



Laboratory for Analytical Chemistry: Molecular Electrochemistry, Electroanalytical Chemistry and Interfacial Chemistry

Akio Ichimura (Professor)

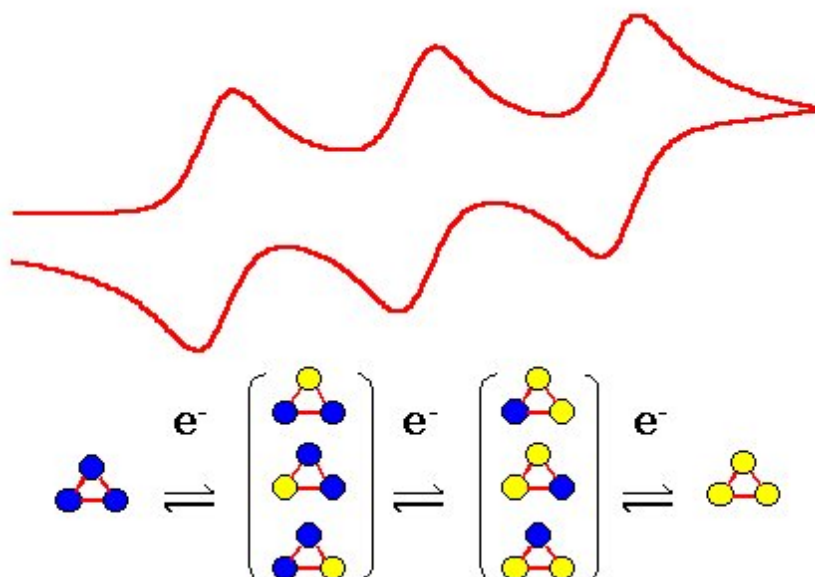
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1. Current Research and Principal Research Interests

My research interests are primarily in the area of molecular electrochemistry including electroanalytical chemistry. Many of the projects are interdisciplinary in nature and involve collaboration with scientists in inorganic chemistry, physical chemistry, and the environmental sciences. Some of our current projects are listed below.

Redox properties of multinuclear metal complexes. An electron is the simplest chemical reagent. We have increasingly recognized the role of electron-transfer (ET) reactions in the laboratory and in nature. Our research focuses sharply on the ET properties of multinuclear metal complexes, with a primary aim of understanding how the structure and reactivity of the complex is changed by addition or removal of electrons. We use mainly voltammetry experiments to realize the redox mechanism. Many of our electrochemical experiments are properly interfaced with spectroscopic instruments that enable us to use optical spectroscopy and magnetic resonance spectroscopies to characterize ET products and intermediates. We have been developing new and universally applicable *in-situ* spectroelectrochemical techniques in uv.-vis.-near IR region to characterize stable mixed-valence states that are formed in each one-electron redox process of multinuclear complexes having multi-redox metal centers as well as to detect intermediates in the redox processes.

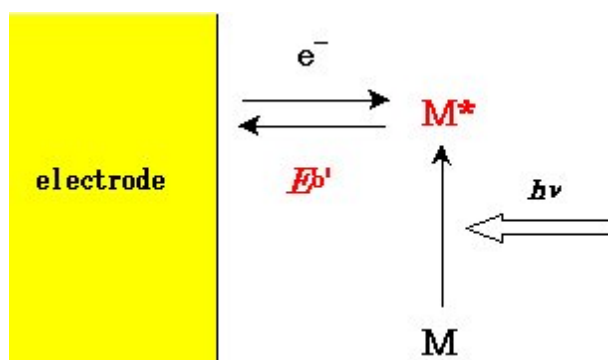


Three stepwise one-electron redox processes and two mixed-valence states



In-situ spectroelectrochemical cell consisting of an optically transparent thin-layer electrode, a mirror and a two-way optical fiber

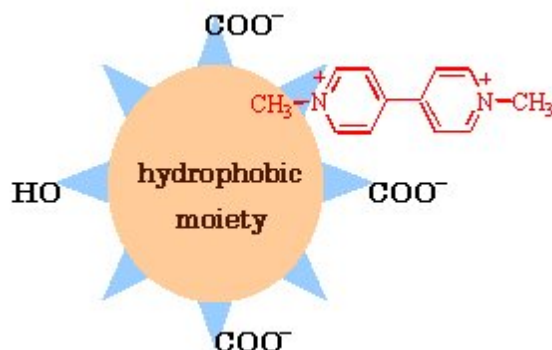
Direct voltammetric measurements of excited state redox potentials. Excited state species are more easily oxidized and reduced than the corresponding ground state species. There have been many studies of photoinduced electron transfer reactions utilizing the strong reducing and oxidizing ability of the excited state species. We have so far estimated redox potentials of excited state species using the ground state redox potentials and the energy gap between the 0th vibrational levels of the ground and excited states. The estimated values, however, contain uncertainties of 100 mV or more. Now we fully recognize that direct measurements of the excited state redox potentials by a precise voltammetric method are of great value for the studies of photoinduced electron transfer reactions. We now choose porphyrins and metalloporphyrins as the target compounds, which have been widely used for the construction of artificially photosynthetic and photoenergy conversion systems.



