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＜招待講演＞

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「アジアへ広がる電気分析化学の真髄」

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K1 Structure and reactions at the liquid-liquid interface of ionic liquids

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Ionic liquids (ILs) are promising materials for electrochemical devices. To maximize the performance of such devices, it is important to understand and control the molecular-level structure of ILs at the electrochemical interfaces. Several unique features have been found at the IL interfaces. The most prominent one would be the spontaneous formation of ionic multilayers at the IL interfaces, revealed using interface-selective techniques such as x-ray reflectometry (XR) [1-4], neutron reflectometry (NR) [5], and molecular dynamics (MD) simulation [6,7]. From the electrochemical point of view, the behavior of ILs in the electrical double layer (EDL) is also unique due to excluded-volume and local-coulombic interactions between neighboring ions, leading to camel-shape potential dependence of the capacitance confirmed by NR [5], MD [7], and zero-frequency capacitance measurements [8-10]. In this presentation, I will focus on the structure at the liquid/liquid electrochemical interface of ILs, such as the IL/water, IL/mercury, and IL/oil interface. I will also introduce an application of such soft interfaces of ILs as formation sites for unique nanostructures of metals such as Au [11-14], Pt [15], and Pd [14,16].

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K2 Hydrophobicity and Pseudo-Capacitance Control of Polyaniline for Solid-Contact Ion-Sensing

Yu-Fu Chen, Yi-Min Wu, and Lin-Chi Chen* (Department of Biomechatronics Engineering, National Taiwan University, Taipei, Taiwan)

Introduction: Solid-contact (SC) ion-sensing is an emerging solid-state ion sensor technology, which uses an electroactive SC layer (*e.g.*, a conducting polymer) to replace the bulky internal reference solution in an ion-selective electrode (ISE) and eliminates the use of silver electrodes. Thus, it has the advantages of size, cost, fabrication flexibility and miniaturization. In principle, an SC layer conducts ion-to-electron transduction (IET) to convert the concentration of a target ion (detected by an ion-selective membrane, ISM) into an electrical potential signal (measured at the electrode) through a field effect. Moreover, an ideal SC layer must be able to resist the permeation of a water layer from the sample solution to avoid interfering ions. Hence, an SC layer with high hydrophobicity and pseudo-capacitance is favored. Here, we report a novel idea for attaining high hydrophobicity and pseudo-capacitance of a polyaniline (PANI) SC layer at the same time via deposition control and demonstrate its benefits for SC ion-sensing.

Experimental: The PANI SC layer was electrodeposited on a screen-printed carbon electrode (SPCE) in a monomer bath via cyclic voltammetry (CV). The CV deposition rate (mV/s) was tuned to control the film thickness and surface morphology of PANI. SEM, contact angle (CA), and electrochemical measurements were done to characterize the PANI layers grown at different CV deposition rates. The SC-ISEs of Na⁺, K⁺, Cl⁻, and Ca²⁺ were fabricated with different PANI SC layers and corresponding ISMs coated atop. The sensing performance factors of the SC-ISEs were then studied with respect to the hydrophobicity and pseudo-capacitance of PANI.

Results and discussion: The CV deposition is an effective method to tune the hydrophobicity and pseudo-capacitance of a PANI SC layer. When the CV deposition rate is slower than 20 mV/s, a thick film with a nano-fibrous surface is formed so that the quasi-superhydrophobicity (CA = 138°) and high pseudo-capacitance (up to 4.61 mF) are attained. By contrast, the film grown faster (with the rate > 50 mV/s) has a decreased CA (< 85°) and capacitance value (< 0.95 mF). Therefore, the SC-ISEs fabricated with the PANI layer grown slower show enhanced performance factors, including high sensitivity, high water layer resistance, low potential drift, and low detection limit as compared to those with the PANI layer grown faster.

