



Title	Mechanistic study of formic acid oxidation reaction on noble metal electrodes [an abstract of entire text]
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Citation	北海道大学. 博士(環境科学) 甲第12681号
Issue Date	2017-03-23
Doc URL	http://hdl.handle.net/2115/65606
Type	theses (doctoral - abstract of entire text)
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博士論文要約

貴金属電極におけるギ酸酸化反応機構に関する研究

(Mechanistic study of formic acid oxidation reaction on noble metal electrodes)

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2017年3月

Fuel cells serve as a viable candidate for renewable and sustainable energy sources, which greatly facilitates the transition to an economy with less or no CO₂ emission. Since it is the anode half-cell reaction in direct formic acid fuel cells, a promising energy source for portable electronic devices, and also a model reaction for the oxidation of small organic molecules, this PhD thesis focuses on the electrochemical formic acid/formate oxidation reaction. Formic acid is oxidized to CO₂ through the so-called dual-pathway mechanism: via a reactive intermediate or a poisoning CO intermediate, known as the direct and indirect pathways, respectively. While the activity of commonly used Pt and Pt-based catalysts is intriguing, the direct oxidation of formic acid to CO₂ is still inefficient because the CO intermediates generated through the indirect pathway blocks the active sites and reduces the overall cell efficiency. A catalyst that selectively facilitates the direct pathway is highly demanded for achieving higher fuel cell efficiency. To this end, a design process more deeply rooted in the molecular-level understanding of the direct pathway is essential. Nevertheless, the

chemical nature if the reactive intermediate in the direct pathway has been remained elusive.

Interfacial properties during catalysis provide critical insights into the reaction mechanism. Throughout this PhD thesis, a specific vibrational spectroscopy, *in-situ* surface-enhanced infrared absorption spectroscopy with the ATR configuration (ATR-SEIRAS), has been employed in selectively probing molecular dynamics during electrochemical formic acid oxidation reaction. While the conventional IR technique, infrared reflection-absorption spectroscopy (IRAS), has been largely applied to directly monitor the intermediate on catalyst surfaces, for this purpose, the ATR-SEIRAS technique is superior to the IRAS technique. To minimize the interference of the bulk solution, IRAS requires the use of a very thin-layer cell in which the electrode is separated from the prism with typically 1~10 μm , which limits mass transport between the thin-layer and the reservoir. In contrast, with the ATR-SEIRAS technique, the incident IR beam hits the back of the IR-transparent prism so that the obtained IR signal is not interfered by the bulk solution and mass transport is not restricted in the cell. Furthermore, the IR absorption by adsorbed molecules on the electrode is enhanced by the factor of approximately $10^1\sim 10^3$ due to the surface-enhanced infrared absorption effect. This effect decays with increasing the distance (r) from the electrode by the factor of $1/r^3$ so that it is significant at the electrode surface and mainly confined to the first adsorbed layer. In addition, the surface selection rule allows us to know the orientation of the adsorbed molecule because only the molecular vibrations that have transition dipole moments perpendicular to the electrode surface are detected. This PhD

this thesis shows how we can use this SEIRAS technique on a variety of different metal surfaces, which really have different surface structures and intermediate dynamics.

With a combination of *in-situ* ATR-SEIRAS and electrochemical techniques, the principal goal of this PhD thesis is to gain a better understanding of the mechanism of formic acid/formate oxidation reaction on noble metal electrodes against pH and applied potentials, especially focusing on the direct pathway, and identify the molecular origin responsible for catalytic activity. Phenomenological correlations between specific surface-bound intermediates and catalytic activity would provide key tips for novel catalyst discovery.

Before getting into the formic acid/formate oxidation reaction, the adsorption properties of phosphate anions at Au surfaces have been systematically investigated over a wide range of pH in Chapter 3. The properties of phosphate anion adsorption has big implications on (1) mechanistic studies in electrochemistry that utilize phosphate buffer solutions to maintain the electrolyte pH, (2) physiological and bio-related research fields in which phosphate buffer solutions at neutral pH are very commonly used in a cell culture, (3) developments of practical applications because phosphoric acids and phosphate buffer solutions are utilized in fuel cells and biosensors. One point that matters is its complexity arising from the polyprotic nature of phosphate anions. Although phosphate anion adsorption at electrochemical interfaces has been studied using IRAS and surface-enhanced Raman spectroscopy (SERS) techniques, the geometry and state of the adsorbed phosphate and their pH dependence have been remained unknown. IRAS has an inherent limitation associated with the thin-layer cell

configuration. Since mass transport between the thin-layer and the reservoir is severely limited and hence the adsorption of ions at the electrode surface reduced their concentration in the thin-layer, negative IR absorption bands of the species in the bulk solution are superposed on positive IR absorption bands of the species adsorbed on electrode surface. This superposition issue becomes particularly critical when the vibrational frequencies of the adsorbed species and the species in the bulk solution appear close enough to overlap and cancel each other, resulting in the distorted IR spectra. SERS measurements are limited only to the coinage metals (Au, Ag, Cu etc.). In addition, in order to get a desired surface enhancement effect, the electrode surface has to be roughened by a repeated oxidation-reduction cycles, which may complicate the electrode surface that are subjected to be measured. All these limitations can be overcome by the ATR-SEIRAS technique.

