

Non-Pt Anode Catalysts for Alkaline Direct Alcohol Fuel Cells

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Abstract: Pd- and Au-based binary catalysts have been tested as non-Pt anode catalysts for alkaline direct alcohol fuel cells toward the electrooxidation of methanol, ethanol, and ethylene glycol. The activity of Pd for alcohol oxidation is very low in acid but relatively high in alkaline, in which an onset potential can be observed around 0.4 V (vs RHE). After incorporation of Ru, the onset potential shifts negatively ca. 0.15 V. It is notable that Pd-Ru is extremely active for ethanol oxidation, and the current density is four times that on Pt-Ru within 0.3–0.4 V. Whereas Au is inert in acid for the electrooxidation of alcohol, but it is somewhat active in alkaline. An anodic current of alcohol oxidation can be observed in alkaline at potentials positive than 0.6 V (vs RHE). Au-Ru exhibits higher activity than Au at relatively positive potentials, but it does not cause a negative shift in the onset potential, which may imply that the dissociative adsorption of alcohol molecules on the Au surface is the rate-determining step at relatively negative potentials.

Key Words: palladium; gold; ruthenium; alcohol; electrooxidation; alkaline

Taking advantages of liquid fuels, direct alcohol fuel cells (DAFC) do not need to deal with the problem of hydrogen storage, and thus have been regarded as a very promising fuel cell technique in the future. However, the current DAFC technique uses strong acidic ion-exchange membranes as the electrolyte and relies on Pt-based catalysts severely, which disables it from widespread applications. One possible solution for DAFC is to make use of alkaline polymer electrolytes. In alkaline media, the activity of catalysts is usually considerably higher than that in acid; some metals (e.g., Pd and Au) that have little catalytic activity in acid can even exhibit notable activity in alkaline.

In recent years, considerable progress has been achieved in developing alkaline polymer electrolytes [1–3]; hence, the research on non-Pt alkaline polymer electrolyte fuel cells becomes a realistic topic. For alkaline DAFC, non-Pt cathode catalysts are already available. For example, both Ag and MnO₂ are good catalysts for the oxygen reduction reaction with high tolerance to alcohol fuels [4]. However, there are few reports on non-Pt anode catalysts for alcohol oxidation.

In comparison with Pt, Pd and Au are relatively abundant and less expensive. For most fuel cell reactions, however, the

catalytic activities of Pd and Au are considerably lower than that of Pt, especially in acid. Although there are some preliminary reports on attempting to use Pd as an alcohol oxidation catalyst in alkaline [5–7], this kind of study, with respect to the tremendous reports on Pt-based catalysts, is still at the beginning phase. Moreover, the research of Au toward alcohol electrooxidation is further premature. In this study, we focus on the topic of non-Pt anode catalysts for alkaline DAFC. Pd- and Au-based binary catalysts have been tested for the electrooxidation of methanol, ethanol, and ethylene glycol.

1 Experimental

1.1 Catalyst preparation and XRD characterization

Au/C, Au-Ru/C, Pd/C, and Pd-Ru/C catalysts with a metal loading of 20% were prepared using the impregnation method that involved an impregnation step and a reduction under H₂ atmosphere. Taking the preparation of Pd-Ru/C for example, PdCl₂ and RuCl₃ with certain Pd/Ru atomic ratio were dissolved in distilled water with a small addition of hydrochloric acid (0.1 mol/L). Vulcan XC-72 carbon powder (Carbot) was

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preheated at 110°C in air and poured into the precursor solution. After alternate blending by sonication and heating stirring, a smooth thick slurry was obtained as the resultant. The slurry was left in an oven at 60°C overnight. After grinding with an agate mortar, the agglomerates were heated in a tube furnace under H₂ flow for 2 h (for Pd/C and Pd-Ru/C at 350°C; for Au/C and Au-Ru/C at 120°C) and then cooled down in Ar atmosphere.

