Pt-Catalyzed D-Glucose Oxidation Reactions for Glucose Fuel Cells

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Glucose fuel cells have received increased attention in recent years for both external and implantable applications. As fuel cells, they show great potential for generating green electricity through biomass conversion, since glucose is a dominant component of biomass products. In addition, the standard Gibbs energy change of complete glucose oxidation to CO$_2$ and H$_2$O is negatively high at approximately -2,870 kJ mol$^{-1}$, corresponding to the maximum theoretical glucose fuel cell voltage of approximately 1.24 V. Glucose fuel cells can help lead the energy transition away from greenhouse gas emitting fossil fuels and towards renewable energy sources. Another field of application is the use-case as implantable fuel cells. For instance, glucose fuel cells promise to harvest energy from the human body and can therefore be used as power implantable biomedical devices.

To rationally design and engineer glucose fuel cells for both external and implantable applications, it is paramount to understand the catalytic processes that occur at both electrodes, and to develop catalysts that can perform well at temperatures close to room temperature. Because the glucose oxidation reaction is complex and the overpotential is high, the anode is a critical component of the glucose fuel cell. To date, many studies have focused on employing enzymes such as glucose oxidase for the catalysis of the glucose oxidation reaction. This enzyme has the benefit of being a highly selective and active catalyst and enzymatic glucose fuel cells have been successfully implanted in rats. However, enzymes deactivate easily and lack long-term stability when they are isolated and stabilized on an electrode, leading to short glucose fuel cell lifetimes of the order of several weeks. In addition, they show relatively poor charge transfer behavior, owing to the complexity of the enzyme molecules. Thus, abiotic catalysts have gained significant attention in recent years as a strategy to overcome these disadvantages. Abiotic catalysts include pure or alloyed noble metals that are often modified on carbon in the form of carbon nanotubes or activated carbon. They show great potential for generating green electricity through cyclic voltammetry and electrochemical quartz crystal microbalance (EQCM) measurements to clarify the adsorption/desorption behavior of these intermediate species. In addition, the effects of alloying Pt with Pd to further enhance the catalytic activity were discussed, based on the glucose oxidation mechanism described later.

**Experimental**

**Preparation of the catalysts.**—All reagents other than commercial platinum on graphitized carbon (Pt/C; 20% Pt/Vulcan XC72, Sigma-Aldrich Co. LLC.) were purchased from Nacalai Tesque, Inc. and used without further purification. To synthesize the Pt-Pd and Pt-Pd catalysts, 0.2 ml of 8 wt.% H$_2$PtCl$_6$ aqueous solution, prepared by dissolving H$_2$PtCl$_6$ in deionized water, 2 g of KOH, and 3.5 or 7 mg of PdCl$_2$ were mixed and dissolved in a mixed solvent containing 24 ml of N,N-dimethylformamide (DMF) and 16 ml of ethylene glycol (EG). After stirring the solution for 12 h, the resultant viscous solution was transferred into a 100 ml Teflon-lined autoclave. The autoclave was maintained at 170 °C for 8 h and then cooled to room temperature. The black products were collected by centrifugation, washed threefold with ethanol and deionized water, and subsequently dried at 60 °C overnight.

**Preparation of the working electrode.**—K$^+$-ion-exchanged Nafion solution was prepared as a binder by mixing 10 ml of 5 wt % Nafion (Sigma-Aldrich Co. LLC.) and 5 ml of 0.1 M KOH aqueous solution.
of glucose continues. By considering the glucose-free voltammogram as a baseline, anodic peaks (declines in cathodic current) were also observed during the negative potential sweep at approximately 0.5 and 0.75 V vs RHE in the presence of glucose. The emergence of anodic peaks during the negative potential sweep suggests that oxidative intermediates were adsorbed on the catalyst surface during the positive potential sweep, thereby inhibiting the oxidation reaction, while desorption of the intermediates occurred during the negative potential sweep. However, the details of these processes remain unclear.

We therefore proceeded to investigate the adsorption/desorption behavior by measuring the current density and corresponding mass change of the Pt electrode using an EQCM, \textsuperscript{16-20} as shown in Fig. 1a. The shape of the voltammogram differed slightly from that shown in Fig. 1a because of the difference in the electrodes and potential ranges (a: GC-RDE modified with Pt/C rotated at 1,600 rpm up to 1.3 V vs RHE and b: Pt-QCM electrode without rotation up to 1.1 V vs RHE to avoid the effect of the oxygen evolution reaction). Nevertheless, it is evident that the mass decreased during the negative potential sweep and increased during the positive potential sweep, suggesting that desorption occurred during the negative potential sweep and adsorption occurred during the positive potential sweep. The mass change below 0.4 V vs RHE is much larger than that above 0.4 V vs RHE during both the negative and positive potential sweeps.

