elemental compositions of the Pt/Au and Pd/Au NWAs electrodes were measured by an EDAX. The morphology information was investigated by FE-SEM (JEOL JSM-7000F). The real surface area of the Au NWA electrode was estimated in the oxygen region in  $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ . The electrochemical activity for EOR was inspected by cyclic voltammetry in [1 mol dm<sup>-3</sup> KOH + 1 mol dm<sup>-3</sup> ethanol] and  $[1 \mod dm^{-3} H2SO4 + 1 \mod dm^{-3} ethanol]$  solutions. Similar conditions were used for the investigation of methanol oxidation. The electrochemical stability of the as-prepared electrodes for ethanol electro-oxidation was studied by chronoamperometric measurements at 0 V in  $[1 \text{ mol } dm^{-3} \text{ KOH} + 1 \text{ mol } dm^{-3} \text{ ethanol}]$ solution. The electrocatalytic activity of Au, Pt/Au, and Pd/Au NWA was normalized to the real surface area of Au nanowires. Similarly, current from the Pt and Pd NWA was normalized to the calculated (see below in the text) surface area of Pt and Pd electrodes, respectively.

#### 3. Results and discussion

The SEM image of the Au NWA is presented in Fig. 1(a). The electrode consists of closely packed nanowires with a uniform diameter (ca. 55 nm) and length (ca. 600 nm). Similarly, Pd and Pt nanowires were also investigated and their length was found to be around 300 nm and 400 nm, respectively. After the upper layer material deposition, EDAX analysis was performed to confirm the modification. In the case of the Pt/Au system, the Pt loading was too low to be detected by EDAX, unless the Pt deposition time was longer than 30 min. After 30 min of modification, the amount of Pt was less than 1 at% and Pt particles could be observed on the SEM image (Fig. 1(b)).

The real surface areas of the Au electrodes were investigated by cyclic voltammetry. The measurements were performed in  $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$  at a potential scan rate of  $50 \text{ mV s}^{-1}$ . The charge obtained by the integration of the cathodic peak for the reduction of gold oxide was  $8410 \,\mu\text{C cm}^{-2}$ . Considering the charge associated with the reduction of the gold oxide monolayer to be  $400 \,\mu\text{C cm}^{-2}$  [29] for a polycrystalline Au electrode, the roughness

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Roughness factors of the electrodes.

Electrode	Au, Pt/Au, Pd/Au	Pt	Pd
Roughness factor	21	13	10

factor (ratio of the real surface area of the electrode to its geometric area) was about 21 for the Au NWA. It was difficult to measure Pt/Au and Pd/Au electrodes surface area by electrochemical methods. It can be assumed that the mantle side roughness of the Pd and Pt nanowires is the same with that of Au nanowires, as the same AAO template was used. Thus, combining data from the SEM (length of nanowires and roughness of the side wall) and data from electrochemical surface area measurements of Au nanowires we can conclude that the roughness factor of Pd and Pt NWAs are approximately 10 and 13, respectively. For Pt/Au and Pd/Au electrodes the current was normalized by the real surface area of Au NWA. The roughness factors of all electrodes used in the current work are summarized in Table 1. Below, the current densities obtained from the electrodes and divided by roughness factor are stated as nanowires area normalized current.

The qualitative results on the relative amount of Pt and Au on the surface of Pt/Au NWA can be obtained from the CV shown in Fig. 2. The CV scans were taken in the potential region of -0.2 V to 1.6 V vs. Ag/AgCl. The peaks appearing at +0.46 V and +0.99 V originate from platinum oxide and gold oxide reduction, respectively. As can be seen, the Pt surface area increased (Pt oxide reduction peak) with Pt deposition time increasing meanwhile the Au surface area decreased (Au oxide reduction peak). It is clear that amount of deposited Pt is increasing with increase in Pt deposition time.



Fig. 2. Cathodic part of CV curves taken in 0.5 mol dm $^{-3}$  H<sub>2</sub>SO<sub>4</sub> solution on Au, Pt, and Pt/Au NWA electrodes with Pt deposition time indicated.