The X-ray diffraction (XRD) patterns were obtained on a Shimadzu XRD-6000 X-ray diffractometer using Cu K_α radiation source ($\lambda = 0.154056$ nm) operating at 20 mA and 40 kV. The scanning range was 20° to 90°, and the scanning rate was 4°/min.

1.2 Electrocatalytic activity evaluation of the catalysts

The electrocatalytic activities of the as prepared catalyst toward alcohol oxidation were characterized using the ink electrode method. A certain amount of the catalysts was ultrasonicated in an ethanol solution of 2 mg/ml ethyl cellulose until a uniform ink was achieved. The suspension was pipetted quantitatively onto a glassy carbon that was polished beforehand. The coated electrode was then dried under an infrared lamp. To make the catalyst layer totally hydrophilic, the electrode was immersed repeatedly into a 1 mol/L NaOH solution until the electrode surface was uniformly covered with water.

A thermostatic electrochemical cell, equipped with the working electrode, a platinum coil counter electrode, and a salt bridge connected to the reference electrode compartment, was used for all electrochemical measurements. To avoid the influence of Cl⁻, a reversible hydrogen electrode (RHE) with the same electrolyte (1 mol/L NaOH) as in the electrochemical cell was used. Electrode potentials reported in this article are all referred to RHE.

For alcohol electrooxidation experiments, the cell temperature was maintained at 60°C. After being deoxygenated with Ar for 10 min, linear scanning voltammetry was conducted from the open circuit potential to an upper limit with a scanning rate of 1 mV/s. The anodic current was converted to mass specific activity according to the catalyst loading. With careful controls, the error in the catalytic activity thus evaluated was within $\pm 5\%$.

2 Results and discussion

2.1 XRD characterization of the catalysts

The XRD patterns of Pd/C, Pd-Ru/C, Au/C, and Au-Ru/C are shown in Fig. 1. The (220) peak of the face-centered cubic (fcc) structure was fitted to a Lorentz lineshape on a linear background so as to obtain the peak maximum and the full width at half maximum, which were then employed to calcu-

late the particle size of the catalyst using the Scherrer equation. The particle diameter thus estimated was ca. 24 nm for the Au-based catalysts and ca. 10 nm for Pd/C. The Pd-Ru/C catalysts seemed to be extremely small, and the particle size could not be calculated from the XRD results.

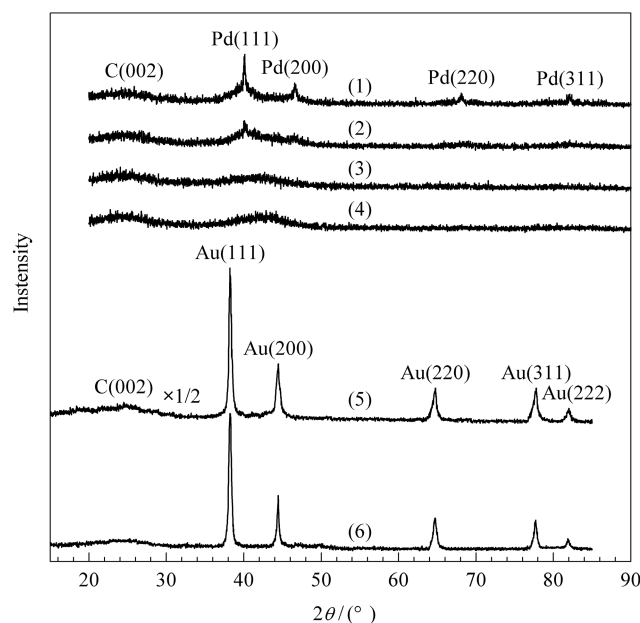


Fig. 1 XRD patterns of different catalysts (1) Pd/C, (2) Pd-Ru(2:1)/C, (3) Pd-Ru(1:1)/C, (4) Pd-Ru(1:2)/C, (5) Au/C, (6) Au-Ru(1:1)/C (All in atomic ratio.)