K3 Nanoscale Electrochemical Imaging of Single Nuclear Pore Complexes

Shigeru Amemiya (Department of Chemistry, University of Pittsburgh, Pennsylvania, USA)

Introduction: In this presentation, the application of nanoscale scanning electrochemical microscopy (SECM) for the imaging of single nuclear pore complexes (NPCs) is discussed. The NPC solely transports both small molecules and macromolecules between the nucleus and cytoplasm of a eukaryotic cell to play imperative biological and biomedical roles. The NPC is crucial to the regulation of gene expression and is linked to many human diseases including cancers and neuronal diseases. In this work, we enable SECM permeability imaging of single NPCs with a spatial resolution of ~30 nm. The spatial resolution is high enough to distinguish “plugged” and “unplugged” states of NPC. We determine the impermeability of “plugged” NPC to unambiguously conclude that plugs are not permeable central transporters of the NPC but are impermeable cargos, e.g., ribonucleoproteins, captured during translocation through the NPC. These two origins have been debated for decades because they cannot be distinguished by structural imaging of plugged NPCs using cryoelectron tomography and atomic force microscopy.

Experimental: Permeability imaging by nanoscale SECM was established for single solid-state nanopores by our group^{1,2} and applied for single NPCs in this work. Nanopipet-supported interfaces between two immiscible electrolyte solutions were employed as nanotips with diameters of ~30 nm. A homebuilt SECM instrument with an isothermal chamber was used to image the nuclear envelope of the *Xenopus* oocyte nucleus in buffer solutions after the nuclear envelope was spread on a glass plate and fixed by glutaraldehyde.

Results and discussion: SECM images of individual NPCs were obtained successfully by scanning ~30 nm-diameter nanopipet tips to electrochemically detect small probe ions, i.e., tetrabutylammonium. The tip current decreased as the tip moved over each NPC, which hindered the diffusion of probe ions to the tip. The density of NPCs in the SECM images agreed with that determined by AFM. The cross-sections of SECM images of plugged NPCs fitted well with finite element simulation of an impermeable pore to indicate that the plug is a captured macromolecule, which blocks the NPC, not a transporter, which is highly permeable to small probe ions.³

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K4 More than a Liquid Junction: Effect of Stirring, Flow Rate, and Inward and Outward Electrolyte Diffusion on Reference Electrodes with Nanopore and Capillary Junctions

Evan L. Anderson, Blair K. Trout, and Philippe Bühlmann (Department of Chemistry, University of Minnesota, Minneapolis, USA)

Introduction: As electroanalytical sensors based on novel materials have reached exceptional stabilities with drifts in the low $\mu\text{V}/\text{h}$ range and long-term and calibration-free measurements gain more and more attention, reference electrode designs that used to be satisfactory for most users do not satisfy the needs of new challenging applications.

Nanoporous Glass Frits: The Henderson equation is usually used to calculate liquid junction potentials between miscible electrolyte solutions. However, the potentials of reference electrodes that comprise an electrolyte-filled nanoporous glass frit may also be affected by charge screening. When the Debye length approaches or surpasses that of the glass pore diameter, reference potentials depend on the composition of the bridge electrolyte, the pore size of the frit, and the concentration of electrolyte in the sample. Stirring of samples may alter the reference potential as it affects the electrolyte concentration in the section of the nanoporous glass frits that is facing the sample solution. When the flow rate of bridge electrolyte into the sample is small, convective mass transport of sample into the nanoporous frit occurs. The depth of penetration into the frits is only a few nanometers but—despite the use of concentrated salt bridges—this is enough to affect the extent of electrostatic screening when samples of low ionic strength are measured. Importantly, because flow through nanoporous frits is slow, mass transport through such frits is dominated by diffusion. Consequently, reference electrode frits with low flow rates become contaminated with sample components.

Capillary Junctions: Commonly used reference electrodes with free-flowing junctions often suffer either from experimental difficulties in assuring a minimum flow rate or from excessive flow rates that require frequent replenishing of bridge electrolyte. To this end, we developed a reference electrode which contains a concentrated electrolyte that contacts samples through a $10.2\ \mu\text{m}$ capillary. By applying a minimal pressure of $10.0\ \text{kPa}$, a flow rate of $100\ \text{nL}/\text{h}$ is achieved. This maintains a constant liquid junction potential, as evidenced by a potential stability of $0.7 \pm 4.8\ \mu\text{V}/\text{h}$.

