

Production of Polyhydroxybutyrate Utilizing Molasses as Cheap Carbon Source

Siti Baidurah,^{*1} Khok Yong Sen,¹ M. Hazwan Hussin²

¹ School of Industrial Technology, Universiti Sains Malaysia, 11800 Minden, Penang, Malaysia

² School of Chemical Sciences, Universiti Sains Malaysia, 11800 Minden, Penang, Malaysia

*Email: sitibaidurah@usm.my

Polyhydroxybutyrate (PHB) synthesized by many microorganisms such as *Cupriavidus necator*, *Bacillus megaterium* under stressed condition like high carbon sources, low nitrogen source and high osmotic pressure. PHB is a type of fully biodegradable polyester that categorizes under the polyhydroxyalkanoate family. PHB offers various advantages over petrochemical derived plastic, in terms of biocompatible, biodegradable, and nontoxic. However, the current production cost of PHB is much expensive than polyethylene and polypropylene partly due to high substrate cost. Therefore, molasses are proposed to be used as the main carbon source during bacteria cultivation due to its abundance in Malaysia, high sugar content and low cost. *C. necator* is the microorganism widely used for PHB production. In this study, the main components of molasses such as total sugar content, glucose, sucrose and fructose content, nitrogen content, moisture content, total dry matter and inorganic matter content were determined. Various types of pretreatment on molasses (acid pretreatment, alkaline pretreatment, thermal pretreatment, microwave assisted acid pretreatment, hydrothermal oven acid pretreatment, hydrothermal acid pretreatment) were conducted in order to promote sucrose hydrolysis, thus, will increase the fructose and glucose concentration. The sucrose, fructose and glucose content of different pretreated molasses were determined using high performance liquid chromatography (HPLC). The pretreated molasses with highest fructose and glucose concentration was used for subsequent fermentation and the cell dry weight and PHB content was compared with untreated molasses. The molasses consists of 34.5 % sucrose, 5.9 % glucose and 5 % fructose respectively. The moisture content and total dry matter of molasses are 15.8 % and 84.2 % respectively. The hydrothermal acid pretreated molasses (oil bath) contains the highest fructose and glucose content which are 21.3 % and 20.3 % respectively. Although the hydrothermal acid pretreated molasses have the highest fructose and glucose content, the cell dry weight and PHB produced by *C. necator* using hydrothermal acid pretreated molasses (oven) is the highest which are 2.9 g and 27 % respectively. The authors gratefully acknowledge RUI Grant 1001/PTEKIND/8011022 for the financial support.

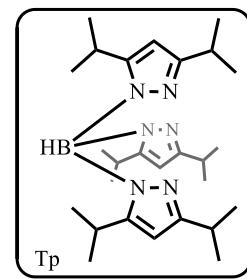
Sulfur Atom Oxidation of Aminothiophenol by Cobalt(II) Complex

Kazunari Ohira¹, Hidehito Komatsuzaki¹, Tomohiro Agou², Yuya Tanaka³, Michito Yoshizawa³, Munetaka Akita³, Jun Nakazawa⁴, Shiro Hikichi⁴

¹National Institute of Technology, Ibaraki College, Japan, 312-8508, ac17402@gm.ibaraki-ct.ac.jp

²Ibaraki University, ³Tokyo Institute of Technology, ⁴Kanagawa University

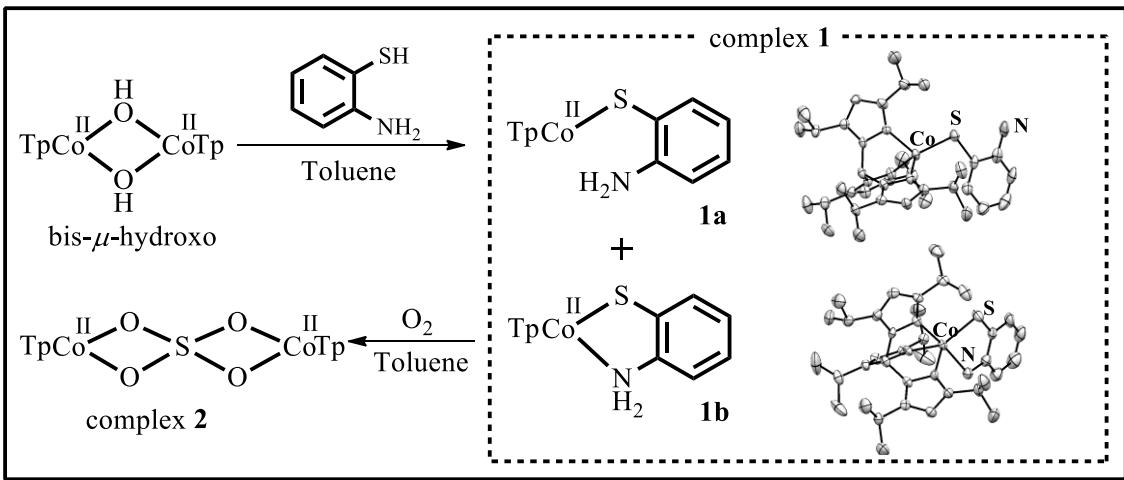
Cysteine dioxygenase (CDO) catalyzes sulfur-atom dioxygenation of cysteine by using molecular oxygen to give cysteine sulfenic acid. Therefore, mimicking of the sulfur atom oxidation of the sulfur-containing ligands in the metal complexes is well-researched. We have reported sulfur-atom oxidation of thiophenolato and thioacetate ligand by cobalt(II) complexes. In this study, we report on the synthesis and dioxygen activation of a cobalt(II) aminothiophenolato complex capped by hydrotris(3,5-diisopropyl-1-pyrazolyl)borate ligand (Tp).



