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## **CURRENT ACTIVITIES and PRESENTATIONS**



# **LABORATORY OF MATERIALS FOR SUSTAINABLE ENGINEERING**

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Assist. Prof. Hisayoshi Matsushima in Yamanashi University was promoted to the Assoc. professor of our laboratory from April 2014. Mrs. Takagi is working as a secretary of the laboratory from August 2014.

Our research activities are concerned with molten salts electrolysis, water electrolysis, surface sciences about metal surface, and fuel cell.

Current topics on research are in the following:

(1) Electrorefining of Na for recycling of used Na-S secondary batteries

To develop electrorefining process of metallic Na from the used Na-S battery. There is no electrorefining process of sodium in the industrial scale. We were

investigated NaFSI-TEATFSI ionic liquid as candidate of the electrolytic melt. In the electrorefining experiment for more than 20 hours, 99.98% pure Na was obtained from simulated Na in used Na-S battery.

(2) Electrodeposition of Al-Zr alloys in chloride molten salt

To improve the corrosion resistance of Al in chloride solutions, electrodeposition of Al-Zr alloys of various compositions was carried out at 448 K by constant potential control in  $\text{AlCl}_3$ -NaCl-KCl molten salt containing  $\text{ZrCl}_4$ . The electrodeposition was performed by constant potential electrolysis from -1.4 to -1.6 V.

(3) Development of Al- $\text{Cl}_2$  cell in ionic liquid

To develop an aluminum-chlorine cell, an electrochemical cell consisting of an aluminum anode and a graphite cathode was developed and evaluated in EMIC- $\text{AlCl}_3$  ionic liquid.

The relationship between current density and cell voltage in the cell showed an almost linear relation. The output characteristics of the cell depend on the configuration of the graphite cathode, the current density with a circular cone type cathode at 0.5 V was about 40 % better than that of a cylindrical type graphite cathode.

(4) Investigation of Li metal surface by surface observation

Li metals in some non-aqueous solution were evaluated by surface observation. Dendrite growth on the Li surface was observed in several kinds of solvents.

(5) In-situ observation of electrochemical interfacial phenomena by Video-AFM

We have developed the atomic force microscopy with fast scanning rate (Video-AFM) and in-situly observed the electrochemical nucleation/dissolution. At the present, Cu electrodeposition/dissolution on HOPG substrate has been investigated in aqueous sulfuric acid solution. The video-AFM demonstrated that the Cu deposits was started at the convex points and defects on the surface.

(6) Hydrogen isotope separate by fuel cell

We are exploring the possibility of hydrogen isotope separation by using PEM fuel cell. The kinetic parameters of hydrogen or deuterium oxidation reaction (HOR or DOR) are investigated by rotating disc electrode (RDE). The separation factor of D/H during PEM operation will be measured by quadrupole mass spectroscopy (Q-mass).

(7) NIR study for Nafion membrane below freezing temperature

We in-situly apply near infrared spectroscopy (NIR) for Nafion membrane below freezing temperature. Simultaneously, we carry out the impedance measurement in order to research the conductivity mechanism of the polymer.

#### Other Activities

Prof. Ueda was invited 2014 ECS and SMEQ Joint International Meeting, Cancun, Mexico, October 5-9, 2014 and presented keynote lecture entitled by "Electrorefining of Na in Hydrophobic Ionic Liquid".

Prof. Ueda attended 2nd International Conference on Ionic Liquids in Separation and Purification Technology, and present paper entitled by "Electrorefining of Na in TBATFSI-NaTFSI ionic liquids", Toronto, Canada, June 29- July 2, 2014.

## Presentations

T. Teshima, M. Ueda, T. Ohtsuka, Electrodeposition of Al-Zr alloy in  $\text{AlCl}_3$ - NaCl-KCl containing  $\text{ZrCl}_4$ , Winter Meeting of Hokkaido Branch of Jpn. Inst. Metals and ISIJ, Sapporo, January 23-24, 2014.

S. Honda , A. Hyono, M. Ueda, Electrodeposition of Al-Sn-Cu alloy in  $\text{AlCl}_3$ -NaCl-KCl molten salt containing  $\text{SnCl}_2$  and  $\text{CuCl}_2$ , Winter Joint Meeting of Hokkaido Branch of Chemistry-related Societies, Sapporo, January 28-29, 2014.

J. Nunomura , A. Hyono, M. Ueda, T. Ohtsuka, Effect of alloy elements in aluminum anode for Al- $\text{Cl}_2$  cell characteristics, Winter Joint Meeting of Hokkaido Branch of Chemistry-related Societies, Sapporo, January 28-29, 2014.

S. Shibuya, A. Hyono, T. Ohtsuka, M. Ueda, The in-situ Raman measurement of the lithium metal electrode surface during the charging and discharging in propylene carbonate, The 129th Meeting of The Surface Finishing Society, Tokyo University of Science, Chiba, March 13-14, 2014.

S. Honda, A. Hyono, M. Ueda, Electrodeposition of Al-Sn-Cu alloy from low temperature chloride molten salt using the constant potential electrolysis and constant potential pulse electrolysis, The 81st meeting of ECSJ, Kansai University, Osaka, March 29-31, 2014.

H. Matsushima, Research for electrochemical interfacial phenomena targeting for hydrogen energy society, Material Seminar, Sapporo, April 25, 2014.

Chika Namekata, Toshiaki Ohtsuka, and Mikito Ueda, Effect of Additive for Smooth Al Electroplating in  $\text{AlCl}_3$ -EMIC Ionic Liquid, Anodizing Science and Technology 2014, Sapporo, June 4-6, 2014.

Hiroki Murakoshi, Kazuhisa Azumi, and Mikito Ueda, Optimization of Electrodeposition Al on Mg Alloy from the Molten Salt Bath, Anodizing Science and Technology 2014, Sapporo, June 4-6, 2014.

Koji Fushimi, Kazunori Kurauchi, Takayuki Nakanishi, Yasuchika Hasegawa, and Mikito Ueda, Ellipso-microscopic Imaging of Anodized Titanium Surface under UV-light Irradiation, Anodizing Science and Technology 2014, Sapporo, June 4-6, 2014.

Mikito Ueda, Ryuich Inaba, and Toshiaki Ohtsuka, Electrorefining of Na in TBATFSI-NaTFSI ionic liquids, 2nd International Conference on Ionic Liquids in Separation and Purification Technology, Toronto, Canada, June 29- July 2, 2014.

Y. Yasui, A. Hyono, H. Matsushima, T. Ohtsuka, M. Ueda, Evaluation of as an electrolyte of NaFSI-TEATFSI mixed ionic liquid for Na electrorefining, Summer meeting 2014 of Hokkaido branch of The Chemical Society of Japan, Hokkaido, Tomakomai National College of Technology, July 12, 2014.

Mikito Ueda, Materials science study using molten salt and ionic liquid, Summer meeting 2014 of Hokkaido branch of The Chemical Society of Japan, Hokkaido,

Tomakomai National College of Technology, July 12, 2014.

Mikito Ueda, Aluminum alloys plating using molten salts and ionic liquid, The 130th Meeting of The Surface Finishing Society, Kyoto University, Kyoto, September 22-23, 2014.

C. Namekata, A. Hyono, H. Matsushima, T. Ohtsuka, M. Ueda, Effect of electroplating thickness for the surface smoothness in the Al electroplating from ionic liquid, The 130th Meeting of The Surface Finishing Society, Kyoto University, Kyoto, September 22-23, 2014.

H. Murakoshi, K. Azumi, M. Ueda, Optimization of Al plating from the molten salt bath for AZ31 alloy, The 130th Meeting of The Surface Finishing Society, Kyoto University, Kyoto, September 22-23, 2014.

H. Matsushima, In-situ observation study for relationship between hydrogen evolution and metal interface, Fall meeting of the Japan institute of metals and materials, Nagoya, September 24-26, 2014.

Y. Yasui, A. Hyono, H. Matsushima, T. Ohtsuka, M. Ueda, Electrodeposition of Na on Fe cathode in Na electrorefining, Meeting of ECSJ 2014, Hokkaido University, Sapporo, September 27-28, 2014.

A. Tsuruta, M. Ueda, H. Date, T. Fujii, Electrodeposition of Si in TFSI ionic liquids, Meeting of ECSJ 2014, Hokkaido University, Sapporo, September 27-28, 2014.

S. Shibuya, A. Hyono, H. Matsushima, M. Ueda, Kinetic study of isotope separation in the hydrogen electrode reaction, Meeting of ECSJ 2014, Hokkaido University, Sapporo, September 27-28, 2014.

Mikito Ueda, Electrorefining of Na in Hydrophobic Ionic Liquid, 2014 ECS and SMEQ Joint International Meeting, Cancun, Mexico, October 5-9, 2014.

R. Nakanishi, A. Hyono, H. Matsushima, M. Ueda, Al electrodeposition to porous Ni in EMIC-AlCl<sub>3</sub> ionic liquid, The 46th Symposium on Molten Salt Chemistry, Kazusa Akademia Hall, Chiba, November 13-14, 2014.

## Facilities and Capabilities

Ellipsometer: Rotating-analyzer type of automated ellipsometer with 632.8 nm wavelength of light and null-method ellipsometer for multiple-angle-of-incidence measurement.

Potential Modulation Reflectance: Wavelength region from 350 to 800 nm

Raman Scattering Spectrometer: Bunko Keiki, single type of spectrometer equipped by high sensitive CCD.

FT-IR Spectrometer: JASCO FT/IR 4200 equipped with MCT detector, IR-RAS apparatus and IR microscopy system.

QCM system for in-situ gravimetry of surface layer on metals.

Electrochemical AC Impedance: NF Circuit Design 5020 FRA and 5095 FRA equipped with a specially designed potentiostat.

ICP atomic emission spectrometer: Thermo i-CAP 6000.

Carl Fischer moisture measuring system: Metrohm 852 titrando.

Evaporator: Eyela SB1100.

Electrochemistry apparatuses.

Optical Microscopy.

Electrochemical Corrosion Rate Monitor System.

Molten salt ion-exchange apparatus for glass.

Luminescence apparatus for thin surface layer equipped with He-Cd UV laser.

Video scanning rate Atomic Force Microscopy (Video-AFM).

Quadrupole Mass Spectroscopy (Q-Mass): ULVAC Quless CGM-052.

Rotating Disc Electrode (RDE) system.

Near Infrared Spectrometer: Ocean optics NIR256-2.1



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The research activities of the laboratory are directed towards the development of advanced oxide films and nanomaterials utilizing anodizing process, sol-gel process and PVD for possible applications including novel fuel cells, air batteries, photovoltaic cells, corrosion protection, self-cleaning surfaces and capacitors. We are also interested in surface analytical techniques with nanoscale resolution for a better understanding of the interfacial phenomena of metal and semiconductor electrodes in relation to electrochemical devices for energy storage and conversion, corrosion, passivation and surface finishing.

Current topics on research are in the following:

(1) Intermediate-temperature fuel cells

We successfully fabricated gas-tight silicate and phosphate nanofilms, which show efficient proton conductivity even in dry atmosphere at intermediate temperatures (200-400°C). Utilizing the proton-conducting nanofilms as an electrolyte membrane, we designed a hydrogen membrane fuel cells (HMFCs). In HMFCs, palladium foil was used as a hydrogen-permeable anode and we succeeded power generation. We also found that the  $ZrO_2$ - $WO_3$ - $SiO_2$  films formed by anodizing of magnetron-sputtered Zr-W-Si alloys reveal high proton conductivity even below 200°C.

(2) Tailoring of self-organized porous anodic oxides on various metals

Recently, we have found that phosphate-glycerol solution at elevated temperature is a new electrolyte to form self-organized porous anodic films on various valve metals. We have already successfully developed self-organized porous anodic films on titanium, niobium and aluminum in the hot phosphate-glycerol electrolyte. For titanium, we succeeded to obtain mesoporous crystalline anatase films without post annealing. In addition, using organic electrolytes containing fluoride ions, self-organized nanoporous anodic films have been successfully developed on iron and stainless steel. The growth behavior and their properties have been examined in detail.

(3) Fabrication of superhydrophobic and superoleophobic surfaces

One of the important factors to control the surface wettability of solid materials is surface geometry. Hierarchical porous surface morphology is of particular importance to obtain superhydrophobic surfaces together with surface energy of solid materials. Further precise control of the surface geometry resulted in the formation of superoleophobic surfaces, on which oil droplets were readily rolled off. Utilizing porous anodic films, we developed hierarchical surfaces on aluminum and aluminum alloys and obtained superoleophobic surfaces after coating with a fluoroalkyl monolayer, which had the lowest surface energy.

#### (4) Novel dielectric films formed by anodizing

One of the important practical applications of the anodic films on valve metals is dielectric in electrolytic capacitors. We have examined dielectric properties of the anodic films formed on a range of novel valve metal alloys. Detailed investigations on the significant enhancement of capacitance by forming nanocomposite anodic films, consisting of nanocrystalline tetragonal  $ZrO_2$  phase and an amorphous matrix, have been conducted.

#### Other activities

Prof. H. Habazaki presented invited lectures entitled “Formation of  $ZrO_2$ -based Nanocomposite Anodic Films with High Capacitance” at the 2<sup>nd</sup> International Symposium on Anodizing Science and Technology (AST2014), which was held on 4-6 June 2014 at Sapporo, “Electrochemical fabrication of micro-/nano-dual scale rough surfaces for super-repellency for various liquids” at 10th International Symposium on Electrochemical Micro & Nanosystem Technologies, which was held on 5-8 November 2014, Okinawa Convention Center, Ginowan, and “Pt-supported Platelet Carbon Nanofibers for Oxygen Reduction Reaction” at 5th Symposium on Academic Exchange and Collaborative Research Competence Center for Materials & Processes, ETH Zürich (MaP) and Graduate School of Engineering, Hokkaido University, held on 27-28 November 2014, at ETH Zurich.

Associate Prof. Y. Aoki presented invited lectures entitled “Reversible Redox Behavior of  $NdCrO_4$  by Insertion/Desertion of Proton through Gas-Solid Reaction” at Solid State Proton Conductors-17 (SSPC-17), which was held on 14-19 Sept. 2014 at Seoul, Korea, and “Joint Japan-German research using the ‘French element’ Gallium for next generation electronics” at German JSPS Meeting in Chitose, which was held on 17 May at Chitose Institute of Science and Technology, Chitose.

Assist. Prof. E. Tsuji presented invited lectures entitled “Photoelectrochemical Applications of Crystalline  $TiO_2$  Nanochannel Films Anodized in Fluoride-free Electrolytes” at International Conference of Smart Systems Engineering 2014, which was held on 15-17 October 2014 at Yonezawa, Japan.

## Presentations

C. Kura, Y. Aoki, E. Tsuji, H. Habazaki, “Resistive Switching Behavior of Amorphous TiO<sub>x</sub> Thin Films prepared by Reactive Sputtering Process”, 1st International Symposium on “Ambitious Leader’s Program for Fostering Future Leaders to Open New Frontiers in Material Science”, March 7, Hokkaido University, Hokkaido, 2014.

Masahiro Seo, Hiroki Habazaki, Masayuki Inaba, Mitsutoshi Yokomizo, Takumi Wakabayashi, Takenori Nakayama, “In-situ X-ray absorption spectroscopy of Sn adsorption structure on Ni”, Zairyo-to-Kankyo 2014, May 18-20, Tokyo, 2014.

Y. Aoki, R. Nonaka, E. Tshuji, H. Habazaki, “Hydrogen membrane fuel cell based on amorphous electrolyte thin films”, 2014 E-MRS Spring Meeting, May 26-30, Lille, France, 2014.

F. Kataoka, E. Tsuji, Y. Aoki, S. Nagata, H. Habazaki, “Formation of Anodic Films on Magnesium in Ethylene Glycol-H<sub>2</sub>O Electrolytes Containing Fluoride”, 2nd International Symposium on Anodizing Science and Technology, June 4 -6, Chateraise Gateaux Kingdom Sapporo Hotel & Spa Resort, Sapporo, 2014.

Kohei Kobayashi, Etsushi Tsuji, Yoshitaka Aoki, Shinji Nagata and Hiroki Habazaki, “Characterization of Anodic Films Formed on Ti-Zr Alloys”, June 4- 6, Chateraise Gateaux Kingdom Sapporo Hotel & Spa Resort, Sapporo, 2014.

T. Yamasaki, E. Tsuji, Y. Aoki S.-G Park and H. Habazaki “Pt/Platelet Carbon Nanofibers Synthesized by Liquid Phase Carbonization in Porous Anodic Alumina Templates for Oxygen Reduction Reaction”, June 4 -6, Chateraise Gateaux Kingdom Sapporo Hotel & Spa Resort, Sapporo, 2014.

Yoshiki Konno, Etsushi Tsuji, Yoshitaka Aoki, Toshiaki Ohtsuka, Hiroki Habazaki, “Formation of Composite Coatings of Porous Anodic Oxide/Polypyrrole on Iron”, June 4-6, Chateraise Gateaux Kingdom Sapporo Hotel & Spa Resort, Sapporo, 2014.

Y. Nakayama, E. Tsuji, Y. Aoki, and H. Habazaki, “Potentiodynamic Study of

the Formation of Anodic Alumina Films in Oxalic Acid Electrolyte”, June 4 -6, Chateraise Gateaux Kingdom Sapporo Hotel & Spa Resort, Sapporo, 2014.

Soo-Gil Park, Jin-Kwon Choi, Hong-Il Kim, Dal-Woo Shin, Sung-Han Kim, Moon-Su Lee, Hiroki Habazaki, “Control the Pore Size of AAO Templates for Electrochemical Capacitors”, June 4-6, Chateraise Gateaux Kingdom Sapporo Hotel & Spa Resort, Sapporo, 2014.

Shiki Matsuura, Etsushi Tsuji, Yoshitaka Aoki, and Hiroki Habazaki, “Cyclic Voltammometric Study of the Formation of Crystalline TiO<sub>2</sub> Mesoporous Anodic Films in Hot Phosphate/glycerol Electrolytes”, June 4-6, Chateraise Gateaux Kingdom Sapporo Hotel & Spa Resort, Sapporo, 2014.

Khurram Shahzad, Etsushi Tsuji, Yoshitaka Aoki, Shinji Nagata, Hiroki Habazaki., “On the Influence of Electric Field on Dissolution Rate of Anodic Films on Iron” June 4-6, Chateraise Gateaux Kingdom Sapporo Hotel & Spa Resort, Sapporo, 2014.