K5 Mechanism of Emulsion Formation in an Organic Solvent in the Presence of Hydrated Ions

○ Vladimír Mareček

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A two-electrode cell comprising a liquid/liquid interface has been used to study the water clusters formation in the organic solvent phase following the tetraalkylammonium chloride (TAACl) transport from the aqueous phase. The partition of chloride ions is controlled by the interfacial potential difference induced by the distribution of a common TAA⁺ ions in both phases. The transfer of hydrated chloride ions is accompanied by the transfer of TAA⁺ ions which concentration

at the aqueous side of the interface can be monitored by the open circuit potential (OCP) measurement. The amount of TAACl transported at a given potential to the organic phase exceeds amount of TAACl which could be dissolved. It results in the water clusters formation in the organic solvent phase. The presented mechanism of this process involves an additional water transport to the organic phase completing dissolved water consumed by the water clusters formation. At higher concentration of TAACl in the aqueous phase this process leads to the formation of emulsion in the organic phase.

The analysis of OCP transients lead to the following mechanism of the water clusters formation. In the first step the TAACl is transported to the organic phase to fulfill the partition of chloride anions. In the next step the chloride ions dissolved in the organic phase form the water clusters utilizing the initial presence of water in the organic phase and water transported by chloride ions. The expended water in the organic phase is replenish by its diffusion from the aqueous phase to fulfill the equilibrium. At any distance from the interface the partition of TAACl between the organic phase and the water clusters must be fulfilled. It can be expected that the partition of TAACl will be influenced by the water cluster size.

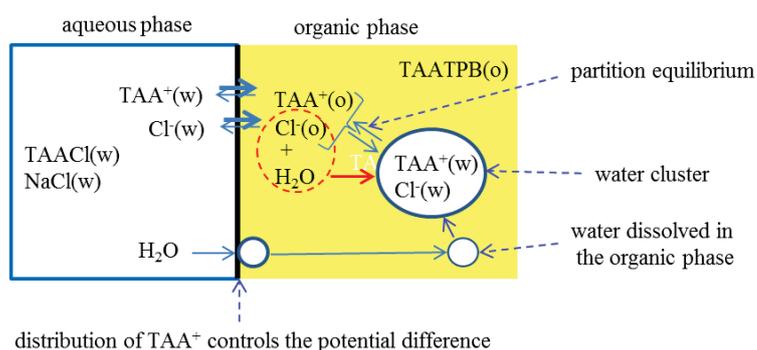


Figure 1: A cartoon depiction of the mechanism of water clusters formation at a water/organic solvent interface associated with the superfluos extraction of TAACl into the organic phase.

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K6 Extracellular Electron Transfer: How about Different Mechanisms Run in Parallel?

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Introduction:

In order to reduce solid-state electron acceptor, microorganisms need to carry out extracellular electron transfer (EET) mechanisms to facilitate respiration. Bacterial nanowires are specialized appendages that provide a larger surface area and a possible way for non-motile cells to attach to the desired solid-state electron acceptors over a long distance. In addition to bacterial nanowires, it has been found that some bacteria are capable of secreting flavins that can boost current generation. It is undoubted that EET capable bacteria are versatile, which is possibly carry out multi mechanisms simultaneously to implement a smooth respiration with solid-state electron acceptor. Since it is a booming era for EET study, in this talk, I will collect the results people have found in these year to point out that there are still something unclear about EET-capable microorganisms.

Experimental:

Atomic force microscopy was used to explore bacterial nanowires, and cyclic voltammetry was used to understand the electrochemical characteristics of microbial electrodes.

