



HOKKAIDO UNIVERSITY

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学 位 論 文 題 名

The Effect of pH on Electrocatalytic Oxidation of Small Organic Molecules on Platinum
Studied by Surface-Enhanced Infrared Absorption Spectroscopy Coupled with
Electrochemical Techniques

(白金表面における小有機化合物の電極触媒酸化反応に及ぼす pH の影響に関する表面増強赤外吸収分
光ならびに電気化学的手法による研究)

Recently, scientific and technological researches have focused on the development of clean, efficient power sources to diminish CO₂ emission coming from combustion of fuels and to avoid energy crisis. One of the most encouraging of these is fuel cells using small organic molecules such as formic acid and methanol. Despite extensive research, however, there still remain many technical difficulties, some of which come from our poor understanding of the mechanism of (electro)chemical reactions taking place in fuel cells. Under these circumstances, I have studied the electrocatalytic oxidation of formic acid and methanol on Pt electrodes at the molecular scale by using surface-enhanced infrared absorption spectroscopy in the ATR mode (ATR-SEIRAS) coupled with electrochemical techniques.

Owing to the technological importance, electrocatalytic oxidation of formic acid and methanol to CO₂ on Pt in acidic media has been studied intensively for more than four decades mostly by electrochemical techniques, from which a dual pathway mechanism has been proposed and this mechanism is now generally accepted. This mechanism consists of a main reaction pathway via an active intermediate and a pathway involving a poisoning species that is oxidized to CO₂ at high potentials. Carbon monoxide was identified as the poisoning species in the 1980s, while the intermediate in the non-CO pathway is still unclear. Recent SEIRAS studies found that a formate species is adsorbed on Pt electrodes with a bridge-bonded configuration during the oxidation of formic acid and methanol in acidic media and the bridge-bonded adsorbed formate (HCOO_{ads}) was proposed to be the reactive intermediate in the non-CO pathway. In formic acid oxidation, however, there exists a claim that the bridge-bonded adsorbed formate is a site-blocking spectator and that formic acid is directly oxidized via a weakly adsorbed molecular formic acid (HCOOH) precursor. To unveil the real reaction mechanism, formic acid is investigated intensively over a wide range of pH (0-12) in the present study, because the previously proposed two pathways was expected to be distinguished by examining the pH dependence of the reaction. By combining kinetic information obtained from electrochemical measurements and structural information of adsorbed species on the electrode obtained by SEIRAS, it is shown that the both previously proposed pathways are negligible, if any, and a new pathway in which formate (HCOO⁻) is directly oxidized is

proposed. The validity of the pathway is confirmed by a mathematical kinetic modeling of the reaction. An additional important finding of the work is that the oxidation rate becomes maximal at a pH close to the pK_a of formic acid. The significance of the present study goes beyond this relatively simple electrocatalytic system because the rule that the optimal reaction conditions are predicted by pK_a of the molecule of interest is the general one applicable to other decoupled proton-electron transfer reactions, including the oxidation of methanol and formaldehyde.

The thesis is composed of 6 chapters. In Chapter 1, the motivation and importance of the present work are described together with brief summaries of preceding related work and the principle of SEIRAS. In Chapter 2, experimental details are described. Chapter 3 is devoted to oxidation of CO adsorbed on Pt, the poisoning species in the oxidation of other small organic molecules, where different oxidation behaviors in acidic and alkaline media are compared and discussed. In Chapter 4, the oxidation of formic acid/formate described before is discussed extensively. In Chapter 5, the pH dependence of methanol oxidation is discussed. On-line analysis of the electrolyte solution by HPCL shows that formaldehyde and formic acid are produced as byproducts. Through these experiments, it is shown that methanol is eventually oxidized to CO_2 in acidic and neutral media while the reaction is terminated at formate production in alkaline media. Finally, the work is summarized in Chapter 6.

Throughout the chapters, the importance of pH variation in electrocatalysis is emphasized.