The cobalt(II) aminothiophenolato complex **1** was synthesized by dehydration condensation reaction of a dimeric cobalt(II,II) bis- μ -hydroxo complex with *o*-aminothiophenol. Results of X-ray crystallographic analysis revealed that complex **1** has two structures; 4-coordinate structure (**1a**) in which the aminothiophenolato coordinates to cobalt(II) by unidentate mode, and 5-coordinate structure (**1b**) in which the aminothiophenolato coordinates to by bidentate mode.

When the complex **1** (mixture of **1a** and **1b**) reacted with O₂, sulfur-atom oxidation of the aminothiophenolato ligand progressed to give a dimeric cobalt(II,II) μ -sulfanato complex **2**.

In order to elucidate the reaction mechanism, a zinc(II) aminothiophenolato analog **3** was synthesized and the reactivity with O₂ was investigated. As the result, the complex **3** did not react with O₂ resulted in dioxygen activation occurs on the cobalt(II) center of complex **1**.



Crystallization Behavior of Sodium Transition Metal Silicate Glasses

Miyuri Terasawa, Tsuyosi Honma and Takayuki Komatsu

Nagaoka University of Technology, Nagaoka, Japan 940-2114, honma@mst.nagaokaut.ac.jp

Material development in sodium ion batteries will be interested in being composed of non-rare metal oxides. Silicon is the second most abundant in the crust, and the cathode active material composed of transition metal and sodium is attractive from the viewpoint of resource and price. Therefore, this study aimed at the preparation of $\text{Na}_2\text{O}-\text{FeO}-\text{MnO}-\text{SiO}_2$ glass and elucidation of the crystallization behavior.

In this study, Optically transparent and electrical conductive glass-ceramics have successfully prepared from $1\text{Na}_2\text{O}-0.5\text{MnO}-0.5\text{FeO}-1\text{SiO}_2$ ($\text{Na}_2\text{Mn}_{0.5}\text{Fe}_{0.5}\text{SiO}_2$) glass by heat-treatment. Crystallization tendency is sensitively depends on valence state of transition metal oxide. For the as quenched glass melted at 1400°C for 15minutes, exhibits two exothermic peaks in the results of differential thermal analysis. Optically transparent glass-ceramics obtained at 493°C 3h shows simple x-ray diffraction patterns those are traditionally corresponding cubic phase with a lattice constant of 0.74511 nm. When the heat treatment temperature increase above 610°C , monoclinic Na_2MSO_4 ($M = \text{Mn, Fe}$) phase are appeared. Therefore, it was considered that the crystal phase precipitated in the low temperature region is a thermodynamic metastable phase. Furthermore, transparent glass-ceramics showed an order magnitude higher electrical conductivity than that of glass and monoclinic phase.

Crystallization Behavior and Electrochemical Performance of Na₂O-TiO₂-SiO₂ Glass and Glass-Ceramics for Sodium Ion Battery

Kaito Ryo, Tsuyoshi Honma, Takayuki Komatsu

Nagaoka University of Technology, Nagaoka, Japan, 940-2188, honma@mst.nagaokaut.ac.jp

Sodium ion battery is expected to be developed as a substitute material for post lithium ion batteries. In the case of graphite and silicon which are currently mainly used in the negative electrode, it's impossible to remove and insert sodium. Therefore, it's necessary to develop an alternative negative electrode material. Some sodium titanates are promising anode materials for sodium ion batteries. In sodium titanate crystals, the change in volume due to sodium insertion and removal is small, so it's a negative electrode material suitable for long-term cycling^[1]. In this study, preparation of Na₂O-TiO₂-SiO₂ ternary glass and characterization as sodium ion battery negative electrode were carried out.

Glasses of 20Na₂O-(40+x)TiO₂-(40-x)SiO₂ (x=0,5,10,15,20) were prepared by melt quenching method. Transparent glasses were obtained at x = 0 ~ 10, and heat treatment was carried out at these crystallization temperatures in these samples. Na_{0.23}TiO₂ crystals are precipitated from each sample and it has been reported that this crystal functions well for sodium ion battery. Translucent crystallized glass was obtained in the sample of 20Na₂O-50TiO₂-30SiO₂, and observation with a polarizing microscope suggested that sub-microscopic particles were precipitated. The crystallization behavior and charge / discharge characteristics of this sample were examined by changing the heat treatment temperature, and the activity increases as the crystallinity increased.

