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Author(s)	矢口, 桃
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学 位 論 文 内 容 の 要 旨

博士 (環境科学)

氏 名 矢 口 桃

学 位 論 文 題 名

Mechanistic study of formic acid oxidation reaction on noble metal electrodes

(貴金属電極におけるギ酸酸化反応機構に関する研究)

In this thesis, the mechanism of the electrochemical formic acid/formate oxidation reaction was systematically investigated on various noble metal electrodes. Throughout the thesis, *in-situ* surface-enhanced infrared absorption spectroscopy with the ATR configuration (ATR-SEIRAS) coupled with electrochemical techniques is used that enables direct observation of the electrified interface at a molecular scale.

Chapter 3 highlights the difference in the pK_a between the species at the interface and in the bulk solution. Systematic investigations of phosphate anion adsorption on polycrystalline Au over a wide range of pH reveal that there are two different adsorbed phosphate species. The pH-dependences of the integrated band intensity of these two adsorbed phosphate suggest that the acid-base equilibrium of these two adsorbed phosphate species appears at pH around 7. Although the acid-base equilibrium at similar pH is the one between HPO_4^{2-} and H_2PO_4^- in the bulk solution, the H/D exchange studies and DFT calculations indicate the acid-base equilibrium between the adsorbed HPO_4 and PO_4 at the interface. Together, the adsorbed phosphate species are revealed as the HPO_4 and PO_4 adsorbed via three O atoms on Au at $\text{pH} < 7$ and $\text{pH} > 8$, respectively.

Chapter 4 formulates a reaction mechanism of the electrocatalytic oxidation of formic acid/formate on polycrystalline Au, Pt and Pd. The oxidation current on all materials increases with increasing the molar fraction of formate ion in the bulk solution, suggesting that the dominant reactant is the formate ion and it is universal. A volcano-shaped pH-current correlation, peaking at pH 4-5, is found on Au and Pt, while not on Pd. At $\text{pH} < 5$, the least and most active material is Au and Pt, respectively. Pd is highly active under neutral and alkaline conditions. Surface-adsorbate profiles against applied potentials and pH reveal that the coverage of the adsorbed

bridge-bonded formate (HCOO_{B}) displays linear correlation with the oxidation current on Au, but not on Pt and Pd. With the Tafel analyses, it is revealed that HCOO_{B} is the reactive intermediate and its chemical decomposition is the rate-determining step on Au. In contrast, HCOO_{B} does not play a critical role in catalysis on Pt and Pd. The dominant route on Pt and Pd is the direct pathway via a reactive intermediate, which is not HCOO_{B} , with the rate-determining adsorption of formate ion involving single electron-transfer. In addition, it is also revealed that the observed activity decay at $\text{pH} > 5$ on Au and Pt is caused due to the specific adsorption of phosphate anions from the electrolyte that act as inhibitor. Together, it is suggested that the difference in the dominant reaction route on each material leads to the difference in the catalytic activity.

In summary, the mechanistic basis of electrochemical formic acid/formate oxidation reaction was rationally established by using a combination of ATR-SEIRAS and electrochemical techniques. Since the electrochemical formic acid/formate oxidation reaction is one of the important electrochemical reactions employed in fuel cells applications, a better understanding of the reaction mechanism can contribute to the rational design of more effective electrocatalysts. In this context, this thesis is focused on the fundamental aspects of chemical process and reaction occurring at the electrode-electrolyte interface yet related to the implementation of future renewable energy technology.