

称号及び氏名 博士（工学） Lam Thi Xuan Binh

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論文名 「Development of Highly Active Electrocatalysts for
Glycerol Oxidation Reaction
(グリセリン酸化反応用高活性電極触媒の開発)」

論文審査委員 主査 井上 博史

副査 長岡 勉

副査 松岡 雅也

論文要旨

Biodiesel fuel (BDF) attracts attention as carbon-neutral fuel in the same way as bioethanol. As the production of BDF increases, the production of the glycerol byproduct is also increasing. Glycerol is used for pharmaceuticals, cosmetics, food additives, synthetic raw materials, and anti-freeze. However, it is important to develop new uses for glycerol to cope with the mass production of BDF. Direct alcohol fuel cells (DAFCs), in which alcohols such as methanol and ethanol are used as fuels, have attracted considerable interest because the alcohols have a high energy density and are easy to handle, store, and transport compared with pure hydrogen. The use of glycerol as a fuel for DAFCs is promising, because direct glycerol fuel cells (DGFCs) are expected to produce electricity with a low environmental load and to be energy efficient.

So far transition metals such as Pt, Au, Ni and Pd have been applied to electrocatalysts for GOR. In general, active electrocatalysts have more negative onset potential of the GOR current (E_{onset}), and higher peak GOR current density per electrochemical surface area (j_p). The more negative E_{onset} and higher j_p lead to higher operating voltage and higher power density of DGFC, respectively. Pt has the most negative E_{onset} among metal electrocatalysts reported to date, whereas Au has the highest j_p . However, Pt is insufficient for j_p , whereas Au is so inferior to Pt in E_{onset} .

The purpose of this study is to develop highly active electrocatalysts for GOR in alkaline

medium. For this purpose, in this study the alloying of Pt or Pd, which had the next lowest E_{onset} in alkaline medium and was less expensive than Pt, with some foreign metals to exhibit a synergistic effect and the search for alternative metals for Pt were carried out. Moreover, the effect of the Ag modification on the mechanism of GOR on Pd was investigated by analyzing adsorbing species produced on bare and Ag-modified Pd electrodes by in situ infrared reflectance absorption spectroscopy (IRRAS).

This thesis consists of five chapters, and the content of each chapter is as follows.

Chapter 1 includes discussion of research background which also consists of purpose of the research work and summary of this study.

In chapter 2, the PdAg and PdAu nanoparticle-loaded carbon black (PdAg/CB and PdAu/CB) catalysts were prepared at room temperature by a wet method, and their electrocatalytic activity and durability for GOR in alkaline medium were evaluated. The mean sizes of PdAg and PdAu alloy nanoparticles loaded on CB were 2.3–3.7 nm. TG-DTA and XPS confirmed that the stabilizer was completely removed by washing. XRD and EDX showed that the bulk composition of the PdAg and PdAu alloys was controlled by the molar ratio of the mixed precursors. However, the Pd3d, Ag3d, and Au4f core-level binding energy shifts in the XPS data indicated that the surface composition of the PdAg and PdAu alloys was Ag-enriched and Pd-enriched, respectively, which was supported by their cyclic voltammograms (CVs) in an Ar-saturated 1 M KOH solution. In the forward sweep of CVs in 1 M KOH solution containing glycerol, the E_{onset} for the PdAg/CB electrodes was 0.10–0.15 V more negative than for the Pd/CB electrode, which was attributed to the electronic effect. The j_p for PdAg/CB was higher than for Pd/CB, whereas the ratio of GOR peak current densities in the backward and forward sweeps of CVs (j_b/j_f) was smaller, which suggested that PdAg/CB had a higher tolerance to the poisoning species than Pd/CB. In contrast to the Pd/CB electrode, the ratio of the GOR current density at 60 and 5 min (j_{60}/j_5) for the PdAg/CB electrodes was higher at more negative potentials, which indicated that the electronic effect retarded the poisoning of the active Pd sites by adsorbed carbonaceous intermediates. Moreover, the PdAu/CB electrodes exhibited a similar E_{onset} to the Pd/CB electrode and the j_p was higher than for the PdAg/CB and Pd/CB electrodes owing to the bi-functional effect. However, the j_b/j_f ratio for the PdAu/CB was higher than that for the Pd/CB electrode. The GOR can restart on the active Pd surface recovered by the reduction of Pd oxide because the onset potentials of the oxidation in the backward sweep are superimposed on the potentials of the high GOR current that flowed in the forward sweep, which may also explain higher the j_b or j_b/j_f ratio for the PdAu/CB electrodes. The j_{60}/j_5 ratio for the PdAu/CB electrodes was higher for more positive potentials, similar to the Pd/CB electrode.

In chapter 3, two types of metal and alloy nanoparticle catalysts with catalytic activity over Pt were developed. The first catalyst was rhodium nanoparticle-loaded carbon black (Rh/CB) prepared by a wet method. In the CV of the Rh/CB electrode, the redox waves due to hydrogen

adsorption/desorption and the surface OH monolayer formation/reduction were observed at more negative potentials than the Pt/CB and Pd/CB electrodes for reference. The E_{onset} at the Rh/CB electrode was ca. -0.55 V vs. Hg/HgO, which were 0.10 V more negative than the Pt/CB electrode, indicating that Rh was a fascinating metal for reducing the overpotential for GOR. In the potentiostatic electrolyses, the decrease in the GOR current density at the Rh/CB electrode with time was suppressed compared to that at the Pt/CB electrode. Therefore the tolerance to poisoning for the Rh/CB electrode was superior to that for the Pt/CB electrode.

