

Short communication

Electro-oxidation of methanol and formic acid on PtRu and PtAu for direct liquid fuel cells

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Abstract

The use of a PtAu catalyst as an anode catalyst for the oxidation of formic acid in direct formic acid fuel cells is described. Catalytic activities of PtAu and PtRu anodes were studied using a linear sweep voltammetry technique in a single cell configuration. PtAu showed a lower on-set potential and a larger current density than that of PtRu in formic acid oxidation. In addition, the maximum power densities at 30 °C for PtAu and PtRu were 94 and 74 mW cm⁻², respectively. In order to evaluate long-term durability, the single cells were operated for hundreds of hours with a 6 M aqueous formic acid solution at 60 °C under 100 mA cm⁻². The difference in performance between PtAu and PtRu after 500 h reached ca. 90 mV in direct formic acid fuel cells.

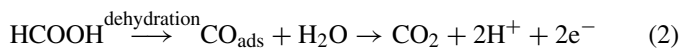
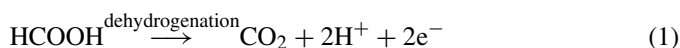
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1. Introduction

Formic acid has recently attracted attention as an alternative fuel for direct liquid fuel cells (DLFCs) due to its high theoretical open circuit voltage (1.45 V) and reduced fuel cross-over compared to methanol. In addition, formic acid is a strong electrolyte that facilitates proton transport in catalyst layers [1–6].

The mechanism of formic acid oxidation on platinum is well-established, the so-called dual pathways which are dehydrogenation and dehydration, represented by Eqs. (1) and (2) [7–12]:



The preferred reaction for the complete oxidation of formic acid is a dehydrogenation reaction (Eq. (1)), which CO₂ is

directly formed through the formation of active intermediates. In contrast, formic oxidation via a dehydration reaction (Eq. (2)) produces adsorbed carbon monoxide (CO_{ads}) which acts as a poisoning agent and must be further oxidized to CO₂. Markovic et al. investigated CO coverage as a function of potential in formic acid solutions for pure Pt, pure Ru and PtRu alloy surfaces [11]. Formic acid oxidation on a pure Pt surface at potentials from 0.2 to 0.7 V mainly occurred via dehydrogenation and CO_{ads} coverage readily increased with increasing potential, leading to an accumulation of CO_{ads}. On the other hand, the reaction on pure Ru took place by dehydration to form CO_{ads}, even at a very low potential, ca. 0.05 V, due to the strong interaction of Ru with formic acid leading to saturation coverage of CO_{ads}. At 0.7–0.8 V, CO_{ads} coverage on pure Ru finally dropped to zero by the subsequent oxidation to CO₂. As a synergic effect of alloying, PtRu showed a much higher activity than pure Pt due to the rapid dehydrogenation reaction on Pt and the enhancement in CO₂ production rate by the effective removal of CO_{ads} formed in the dehydration reaction, which is referred to a bifunctional mechanism analogous to methanol oxidation. Ross [13] pointed out that PtRu alloy is not the best catalyst for formic