In detail, the mass change per one mole of electrons transferred was calculated in several potential ranges, as shown in Table 1. During the positive potential sweep, the mass change was +167.9 g mol\(^{-1}\) in the potential range of 0.1–0.2 V vs RHE, which is similar to the molecular weight of glucose (180 g mol\(^{-1}\)). This result suggests that the oxidative adsorption of glucose via one-electron reaction mainly occurs at 0.1–0.2 V vs RHE during the positive potential sweep. This well agrees with the conclusion derived by Beden et al., from their spectroscopic study, that an adsorbed intermediate was formed on Pt by dehydrogenation of a more reactive axial H atom bonded to the anemic carbon of glucose in the \(\beta\)-D-glucopyranose form at lower potentials as follows:\textsuperscript{16}

\[ E(V\text{ vs}\ RHE) = E(V\text{ vs}\ Ag/AgCl,\ sat.KCl) + 0.05916\ \text{pH} + 0.197\ V \]  

\[ \text{Pt} + \text{HO}-\text{H}_{\text{anomeric}} + \text{H}_{\text{axial}}^+ + e^- \]  

All current densities were obtained using the geometric areas of the working electrode parts exposed to electrolytes (GC-RDE: 0.2 \(\times\) 0.2 \(\times\) \(\pi\) cm\(^2\), QCM electrode: 0.25 \(\times\) 0.25 \(\times\) \(\pi\) cm\(^2\), and fuel cell electrode: 0.65 \(\times\) 0.65 \(\times\) \(\pi\) cm\(^2\)).

Results and Discussion

The typical cyclic voltammograms for a GC-RDE modified with the Pt/C catalyst, measured in 0.1 M Na\(_2\)SO\(_4\) aqueous electrolyte with different glucose concentrations, are presented in Fig. 1a. While no significant peaks were observed with the glucose-free electrolyte, three anodic peaks were observed during the positive potential sweep at approximately 0.4, 0.75, and 0.95 V vs RHE. The current density increased with increasing glucose concentration, and therefore, these peaks correspond to the oxidation of glucose or its oxidative intermediates. As can be seen in the glucose-free cyclic voltammogram, a relatively strong capacitive behavior is observed, which offsets the current density to positive during the positive potential sweep and to negative during the negative potential sweep in this system. Therefore, even if the current density drops below zero after the reversal to the negative potential sweep, the oxidation...
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Overall, in the occupation of active Pt sites by OHads, lowers the current density for the direct oxidation of the adsorbed glucose. However, the significantly small anodic peak in Fig. 1b and relatively large peak in Fig. 1a in the range 0.9–1.0 V vs RHE, observed only during the positive potential sweep, suggest that OHads can also promote the indirect oxidation of glucose, possibly by C–O–C bond breakage. Furthermore, once the adsorbed glucose was consumed at higher potentials, most of the active Pt sites were occupied by OHads, leading to a decline in the anodic current at 0.9–1.0 V vs RHE. However, the amount of OHads decreases by the subsequent negative potential sweep, and a refreshed Pt surface appears, providing active sites for glucose oxidation. In this way, an increase in the current density corresponding to direct glucose oxidation is observed during the negative potential sweep.

Table 1 shows also the mass changes during the negative potential sweep. Above 0.4 V vs RHE, the mass change is very small (approximately –2 g mol\(^{-1}\)), even though there is an anodic peak in the potential range of 0.8–0.4 V vs RHE, suggesting the steady oxidative adsorption of glucose and subsequent desorption of δ-glucolactone. Below 0.4 V vs RHE, the mass change is approximately –80 g mol\(^{-1}\) (smaller than the molecular weight of glucose: 180 g mol\(^{-1}\)), which suggests that the reductive desorption of the dehydrogenated glucose dominates the current, but that reductive hydrogen adsorption also occurs.

Based on the above results and discussion, the oxidation of glucose can be divided into two pathways, namely direct and OHads-mediated oxidation. Both pathways start from the oxidative dehydrogenation of glucose, resulting in the adsorption of glucose on the Pt surface. The direct oxidation of the adsorbed glucose to weakly adsorbed δ-glucolactone and gluconic acid then proceeds, while oxidation aided by OHads also occurs at higher potentials (above 0.8 V vs RHE), where sufficient OHads is generated. Thus, an increase in the amount of OHads is a possible strategy to promote glucose oxidation at higher potentials.