Katsutoshi Nakayama, Etsushi Tsuji, Yoshitaka Aoki, and Hiroki Habazaki, “Fabrication of Superoleophobic Hierarchical Surfaces on Aluminum by Chemical Etching and Anodizing”, June 4-6, Chateraise Gateaux Kingdom Sapporo Hotel & Spa Resort, Sapporo, 2014.

Y. Konno, E. Tsuji, Y. Aoki, T. Ohtsuka, H. Habazaki, “Removal of fluoride species from the porous anodic oxide – polypyrrole composite coating on iron”, The 3rd Fronthier Chemistry Center International Symposium “Chanlleges at the Frontier of Chemical Sciences”, June 13-14, Hokkaido Univ., Sapporo, 2014.

K. Shahzad, E. Tsuji, Y. Aoki, S. Nagata, H. Habazaki, “Effect of sweep rate on formation of nanostructured iron oxide films under potentiodynamic anodizing”, The 3rd Fronthier Chemistry Center International Symposium “Challenges at the Frontier of Chemical Sciences”, June 13-14, Hokkaido Univ., Sapporo, 2014.

T. Kimura, T. Yano, E. Tsuji, Y. Aoki, H. Habazaki, “Oxidation of type 430 stainless steel covered with aluminosilicate thin coating at elevated temperatures”, Int. Symp. on High-temperature Oxidation and Corrosion (ISHOC 2014), June

23-27, Hakodate Kokusai Hotel, Hakodate, 2014.

Y. Aoki, “Bulk Mixed Ion Electron Conduction in Amorphous Gallium Oxide Causes Memristive Behaviour”, 7th Nagoya Univ.-Tsinghua Univ.-Toyota Motor Corp.-Hokkaido Univ. Joint Symposium — Materials Science and Nanotechnology for the 21st Century —, 21-24 July, Hokkaido Univ., Sapporo, 2014.

C. Kura, Y. Aoki, E. Tsuji, H. Habazaki, “Resistive switching of Highly-Nonstoichiometric GaOx Thin Films with Low valence state Ga<sup>+</sup> cation having (4s)<sup>2</sup> lone pair electrons”, 7th Nagoya Univ.-Tsinghua Univ.-Toyota Motor Corp.-Hokkaido Univ. Joint Symposium — Materials Science and Nanotechnology for the 21st Century —, 21-24 July, Hokkaido Univ., Sapporo, 2014.

T. Yamasaki, E. Tsuji, Y. Aoki, S-G. Park, H. Habazaki, “Highly Dispersed Pt Deposition on Platelet Structure Carbon Nanofiber Synthesized by Liquid Phase Carbonization”, 7th Nagoya Univ.-Tsinghua Univ.-Toyota Motor Corp.-Hokkaido Univ. Joint Symposium — Materials Science and Nanotechnology for the 21st Century —, 21-24 July, Hokkaido Univ., Sapporo, 2014.

H. Takano, K. Izumiya, N. Kumagai, H. Habazaki, K. Hashimoto, “Characterization and catalytic properties of Ni/Ca-doped ZrO<sub>2</sub> for CO<sub>2</sub> methanation” 7th Nagoya Univ.-Tsinghua Univ.-Toyota Motor Corp.-Hokkaido Univ. Joint Symposium — Materials Science and Nanotechnology for the 21st Century —, 21-24 July, Hokkaido Univ., Sapporo, 2014.

E. Tsuji, Y. Taguchi, Y. Aoki, H. Habazaki, “Size-selective Photocatalytic Decomposition of Organic Molecules Using Anodic Crystalline TiO<sub>2</sub> Mesoporous Films”, 20th International Conference on Photochemical Conversion and Storage of Solar Energy, July 27-August 1, 2014, Berlin, Germany, 2014.

F. Di Franco, A. Zaffora, M. Santamaria, F. Di Quarto, E. Tsuji, H. Habazaki, “Tuning of solid state properties of Al-Ta mixed oxides”, 65th Annual Meeting of the International Society of Electrochemistry, August 31-September 5, 2014, EPFL, Lausanne, 2014.

H. Habazaki, F. Kataoka, E. Tsuji, Y. Aoki, S. Nagata, “Efficient Growth of

Anodic Films on Magnesium in Fluoride-containing Electrolytes”, 65th Annual Meeting of the International Society of Electrochemistry, August 31 -September 5, 2014, EPFL, Lausanne, 2014.

M. Seo, H. Habazaki, M. Inaba, M. Yokomizo, T. Wakabayashi, T. Nakayama, “Inhibition Effect of  $\text{Sn}^{2+}$  on Corrosion of Ni and Sn Adsorption Structure”, 65th Annual Meeting of the International Society of Electrochemistry, August 31 - September 5, 2014, EPFL, Lausanne, 2014.

E. Tsuji, Y. Taguchi, Y. Aoki, H. Habazaki, “Nanostructural Control and Photocatalytic Application of Anodic  $\text{TiO}_2$  Nanochannel Films”, 10th International Symposium on Electrochemical Micro & Nanosystem Technologies, 5-8 November, Okinawa Convention Center, Ginowan, 2014.

T. Yamasaki, E. Tsuji, Y. Aoki, S.G. Park, H. Habazaki, “Influence of Graphitization Degree on the Durability of Pt/Platelet Carbon Nanofibers Electrocatalysts for Oxygen Reduction”, 10th International Symposium on Electrochemical Micro & Nanosystem Technologies, 5-8 November, Okinawa Convention Center, Ginowan, 2014.

K. Kikutani, Y. Aoki, E. Tsuji, H. Habazaki, “Proton conductivity of amorphous zirconium phosphate thin film formed on various substrates”, 10th International Symposium on Electrochemical Micro & Nanosystem Technologies, 5 -8 November, Okinawa Convention Center, Ginowan, 2014.

C. Kura, Y. Aoki, E. Tsuji, H. Habazaki, “Fabrication of  $\text{TiN}_{1-x}$  membranes on porous oxide substrate by reactive RF sputtering”, 2nd International Symposium of Ambitious Leader’s Program Fostering Future Leaders to open new Frontiers in Materials Science: Ambition Across the Disciplines, 11-12 December, Hokkaido University, Hokkaido, 2014.

## **Facilities and Capabilities**

DC and RF magnetron sputtering: Shimadzu SP-2C, suitable for preparation of various metallic thin films as well as oxide and nitride films.

FT-IR spectrometer: Jasco FT-IR350, equipped with DR and RAS attachments.

Ultramicrotomy: RMC MT-7 and PT-X, suitable for the preparation of electron transparent TEM sections.

AFM: SII SPA-400 system with conductive AFM mode as well as contact and tapping modes.

Impedance analyzer: Solartron 1260, measurable in the frequency range of 10  $\mu$ Hz to 32 MHz.

Contact angle meters: Kyowa Interface Science, Dropmaster system, to evaluate superhydrophobicity solid surface.

Q-mass: Balzers Quadstar421 system for mass analysis of gases with mass number of less than 200.

Tribometer: CSM pin-on-disk tribometer for wear and friction characterization of coated materials



## **ECO-PROCESSING LABORATORY**

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### **Foreign Researchers**

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### **Technical Staffs**

M. Kitamura, H. Noguchi, E. Takahashi, M. Tanaka, A. Yamase

### **Students**

M. Baba, K. O. Ito, O. Nishinaga, R. Ishida(deceased), T. Wakamatsu,  
J. Kawashima, H. Takai, D. Nakajima, H. Hada, F. Matsuura,  
S. Akiya, S. Oki, N. Suzuki, A. Takenaga, R. Nashimoto

Prof. Ryosuke O. Suzuki merged as the professor of the laboratory of Eco-processing from Kyoto University on March 2006. He studies the non-ferrous metallurgy based on the molten salt electrolysis. His research activities are directed to design the economical and environment-friendly processes for materials production at high temperatures. The extraction metallurgy of the refractory metals such as Nb and Ta, and of valve metals such as Ti, V and Zr, serves many topics when the electrolysis of CaO in the molten CaCl<sub>2</sub> is applied. The electrolysis of CO<sub>2</sub> gas is one of the extreme cases in oxide decomposition. The thermoelectric power generation is designed from the view of material design and heat exchange.

Dr. Kikuchi joined as an associate professor from laboratory of interface microstructure analysis on May 2010, and he began to study the micro- and nano-structure fabrication by electrochemical techniques such as anodizing, electrochemical etching, and electrodeposition. Electroless calcium reduction of titanium, zirconium, neodymium, and iron oxides in calcium chloride molten salt at high temperature was also investigated for novel electronic device fabrication and recycling of these metals.

Dr. Natsui joined as an assistant professor from Tohoku University on April 2013. His research activities are directed to design the low-carbon ferrous metallurgy by using current numerical simulation technology such as discrete element method, its coupling to CFD, and particle based hydrodynamics. And he began to develop the rapid electro-reduction system by emulsified molten salt at high temperature.

Current topics on corrosion research are in the following:

(1) Molten salt electrolysis of  $\text{CaCl}_2$

Reduction of the oxides of Ti, Nb and Ta are studied, when the CaO dissolved in the molten  $\text{CaCl}_2$  is electrochemically decomposed to form metallic calcium. A low oxygen potential produces the metallic powders at the cathode. The reduced metallic powder is prepared directly from the oxides. The mechanism of this proposal is examined from the electrochemistry and thermodynamics.  $\text{CO}_2$  gas reduction catches the current interests in the morphology of precipitated carbon particles.

(2) Micro- and Nano-structure fabrication by anodizing

Anodic porous alumina has been widely investigated as a nanostructure template in various nano-applications. The nano-morphology of porous alumina is limited by the narrow range of electrolyte species used for anodizing. Therefore, the discovery of additional electrolytes would greatly expand the applicability of porous alumina. We have been working on new electrolytes, such as selenic, squaric, croconic, rhodizonic, acetylenedicarboxylic, ketoglutaric, and acetonedicarboxylic acid, for anodic porous alumina fabrication. Our novel

anodic porous alumina can be used as a nanotemplate for various nanostructures in 100-, 10-, and sub-10-nm-scale manufacturing. In addition, ultra-high density single nanometer-scale anodic alumina nanofibers consisting of an amorphous, pure aluminum oxide were successfully fabricated via pyrophosphoric acid anodizing. The aluminum surface covered by the anodic alumina nanofibers exhibited ultra-fast superhydrophilic behavior, with a contact angle of less than  $1^\circ$ , within 1 second.

### (3) Low-carbon ferrous metallurgical design

In a ferrous metallurgical process, multiphase flow plays an important role in increasing the efficiency by stirring liquid mechanically or by injecting a gas. Owing to the difficulty of direct observation in a high-temperature system or real furnace experiment, numerical analysis is useful and studied. We presents a new particle-based simulation scheme for gas-liquid flow. We improved the numerical stability, which is generally a problem with the particle method, and verified the model's accuracy for fundamental gas-liquid flow analysis. This scheme is also applicable to phenomena in an actual process that includes many dispersal phases.

Other activities

### (4) Thermoelectric power generation

An optimization of the thermoelectric generation is mathematically designed for the highest output. This work links with energy harvesting to conduct the electrolysis. The utilization of solar energy is challenged using cheap materials such as water.

### (5) Electro-reduction in suspended molten salt

The electrochemical reduction of metal oxides is an important process in active metal production. The OS process has revolutionised molten salt electrolysis; however, it still has diffusion and oxide rebuild-up issues. We attempted the electro-reduction in suspended molten salt with gas flow. This approach expects increasing reduction rate and eliminates some of these issues.

Prof. Suzuki made the keynote lecture on Production of Pure Ti Powder at the

4th International Round Table on Titanium Production in Molten Salts held at Shanghai University. Dr. Kikuchi made the invited lectures at the 31<sup>th</sup> Anodizing Research Society Conference and the Autumn Meeting of Electrochemical Society of Japan.

The following foreign scientists visited this laboratory: Prof. Kevin C.-W. Wu (Taiwan), Dr. Sorapong Pavasupree (Thailand), Prof. Frank F. S. Shieu (Taiwan). Dr. X.-N. Meng returned to Northeastern University, China, after working for 2 years as JSPS postdoctoral fellow.

## Presentations

Anodizing in etidronic acid solution and their structural color generation; O. Nishinaga, T. Kikuchi, S. Natsui and R. O. Suzuki : The 31<sup>th</sup> Anodizing Research Society Conference, Oi-machi, Kanagawa, Japan, Nov., 2014.

Effect of electrolyte species on the growth behavior of anodic porous alumina; T. Kikuchi : *ibid.*

Carbon Recycling by Electrochemical decomposition of CO<sub>2</sub> in high-temperature LiCl-KCl molten melt; S. Natsui : POWTEX TOKYO 2014 (The 20th International Powder Technology Exhibition Tokyo), 27 Nov., 2014, Tokyo Big Sight, Japan.

CO<sub>2</sub> gas enrichment by the decomposition of CO<sub>2</sub> gas in CaCl<sub>2</sub>-CaO molten salt; F. Matsuura, H. Hada, T. Wakamatsu, S. Natsui, T. Kikuchi and R. O. Suzuki : The 46th Symposium on Molten Salt Chemistry, 13-14 Nov., 2014, Kazusa Academia Hall, Kisarazu, Chiba, Japan.

Reduction of titanium oxide and evolution of anode gas by electrolysis in CaCl<sub>2</sub>-CaO molten salt; H. Hada, H. Noguchi, S. Natsui, T. Kikuchi and R. O. Suzuki : *ibid.*

Electrochemical measurement and direct observation of CO<sub>2</sub> decomposition behavior in LiCl-KCl melt; S. Natsui, M. Kitamura, T. Wakamatsu, T. Kikuchi and R. O. Suzuki : *ibid.*

CO<sub>2</sub> decomposition behavior by electrolysis in LiCl-Li<sub>2</sub>CO<sub>3</sub> molten salt; T. Wakamatsu, F. Matsuura, M. Kitamura, S. Natsui, T. Kikuchi and R. O. Suzuki : ibid.

Reduction of CaTiO<sub>3</sub> by electrolysis in the molten salt (CaCl<sub>2</sub>-CaO) and cathode shape; H. Noguchi, H. Hada, S. Natsui, T. Kikuchi and R. O. Suzuki : ibid.

Production of Pure Ti Powder from CaTiO<sub>3</sub> Using Electrolysis in CaCl<sub>2</sub>-CaO Melt; R. O. Suzuki : The 4th International Round Table on Titanium Production in Molten Salts, 3-7 November 2014, Shanghai University, Shanghai, China.

Performance analysis of thermoelectric modules using polyhedron elements; X.-N. Meng and R. O. Suzuki : 11th Annual Meeting of Thermoelectric Society of Japan, 29-30 Sept., 2014, NIMS., Tsukuba, Ibaraki, Japan.

Optimization of Thermoelectric Systems Using Radiative Heat; K. Ito and R. O. Suzuki : ibid.

Fabrication of micro-porous alloy by calciothermic reduction for electrolytic capacitor applications ; T. Kikuchi, M. Yoshida, S. Natsui, H. Habazaki and R. O. Suzuki : The Autumn Meeting of Electrochem. Soc. of Jpn., Sapporo, Japan, Sep., 2014.

Conversion of CO<sub>2</sub> to CO by electrolysis in molten LiCl-Li<sub>2</sub>CO<sub>3</sub>; T. Wakamatsu, F. Matsuura, H. Hada, S. Natsui, T. Kikuchi and R. O. Suzuki : 168th Annual Meeting of Iron and Steel Institute of Metals (Fall session), 24-26 Sept., 2014, Nagoya Univ., Nagoya, Aichi, Japan.

CO gas production from CO<sub>2</sub> gas by electrolysis in molten salt; F. Matsuura, H. Hada, T. Wakamatsu, S. Natsui, T. Kikuchi and R. O. Suzuki : ibid.

Reduction of CaTiO<sub>3</sub> by molten salt electrolysis; H. Hada, H. Noguchi, S. Natsui, T. Kikuchi and R. O. Suzuki : ibid.

Characterization of Liquid Trickle Flow in Poor Wettability Packed Bed; S. Natsui, T. Kikuchi, R. O. Suzuki, T. Kon, S. Ueda and H. Nogami : ibid.

Influence of Wettability on Interparticle Droplet Holdup; T. Kon, S. Natsui, S.

Ueda, N. Maruoka and H. Nogami : *ibid.*

3-dimensional numerical analysis of metal emulsion using multiphase particle method; H. Takai, S. Natsui, T. Kumagai, T. Kikuchi and R. O. Suzuki : *ibid.*

Effect of graphite electrodes on the CO<sub>2</sub> reduction by calciothermic reduction; R. Ishida, T. Kikuchi, S. Natsui, N. Sakaguchi and R. O. Suzuki : 155th Annual Meeting of Japan Institute of Metals (Fall session), Nagoya, Japan, Sep., 2014.

Clarification of the tension instability and dispersion mechanisms of molten metal-slag interfaces; S. Natsui, H. Takai, T. Kumagai, T. Kikuchi and R. O. Suzuki : Shigen-Sozai 2014 (Annual Meeting of The Mining and Materials Processing Institute of Japan), Kumamoto, Japan, Sep. 2014.

3D Numerical Analysis of Gas-Liquid-Liquid Multiphase Flow Using Particle Method, H. Takai, S. Natsui, Takehiko Kumagai, T. Kikuchi and R. O. Suzuki : *ibid*

Anodizing of aluminum in etidronic acid - Fabrication of highly ordered porous alumina with large cell diameter; O. Nishinaga, T. Kikuchi, S. Natsui and R. O. Suzuki : The 130th Annual Meeting of Surf. Finish. Soc. Jpn., Kyoto, Japan, Sep., 2014.

Fabrication of porous tungsten oxide films and their photocatalytic activities; J. Kawashima, T. Kikuchi, S. Natsui and R. O. Suzuki : *ibid.*

Fabrication of anodic porous alumina in ketoglutaric acid solution; D. Nakajima, T. Kikuchi, S. Natsui and R. O. Suzuki : *ibid.*

Fabrication of anodic porous alumina via anodizing in cyclic oxocarbon acid; T. Kikuchi, D. Nakajima, J. Kawashima, S. Natsui and R. O. Suzuki : *ibid.*

CO<sub>2</sub> Decomposition by Electrolysis in CaCl<sub>2</sub>-CaO Melt; R. O. Suzuki, T. Uchiyama, T. Wakamatsu, K. Otake, M. Kitamura, S. Natsui, N. Sakaguchi and T. Kikuchi : 65th Annual Meeting of the International Society of Electrochemistry, 31 August - 5 September, 2014 EPFL, Lausanne, Switzerland.

