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学位論文題目 Redox Behavior of Ru Complexes Modified on Carbon
Electrode Surface and Reactivity toward Electrochemical
CO₂ Reduction

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論文内容の要旨

Functionalized surface with biological or redox active molecules has numerous applications for molecular electronics, energy conversion, chemical or biological sensors, and electrochemical catalysts. Electrochemical reactions using functionalized electrodes have led to supplementary advantages in terms of enhancement of catalytic efficiency because of minimizing the amounts of catalysts and facilitating electron transfer between catalysts and electrodes. The author's group has developed homogeneous ruthenium catalysts for electrochemical CO₂ reduction, water oxidation, and alcohol oxidation. For example, [Ru(bpy)(trpy)(CO)]²⁺ (bpy = 2,2'-bipyridine; trpy = 2,2':6',2''-terpyridine) stably works as a molecular catalyst for CO₂ reduction under the electrolysis at potentials more negative than -1.6 V (vs. Ag/Ag⁺). Self-assembled thiolate monolayers (SAMs) on a gold surface have widely been utilized as modified electrodes because of the easiness of preparation. Electrochemical potential windows of SAMs, however, are relatively narrow since thiolate group desorbs from the gold surface at potentials more negative than -1.0 V (vs. SCE) in aqueous media. Thus, there is a strict limitation of SAMs electrode for application to electrochemical reductions. Among various methodologies for optimizing of functionalized electrodes, electrografting through irreversible reduction of diazonium moiety linked to redox active groups is a feasible process to prepare modified electrodes with strong C-C bonds between redox-active molecules and surfaces of carbon electrodes. In this study, the author modified [Ru(bpy)(trpy)(X)]ⁿ⁺ on a surface of carbon electrode with C-C bonds, and investigated the redox behavior of the modified electrodes including catalytic ability for electrochemical CO₂ reduction.

In chapter 2, the framework composed of [Ru(bpy)(trpy)Cl]⁺ was immobilized on carbon electrodes with C-C bond by two methods; one is that using so called the click chemistry (click chemistry modification), in which an acetylene group bond to terpyridine of ruthenium complex is allowed to react with phenylazide linked to surfaces of carbon electrodes, and the other is electrochemical reduction of a diazonium complex [Ru(bpy)(trpy-ph-N₂)Cl]²⁺ on carbon electrodes (electrografting modification). The modified electrode prepared by the click chemistry would form mono or quasi-monolayer on surfaces of carbon electrodes. On the other hand, the modified electrode prepared by electrochemical reduction of a diazonium complex is more likely to form poly-film of the [Ru(bpy)(trpy)Cl]⁺ framework on carbon electrode surfaces. Because electrochemical reduction of a diazonium group generates reactive phenyl radicals, which initially forms a C-C bond with the surface of carbon electrode, and the subsequent generation of phenyl radicals repeatedly attacks on the top of the [Ru(bpy)(trpy-ph)Cl]²⁺ layers formed on the glassy carbon electrode. The modified electrode was relatively stable in aqueous media, since a decrease of the peak currents of the Ru^{II}/Ru^{III} redox couple of the modified electrode was less than 5 % in 4 hour. The modified carbon electrode obtained by electrochemical reduction of [Ru(bpy)(trpy-ph)Cl]⁺ showed catalytic currents for electrochemical CO₂ reduction in the cyclic voltammogram (CV) under CO₂

atmosphere. The amounts produced in the electrochemical CO₂ reduction, however, would be too small to conduct gas chromatography and electrophoresis analysis. On the other hand, high surface concentrations of the catalysts on the electrode will increase the amounts of the products in the electrochemical CO₂ reduction. Electrochemical reduction of [Ru(bpy)(trpy-ph-N₂)Cl]²⁺ on carbon electrodes did not produce high coverage of multi-layer film on the electrode due to incomplete generation of [Ru(bpy)(trpy-ph-N₂)Cl]²⁺ in situ.

