



Title	Spectroelectrochemical Study of Electron Transfer Steps at ITO Electrode Modified by Molecular Layer with Viologen Moieties with and without Pt Complexes [an abstract of dissertation and a summary of dissertation review]
Author(s)	Kurniawan, Cepi
Citation	北海道大学. 博士(理学) 甲第12318号
Issue Date	2016-03-24
Doc URL	http://hdl.handle.net/2115/61837
Rights(URL)	http://creativecommons.org/licenses/by-nc-sa/2.1/jp/
Type	theses (doctoral - abstract and summary of review)
Additional Information	There are other files related to this item in HUSCAP. Check the above URL.
File Information	Cepi_Kurniawan_abstract.pdf (論文内容の要旨)



[Instructions for use](#)

学位論文内容の要旨

博士の専攻分野の名称 博士 (理学) 氏名 セピ クルニアワン

学位論文題名

Spectroelectrochemical Study of Electron Transfer Steps at ITO Electrode Modified by Molecular Layer with Viologen Moieties with and without Pt Complexes

(ITO 電極上に構築したビオロゲン分子層における白金錯体での電子移動過程の分光電気化学測定による研究 —白金錯体存在の効果—)

The development of highly efficient catalysts for energy conversion should have a significant impact on the future energy systems. For example, generation of hydrogen from electricity requires the reduction of two protons by two electrons to form H₂. Platinum metal efficiently catalyzes this reaction, but its high cost and low abundance require effective use of Pt atoms. The utilization of molecular catalyst based on Pt complexes is one of the best solutions for this issue. The immobilization of a molecular catalyst onto a solid surface maintaining its catalytic activity is one of the major challenges in achieving highly efficient catalyst. Preparation and characterization of various metal complexes have been reported not only to achieve a well-ordered reaction site but also for the detailed understanding of reaction mechanism. The previous report demonstrated that Pt-complex incorporated within viologen layers on silicon acts as an efficient electrocatalyst for hydrogen evolution reaction (HER). The Pt(II) state was not changed into metallic state and Pt aggregation was not observed after HER, suggesting that HER is catalyzed by Pt complex-based “confined molecular catalyst”. It was also suggested that the viologen moiety act as an electron transfer mediator during HER. However, there is no direct evidence for an electron to be transferred through viologen moiety or directly transferred from electrode to Pt-complex. To design better confined molecular catalyst system, it is important to clarify how electron is transferred through molecular layer.

In the present thesis, in situ UV-Vis spectroelectrochemistry was used to monitor electrogenerated intermediate during HER catalyzed by Pt complex incorporated within viologen layers, which are constructed on indium tin oxide (ITO), a transparent electrode, so that electron transfer steps are directly probed.

The structure of the thesis is as follows:

Chapter 1 is the introduction to the thesis, in which molecular catalyst, viologen, ITO functionalization,

and characterization techniques of modified electrode are briefly described.

In Chapter 2, the experimental details including materials, sample preparation, experimental setups, and measurements are provided.

In Chapter 3, the construction of viologen on ITO by surface coupling reactions are discussed. The first step is the attachment of bromoalkylsilane to ITO surface by silane coupling reaction. Then viologen layers are constructed by subsequent reaction with bipyridine and bromobutane. Reaction time dependencies of surface coverage of silane coupling reaction and viologen formation are followed by IR and electrochemical response.

In Chapter 4, viologen layers constructed on ITO substrates are characterized both by cyclic voltammetry (CV) and chronoamperometry (CA) coupled with UV-Vis absorbance spectroscopy. The CVs and absorbance spectra of methyl viologen (MV) in solution are used as a reference since the spectroelectrochemical properties of MV are well-known. Two redox peak was observed in CVs of viologen monolayer on ITO (1LV-ITO) corresponding to the formation of radical cation ($V^{\bullet+}$) and neutral viologen (V^0) species centered at -0.40 and -0.82 V, respectively. The existence of different viologen state was also observed in steady state UV-Vis spectra of 1LV-ITO, depending on the potential. The transient absorbance spectra obtained upon potential step show that $V^{\bullet+}$ and V^0 species are formed and disappeared upon potential step from 0 V to potentials more negative than the corresponding redox potentials and from the negative potentials to 0 V, respectively, within ca. 200 μ s.

In Chapter 5, the role of viologen moiety during HER catalyzed by Pt complex incorporated in viologen layer is examined both by CV and CA coupled with UV-Vis absorbance spectroscopy. After Pt incorporation in viologen layers, the peaks related to the viologen moieties are not observed in CV and the large cathodic current due to HER flows. The cathodic currents are dependent on number of viologen layers, i.e., the amount of Pt complex. No peaks related to the viologen species are observed in the steady state UV-Vis spectra. However, the transient absorbance spectra obtained upon the potential step to the potentials more negative than the reversible hydrogen electrode potential shows the presence of $V^{\bullet+}$. The absorbance due to $V^{\bullet+}$ decays within ca. 1 ms, confirming the existence of $V^{\bullet+}$ species as an intermediate. These results show that electron is transferred first to viologen to form $V^{\bullet+}$ species and then transferred to Pt complex, which catalyzes HER.

In Chapter 6, the most important conclusions are summarized and a brief prospect for the future work.