Direct Observation of CO<sub>2</sub> Decomposition Behavior by Electro-reduction in LiCl-

KCl Eutectic Melt; S. Natsui, M. Kitamura, T. Wakamatsu, T. Kikuchi and R. O. Suzuki : *ibid.*

CO<sub>2</sub> Decomposition by Electrolysis in Molten LiCl-Li<sub>2</sub>CO<sub>3</sub>; T. Wakamatsu, T. Uchiyama, S. Natsui, T. Kikuchi and R. O. Suzuki : *ibid.*

Development of oxide and silicide thermoelectric materials and modules; R. Funahashi, Y. Matsumura, R. O. Suzuki, S. Katsuyama, T. Takeuchi, E. Combe and T. Barbier : 5th International Congress on Ceramics (ICC5), Beijing, 18th August, 2014.

CO gas formation from CO<sub>2</sub> using molten salt electrolysis; F. Matsuura, T. Wakamatsu, H. Hada, S. Natsui, T. Kikuchi and R. O. Suzuki : Summer session of FY\_2014, Hokkaido committee of both JIM and ISIJ, 28 July, 2014, Hokkaido Univ., Sapporo, Hokkaido, Japan.

Shape optimization of thermoelectric generator under constant heat flux; K. Ito and R. O. Suzuki : *ibid.*

CO<sub>2</sub> decomposition by electrolysis in LiCl-Li<sub>2</sub>CO<sub>3</sub> melt using ZrO<sub>2</sub> anode; T. Wakamatsu, T. Uchiyama, S. Natsui, T. Kikuchi and R. O. Suzuki : *ibid.*

CO<sub>2</sub> gas decomposition by low temperature molten chloride electrolysis; H. Hada, T. Uchiyama, T. Wakamatsu, F. Matsuura, S. Natsui, T. Kikuchi and R. O. Suzuki : *ibid.*

Effect of electrolyte solution on the growth behavior of anodic oxide films; D. Nakajima, T. Kikuchi, S. Natsui and R. O. Suzuki : *ibid.*

Fabrication of tungsten oxide films via anodizing; J. Kawashima, T. Kikuchi, S. Natsui and R. O. Suzuki : *ibid.*

Modeling of Gas-Liquid-Liquid Flow using 3-dimensional Multi-phase Particle Method; H. Takai, S. Natsui, T. Kikuchi and R. O. Suzuki : *ibid.*

Simulation analysis for thermoelectric elements having the tilted polyhedron shape; X.-N. Meng and R. O. Suzuki : 33<sup>rd</sup> International Conference on Thermoelectrics, (ICT2014), July 6-10, 2014, Renaissance Nashville Hotel,

Nashville, Tennessee, USA.

Dimension of thermoelectric power generation module under constant heat flux; K. O. Ito and R. O. Suzuki : *ibid.*

Development of new silicide thermoelectric modules; R. Funahashi, Y. Matsumura, R. O. Suzuki, S. Katsuyama, T. Takeuchi, E. Combe and T. Barbier : *ibid.*

Fabrication of Highly Ordered Anodic Porous Alumina by Selenic Acid Anodizing; O. Nishinaga, T. Kikuchi, S. Natsui and R. O. Suzuki : AST2014, 2nd International Symposium on Anodizing Science and Technology, Sapporo, Japan, June, 2014.

Heat and Mass Transfer Simulation of Low-carbon Blast Furnace using DEM-CFD; S. Natsui, T. Kikuchi and R. O. Suzuki : Spring Annual Meeting of The Society of Powder Technology, Japan, Kyoto, Japan, 29-30 May, 2014.

3-Dimensional Numerical Analysis of Molten Metal-Slag-Gas Multiphase Flow Using Particle Method; S. Natsui, H. Takai, T. Kikuchi and R. O. Suzuki : Annual Meeting of The Mining and Materials Processing Institute of Japan, Tokyo, Japan, 26-28 March, 2014.

CO<sub>2</sub> decomposition using zirconia and molten salt; R. O. Suzuki, T. Kikuchi, N. Sakaguchi, M. Ueda, T. Kumagai, S. Natsui, I. Ogino, T. Uchiyama, T. Wakamatsu, R. Ishida, M. Kitamura, F. Matsuura and H. Hada : 167th Annual Meeting of Iron and Steel Institute of Metals (Spring session), 21-23 March, 2014, Tokyo Inst. Tech., Tokyo, Japan.

Numerical Analysis of Metal Emulsion Using 3-dimensional Multiphase Particle Method; H. Takai, S. Natsui, T. Kumagai, T. Kikuchi and R. O. Suzuki : *ibid.*

Simulation of Gas-Liquid Dispersion Behavior Using Multiphase Particle Method; S. Natsui, H. Takai, T. Kumagai, T. Kikuchi and R. O. Suzuki : *ibid.*

T. Wakamatsu, T. Uchiyama, S. Natsui, T. Kikuchi, R. O. Suzuki, U. Hatanaka and K. Ohno : 154th annual meeting of Japan Institute of Metals (Spring session), 21-23 March 2014, Tokyo Inst. Tech., Tokyo, Japan.



Effect of iron catalyst on the calciothermic reduction of CO<sub>2</sub> and synthesis of CNTs; R. Ishida, T. Kikuchi, S. Natsui, N. Sakaguchi and R. O. Suzuki : *ibid.*

Nanostructure fabrication via selenic acid anodizing; O. Nishinaga, T. Kikuchi, S. Natsui and R. O. Suzuki : The Winter Joint Meeting of the Hokkaido Branch of Academic Societies of Chemistry, Sapporo, Japan, Jan., 2014.

Fabrication of anodic porous alumina via anodizing in Meldrum's acid solution; A. Sado, T. Kikuchi, S. Natsui and R. O. Suzuki : *ibid.*

CO gas formation from CO<sub>2</sub> gas using molten salt electrolysis; F. Matsuura, T. Uchiyama, T. Wakamatsu, S. Natsui, T. Kikuchi and R. O. Suzuki : Winter session of FY2013, Hokkaido committee of both JIM and ISIJ, 23 -24 Jan., 2014, Hokkaido Citizens Actives Center, Hokkaido, Japan.

Growth behavior of nanoporous alumina via anodizing in squaric acid solution; T. Yamamoto, T. Kikuchi, S. Natsui and R. O. Suzuki : *ibid.*

Fabrication of CNTs via calciothermic reduction of CO<sub>2</sub>; R. Ishida, T. Kikuchi, S. Natsui, N. Sakaguchi and R. O. Suzuki : *ibid.*

## **Facilities and Capabilities**

X-ray diffractometer: Philips X'Pert Pro. A set for thin film XRD and powder XRD, and another set for high temperature XRD using Pt heating planer stage or Al<sub>2</sub>O<sub>3</sub> crucible with RF heating.

Oxygen and Nitrogen Analyzer: LECO TC-600. Inert gas extraction with carbon crucible and infrared absorption method. 5mass%-0.05 mass ppm.

Sulfur and Carbon Analyzer: LECO CS-600. Carbon and nitrogen are converted to CO and NO gas by burning in O<sub>2</sub> gas with RF heating and they are detected by the infrared absorption method.

CO/CO<sub>2</sub> Gas Analyzer IR-400: 4 sets. Yokogawa

Gas Chromatography, Shimazu

NO/SO<sub>2</sub> Gas Analyzer IR-400: Yokogawa. In the range of 0.1 vol% and 2 vol%.

Constant voltage generators: Takasago Electrics. 4 sets. Max.50V and 20 A.

High voltage amplifier: Takasago Electrics. 100V-8000V.

Thermal Analyzers: SII EXSTAR-6000 TG/DTA. With Pt heater up to 1500C.

Thermal Conductivity Measuring Unit: Kyoto Electrics. Hot disk method at room temperature.

## **AFFILIATE MEMBERS**



## **AFFILIATE MEMBER**

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### **Students**

Masaki Aomi, Ali Shaaban, Yusuke Sato, Yuto Nagai, Shohei Yamazoe, Keishi Inoue, Hiroki Murakoshi, Satoshi Oguma, Takumi Kato, Yuto Yoshikawa

Our group has been investigated various research subjects related to corrosion engineering, surface finishing of metals, and development of new technologies of electrochemistry related to energy and environment. Current topics are followings:

(1) Controlling co-electrodeposition of metals by using a double counter electrode electrodeposition system.

A double counter electrode electrodeposition system was developed to enable co-electrodeposition of Al and Zn with a desired composition. This system switches the active counter electrodes of different metals as a metal ion source to alter the composition of an EMIC-AlCl<sub>3</sub>-based ionic liquid bath. Using an integrated counter electrode composed of Al and Zn plates and a thin electrolyte cell, Al and Zn were co-electrodeposited on a Cu plate substrate by the galvanostatic pulse method. The effects of electrodeposition current density, distance between the working and counter electrodes, and electric charge ratio of anodic dissolution on the Al and Zn counter electrodes on the composition of coatings were examined. Experimental results confirmed that current density and charge ratio affected the composition of the coatings. On the other hand, the distance between the counter and the working electrode showed a rather complicated effect on the coating composition. This was explained by the transition of the transport mechanism of Zn ions supplied from the Zn counter

electrode to the working electrode surface via the ionic liquid bath depending on the distance.

## (2) Application of coupling photocurrent method to atmospheric corrosion

A coupling photocurrent method developed in this laboratory enables in-situ measurement of semiconductor properties corroding in wet and dry corrosion condition. In this method, a couple of specimen of same metal was irradiated by UV or Vis light emitted from LED pulse modulated and coupling current responding to the light modulation frequency was detected by using a lock-in amplifier. One of two specimen was corroded by NaCl dispersion to enable asymmetric corrosion progress on two specimens and thus coupling current was activated from corroding specimen to the other. This method was applied to hot-dip Zn-Al alloy coated steel and Cu plate placed in a wet and dry chamber. In case of Zn-Al alloy coatings, response of n-type ZnO ( $E_{BG} = 3.2$  eV) and p-Si ( $E_{BG} = 1.1$  eV) were observed for UV and Vis light, respectively, changing with corrosion progress. Dependence of coupling photocurrent on bias between the two electrodes confirmed the n-type or p-type response. Cu sample also revealed coupling photocurrent to the visible light irradiation due to formation of Cu oxide with p-type semiconductor properties.

## (3) Photo-electrochemical investigation of low-Cr alloyed iron

Corrosion behavior of iron (99.5%, 4N and 5N) and low-Cr (up to 7%) alloyed iron was investigated by measuring the electrochemical polarization, photocurrent spectra, and impedance spectra in pH 3 phosphate solution. The samples were also subjected to the outdoor exposure test for a several months. In the exposure test, Fe7%Cr showed slightly better corrosion resistivity than the others. In the laboratory tests, all iron samples and low Cr alloyed iron samples showed similar n-type semiconductor properties under the anodic polarization condition due to formation of the iron passive films. On the other hand intensity of photocurrent decreased with increase anodic oxidation time on Fe7%Cr alloy while change in spectra was not clear. Such transition of photocurrent response should be related to the compositional changes of the

passive film under the anodic polarization in the acidic solution such as enrichment of Cr ions and thinning of the passive films.

#### (5) Electrochemical CO<sub>2</sub> reduction in hydrophobic ionic liquid

Electrochemical reduction of CO<sub>2</sub> to methane in EMIm-TFSI (1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide) ionic liquid had been investigated. EMIm-TFSI was known to absorb CO<sub>2</sub> gas and thus considered as an electrolyte medium for electrochemical CO<sub>2</sub> reduction. Two compartments electrochemical cell composed of ionic liquid bath with Cu cathode and KOH aqueous solution bath with Pt anode separated by a proton conducting membrane was used for efficient reaction. Methane and hydrogen gas sensors placed at the gas outlet of the cell confirmed formation of CH<sub>4</sub> and H<sub>2</sub> gases under the cathodic polarization of Cu electrode in ionic liquid saturated with CO<sub>2</sub> gas. Currently gas chromatograph is building into to the gas line of the system for quantitative analysis to find the optimum polarization condition.

#### (6) Corrosion monitoring of Cu foil embedded in swelled bentonite clay

Cu has been considered as a candidate for metal container of high level radioactive nuclear waste vitrification produced in nuclear power plants. The containers are required to separate their contents from human sphere for very long term as 10000 years. To achieve this, it is planned that the containers are covered with bentonite clay layer as a mechanical buffer and a transportation barrier and stored at repository deep underground around 500 m. Corrosion resistivity of metal container for long period is thus important issue to ensure the long-term repository of nuclear waste. Metal corrosion may progress in the condition of high temperature due to residual nuclear fission reaction, contacting with water passed through bentonite clay containing various ions such as carbonate, sulfate and chloride, changing oxygen level from atmosphere level to almost zero level depending on the repository stage and high mechanical stress due to rock pressure after sealing the repository. To evaluate the actual corrosion rate of Cu embedded in swelled bentonite clay, an integrated corrosion monitoring system was built including in-situ measurement of resistometry,

impedance, corrosion potential and coupling current between two Cu foil specimens under controlling temperature and oxygen level for long period as a few months. In the test experiments, it was confirmed that the corrosion behavior of Cu in swelled bentonite clay differed considerably from that in the aqueous solutions containing similar ions.

(7) Promotion of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> formation on an Ni–Al alloy using a Ni–Fe<sub>2</sub>O<sub>3</sub> nano-composite seeding layer

Thin seeding layers of Ni and Ni–Fe<sub>2</sub>O<sub>3</sub> composites were successfully formed on an Ni50Al alloy using the pulse electrodeposition method (PED) from a Watts bath in order to promote  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> formation for improving the high temperature oxidation resistance of the Ni50Al alloy. The conditions for the PED and the effects of these seeding layers on Al<sub>2</sub>O<sub>3</sub> scale formation on the Ni50Al alloy were investigated. The coated samples showed thicker oxide scales than bare Ni50Al samples in oxidation tests at 1000 °C in air. At the initial stage of oxidation (1 h), a single layer scale composed of blade-like crystals of metastable  $\theta$ -Al<sub>2</sub>O<sub>3</sub> was formed. The oxide scales formed on the PED coated samples had a multilayered structure consisting of an inner layer of either a mixture of  $\theta$ - and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> or of single-phase  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, intermediate NiAl<sub>2</sub>O<sub>4</sub> layer and an outer NiO layer. The Ni- seeding layer was found to delay the phase transformation of  $\theta$ - to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> to 100 h of oxidation. Addition of 3.1% Fe<sub>2</sub>O<sub>3</sub> to the Ni-seeding layer accelerated the transformation of  $\theta$ - to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> after 9 h of oxidation. Further addition of Fe<sub>2</sub>O<sub>3</sub> nano-powder (5.2%–7.4%) to the Ni-seeding layer successfully suppressed the  $\theta$ -Al<sub>2</sub>O<sub>3</sub> formation even at 1 h of oxidation.

## Presentation

K. Azumi; Development of corrosion monitoring resistometry for field works, Annual meeting of Japan Society of Corrosion Engineering 2014, Yonago, Nov. 26-28, 2014.



Y. Sato, K. Azumi; An-Zn plating from ionic liquid bath using a double counter electrodeposition method, The 130th Annual Meeting of Surf. Finish. Soc. Jpn., Sept. 22-13, Kyoto university of science, 2014.

H. Murakoshi, K. Azumi, M. Ueda; Optimization of Zn plating on AZ31 alloy from molten salt bath, *ibid.*

K. Azumi; In-situ atmospheric corrosion monitoring using resistometry, EuroCorr2014, Pisa, Italy, Sept. 7-11, 2014.

Y. Sato, K. Azumi; Electrocodeposition of Al-Zn alloy by using double counter electrodes system, *ibid.*

K. Azumi; Recent progress in electrochemistry using ionic liquid, NTTH Symposium, Sapporo, Japan, July 21–24, 2014.

N. Murakami; Atmosphere dependence of electric conductivity of polypyrrole, *ibid.*

S. Kashima; Fabrication and characteristics of poly (3- octyloxythiophene) thin film transistor, *ibid.*

A. Shaaban, K. Azumi, and S. Hayashi; Effect of nano metal coatings on growth kinetics of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> formed on Ni-50Al alloy, ISHOC 2014, Hakodate, June 23-27, 2014.

A. Shaaban, S. Hayashi, K. Azumi; Effects of nano coatings on high temperature oxidation kinetics of NiAl Alloy, FCC symposium, Hokkaido Univ., June 13-14, 2014.

Y. Sato, K. Azumi; Electrocodeposition of Al-Zn layer by using double counter electrodes method, *ibid.*

H. Murakoshi, K. Azumi, and M. Ueda; Optimization of electrodeposition Al on Mg Alloy from the molten salt bath, AST2014, Barato, June 4-6, 2014.

Y. Nagai, K. Azumi; Corrosion monitoring of metals embedded in bentonite clay, *ibid.*

S. Yamazoe, K. Azumi; In-situ coupling photocurrent method for atmospheric corrosion", *ibid.*

Sato and K. Azumi; Electrodeposition of Al-Zn alloy layer by applying double counter electrodes system, *ibid.*

A. Shaaban, K. Azumi, S. Hayashi ; Effect of nano metal coatings on growth kinetics of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> Scale Formed on Ni-50Al Alloy, 9th Intern. Conf. Microscopy of Oxidation, University of Nottingham, UK, April 14-16, 2014.

K. Azumi, Y. Tsugawa ; Application of water absorbing polymer to electrolytic probe for corrosion monitoring, Annual meeting of Japan Society of Corrosion Engineering, 2014, Tokyo, May 18-20, 2014.

H. Murakoshi, K. Azumi, M. Ueda ; Optimization of Al deposition on Mg alloy from molten salt bath, The 129th Annual Meeting of Surf. Finish. Soc. Jpn., March 13-14, Tokyo university of science, 2014.

Y. Sato, K. Azumi; Al-Zn alloy plating by using a double counter electrodeposition method , 81th Annual meeting of Japan Society of Electrochemistry, Kansai university, March 29-31, 2014.

S. Yamazoe, K. Azumi; Development of in-situ coupling photocurrent method for atmospheric corrosion, *ibid.*

K. Inoue, K. Azumi, S. Kajiyama; Comparison of electrochemical properties of iron with different purity, *ibid.*

K. Azumi; Development of a new measurement method of atmospheric corrosion, NIMS-HU seminar, NIMS, Feb. 21, 2014.

K. Inoue, K. Azumi; Photoelectrochemical response of passive film formed on high purity iron, Winter Joint Meeting of the Hokkaido Branch of the Chemistry Related Societies, Sapporo, Jan. 28-29, 2014.

