

学 位 論 文 題 名

In situ Investigation of Electrode/Solution Interface by
Infrared Spectroscopy

(赤外分光法による電極溶液界面のその場研究)

学位論文内容の要旨

In the present thesis, reaction mechanisms and kinetics on the electrode / solution interfaces have been investigated by *in situ* infrared (IR) spectroscopy. Quantitative analysis of the electrochemical behaviors on electrode / solution interface at a molecular level is very crucial to understand the relationship between the electrochemical reactivity and surface structure of electrode. *In situ* IR spectroscopy with high surface sensitivity is suitable for such purpose. In the present thesis, electro-oxidation of dimethyl ether (DME) on platinum electrodes and electrochemical processes on organic thin film modified electrodes have been evaluated by *in situ* IR spectroscopy.

Chapter 1 presents a general review for applications of several surface analysis techniques on investigating the electrochemical interfaces under *in situ* conditions. These techniques include scanning probe microscopy (SPM), IR spectroscopy, Raman scattering, sum frequency generation (SFG) and differential electrochemical mass spectroscopy (DEMS). Principles and selective research examples have been described. In particular, vibrational spectroscopy techniques that have been applied in probing molecular structure on electrocatalytic reactions are discussed in detail. Finally, the purpose and outline of the present thesis are given.

In Chapter 2, the electrochemistry and *in situ* IR spectroscopy have been employed to study electro-oxidation of DME, which is a promising fuel in direct fuel cells applications, on both Pt polycrystalline and single crystal electrodes in acid solution. The first positive-going potential sweep on Pt polycrystalline electrode shows a small anodic peak ($E < 0.4\text{V}$ vs. RHE) and large anodic peaks ($E > 0.5\text{V}$), corresponding to the dissociation and bulk oxidation reactions of DME molecules, respectively. *In situ* IR measurement confidently identified adsorbed $\text{CH}_3\text{OCH}_2\text{-}$ and carbon monoxide (CO) species as reaction intermediate and product for DME dissociation process at low potential region, in which DME undergoes an initial dehydrogenation and a successive CO formation reaction on electrode surface. The kinetics of DME

dissociation process has been analyzed by a consecutive reaction model based on the time-resolved IR observations. DME dissociation reaction is considered as a combination of catalytic dehydrogenation step and electrocatalytic CO formation step. In dehydrogenation process, the cleavage of C-H bond of DME molecule is activated by surface Pt atoms. In CO formation process, adsorbed $\text{CH}_3\text{OCH}_2^-$ is further electrochemically oxidized to CO, which is significantly affected by electrode potential. Influences from anion and hydrogen adsorption on the DME dissociation kinetics have also been discussed. $\text{CH}_3\text{OCH}_2^-$ and CO have also been identified in DME dissociate process on Pt single crystal electrode, especially on Pt (100) surface. Although no reaction intermediate can be observed for DME bulk oxidation process on the high potential region, possible reaction mechanisms have been discussed in comparison with those proposed in UHV system.

In Chapter 3, self-assembled monolayers (SAMs) terminated by different metal complexes, which are expected to provide novel functionalities on electrode surface, have been studied by electrochemistry and *in situ* IR measurements. *In situ* IR measurement shows that CO-ligands of the SAM terminated by tri-ruthenium clusters (Ru_3 -SAM) desorb from the SAM quickly under UV irradiation, indicating a UV-induced CO desorption process. Various ligands such as solvent, NO and tri-ruthenium complex can be further immobilized on the surface under electrochemical controls. In particular, *in situ* time-resolved IR spectra indicate that the immobilization of a tri-ruthenium complex to the SAM surface under potential control exhibits considerably high reaction rate and efficiency in comparison with previous works carried out at rest potential. By utilizing these photochemical and electrochemical features, the SAM with spatially desired architectures, has been successfully fabricated on the gold electrode surface, which has been characterized by electrochemistry, *in situ* IR and spatially resolved SFG measurements. On the other hand, the ferrocene terminated SAMs with two different chain structures, normal alkyl chain and novel norbornylogous bridge, have also been characterized by *in situ* IR measurement. Both SAMs undergo potential-induced orientation change, while SAM with a norbornylogous bridges chain show higher tolerant ability upon potential due to the rigid chain structures.

In Chapter 4, to understand the structures and functionality of biological membrane, the formation and potential-induced structural changes of lipid bilayer is investigated by *in situ* IR spectroscopy. *In situ* time-resolved IR spectra shows that lipid bilayer of dipalmitoylphosphatidylcholine (DPPC) molecules can be constructed on the gold electrode surface by potential-induced vesicle fusion. The supported DPPC bilayer undergoes a reversible structure change during potential sweep on gold surface in aqueous solution. In contrast, the lipid bilayer of dioctadecyldiammonium bromide (DODAB) molecules can be constructed at

the rest potential. The potential effect on the formation and structure change of lipid bilayer is discussed.

