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論文要旨

Direct alcohol fuel cells (DAFCs), which use low-molecular weight alcohols as fuel, have attracted the attention of many scientists as alternative power sources for portable electrical appliances. Ethanol is one of the most attractive alcohol fuels for DAFCs due to its low toxicity and high energy density. Ethanol is also a carbon-neutral fuel and easily obtained via the fermentation of sugar-containing raw materials. However, ethanol oxidation reaction (EOR) has very sluggish kinetics. Particularly, the C–C bond is difficult to break, which inhibits the oxidation to CO₂ and limits the practical use of DEFCs. For these issues, many studies have been done on the electrocatalysis of noble metals for EOR. Among them, Pt is known as the most common noble metal with high EOR activity. However, Pt is easily poisoned by carbonaceous intermediates formed in EOR. Bimetallic electrocatalysts can reduce the content of noble metals, which brings low cost, and can exhibit higher catalytic activity than original noble metals due to the positive effect of the second metals. Various second metals have been proposed for use in Pt-based bimetallic catalysts. Recently, many scientists have expressed that Sn was the best partner for Pt in EOR. It was reported in studies on EOR using PtSn and PtSnO_x that Pt accelerated the dissociative adsorption of ethanol molecules, whereas Sn species including SnO_x provided OH sources to oxidize the carbonaceous intermediates adsorbed on Pt, which is known as a bi-function effect. Meanwhile, Rh is also a valuable metal because it can promote the C–C bond cleavage of ethanol molecules although Rh itself does not have impressive catalytic activity. The activity and

durability for EOR of bimetallic nanoparticle electrocatalysts including Sn and Rh as the second metal have been reported so far, but kinetics and mechanism of EOR have also been discussed without detailed analysis. In this study, Pt with different SnO₂ coverages and Pt_xRh_{1-x} solid solutions with different compositions were prepared as a model electrode and used for precisely analyzing the kinetics and mechanism of EOR and discussing the role of each element.

On the other side, Pd is known as a promising metal for EOR in alkaline media because Pd had higher EOR activity than Pt in alkaline media. Pd-based binary catalysts have also been prepared to reduce the content of expensive Pd and improve the catalytic activity. The modifications with Au, Ni, Sn, etc. have been proved to facilitate the EOR activity. For more effective cost of binary catalyst and the formation of intermetallic compound, inexpensive zinc as a favorable element for Pd-based binary catalyst is promising. However, since Zn is easily soluble in the alkaline medium, few papers have mentioned the stability of PdZn on EOR in alkaline media. In this study, two types of PdZn electrocatalysts including the intermetallic compound and substitutional solid solution were prepared and employed for the EOR in the alkaline medium.

This thesis contains five chapters, and the content of each chapter is as follows:

Chapter 1 reviews the research background knowledge, purpose, and summary of the current research work.

In chapter 2, Pt_xRh_{1-x} solid solutions with different compositions (Pt_{0.76}Rh_{0.24}, Pt_{0.54}Rh_{0.46}, and Pt_{0.27}Rh_{0.73}) were prepared by the arc-melting method. The bulk and surface compositions of each solid solution were determined by energy-dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS), respectively. The lattice constant as a function of bulk composition followed the Vegard equation, indicating that all the Pt_xRh_{1-x} alloys formed solid solutions. For each solid solution, the surface composition estimated by XPS is quite similar to the bulk composition estimated by EDX. The CO-stripping voltammograms demonstrated that the onset potential (E_{onset}) of CO oxidation shifted negatively as the Pt content in the solid solutions decreased, which indicated an enhancement of CO-poisoning resistance for the solid solutions with lower Pt contents. The EOR activity of each alloy was evaluated with the linear sweep voltammogram (LSV) in an Ar-saturated (0.1 M HClO₄ + 1 M ethanol) solution. Among the alloys, Pt_{0.54}Rh_{0.46} gave the highest specific activity of 312 $\mu\text{A cm}^{-2}$ which was about 1.8 to 2.5 times higher than Pt and Rh, whereas the E_{onset} of each solid solution was lower than that of Pt. The change was attributed to the ligand effect because the alloying of Pt and Rh altered the electronic state of Pt. The *in situ* infrared reflection-absorption spectroscopy clearly illustrated the increase of a peak at 2343 cm^{-1} assigned to CO₂ at potentials above 0.5 V for Pt_xRh_{1-x} electrodes, suggesting the enhancement in CO₂ selectivity of Pt_xRh_{1-x} solid solutions compared to Pt electrode.