K. Suetake, K. Azumi; Efficient electrochemical CO<sub>2</sub> reduction using ionic liquid, *ibid.*

H. Murakoshi, K. Azumi; Optimization of Al plating on Mg alloys from molten salt bath, *ibid.*

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## **Students**

J.-S. Lee, Y. Takabatake, H. Ikeyama, M. Jin, K. Yanagisawa, Y. Yamamoto, M. Goto

The research activities of the laboratory are directed to the materials surface science and engineering. We are interested in the micro-electrochemistry for a better understanding of the interfacial phenomena of metal and semiconductor electrodes in relation to electrochemical devices, corrosion, passivation, and surface finishing.

Current topics on research are as follows:

### (1) Grain-dependent Passive State of Iron Single Grains in Sulfuric Acid

Passivation of single grains on a polycrystalline pure iron was investigated in sulfuric acid with a micro-capillary-cell. Passivation behavior of the iron single grains under potentiostatic polarization depended on the crystallographic orientation of a substrate iron surface. Electrochemical impedance spectroscopy and cathodic reduction of the surface passivated on single grains revealed that the charge transfer resistance and the thickness of passive films depended on the orientation and that the thicker oxide film exhibited the smaller resistivity. XPS analysis evaluated that the composition of the film varied among the surface orientations. It was suggested that the structure of the passive film depended on the orientation of the iron substrate due to different surface energy and work function on each crystallographic orientation of bcc iron.

### (2) Corrosion Behavior of Dual-Phase Carbon Steel and Super Duplex Stainless Steel

Corrosion behavior of high-purity dual-phase carbon steel composed of only ferrite and martensite phases in 0.1 M sulfuric acid was investigated by both macro- and micro-electrochemical methods. The dual-phase steel corrodes non-uniformly due to galvanic coupling between its microstructures as well as self-corrosion of each phase. Hydrogen evolution reaction on galvanic-coupled martensite accelerates iron dissolution reaction of ferrite, though the corrosion rate of martensite was three-times larger than that of ferrite due to the self-corrosion in the acid. Totally, ferrite phases corrode selectively and the degree of selective corrosion was about two-times larger than martensite phases.

Corrosion behavior of super duplex stainless steel (SDSS) in acidic chloride solution was also investigated electrochemically. Potentiostatic polarizations of SDSS at -0.377 and -0.447 V<sub>SHE</sub> resulted in selective dissolution of gamma- and alpha-phases, respectively, and were utilized for fabricating single-phase electrodes. Potentiodynamic polarization curve of SDSS could be calculated from those of single-phase electrodes. The higher corrosion current density and less noble corrosion potential of alpha-phase characterized by galvanic connection with gamma-phase indicated that alpha- and gamma-phases were functioned as the anode and the cathode, respectively, in the corrosion of SDSS.

(3) *In-situ* observation of passive surface by using an ellipso-microscope and electrochemical impedance spectroscopy during UV-light irradiation

Photo-corrosion of an anodized titanium surface in 0.05 mol dm<sup>-3</sup> sulfuric acid solution was investigated by using an in situ electrochemical ellipso-microscope. Irradiation of UV-light on an anodized surface, which showed a patch-like bright image on an ellipso-microscopic view due to non-uniform growth of the oxide film, under potentiostatic polarization allowed the flow of a photo-induced anodic current and changed the brightness and patch pattern in the image. This indicates that the irradiation promotes photo- electrochemical reaction, resulting in a change in the thickness and/or structure of the oxide film on the surface. The film change was dependent not only on power density of the irradiation light but also on applied potential during the irradiation and crystallographic orientation of the substrate. Pitting initiation during potentiodynamic polarization in the acid with bromide ions was also

monitored using the ellipso-microscope. The irradiation resulted in pitting initiation at lower potentials than those in a non-irradiated condition.

#### (4) Fabrication of Multichannel Microelectrode-array and Its Application

Scanning probe technique such as an SECM enables to visualize the electrochemical activity on a specimen electrode. However, it is not suitable to pursue the relatively rapid reaction of the electrode such as an initiation of pitting corrosion. In order to overcome this problem, a microelectrode-array has been fabricated by MEMS technologies in collaboration with Nanotechnology Platform, Waseda University. Simultaneously, a numerical calculation of diffusion problem on the microelectrode array has been conducted.  $10 \times 10$ - channels array structure with a microelectrode diameter of 10  $\mu\text{m}$  successfully showed limiting currents flowing through 100 microelectrodes independently. Interference effect between electrodes in the array was also simulated. These results have been used to re-design the array.

#### (5) Exploring New SECM Redox Mediator for Corrosive Surface

SECM is an effective tool for investigating the corrosive interface. Conventionally, it has been used to image passive metal surface by combination of redox mediator of ferro- or ferri-cyanide ions. In order to extend the application of SECM measurement in corrosion research, new method and new mediator are explored. One of candidates for new redox mediator is ferrocenemethanol. DFT of ferrocenemethanol as well as other mediator molecules was carried out and revealed the dependence of the redox potential on LUMO state of the molecule. Though ferrocenemethanol has a similar redox potential with ferro-/ferri-cyanide ions, ferrocenemethanol shows a lateral resolution better than ferrocyanide ions during SECM imaging of passive surface on dual phase carbon steel.

#### (6) Convection-dependent Hydrogen Permeation into a Carbon Steel Sheet

In order to avoid hydrogen embrittlement of carbon steel sheet, basic research for mechanism and kinetics of hydrogen penetration is necessary. The Devanathan-Stachurski double electrochemical cell for measurement of hydrogen-permeation into a steel sheet was extended to an electrolyte-flowing design. Increase in flow rate of the entry cell induces increase in hydrogen- evolution current at the entry electrode but decrease in hydrogen-permeation

current at the hydrogen-exit electrode. Hydrogen-permeation is actualized by a sinusoidal perturbation of the entry-flow rate. The hydrogen-permeation response, i.e., phase shift of the detection current from the evolution current, was proportional to the square root of flow rate frequency and was dependent on sheet thickness. The sinusoidal perturbation of entry-flow rate is a new factor influencing hydrogen-permeation into the sheet.

#### Other Activities

In June, Dr. Koji Fushimi, Mr. Jun-Seob Lee, and Mr. Yu Takabatake attended to 2nd International Symposium on Anodizing Science and Technology (AST2014) and presented three papers. Mr. J.-S. Lee and Mr. Y. Takabatake also attended to The 3rd Frontier Chemistry Center International Symposium “Challenge at the Frontier of Chemical Sciences” and presented two papers. Mr. Y. Takabatake won FCC Poster Award. In August, Dr. K. Fushimi, Mr. Kei Yanagisawa, and Mr. Yudai Yamamoto attended to 65th ISE Annual Meeting, Lausanne, Switzerland and presented three papers. In September, Dr. K. Fushimi, Mr. J.-S. Lee, and Mr. Y. Takabatake attended to Eurocorr2014, Pisa, Italy and presented three papers. In November, Dr. K. Fushimi and Mr. J.-S. Lee attended to 19th International Corrosion Congress, Jeju, Korea and presented a keynote lecture entitled “Anodic Dissolution Sequence of Super Duplex Stainless Steel in an Acidic Chloride Solution” and a paper.

### **Presentations**

K. Fushimi, K. Kurauchi, T. Nakanishi, Y. Hasegawa, M. Ueda, “Ellipso-microscopic Imaging of Anodized Titanium Surface under UV-light Irradiation”, 2nd International Symposium on Anodizing Science and Technology (AST2014), Jun. 4-6, Sapporo, Japan (Oral presentation).

Y. Takabatake, K. Fushimi, T. Nakanishi, Y. Hasegawa: “Anodic Oxide Film Formed on Iron Dependinh on Crystallographic Orientation”, 2nd International Symposium on Anodizing Science and Technology (AST2014), Jun. 4 -6, Sapporo, Japan (Poster).

J.-S. Lee, K. Fushimi, T. Nakanishi, Y. Hasegawa: “Generation of Sulfide Ions

from Ag-Microelectrode on Iron Electrode”, 2nd International Symposium on Anodizing Science and Technology (AST2014), Jun. 4 -6, Sapporo, Japan (Poster).

J.-S. Lee, K. Fushimi, T. Nakanishi, Y. Hasegawa: "Reduction of Ag<sub>2</sub>S-microelectrodes as Sulfide Ion Generator ", The 3rd Frontier Chemistry Center International Symposium “Challenge at the Frontier of Chemical Sciences”, Jun. 13-14, Sapporo, Japan (Poster).

Y. Takabatake, K. Fushimi, T. Nakanishi, Y. Hasegawa: "Effect of Metallographic Structure on Electrochemical Oxidation of Pure Iron", The 3rd Frontier Chemistry Center International Symposium “Challenge at the Frontier of Chemical Sciences”, Jun. 13-14, Sapporo, Japan (Poster).

K. Yanagisawa, K. Fushimi, T. Nakanishi, Y. Hasegawa, T. Kawano, M. Kimura, “Corrosion of dual-phase carbon steel in 0.1 mol dm<sup>-3</sup> sulphuric acid aqueous solution”, 65th ISE Annual Meeting, Aug. 31-Sep. 5, Lausanne, Switzerland (Poster).

Y. Yamamoto, K. Fushimi, T. Nakanishi, Y. Hasegawa, M. Saito, T. Homma, “Redox reaction current on multi-microdisc electrode”, 65th ISE Annual Meeting, Aug. 31-Sep. 5, Lausanne, Switzerland (Poster).

Y. Takabatake, K. Fushimi, T. Nakanishi, Y. Hasegawa, “Micro-electrochemical reactivity of iron single crystal grain during anodic polarisation in 0.05 mol dm<sup>-3</sup> sulphuric acid aqueous solution”, 65th ISE Annual Meeting, Aug. 31 -Sep. 5, Lausanne, Switzerland (Oral presentation).

K. Fushimi, K. Kurauchi, T. Nakanishi, Y. Hasegawa, M. Ueda, T. Ohtsuka; “Non-uniformity of Anodized Titanium Surface under UV-light Irradiation Observed by Ellipso-microscopy, Eurocorr 2014, Sep. 8-12, Pisa, Italy (Oral presentation).

Y. Takabatake, K. Fushimi, T. Nakanishi, Y. Hasegawa; “Grain-dependency of passive oxide film formed on iron in sulphuric acid”, Eurocorr 2014, Pisa, Italy, Sep. 8-12, Pisa, Italy (Oral presentation).



J.-S. Lee, K. Fushimi, T. Nakanishi, Y. Hasegawa; “Development of a Liquid-phase Sulfide Ion Gun for Localized Sulfidation of Metal Surfaces”, Eurocorr 2014, Sep. 8-12, Pisa, Italy (Oral presentation).

K. Fushimi, K. Kurauchi, T. Nakanishi, Y. Hasegawa, M. Ueda, T. Ohtsuka; “Ellipso-microscopic Observation of Titanium Surface under UV-light Irradiation”, 19th International Corrosion Congress, Nov. 2-6, Jeju, Korea (Oral presentation).

J.-S. Lee, K. Fushimi, T. Nakanishi, Y. Hasegawa, Y.-S. Park; “Anodic Dissolution Sequence of Super Duplex Stainless Steel in an Acidic Chloride Solution”, 19th International Corrosion Congress, Nov. 2-6, Jeju, Korea(Keynote lecture).

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T. Sasaki, T. Yamaguchi, K. Igarashi, H. Mizukami, R. Sakaki, F. Nishino, L. Rao, and R. Itzinger

Mr. Lalith Rao, School of Mechanical Sciences, Indian Institute of Technology Bhubaneswar, India, joined our group as internship student from 16th May 2014 to 16th July 2014. Ms. Regina Itzinger, Johannes Kepler University Linz, Austria, joined our group as internship student from 14th July 2014 to 5th September 2014.

Research work of our group directs toward (1) effect of metal cations on passive film structure of aluminum alloys in model tap water, (2) effect of CH<sub>3</sub>COONa concentration on oxide film composition and corrosion behavior of 13 % Cr stainless steel in model oil and gas environments, (3) Effect of surface condition on hydrogen permeation behavior of zinc coated steels during cyclic wet and dry corrosion (4) Formation of layer structured porous type anodic alumina locally by solution flow type micro-droplet cell, (5) effect of water layer thickness on oxygen reduction reaction on zinc coated steels, (6) formation of multi layer structure of Cu-Ni with nano-size thickness and its property, and 7)Field exposer test in cold and heavy snow district.

Current topics on research are in the following:

(1) Effect of metal cations on passive film structure of aluminum alloys in model tap water

It has been reported that the corrosion rate of aluminum alloy in model tap water is affected by kind of metal cation in the media, and the effect can be

explained by metal cation hardness which based on the hard and soft acid and base, HSAB, concept. It is, however, not clear the influence of substrate on the change of passive film structure. The effects of metal cations (Na, Mn and Zn) on the passive film structure of two types of aluminum alloys (A3003 and A5052) were examined by immersion test, potentiodynamic polarization and electrochemical impedance method. From immersion tests, rest potential tends to raise the metal cation hardness, and its of A3003 was about 0.3 V larger than that of A5052. The current density of both alloys were decreased with increasing of metal cation hardness. From the electrochemical impedance observation, film resistance on A3003 is generally larger than that of A5052.

(2) Effect of  $\text{CH}_3\text{COONa}$  concentration on oxide film composition and corrosion behavior of 13 % Cr stainless steel in model oil and gas environments

An acetic acid is the most common organic acid in oil and gas environments, therefore, acetate ions sometimes used in simulated oil and gas environments. However, the role of acetic ions in corrosion behavior and surface film structure. In this year, the effect of  $\text{CH}_3\text{COONa}$  addition, temperature and immersion time on surface film thickness was examined. Addition of  $\text{CH}_3\text{COONa}$  and longer immersion time lead to small hole formation and surface color change. From XPS analysis results, even in high concentration of  $\text{CH}_3\text{COONa}$  and high temperature, surface film thickness less than 5 nm. The film thickness, however, is affected by immersion condition. Permeated hydrogen formed during corrosion detected by micro electrochemical technique and Laser irradiation

(3) Effect of surface condition on hydrogen permeation behavior of zinc coated steels during cyclic wet and dry corrosion

The wet and dry corrosion test with constant dew point test was applied to investigate the effects of composition and corrosion products on the hydrogen permeation behavior of Zn and Zn alloy coated steels, and uncoated steels during wet and dry corrosion tests. Independent of the specimen composition and the area of the formed scratches, the hydrogen permeation current and the corrosion products were observed. The hydrogen permeation current of the steels with the formed scratches decreased with number of cycles of the wet and dry tests. Except in the first cycle there were no significant changes in the current with cycle

number on steels without formed scratches. It was suggests that the composition, scratch, and corrosion products play an important role in the hydrogen permeation behavior during wet and dry corrosion.

An area-selective technique for electrochemical hydrogen detection with laser local activation (focused pulse YAG laser irradiation) was developed, and this technique was applied to measure hydrogen permeation behavior of iron at selected areas.

(4) Formation of layer structured porous type anodic alumina locally by solution flow type micro-droplet cell

A solution flow-type micro droplet cell with co-axial dual capillary tubes (Sf-MDC) was applied to form porous type anodic alumina film with layered structure at selected areas. The anodizing process with different repetition numbers, yielding different oxide layer numbers was performed with the Sf-MDC. The fine structure between the layers and its formation mechanism have not been clarified. The purpose of this year is to clarify the fine structure between the layers of formed porous type anodic alumina films, and also determine the formation mechanism of the layered structure in the formed films. The investigation of cross sections of the formed oxide showed that the pore diameter widened at the boundary between layers. From a simulated anodizing process with the Sf-MDC, the reason for this modification of the pores was suggested to be intermittent anodizing with processes of drying up of the solution of the pores and widening at the bottom of the pores.

(5) Effect of water layer thickness on oxygen reduction reaction on zinc coated steels

It is well known that thickness of water layer plays an important role in cathodic reaction of atmospheric corrosion. However, the relationship between water layer thickness and oxygen limiting current is not clear. In this study, micro electrode technique was applied to investigate oxygen limiting current change with water layer thickness on zinc coated steels. In the thickness range form 0.2 mm to 1mm, the oxygen limiting current increase with decreasing water layer thickness that expect from oxygen diffusion.

6) Multi layer structured of Cu-Ni with nano-size thickness film formation and its property

DC electro-deposition Cu-Ni nano thickness multi layer formation machine was developed. Using Ti as substrate, makes it possible to peel off the formed Cu-Ni film easily. The layer structure was observed by FIB-SEM and layer composition by RBS. From simulation of RBS results, Cu and Ni layered structure was detected, however it become unclear with increasing each layer thickness. The tensile tests results showed strength of the formed Cu-Ni films were almost same strength as same thickness of Cu or Ni. It was success fully recorded the crack propagation under optical microscope.

7) Field exposer test in cold and heavy snow district

The filed exposer test for corrosion of steels in cold and heavy snow district as Sapporo and Akkeshi in Hokkaido is carrying out in this year. This exposer test is a joint research work of e-Asia corrosion mapping project and, NIMS. A one year exposure tests sample was finished and new exposure samples of each steels was set.

Other activities

In February, Assoc. Prof. Sakairi attended 1st international conference on structural integrity (ICONS-2014) at Kalpakkam India, and presented papers entitled "Electrochemical noise evaluation of metal cation effects on galvanic corrosion of aluminum alloys in low concentration of chloride ion containing solutions".

In June, Assoc. Prof. Sakairi and Mr. Sasaki attended 2nd International symposium on anodizing surface and technology, AST2014 at Sapporo, Japan, and presented a paper entitled "Electrochemical noise evaluation of metal cation effects on galvanic corrosion of aluminum in model tap waters" and "Analysis of passive film structure formed on A3003 in sulfate solutions".

In September Assoc. Prof. Sakairi and Mr. Sasaki attended AGH-HU joint symposium at Krakow, Poland, and present papers entitled "Pulsed Laser and micro-electrochemical techniques applied for detection of permeated hydrogen during wet/dry corrosion" and "XPS analysis of surface films formed on aluminum alloys in sulfate solutions".

In September, 65th ISE annual meeting at Lausanne, present a poster entitled "Area selective Porous type Aluminum Anodic Oxide Film Formation by Solution flow type Micro-droplet Cell".

In September, Assoc. Prof. Sakairi attended EUROCORR2014 at Pisa Italy, and presented a paper entitled "Electrochemical noise analysis on modified 13%Cr stainless steels in sour environments under stress".

In October, Assoc. Prof. Sakairi attended the seventh international symposium on marine corrosion and control, Nanjing, China, and presented a paper entitled "Metal cation effects on galvanic corrosion behavior of A2024 aluminum alloy with electrochemical noise."