REFERENCES

- [1] H.Usui et al., ACS Appl. Mater. Intefaces 2015, 7, 6567-6573

Compressive Processing of Waste-Based Geopolymers: Effecting NaOH Concentration on the Microstructure of Clay Waste

Sitthisak Prasanphan¹, Sirithan Jiemsirilert^{1,*}, Takaomi Kobayashi², Anucha Wannagon³

¹*Research Unit of Advanced Ceramics, Department of Materials Science, Faculty of Science, Chulalongkorn University, Bangkok, 10330, Thailand*

²*Department of Materials Science and Technology, Nagaoka University of Technology, 1603-1 Kamitomioka, Nagaoka, Niigata 940-2188, Japan*

³*National Metal and Materials Technology Center, 114 Thailand Science Park, Phahonyothin Road, Khlong Nueng, Khlong Luang, Pathum Thani 12120, Thailand*

*E-mail: sirithan.j@chula.ac.th

In the present study, geopolymer samples were prepared from waste of clay washing process with the major chemical components of muscovite, mica, and kaolin. The clay residues were molded by using compressive process for geopolymers in the presence of alkali activator solution. Prior to using the raw material for the geopolymer, the waste was calcined at 700 °C for 1 hour. The geopolymers were formed by hydraulically pressing with compressive machine at approximately 20 MPa for 1 minute and then the geopolymer samples were kept for 7 days at room temperature, as shown in Fig. 1. The effect of NaOH concentration on the microstructure and compressive strength of waste-based geopolymer was studied. Furthermore, the effect of NaOH concentration on the geopolymers reaction was studied by DSC. This method indicated that the geopolymers reaction increased at higher NaOH concentrations, resulting in greater compressive strength. The compressive strength of the geopolymers synthesized with NaOH concentration at 10 M was approximately 22.58% higher than that synthesized at 4 M NaOH in the slurry, which was equal to 26.98 MPa. In Fig. 2, the SEM micrographs of the geopolymers samples displayed more denser in the geopolymers matrices when the NaOH concentration was increased. The values of BET and pore volume of the geopolymers matrix were decreased with increase in NaOH concentration in the compressive processing, suggesting dense microstructure. In conclusion, compressive processing was effective for dense matrix of calcined waste-based geopolymers.



Fig. 1. Geopolymer samples.

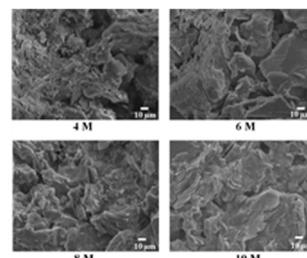


Fig. 2. SEM micrographs of the geopolymers samples displayed more denser in the geopolymers matrices.

Simple and Environment Friendly Preparation of Silver Nanoparticles by Using Silver-Containing Glass Powder – Effects of Glass Composition on Generation of Silver Nanoparticles

Yasutaka Mori, Aoi Yamamoto

*Dept. of Applied Chemistry and Chemical Engineering, National Institute of Technology, Toyama college,
Toyama, Japan 939-8630, yamori@nc-toyama.ac.jp*

Silver-containing glass, which is usually used as antibacterial materials, can sustainably release Ag⁺ ions into aqueous environments. In our previous work, we developed a simple and environmentally friendly method to prepare size-controlled spherical silver nanoparticles (Ag NPs) by heating of a mixture of silver-containing glass powder and an aqueous solution of glucose [1]. The size of generated Ag NPs by this method was increased proportionally with the square root of the glucose concentration in the range of 0.25-8.0 wt%, which was corresponding to particle sizes of 3.5-20.0 nm. Although the composition of silver-containing glass powder used in this method for generation of Ag NPs, the composition of the glass powder used in the previous work was supplied as an antibacterial material and its composition was not disclosed.

In this work, we investigated effects of glass composition on generation of Ag NPs by the method. Four component glasses consisted of various compositions of B₂O₃, SiO₂, Na₂O, and Ag₂O were prepared by melting method at 1000°C. Compositions of SiO₂ and B₂O₃ were varied and those of Na₂O and Ag₂O were fixed at 15 and 1 wt%, respectively. Prepared bulk glass was grained with a hammer mill and a planetary ball mill to fine powder. The glass powder was mixed with 2wt% glucose aqueous solution and then heated at 95°C. The average diameters of generated Ag NPs were slightly decreased from 10.6 to 8.7 nm with the composition of SiO₂ in a range of 15-40 wt%. Glass powder with 10 wt% of SiO₂ generated Ag NPs with wide size distribution and an average diameter of 8.7±3.7 nm. Glass powder with 5 wt% of SiO₂ generated bulk silver and did not produce Ag NP. Generation rates of Ag NPs were increased with the composition of SiO₂ in a range of 10-40 wt%. It was considered that SiO₂ was essential for nanoparticle generation and promoted dissolution of glass powder during reaction.