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acid oxidation because in the potential region of 0–0.2 V Pt interacts with formic acid too weakly and Ru interacts with formic acid too strongly, so that the CO_{ads} formed in the dehydration reaction cannot be oxidized to CO_2 in this potential region on either surface. In addition to PtRu alloy, platinum surfaces have been modified by electrodeposition, not involving the formation of alloy, with various elements such as Pd, Pb, As, and Bi attempts to avoid poisoning and the resulting products show an increase in apparent reaction rate for formic acid oxidation. Rice et al. [14] and Larsen and Masel [15] investigated the catalytic activity of a PtPd catalyst for formic acid oxidation compared to that of PtRu in which Pd or Ru was spontaneously deposited on Pt black. From anode polarization and CO stripping experiments, it was concluded that the addition of palladium enhanced the rate of oxidation of formic acid via a direct dehydrogenation reaction which was not inhibited by CO_{ads} , while added ruthenium suppressed the direct pathway and accelerated the oxidation of CO_{ads} . The mechanism by which Pb deposited on Pt enhances formic acid oxidation has been attributed to an electronic effect, in which electronic interactions between Pb and Pt surface alter the electronic properties of their surfaces, thus accounting for the catalytic effect [16,17]. The most plausible mechanism for the enhancement of formic acid oxidation by a second element, such as Pd, As and Bi, is the so-called the third-body effect, in which the addition of a second element (third-body) to Pt reduces the number of adsorption sites for CO due to geometrical hindrance and their surface is poisoned by the CO_{ads} to a lesser extent than a pure Pt surface [18,19]. The high catalytic activity for a Bi modified Pt electrode can be explained by electronic effects, instead of a third-body effect [20]. In spite of these studies of Pt-based catalyst, formic acid oxidation on pure gold electrodes has been extensively investigated [21–26]. Weaver and co-worker [25] and Koper and co-workers [26] explored formic acid oxidation on gold by a combination of electrochemistry and surface-enhanced Raman spectroscopy (SERS) and proposed that the main reaction occurs via dehydrogenation with negligible CO poisoning by dehydration reactions. However, these works on gold had limitations, in that the formic acid oxidation started at a high potential, above 0.7 V versus RHE, in order for the system to be used in fuel cell applications.

In this paper, we report that a PtAu alloy, combined with two elements of the most extensively studied and positive materials, would be a good anode catalyst in direct formic acid fuel cell (DFAFC). Before comparing the catalytic activity of the new catalyst, the effect of formic acid concentration on single cell performance was investigated. Finally, we determined the catalytic activity of PtAu for formic acid oxidation under actual fuel cell conditions and the performance of DFAFC is compared with PtRu.

2. Experimental

2.1. Catalyst synthesis

Unsupported PtAu alloy nanoparticles were synthesized by a conventional borohydride reduction method combined with freeze-drying. Metal salts ($\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ and $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$,

Aldrich Chem. Co.) in the desired stoichiometry were completely dissolved in Millipore water. After stirring for several hours, the solutions were reduced by adding 0.2 M NaBH_4 (Aldrich Chem. Co.). A threefold excess of reducing agent over the valences of the metal salts was used, which was sufficient to completely reduce the salts to the elemental state. After precipitation, the resulting materials were washed with Millipore water several times and freeze-dried using liquid N_2 without any heat-treatment.

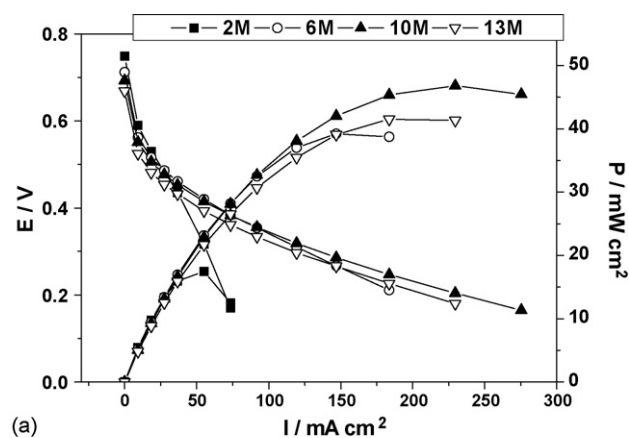
2.2. Fuel cell testing

Different catalysts, such as PtAu black, Pt black (Johnson Matthey, Hi-SPEC 1000) and PtRu black (Johnson Matthey, Hi-SPEC 6000), were used for the anodes and Pt black (Johnson Matthey, Hi-SPEC 1000) was used for the cathode. Electrodes were fabricated by dispersing appropriate amounts of unsupported catalysts powder in a deionized water, iso-propyl alcohol (IPA), and 5% Nafion[®] solution (1100 EW, Dupont), sonicating the solution for 5 min and then applying catalyst inks to a carbon cloth (E-TEK) by spraying at 75 °C. The catalyst loading for the anode and cathode was approximately 3 mg cm^{-2} and the geometrically active area of the electrode was 10 cm^2 . Membrane-electrode assemblies (MEAs) were prepared by hot pressing with Nafion[®] 115 at a temperature of 140 °C and a pressure of 70 kgf cm^{-2} for 150 s.