In November, Assoc. Prof. Sakairi attended 16th international corrosion congress, 16th ICC, at JeJu, Korea, and presented a paper entitled "Improvement of corrosion resistance of aluminum with wettability controlled porous oxide films."

In November-December, Assoc. Prof. Sakairi attended Forschung und Studium in Japan at Universität Wien, Aula Am Campus, Viena, Austria and Hokkaido University–University of Bremen Inter-University Exchange Seminar at Bremen, Germany, and during this trip he and Prof. Nawa also visited Prof. A. Hassel, Johannes Kepler University Linz and discuss about future corroboration.

## **Presentations**

Analysis of passive films formed on A3003 in diluted sulfates solutions by XPS, R. Sasakai, M. Sakairi, and Y. Kaneko, The Winter Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and ISIJ, Sapporo, January, 2014.

Anodic oxide film growth rate change with repetition number during Sf-MDC anodizing, T. Yamaguchi and M. Sakairi, The Hokkaido Secs. of Chem. Soc. Jpn. And Jpn. Soc. Anal. Chem. Sapporo, January, 2014.

Evaluation of metal cation effects on galvanic corrosion of aluminum alloys in low chloride ion containing solutions with electrochemical noise, M. Sakairi, K. Otani, and R. Sasaki, ICONS2014, Kalpakkam, India, February, 2014.

Formation of porous alumina film locally by Sf-MDC, M. Sakairi and T.

Yamaguchi, The 129th meeting of Surf. Fin. Soc. JPN, Tokyo, March, 2014.

Formation of Cu-Ni multi layer by electro-deposition and investigation of the property, M. Sakairi, S. Miura, K. Ohkubo and S. Nagata, The 81th spring meeting of Electrochemistry Japan, Osaka, March, 2014.

Influence of metal cation on corrosion behavior of Al alloy in fresh waters, M. Sakairi, K. Otani, R. Sasaki and A. Kaneko, The Hokkaido Sec. of Light metal soc., Sapporo, April, 2014.

Detection of permeated hydrogen during wet/dry corrosion at laser machined scratch formed on coated steels, M. Sakairi, S. Takagi and K. Igarashi, Zairyo-to-Kankyo 2014, Tokyo, May, 2014.

Investigation of passive film formed on Al alloy in fresh water containing metal cations, R. Sasaki, M. Sakairi, and A. Kaneko, *ibid*.

Electrochemical noise evaluation of metal cation effects on galvanic corrosion of aluminum in model tap waters, M. Sakairi, K. Otani, R. Sasaki, and A. Kaneko, ASST2014, Sapporo, June, 2014.

Analysis of passive film structure formed on A3003 in sulfate solutions, R. Sasaki, M. Sakairi, and A. Kaneko, *ibid*.

Analysis of passive film formed on 13Cr steel in acid NaCl solutions, Summer Joint Meeting The Hokkaido Secs. of Chem. Soc. Jpn. And Jpn. Soc. Anal. Chem., Tomakomai, July, 2014.

Effect of alloying elements on passive film structure formed on Al alloys, R. Sasaki, M. Sakairi, and A. Kaneko, The Summer Joint Meeting of The Hokkaido Secs. of Jpn. Inst. Metals and ISIJ, Sapporo, July, 2014.

Hydrogen permeation behavior at scratch formed on Zn coated steel during wet/dry corrosion, K. Igarashi, M. Sakairi, and S. Takagi, *ibid*.

Exploring the Use of High Cr Oxide Dispersion Strengthened Steels Cladding in Fuel Reprocessing Environment, S. Ningshena, M. Sakairi, K. Sukuzi, S. Ukai, and U. Kamachi Mudali, International conference on Advancements in Materials,

Health and Safety towards Sustainable Energy & Environment (MHS-2014), Chennai, India, August, 2014.

Pulsed Laser and micro-electrochemical techniques applied for detection of permeated hydrogen during wet/dry corrosion, M. Sakairi and S. Takagi, AGH-HU joint symposium at Krakow, Poland, September, 2014.

XPS analysis of surface films formed on aluminum alloys in sulfate solutions, R. Sasaki, M. Sakairi, and A. Kaneko, *ibid.*

Area selective Porous type Aluminum Anodic Oxide Film Formation by Solution flow type Micro-droplet Cell, M. Sakairi, T. Yamaguchi, and K. Fushimi, Lausanne, Switzerland, September, 2014.

Electrochemical noise analysis on modified 13%Cr stainless steels in sour environments under stress, M. Sakairi, J. Tatehara and Y. Mizukami, and H. Hashizume, Eurocorr2014, Pisa, Italy, September, 2014.

Microstructural Characterization and Corrosion Resistance of Mechanically Alloyed Oxide dispersion strengthened steels, S.Ningshen, M. Sakairi, K. Suzuki, S. Ukai, and U. Kamachi Mudali, DAE-BRNS National Conference on Current Trends in Advanced Materials (CTMat-2014), Kolkata, India, September, 2014.

Local porous anodic alumina film formation by Sf-MDC, M. Sakairi and T. Yamaguchi, Autumn meeting of Jpn. Inst. Metals, Nagoya, September, 2014.

Effect of cations on electrochemical noise obtained during galvanic corrosion of Al in model tap water, M. Sakairi, K. Otani, R. Sasaki, and A. Kaneko, Autumn meeting of Electrochemical Society Japan, Sapporo, September, 2014.

Corrosion behavior of Al alloys in model tap water, R. Sasaki, M. Sakairi, A. Kaneko, Corrosion dream2014, Osaka, October, 2014.

Metal cation effects on galvanic corrosion behavior of A2024 aluminum alloy with electrochemical noise, M. Sakairi, A. Kaneko, and R. Sasaki, The seventh international symposium on marine corrosion and control, Nanjin, China, October, 2014.



Formation of hydrophobic surface on aluminum by anodizing and drying treatment, M. Sakairi and V. Goyal, The 127th Autumn meeting of Jpn. Light Metal Soc., Tokyo, November, 2014.

Relationship passive film structure and corrosion behavior of 13Cr stainless steels in acid NaCl solutions, H. Mizukami, M. Sakairi, s. Hashizume, and T. Taniguchi, The 61st discussion meeting of Zairyo-to-Kankyo, Yonago, November, 2014.

Effect of metal cation in model tap water on electrochemical behavior of Al alloys, *ibid.*

Improvement of corrosion resistance of aluminum with wettability controlled porous oxide films, M. Sakairi and V. Goyal, 16th International corrosion congress, Jeju, Korea, November, 201



**ABSTRACT of PUBLICATIONS**



# **Electrorefining of Sodium in Sodium Bis(trifluoromethane)sulfonylimide and Tetrabutylammonium Bis(trifluoromethane)sulfonylimide Mixture Ionic Liquids for Metallic Sodium Recycling**

M. Ueda, R. Inaba, H. Matsushima and T. Ohtsuka

ECS Electrochemistry Letters, **4**, E1-E3 (2014)

To develop an electrorefining process for sodium to enable recycling of used sodium-sulfur batteries, a non-aqueous electrolyte with low melting point was investigated. A mixed ionic liquid of NaTFSI (sodium bis (trifluoromethane) sulfonylimide) - TBATFSI (tetrabutylammonium bis (trifluoromethane) sulfonylimide) was selected for the electrolyte. From AC impedance measurements, a maximum ionic conductivity of  $16 \text{ mS cm}^{-1}$  was established of 20 mol% NaTFSI-TBATFSI concentration at 433 K. Electrorefining for 20 hours was carried out with a stable voltage under constant current electrolysis. Liquid pure sodium was electrodeposited by the constant current electrolysis. The calcium content in the sodium cathode was decreased from 250 to 52 ppm by the electrorefining.

## **Observation of Three-Phase Interface during Hydrogen Electrode Reactions in Unitized Regenerative Fuel Cell**

W. Majima, H. Matsushima, Y. Fukunaka and M. Ueda

Journal of The Electrochemical Society, **161**, F1002-F1005 (2014)

The dynamic behavior of the meniscus of a potassium hydroxide and sulfuric acid droplet on a platinum electrode was studied using a charge-coupled device (CCD) camera and confocal laser microscopy. The three-phase interface was investigated during the hydrogen oxidation reaction (HOR) and the hydrogen evolution reaction (HER). Contact angle measurements revealed a spreading interface during the HER whereas the droplet shape remained unchanged during the HOR for both droplets. The overhead view revealed the formation of many fine droplets near the meniscus boundary during the HOR in the alkaline electrolyte, which agrees with previous results for the oxygen reduction reaction (ORR). The correlation of these observations with electrochemical data and differences in the results between the HOR and the HER suggest that the motion of the meniscus was induced by local pH and temperature gradients, presumably caused by a non-uniform reaction because of the limitations of the dissolved gas.

## Output Characteristics of a Circular Cone Type Graphite Cathode for Al-Cl<sub>2</sub> Fuel Cells in AlCl<sub>3</sub>-EMIC Ionic Liquid

J. Nunomura, M. Ueda, and T. Ohtsuka

Z. Phys. Chem, **228**, 685-689(2014)

To improve the reduction efficiency of chlorine electrodes in aluminum-chlorine cells, this reports a circular cone type graphite cathode, with an electrochemical cell consisting of an aluminum anode and the graphite cathode evaluated in EMIC-AlCl<sub>3</sub> ionic liquid. The current density in the circular cone type cathodes with different cone angles exhibited a maximum value at 40°, and the current density at cell voltage of 0.5 V was about 25 mA cm<sup>-2</sup>. This value is about 80% larger than that of a cylindrical type graphite cathode. In a circular cone type cathode with a 40° angle, the maximum power density recorded was 15.3 mW cm<sup>-2</sup>.

## Improvement of Protective Polypyrrole Film for Corrosion of Zinc-Coated AZ91D Alloy

Nan Sheng, YanHua Lei, Mikito Ueda, and Toshiaki Ohtsuka

Progress in Organic coating, **77**, 1724-1734 (2014)

To improve the protection against the corrosion of AZ91D magnesium alloy provided by conducting polypyrrole (PPy) films, optimization of the electrochemical synthesis of the PPy film was investigated. The bi-layered PPy film was prepared under constant current control, first in a sodium tartrate solution containing molybdate and second in a sodium dodecylsulfate (DS) solution (after the AZ91D alloy was covered by zinc electroplating). Corrosion testing of the zinc-coated AZ91D alloy covered with the PPy film was performed in 3.5% NaCl solution. The more protective PPy film doped with tartrate ions (PPy-Tart film) was formed by the lower current density (CD). Doping of molybdate ions ( $\text{MoO}_4^{2-}$ ) into the PPy-Tart film significantly improved its corrosion protection properties. When the PPy-Tart- $\text{MoO}_4$  layer was covered by an outer PPy layer doped with DS ions, the corrosion protection was further improved. The imposition of ultrasonic waves during the electropolymerization of the inner PPy-Tart- $\text{MoO}_4$  layer was effective in the improvement of corrosion protection. The bi-layered PPy-Tart- $\text{MoO}_4$ /PPy-DS film prepared under ultrasonic irradiation maintained the zinc-coated AZ91D alloy in the passive state during the corrosion test in NaCl solution for 221 h, during which no corrosion products appeared.



## **Influence of pH on the Synthesis and Properties of Polypyrrole on Copper from Phytic Acid Solution for Corrosion Protection**

Y. Lei, N. Sheng, A. Hyono, M. Ueda, T. Ohtsuka

*Progress in Organic Coatings*, **77**, 774-784 (2014)

Polypyrrole (PPy) films were deposited on copper from “green” inhibitor of phytic acid solution for corrosion protection of copper. The corrosion protection property of the PPy layer was studied by an immersion test in a NaCl aqueous solution. The polymerization process of PPy on copper changed with the pH values of phytic acid solution and current density applied. When one oxidized bare copper in phytic acid solution at various pHs containing pyrrole monomer, a thin layer consisting of complex compound of Cu-phytate was firstly formed, followed by the formation of the PPy layer doped with phytate anion on the complex compound layer. The complex compound layer passivated the copper surface and its thickness increased with the lower pH value of the solution and the lower current density applied. It was found that the PPy coating prepared in the phytic acid solution at pH 4 exhibit the most protective property against copper corrosion.

## **Effect of Benzotriazole(BTA) Addition on Polypyrrole Film Formation on Copper and Its Corrosion Protection**

Y. Lei, N. Sheng, A. Hyono, M. Ueda, T. Ohtsuka

Progress in Organic Coatings, **77**, 339-346 (2014)

Benzotriazole (BTA) was added in a conducting Polypyrrole (PPy) film prepared on copper in oxalic acid aqueous solution containing pyrrole monomer to improve corrosion protection by the PPy film and reduce copper corrosion. When BTA was added in the preparation solution, the copper surface was covered by a BTA–Cu complex layer before the anodic polymerization of PPy was started. On the copper surface with the BTA layer, the initial dissolution of copper was inhibited and the PPy polymerization-deposition was started immediately after the anodic current was imposed. The PPy film thus formed was doped with oxalic ions and ionized BTA and was homogeneous in thickness and strongly adhesive. The PPy film containing BTA protected the copper from corrosion in 3.5 wt.% NaCl solution. In 400 h of immersion, copper dissolution was inhibited with 80% protection efficiency relative to that of bare copper.

## Gas Sensing Properties of the Nanostructured Anodic Zr–W Oxide Film

R. M. Vázquez, A. Mozalev, R. Calavia, F. Gispert-Guirado, X. Vilanova, H. Habazaki and E. Llobet

Sensors and Actuators B: Chemical, **204**, 588-595 (2014)

The sensing properties of nanostructured Zr–W mixed oxide film have been investigated. The film was prepared via anodizing a sputter-deposited Zr–W alloy layer through nanopores in an anodic alumina layer superimposed on the alloy. The morphology, structure and chemical composition of the film were examined by SEM and XRD. The film consists of an array of self-ordered nanocolumns protruding from a continuous thin oxide layer. The initially amorphous film material crystallizes to monoclinic  $\text{WO}_3$  and orthorhombic  $\text{ZrO}_2$  due to a high temperature annealing in air. A sensor employing the  $\text{ZrO}_2$ – $\text{WO}_3$  oxide film as active layer was fabricated and used for detecting various concentrations (1–1000 ppm) of  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{NO}_2$  at temperatures up to 300 °C. In hydrogen detection experiments, the sensor was very fast, with a response time of 19 s, and highly sensitive to hydrogen, with a response value of up to 50, while showing incomparably weaker and slower responses to carbon monoxide, ethanol and nitrogen dioxide. The features of the films revealed to date are of importance for improving the chemical, structural and exploitation stability of nanostructured tungsten-oxide-based films and their selectivity in hydrogen gas detection.

## **Morphological Control of Anodic Crystalline TiO<sub>2</sub> Nanochannel Films for Use in Size-selective Photocatalytic Decomposition of Organic Molecules**

E. Tsuji, Y. Taguchi, Y. Aoki, T. Hashimoto, P. Skeldon, G. E. Thompson and H. Habazaki

*Applied Surface Science*, **301**, 500-507 (2014)

We report the size-selective photocatalytic decomposition of organic molecules using crystalline anodic TiO<sub>2</sub> nanochannel films as the photocatalyst. The porous TiO<sub>2</sub> films were formed by anodizing titanium at 20 V in glycerol electrolyte containing various amounts of K<sub>3</sub>PO<sub>4</sub>, K<sub>2</sub>HPO<sub>4</sub>, and KH<sub>2</sub>PO<sub>4</sub> at 433K. Regardless of the electrolyte composition, the as-formed TiO<sub>2</sub> films had a crystalline anatase structure. The basicity of the electrolyte markedly influenced the morphology of the TiO<sub>2</sub> nanochannel films; more regular nanochannels developed with increasing basicity of the electrolyte. Because the diameter of the nanochannels in the films formed in a basic electrolyte was as small as similar to 10 nm, the anodic TiO<sub>2</sub> nanochannel films with a thickness of 5  $\mu$ m revealed a selective photocatalytic decomposition of methylene blue (MB) in a mixture of MB and direct red 80 (DR) kept under UV irradiation. The importance of the diameter of the nanochannels and their uniformity for size-selective decomposition of organic molecules were investigated.

## **In Situ X-Ray Absorption Spectroscopy Study of Sn Underpotential Deposition on Ni from Perchloric Acid**

M. Seo, H. Habazaki, M. Inaba, M. Yokomizo, T. Wakabayashi and T. Nakayama

Journal of the Electrochemical Society, **161**, H195-H202 (2014)

In situ X-ray absorption spectroscopy (XAS) was applied to investigate the Sn underpotential deposition (UPD) on Ni surface from 0.2 M HClO<sub>4</sub> solution containing 10<sup>-3</sup> M Sn<sup>2+</sup> with relation to the inhibition effect of Sn on aqueous corrosion of Ni. The periodical emersion method under potentiostatic polarization, using the surface-roughened Ni plate (surface roughness S-r = 78.3) as a working electrode was employed to detect sensitively the sub-monolayer coverage of Sn on Ni. The Sn K-edge absorption spectra in a scanning XAS mode were measured by monitoring the Sn K-alpha 1 fluorescence line. The Sn K-edge absorption near-edge structure (XANES) in the Sn-UPD potential region has revealed that the Sn-UPD layer on Ni is oxygenated. The extended X-ray absorption fine structure (EXAFS) analysis was performed with a two shell fit of the nearest neighbor Sn-Ni and Sn-O interactions, assuming that the uppermost Ni surface exposed to the solution is mainly oriented to the (111) plane. The results have indicated that Sn atoms are substituted like a surface alloy at face- center-cubic sites in the first Ni layer and further bonded with oxygen atoms. The strong inhibition effect of Sn on aqueous corrosion of Ni is ascribed to the bond between Sn and O atoms in addition to the bond between Sn and Ni atoms.

# Electrochemical Analysis of Hydrogen Membrane Fuel Cells with Amorphous Zirconium Phosphate Thin Film Electrolyte

R. Nonaka, Y. Aoki, E. Tsuji, S. Nagata and H. Habazaki

Electrochemistry, **82**, 859-864 (2014)

An electrochemical analysis was conducted with respect to a hydrogen membrane fuel cell (HMFC) comprising proton-conducting, amorphous zirconium phosphate,  $\alpha$ -ZrP<sub>2.5</sub>O<sub>8.9</sub>H<sub>1.3</sub>, thin film electrolyte supported on a dense Pd anode. The HMFC gave rise to an OCV of 1.0 V, but the maximum power density was limited and was about 1 mW cm<sup>-2</sup> at 400°C. The impedance spectroscopy revealed that the interfacial polarizations were decreased by two orders of magnitude when the cell configuration was changed from the fuel cell setup to the hydrogen concentration cell with an anode symmetric configuration. These results indicated that the polarization losses at the solid-solid anode interface are not a main contribution to the voltage loss of the HMFC. The large cathode polarization might be attributed to the lessened conductivity of amorphous zirconium phosphate electrolyte thin film formed on a precious metal electrode.