REFERENCES

- [1] Mori, Y., et al., Simple and environmentally friendly preparation and size control of silver nanoparticles using an inhomogeneous system with silver-containing glass powder, J Nanopart Res, 13 (2011), 2799-2806

Separation Performance of Zeolite–Polymer Composite Membranes for Alkali Metal Ions

Tatsuki Inamoto, Lisa Nakajima and Takaomi Kobayashi

Nagaoka University of Technology, 1603-1 Kamitomioka, Nagaoka , Niigata, Japan 940-2188,

takaomi@nagaokaut.ac.jp

Zeolite composited membranes, which were composed of polyethersulfone (PES) and natural zeolite (mordenite) and other five kinds of synthesized zeolites (A-3 zeolite, 620 zeolite, 642 zeolite, 890 zeolite and 990 zeolite), were each prepared via phase inversion process. Then, the adsorption and ion exchange abilities were investigated in the zeolite composition membrane for separation of alkali metal ions. The zeolite content was 58.8wt % in the composite membranes which was used for with dead-end membrane filtration. The permeation adsorption process of the aqueous solution containing five kinds of alkali metal ions (Li^+ , Na^+ , K^+ , Mg^{2+} and Ca^{2+}) was tested by the membrane permeation process and the adsorption performance of each zeolite composition membrane was investigated. Here, the permeation was carried out using 50 ml of the aqueous mixtures with each 0.5 mM concentration of the alkali metal ion. The aqueous solution was filtrated under 0.4 MPa by using AMIKON membrane cell (50 ml volume). The composition membrane used had 45 mm size in the diameter as looked in Figure 1. The cross section view (bottom) showed porous membrane including zeolite powders. After permeation experiment, the residual ion concentration of the alkali metal ions was detected by atomic absorption spectrophotometry. Figure 2 shows residual % of each ion with permeation solution. As a result, it was revealed that A-3 composite membrane was effected on the adsorptivity to Li^+ , Mg^{2+} and Ca^{2+} and 642 zeolite membrane for K^+ , Mg^{2+} and Ca^{2+} . It was concluded that Na^+ substituted zeolites of A-3 and 642 were more effective in the separation of alkali metal ions, when the zeolite was composited in the membrane.

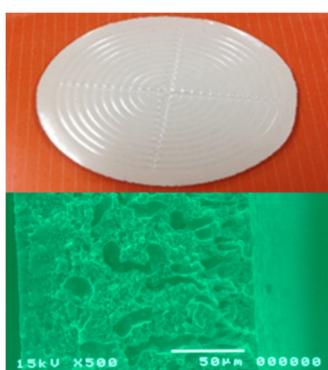


Fig.1 Pictures of view
of the A-3 zeolite
composite membrane
and the cross section.

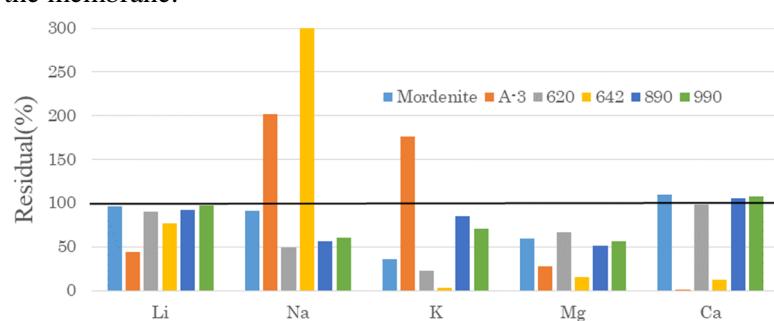


Fig.2 Adsorption experiments of alkali metal ions
with the zeolite composition membrane.

Synthesis and Evaluation of High Adsorbability in Ceria Photocatalysts for Water Treatment

Yusaku Mochizuki¹, Ryo Shoji¹, Yasukazu Kobayashi², Noriko Yamauchi³, Kazunori Sato⁴

¹*National Institute of Technology, Tokyo College, Tokyo, Japan 193-0997, mochisaku1113@gmail.com*

²*The University of Tokyo, Tokyo, Japan 113-8656*

³*Ibaraki University, Ibaraki, Japan 316-8511*

⁴*Nagaoka University of Technology, Niigata, Japan 940-2188*

Along with the rapid development of industries, water contaminations caused by persistent organic pollutants and heavy metal ions are occurring particularly in developing countries. According to the drinking-water standard of World Health Organization criteria, the concentration of these pollutants in discharged water are required to be decreased down to the ppb level. Compared with the adsorption and precipitation methods, the photocatalytic oxidation method using semiconductor photocatalysts is an advantageous technology for removal of these pollutants at low concentrations.