**Fig. 3.** CVs in 1 mol dm<sup>-3</sup> KOH +1 mol dm<sup>-3</sup>  $C_2H_5$ OH for Au NWA decorated by (a) Pt and (b) Pd with Pt (Pd) deposition time indicated. The corresponding dependence of the ethanol oxidation peak currents on the (c) Pt and (d) Pd decoration time. The dashed and dotted lines show the current densities from the Au and Pt (Pd) NWA. The current densities are normalized to the real surface area of the Au nanowire array. The scan rate was 50 mV s<sup>-1</sup>.

At the same moment the amount of available Au sites is decreasing, though, even after 20 min. of Pt deposition the Au nanowires surface is not fully covered by platinum. During the chemical reduction of platinum ions on the gold by the reducing agent, randomly distributed Pt nanoparticles are formed, as was shown in Fig. 1(b). Thus, even after 30 min of Pt deposition there are still available Au sites as Pt does not form solid film but rather Pt nanoparticles randomly distribute on the surface of Au. For some samples, the Pt oxide reduction peak potential shift to more positive values is seen. This result, in principle, may indicate on the *d*-band center shifting of Pt particles [30]. Though, the detail analysis of the peaks reveals that peak of oxygenated surface species reduction on the samples with short Pt deposition time (1 min and 3 min) have the same position as that of pure Pt NWA. Only samples with longer Pt deposition time exhibit the shift. Nonetheless, as was pointed out by Tegou et al. [31], cyclic voltammetry is probably not sensitive enough to reveal the difference in the Pt-O bonds strength or shift in *d*-band center. More recent results by the same group revealed that even the interpretation of Pt-O surface species striping peaks is problematic. Indeed, the conflicting results were found by different groups as discussed by Tegou et al. in Ref. [32]. Application of X-ray photoelectron spectroscopy combined with an electrochemical cell (EC-XPS) in the investigation of CO tolerance at pure Pt and Pt alloys showed the existence of core level shifts (shifts in Fermi level and d-band center position) in Pt atoms electronic structure by the alloying [33]. The similar investigation of the Pt/Au system should be performed to find (if any) the changes in Pt atoms electronic structure by Au. The Au oxide reduction peaks remain at the same position, which supports the conclusions made by Tegou.

The cyclic voltammograms in  $[1 \mod dm^{-3} \text{ KOH} + 1 \mod dm^{-3} \text{ C}_2\text{H}_5\text{OH}]$  solution for the Pt/Au electrodes after Pt deposition over various times are shown in Fig. 3(a). The onset potential of the EOR for all of the modified electrodes was about -0.6 V, which is much

lower than that for a bulk gold electrode [34]. The oxidation current abruptly decreases at around 0.2 V, due to the formation of Pt oxide which blocks the adsorption of the active species to the electrode surface. The EOR peak current variations were accompanied by peak potential shifts depending on the Pt modification time. For short modification times, the peak current rises with increasing the time (1 min and 3 min). When the Pt deposition time exceeds 3 min, the peak current decreases and reaches values close to those for the pure Pt NWA electrode when the time is over 30 min. We can conclude that there is an optimal amount of Pt that leads to the maximum activity of the electrode. The peak current on  $Pt_{3\min}/Au$  NWA was  $266 \text{ mA cm}^{-2}$  (normalized to the electrode geometric area) or 12.7 mA cm<sup>-2</sup> (normalized to the nanowires surface area) and the peak position was 0.19 V for this sample. It is worth mentioning that the peak position on the CV curves shifts to more positive potentials for the electrodes with a higher peak current. Thus, the potential of ethanol oxidation, as well as its current, depends on the amount of shell material. As the origin of the peak decrease is the electrode passivation by oxides formation rather than ethanol mass-transfer limitation, it is most likely that ethanol oxidation diminishes the surface oxidation. The corresponding graph of the peak current versus the deposition time is shown in Fig. 3(c). The extremely high activity of the Pt/Au NWA electrodes (the maximum peak current was 3.7 times higher than on the pure Pt NWA electrode) cannot be explained by the increase in the surface area due to the deposition of Pt particles, because this mechanism cannot explain the maximum in the electrode activity. The Pt surface area was much lower on  $Pt_{3 min}/Au$  than on  $Pt_{180min}/Au$ , but the activity was much higher. SEM analysis also did not show any difference in the roughness of Au and Pt<sub>3 min</sub>/Au nanowires. The EOR peak current densities are also much higher than the summation of the EOR currents on the pure Au and pure Pt NWA electrodes, so we may conclude that there exist a synergistic effect resulting from the interaction between the Au substrate and the Pt outer layer [25,35,36]. As Pt and Au are both