## **Fabrication of Superoleophobic Hierarchical Surfaces for Low-surface-tension Liquids**

K. Nakayama, E. Tsuji, Y. Aoki and H. Habazaki

RSC Advances, **4**, 30927-30933 (2014)

This study demonstrates the fabrication of hierarchical surfaces with super-repellency even for low-surface-tension liquids, including octane (surface tension of  $21.7 \text{ mN m}^{-1}$ ). Dual-pore surfaces were prepared by a combination of practical wet processes on an aluminium substrate: chemical etching, anodizing, and organic monolayer coating. The size of the larger pores formed by the chemical etching of aluminium is controlled by the concentration of HCl in the  $\text{CuCl}_2/\text{HCl}$  etching solution. The etched aluminium is then anodized to introduce nanopores, followed by a pore-widening treatment that controls the nanopore size and porosity. The repellency for low-surface-tension liquids is enhanced by increasing the size of the larger pores as well as the porosity of the walls of the larger pores in this dual-pore morphology. Under optimized morphology with a fluoroalkyl-phosphate monolayer coating, an advancing contact angle close to  $160^\circ$ , a contact angle hysteresis of less than  $5^\circ$  and a sliding angle of  $10^\circ$  is achieved even for octane.

## **Formation-structure-properties of Niobium-oxide Nanocolumn Arrays via Self-organized Anodization of Sputter-deposited Aluminum-on-niobium Layers**

A. Mozalev, R. M. Vazquez, C. Bittencourt, D. Cossement, F. Gispert-Guirado, E. Llobet and H. Habazaki

Journal of Materials Chemistry C, **2**, 4847-4860 (2014)

Nanostructured niobium oxide (NO) semiconductors are gaining increasing attention as electronic, optical, and electro-optic materials. However, the preparation of stable NO nanofilms with reproducible morphology and behavior remains a challenge. Here we show a rapid, well-controlled, and efficient way to synthesize NO films with self-organized columnlike nanostructured morphologies and advanced functional properties. The films are developed via the growth of a nanoporous anodic alumina layer, followed by the pore-directed anodization of the Nb underlayer. The columns may grow 30-150 nm wide, up to 900 nm long, with an aspect ratio of up to 20, being anchored to a thin continuous oxide layer that separates the columns from the substrate. The as-anodized films have a graded chemical composition changing from amorphous Nb<sub>2</sub>O<sub>5</sub> mixed with Al<sub>2</sub>O<sub>3</sub>, Si-, and P-containing species in the surface region to NbO<sub>2</sub> in the lower film layer. The post-anodization treatments result in the controlled formation of Nb<sub>2</sub>O<sub>5</sub>, NbO<sub>2</sub>, and NbO crystal phases, accompanied by transformation from nearly perfect dielectric to n-type semiconductor behavior of the films. The approach allows for the smooth film growth without early dielectric breakdown, stress-generated defects, or destructive dissolution at the respective interfaces, which is a unique situation in the oxide films on niobium. The functional properties of the NO films, revealed to date, allow for potential applications as nanocomposite capacitor dielectrics and active layers for semiconductor gas microsensors with the sensitivity to ethanol and the response to hydrogen being among best ever reported.



# Nanostructured Anodic-alumina-based Dielectrics for High-frequency Integral Capacitors

A. Mozalev, M. Sakairi, H. Takahashi, H. Habazaki and J. Hubálek

Thin Solid Films, **550**, 486-494 (2014)

Three types of thin solid films with the nanoscale inner structures were synthesized by sputtering-deposition and anodizing of Al layer, Al-1.5 at.% Si alloy layer, and Al/Ta bilayer on Si wafers. All the anodic films comprised 1  $\mu\text{m}$  thick nanoporous alumina layer as the key component. The essential differences were due to the silicon impurities (AlSi alloy) and the array of nanosized tantalum oxide protrusions in the alumina barrier layer (Al/Ta bilayer). The films were examined by scanning and transmission electron microscopy and electrochemical impedance spectroscopy. Integral capacitors utilizing the anodic films as dielectrics combine the small-value capacitance ( $6.5 \text{ nF cm}^{-2}$ ) with the excellent properties of high withstand field strength ( $1.7\text{--}2.7 \text{ MV cm}^{-1}$ ), low leakage current ( $(3\text{--}20) \times 10^{-12} \text{ A mm}^{-2}$  at  $1.0 \text{ MV cm}^{-1}$ ), and low loss tangent ( $\text{tg}\delta = (4\text{--}6) \times 10^{-3}$ ). The revealed dispersion of dielectric constant, although within 10%, and the presence of loss peaks on the temperature and frequency dependencies of  $\text{tg}\delta$  denote the influence of ion-relaxation mechanism on dielectrics' polarizability, with the characteristic times ranging from 10 to 145  $\mu\text{s}$  depending on the dielectric type. By selecting appropriate technological and electrolytic conditions, the functionality of the capacitors can be optimized to meet the needs of a specific range, from 1 kHz to about 300 MHz operating frequencies.

## **Characterization of Self-Assembled Monolayer on Anodized Aluminum by XPS, AFM and Low-Voltage SEM**

H. Habazaki, H. Sato, E. Tsuji, Y. Aoki and K. Shimizu

ECS Transactions, **58**, 75-83 (2014)

Organic layers of tetradecylphosphonic acid (TDP) and octadecyltriethoxysilane (OES) are formed on flat anodized aluminum surfaces by a simple immersion process. The organic layers are characterized by dynamic contact angle measurements for water, AFM, low-voltage SEM and angle-resolved XPS. The results indicate that a self-assembled monolayer is formed using TDP, but not for OES. Plasma surface treatment prior to the coating was found to significantly influence the formation of organic layers.

# The Effects of Film Thickness and Incorporated Anions on Pitting Corrosion of Aluminum with Barrier-type Oxide Films Formed in Neutral Borate and Phosphate Electrolytes

H. Habazaki, R. Nishimura, K. Okitsu, H. Inoue, I. Kiriya, F. Kataoka, M. Sakairi and H. Takahashi

Journal of Solid State Electrochemistry, **18**, 369-376 (2014)

The pitting corrosion behavior of high-purity aluminum covered with barrier-type anodic films, which are formed in neutral borate and phosphate electrolytes, has been examined in 0.5 mol dm<sup>-3</sup> NaCl solution at an applied potential of -0.6 V versus Ag/AgCl, which is slightly nobler than the pitting potential of -0.64 V in the same solution. The pitting current density,  $i_p$ , increased with time after an incubation time,  $t_i$ . The double logarithmic plot of  $i_p$  and polarization time,  $t$ , reveal two straight lines, which are separated at the time,  $\tau$ . The slope becomes larger after  $\tau$  for the specimens anodized in the phosphate electrolyte, while it becomes smaller for those in the borate electrolyte. Both the  $t_i$  and  $\tau$  increase with the thickness of the anodic films, and at the similar film thickness, they are much larger for the anodic films formed in the phosphate electrolyte than for those in the borate electrolyte. The corrosion process can be divided into three stages: the incubation period up to  $t_i$ , the pit nucleation period before  $\tau$ , and the pit growth period after  $\tau$ . We have discussed the different pitting corrosion behavior of the aluminum specimens covered with the anodic films formed in the borate and phosphate electrolytes in terms of ion selectivity of the anodic films.

## Highly Enhanced Corrosion Resistance of Stainless Steel by Sol-Gel Layer-by-Layer Aluminosilicate Thin Coatings

H. Habazaki, T. Kimura, Y. Aoki, E. Tsuji and T. Yano

Journal of the Electrochemical Society, **161**, C57-C61 (2014)

In this study, aluminosilicate sol-gel coatings were deposited on Type 430 stainless steel by multiple spin casting cycles. Amorphous aluminosilicate coatings, 65 nm thick, were prepared from precursor solutions with 50, 100, and 500 mmol dm<sup>-3</sup> total concentrations of aluminum and silicon species (molar ratio of Al/Si = 1/4) by 10, 5, and 1 spin casting cycles, respectively. Although the obtained coatings had a similar composition with a molar ratio of Al/Si = 25/75, the coatings with increased density were formed by reducing the concentration of precursor solution. The pitting potentials of the coated stainless steels, measured by potentiodynamic polarization in 3.5% NaCl solution, increased remarkably (to 1.1 V vs Ag/AgCl) with a decrease in the concentration of precursor solution. Cyclic corrosion tests, consisting of 30 cycles of spraying of 5% NaCl solution at 35°C for 2 h, drying at 60°C for 4 h, and wetting at 50°C and >95% relative humidity for 2 h, revealed highly improved corrosion resistance. Layer-by-layer sol-gel deposition using diluted precursor solutions is an effective way to obtain highly protective coatings.

## Efficient Growth of Anodic Films on Magnesium in Organic Electrolytes Containing Fluoride and Water

H. Habazaki, F. Kataoka, E. Tsuji, Y. Aoki, S. Nagata, P. Skeldon and G. E. Thompson

Electrochemistry Communications, **46**, 30-32 (2014)

Abstract the present study reports, for the first time, the highly efficient formation of barrier-type anodic films, with flat and parallel metal/film and film/electrolyte interfaces, on magnesium in ethylene glycol electrolytes containing ammonium fluoride and water. The anodizing voltage increases linearly with time during galvanostatic anodizing at  $10 \text{ A m}^{-2}$  up to 350 V. The anodic film formed to 200 V is 247 nm thick, containing a crystalline  $\text{MgF}_2$  phase. Analysis by Rutherford backscattering spectroscopy discloses the film composition of  $\text{MgF}_{1.8}\text{O}_{0.1}$  and Pilling–Bedworth ratio (PBR) of 1.67. The PBR value greater than unity and the formation of chemically stable fluoride-based films may contribute to the film growth at high current efficiency.

## **Mixed Proton Electron Conductivity of Calcium Chromate(V) Apatite**

Y. Aoki, K. Kikutani, E. Tsuji and H. Habazaki

ECS Electrochemistry Letters, **3**, F61-F64 (2014)

This is the first report to investigate on the electrical conductivity of unusual high valence state pentavalent chromium oxides in terms of defect thermodynamics. Calcium chromium(V) apatite was prepared as a single phase, and the electrical conductivity was examined as a function of oxygen partial pressure  $p_{O_2}$ . The conductivity was increased at higher  $p_{O_2}$  in wet atmosphere but it was not dependent on  $p_{O_2}$  in dry atmosphere. The water concentration cell gives stable electromotive force. The features disclosed that the chromium(V) apatite reveals proton electron mixed conductivity under wet oxidative condition.

## **Electrochemical Properties of Heated Carbon Nanofibers for Lithium Ion Capacitor**

S.-K. Ahn, J.-J. Yang, H.-I. Kim, H. Habazaki and S.-G. Park

Chemistry Letters, **43**, 898-900 (2014)

We have investigated the effects of heat treatment on the electrochemical properties of carbon nanofibers (CNFs) for use as an anode material in lithium ion capacitors. The CNFs were fabricated by liquid-phase carbonization on a porous alumina template that was anodized in oxalic acid at 40 V for 30 min and subjected to a pore-widening process in phosphoric acid at room temperature. The CNFs were heated at temperatures of 600, 1000, and 1400 °C to facilitate rearrangement of the carbon structure.

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# **Bulk Mixed Ion Electron Conduction in Amorphous Gallium Oxide Causes Memristive Behavior**

Y. Aoki, C. Wiemann, V. Feyer, H.-S. Kim, C. M. Schneider, H. Ill-Yoo and M. Martin

Nature communications, **5**, 3473/1-/9 (2014).

In thin films of mixed ionic electronic conductors sandwiched by two ion-blocking electrodes, the homogeneous migration of ions and their polarization will modify the electronic carrier distribution across the conductor, thereby enabling homogeneous resistive switching. Here we report non-filamentary memristive switching based on the bulk oxide ion conductivity of amorphous  $\text{GaO}_x$  ( $x \sim 1.1$ ) thin films. We directly observe reversible enrichment and depletion of oxygen ions at the blocking electrodes responding to the bias polarity by using photoemission and transmission electron microscopies, thus proving that oxygen ion mobility at room temperature causes memristive behaviour. The shape of the hysteresis  $I$ - $V$  curves is tunable by the bias history, ranging from narrow counter-8 figure loops to wide-hysteresis, triangle loops as found in the mathematically-derived memristor model. This dynamical behaviour can be attributed to the coupled ion drift and diffusion motion and the oxygen concentration profile acting as state function of the memristor.

## Effect of Sn<sup>2+</sup> on Anodic Dissolution of Ni in Perchloric Acid

Masahiro Seo, Atsushi Hyono, Hiroki Habazaki and Takenori Nakayama

Journal of the Electrochemical Society, **161**, C550-C556 (2014)

The effect of Sn<sup>2+</sup> on anodic dissolution of nickel was investigated in deaerated 0.2 M HClO<sub>4</sub> solution containing Sn<sup>2+</sup> at room temperature. It has been found that the addition of 10<sup>-3</sup> M Sn<sup>2+</sup> inhibits completely the anodic dissolution of Ni. In contrast, tin itself is not passivated in 0.2 M HClO<sub>4</sub> irrespective of the addition of 10<sup>-3</sup> M Sn<sup>2+</sup>. Besides, the anodic dissolution of Ni is not inhibited by the surface coating with Sn (IV) colloid which mainly consisting of hydrous or amorphous nano-crystalline SnO<sub>2</sub>. X-ray photoelectron spectroscopy (XPS) analysis used to supplement our recent X-ray absorption spectroscopy (XAS) results has indicated that the inhibition effect of Sn<sup>2+</sup> on anodic dissolution of Ni is associated with the underpotential deposition (UPD) of Sn on Ni. The metallic bond between Sn and Ni in Sn-UPD layer on Ni is prerequisite to the formation of Sn (II) residue adhesive to the Ni substrate at the more noble potential that brings the inhibition effect on anodic dissolution of Ni. Moreover, the difference between inhibition effects of Sn<sup>2+</sup> and Pb<sup>2+</sup> on anodic dissolution of Ni was discussed on basis of the difference between Sn- and Pb-UPD on Ni.



# Fabrication of a Micro-Porous Ti-Zr Alloy by Electroless Reduction with a Calcium Reductant for Electrolytic Capacitor Applications

Tatsuya Kikuchi, Masumi Yoshida, Yoshiaki Taguchi, Hiroki Habazaki and Ryosuke O. Suzuki,

Journal of Alloys and Compounds, **586**, 148-154 (2014)

A metallic titanium and zirconium micro-porous alloy for electrolytic capacitor applications was produced by electroless reduction with a calcium reductant in calcium chloride molten salt at 1173 K. Mixed  $\text{TiO}_2$ -70 at%  $\text{ZrO}_2$  oxides, metallic calcium, and calcium chloride were placed in a titanium crucible and heated under argon atmosphere to reduce the oxides with the calcium reductant. A metallic Ti-Zr alloy was obtained by electroless reduction in the presence of excess calcium reductant and showed a micro-porous morphology due to the sintering of each of the reduced particles during the reduction. The residual oxygen content and surface area of the reduced Ti-Zr alloy decreased over time during the electroless reduction. The element distributions were slightly different at the positions of the alloy and were in the composition range of Ti-69.3 at% to 74.3 at% Zr. A micro-porous Ti-Zr alloy with low oxygen content (0.20 wt%) and large surface area ( $0.55 \text{ m}^2 \text{ g}^{-1}$ ) was successfully fabricated by electroless reduction under optimal conditions. The reduction mechanisms of the mixed and pure oxides by the calcium reductant are also discussed. [dx.doi.org/10.1016/j.jallcom.2013.10.052](http://dx.doi.org/10.1016/j.jallcom.2013.10.052)

## **Fabrication of Anodic Porous Alumina by Squaric Acid Anodizing**

Tatsuya Kikuchi, Tsuyoshi Yamamoto, Shungo Natsui and Ryosuke O. Suzuki

*Electrochimica Acta*, **123**, 14-22 (2014)

The growth behavior of anodic porous alumina formed via anodizing in a new electrolyte, squaric acid (3,4-dihydroxy-3-cyclobutene-1,2-dione), is reported for the first time. A high-purity aluminum foil was anodized in a 0.1 M squaric acid solution at 293 K and a constant applied potential of 100-150 V. Anodic oxides grew on the aluminum foil at applied potentials of 100-120 V, but a burned oxide film was formed at higher voltage. Anodic porous alumina with a cell size of approximately 200–400 nm and sub-100-nm-scale pore diameter was successfully fabricated by anodizing in squaric acid. The cell size of the anodic oxide increased with anodizing time because of the uneven growth of the porous layer. The anodic porous alumina obtained by squaric acid anodizing consists of amorphous  $\text{Al}_2\text{O}_3$  containing 5-6 at% carbon from the electrolyte. [dx.doi.org/10.1016/j.electacta.2013.12.186](https://doi.org/10.1016/j.electacta.2013.12.186)

## **Rapid Reduction of Titanium Dioxide Nano-particles by Reduction with a Calcium Reductant**

Tatsuya Kikuchi, Masumi Yoshida, Shiki Matsuura, Shungo Natsui, Etsuji Tsuji, Hiroki Habazaki and Ryosuke O. Suzuki

Journal of Physics and Chemistry of Solids, **75**, 1041-1048 (2014)

Micro-, submicron-, and nano-scale titanium dioxide particles were reduced by reduction with a metallic calcium reductant in calcium chloride molten salt at 1173 K, and the reduction mechanism of the oxides by the calcium reductant was explored. These oxide particles, metallic calcium as a reducing agent, and calcium chloride as a molten salt were placed in a titanium crucible and heated under an argon atmosphere. Titanium dioxide was reduced to metallic titanium through a calcium titanate and lower titanium oxide, and the materials were sintered together to form a micro-porous titanium structure in molten salt at high temperature. The reduction rate of titanium dioxide was observed to increase with decreasing particle size; accordingly, the residual oxygen content in the reduced titanium decreases. The obtained micro-porous titanium appeared dark gray in color because of its low surface reflection. Micro-porous metallic titanium with a low oxygen content (0.42 wt%) and a large surface area ( $1.794 \text{ m}^2 \text{ g}^{-1}$ ) can be successfully obtained by reduction under optimal conditions. [dx.doi.org/10.1016/j.jpcs.2014.04.016](https://doi.org/10.1016/j.jpcs.2014.04.016)