Cerium oxide, CeO₂, as a stable solid oxide has received much attention for its unique characteristics. The oxide possesses a high oxygen storage and releasing ability derived from the redox cycle between Ce³⁺ and Ce⁴⁺. The oxide therefore plays a great role as a photocatalyst for photo-redox reaction against adsorbed substances. It has been reported that two-phase mixture of CeO₂ matrix and its compounds with other lanthanoid oxides showed a high photocatalytic oxidation performance for the recovery of lead ions dissolved in water. However, because of the small surface area and low adsorbability, the crystalline CeO₂ particles exhibit the low reaction efficiency. We have developed fine CeO₂ particles having a high specific surface area, which is favorable for providing a much larger number of adsorption sites, with a unique hard-template method. We have also investigated their removal performance for the harmful substances dissolved in water.

The CeO₂ particles prepared by the hard-template method had a surface area (28.3 m²/g) much larger than that of conventional CeO₂ particles (1.6 m²/g). The high adsorbability in the CeO₂ photocatalyst particles resulted in an excellent removal performance for methylene blue dye.

The XRD and XPS analyses revealed that the synthesized CeO₂ has the face-centered cubic structure as the matrix phase and the surface structure coexisting both Ce³⁺ and Ce⁴⁺ ions. Moreover, we found that a large amount of oxygen defects and surface hydroxyl groups, both of which can be effective adsorption sites for reactants, exist on the surface of the fine CeO₂ particles.

**Particle Orientation Behavior in Colloidal Processing
with UV Curable Binder Under a Rotating Magnetic Field**

Shoko BABA, Satoshi TANAKA

Nagaoka University of Technology, Nagaoka, Japan 940-2188, stanaka@vos.nagaokaut.ac.jp

Crystal-orientation using the colloidal processing in a high magnetic field is effective for improving property of the polycrystalline ceramics. We have examined on the colloidal processing with UV curable binder, and reported fabrication of a particle-oriented $(\text{Sr,Ca})_2\text{NaNb}_5\text{O}_{15}$ green sheet. The polymerization by the UV light could shorten the duration time in the magnetic field to several ten seconds. The objective of this study is to examine the influence of experimental parameters on the orientation degree of the green sheet. In principle, the orientation degree depends on the magnetic flux density, duration time in the magnetic field, and the viscosity of the slurry. Here, the viscosity could be controlled with temperature. The slurry was cast on a PET film and placed in magnetic fields with 2 - 10 T. After duration of various seconds, UV light was irradiated to the tapes in the magnetic field.

In the magnetic field with 10T, the Lotgering factor is saturated in several seconds, whereas it increases gradually with increasing the duration time at 6T (Fig.1). Fig. 2 shows orientation time plotted as a function of viscosity divided by the square of magnetic flux density. The result shows that the orientation time of particles in a slurry under a magnetic field can be accurately estimated from the magnetic flux density and the slurry viscosity used to prepare the green sheet.

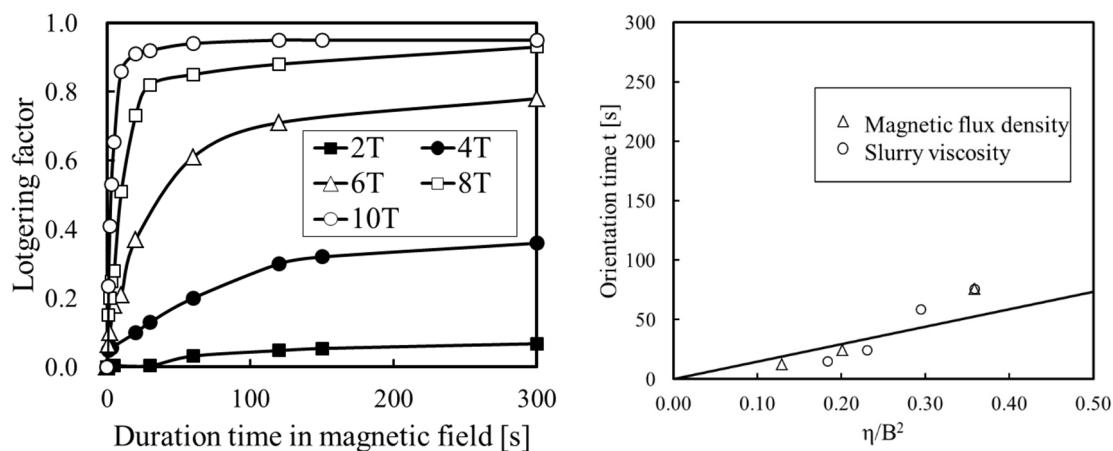


Fig.1 The orientation degree of prepared by various duration times in rotating magnetic field of each magnetic flux density at 20 .

Fig.2 Time required for particle orientation plotted against the viscosity of slurry divided by the square magnetic flux density.