In chapter 3, the author isolated a diazonium complex, [Ru(bpy)(trpy-ph-N₂)(CO)]³⁺, and modified the [Ru(bpy)(trpy)(CO)]²⁺ framework on the surface of glassy carbon electrodes with a C-C bond by electrochemical reduction of the diazonium complex, [Ru(bpy)(trpy-ph-N₂)(CO)]³⁺, and investigated the catalytic ability of the modified electrode toward electrochemical CO₂ reduction. A diazo complex, [Ru(bpy)(trpy-ph-N₂)(CO)](PF₆)₃, was obtained by the reaction of [Ru(bpy)(trpy-ph-NH₂)(CO)](PF₆)₂ with NaNO₂. Controlled potential electrolysis of [Ru(bpy)(trpy-ph-N₂)(CO)](PF₆)₃ in CH₃CN at -1.0 V using a glassy carbon electrode formed multi-layer films composed of the [Ru(bpy)(trpy)(CO)]²⁺ framework. The coverage of the complex on GC was estimated as 3.1 × 10⁻¹⁰ mol cm⁻² from the CV, which is ca. 60 times concentrated compared with that of multi-layer films composed of the [Ru(bpy)(trpy)Cl]⁺ framework on carbon electrodes. The modified electrode covered with the multi-layer [Ru(bpy)(trpy-ph)(CO)]²⁺ films also showed catalytic activity for electrochemical CO₂ reduction, and produced CO and HCOOH. However, the modified electrode rapidly lost the catalytic ability for CO₂ reduction in 0.5 hour. Scanning electron micrographs (SEM) measurements of the modified electrode indicated detachments of the multi-layer [Ru(bpy)(trpy-ph)(CO)]²⁺ films from the GC electrode after electrochemical CO₂ reduction. The stability of the Ru complexes modified electrodes was evaluated by the changes of the peak currents of the Ru^{II}/Ru^{III} redox couple. Taking into accounts that multi-layer [Ru(trpy)(trpy-ph)]²⁺ and [Ru(bpy)(trpy-ph)(CO)]²⁺ films showed the reversible Ru^{II}/Ru^{III} couple around 1.0 V and 1.66 V, respectively, the former was used to evaluate the stability of the modified electrodes.

In chapter 4, the author investigated the stability of the multi-layer [Ru(trpy)(trpy-ph)]²⁺ film generated by electrochemical reduction of a diazonium complex, [Ru(trpy)(trpy-ph-N₂)]³⁺, on a glassy carbon electrode according to a literature. The CV of the multi-layer [Ru(trpy)(trpy-ph)]²⁺ films on a carbon electrode displayed the Ru^{II}/Ru^{III} and the trpy/trpy⁻ redox couples at 0.95 V and -1.50 V, respectively. The peak currents of the Ru^{II}/Ru^{III} redox couple decreased by ca. 5 % after 50 cycle of the potential scans between 0.40 V and 1.40 V (vs. Ag/Ag⁺). On the other hand, the decrease of the peak currents of the Ru^{II}/Ru^{III} (or trpy/trpy⁻) redox couple was ca. 20 % in the similar 50 cycle of the potential scans between -0.70 V and 1.40 V. Thus, negative potential scans of the modified electrode gave more damages on the redox reactions of multi-layer [Ru(trpy)(trpy-ph)]²⁺ films compared with positive potential ones. In fact, the controlled potential electrolysis of the multi-layer [Ru(trpy)(trpy-ph)]²⁺ films under the same condition of CO₂ reduction (at -1.70 V for 0.5 h) decreased by about 50 % of the peak currents of the trpy/trpy⁻ redox couple. Moreover, existence of Ru complexes on the carbon

electrode after the electrolysis was confirmed by XPS measurements.