**Fig. 4.** (a) CAs in 1 mol dm<sup>-3</sup> KOH +1 mol dm<sup>-3</sup> C<sub>2</sub>H<sub>5</sub>OH taken on Pt/Au NWA electrodes with Pt deposition time indicated. The applied potential was 0 V vs. Hg/HgO. (b) The effect of positive (0.75 V, 5 s) and negative (-0.65 V, 10 s) voltage pulses on the ethanol oxidation current on Pt<sub>3 min</sub>/Au NWA.

noble metals the segregation of the surface layer is unlikely. This is different to the most core-shell systems with non-noble core material, e.g. Ni, Fe, Co, where such segregation leads to the formation of Pt surface of few monolayer thickness [31]. In this case, the active material is, undoubtedly, platinum. As Pt and Au both can catalyze the electrooxidation of ethanol the exact position of active sites, that is either Pt or Au or, which is most like, Au-Pt interface, is not clear. However, synergetic phenomena seem to be crucial. This synergistic effect also affects EOR mechanism on Pt/Au NWA electrodes as the hysteresis between the anodic and cathodic scan are different as the Pt deposition time increased. The size of the hysteresis loop (e.g. below -0.25 V on Pt<sub>3 min</sub>/Au) is often related to the poisoning of the surface [37]. The hysteresis loop width increases with the Pt deposition time, and it is smaller than that on Pt NWA when Pt deposition time is shorter than 5 min. This fact may suggest that there are less strongly adsorbed species during the reaction. Though, the mechanism should be further studied by other techniques such as FT-IR or SERS.

We found that such synergistic effect was only observed for EOR in alkaline media. The electrocatalytic activity toward the EOR in acidic solution and the methanol oxidation in both alkaline and acidic solutions was measured on the Pt/Au NWA electrodes. However, the activity was found to be much lower than that for the EOR in alkaline medium, and it was simply proportional to the Pt surface area for these reactions.

The similar dependence of the electrocatalytic activity of ethanol oxidation in the 1 M KOH solution on the upper layer modification time was also observed on Pd/Au NWA electrodes as can be seen from Fig. 3(b). The corresponding curves for the peak current densities versus the shell metal deposition time are shown in Fig. 3(d). The optimum decoration time for Pd on Au was 5 min. By comparing the two kinds of electrodes, the Pt3 min/Au NWA electrode shows slightly higher electrocatalytic activity. It is worth to note, that Pd-based electrodes are reported by other researches [16,38] to be better than Pt-based for EOR in alkaline media. The onset of the C<sub>2</sub>H<sub>5</sub>OH oxidation on Pt modified electrode starts at lower potential than that on Pd/Au NWA. On the other hand, peak potential of ethanol oxidation is ca. 100 mV more negative for Pd/Au NWA. The other interesting observation is the current profile during negatively going sweeps. The peak current ratio of the backward to forward scans  $(I_b/I_f)$  is usually used as a measure of the surface poisoning by CO or CO-like surface species. Comparing the CV profiles for Pt/Au NWA and Pd/Au NWA it is most likely that the peak on the backward scan is due to the poisons oxidation rather than ethanol oxidation (similar diffusion conditions in both case would result in similar profile). The ratios  $I_{\rm b}/I_{\rm f}$  for the electrodes with optimal shell coverage, i.e.  $Pt_{3 min}/Au$  and  $Pd_{5 min}/Au$  NWAs were 0.31 and 1.05, respectively. The results for the  $\mathrm{Pd}_{5\,\mathrm{min}}/\mathrm{Au}$  NWA is similar to that obtained on Au/Pd NW and Pd@Au/C electrodes [19,24]. At the same time Pt<sub>3 min</sub>/Au shows much better result.