Synthesis and Property of Cobalt(II) Complex with Sulfur-Containing Ligand

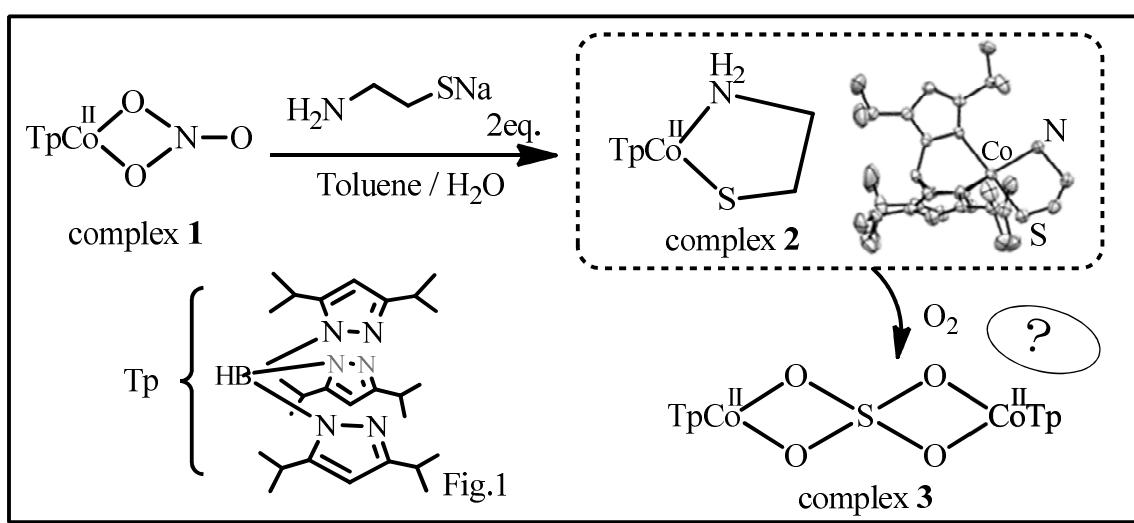
Shun Tadokoro¹, Hidehito Komatsuzaki¹, Tomohiro Agou², Yuya Tanaka³,
Michito Yoshizawa³, Munetaka Akita³, Jun Nakazawa⁴, Shiro Hikichi⁴

¹National Institute of Technology, Ibaraki College, Japan, 312-8508, ac18401@gm.ibaraki-ct.ac.jp

²Ibaraki University, ³Tokyo Institute of Technology, ⁴Kanagawa University

Cysteamine dioxygenase (ADO) introduces two oxygen atoms from O₂ into sulfur atom of cysteamine to generate cysteamine sulfenic acid. There are unclear points for ADO such as coordination environment of metal center, active intermediate, and reaction mechanism. In this research, for the purpose of elucidating the sulfur atom oxidation mechanism of ADO, we synthesized a cobalt(II) cysteaminato complex capped by hydrotris(3,5-diisopropyl-1-pyrazolyl)borate ligand (=Tp in Fig.1) and we checked reactivity of complex **2** with O₂.

The cobalt(II) cysteaminato complex **2** was synthesized from the ligand exchange reaction of a cobalt(II) nitrate complex **1** and sodium cysteaminato. As a result of the X-ray analysis, we found that complex **2** has a monomeric 5-coordinate structure ($\tau=0.44$) due to bidentate coordination of cysteaminato ligand. When the complex **2** reacted with oxygen molecule, the solution color changed from red to brown. From mass spectrum measurement, we assigned to a sulfanato complex **3** as one of the reaction products. The synthesis and property of analogous complex of **2** would be also reported in this presentation.



Crystal-Oriented Tetragonal Lithium Sodium Potassium Niobate Ceramics

Yuuki. Ono, and Satoshi.Tanaka

Nagaoka University of Technology, Nagaoka, 940-2188, Japan

stanaka@vos.nagaokaut.ac.jp

(Li_xNa_yK_z)NbO₃ (LNKN) ceramic has well-balanced piezoelectric properties and better environmental compatibility. The properties of LNKN can be improved by controlling the microstructure as crystal orientation. The objective of this study is to fabricate crystal-oriented LNKN ceramic by a colloidal processing in a magnetic field, and to demonstrate improvement of their piezoelectric properties.

LNKN particles with tetragonal crystal system was synthesized by a solid phase reaction. A dispersed slurry was prepared by a ball-milling of powder, 2-propenol, and a dispersant. The slurry was poured into a mold and set in the superconducting magnet 10T until drying. A random LNKN sample was also fabricated as a reference. The powder compacts were sintered at 1000 °C under the oxygen atmosphere. The orientation of the powder compact and ceramics were evaluated by powder X-ray Diffraction (XRD). The Polarization-Electric field (P-E) hysteresis loops were analyzed by a Sawyer-tower circuit, and the piezoelectric d₃₃ constant was measured by the d₃₃ meter after polarization treatment.

The XRD pattern of the powder compact showed the c-axis orientation to the magnetic field. The c-axis-oriented structure changed to the c- and a-axis orientation after sintering. This is because the sample has undergone a phase transition from tetragonal to cubic at higher temperature. The relative density of sintered LNKN ceramics were ~96%. While the hysteresis loop of the oriented LNKN was almost same with that with random structure, the d₃₃ of oriented sample was 143 pC/N and higher than non-oriented sample 103 pC/N.