Results and discussion:

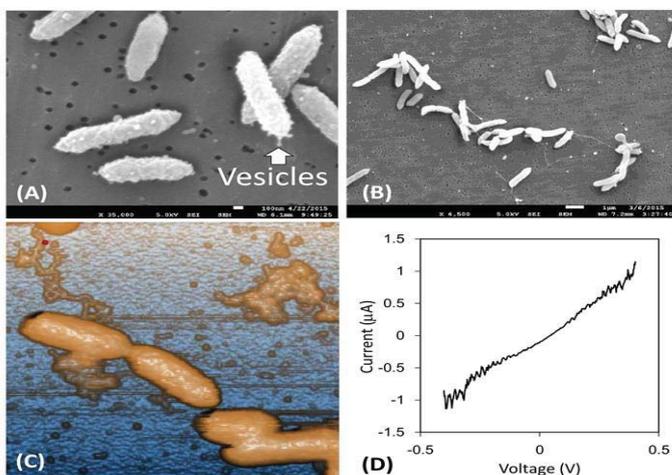


Figure. *Geobacter sulfurreducens* PCA growth pattern in a chemostat (A) a vesicle-like structure formation; (B) a bacterial nanowire structure observed; (C) bacterial nanowire observation using contact atomic force microscopy; (D) conductance measurement of the bacterial nanowire.

K7 Carbon Nanotube Platform for Bioelectrochemistry

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Carbon nanotubes have some advantages as an electrode such as high electric conductivity and high surface area. On the other hand, there are some disadvantages such as defects (carbon oxidized functional group), impurity compounds and bundled structure, which would relate to a lack of repeatability. I would introduce my previous researches [1] and discuss the advantage and disadvantage of carbon nanotubes in bioelectrochemistry.

1. Preparation of single-walled carbon nanotube modified electrode

We synthesized single-walled carbon nanotubes (SWCNTs) ourselves because of repeatability. The SWCNTs were directly synthesized on a metal and a carbon surface by using CVD method. For bioelectrochemistry, the SWCNTs were synthesized on a gold electrode. The SWCNT synthesis was perfectly controlled the synthesis conditions, especially humidity, which produces exactly same SWCNTs each synthesis in the viewpoint of the defect, diameter and bundled structure of the SWCNTs. Our synthesized SWCNTs were 1~2 nm in a diameter, and very few defect from results of TEM and Raman spectroscopy.

2. Bioelectrochemistry at SWCNT

Cytochrome c: Cytochrome c is one of the typical standard redox protein to understand the surface condition. The redox reaction of cytochrome c was not observed at as-grown, high-quality SWCNTs. Well-defined diffusion-controlled redox wave of cytochrome c was observed at SWCNTs with oxidized carbon species such as C-O, C=O and O-C=O induced by UV-ozone treatment. The redox reaction was inhibited immediately by SWCNT surface contamination when the SWCNT was exposed under atmosphere.

NADH: Two main oxidation peaks of β -nicotinamide dinucleotide (NADH) at the SWCNTs were due to adsorbed and diffused species, which was strongly related to the SWCNT surface defect.

Laccase: The interface between laccase and SWCNTs was improved by modification with the steroid biosurfactant, especially sodium cholate, resulting in obtaining large catalytic O₂ reduction current at starting from a potential very close to the redox equilibrium potential of the oxygen/water couple.

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K8 Improvement of optical properties for cadmium-free quantum dot fluorophores

Taro Uematsu (Graduate School of Engineering, Osaka University, Japan)

Introduction: Semiconductor nanoparticles (quantum dots, QDs) are photoluminescent (PL) materials represented by cadmium selenide (CdSe), and they have recently been applied to the color conversion materials used in display devices due to prominent monochromaticity of their PL. Unfortunately, the use of cadmium compounds is no longer allowed for commercial products and alternative materials have been proposed. Silver indium sulfide (AgInS_2) QDs are one of the cadmium-free candidates that our group have contributed to development, but the lack of PL monochromaticity deriving from multiple defect levels was the largest problem. Recently, we have successfully generated a narrow band-edge PL from the AgInS_2 QDs and solved the problem over ten years. The key factor for the observation of band-edge emission was surface passivation by III-VI semiconductors, indium and gallium sulfides (InS_x and GaS_x) to form core/shell structure. Unlike the famous zinc sulfide shell, III-VI semiconductor shells had an amorphous nature that is unusual as QDs' shell. Probably, the amorphous nature helps to create a defect-free interface between the AgInS_2 cores, as well as a better matching of valences (In^{3+} vs. Zn^{2+}) at the interface. More recently, we attempted to improve the AgInS_2 cores that are as important as GaS_x shells. Synthesis of ternary compound semiconductor nanoparticle materials are more difficult than binary materials because two kinds of metals with different reactivity are involved in the reaction. A dropwise addition of reactive sulfur precursors into a preheated metal solution created monodispersed AgInS_2 nanoparticles by the two-step reaction through Ag_2S nanoparticle intermediates.