In Chapter 5, several functional materials have been evaluated by IR reflection absorption spectroscopy (IRAS). (1) Hydrogen bonding effect on composite thin film of porphyrin and C₆₀, as electrode materials in solar cells, has been studied by IRAS measurement. ZnP-acid and C₆₀-acid in the composite films exhibit a remarkable hydrogen-bonding interaction and also show a relatively higher performance in solar cell, indicating that the hydrogen-bonding interaction between donor and acceptor composites is important for their possible applications in solar cells. (2) The redox behavior of cofacial ruthenium porphyrin dimmers is characterized by *in situ* IRAS measurements. The IR band shifts of carbonyl groups can be used to determine the different electron-localization states during redox processes. Time-resolved IR spectra show that, the oxidation of Ru centers proceeds through the first oxidation of porphyrin rings. (3) The carbonyl-ruthenium substituted Keggin-type silicotungstate has been characterized by *in situ* IRRAS measurements in electrolyte solutions with the redox processes on Ru ions and polyoxotungstates. The IR band of carbonyl group shifts largely (90 cm⁻¹) for redox reaction of Ru ions, while shifting slightly (18 cm⁻¹) for redox reaction of polyoxotungstates, indicating different electron localization states during the redox process of ruthenium-substituted polyoxotungstates.

In Chapter 6, general conclusion and future prospect are given.

The present work demonstrates that *in situ* infrared spectroscopy is a powerful method to investigate the reaction kinetic and mechanism on the electrode / solution interface with a molecular level. The interfacial structural information is extremely useful to understand and to control the properties of functional materials in electrochemistry.

学位論文審査の要旨

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(赤外分光法による電極溶液界面のその場研究)

電気化学反応は固液界面における電子移動過程であり、燃料電池や腐食防食、機能性材料、センサーなどの様々な応用分野と密接に関係している。電気化学反応の反応速度や反応機構は固液界面における原子や分子の配列構造に強く相関し、その構造解明と制御が極めて重要である。伝統的な電気化学計測には、電流電位曲線を主に使用しているが、同じ電位で複数の反応が同時に進行する場合、電流応答を定量的に解析することが非常に困難となる場合がある。申請者は、分子構造に極めて敏感である赤外振動分光測定を、電極溶液界面における有機小分子や金属錯体自己組織化単分子膜の電気化学反応が起こるその場での計測に応用し、そこから得られた界面分子構造の情報を電気化学反応の速度論と反応機構の解析に活用し、分子レベルで電極反応の触媒反応活性と電極溶液界面分子構造の関係について研究した。

申請者は燃料電池の燃料として期待されているジメチルエーテル(CH_3OCH_3 , DME)の電気化学的酸化の反応速度論と反応機構について、白金多結晶及び白金単結晶電極を用い、その場赤外分光法により詳しく調べた。その結果、低い電位側において、白金電極表面にDME分子は電気化学的に酸化分解反応が進行し、反応中間体である $(\text{CH}_3\text{OCH}_2)_{\text{ad}}$ と $(\text{CO})_{\text{ad}}$ が電極表面に吸着されていることをその場赤外分光法により観測した。これらの反応中間体の電位依存性を詳細に解析した結果、DME分子は白金電極表面に、まず脱水素反応により $(\text{CH}_3\text{OCH}_2)_{\text{ad}}$ と生成され、さらに安定な中間体である $(\text{CO})_{\text{ad}}$ まで酸化されることで分解反応は進行することが分かった。申請者は二段階連続反応の速度論モデルを提案し、その場赤外

測定から得られた各中間体の吸着率により、各反応ステップの反応速度定数およびその電位依存性を決定した。その解析結果によると、 $(\text{CH}_3\text{OCH}_2)_{\text{ad}}$ の生成速度があまり電極電位に依存せず、白金電極表面の触媒作用により脱水素反応が進行するのに対して、 $(\text{CO})_{\text{ad}}$ の生成速度は、電極電位に強く依存し、電極触媒的な反応過程であることが分かった。さらに、種々の表面原子構造をもつ白金単結晶電極を用いた検討した結果、Pt(100)電極表面においてのみ、上記の中間体が観測されたので、上記の反応機構は主に(100)ドメン上に進行することが示唆された。これらの研究成果はDMEの燃料電池の電極触媒開発に役に立つものとする。

申請者はさらにその場赤外分光法を用い、分子構造の観点からルテニウム金属三核錯体の自己組織化単分子膜で修飾された電極表面反応の機構解明と反応制御を試みた。申請者は、自己組織化単分子膜内のルテニウム金属錯体部位の酸化還元状態を電気化学的制御により、ルテニウム金属錯体の配位能力を制御できることを見出し、種々の配位子を高い効率で電極表面に導入することに成功した。その場赤外分光測定により、電気化学的測定では全く区別がつかないか、または不安定で測定が困難である反応生成物や反応中間体を素早く捕えると同時に、それぞれの反応速度論を解析することもできた。特に光化学的制御を導入し、電気化学的制御との組み合わせにより、電極表面に金属多核錯体の異なる配位子空間構造の形成を試み、赤外分光測定と他の分光測定手法により、分子レベルでその反応過程を解析した。この研究は新規電極触媒や高感度センサーの研究開発に役に立つものとする。

こうした申請者の一連の研究は、これまでに伝統的な電気化学的測定のみでは解析が困難である電極溶液界面の反応速度論や反応機構について、その場赤外分光法を用い分子レベルで検討することができ、基礎研究のみならず、応用研究でも重要なインパクトを与えるものとする。審査委員一同は、これらの成果を高く評価し、また研究者として誠実かつ熱心であり、言葉の困難を克服し、長期にわたり研究と勉強に努力し続け、大学院博士課程における研鑽や修得単位などもあわせ、申請者が博士（環境科学）の学位を受けるのに十分な資格を有するものと判定した。