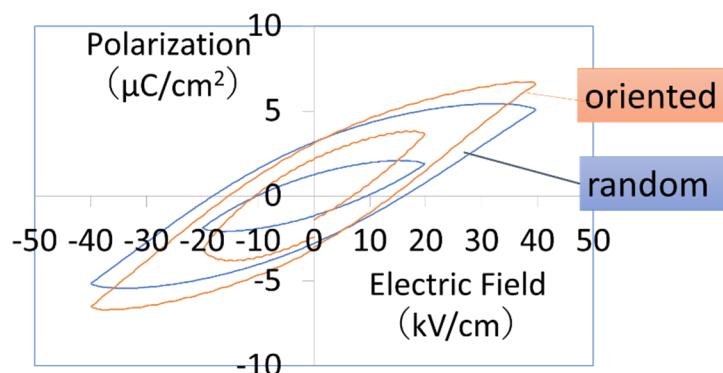


Fig. 1 P-E hysteresis loops of oriented and random LNKN ceramics.

Photodegradation of Bisphenol a Dissolved in Water by Gd₂O₃-CeO₂

Fumiya Sato, Kazuhiro Yamamoto, Kazunori Sato

Nagaoka University of Technology, Nagaoka, Japan 940-2188, s153334@stn.nagaokaut.ac.jp

The lanthanide oxides (Ln_2O_3 ($\text{Ln} = \text{La, Sm, Gd}$)) have different cation radii and valence from cerium oxide (CeO_2), which is the stable solid oxide in the cerium-oxygen system. The separate incorporation of these lanthanide oxides into CeO_2 results in a formation of face-centered cubic structure with a metastable two-phase microstructure consisting of the CeO_2 matrix phase and the $\text{Ce}_{1-x}\text{Ln}_x\text{O}_{2-y}$ compound or solid-solution phase. We have found that this two-phase structure shows a high catalytic activity for the removal of lead ions and bisphenol A (BPA) dissolved in water. The photocatalytic activities were observed only for the samples prepared by a mixture of Ln_2O_3 and CeO_2 starting particles heated at a fixed temperature for a fixed period of time. The specific two-phase microstructure is favorable for an efficient separation of electrons and holes excited by photo-irradiation and contributes to a degradation of BPA. We have investigated an influence of Gd_2O_3 addition to CeO_2 on the degradation activity of BPA dissolved in water. The mixture of CeO_2 and Gd_2O_3 was fired at 1723 K for 10 h in air. The contents of Gd_2O_3 were fixed 5 to 20 mol% in the $\text{Gd}_2\text{O}_3\text{-CeO}_2$ (5 GDC to 20 GDC, respectively). 50 mg of sample was dispersed in a 10 ppm BPA aqueous solution and irradiated with a light source in the wavelength range 370 to 450 nm for 3 h using a Hg-Xe lamp (200 W) equipped with a cut filter. The degradation ability was examined by measuring the residual BPA concentration in the solution with a uv-vis spectrophotometer. 10 GDC showed the highest degradation ability. The X-ray diffraction method revealed that an appropriate ratio of the $\text{Ce}_{1-x}\text{Gd}_x\text{O}_{2-y}$ phase increased the ability of BPA degradation. The reaction mechanism is discussed based on these experimental results.

Photochemical Reduction of Carbon Dioxide Dissolved in Water by La₂O₃-CeO₂ Composite

Ryota Suzuki, Kazuhiro Yamamoto, Kazunori Sato

Nagaoka University of Technology, Nagaoka, Japan 940-2188, s153338@stn.nagaokaut.ac.jp

We have found that an efficient activity for the photocatalytic reduction of carbon dioxide appears by the formation of the two-phase structure in x mol%Ln₂O₃(Ln = La, Gd)-CeO₂ (LDC and GDC, respectively) particles prepared by the solid-state reaction method. The specific two-phase structure was formed by heating a mixture of an appropriate ratio of Ln₂O₃ and CeO₂ starting particles at a fixed temperature for a fixed period of time. The similar photocatalytic activity was also found for the removal of lead ions and bisphenol A dissolved in water. The photocatlytic reduction of carbon dioxide resulted in a production of methane, whose selectivity is controlled by dispersing the most effective auxiliary photocatalyst fine particles on the surface of the LDC and GDC particles. Photoelectrodepositions of platinum, gold, and copper respectively did not show a uniform particle dispersion, which seems specific to near the corners and the edges of the LDC and GDC particles. The mechanism of carbon dioxide reduction is discussed in relation to the role of these auxiliary catalysts and the microstructure of the LDC particles in detail.