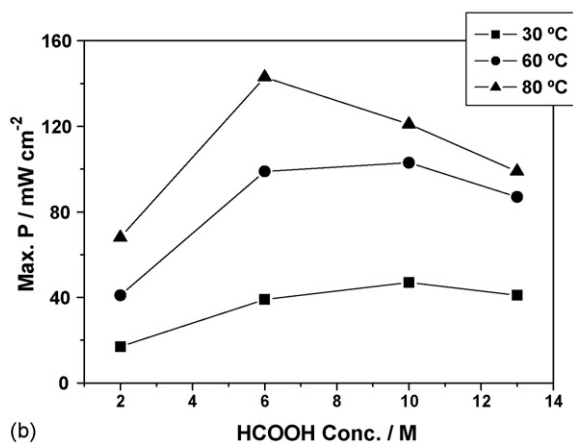
Cell performance was evaluated using a DFAFC single cell and was measured with a potentiometer which recorded the cell voltage under constant current conditions. Different concentrations of formic acid were supplied to the anode at a rate of 5 mL min^{-1} and humidified air (or oxygen) was supplied at 250 sccm at a zero back pressure. To evaluate catalytic activity for formic acid electro-oxidation in the fuel cell test configuration, cyclic voltammetry (CV) was carried out with flowing deionized water at the anode, working electrode, and flowing of hydrogen at the cathode served as a counter electrode as well as a dynamic hydrogen electrode (DHE). After obtaining the base voltammogram, the formic acid solution was fed to the anode and H_2 was fed to cathode.

3. Results and discussion

Fig. 1(a) compares the polarization curves for the MEA consisting of a Pt anode and a Pt cathode as a function of formic acid concentration. As expected, the open circuit voltage (OCV) decreased with increasing formic acid concentrations. For example, OCVs for 2, 6, 10, and 13 M formic acid solutions were 0.75, 0.71, 0.69, and 0.67 V, respectively, which show evidence of formic acid crossover similar to, but less than methanol. For the case of 2 M formic acid, the cell voltage rapidly dropped, due to limitations in mass transport. The maximum power density generated in DFAFC at 30 °C increased with increasing formic acid concentrations up to 10 M formic acid, and then decreased at concentrations above 10 M formic acid solution. This might be due to formic acid crossover. A similar trend was observed for all temperatures as shown in Fig. 1(b). It is noteworthy that the optimum concentration of formic acid for the best perfor-



(a)



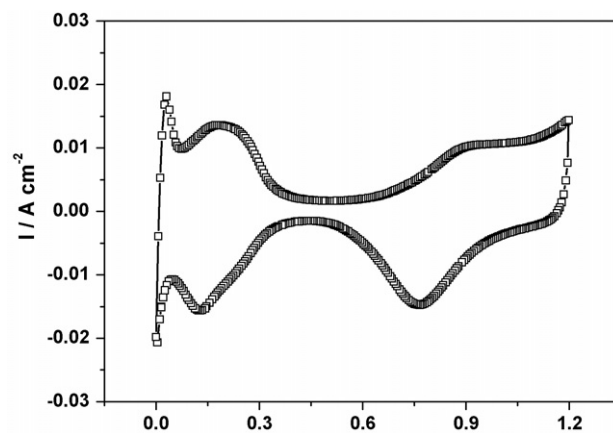
(b)

Fig. 1. (a) Single cell performance of DFAFC at 30 °C and (b) comparison of maximum power density using different concentrations of formic acid. The MEA consisted of a Pt anode and a Pt cathode.

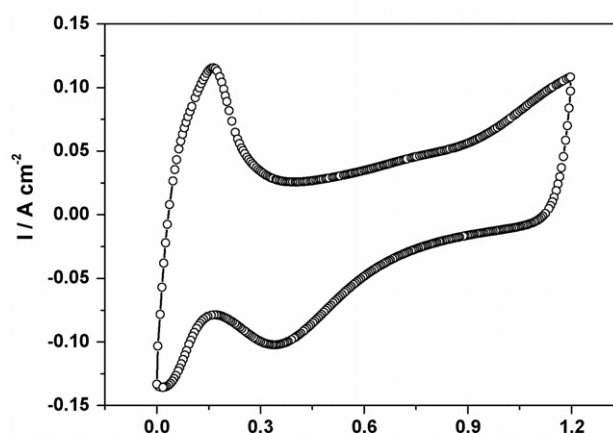
mance differs slightly with cell temperature and changed from 10 to 6 M with increasing temperature.