## **Fabrication of Anodic Nanoporous Alumina via Acetylenedicarboxylic Acid Anodizing**

Tatsuya Kikuchi, Osamu Nishinaga, Shungo Natsui and Ryosuke O. Suzuki

ECS Electrochemistry Letters, **3**, C25-C28 (2014)

The nano-morphologies of anodic porous alumina formed via anodizing in a new electrolyte, acetylenedicarboxylic acid (ADCA), are described. Anodic oxides grew uniformly on the aluminum at voltage of 87.5–95.0 V, but a burned black oxide film was formed at higher voltage. The burning voltage and the current density under steady-state oxide growth decreased with solution temperature. An anodic porous alumina film with a cell size of 250 nm and nanopores measuring 100 nm could be successfully obtained by ADCA anodizing. The anodic porous alumina possessed numerous non-straight nanopores due to the branching and extinction of the nanopores during anodizing. [dx.doi.org/10.1149/2.0071407eel](https://doi.org/10.1149/2.0071407eel)

## **Fabrication of Anodic Porous Alumina via Anodizing in Cyclic Oxocarbon Acids**

Tatsuya Kikuchi, Daiki Nakajima, Jun Kawashima, Shungo Natsui and Ryosuke O. Suzuki

Applied Surface Science, **313**, 276-285 (2014)

The growth behavior of anodic porous alumina formed by anodizing in novel electrolyte solutions, the cyclic oxocarbon acids croconic and rhodizonic acid, was investigated for the first time. High-purity aluminum specimens were anodized in 0.1 M croconic and rhodizonic acid solutions at various constant current densities. An anodic porous alumina film with a cell size of 200–450 nm grew uniformly on an aluminum substrate by rhodizonic acid anodizing at 5–40 A m<sup>-2</sup>, and a black, burned oxide was formed at higher current density. The cell size of the porous alumina increased with current density and corresponding anodizing voltage. Anodizing in croconic acid at 293 K caused the formation of thin anodic porous alumina films as well as black, thick burned oxides. The uniformity of the porous alumina improved by increasing the temperature of the croconic acid solution, and anodic porous alumina films with a uniform film thickness were successfully obtained. Our experimental results showed that the cyclic oxocarbon acids croconic and rhodizonic acid could be employed as a suitable electrolyte for the formation of anodic porous alumina films. [dx.doi.org/10.1016/j.apsusc.2014.05.204](https://doi.org/10.1016/j.apsusc.2014.05.204)

## Self-Ordering Behavior of Anodic Porous Alumina via Selenic Acid Anodizing

Tatsuya Kikuchi, Osamu Nishinaga, Shungo Natsui and Ryosuke O. Suzuki

*Electrochimica Acta*, **137**, 728-735 (2014)

The self-ordering behavior of anodic porous alumina that was formed by anodizing in selenic acid electrolyte ( $\text{H}_2\text{SeO}_4$ ) at various concentrations and voltages was investigated with SEM and AFM imaging. A high purity aluminum foil was anodized in 0.1-3.0 M selenic acid solutions at 273 K and at constant cell voltages in the range of 37 to 51 V. The regularity of the cell arrangement increased with increasing anodizing voltage and selenic acid concentration under conditions of steady oxide growth without burning. Anodizing at 42 -46 V in 3.0 M selenic acid produced highly ordered porous alumina. By selective dissolution of the anodic porous alumina, highly ordered convex nanostructures of aluminum with diameters of 20 nm and heights of 40 nm were exposed at the apexes of each hexagonal dimple array. Highly ordered anodic porous alumina with a cell size of 102 nm from top to bottom can be fabricated by a two-step selenic acid anodizing process, that includes the first anodizing step, the selective oxide dissolution, and the second anodizing step. [dx.doi.org/10.1016/j.electacta.2014.06.078](https://doi.org/10.1016/j.electacta.2014.06.078)

## **Growth Behavior of Anodic Oxide Formed by Aluminum Anodizing in Glutaric and Its Derivative Acid Electrolytes**

Daiki Nakajima, Tatsuya Kikuchi, Shungo Natsui and Ryosuke O. Suzuki

Applied Surface Science, **321**, 364-370 (2014)

The growth behavior of anodic oxide films formed via anodizing in glutaric and its derivative acid solutions was investigated based on the acid dissociation constants of electrolytes. High-purity aluminum foils were anodized in glutaric, ketoglutaric, and acetonedicarboxylic acid solutions under various electrochemical conditions. A thin barrier anodic oxide film grew uniformly on the aluminum substrate by glutaric acid anodizing, and further anodizing caused the film to breakdown due to a high electric field. In contrast, an anodic porous alumina film with a submicrometer-scale cell diameter was successfully formed by ketoglutaric acid anodizing at 293 K. However, the increase and decrease in the temperature of the ketoglutaric acid resulted in non-uniform oxide growth and localized pitting corrosion of the aluminum substrate. An anodic porous alumina film could also be fabricated by acetonedicarboxylic acid anodizing due to the relatively low dissociation constants associated with the acid. Acid dissociation constants are an important factor for the fabrication of anodic porous alumina films. [dx.doi.org/10.1016/j.apsusc.2014.10.014](https://doi.org/10.1016/j.apsusc.2014.10.014)

# Ultra-High Density Single Nanometer-Scale Anodic Alumina Nanofibers Fabricated by Pyrophosphoric Acid Anodizing

Tatsuya Kikuchi, Osamu Nishinaga, Daiki Nakajima, Jun Kawashima,  
Shungo Natsui, Norihito Sakaguchi and Ryosuke O. Suzuki,

Scientific Reports, **4**, 7411 (2014)

Anodic oxide fabricated by anodizing has been widely used for nanostructural engineering, but the nanomorphology is limited to only two oxides: anodic barrier and porous oxides. Therefore, the discovery of an additional anodic oxide with a unique nanofeature would expand the applicability of anodizing. Here we demonstrate the fabrication of a third-generation anodic oxide, specifically, anodic alumina nanofibers, by anodizing in a new electrolyte, pyrophosphoric acid. Ultra-high density single nanometer-scale anodic alumina nanofibers ( $10^{10}$  nanofibers/cm<sup>2</sup>) consisting of an amorphous, pure aluminum oxide were successfully fabricated via pyrophosphoric acid anodizing. The nanomorphologies of the anodic nanofibers can be controlled by the electrochemical conditions. Anodic tungsten oxide nanofibers can also be fabricated by pyrophosphoric acid anodizing. The aluminum surface covered by the anodic alumina nanofibers exhibited ultra-fast superhydrophilic behavior, with a contact angle of less than 1°, within 1 second. Such ultra-narrow nanofibers can be used for various nanoapplications including catalysts, wettability control, and electronic devices. [dx.doi.org/10.1038/srep07411](https://doi.org/10.1038/srep07411)



## **Porous Anodic Oxide Films on Aluminum and Their Nanofabrication (Review)**

Tatsuya Kikuchi, Daiki Nakajima, Osamu Nishinaga, Shungo Natsui and Ryosuke O. Suzuki,

Journal of Japan Institute of Light Metals, **64**, 476-482 (2014)

In this review article, we introduce the fundamentals of barrier and porous type anodic oxide films formed via anodizing of aluminum. We also introduce the various electrolyte species used for porous alumina fabrication and describe the self-ordering conditions during anodizing in these electrolyte solutions. Highly ordered anodic porous alumina can be successfully fabricated via anodizing under the optimum electrochemical conditions. Various nanoapplications using ordered porous alumina such as optical and electronic devices are also introduced.

[dx.doi.org/10.2464/jilm.64.476](https://doi.org/10.2464/jilm.64.476)

# Multiphase Particle Simulation of Gas Bubble Passing through Liquid/Liquid Interfaces

Shungo Natsui, Hifumi Takai, Takehiko Kumagai, Tatsuya Kikuchi and Ryosuke O. Suzuki,

Materials Transactions, **55**, [11] 1707-1715 (2014)

A newly developed computational fluid dynamics (CFD) model based on a multi-phase particle method is presented for predicting the entrainment behavior of liquid metal into slag due to rising single bubble. By comparing results calculated using this model against experimental data, it was found that the transient behavior of bubbles and the two immiscible liquids can be accurately estimated by this method. The rupturing of the thin water film surrounding the bubble was less reliably predicted, but this 3-dimensional unsteady numerical model still nevertheless provides valuable new information for directly predicting the change in the liquid/liquid interface over time. Such prediction of continuous change in an interface has not been possible by more conventional methods, and thus further improvement in the accuracy of this simulated model may well be the only way to non-empirically predict the metal-slag interface area in actual processes.

[dx.doi.org/10.2320/matertrans.M2014245](https://doi.org/10.2320/matertrans.M2014245)

# **Numerical Analysis of Carbon Monoxide-Hydrogen Gas Reduction of Iron Ore in a Packed Bed by an Euler-Lagrange Approach**

Shungo Natsui, Tatsuya Kikuchi and Ryosuke O. Suzuki

Metallurgical and Materials Transactions B, **45**, [6] 2395-2413 (2014)

In recent years, various methods to decrease carbon dioxide emissions from iron and steel making industries have been developed. The latest blast furnace operation design is intended to induce the low reducing agent operation, highly reactive material is considered a promising way to improve reaction efficiency. Another method utilizes hydrogen in the blast furnace process for highly efficient reduction. Mathematical modeling may help to predict complex in-furnace phenomena, including momentum, heat, and mass transport. However, the current macroscopic continuum model gives no information on the individual particles. In this work, a new approach based on the discrete element method was introduced to consider the interaction between particles under fluid flow in accordance with the arrangement and properties of individual particles. We used an Euler–Lagrange method to precisely understand the influence of the reaction conditions on the behavior of coke and ore particles in three dimensions. The heterogeneity of the reaction rate and temperature distribution was observed to be influenced by the particle arrangement. The endothermic and exothermic reactions influenced each other in the packed bed. Temperature distributions nearly correlated with the gas velocity distribution because convection processes greatly affected the reaction rate. Although convection heat transfer was not a dominant issue in the packed bed, promotion of the reaction by a gas flow was effective.

[dx.doi.org/10.1007/s11663-014-0132-x](https://doi.org/10.1007/s11663-014-0132-x)

# Stable Mesh-free Moving Particle Semi-implicit Method for Direct Analysis of Gas-Liquid Two-Phase Flow

Shungo Natsui, Hifumi Takai, Takehiko Kumagai, Tatsuya Kikuchi and Ryosuke O. Suzuki,

Chemical Engineering Science, **111**, 286-298 (2014)

In a metallurgical process, gas–liquid flow plays an important role in increasing the efficiency by stirring liquid mechanically or by injecting a gas. Owing to the difficulty of direct observation in a high-temperature system or real furnace experiment, numerical analysis is useful and widely studied. However, flexible treatment of complicated free surface behavior such as fragmentation and coalescence of liquids is still a difficult problem. This paper presents a new particle-based simulation scheme for gas–liquid flow. We improved the numerical stability, which is generally a problem with the particle method, and verified the model’s accuracy for fundamental gas–liquid flow analysis.

Because all the phases were discretized as particles in Moving Particle Semi-implicit (MPS) method, the proposed model can track the movement of both the gas and liquid phases directly. A large difference in the real density between the gas and liquid phases makes the gas–liquid interface behavior unstable. This study proposed an optimization of the weakly compressible Poisson equation, an initial particle arrangement, and a smoothed interface density in order to stabilize the multi-density flow analysis. This model guarantees conservation of the fluid volume even for a high-density-ratio flow like that at a gas–liquid interface. Therefore, a gas–liquid interface has been represented with high accuracy. We believe that this scheme is also applicable to phenomena in an actual process that includes many dispersal phases.

[dx.doi.org/10.1016/j.ces.2014.02.038](https://doi.org/10.1016/j.ces.2014.02.038)

## **Ionic Conduction of Oxygen and Calciothermic Reduction in Molten CaO-CaCl<sub>2</sub>**

Ryosuke O. Suzuki, Daisuke Yamada, Shogo Osaki,  
Reyna F. Descallar-Arriesgado and Tatsuya Kikuchi

in "Molten Salts Chemistry and Technology", ed. by Marcelle Gaune-Escard,  
Geir Martin Haarberg, John Wiley & Sons, Chichester, West Sussex, UK,  
ISBN: 978-1-118-44873-1 (2014) pp.115-122.

Oxygen conductive nature of CaO-CaCl<sub>2</sub> melt was confirmed by EMF method at the high oxygen partial pressure,  $PO_2 > 10^{-19}$  atm at 1073-1173 K, while the stable EMF could not be obtained at the low  $PO_2$ . A disk of the oxygen conductive La<sub>0.8</sub>Sr<sub>0.2</sub>Ga<sub>0.8</sub>Mg<sub>0.15</sub>Ni<sub>0.05</sub>O<sub>3</sub> or La<sub>0.8</sub>Sr<sub>0.2</sub>Ga<sub>0.8</sub>Mg<sub>0.2</sub>O<sub>3</sub> was used as the oxygen absorbing anode. The reduction of NiO powder to metallic Ni at cathode and the simultaneous O<sub>2</sub> gas evolution inside the anode indicate the oxygen ionic conduction in the used ceramic pellets as well as in the molten salt. The electric isolation of the NiO powder from the cathode confirmed that the calciothermic reduction occurs through the electrolysis of CaO in the CaCl<sub>2</sub> melt, which is also verified by the CaO concentration dependency of current. [dx.doi.org/10.1002/9781118448847.ch2a](https://doi.org/10.1002/9781118448847.ch2a)

## Thermoelectric Analysis for Helical Power Generation Systems

Xiangning Meng, Takeyuki Fujisaka and Ryosuke O. Suzuki

J. Electron. Mater., **43**, [6] 1509-1520 (2014)

The performance of a three-dimensional helical thermoelectric generation (TEG) system is examined by exposing it to a temperature difference with hot and cold sources. The helical paths for the two thermal fluids give the TEG device the potential to efficiently convert thermal energy. The characteristic performance of the helical system is numerically analyzed by using the finite - volume method in a compact system. The helical system is compared with a straight system in which all the thermoelectric (TE) elements present equivalent geometry. The difference in the TE performance between the two systems is not significant when the TE surfaces are maintained at constant temperatures. Both the electromotive force and the current in the TEG system increase linearly with the temperature difference  $\Delta T$  applied at the two module surfaces. The current preferentially flows through a main path determined by the geometry of the TE element. The merits of the helical design are its compactness, space saving, and smooth fluid flow due to gravity, compared with the straight system. [dx.doi.org/10.1007/s11664-013-2768-8](https://doi.org/10.1007/s11664-013-2768-8)

## Thermoelectric Analysis for Pai-type Thermoelectric Module with Tilted Elements

Xiangning Meng, Takeyuki Fujisaka, Keita O. Ito and Ryosuke O. Suzuki

Materials Research Innovations, **18**, Suppl.4, S4-116-121 (2014)

Thermoelectric (TE) legs in the  $\Pi$ -type module for TE generation are tilted as a shape of parallelogram, and three-dimensional flows of heat and electric charge are examined by using a numerical analysis of finite-volume method. The distributions of temperature and current density are significantly dependent on the module configuration and leg shape. The shortest path is chosen preferentially as mainstream of current. The  $\Pi$ -type module is the most favorable because the maximum performance is obtained in case that the tilting angle is  $90^\circ$ . Under the constant temperature difference, the charge-transporting ability of the stream is governed by the path length.

[dx.doi.org/10.1179/1432891714Z.000000000654](https://doi.org/10.1179/1432891714Z.000000000654)

## **Thermoelectric Analysis for a Three-Dimensional Power Generator in Helical**

Xiangning Meng, Takeyuki Fujisaka, Keita O. Ito and Ryosuke O. Suzuki

Key Engineering Materials, **617**, 260-264 (2014)

Thermoelectric (TE) phenomenon of a helical generator is numerically analyzed by using the finite-volume method in combination with a three-dimensional finite-element (FE) model. The distributions of temperature and current density are significantly influenced by the generator dimension. The output power of helical generator is also affected by the geometric parameter, such as the helical pitch. The output power and conversion efficiency of helical generator are better than those of straight generator where all the TE elements aligned in a straight line. The helical geometry has a satisfactory potential to be a good TE generator.

[dx.doi.org/10.4028/www.scientific.net/KEM.617.260](https://doi.org/10.4028/www.scientific.net/KEM.617.260)



# Optimization of Module Shape in Thermoelectric Power Generation

Ryosuke O. Suzuki and Takeyuki Fujisaka

Key Engineering Materials, **617**, 251-255 (2014)

Heat and electric charge transfer through the thermoelectric (TE) module were analyzed numerically. The thermal heat can expand or shrink in the trapezoid shape in comparison with the conventional  $\Pi$  type module, and the output and efficiency from the module with trapezoid TE elements was examined from the view of shape optimization. The temperature profile and some thermoelectric properties were calculated using the infinite volume method and the original code. The temperature profile in the module showed a complex distribution in the TE elements, however, the efficiency in power generation did not change from that of the rectangular TE module.

[dx.doi.org/10.4028/www.scientific.net/KEM.617.251](https://doi.org/10.4028/www.scientific.net/KEM.617.251)

# **Light-Concentration Characteristic of Water Lens and its Application to Thermoelectric Generation**

Keita O. Ito, Hongtao Sui, Hidetoshi Hakozaki, Hiroshi Kinoshita and Ryosuke O. Suzuki

Key Engineering Materials, **617**, 247-250 (2014)

A water lens was used to concentrate sunlight on the surface of a thermoelectric (TE) module in order to heat it. The shape of this water lens could be flexibly adjusted to compensate for solar altitude changes. The light condensed by the water lens produced a large energy distribution on the top of the module. In this study, we simulated the power generation properties when the top of the module was heated by light with a certain condensing distribution. The simulation results revealed that the energy distribution had little effect on the TE generation if the solar light was effectively condensed on a plate with a condensing width of a few millimeters.