Electroanalytical chemistry in nonaqueous solvents. Electrochemical use of nonaqueous solvents has spread from laboratory experiments to the industrial field including lithium secondary batteries. Many of the ET reactions in biological systems take place at a relatively hydrophobic reaction field. We are studying nonaqueous electroanalytical chemistry to reveal fundamentally important aspects of the redox reactions in nonaqueous and pseudo-nonaqueous electrolyte solutions. Precise measurements of redox potentials by voltammetric techniques provide us better understanding of solvation of redox active species. Furthermore, we are developing a universal reference electrode independent of solvent properties and estimating its absolute potential. Using this reference electrode, we can correctly compare redox potentials which are measured under different nonaqueous solution conditions.

Chemical characterization of humic acid. Humic acid is a fascinating substance that can have profound environmental consequences. The ability to form complexes with toxic metal ions and organic agricultural chemicals has been recognized by researchers interested in their migration and mobilization. The micellar properties also show the ability to play important roles in the

solubilization and transport of hydrophobic substances. We are applying electroanalytical techniques involving ion-transfer voltammetry between immiscible aqueous and organic solutions to chemical characterization of humic acid, in connection with redox reactivity, hydrophobicity, and ionic exchange ability. We are attempting to quantitatively interpret the interaction of chemical substances of environmental interest with humic acid.



Electrostatic and hydrophobic interaction of methyl viologen (used for a pesticide) and humic acid

2. Selected Publications

1. "Redox Chemistry of Dinuclear Molybdenum Dithiolene Complexes. Interconversion of the Bridging Disulfide and Sulfides", Y. Miki, H. Takagi, A. Ichimura, H. Akashi and T. Shibahara, *Chem. Lett.*, 482-483 (2002).
2. "Unusual Oxidation of Oxo-Peroxomolybdenum(VI) Tetramesitylporphyrin Giving Molybdenum(V) Porphyrin and Dioxygen", T. Fujihara, K. Myougan, A. Ichimura, Y. Sasaki and T. Imamura, *Chem. Lett.*, 178-179 (2001).
3. "Oxo- and Alkoxo-Bridged Dimeric Molybdenum(III) Ethylenediamine Complexes", S. Kiyoda, H. Akashi, A. Ichimura and T. Shibahara, *Chem. Lett.*, 1422-1423 (2000).
4. "Brominated Trihalomethane Formation in Halogenation of Humic Acid in the Coexistence of Hypochlorite and Hypobromite ions", K. Ichihashi, K. Teranishi and A. Ichimura, *Water Res.*, **33**, 477-483 (1999).
5. "Feasible Attachment of a Dinuclear Ruthenium Complex to Gold Electrode Surfaces. A Screening Method to Find Functional Electrodes", H. Takagi, A. Ichimura, T. Yano, I. Kinoshita, K. Isobe, M. Abe, Y. Sasaki, Y. Mikata, T. Tanase, N. Takeshita, C. Inoue, Y. Kimura, S. Endo, K. Tamura and S. Yano, *Electrochemistry*, **67**, 1192-1193 (1999).
6. "Perpendicularly Arranged Ruthenium Porphyrin Dimers and Trimers", K. Funatsu, A. Kimura, T. Imamura, A. Ichimura and Y. Sasaki, *Inorg. Chem.*, **36**, 1625-1635 (1997).
7. "Syntheses and Electrochemistry of Incomplete Cubane-Type Clusters with M_3S_4 Cores (M=Mo,W). X-ray Structures of $[W_3S_4(H_2O)_9](CH_3C_6H_4SO_3)_4 \cdot 9H_2O$, $Na_2[W_3S_4(Hnta)_3] \cdot 5H_2O$, and $(bpyH)_5[W_3S_4(NCS)_9] \cdot 3H_2O$ ", T. Shibahara, M. Yamasaki, G. Sakane, K. Minami, T. Yabuki and A. Ichimura, *Inorg. Chem.*, **31**, 640-647 (1992).

8. "The Dinuclear Palladium(II) Complex of Pyridine-2-thiol. Synthesis, Structure, and Electrochemistry", K. Umakoshi, A. Ichimura, I. Kinoshita, and S. Ooi, *Inorg. Chem.*, **29**, 4005-4010 (1990).

9. "Technetium Electrochemistry. 2. Electrochemical and Spectroelectrochemical Studies of the Bis(tertiary phosphine) (D) Complexes $\text{trans-}[\text{Tc}^{\text{III}}\text{D}_2\text{X}_2]^+$ (X = Cl, Br) and $[\text{Tc}^{\text{I}}\text{D}_3]^+$ ", A. Ichimura, W. R. Heineman, J.-L. Vanderheyden and E. Deutsch, *Inorg. Chem.*, **23**, 1272-1278 (1984).

10. "Reactivity of Coordinated Disulfides. 1. Nucleophilic Cleavage of the Sulfur-Sulfur Bond", A. Ichimura, D. L. Nasco and E. Deutsch, *J. Am. Chem. Soc.*, **105**, 844-850 (1983).

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専 攻 化学

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職 歴	昭和46年4月 から 平成2年3月 まで	大阪市立大学	理学部	助手
	平成2年4月 から 平成4年9月 まで	大阪市立大学	理学部	講師
	平成4年10月 から 平成9年3月 まで	大阪市立大学	理学部	助教授
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主 な 役 職 研 究 科 長 (平成20年7月 ~ 平成22年3月)

学 位 理 学 博 士 (昭 和 54 年 9 月 27 日 大 阪 市 立 大 学)