The electrochemical properties of the new PtAu catalyst for formic acid oxidation were analyzed in single cell fixture using voltammetry and the results were compared to PtRu black. Fig. 2(a) shows voltammograms for PtAu (1:1), in which the hydrogen adsorption/desorption peaks and pre-oxidation peaks for PtAu (1:1) are clearly similar to that of pure Pt. In contrast, the voltammograms for PtRu (1:1) had a thick double layer due to OH adsorption despite the same amount of catalyst loading, 3 mg cm⁻², being used in both cases. In addition, the hydrogen desorption peak, which is directly related to the electrochemically active surface area (EAS), is also different for the two catalysts. This suggests that Au in PtAu alloy and Ru in PtRu alloy have a different stoichiometry for hydrogen adsorption, while the ratio of hydrogen adsorption on a platinum surface was 1:1. Except for the change in the thickness of the voltammograms, no distinct difference in characteristic features was observed.

In order to investigate the catalytic activity of the PtAu (1:1) catalyst for the electro-oxidation of formic acid and methanol compared to PtRu (1:1), 2 M methanol and 6 M formic acid was fed to two different single cells. One contained the PtAu anode (PtAu-based MEA) and the other the PtRu anode (PtRu-based



(a)



(b)

Fig. 2. Voltammograms of (a) PtAu and (b) PtRu anode under conditions of deionized water flowing at the anode and humidified hydrogen flowing at the cathode.

MEA), while the cathode was composed of Pt black in both cases and humidified hydrogen was fed to the cathode. Fig. 3(a and b) shows the linear sweep voltammogram for each anode catalyst at 30 °C. The scan rate was 10 mV s⁻¹ in the range of 0.05–0.60 V, a range in which formic acid and methanol oxidation typically occurs. As shown in Fig. 3(a), PtRu shows a lower on-set potential and a larger current density for methanol oxidation than PtAu. The current densities for the PtRu and PtAu catalysts at 0.40 V are 19.1 and 1.1 mA cm⁻², respectively, and the difference increased with increasing potential. It is well known that CO poisoned Pt can be regenerated by reacting with surface CO with oxygen species associated with Ru to yield CO₂, a reaction that is based on a bifunctional mechanism [27]. The PtAu alloy, however, had no positive effect on methanol oxidation, showing almost the same activity as pure Pt, because Au itself is inactive for methanol oxidation and is not helpful for removing CO_{ads} on the Pt surface [25,26]. In contrast to methanol oxidation, PtAu has a lower on-set potential and a larger current density for formic acid oxidation than PtRu, as shown in Fig. 3(b). For example, the current densities for the PtRu and PtAu catalysts at 0.40 V are 3.8 and 119.2 mA cm⁻², respectively. In addition, the catalytic activity of PtRu in terms of on-set potential and

