白金単結晶(111), (100), (110)電極表面における硫黄種の吸着脱離挙動

(物質・材料研究機構[1]・お茶の水女子大学[2]) ○諸岡 哲朗[1]・Ruttala Devivaraprasad[1]・Elumalai Ganesan[1]・近藤 敏啓[2]・増田 卓也[1]

Adsorption-desorption behavior of sulfur on Pt single crystal electrodes

([1]*National Institute of Materials Science*, [2]*Ochanomizu University*) ○ Tetsuro Morooka,[1] Ruttala Devivaraprasad,[1] Elumalai Ganesan,[1] Toshihiro Kondo,[2] Takuya Masuda[1]

Sulfur poisoning of Pt electrocatalysts due to impurities in fuel hydrogen gas and/or pollution substances in air is a major concern of polymer electrolyte membrane fuel cells because it causes a significant power loss. Understanding the adsorption/desorption behaviors of sulfur species at each face orientation of Pt nanocrystal electrocatalysts is important to prevent and control the sulfur poisoning. In the present study, we investigated the correlation between the electrochemical properties and adsorbed structure of sulfur at Pt (111), (100), (110) surfaces by in situ electrochemical surface analysis. Fig. 1 shows CVs of sulfur-adsorbed Pt(111) electrodes. The adsorption of sulfur interrupted the electrochemical properties characteristic to Pt(111) such as adsorption/desorption of hydrogen and anions. The adsorbed sulfur species was oxidatively removed from the Pt electrode surface by potential cycling with different positive potential limit. When the positive potential limit became more positive, oxidative current corresponding to the oxidation of adsorbed sulfur became larger. In the successive potential cycling, hydrogen adsorption/desorption (-0.2 V - +0.1 V) waves characteristic to the Pt(111) surface became larger with the number of cycles, confirming the oxidative desorption of sulfur species. The oxidative desorption of sulfur occurred at different potentials at different face orientations. The face orientation dependence of sulfur oxidative desorption was discussed on the basis of adsorbed structure of sulfur determined by surface x-ray scattering.

Keywords : Pt single crystal electrode; Sulfur; Fuel cell

燃料電池において、大気・燃料中に含まれる硫黄種が電極触媒である白金ナノ粒子に吸着すると、反応活性サイトが占有され出力が大幅に低下する。こうした被毒を予防・回復するためには、ナノ粒子を構成する各面方位での硫黄種の吸着脱離挙動の解明が重要である。本研究では、白金単結晶表面に硫黄種を吸着させ、吸着構造と被毒効果の相関を明らかにする目的で電気化学測定・表面分析を行った。Fig.1 は硫黄が吸着した Pt(111)電極の電流―電位曲線である。硫黄が吸着すると水素やアニオンの吸脱着といった Pt(111)電極特有の電気化学挙動が阻害された。正電位限界がより正電位になるほど硫黄種の酸化を示す電流が大きく現れるとともに、水素の吸着脱離波（-0.2 V~+0.1 V）が回復した。硫黄種の酸化的分解反応の起こりやすさが面方位によって異なることを明らかにし、表面 X 線散乱法により決定した硫黄の吸着構造の違いに基づいて議論した。

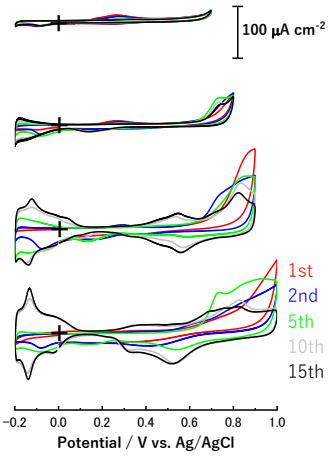

Fig. 1. CVs of the S-adsorbed Pt(111) electrode in 0.1 M $HClO_4$ aqueous solution with a scan rate of 20 mV s^{-1}.