Experimental: Silver acetate and indium acetate was mixed with oleylamine and a small amount of 1-dodecanethiol was added to the mixture to stabilize Ag^+ species. The solution was heated to 140°C in Ar and an oleylamine solution of 1,3-dimethylthiourea was slowly injected by using a syringe pump.

Results and discussion: Figure 1 shows PL spectra for AgInS_2 cores having tetragonal and orthorhombic phases; the tetragonal cores emitted more strongly than the orthorhombic cores. These tendencies have not been changed after the formation of GaS_x shells, where tetragonal $\text{AgInS}_2/\text{GaS}_x$ QDs showed narrow band-edge emission (fwhm = 31 nm) which is still narrower than our recent report.

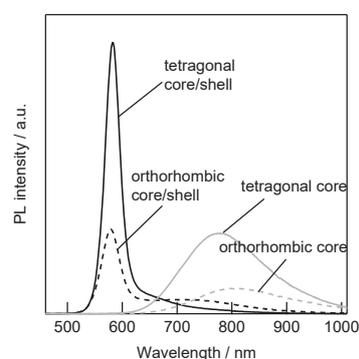


Figure 1. PL spectra for tetragonal- and orthorhombic AgInS_2 core QDs and the corresponding $\text{AgInS}_2/\text{GaS}_x$ core/shell QDs (ex = 450 nm).

I 1 Electrochemical quantitative evaluation of bacterial activity

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Japan)

Introduction: A better understanding of the biological functions of microorganism is required to reduce their threats and increase their usefulness. Therefore, an importance of real-time evaluation of bacterial activity increase for various purposes such as hygiene management, development of antibacterial agents, and effective utilization of bacterial resources.¹ This necessitates a quantitative assessment of metabolic processes, including growth and respiration. Here we would like to introduce the development of electrochemical methods for assessing bacterial activity.

Results and discussion: Electrochemical detection of viable bacterial cells was performed using cell membrane permeable electron mediator and redox active pigment. *Shewanella oneidensis* MR-1 transfers electrons generated within the cell to the extracellular environment via the cytochrome complex in the inner/outer membranes and is one of the most useful bacteria for the recovery of metals, treatment of wastewater, and preparation of microbial fuel cells. By using potentiometric measurements, we have examined intracellular electron generation in bacterial suspensions of *S. oneidensis* supplemented with different carbon sources or ferricyanide, which was almost completely reduced to ferrocyanide during the incubation without affecting bacterial cell viability.² On the other hand, a tetrazolium salt (MTT), which was converted to an insoluble reduction form (formazan) through the respiration of microbial cells.³ The insolubility of this formazan was effectively exploited as a surface-confined redox event. The electrochemical detection of formazan was effectively coupled with the thermal lysis of microbes. The sensitivity of the present technique is up to 10,000-fold higher than that of MTT colorimetry and requires an incubation time of only 1 h, which is approximately 1/4 of that required for other metabolism-based techniques. Furthermore, the measurement of the reduction current of dissolved oxygen provides an effective mean for assessing the respiratory activity of bacteria in suspension.⁴

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I2 **Selective retrieval of single cells with a secretory ability of a target antibody in cell-based arrays using a microwell array electrode**

Tomoyuki Yasukawa, Misaki Hata, Masato Suzuki (Graduate School of Material Science, University of Hyogo, Ako, Japan)

Introduction: This study demonstrates proposed manipulation techniques for retrieving target hybridomas from cell-based arrays selectively by the novel device with microwell arrays that employs dielectrophoresis (DEP) after hybridomas with the secretion of antibodies were discriminated. Individual cells trapped in microwells can be selectively retrieved by regulating the generation of electric fields in individual microwells. The development of series of these techniques could be useful to recover hybridomas producing antibodies with high affinity in large populations of cells without repeated steps of a culture and a limiting serial-dilution.

