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Mechanism of glycerol oxidation reaction on silver-modified palladium electrode in alkaline medium

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ABSTRACT

The silver-modified Pd (Ag/Pd) electrode was prepared by underpotential deposition of Cu adatoms, followed by galvanic displacement with Ag atoms to investigate the effect of silver modification on the catalysis and mechanism for glycerol oxidation reaction (GOR) of Pd. Cyclic voltammograms in alkaline glycerol solution exhibited that the Ag/Pd electrode had ca. 100 mV less positive onset potential of the GOR current density and higher peak current density than the Pd electrode, indicating that the GOR activity of Pd was enhanced by surface modification with Ag atoms. In potentiostatic electrolysis at -0.1 V vs. Hg/HgO, GOR mainly began with the oxidation of a terminal OH group for both electrodes, and glycerate and glycolate were major products. The glycolate production was more active for the Ag/Pd electrode. The *in situ* infrared reflectance-absorption spectra (IRAS) exhibited that GOR products with one or two carbons were detected at lower potentials for the Ag/Pd electrode, indicating that the C–C bond cleavage was facilitated by the Ag modification.

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Introduction

Biodiesel fuel (BDF) as a carbon-neutral fuel is generally produced by the transesterification of fatty acid triglyceride like vegetable oil with methanol under alkaline conditions, and glycerol, which is taken as a bioalcohol, is simultaneously produced [1]. The production of the glycerol byproduct will increase with the BDF production. Glycerol is practically used for pharmaceuticals, cosmetics, botanical extracts, antifreeze, food additives, chemical intermediates, etc. [2]. However, these applications cannot cover the increased BDF production, so the development of another glycerol application is

indispensable. A solution of this issue is to use as a fuel for direct alcohol fuel cell (DAFC). Methanol is a more preferred fuel for DAFC, but direct methanol fuel cell (DMFC) produces carbon dioxide with electricity. This means the CO₂ discharge increases as DMFC is widely provided, which generates an environmental issue. In contrast, direct glycerol fuel cell (DGFC) using bioglycerol can produce electricity with a low environmental load. However, the development of anode catalysts to facilitate GOR to carbonate in alkaline media is an imperative task.

Pt is known to be a highly active element for alcohol oxidation reactions. Pd is more abundant in nature than Pt, and active for the oxidation of various substances in alkaline

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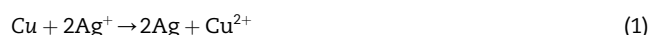
media [3]. So far, a variety of Pd-based binary catalysts have been developed for improving the GOR activity in alkaline media [4–15]. We also reported that PdAg nanoparticle-loaded carbon black catalysts had higher GOR activity than Pd nanoparticle-loaded carbon black catalyst [16]. However, we have not identified the GOR products and clarified the effect of Ag on the GOR mechanism. *In situ* infrared reflection-absorption spectroscopy (IRAS) is often used for the identification of the GOR products, but it may be risky to make a precise determination by itself because the GOR products have similar absorption bands due to the similar molecular structure. In this study, we performed potentiostatic oxidation of glycerol using a bare Pd or Ag monolayer-modified Pd (Ag/Pd) electrode, which was prepared by galvanic displacement of a Cu adlayer underpotentially deposited on a Pd electrode with Ag, and the GOR products were qualitatively and quantitatively analyzed by high performance liquid chromatography (HPLC). Based on this result and *in situ* IRAS data, the GOR mechanism for the bare Pd and Ag/Pd electrodes was discussed.

Experimental

A polycrystalline Pd column (5 mm ϕ \times 5 mm) was used as a substrate in this study. The Pd column was polished with 0.3 and 0.05 μm alumina suspension, followed by sonicating in ultrapure water. Moreover, the Pd column was electrochemically polished in a 0.5 M HClO₄ solution by cycling potential at a sweep rate of 500 mV s⁻¹ in a potential range between 0.3 and 1.2 V vs. RHE.

To estimate electrochemical surface area (ECSA) of the polished Pd electrode, cyclic voltammogram (CV) was measured at 20 mV s⁻¹ in a 0.1 M HClO₄ aqueous solution in a potential range between 0.40 and 1.25 V vs. RHE. ECSA was estimated from the electric charge for the reduction peak of the surface PdO (Q_{red}), assuming charge density of 424 $\mu\text{C cm}^{-2}$ for polycrystalline Pd [17].

The deposition of Ag atoms on the Pd electrode was performed as follows. Briefly, the polished Pd electrode was placed in a Ar-saturated 0.5 M HClO₄ solution containing 2 mM Cu(ClO₄)₂. To form a Cu adlayer on the Pd electrode by underpotential deposition (upd), it was polarized at 0.46 V vs. RHE for 5 min. After that, the Cu adlayer was replaced with Ag by immersing in a 0.01 M HClO₄ aqueous solution containing 5 mM AgClO₄ for 5 min, and the galvanic displacement is represented by eq. (1).