2.2 Electrooxidation of methanol, ethanol, and ethylene glycol on Pd and Pd-Ru

Pd was thought to be inactive for alcohol oxidation in acid and was studied as a methanol-tolerant catalyst for oxygen reduction [8–12]. However, in alkaline, the catalytic activity of Pd toward alcohol oxidation is notable. As seen in Fig. 2, at potentials more positive than 0.4 V, the oxidation of methanol, ethanol, and ethylene glycol occurred on Pd. By comparing the current density at the same potential, the activity sequence of the alcohol oxidation on Pd was ethanol > ethylene glycol > methanol.

Ru can promote the catalytic activity of Pt toward methanol oxidation by providing oxygen-containing species at more negative potentials. It is thus interesting to investigate whether such a promotion effect is also effective for Pd catalysts. As compared in Fig. 2, the catalytic activity of Pd-Ru is considerably higher than that of Pd toward the oxidation of methanol, ethanol, and ethylene glycol. The incorporation of Ru gave rise to a negative shift of 0.15 V in the onset potential. By comparing the current density at 0.4 V (Fig. 3), the activity sequence of Pd-Ru toward the alcohol oxidation was ethanol > ethylene glycol > methanol, and Pd-Ru with 1:1 atomic ratio exhibited the highest activity.

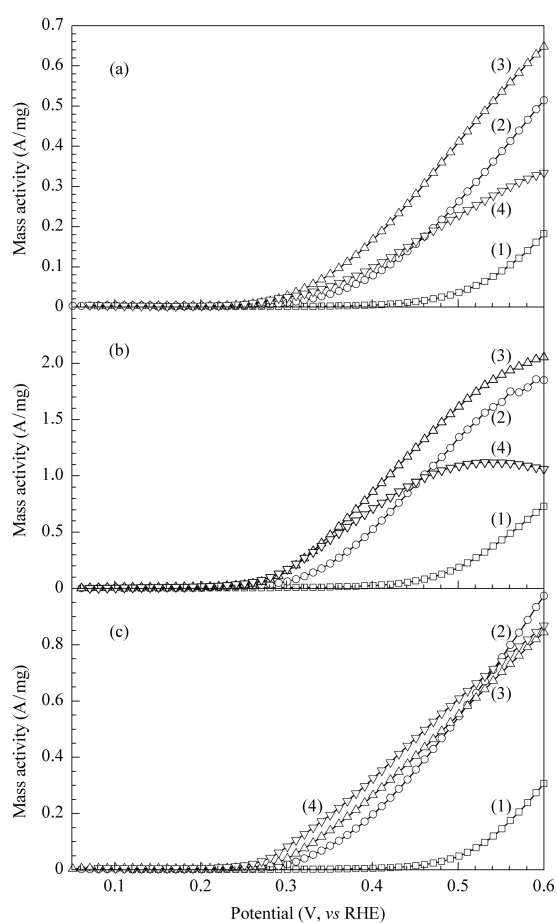


Fig. 2 Mass specific activity comparison for methanol (a), ethanol (b), and ethylene glycol (c) oxidation on Pd/C (1), Pd-Ru(2:1)/C (2), Pd-Ru(1:1)/C (3), and Pd-Ru(1:2)/C (4)

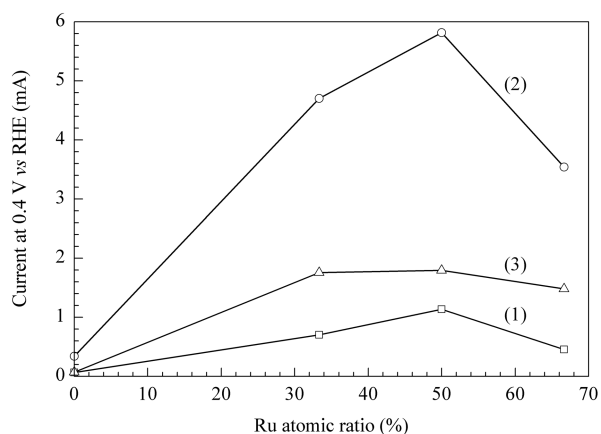


Fig. 3 Relationship between the current of methanol (1), ethanol (2), and ethylene glycol (3) and the Ru content in Pd-Ru/C

