HOKKAIDO UNIVERSITY

Title	Effect of Porous Structure of Carbon Support on CO Tolerance of PEFC Platinum Alloy Anode Catalysts [an abstract of dissertation and a summary of dissertation review]
Author(s)	Narischat, Napan
Degree Grantor	北海道大学
Degree Name	博士(工学)
Dissertation Number	甲第12378号
Issue Date	2016-06-30
Doc URL	https://hdl.handle.net/2115/62484
Rights(URL)	https://creativecommons.org/licenses/by-nc-sa/2.1/jp/
Type	doctoral thesis
File Information	Napan_Narischat_review.pdf, 審査の要旨

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学 位 論 文 審 査 の 要 旨

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Effect of Porous Structure of Carbon Support on CO Tolerance of PEFC Platinum Alloy Anode Catalysts

（PEFC の白金合金　アノード用触媒の CO 耐性への炭素担体の細孔構造の影響に関する研究）

Platinum (Pt) is well known as the best anode catalyst for low temperature polymer electrolyte fuel cells. One of the serious issues in anode catalysts is its low CO tolerance. Therefore, studies to develop electrocatalysts with enhanced CO tolerance for anode electrodes have been actively conducted. Significant efforts to attain high catalytic activities and robustness have been made, by adding a second element such as Ruthenium (Ru) to Pt supported on carbon (Pt/C) or other elements to such Pt–Ru/C catalysts. The CO tolerance of the developed catalysts is strongly dependent on their composition and porous structure of the support material. The enhancement in CO tolerance has been attributed to the bi-functional mechanism, ligand effect (or electronic effect) and the increase in the length of triple phase boundary. As all of these factors are thought to be controllable by adjusting the properties of the catalyst support, this work was conducted to clarify the properties of the support which significantly affect the CO tolerance of the resulting catalyst. This thesis consists of 7 chapters and starts with a chapter giving a general introduction.

In chapter 2, the effect of the activation degree of the carbon support on the CO tolerance of the resulting catalyst was investigated. Resorcinol-formaldehyde carbon gels (RFCs) were used as the support, due to its high pore structure tunability. A series of RFCs were synthesized with a fixed resorcinol to catalyst (R/C) ratio of 1000 and varied activation degrees (burn-offs) of 0, 37, 58 and 88%, and Pt-Ru particles were loaded onto them. A commercial Pt_2Ru_3/C anode catalyst was used as a reference. The catalysts were characterized by powder X-ray diffraction (PXRD), N_2 gas adsorption/desorption experiments, transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM). The CO tolerance of the obtained catalysts were tested through single cell performance analysis using H_2 with CO contamination levels ranging from 100 to 2000 ppm. The prepared Pt_2Ru_3/RFC catalysts showed superior CO tolerance. Especially Pt_2Ru_3/RFC prepared using an RFC with a burn off of 58% (RC1000Ac58) showed the highest CO tolerance. The activation degree could affect the volumes and sizes of mesopores and micropores, resulting in differences in size and dispersion of Pt-Ru particles, and accessibility to the particles all of which govern CO tolerance of the catalyst. Pt_2Ru_3/RC1000Ac58 showed the highest cell voltage of 0.787 V and highest CO tolerance at a CO contamination level of 2000 ppm (0.655 V, only 16.8% overvoltage). Supporting Pt-Ru particles on a carbon support with an optimum activation degree could be a practical method to improve CO tolerance of a Pt-Ru electrocatalyst.

In chapter 3, optimization of the Ru:Pt ratio in Pt-Ru/C catalysts was conducted. Pt-Ru/C Catalysts with Ru:Pt molar ratios of 1.0, 1.3, 1.5, and 2.0 were prepared by the Rapid Quenching Method using 2 different commercial carbons as the support. The carbon supports used were Carbon ECP and Carbon ECP600JD both provided by LION Corporation. The BET surface area of both carbons differed and were 800 and 1400 m^2g^{-1}, respectively. The carbon content of the prepared catalysts was measured using

a thermogravimeter, and the size of the loaded Pt-Ru particles was estimated by PXRD. CO stripping experiments were conducted, followed by CO tolerance tests conducted under the same conditions as in chapter 2. It was found that all of the prepared catalysts showed higher CO tolerance levels than a typical commercial catalyst (Pt_2Ru_3/C catalyst obtained from TKK). When Carbon ECP was used as the support, a catalyst with an Ru:Pt molar ratio of 1.5 (E-1.5 catalyst) showed the highest CO tolerance in accordance with the literature. However, when Carbon ECP600JD was used as the support, a catalyst with an Ru:Pt molar ratio of 1.3 (JD-1.3 catalyst) showed the best performance, and this catalyst exhibited higher CO tolerance than E-1.5 at CO contamination levels of 1000 ppm and 2000 ppm. This result suggests that, in order to maximize CO tolerance, the Ru amount to be added to Pt catalysts should be optimized according to the type of the support.