PtPd and Pt\(_2\)Pd particles were synthesized and evaluated against a commercial Pt/C catalyst because of the easier formation of OHads. OHads, and H\(_2\)Oads on Pd at lower potentials\(^{11}\) (strictly, this also depends on the alloy configuration\(^{25}\)). As can be seen in the X-ray diffraction (XRD) patterns in Fig. 2a, the bimetallic catalysts, PtPd and Pt\(_2\)Pd, both comprise face-centered cubic (fcc) structures. Moreover, the PtPd and Pt\(_2\)Pd particles do not differ significantly and are smaller than 1 μm, as can be seen in the scanning electron microscopy (SEM) images in Fig. 2b and elemental analysis results in Fig. S1 (available online at stacks.iop.org/JES/168/064511/
mmedia).

The electrocatalytic performances of the bimetallic catalysts, PtPd and Pt\(_2\)Pd, for the glucose oxidation reaction were evaluated in 0.1 M Na\(_2\)SO\(_4\) aqueous electrolytes with different concentrations of glucose under N\(_2\) atmosphere. Typical cyclic voltammograms measured in an aqueous electrolyte containing 0.5 M glucose are shown in Fig. 3a, and for comparison, the current densities at 1 V vs RHE during positive potential sweep with various glucose concentrations are shown in Fig. 3b. As can be seen in Figs. 3a and 3b, the current densities for PtPd and Pt\(_2\)Pd are larger than that for Pt/C,

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with PtPd showing the highest current density. The electrochemically active surface area (ECSA) was determined by calculating the Coulombic charge of the hydrogen underpotential deposition in a N₂-saturated 0.1 M HClO₄ aqueous electrolyte. The estimated ECSAs of PtPd, Pt₃Pd, and Pt/C are 53.1 m² g⁻¹, 24.2 m² g⁻¹, and 63.7 m² g⁻¹, respectively (Fig. S2). The current densities for PtPd and Pt₃Pd are larger than that for Pt/C despite the lower ECSAs, indicating that the intrinsic catalytic activity of Pt can be improved by alloying with Pd. Specifically, the current densities at higher potentials are significantly enhanced, possibly because of the increase in the amount of OHads on the Pd surface.

Single-chamber glucose fuel cells were assembled using a N₂-saturated 0.1 M Na₂SO₄ aqueous electrolyte containing 0.5 M glucose, a Pt/C-modified GDL as the cathode catalyst, and PtPd- or Pt₃Pd-modified carbon paper as the anode, as displayed in Fig. 3c. Figures 3d and 3e show the performances of the fuel cell in air with PtPd and Pt₃Pd catalysts, respectively. The fuel cell with PtPd (Fig. 3d) exhibited a maximum power density of 27.6 μW cm⁻², an open-circuit voltage of 0.616 V, and a short-circuit current density of 0.239 mA cm⁻², which surpass the corresponding properties of the fuel cell with Pt₃Pd (Fig. 3e: Maximum power density, 9.84 μW cm⁻²; open-circuit voltage, 0.354 V; and short-circuit current, density 0.095 mA cm⁻²). It should be noted that the cell voltage is determined by the difference between the anode potential and the cathode potential. Therefore, the lowering in the cell voltage corresponds to the increase in the anode potential (and the decrease in the cathode potential), where the indirect glucose oxidation through OHads becomes predominant. These results agree with our prediction that PtPd provides more active sites for OHads than Pt₃Pd, thereby promoting glucose oxidation. The performance is comparable to that of other systems using enzyme-modified electrodes in neutral electrolytes; however, the same procedure should be adopted for the accurate comparison of catalysts because the catalytic activity and cell performance can be changed by many factors, such as the type of electrolyte and electrodes, pH, temperature, and electrode modification procedure.

Conclusions

Glucose fuel cells are of interest for clean energy storage and implantable applications. Despite the promise and proofs of concepts, the oxidation mechanism of glucose remains unclear. In this work, the mechanism of the Pt-catalyzed glucose oxidation reaction
was discussed based on the EQCM results. The oxidation of glucose
was designated as two pathways. Both pathways start from the
adsorption of glucose through oxidative dehydrogenation, which occurs
even at lower potentials above 0.1 V vs RHE. The direct oxidation of
the adsorbed glucose occurs over a wide range of potentials, while the
indirect oxidation proceeds at higher potentials above 0.8 V vs RHE
with the aid of OH_{ads}. The anodic peak during the negative potential
sweep was attributed to the formation of a refreshed catalyst surface
through the reductive desorption of OH_{ads}. The alloying of Pt with Pd
improved the electrocatalytic activity for the glucose oxidation reaction
because Pd enhances OH_{ads} formation and promotes indirect glucose
oxidation. Collectively, this signifies a novel approach for the design of
catalysts for glucose oxidation reaction. A single-chamber glucose fuel
cell was prototyped with the PtPd catalyst and a neutral aqueous
electrolyte, showing a performance comparable to that of glucose fuel
cells with enzyme-modified electrodes.

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