Experimental: The device comprises the upper substrate with indium-tin-oxide (ITO) microband electrodes and the lower substrate with microwell arrays on ITO microband electrodes. Hybridomas producing an anti-rabbit serum albumin (RSA) antibody suspended in the DEP medium were introduced in the channel. AC signal (3 MHz, 2 Vpp) was then applied to the upper and lower microband electrodes with opposite phase to form a cell-based array. Anti-RSA antibodies secreted from hybridomas trapped in the microwells were captured by RSA immobilized on the electrodes. Cell arrays were then treated with anti-mouse IgG antibody conjugated with Alexa 488 (a secondary antibody). Thereafter, a repulsive force of negative dielectrophoresis (n-DEP) was employed to retrieve the target hybridomas from the microwell array. To retrieve the target hybridoma, an AC signal in the n-DEP frequency region was applied to a pair of microband electrodes above and below the microwell with the target hybridoma.

Results and discussion: Cell-based arrays were formed with the occupancy efficiency of over 90% in a few seconds by p-DEP. Antibodies secreted in microwell arrays were captured to discriminate target hybridomas in a few hours without repeated steps of a culture and a limiting serial-dilution. Furthermore, hybridomas trapped in microwells were retrieved from the cell-based array by applying an AC signal to band electrodes. The sequential system for forming cell-based arrays, discriminating hybridomas secreting specific antibodies, and retrieving target hybridomas was developed by using the novel microwell array device comprising 3-D microband array electrodes with an orthogonal arrangement.

I3 Application of Electrochemical Measurement Technique in Cell study and Oxidative Stress

Shigenobu Kasai

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Abstract

Oxidative stress is induced by imbalance in redox state in living body and associated with ROS related diseases, for example, inflammation, allergy, aging and various adult diseases. Visualization of oxidative stress is indicative of a significant for diagnostic purpose visualization techniques of oxidative stress, which leads to a practical diagnostic device that contributes to the social demands on health and welfare. In this research, we introduce the following two electrochemical measurement cases.

Mastitis is a generic term for biological reactions leading to damage of mammary gland tissue, which occurs when intestinal microbes invade into mammary glands. Currently, Somatic cell count (SCC) is widely used as mastitis diagnosis method utilizing the fact that a large number of somatic cells are present in the milk of mastitis cattle. However, it is difficult to know whether the immune cells increase at the early stage of mastitis and early diagnosis is difficult. We have evaluated respiratory activity and respiratory burst of immune cells by Scanning electrochemical microscopy (SECM). In this study, attention was paid to the fact that neutrophils are particularly likely to increase among somatic cells, and evaluation of respiratory activity can be used as a marker for the diagnosis of mastitis.

Cell sheets have been studied for the purpose of regenerating dysfunctional tissue, and it has also been reported that whole-body transplantation of autologous cultured epidermis was actually successful. However, there are few simple methods to test activity after cell sheet preparation. In this study, we aimed to reproduce the sunburn condition on a part of normal human epidermal keratinocyte sheet by ultraviolet irradiation and to evaluate its activity using Bio-LSI. We monitor the oxygen reduction current of the epidermal cell sheet in real time, and report the results of imaging the respiratory burst phenomenon similar to that of immune cells as the area irradiated with ultraviolet light.

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I4 Preparation of glucose sensor using electrodeposition method and its application to in vivo measurement

Mikito Yasuzawa* and Masashi Kurashina (Department of Applied Chemistry, Tokushima University, Japan)

Introduction: Development of implantable glucose sensors for a continuous glucose monitoring system (CGMS) has provided significant benefit, since it not only provide instant glucose level but also its continuous trend, which help to provide effective treatment. However, commonly 1 cm in length is requested to be injected in the tissue for the sensor placement and the development of lower invasive CGMS is longed to improve the patients quality of life. We have previously reported that the sensor response of a fine tapered needle type glucose sensor, which has a sensing region at the tip, showed good correlation with blood glucose value, even though the sensor device was implanted in the skin for a length of 1.0 mm¹⁾. This result indicate that the glucose measurement in dermis have potential to provide valuable information for blood glucose management. Nevertheless, low-invasive sensor require sensing region miniaturization and improvement of sensor sensitivity is indispensable. Here, we report various procedures to increase the sensitivity of the glucose sensor based on the immobilization of enzyme using electrodeposition method.