The resultant Ag-modified Pd electrode is named Ag/Pd.

The atomic radius of Cu is shorter than that of Pd, so Cu atoms epitaxially adsorb on Pd atoms [18]. The upd of Cu hardly occurs on the Ag surface [19]. Thus the coverage (θ_{Cu}) of the Cu adlayer deposited by upd was estimated as follows. At first, the electric charge for the Cu-upd ($Q_{\text{Cu}}(\text{Pd})$) on the Pd electrode in a (0.5 M HClO₄ + 2 mM Cu(ClO₄)₂) aqueous solution at 0.46 V vs. RHE for 5 min was evaluated, and then the θ_{Cu} value was calculated with the following equation;

$$\theta_{\text{Cu}} = Q_{\text{Cu}}(\text{Pd})/Q_{\text{red}} \quad (2)$$

In this study $Q_{\text{Cu}}(\text{Pd})$ and Q_{red} were evaluated to be 52.9 and 86.7 μC , respectively, so θ_{Cu} was estimated as 0.61. Next, the coverage (θ_{Ag}) of the Ag monolayers was estimated as follows. The electric charge for the Cu upd ($Q_{\text{Cu}}(\text{Ag/Pd})$) on the Ag/Pd electrode in a (0.5 M HClO₄ + 2 mM Cu(ClO₄)₂) solution at 0.31 V vs. RHE, at which θ_{Cu} was equal to Q_{red} , for 5 min was evaluated, and then the θ_{Ag} value was calculated with the following equation;

$$\theta_{\text{Ag}} = 1 - Q_{\text{Cu}}(\text{Ag/Pd})/Q_{\text{red}} \quad (3)$$

In this study $Q_{\text{Cu}}(\text{Ag/Pd})$ was evaluated as 29.8 μC , so θ_{Ag} was estimated as 0.66.

The chemical states of Pd and Ag for the Ag/Pd electrodes were analyzed by X-ray photoelectron spectroscopy (XPS). The X-ray source was Mg K α at 1253.6 eV operating at 10 kV and 20 mA. The base pressure of the system was 1.3×10^{-7} Pa.

For CV measurement, a Pt plate and a reversible hydrogen electrode (RHE) or Hg/HgO electrode were used as the counter and reference electrodes, respectively. The CVs of the Pd and Ag/Pd electrodes in 1 M KOH aqueous solutions containing 5 mM glycerol and the GOR products with three carbons such as glyceraldehyde, glycerate, tartronate, dihydroxyacetone, hydroxypyruvate and mesoxalate were measured at 20 mV s⁻¹ in a potential range between -0.6 and 0.1 V vs. Hg/HgO. For potentiostatic electrolysis, a two-compartment cell that was separated by an anion exchange membrane (AGC Engineering, Selemion[®]) was used with a Pd or Ag/Pd sheet (3 \times 1 cm²) working electrode, a Pt plate counter electrode and Hg/HgO reference electrode. The electrolyte was a 1 M KOH aqueous solution containing 0.5 M glycerol. The applied potential was -0.1 V vs. Hg/HgO. 100 μL of the electrolyte solution was collected every 1.5 h for HPLC measurement. A qualitative and quantitative analysis of various products was performed at 35 $^{\circ}\text{C}$ using high performance liquid chromatograph (Agilent Technology, Infinity II) and Sugar SH1011 column (Shodex). The eluent was a 5 mM H₂SO₄ aqueous solution and the detection was performed with a refraction index detector and an ultraviolet detector ($\lambda = 210$ nm).

The electrochemical cell for *in situ* IRAS was coupled at its bottom with a CaF₂ prism beveled at 60 $^{\circ}$ from the surface normal. IRAS spectra were recorded with a resolution of 4 cm⁻¹ between 400 and 4000 cm⁻¹ at various potentials. The applied potential was changed with every 0.1 V from -0.6 to 0.1 V and then from 0.1 to -0.6 V. IR spectra were calculated as the difference in absorbance between sample and reference spectra. The spectrum recorded at -0.6 V was used as a reference to spectra recorded at other potentials.

All electrochemical experiments were performed at room temperature.

Results and discussion

Electrochemical and spectroscopic properties of the Ag/Pd electrode

Fig. 1 shows stripping voltammograms of the Cu adlayer formed on the Pd electrode at 0.31 and 0.46 V vs. RHE in an Ar-saturated 0.5 M HClO₄ containing 2 mM Cu(ClO₄)₂ for 5 min. In

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