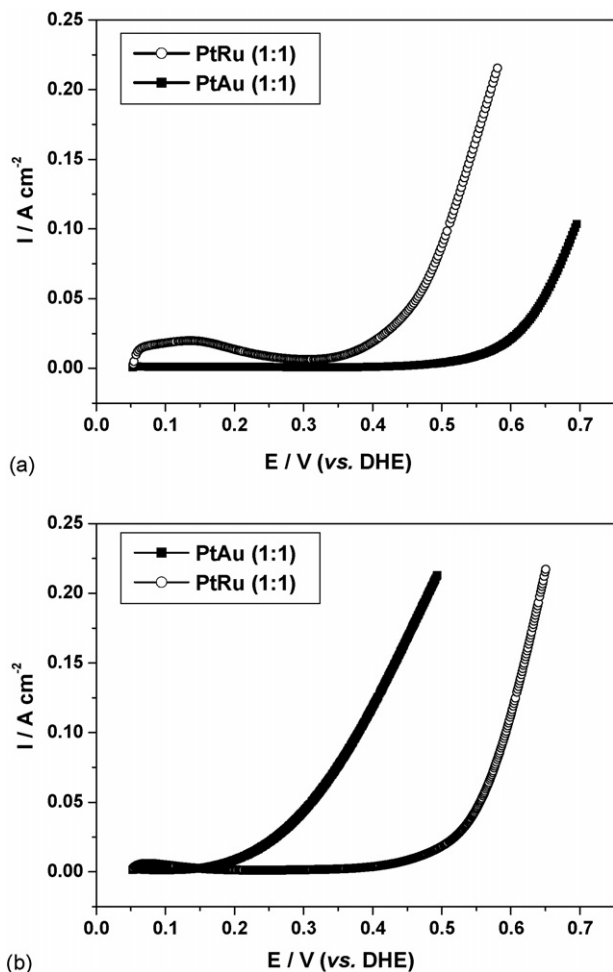


Fig. 3. Current vs. potential plot for PtAu-based MEA and PtRu-based MEA. The anode was fed with (a) 2 M methanol and (b) 6 M formic acid solution, respectively, while humidified hydrogen was fed to the cathode.

current density for formic acid oxidation is much less than that for the oxidation of methanol, which results from the instantaneous dehydration of formic acid on Ru in the PtRu alloy at low potentials, leading to saturation coverage of CO_{ads} [13]. The promotion of formic acid oxidation by a PtAu alloy has been explained by the third-body effect mentioned above [28] and the catalytic activity of pure Au might be one of the reasons for this enhancement [23,26]. It is noteworthy that, from our results, formic acid oxidation on PtAu catalyst starts even at 0.10 V and a significant amount of oxidation current occurs in the region 0.10–0.40 V, which is the most important region for catalytic activity in fuel cell performance. It should be noted that the not only the third-body effect but also the catalytic activity of pure Au is insufficient to explain the reason for the remarkable improvement attained by alloying Pt and Au. Therefore, this enhancement by PtAu could be explained by the fact that electro-oxidation of formic acid by PtAu produces mainly CO_2 as a final product via a direct dehydrogenation reaction because it is not necessary to adsorb oxygen species such as OH compared to methanol oxidation. A more detailed mechanistic understanding of the origin of enhancement will be reported from this group. Thus, we conclude that the half substitution of Au for Pt resulted

in an enhancement in intrinsic catalytic activity for formic acid oxidation. Further, the on-set potential for formic acid oxidation on PtAu is lower than that for methanol oxidation on PtRu and the current density for formic acid on PtAu is larger than that for the methanol oxidation on PtRu.

Fig. 4 shows the performances of single cells measured at 30 °C using 6 M formic acid. As shown in Fig. 4(a), the OCVs of the single cells with a PtAu anode and a PtRu anode were ~ 0.77 and ~ 0.61 V, respectively, and the difference between these OCVs is ~ 0.16 V. As is clearly shown in Fig. 3(b), PtAu begins to oxidize formic acid at 0.10 V, a more negative potential than PtRu. This is directly reflected in the difference in OCVs for both catalysts. At 0.50 V, where the activation polarization is dominantly affected by the catalytic activity, the current density of PtAu is several times higher than that of PtRu which are 66.3 and 9.2 mA cm^{-2} , respectively. In addition, the maximum power densities for PtAu and PtRu are 94 and 74 mW cm^{-2} , respectively. For the PtAu-based MEA, the maximum power density was maintained at 76 mW cm^{-2} despite changing oxygen to air (Fig. 4(b)). These findings provide evidence for a higher catalytic activity of PtAu for formic acid oxidation compared to PtRu. This improved activity by the new PtAu catalyst was also evaluated over long periods of time because catalyst durability is an important issue in practical applications.