[dx.doi.org/10.4028/www.scientific.net/KEM.617.247](https://doi.org/10.4028/www.scientific.net/KEM.617.247)

## **Simulation of a thermoelectric module having parallelogram elements**

Xiangning Meng, Takeyuki Fujisaka, Keita O. Ito and Ryosuke O. Suzuki

Materials Transaction, **55**, [8] 1219-1225 (2014)

A thermoelectric (TE) module with two different thermal sources for power generation is studied in this work. Here, a conventional  $\Pi$ -type module is tilted in the shape of a parallelogram. A numerical analysis is conducted by using the finite volume method to examine three-dimensional (3-d) flows of heat and electric charge. The module configuration and the shape of the elements determine the distribution of temperature and current density inside the TE module. Further, the shortest path is chosen preferentially as the path of the current, depending on the geometry of the TE elements. Although the distribution of current density depends greatly on the module configuration, the TE output power is not affected by the parallel and symmetrical configurations in the two equivalent modules. Thus, the conventional TE module with  $\Pi$ -type elements is the most favorable, and maximum performance is obtained for a tilting angle of  $90^\circ$  because of the lowest internal electric resistance. [dx.doi.org/10.2320/matertrans.E-M2014822](https://doi.org/10.2320/matertrans.E-M2014822)

## New n-type Silicide Thermoelectric Material with High Oxidation Resistance

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Mater. Res. Soc. Symp. Proc. **1490**, [1] 103-112 (2013)

In order to achieve waste heat recovery using thermoelectric systems, thermoelectric materials showing high conversion efficiency over wide temperature range and high resistance against oxidation are indispensable. A silicide material with good n-type thermoelectric properties and oxidation resistance has been discovered. The composition and crystal structure of the silicide are found out  $Mn_3Si_4Al_2$  (abbreviated as 342 phase) and hexagonal  $CrSi_2$  structure, respectively. Element substitution of Mn with 3d transition metals is succeeded. Enhancement of Seebeck coefficient is observed in a Cr-substituted sample. The maximum dimensionless thermoelectric figure of merit  $ZT$  is 0.3 at 573 K in air for the  $Mn_{2.7}Cr_{0.3}Si_4Al_2$  sample. Electrical resistivity of the  $Mn_3Si_4Al_2$  bulk sample holds constant value for 48 h at 873 K in air. This is due to formation of oxide passive layer on the surface of the bulk sample. The 342 phase is a promising n-type material with a good oxidation resistance in the middle temperature range of 500-800 K.

[dx.doi.org/10.1557/opl.2013.117](https://doi.org/10.1557/opl.2013.117)

## Using a Water Lens for Light Concentration in Thermoelectric Generation

Keita O. Ito, Hongtao Sui, Hidetoshi Hakozaiki, Hiroshi Kinoshita and Ryosuke O. Suzuki

J. Electr. Mater., **43**, [6] 2086-2093 (2014)

A water lens is employed to concentrate sunlight on the surface of a thermoelectric module in order to heat it. This water lens can change its shape flexibly and is adjustable to solar altitudes. The lens shape and light path were simulated for the cases when the light is incident at an angle to the water surface, parallel to the central axis of the half-cylindrical water lens, and when the light is focused on a plate. A condensing ratio larger than 70 is achieved when the incident light is closer to the normal of the water surface and if the optimal lens shape is maintained.

[dx.doi.org/10.1007/s11664-013-2965-5](https://doi.org/10.1007/s11664-013-2965-5)

## Effects of Nano Metal Coatings on Growth Kinetics of $\alpha$ -Al<sub>2</sub>O<sub>3</sub> Formed on Ni-50Al Alloy

A. Shaaban, S. Hayashi, K. Azumi

*Oxidation of Metals* 82:85-97 (2014).

The effects of pure metal coatings, including Ni, Fe and Cr, on long-term oxidation kinetics, surface morphology and structure were studied. Ni-50Al alloy and Ni-coated, Fe-coated and Cr-coated samples were pre-oxidized at 900 °C in air. They were then oxidized isothermally at 1,000 °C in air. The bare Ni-50Al alloy oxidized rapidly during the initial stage of oxidation due to the formation of  $\theta$ -Al<sub>2</sub>O<sub>3</sub>, but the oxidation rate decreased after  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> had developed. Oxidation of the Ni-coated sample was slow from the beginning of oxidation even though the  $\theta$ -Al<sub>2</sub>O<sub>3</sub> was predominated for a longer oxidation time. No  $\theta$ -Al<sub>2</sub>O<sub>3</sub> developed on the Cr and Fe-coated samples, but the oxidation rates of these samples were much faster than those of bare and Ni-coated samples. Cross-sectional images revealed that the grain size of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, which formed on Cr and Fe-coated samples, was smaller than those of bare and Ni-coated samples. These metal coatings affected the microstructure of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and they showed a strong effect on the growth rate of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> in the steady-state oxidation stage.

[DOI 10.1007/s11085-014-9478-3](https://doi.org/10.1007/s11085-014-9478-3)

## Prospect of Corrosion Resistive Aluminum Plating Process on Magnesium Alloys

K. Azumi, M. Ueda and Y. Hang

*J. Japan Inst. Light Metals*, **64** 15-20 (2014).

Fundamental aspect of plating process of Mg alloys from the view points of corrosion engineering is introduced. Weak corrosion resistivity of Mg alloys must be considered not only in the practical use but also even in each step of plating process for corrosion protection coatings. For example, different electrochemical activity of  $\alpha$ - and  $\beta$ - phases in AZ91D Mg alloy induces non-uniform dissolution on the surface of these phases and thus degrades the uniformity in the following processes. Combination of acidic agents, hydrochloric acid which promotes uniform but phase-dependent dissolution and hydrofluoric acid which promotes formation of insoluble Mg fluoride layer, can mitigate non-uniform dissolution of  $\alpha$ - and  $\beta$ - phases. Phase dependent non-uniform metal deposition also progresses on  $\alpha$ - and  $\beta$ - phase surfaces in zincating and main coating processes. Such non-uniformity is induced by the degradation of substrate surfaces during the process and low activity, *i.e.*, inefficient charge transfer, for metal deposition reaction. Protection and activation of the substrate surface are effective strategy to overcome such difficulties. Predeposition of Cu nanoparticles on the substrate prior to the deposition processes could improve considerably the uniformity, adhesivity and protection ability of deposits due to induction of high efficient charge transfer path with high density to the substrate surface resulting in high density nucleation of deposits.

## Convection-dependent Hydrogen Permeation into a Carbon Steel Sheet

K. Fushimi, M. Jin, T. Nakanishi, Y. Hasegawa, T. Kawano, M. Kimura

*ECS Electrochem. Lett.* **3** (2014) C21-C23.

The Devanathan-Stachurski electrochemical cell for measurement of hydrogen-permeation into a steel sheet was extended to an electrolyte-flowing design. Increase in flow rate of the entry cell induces increase in hydrogen evolution current at the entry electrode but decrease in hydrogen-permeation current at the hydrogen-exit electrode. Hydrogen-permeation is actualized by a sinusoidal perturbation of the entry-flow rate. The hydrogen-permeation response, i.e., phase shift of the detection current from the evolution current, was proportional to the square root of flow rate frequency and was dependent on sheet thickness. The sinusoidal perturbation of entry-flow rate is a new factor influencing hydrogen-permeation into the sheet.

DOI: 1149/2.011406eel



## **Corrosion Behaviour of Ferrite and Austenite Phases on Super Duplex Stainless Steel in a Modified Green-death Solution**

J.-S. Lee, K. Fushimi, T. Nakanishi, Y. Hasegawa, Y.-S. Park

*Corros. Sci.* **89** (2014) 111-117.

Corrosion behaviour of super duplex stainless steel (SDSS) in acidic chloride solution was investigated electrochemically. Potentiostatic polarisations of SDSS at  $-0.377$  and  $-0.447$   $V_{SHE}$  resulted in selective dissolution of  $\gamma$ - and  $\alpha$ -phases, respectively, and were utilized for fabricating single-phase electrodes. Potentiodynamic polarisation curve of SDSS could be calculated from those of single-phase electrodes. The higher corrosion current density and less noble corrosion potential of  $\alpha$ -phase characterised by galvanic connection with  $\gamma$ -phase indicated that  $\alpha$ - and  $\gamma$ -phases were functioned as the anode and the cathode, respectively, in the corrosion of SDSS.

DOI: 10.1016/j.corsci.2014.08.014

## Growth and Degradation of Anodic Oxide Film on Titanium in Sulphuric Acid Observed by Ellipso-microscopy

K. Fushimi, K. Kurauchi, Y. Yamamoto, T. Nakanishi, Y. Hasegawa, T. Ohtsuka

*Electrochim. Acta* **144** (2014) 56-63.

The surface of polycrystalline titanium polarised anodically in 0.05 mol dm<sup>-3</sup> sulphuric acid was monitored using an ellipso-microscope. During dynamic polarisation, a patch-like bright image was seen on an ellipso-microscopic view, and the brightness and image changed with increase in potential. The change in the brightness and image mainly corresponded to growth of an anodic oxide film on the surface. An *in situ* monitoring using the ellipso-microscope revealed that the film formation rate was dependent on the crystallographic orientation of the substrate. Breakdown of the film induced in a solution containing bromide ions was also monitored using the microscope. Prior to the pitting propagation, the surface was partially changed with flow of a large anodic current. AES measurement revealed that the formation of bromo-oxide resulted in localised film degradation followed by pitting corrosion.

DOI: 10.1016/j.electacta.2014.08.082

## Grain-dependent Passivation of Iron in Sulfuric Acid Solution

Y. Takabatake, K. Fushimi, T. Nakanishi, Y. Hasegawa

*J. Electrochem. Soc.* **161** (2014) C594-C600.

Passive films formed on single grains of a polycrystalline pure iron substrate were investigated in  $0.05 \text{ mol dm}^{-3}$  sulfuric acid with a micro-capillary cell (MCC). Passivation behavior under the condition of potentiostatic polarization was strongly dependent on the crystallographic orientation of the substrate surface. Electrochemical impedance spectroscopy revealed that the charge transfer resistance of the passivated surface was determined by the substrate orientation. Galvanostatic reduction and XPS analysis of the surface passivated using the MCC showed that the substrate orientation affected the chemical state of iron in the oxide. The results suggested that the aging of the passive film formed on the iron substrate depended on its crystallographic orientation due to the differences in surface energy of the substrate surface that has a bcc lattice structure. It was concluded that the grain dependency on the electric property of the passive film arose from the compositional differences of the oxide film.

DOI: 10.1149/2.0901414jes

## **The Corrosion Resistance and Passive Film Compositions of 12% Cr and 15% Cr ODS Steels in Nitric Acid Media**

S. Ningshen, M. Sakairi, K. Suzuki and S. Ukai

Corrosion Science, **78**, 322-334 (2014).

The passive film compositions and corrosion resistance of 12% Cr and 15% Cr oxide dispersion strengthened (ODS) steels in 3 M HNO<sub>3</sub> to 9 M HNO<sub>3</sub> was evaluated. The potentiodynamic polarization plots exhibited a shift in corrosion potential, and higher passive current density with increasing HNO<sub>3</sub> concentrations. In 12% Cr ODS steel, high corrosion rate was observed in all HNO<sub>3</sub> concentrations. However, low corrosion rate observed in 15% Cr ODS steel was attributed to Al<sub>2</sub>O<sub>3</sub> enrichment. The TEM analysis indicated a complex Y<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub> formation in 15% Cr ODS steel, and this may have a role in suppressing intergranular corrosion attack.

## **The Surface Characterization and Corrosion Resistance of 11% Cr Ferritic/Martensitic and 9-15% Cr ODS Steels for Nuclear Fuel Reprocessing Application**

S. Ningshena, M. Sakairi, K. Suzuki, and S. Ukai

Journal of Solid State Electrochemistry, **18**, 411-425 (2014)

In spent fuel nuclear reprocessing plant, nitric acid is the main medium used in PUREX method. The passive film compositions and corrosion resistance of 11 % Cr ferritic/martensitic and 9–15 % Cr oxide dispersion strengthened steels in different nitric acid concentrations were studied. The open circuit potential is shifted toward more noble potential as the concentrations increased from 1 M HNO<sub>3</sub> to 9 M HNO<sub>3</sub> in all the investigated alloy steels. The results of the potentiodynamic polarization plots also exhibited a shift in corrosion potential as the concentrations increased from 1 M to 9 M HNO<sub>3</sub>. This shift is undesirable because of risk of overshooting the potential beyond passive region and may result into transpassive corrosion. The X-ray photoelectron spectroscopy results of the passive film analysis are composed mostly of Fe<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, and Y<sub>2</sub>O<sub>3</sub>, and the depth profile of Fe and Cr concentrations vary depending upon the nitric acid concentration. The surface morphology after the corrosion test does not show intergranular corrosion attack at the nitric acid concentrations studied. It is desirable that materials for use in nitric acid service are resistant to such corrosion induced degradation.

## **Effect of Metal Cations on Corrosion Behavior and Surface Film Structure of the A3003 Aluminum Alloy in Model Tap Waters**

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The effect of the metal cations,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Ni}^{2+}$ , on the oxide film structure and morphology changes during long-term immersion corrosion tests of aluminum alloy (A3003) in model tap waters was investigated by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy. The effect of the metal cations on the corrosion behavior was also investigated with mass change and electrochemical tests. The hardness of the metal cations, X, based on the hard and soft acids and bases (HSAB) concept was applied to explain the effect of metal cations on the passive oxide film structure and corrosion resistance. The mass change rate and corrosion current density decreased with increasing metal cation hardness. The XPS results showed that hard metal cations like  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$  were incorporated in the oxide films, while the four soft metal cations were not incorporated in the oxide films. The results are in good agreement with those which could be expected from the HSAB hardness of the metal cations.

# **Evaluation of Metal Cation Effects on Galvanic Corrosion Behavior of the A5052 Aluminum Alloy in Low Chloride Ion Containing Solutions by Electrochemical Noise Impedance**

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The effects of metal cations on the galvanic corrosion behavior of the A5052 aluminum alloy in low chloride ion containing solutions (tap water) were examined by electrochemical noise impedance. The electrochemical noise impedance and conductance were calculated by the power spectral density (PSD) of the galvanic current and potential. The oscillations in the galvanic current correlate well with the oscillations in the potential. The total charge (summation of galvanic current) during galvanic corrosion tests was suppressed by the addition of  $\text{Ca}^{2+}$ , while it was increased with  $\text{Mg}^{2+}$  addition. Only a small effect on mean impedance and conductance was observed in solutions with  $\text{Cu}^{2+}$  and  $\text{Mg}^{2+}$ , while addition of  $\text{Ca}^{2+}$  strongly influences both the mean impedance and conductance. These results may be explained by the passive film structure changes due to the metal cations. The results obtained in this study indicate that metal cations play a very important role in the corrosion behavior of A5052 aluminum alloys in tap water.

## **Line Shaped Porous Type Anodic Oxide Film Formation on Aluminum by Sf-MDC with Coated Pt Wire Electrode**

T. Yamaguchi and M. Sakairi

Journal of the Surface Finishing Society of Japan, **65**, 385-390 (2014)

It is possible to form highly ordered porous type anodic oxide film by anodizing in acid solutions such as oxalic acid, phosphoric acid, and sulfuric acid, and both pore size and thickness are controlled by the anodizing condition. Therefore, porous type anodic oxide films are widely used and studied. However, almost all research on area-selected anodizing is carried out with mask-processes. The solution flow type micro-droplet cell (Sf-MDC) has been applied to form thick porous type aluminum anodic oxide film locally. By coating a side wall Pt wire electrode, it is possible to reduce the width of the formed anodic oxide line without changes in the film formation reaction. Up to ten repeated passes, there is no change in the oxide film growth rate; the width of the oxide lines was observed by a coated Sf-MDC electrode. (Japanese)



## **Evaluation of Metal Cation Effects on Galvanic Corrosion of Aluminum Alloys in Low Chloride Ion Containing Solutions with Electrochemical Noise**

M. Sakairi, K. Otani, and R. Sasaki

Procedia Engineering, **86**, 589-596 (2014),

The effect of metal cations on the galvanic corrosion behavior of A3003 aluminum alloy in low concentration of chloride ion containing solutions (tap waters) was examined by electrochemical noise impedance. The electrochemical noise impedance and conductance were calculated by the power spectrum density of the galvanic current and potential. The sum of the galvanic current during galvanic corrosion tests was suppressed by the addition of  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$ , while it was increased with  $\text{Mg}^{2+}$  addition. These results may be explained by the passive film structure changes due to the metal cations. The results obtained in this study indicate that metal cations play an important role in the corrosion behavior of A3003 aluminum alloys in tap water.

## **Oxide Films on Nickel-base Alloys in Water at 360 °C under PWR Environment**

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Proceedings of 16th International Congress Environmental Degradation of  
Metals in Nuclear Power Systems (2014)

The oxide film on the nickel-base alloys exposed to the PWR environment at 360°C in water containing 500 ppm B and 2.0 ppm Li was analyzed by ellipsometry, Raman spectroscopy, IR-reflection absorption spectroscopy, Auger electron spectroscopy, SEM, and laser scanning microscope. The oxide film on the alloys consisted of the flat layer enriched by Cr oxide and the protuberance particles enriched by Ni and Fe oxides. The number of the protuberance particles was increased with the tensile stress added. The protuberance oxide particle was assumed to emerge from the crack site of the flat oxide layer induced by the inner stress in the oxide or by the tensile stress loaded from the outside.

## **Electrochemical Noise Analysis on Modified 13%Cr Stainless Steels in Sour Environments under Stress**

M. Sakairi, J. Tatehara, Y. Mizukami, and S. Hashizume

Proceedings of EUROCORR2014, No. **7095** (2014)

Electrochemical noise analysis technique was applied to predict initiation or propagation of pitting events, which is lead to SCC or SSC. It is also try to clarify the relationship between features of PSD and initiation of crack or pitting corrosion during immersion corrosion tests by using consecutive PSD calculation technique. Consecutive average PSD can be calculated from rest potential data, and the peaks of the average PSD shows good correlation with rest-potential changes. The average PSD peaks enhances the rest-potential changes. The enhancement by PSD make it possible to monitor initiation of localized corrosion events in sour environments.

# **Metal Cation Effects on Galvanic Corrosion Behavior of 2024 Aluminum Alloy with Electrochemical Noise**

M. Sakairi, A. Kaneko, and R. Sasaki

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The corrosion behavior of some aluminum alloys strongly depends on the kinds of metal cations in the environments. However, only a few reports have focused on the effect of metal cations on galvanic corrosion of aluminum alloys in fresh or tap waters. In the present study, electrochemical noise analysis based impedance technique was applied to evaluate the effect of metal cations on galvanic corrosion of an aluminum alloys in model tap waters. The current fluctuations and potential fluctuations showed good correlation. While, in  $Mg^{2+}$  and  $Ca^{2+}$  added solutions, no changes in potential and current were observed. The total charge (summation of the current density from 0 to 86.4 ks) changed with kind of metal cation. These results clearly indicated that the galvanic corrosion rate was strongly affected by the kind of metal cations.