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論　　文　　名　「Development of Electrocatalysts toward Complete Oxidation of Ethanol
（エタノールの完全酸化を目指した電極触媒の開発）」

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論文要旨

Direct alcohol fuel cells (DAFCs) have increasingly attracted attention in their applications to alternative power sources for portable electric devices to lithium ion batteries. Among alcohols, ethanol is more attractive than methanol because it has lower toxicity and higher energy density. Ethanol, moreover, is a carbon-neutral fuel, and can be easily produced in great quantity by fermentation of sugar-containing raw materials. However, ethanol oxidation reaction (EOR) has very sluggish kinetics, and the C-C bond in an ethanol molecule is hard to break, which inhibits complete oxidation to CO_2. Pt-based binary anode catalysts have demonstrated high catalytic activity for EOR. Many studies have proved PtSn alloy and Pt/SnO_x were the most promising catalysts for EOR. In these catalysts Pt facilitated the adsorption and dissociation of ethanol, while Sn provided OH species for the oxidation of CO intermediates strongly adsorbed on Pt, which is known as a bi-functional effect. The main product, however, was not CO_2, but acetaldehyde and acetic acid, the partial EOR products, which were unfavorable for the operation of direct ethanol fuel cells (DEFCs). Another binary catalyst with a composition of PtRh was effective for the C-C bond cleavage or CO_2 formation, although the EOR activity was low. Recently, ternary Pt-Sn-Rh catalysts prepared by various methods have been reported to be very effective for EOR because they had lower onset potential for EOR current density (E_{onset}) and higher EOR current density (j_{EOR}), and also facilitated

the C-C bond cleavage. It was proved that all three constituents were needed for the cleavage of the C-C bond in ethanol to form CO_2 with keeping EOR activity. However, there have been only a few researches about atomic arrangement at active sites so far. Considering the previous results, I built a hypothesis in which Pt and Sn (or SnO_x) sites should be separated by Rh atoms for selective CO_2 formation.

The purpose of this study is to verify my hypothesis, and establish how to prepare atomic arrangement-controlled Pt/Rh/SnO_2 nanoparticle-loaded carbon black (Pt/Rh/SnO_2/C) catalyst. For this purpose, I first developed two ways to deposit Rh and SnO_2 on a polycrystalline Pt model electrode where the Pt and SnO_2 sites were separated by Rh atoms. Then I characterized the atomic arrangement-controlled Pt/Rh/SnO_2 electrodes, and evaluated their EOR activity and CO_2 selectivity by electrochemical measurements and *in situ* infrared reflection-adsorption spectroscopy (IRAS), respectively. Next, toward the application to DEFCs, I developed how to prepare the atomic arrangement-controlled Pt/Rh/SnO_2/C nanoparticle catalyst, and evaluated its EOR activity and CO_2 selectivity by the electrochemical and spectroscopic measurements.

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

Chapter 1 includes discussion of the research background knowledge as well as the purpose and summary of the current research work.

In chapter 2, the atomic arrangement-controlled Pt/Rh/SnO_2 electrode was prepared by depositing SnO_2 on a Pt model electrode, followed by depositing Rh after CO adsorption and then CO stripping at a specific potential, which is named a limited CO stripping method. Sn was deposited on a Pt electrode by potentiostatic method, and oxidized to SnO_2 in air. The coverage of SnO_2 on Pt electrode was 0.23. After the limited CO stripping, only CO molecules adsorbed on Pt sites adjacent to SnO_2 were removed, and Rh was deposited by galvanic replacement with atomic hydrogen adsorbed on the exposed Pt sites, which is named an H-upd method (controlled Pt/Rh/SnO_2(h)). For comparison, Rh was randomly deposited by the H-upd method without the limited CO stripping (normal Pt/Rh/SnO_2(h)). The Rh contents of the normal and controlled Pt/Rh/SnO_2(h) electrodes were 0.09 and 0.04, respectively. The j_{EOR} value of the controlled Pt/Rh/SnO_2(h) electrode at 0.6 V (vs. RHE) was similar to that of the Pt/SnO_2 electrode, and ca. 3 times as high as that of the Pt electrode. However, the j_{EOR} value of the normal Pt/Rh/SnO_2(h) electrode was ca. 1.5 times as high as that of the Pt/SnO_2 electrode. The E_{onset} value for the Pt/SnO_2 and both Pt/Rh/SnO_2(h) electrodes was 0.1 V and 0.2 V lower than that for the Pt electrode, respectively. The *in situ* IRAS exhibited that for the normal Pt/Rh/SnO_2(h) electrode, the formation of acetic acid was predominant over that of CO_2, whereas the controlled Pt/Rh/SnO_2(h) electrode with lower EOR activity was superior in CO_2 selectivity to the normal one.

In order to increase the EOR performance, the Sn coverage was enhanced and Rh was deposited by potentiostatic method instead of the H-upd method after the limited CO stripping (controlled

$Pt/Rh/SnO_2$(p)). The controlled $Pt/Rh/SnO_2$(p) electrode had the Sn coverage of 0.42 and the Rh content of 0.28. The j_{EOR} value of this electrode at 0.6 V was ca. 4 times as high as that of the Pt electrode. The E_{onset} value for the Rh/Sn/Pt electrode was 0.2 V lower than that for the Pt electrode. The *in situ* IRAS exhibited that the controlled $Pt/Rh/SnO_2$(p) electrode greatly suppressed the formation of acetic acid, leading to the selective CO_2 formation.