In chapter 4 the effect of the porous structure of the carbon gel support on the CO tolerance of the resulting catalyst was examined. As the porous structure of carbon gels can be varied by adjusting the R/C ratio at which they are synthesized, a series of carbon gels were synthesized at different R/C ratios (i.e., 200, 800 and 1000) and were activated to the same degree of 58% using CO_2. Then, Pt_2Ru_3 nanoparticles were supported onto the obtained carbons. The synthesized catalysts were characterized by PXRD, N_2 gas adsorption/desorption experiments, and STEM. The performance and CO tolerance of the obtained catalysts were tested using the same method and conditions as in previous chapters. The results revealed that catalysts having a large volume of mesopores show a significantly higher CO tolerance. Among the tested catalysts, Pt_2Ru_3 nanoparticles supported on a carbon gel synthesized with an R/C ratio of 1000 and activated to a burn-off of 58%, which has a high mesopore volume of 2.08 cm3 g^{-1} showed the highest CO tolerance. The cell voltage was the highest even in the presence of 2000 ppm CO (0.655 V) whereas the cell using a commercial Pt_2Ru_3/C catalyst showed only a voltage of 0.570 V in the presence of 500 ppm CO.

In chapter 5, the effect of SnO_2 decoration of the support was studied. Pt-Ru/SnO_2/C catalysts were prepared by the Rapid Quenching Method. The preparation conditions of Pt-Ru/SnO_2/C were controlled so that the structure and morphology of the loaded Pt-Ru particles would be the same as the previously studied Pt-Ru/C catalysts. Pt-Ru/SnO_2/C and commercial Pt-Ru catalysts were characterized by PXRD and STEM. Electrochemical activities were evaluated by CO stripping voltammetry, single cell tests, in situ infrared reflection–absorption spectroscopy (IRRAS), and surface-enhanced infrared absorption spectroscopy (SEIRAS). Pt-Ru/SnO_2/C catalyst showed the same structure, morphology, and catalytic activity for hydrogen oxidation reaction (HOR) in the absence of CO as Pt-Ru/C catalyst. Both the activity of electrochemical CO oxidation and the Pt-CO bond strength were quantitatively evaluated. The addition of SnO_2 was found to lead to the decrease in Pt-CO bond strength, which is thought to lead to the increase in CO tolerance while maintaining HOR activity.

In chapter 6, the effect of the ionomer (Nafion) content in the catalyst layer of membrane electrode assemblies (MEAs) was examined. MEAs with varied Nafion to catalyst (I/C) ratios, from 1:9 to 1:1, were prepared using Pt_2Ru_3/RFC and commercial Pt_2Ru_3/C catalysts. Then these catalysts were characterized by N_2 gas adsorption/desorption experiments, STEM and their CO tolerance was evaluated using a PEFC single cell. According to the triple-phase boundary (TPB) theory, the transportation of protons through ion-conducting Nafion can enhance or inhibit the efficiency of a fuel cell. Experimental results confirmed that insufficient loading of Nafion could seriously reduce MEA efficiency, while excess loading of Nafion might reduce the accessibility of gases to the inner surfaces of the catalyst support, also leading to a reduction in MEA efficiency. CO tolerance was also found to be affected by the amount of Nafion loading. The optimum amount of Nafion did not directly depend on either the I/C ratio or the surface area of a support. It was found, however, that the pore diameter and the pore volume of mesopores in the catalyst support are critical factors in enhancing CO tolerance.

In chapter 7, general conclusions were drawn. The effects of porous structure, SnO_2 decoration and Nafion content to the CO tolerance of Pt-Ru/RFC catalysts have been revealed. The present work proposes the key factors to obtain an anode catalyst for PEFC with a high CO tolerance. Finally, a novel CO tolerant Pt_2Ru_3/RFC catalyst which can operate under an atmosphere contaminated with 2000 ppm CO was successfully synthesized.

Considering these research achievements, we conclude that the author is eligible to receive a doctoral degree of engineering from Hokkaido University.