2.3 Comparison of Pd-Ru and Pt-Ru catalysts

According to the above results, it may be inferred that the catalytic mechanism of Pd-Ru catalyst is probably similar to that of Pt-Ru catalyst, namely, Pd catalyzes the dissociative

adsorption of alcohol molecules, and Ru catalyzes the dissociative adsorption of water to produce oxygen-containing species (OH_{ads}) at a more negative potential. At the interface of Pd and Ru surfaces or being transferred from Ru to Pd surface, OH_{ads} species react with poisoning intermediates strongly adsorbing on the Pd surface and thus promote the entire electrooxidation process.

We also compared the activities between Pd-based catalysts and the Pt-Ru catalyst in alkaline toward alcohol oxidations. As illustrated in Fig. 4, for the oxidation of methanol and ethylene glycol, the activity of Pd-Ru is higher than that of Pd but still lower than that of Pt-Ru. However, for ethanol oxidation, Pd-Ru exhibits an exceptional high activity. At potentials ranging from 0.3 to 0.4 V, the mass specific activity of Pd-Ru is almost 4 times that on Pt-Ru. After 0.45 V, the anodic current on Pt-Ru starts to decline; while on Pd-Ru, the current continues to increase and reaches a mass specific activity of 1.5 A/mg at 0.5 V. The particularly high activity of the Pd-Ru catalyst toward ethanol oxidation reveals the scientific and technological significance of this kind of catalyst.

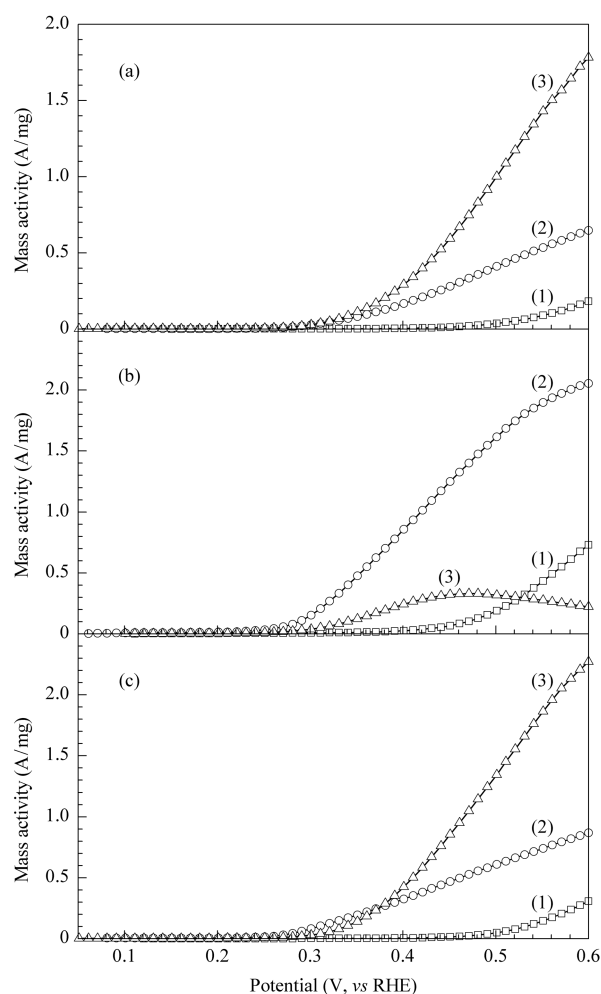


Fig. 4 Mass specific activity comparison for methanol (a), ethanol (b), and ethylene glycol (c) oxidation on Pd/C (1), Pd-Ru(1:1)/C (2), and Pt-Ru (1:1)/C (3)

2.4 Electrooxidation of methanol, ethanol, and ethylene glycol on Au and Au-Ru

Au is inert in acid toward alcohol oxidations, but it is somewhat active in alkaline. As shown in Fig. 5, the anodic current of alcohol oxidations on Au can be observed at potentials more positive than 0.6 V. Among the alcohol molecules being investigated under such conditions, the activity of methanol turned out to be the lowest while that of ethylene glycol was the highest.