In chapter 3, another atomic arrangement-controlled $Pt/Rh/SnO_x$ electrode was prepared by depositing Rh on a Pt model electrode, followed by depositing Sn only on Rh (tandem $Pt/Rh/SnO_x$). The deposition of Rh and Sn was performed by the H-upd method. For comparison, Sn was randomly deposited on Rh-deposited Pt (Pt/Rh) electrode by the H-upd method (random $Pt/Rh/SnO_x$). The deposited Sn was considerably oxidized to SnO and SnO_2 in air. The covarages of SnO_x and Rh for the random $Pt/Rh/SnO_x$ were 0.36 and 0.22, respectively, and those for the tandem $Pt/Rh/SnO_x$ were 0.07 and 0.28, respectively. The Pt/Rh electrode exhibited the similar E_{onset} and j_{EOR} to the Pt electrode. However, both $Pt/Rh/SnO_x$ electrodes were 5 times as high in j_{EOR} as the Pt and Pt/Rh electrodes. The E_{onset} values of these two ternary catalysts were about 0.1 V lower than the Pt and Pt/Rh electrodes. *In situ* IRAS exhibited that the tandem $Pt/Rh/SnO_x$ electrode selectively formed CO_2 without the formation of acetic acid, whereas the random $Pt/Rh/SnO_x$ electrode still formed acetic acid. The latter suggests SnO_2 was deposited on not only Rh but also Pt surface.

In chapter 4, based on findings obtained in chapter 2, the atomic arrangement-controlled $Pt/Rh/SnO_2/C$ was prepared by depositing Rh on Pt/SnO_2(3:1) nanoparticle-loaded carbon black ($Pt/SnO_2/C$) by H_2 reduction method after the limited CO stripping (controlled $Pt/Rh/SnO_2/C$). For comparison, Rh was randomly deposited on $Pt/SnO_2/C$ by the same method without the limited CO stripping (normal $Pt/Rh/SnO_2/C$). The size of nanoparticles for the normal and controlled $Pt/Rh/SnO_2/C$ was estimated as 2.8 nm by X-ray diffraction spectroscopy. The Rh contents of the normal and controlled $Pt/Rh/SnO_2/C$ were 5.5 and 5.0 at.%, respectively. The j_{EOR} at 0.6 V for the controlled $Pt/Rh/SnO_2/C$ electrode was ca. 2 and 4 times as high as that for the $Pt/SnO_2/C$ and normal $Pt/Rh/SnO_2/C$, respectively. The E_{onset} for the controlled $Pt/Rh/SnO_2/C$ electrode was the most negative among three catalysts. The *in situ* IRAS exhibited that for the normal $Pt/Rh/SnO_2/C$ electrode acetaldehyde and acetic acid were mainly produced, whereas for the controlled $Pt/Rh/SnO_2/C$ electrode the main products were CO_2 and acetaldehyde, and their production started at 0.2 V. In the latter the amount of CO_2 increased with potential, but that of acetaldehyde did not depend on potential. Thus I succeeded the preparation of the atomic arrangement-controlled $Pt/Rh/SnO_2/C$ with high CO_2 selectivity and high EOR activity.

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

審査結果の要旨

本論文は、直接型エタノール燃料電池のアノード反応であるエタノールの CO_2 への酸化反応を選択的に行わせるための Pt/Rh/SnO_x 触媒の構造制御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） SnO_2 修飾 Pt 電極表面に CO を吸着させた後、0.5 V vs. RHE の電位を印加して SnO_2 に隣接する Pt に吸着した CO のみを酸化除去した。その後、Rh を析出させることにより Rh を Pt と SnO_2 の間に配置させることに成功した。このような Pt/Rh/SnO_2 触媒のエタノール酸化活性は Pt や Pt/SnO_2 触媒より高いことを明らかにした。また、*in situ* 赤外反射−吸収分光法（IRAS）より、Rh の析出位置を制御した触媒では、完全酸化生成物である CO_2 が選択的に生成することを明らかにした。

（２） Rh 修飾 Pt 電極上に 0.5 V vs. RHE の電位を印加しながら CO を電解液に吹き込むと、CO は Pt にのみ吸着することを見出した。これを利用して、Rh 上にのみ Sn を析出させることに成功した（tandem Pt/Rh/SnO_x）。tandem Pt/Rh/SnO_x 触媒のエタノール酸化活性は Pt や Pt/Rh 触媒の約 5 倍であることを明らかにした。また、*in situ* IRAS により、tandem Pt/Rh/SnO_x 触媒では、CO_2 が選択的に生成することを明らかにした。

（３） Pt/SnO_2 ナノ粒子担持カーボン（Pt/SnO_2/C）上に CO を吸着させた後、0.5 V vs. RHE の電位を印加して Sn に隣接した Pt に吸着した CO のみを選択的に酸化除去した。その後、水素還元法により Sn に隣接した Pt にのみ Rh を析出させることに成功した。この触媒のエタノール酸化活性は Pt/SnO_2/C 触媒の約 2 倍であることを明らかにした。また、*in situ* IRAS により、ナノ粒子触媒の場合にも、CO_2 が選択的に生成することを明らかにした。

以上の研究成果は、エタノールの完全酸化触媒の開発にきわめて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。