Electric Power Generation Enhancement in a Solid Oxide Fuel Cell Operating in Methane by Using Oxygen Storage and Release Property of Ce_{1-x}Sr_xO₂

Yohei Sugano, Kazuhiro Yamamoto, Kazunori Sato

Nagaoka University of Technology, Nagaoka, Japan 940-2188, s153337@stn.nagaokaut.ac.jp

Current solid oxide fuel cells (SOFC) utilize hydrogen modified hydrocarbon gases. If hydrocarbon gases can be used directly, heat loss during fuel reforming will be minimized and the power generation efficiency will be improved. Cerium oxide (CeO₂) shows the high ionic conductivity by adding group 2 elements. Strontium oxide (SrO) doped in CeO₂ (Strontia-Doped Ceria: SrDC) has an Oxygen Storage Capacity (OSC) effect, an ability of storing and releasing the lattice oxygen between the solid and gas phases. Methane (CH₄) oxidation reaction is expected to be enhanced by the OSC effect as well as the high oxide-ion conductivity. We have investigated the power generation characteristics of methane by adding an appropriate amount of SrO to CeO₂ and its influence on OSC. Mixed powders of NiO, SrDC, corn starch, stearic acid for the anode, Sm_{0.2}Ce_{0.8}O_{1.9}(SDC) for the electrolyte, Sm_{0.5}Sr_{0.5}CoO₃(SSC) and SDC at a mass ratio of 7: 3 for the cathode were prepared. The NiO and SrDC powders were weighed at a mass ratio of 4:6, then compacted at 15 kN for 1 min and calcined at 1100 °C. The electrolyte was applied by a tape cast method and sintered at 1400 °C for 10 h. The cathode was applied by a tape casting method and sintered at 1200 °C for 5 h. Evaluation of power generation characteristics for methane was made. CH₄ was supplied to the anode at 60 ml · min⁻¹, and O₂ was supplied at 100 ml · min⁻¹ to the cathode. As for the OSC evaluation, the sample weight change was measured by the thermal analysis method (TG-DTA) under air and argon. The observed power density of an SOFC using the SrDC anode for CH₄ was 0.76 W · cm⁻² at 750 °C. The SOFC showed a strong resistance to carbon deposition and stably generated the electric power for long operation hours. This effect is most likely caused by the O²⁻ release from the crystal lattice of SrDC. The enhancement mechanism for the oxidation of CH₄ at the SrDC anode is discussed.

Investigation of Nitriding Treated Ni-free SUS445 as Current Collector for 5V-Class Li-ion Secondary Cell

Neil Ihsan¹, Sayoko Shironita¹, Kenichi Souma^{1,2}, Minoru Umeda^{1,*}

1 Nagaoka University of Technology, 1603-1, Kamitomioka, Nagaoka, Niigata 940-2188, Japan

2 Hitachi Industrial Equipment Systems Co., Ltd, 3 Kanda Neribei, Chiyoda, Tokyo 101-0022, Japan

* *mumeda@vos.nagaokaut.ac.jp*

Li-ion secondary cells have been widely used as a power sources in portable electronic devices and electric vehicles, and further higher operating voltage and higher capacity are required. To realize higher operating voltage, it is necessary to develop a cathode current collector material with high corrosion resistance. In our previous study, it is found that a corrosion resistance of Ni-free stainless steel in an acid aqueous solution is improved by a nitriding heat treatment [1]. Therefore, in this study, the corrosion resistance as the cathode current collector of the nitriding treated Ni-free stainless steel was electrochemically evaluated.

The Ni-free stainless steel SUS445 was nitrided by a heat treatment in N₂ atmosphere at 1473 K for 4 h. The nitriding treated stainless steel is SUS445N. Electrochemical measurement was conducted using a T-type three electrode glass cell. The working electrodes were SUS445N and Al plate. Li foils were used as counter and reference electrodes. The electrolyte was 1 mol dm⁻³ LiPF₆/ethylene carbonate (EC) + dimethyl carbonate (DMC) (1:1v/v%). All electrochemical measurements were performed in Ar atmosphere using a glove box. SUS445N was conducted a potential sweep for 30 min in a range of 0-5 V vs. Li/Li⁺ prior to measure cyclic voltammogram.

The obtained the cyclic voltammograms of SUS445N and Al in 1 mol dm⁻³ LiPF₆/EC+DMC. The Li-ion extraction and insertion of LiCoO₂ and LiNi_{0.5}Mn_{1.5}O₄ take place at 3.7-4.2 V vs. Li/Li⁺ and 4.5-5.2 V vs. Li/Li⁺, respectively. Al is stable until 4.3 V vs. Li/Li⁺, but the dissolution of Al occurs at more positive potential than 4.3 V vs. Li/Li⁺. In the case of LiCoO₂, Al can be used as the cathode current collector. However, Al cannot be used in the case of LiNi_{0.5}Mn_{1.5}O₄. On the other hand, the nitriding treated SUS445N is stable until 5.5 V vs. Li/Li⁺. Therefore, it was found that SUS445N possesses a potential as the cathode current collector material for Li-ion secondary cell.

REFERENCES

- [1] Y. Yu, S. Shironita, K. Nakatsuyama, K. Souma, M. Umeda, Appl. Surf. Sci., 388, (2016) 234-238.