本論文は5章から構成されており、1章の序論では、これまでの電気化学的二酸化炭素の還元反応が紹介されており、分子性触媒を用いた均一系溶液中の電気化学的反応では、電極と触媒分子間の電子の授受が電極表面近傍の電気二重層でのみ行われるため、溶液中の大部分の触媒分子が酸化型で存在し反応に関与できず、反応の効率が悪くなる問題点を指摘している。この問題は、電極上に触媒を修飾した機能性電極を用いることで改善することが期待されるが、調製が簡便な金-硫黄修飾電極では、 -1.0 V (vs. SCE)で、金表面からチオール基の脱離が起こることから、電気化学的二酸化炭素の還元反応では触媒分子と炭素電極を炭素—炭素結合で結合させた修飾電極の有用性を記載している。

2章では、電気化学的二酸化炭素還元能を有するルテニウム錯体にエチニル基を導入し、電極表面をアジド基で修飾した機能性電極とクリックケミストリー反応を起こさせることで、錯体分子と炭素電極を炭素—炭素結合で繋いだ新規のルテニウム錯体修飾電極 Ru-Cl/CM を作成している。また、溶液中で調製したルテニウム—ジアゾニウム塩を炭素電極で電解還元し、錯体分子と炭素電極を炭素—炭素結合で修飾した電極 Ru-Cl/EM も作製をしている。さらに、二酸化炭素気流下の修飾電極 Ru-Cl/EM の電気化学的測定から、同電極は二酸化炭素還元能を持つことを見いだしたが、修飾電極上の錯体の修飾量が少なすぎたため、還元反応の生成物の同定には至らなかったことを記している。

3章では、単離精製したルテニウム—カルボニル—ジアゾニウム塩を用いて、炭素電極による電解還元で修飾電極 Ru-CO/EM を調製すると、炭素電極上の錯体分子の被覆量は、 $3.1 \times 10^{-8}\text{ mol cm}^{-2}$ に達することを明らかにしている。その値は X 線構造解析で決定した錯体分子の最密充填から予想される錯体膜の被覆量の約 180 層程度になることを明らかにしている。また、電極上に修飾したルテニウム錯体の反射吸収スペクトルからルテニウム—カルボニル錯体の存在を同定している。さらに、同修飾電極 Ru-CO/EM を用いて二酸化炭素の電気化学的還元反応を行い、生成物として一酸化炭素およびギ酸の定量を行い、修飾電極 Ru-CO/EM が電気化学的二酸化炭素還元反応に触媒作用を示すことを明らかにしている。修飾電極 Ru-CO/EM による二酸化炭素の生成物量は、均一系での触媒反応に比べると劣るが、反応初期では触媒分子当たりの反応効率は 20 倍程度改善されていることも明らかにしている。

4章では、修飾電極 Ru-CO/EM による電気化学的二酸化炭素還元反応での耐久性を述べている。二酸化炭素還元反応前後の修飾電極表面の SEM 観察により、触媒能の低下は、錯体膜の脱離であることを示している。さらに、幅広い電位に対して安定な類似のルテニウム錯体膜修飾電極を調製し、その耐久性は層の厚さよりは、負側の電位に対して安定性が低いことを見いだしている。また、CV、SEM、および XPS 測定から錯体膜の脱離はルテニウムと配位子との結合開裂による錯体膜の分解であることを示唆している。

5章では、本論文の総括がなされており、炭素電極表面に機能性金属錯体を炭素—炭素結合で結合させた修飾電極は、二酸化炭素還元に対して触媒能を有することから、錯体膜の脱離を抑えて耐久性を改善することで、大きな発展があり得ることを指摘している。

以上の内容で博士論文は構成されており、炭素—炭素結合で繋いだ機能性電極を用いて二酸化炭素の電気化学的還元反応を行った点で独創性があり、一般的な電気化学

的触媒反応の研究に対して新たな方向性を示した点で評価される。また、本論文の一部は既に査読付きの国際雑誌に掲載されており、語学力に関しても学位授与に十分なレベルに達していると判断された。以上より、本論文は博士（理学）の学位授与に値すると審査委員全員一致で判断した。