The second catalyst was PtAg alloy nanoparticle-loaded carbon black (PtAg/CB) prepared by the same method. The mean size of PtAg nanoparticles loaded on CB was 2.1 nm irrespective of the Pt/Ag mole ratio, and increased to 4.0 nm by heat-treatment in N₂ at 200 °C for 15 min. The crystallinity of the PtAg nanoparticles was also improved by heat-treatment. The CVs of the PtAg/CB electrodes had two waves for GOR irrespective of heat-treatment, suggesting that there were two kinds of reaction sites on the Pt surface. The E_{onset} of the first wave was -0.65 V, which was 0.20 V more negative than that for the Pt/CB electrode, and the peak potential of the second wave was positively shifted, suggesting that tolerance to poisoning was improved for the PtAg/CB electrode. In the potentiostatic electrolyses at -0.1 V, the heat-treated PtAg(3:1)/CB electrode exhibited more than 10 times higher GOR current density after 60 min than the Pt/CB electrode.

In chapter 4, Ag-modified Pd disk (Ag/Pd) electrode was prepared by galvanic displacement of Cu underpotentially deposited on a Pd disk electrode with Ag to investigate the effect of the Ag modification on the catalysis and mechanism for GOR of Pd. The coverage of Ag was controllable by the amount of deposited Cu. In the CV of the Pd disk electrode, the redox waves due to the formation/reduction of PdO was reduced by the Ag modification, suggesting that the Pd surface was covered with Ag. The E_{onset} was a little shifted in the negative direction, but the peak potential of GOR at the Ag/Pd electrode was positively shifted. The *in situ* infrared reflectance absorption spectroscopy (IRRAS) was used for the identification of the GOR products. The IRRAS for GOR at the Ag disk electrode exhibited that GOR did not occur at the Ag disk electrode in the potential range between -0.6 and 0.1 V. For the Pd disk electrode, the absorption band assigned to dihydroxyacetone was observed at -0.2 V, and at higher potentials the absorption band assigned to glyceraldehyde and glycerate became stronger than that for dihydroxyacetone. On the other hand, for the Ag/Pd electrode, at -0.2 V the absorption band for dihydroxyacetone was not observed and glyceraldehyde and glycerate were preferentially produced.

Chapter 5 finally concludes this thesis by summarizing the previous chapters.

審査結果の要旨

本論文は、直接型グリセリン燃料電池(DGFC)のアノード反応であるグリセリン酸化反応(GOR)の高活性触媒開発に関する研究成果をまとめたものであり、以下の成果を得ている。

(1) 2種類のPd合金(PdAg、PdAu)ナノ粒子をカーボンブラック(CB)に担持した触媒(PdAg/CB、PdAu/CB)を新規に作製し、Pd合金の組成が前駆体のモル比で制御できることを見出した。また、両触媒ともPdナノ粒子触媒より高いGOR活性と耐被毒性を示すことを明らかにし、これらの特性向上は、PdAg/CBでは主に電子的効果、PdAu/CBでは二元機能効果によるものであることを明らかにした。

(2) Rhナノ粒子を担持したCB(Rh/CB)触媒を新規に作製し、この触媒上でのGORは、最高のGOR活性を示すPtナノ粒子触媒(Pt/CB)よりも負電位側から起こり始めることを見出し、Rh/CBが優れたGOR活性を示すことを明らかにした。また、Rh/CBはPt/CBよりも高い耐被毒性を示すことも明らかにした。

(3) PtAg合金ナノ粒子を担持したCB(PtAg/CB)触媒を新規に作製し、この触媒上でのGORは、Pt/CBやRh/CBよりも負電位側から起こり始めることを見出し、PtAg/CBが優れたGOR活性を示すことを明らかにした。また、PtAg/CBを熱処理することによりGOR電流が増大することを見出した。

(4) Pd電極およびAgを表面修飾したPd(Ag/Pd)電極上でのGOR生成物の同定を赤外反射吸収分光法により行った結果、Pd電極上では、 -0.2 V vs. Hg/HgO でジヒドロキシアセトンが主に生成し、さらに高電位側ではグリセルアルデヒドやグリセリン酸塩が主に生成したのに対し、Ag/Pd電極上では、 -0.2 V でもグリセルアルデヒドやグリセリン酸塩が主に生成することを見出し、Pd上でのGORの生成物分布の電位依存性はAgを表面修飾することにより変化することを明らかにした。

以上の研究成果は、直接型グリセリン燃料電池用高活性アノード触媒の開発指針にきわめて有益な知見を与えるものであり、本分野の学術的・産業的な発展に貢献するところ大である。また、申請者が自立して研究活動を行うのに必要な能力と学識を有することを証したものである。

学位論文審査委員会は、本論文の審査ならびに最終試験の結果から、博士(工学)の学位を授与することを適当と認める。