Experimental: Glucose oxidase (GOx) was used as the enzyme for sensor fabrication. Carbon nanomaterials, such as carbon nanotube (CNT) and graphene, were introduced and Gallen gum powder was employed to obtain dispersed aqueous electrodeposition solution containing GOx. GOx was electrodeposite on Pt electrode by applying a constant potential of 1.3 V (vs. Ag/AgCl). Electropolymerization of o-phenylenediamine was carried out at a constant potential of 0.7 V (vs. Ag/AgCl) to form a polymer film, which increase the stability of the enzyme film. Response current measurement was performed at a constant potential of 0.60 V (vs. Ag/AgCl) for hydrogen peroxide detection.

Results and discussion: Stable dispersed solution containing GOx and CNT was prepared using gellan gum and was applied successfully for the electrodeposition on Pt electrode. The obtained GOx and CNT immobilized electrode performed good glucose sensor response and its sensor sensitivity was two times higher than that without CNT.

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I5 **Different Chemistry of Li- and Na-ion toward Carbon Electrode**

Yasuyuki Kondo¹, Yuko Yokoyama², Yuto Miyahara³, Kohei Miyazaki^{1,3}, and Takeshi Abe^{1,3} (¹Graduate School of Global Environmental Studies, Kyoto Univ., ²Office of Society Academia Collaboration for Innovation, Kyoto Univ., ³Graduate School of Engineering, Kyoto Univ.)

Introduction: It has been well-recognized that lithium-ion batteries (LIB) are the main secondary batteries for portable devices, electric vehicles, etc. Storage of renewable energies has been of great importance for their effective use, and LIB also plays an important role for the storage systems. The storage of renewable energies will be rapidly increased and therefore, other secondary battery systems must be developed because of the resources' limitation. In this sense, sodium-ion batteries have attracted much attention. Graphite has served as a negative electrode of LIB for more than 25 years mainly because of its high capacity (theoretical 372 mAh/g), low potential identical with Li metal, and low cost. The use of graphite is one of the key issues for the success of LIB. Then, we have focused sodium-ion chemistry toward carbon electrode and compared it with lithium-ion.

Intercalation of Li- and Na-ion into graphite: While graphite accepts lithium-ion to form Li-graphite intercalation compound (GIC), reactivity of sodium-ion with graphite is quite low. Little reactivity of sodium-ion with graphite has been a mystery for ca. 50 years. We tried to solve this mystery and the details will be shown in the conference [1, 2].

Insertion of Li- and Na-ion into hard carbon: When organic compounds are heat-treated up to 3000 °C under inert atmosphere, most of them will become graphite. However, some compounds will be still amorphous, and the resultant carbons are called non-graphitizable carbon (or hard carbon). Glassy carbon is one the hard carbons. Hard carbons heat-treated by 1200 °C possess many open pores, and the carbons heat-treated exceeding 1500 °C possess almost no open pores but closed pores. Sodium-ion can easily insert into the hard carbons with closed pores, but lithium-ion cannot [3, 4]. These results have become the second mystery between lithium-ion and sodium-ion.