It is most likely that the highest electrode activity corresponds to the optimal Pt or Pd coverage. At the moment, the main reason of such behavior is not clear. It can be electron donation from Au d-orbital, or optimal Pt-Pt, Pd-Pd, or even Au-Au interatomic distances. Although the mechanism of the synergistic effect on the Pdor Pt-decorated Au NWA is not clear, much effort has been made to explain this behavior resulting from geometric effects and electron transfer mechanisms [25,35,39,40]. In both cases, the d-band center shift, which is crucial in catalysis, was considered [41]. When the lattice of metals (such as Pd and Pt) whose d-band is more than halffilled is expanded parallel to the substrate of metal with large lattice constant (e.g. Au) the overlap between the *d*-electron orbitals of the neighboring Pd or Pt atoms becomes smaller and the bandwidth decreases. To keep the *d*-band occupancy fixed, the energy of the d-states is up-shifted [30]. As a result, the reactivity of the shell atoms increases. The geometric effect is gradually weakened as Pd or Pt layers increased. Besides, the electron transition between the substrate and the shell atoms can take place and, thus, affect the d-band center position [30]. Both the geometric effects and electron transfer between the metal layers depend on the thickness of the upper layer, which can result in the dependence of the catalytic activity on the shell deposition time described above. That is, smaller Pt or Pd deposition times results in the most intense effect. The relatively low activity during very short deposition time is due to small amount of such active material (active sites). Though, at the moment, we cannot provide any experimental confirmation of such *d*-band modification in Pt/Au and Pd/Au NWAs.

The obtained result can also be explained by the effect of deposited ad-layers on the overall surface morphology. Borkowska et al. [42] have shown that methanol oxidation current on activated rough gold electrode highly exceeds the one on an un-activated electrode. The authors proposed that the formation of small crystallites that can trap OH- species is the most important factor for the unusually high activity. Though, Borkowska studied methanol oxidation whereas we report on ethanol oxidation, there can be similarities in the mechanisms. As was proposed by Tremiliosi-Filho et al. [43] adsorbed hydroxide species also plays crucial role in the ethanol oxidation on gold. It is reasonable to propose that a tiny amount of Pt or Pd ad-layer can facilitate such processes. Also, the platinum ad-layer with larger Pt-Pt distance may facilitate the OH<sup>-</sup> adsorption strength (opposite to the effect of OH<sup>-</sup> inhibition for shorter Pt-Pt distances in O<sub>2</sub> reduction Pt alloy electrocatalysts [44,45], though the effect was questioned more recently [46]) and, thus, enhance the overall ethanol oxidation activity. Nonetheless, further studies of such structures should be carried out to explain their unique behavior toward the oxidation of ethanol in alkaline media.

The electrochemical stability of the Pt/Au electrodes for ethanol electro-oxidation was studied by analyzing chronoamperometric (CA) response at 0 V in  $[1 \text{ mol dm}^{-3} \text{ KOH} + 1 \text{ mol dm}^{-3} \text{ C}_2\text{H}_5\text{OH}]$ 

solution (Fig. 4(a)). The variations of current density at initial period of CA on different Pt/Au NWA and Pt NWA electrodes were in good agreement with CV results. Pt<sub>3 min</sub>/Au NWA which had smaller hysteresis loop size on CV curve had the highest electrochemical activity and stability. After few minutes, however, a sharp decay in polarization current for the ethanol oxidation on all Pt/Au electrodes was observed. The possible explanation of such behavior can be the poisoning of electrodes by CO and CO-like species, or oxidation of Pt [9,37].

In order to determine the exact reason of such current decrease, the CA with additional steps were performed. To oxidize any CO or CO-like species further, the potential pulse of 0.75 V over 5 s was applied. Similarly, to reduce any Pt oxide, the potential pulse of -0.6 V over 10 s was applied. Each pulse was applied twice as shown Fig. 4(b). As can be seen, the current density decays sharply at the beginning of CA test. The sharp increase in current density was observed after application of pulse on negative voltage while no current recovery after applying 5 s positive voltage. This implies that Pt oxidation is the main reason for the current decay in CA, and CO poisoning problem is not significant on Pt<sub>3 min</sub>/Au.

#### 4. Conclusions

The Pt- and Pd-decorated gold NWA electrodes with an ultralow Pt or Pd loading show excellent performances for ethanol oxidation in alkaline media as a result of a synergetic effect between the substrate and deposit materials. A similar dependence of the electrocatalytic activity on the shell deposition time was found for studied systems. The maximum activity for the electrodes was achieved after 3–5 min of catalytic metal deposition on Au NWA surface. The Pt-decorated Au NWA electrodes, especially Pt<sub>3 min</sub>/Au NWA, show better stability during the oxidation of ethanol than pure Pt NWA. The nanowire arrays electrodes showed good properties as templates and current collectors allowing for the optimal utilization of noble metals as shells.

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