The incorporation of Ru remarkably promoted the alcohol oxidations on Au, especially for methanol oxidation. However, different from the case of Pt-Ru or Pd-Ru, the incorporation of Ru did not cause a negative shift in the onset potential. A possible reason for this can be that at Au surface, the dissociative adsorption of alcohol molecules is very slow and becomes the rate-determining step of the entire oxidation process at the negative potential region. Since Ru is unable to

accelerate this step, its incorporation does not cause a negative shift in the onset potential.

In the above deduction, the activity difference between Pt and Au for the dissociative adsorption of alcohol molecules is in line with the difference in their activities for hydrogen reaction (hydrogen evolution or oxidation). On the basis of this correlation, one can further speculate that in the composition of a non-Pt catalyst for alcohol oxidation, a component with low hydrogen-overpotential (e.g., Pd and Ni) can be as important as the one to provide surface oxygen-containing species (such as Ru).

3 Conclusions

For the electrooxidation of methanol, ethanol, and ethylene glycol in alkaline media, both Pd and Au exhibit clear activities. The incorporation of Ru remarkably promotes the activities of Pd and Au. Especially, Pd-Ru is extremely active for ethanol oxidation, and the activity is almost four times that on Pt-Ru. Different from that on the surface of Pt or Pd, the dissociative adsorption of alcohol molecules on the Au surface can be the rate-determining step at the negative potential region. It has to be pointed out that this study is only a preliminary study of the electrocatalysis in this regard; detailed investigations are highly required to gain insights into the relevant electrode processes.

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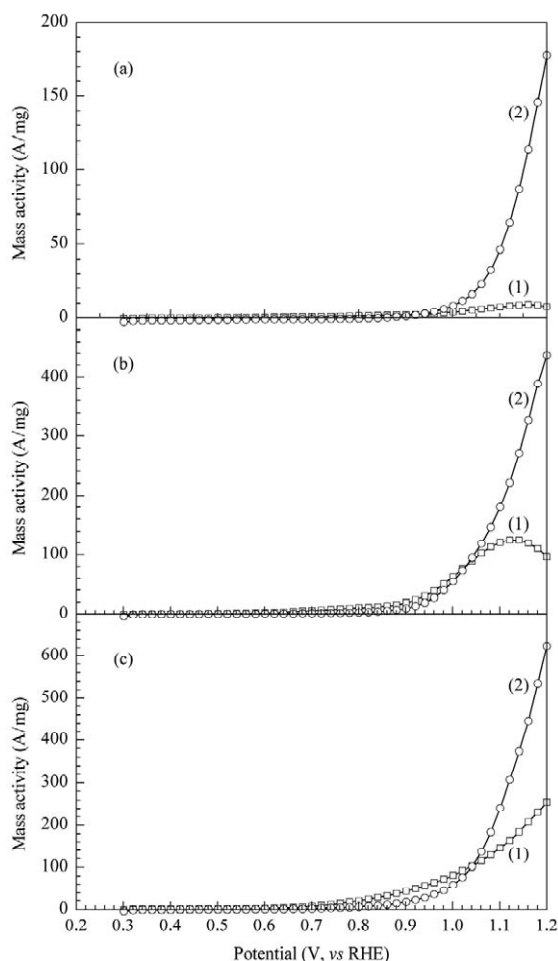


Fig. 5 Mass specific activity comparison for methanol (a), ethanol (b), and ethylene glycol (c) oxidation on Au/C (1) and Au-Ru(1:1)/C (2)