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I6 A Simple EIS Model to Describe Diffusion and Migration inside a Porous Electrode

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The use of an equivalent circuit is helpful to interpret electrochemical impedance spectroscopy (EIS). Transmission-line model (TLM) is a kind of equivalent circuits with a ladder-like structure and several rows of infinitesimally small elements. Usually the values of the elements in a row do not depend on the position in the ladder (uniform model). Impedance values of several uniform TLMs are mathematically obtained¹⁾. If the analytical solution is not available for the assumed model, such as a non-uniform model or even a uniform model with a highly complicated structure, the model is usually transformed to a discrete model with finite-length ladder steps to obtain the impedance values with the aid of some simulation software. Generally there are two different types of the TLMs used in the field of EIS: One is to reflect spatial distributions of the ionic and/or electronic resistances, and the other is to describe diffusion of the active species. As an example in the former meaning, an expansion of the Randles-type circuit for a porous electrode is shown in Fig. 1. However, since the arrayed Warburg elements in Fig. 1 are isolated with each other, there is a limitation that the model can describe only a locally terminated diffusion. The diffusion inside the active material (usually a powdery material) is applicable, whereas that inside the electrolyte solution is not, since the concentration perturbation propagates spatially successively throughout the porous electrode. On the other hand, it is known that a kind of TLMs can describe the diffusion and migration in an electrolyte solution containing several ionic species²⁾. Therefore, an incorporation of such a TLM into Fig. 1 becomes a powerful equivalent circuit to describe the effects of diffusion, migration, and electronic resistance on the faradaic impedance inside a porous electrode. A difficulty lies in the fact that all of the ionic species, not only the active species, contribute the electric double-layer charge/discharge process. An exact modeling of the double-layer capacitance will be discussed.

References

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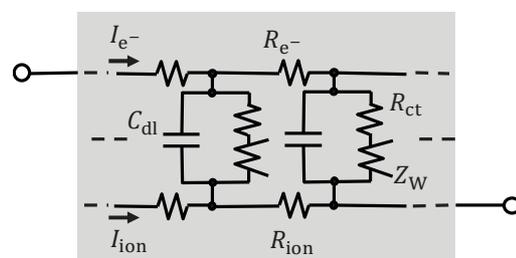


Fig. 1. A TLM for a porous electrode based on a Randles-type equivalent circuit.

I7 *operando* X-ray Absorption Spectroscopic Study on Oxygen Reduction Reaction Kinetics of Pt Monolayer on Pd Core-shell Catalyst

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Introduction: Considering the practical application in PEFCs, more and more researches start focusing on the catalytic properties under moderate temperature as the working temperature of PEFCs is over 70 °C. In this study, we measured ORR activities and coverage of oxygenated species on Pt monolayer-shell Pd-core catalyst from 25 °C to 60 °C. The core-shell catalyst was synthesized by Pt monolayer deposition on Pd/C with the galvanic displacement of Pt from a Cu monolayer obtained by under-potential deposition. *Operando* XAS also used to observe Pt-Pt bond distance of the catalyst, trying to illustrate the ORR activity temperature dependence of Pt shell-Pd core catalyst.

Experimental: Pd/C catalyst (30wt%) made from ISHIFUKU Metal Industry Co., Ltd. was used as core metal. The core-shell catalyst was prepared by depositing Pt monolayer involving the galvanic displacement by Pt of underpotentially deposited (UPD) Cu monolayer. *Operando* XAS measurements for Pd K-edge of Pt/Pd/C core-shell catalyst and Pt L_{III}-edge of Pt/C catalyst and Pt/Pd/C core-shell catalyst were carried out by using synchrotron radiation at the beamlines BL37XU and BL01B1 at SPring-8, Hyogo, Japan.

Results and discussion: The apparent rate constant (k_{app}) in Pt/Pd/C core-shell catalyst possessed the higher ORR activity than Pt/C catalyst at 25°C but the ORR activity started to decrease at 60°C. The coverage of Pt/Pd/C core-shell catalyst was much lower than Pt/C catalyst at 25°C but it dramatically increased with the rising temperature, which could be a part reason of the ORR activity decrease. *Operando* XAS study showed the Pt-Pt bond length of Pt/Pd/C core-shell catalyst was shorter than that of Pt/C catalyst, in the case of the compressive surface strain on the Pd core. As the summarize in Figure 6, the Pt-Pt bond length extension was more significant for Pt/Pd/C core-shell catalyst than Pt/C catalyst at 60°C, which cause the decrease of ORR activity. This structural change of the catalyst was caused by the larger thermal expansion of Pd core as well as the particle size effect of thermal expansion coefficient.

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