Depending on pH, two different adsorbed phosphate species are rationally identified. Corroborated by DFT calculations, the state and geometry of the adsorbed phosphate species at the Au-electrolyte interface and their speciation against pH are, for the first time, rationally demonstrated as HPO_4 and PO_4 at $\text{pH} < 6$ and $\text{pH} > 6$, respectively, highlighting the difference in the $\text{p}K_a$ of phosphate species at the interface and in the bulk solution. Specific adsorption of phosphate anions at Au surfaces is revealed to be both pH- and potential-dependent, which has a significant implication because the use of phosphate buffer solution is inevitable for the systematic survey of the mechanism of formic acid/formate oxidation reaction over a wide range of pH. Anions that are irrelevant to catalysis tend to be regarded as just chemically inert

species that do not involve in catalysis. However, it is explicitly demonstrated that anions in the electrolyte can involve in catalysis and even act as inhibitor during catalysis. Therefore, this PhD thesis raises an alarm to other research fields or applications where phosphate buffer solutions are widely employed to carefully concern the effect of phosphate anion adsorption on electrocatalysis at play.

With the aim of further pushing up the limit of current knowledge, electrochemical formic acid/formate oxidation reaction has been systematically investigated on Au, Pt and Pd electrodes across a wide range of pH in Chapter 4. A key challenge for more efficient catalyst discovery is to understand how to get rid of the indirect pathway while keeping high catalytic activity. While the intermediate in the indirect pathway has been spectroscopically well identified as CO, the intermediate in the direct pathway has been poorly understood. A viable candidate for the intermediate in the direct pathway is the formate adsorbed to metal surfaces via two oxygen atoms, the bridge-bonded formate (HCOO_B). Nevertheless, its detailed kinetic role in catalysis is remained elusive. There are mainly two different interpretations on the role of HCOO_B : either a reactive intermediate or a site-blocking spectator. Previous mechanistic studies have been mostly conducted in extremely acidic conditions until the importance of pH variation in mechanistic studies has become realized. Recently, the strong pH dependence of the reaction rate on Pt has been reported. Despite the knowledge that the catalytic activity is highest near the $\text{p}K_\text{a}$, people have not systematically looked at the surface-bound intermediates and their dynamics spectroscopically as a function of pH and over a wide range of catalytically active

material surfaces. Since the reaction bifurcates into the direct and indirect pathways on Pt and thus it is difficult to obtain mechanistic insights into the direct pathway, reactions on materials that are known to selectively facilitate the direct pathway, Au and Pd, are also examined. Phosphate buffer solutions were used as the electrolyte in order to maintain the local pH at the interface.

On all three materials, the reaction rate increases with increasing pH, in line with the augment of the molar fraction of formate ion in the bulk electrolyte, confirming that it is universal that the oxidation reaction initiates with formate ion and not formic acid molecule. Electrochemical results reveal that Au is the least active, while Pt and Pd are comparable highly active. The optimal pH is found as around 4-5 on Au and Pt, while around 8 on Pd. The observed strong pH-dependence of the formic acid oxidation reaction also suggests that fuel cells with acidic electrolyte solutions are not operated under the optimal conditions. On the basis of the SEIRAS and electrokinetic results, it is revealed on Au that the catalytic current is linearly proportional to the coverage of HCOO_B , demonstrating that the main catalytic route is HCOO_B -mediated with the rate-determining chemical decomposition of a single HCOO_B molecule. This new finding has put an end to the long-lasting controversy on the kinetic role of HCOO_B in formic acid/formate oxidation catalysis on Au surfaces. In contrast, it is revealed on Pt and Pd that the main catalytic route is not HCOO_B -mediated and the rate-determining step is suggested as the adsorption of formate ion that involves a single electron-transfer. To identify the mechanistic origin underlying catalytic activity, the contribution of the HCOO_B -mediated route to the main catalytic route is linked with the corresponding

catalytic active: a catalyst is less active if the contribution of the HCOO_B -mediated route is large (*i.e.*, Au), while a catalyst is highly active if the contribution of the HCOO_B -mediated route is small (*i.e.*, Pt and Pd). Together, the spectroscopic and kinetic basis for the mechanism of formic acid/formate oxidation reaction has been established. The proposed molecular origin responsible for catalytic activity can be applied to more efficient catalyst discovery not only towards the electrochemical formic acid/formate oxidation reaction but also towards other electrocatalytic reactions in which formic acid/formate is involved as one of the reaction intermediates.

In conclusion, this PhD thesis engages in spectroelectrochemical investigations of electrocatalytic formic acid/formate oxidation reaction on Au, Pt and Pd electrodes that provide key tips for more rational design of catalysts for fuel cells applications. While theoretical studies have established phenomenological correlations between catalytic activity and the adsorption energy of the key intermediate, this PhD thesis demonstrates that the molecular understanding of the surface-adsorbate profiles during catalysis can also be a driving force to identify the mechanistic origin behind catalytic activity. The versatility of the ATR-SEIRAS technique is explicitly emphasized in probing the molecular dynamics at the electrode-electrolyte interfaces, applicable for other technologically relevant electrocatalysis. In this context, this PhD thesis is focused on the fundamental understanding of chemical process and reaction occurring at the electrochemical interface yet related to the implementation of future renewable and sustainable energy technologies.