In chapter 3, Sn was deposited on a polycrystalline Pt electrode at -0.2 V vs. reversible hydrogen electrode (RHE) in an Ar-saturated 0.1 M H₂SO₄ solution containing various concentrations of SnCl₂

for 30 s, followed by the exposure to air. The coverage of SnO₂ on Pt (θ_{SnO_2}), which was calculated based on the electrochemical active surface area (ECSA), was proportional to the SnCl₂ concentration, suggesting that θ_{SnO_2} can be controlled by the SnCl₂ concentration. The CO-stripping voltammograms of the SnCl₂-modified Pt (Pt/SnO₂) electrodes with $\theta_{\text{SnO}_2} \leq 0.61$ demonstrated an increase in the Pt-SnO₂ interface, whereas the Pt/SnO₂ electrodes with $\theta_{\text{SnO}_2} > 0.61$ showed a decrease in the Pt-SnO₂ interface. In addition, kinetic analysis of CO-stripping voltammograms at various sweep rates also indicated that CO-stripping reaction for the Pt and Pt/SnO₂ electrodes was a surface reaction and the rate-determining step of the CO-stripping reaction was one-electron oxidation of water to adsorbed OH and the coupling of adsorbed CO and OH for the Pt and Pt/SnO₂ electrodes, respectively. Moreover, further modification of Pt/SnO₂ with Rh adatoms expressed the CO-stripping is limited by the surface diffusion of CO. The EOR activity of Pt/SnO₂ electrodes was evaluated with LSVs in an Ar-saturated (0.1 M HClO₄ + 1 M ethanol) solution. The specific activity at 0.4 V vs. RHE exhibited the highest value for $\theta_{\text{SnO}_2} = 0.61$, whereas E_{onset} was shifted negatively compared to the Pt electrode. Moreover, further modification of Pt/SnO₂ with Rh adatoms also expressed an enhancement in EOR activity.

In chapter 4, the intermetallic and substitutional solid-solution PdZn alloy nanoparticles (NPs) (i-PdZn/C, s-PdZn/C) were prepared via the wet reduction of palladium and zinc precursors in ethanol dispersion of carbon black by sodium tetrahydroborate with and without the following heat-treatment in an autoclave. The structure and average particle size of i-PdZn/C and s-PdZn/C was well-characterized by X-ray diffractometry, XPS, EDX, and transmission electron microscopy. XPS analysis illustrated a strong electronic interaction between Pd and Zn in i-PdZn/C because the binding energy of the peaks assigned to metallic Pd and Zn shifted positively and negatively compared to that of metallic Pd and Zn sheets, respectively. On the contrary, for s-PdZn/C, the binding energy for Pd shifted positively, but only a Zn 2p peak for ZnO was observed, suggesting the surface Zn component was oxidized. The corrosion-resistance tests in 1 M KOH aqueous solution at 20 °C indicated that i-PdZn/C was much more tolerant to alkaline medium than s-PdZn/C. After the tests, s-PdZn NP resulted in a structure of porous Pd NP, whereas i-PdZn NP changed to a core-shell structure in which intermetallic PdZn NP core was covered with a porous Pd shell. Both i-PdZn/C and s-PdZn/C significantly enhanced the EOR activity compared to Pd NP-loaded carbon black (Pd/C). Moreover, the potentiostatic electrolysis for 10000 s demonstrated that i-PdZn/C was superior in durability to Pd/C and s-PdZn/C due to the electronic effect of the intermetallic PdZn core.

Chapter 5 finally summarized previous chapters and gave a general conclusion.

審査結果の要旨

本論文は、直接型エタノール燃料電池のアノード反応であるエタノール酸化反応 (EOR) を高活性に行わせるための 2 種類の金属からなる電極触媒の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) アーク融解法で作製した 3 種類の Pt_xRh_{1-x} 合金はいずれも固溶体を形成し、表面組成とバルク組成がほぼ等しいことを明らかにした。酸性水溶液中、Rh 成分が酸化溶解しない電位での EOR 活性は、表面組成が $Pt_{0.54}Rh_{0.46}$ の場合に最も高いことを見出した。また、赤外反射吸収分光分析より、 $Pt_{0.54}Rh_{0.46}$ ではエタノール分子の C-C 結合の開裂に起因して Pt と Rh 原子上に CO が吸着し、0.5 V vs. RHE 付近からは CO_2 が生成することを明らかにした。

(2) 多結晶 Pt 表面に電析された後、空気酸化されて生成した SnO_2 の被覆率 (θ_{SnO_2}) は、電析浴中の Sn^{2+} 濃度に依存することを見出した。また、 SnO_2 に隣接した Pt 原子に吸着した CO の酸化電気量は $\theta_{SnO_2}=0.61$ のときに最大になることを見出した。CO 酸化ピーク電流の動力学解析より、 SnO_2 被覆 Pt (Pt/SnO_2) 電極での吸着 CO の酸化反応の律速段階は、 SnO_2 に形成された OH と隣接した Pt 上に吸着した CO とのカップリング反応であることを明らかにした。さらに、 Pt/SnO_2 電極での EOR 活性も $\theta_{SnO_2}=0.61$ のときに最大になることを見出した。

(3) カーボンに担持した PdZn 金属間化合物ナノ粒子 (i-PdZn/C) 触媒の合成法を確立した。i-PdZn/C の XPS より Pd から Zn への電子移動が起こっていることを明らかにし、このことが EOR に対する比活性の向上に寄与していることを明らかにした。また、アルカリ水溶液中での i-PdZn/C の Zn 成分の溶解が大幅に抑えられることを見出した。EOR に対する触媒安定性は i-PdZn/C の方が Pd ナノ粒子担持カーボンより優れていることを明らかにした。

以上の研究成果は、高活性や低貴金属量のエタノール酸化触媒の開発に有益な知見を与えるものであり、燃料電池やその関連分野の学術的・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。