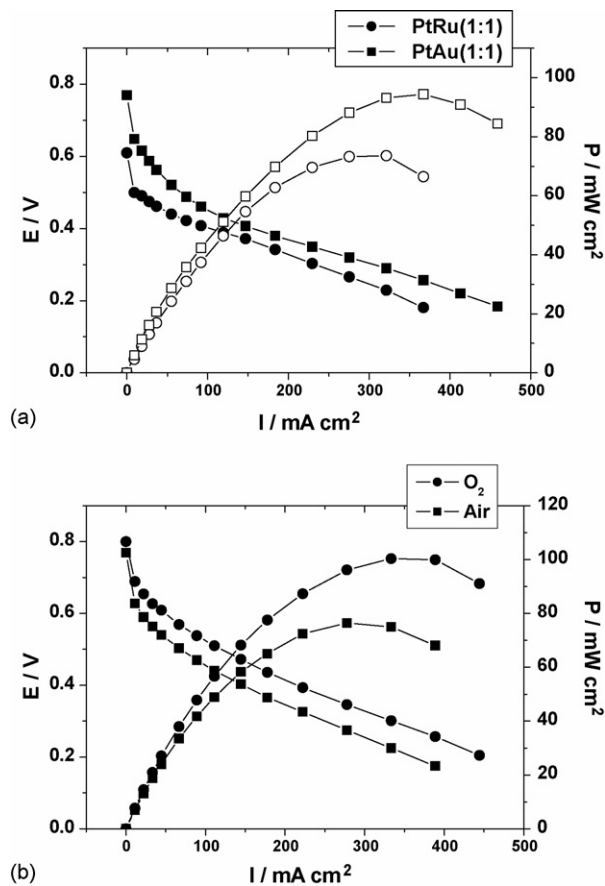


Fig. 4. (a) Single cell performance of PtAu-based MEA and PtRu-based MEA using 6 M formic acid and oxygen at 30 °C and (b) effect of cathode gas on the performance of the PtAu-based MEA.

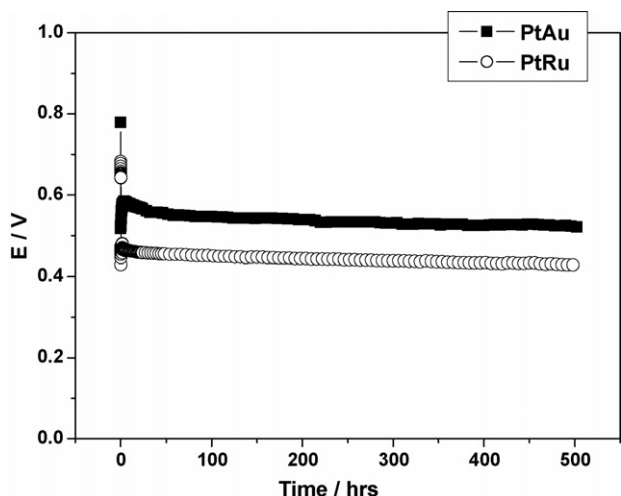


Fig. 5. Change in cell voltage of PtAu-based MEA and PtRu-based MEA during a 500 h life time test under 100 mA cm^{-2} .

Fig. 5 shows results for the long-term stability of a single cell using the PtAu-based MEA and PtRu-based MEA. The cell voltages of the single cells shown in Fig. 5 were measured at a fixed current density of 100 mA cm^{-2} and the temperature of the cell was 60°C . The difference in performance between PtAu and PtRu reached ca. 90 mV in DFAFC after 500 h of operation. In addition, the decay ratio of the cell voltage for PtAu-based MEA did not exceed 10% of initial cell voltage from 0.58 to 0.53 V. Therefore, we conclude that PtAu catalysts have the necessary stability for fuel cell operating conditions as well as a high catalytic activity with respect to formic acid oxidation. In order to identify the mechanism of degradation between PtRu and PtAu in detail, comparative investigations before and after long-term operations are currently underway.

4. Conclusions

A PtAu (1:1) anode catalyst for DFAFC was synthesized by a borohydride reduction method and its electrocatalytic activity was examined in a single cell configuration. PtAu (1:1) showed a high oxidation current in anode polarization and power density in single cell measurements. The improved catalytic activity of PtAu was also maintained in a long-term operation. We therefore conclude that the PtAu catalyst has the potential for use as a DFAFC anode.

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