ANNUAL REPORT

2016

CORROSION RESEARCH

Materials Science and Engineering

Published by

THE CORROSION RESEARCH GROUP

HOKKAIDO UNIVERSITY

No. 45

For additional copies and more information, please write to the group members
Prof. M. Ueda: LABORATORY OF MATERIALS FOR SUSTAINABLE ENGINEERING
Prof. H. Habazaki: INTERFACIAL ELECTROCHEMISTRY LABORATORY
Prof. R. O. Suzuki: ECO-PROCESSING LABORATORY

AFFILIATE MEMBERS
Prof. K. Azumi:
Assoc. Prof. K. Fushimi:
Assoc. Prof. M. Sakairi:

Faculty of Engineering, Hokkaido University
Kita 13, Nishi 8, Kita-ku, Sapporo 060-8628, Japan
Current Activities And Presentations

Laboratory of Materials for Sustainable Engineering ..............................................1
Interfacial Electrochemistry Laboratory .................................................................7
Eco-Processing Laboratory ......................................................................................12
Affiliate Member: Prof. Dr. Kazuhisa Azumi.........................................................20
Affiliate Member: Assoc. Prof. Dr. K. Fushimi.......................................................25
Affiliate Member: Assoc. Prof. Dr. M. Sakairi .........................................................30

Abstract Of Publications

Hydrogen Isotope Separation with an Alkaline Membrane Cell ..........................41
Study of Deuterium Isotope Separation by PEFC ....................................................41
Electrodeposition of Al-Ta Alloys in NaCl-KCl-AlCl₃ Molten Salt Containing TaCl₅ .................................................................42
Aging of Passive Oxide on SUS304 Stainless Steel in a Sulfuric Acid Solution ...42
Utilization of Ionic Liquids as an Electrolyte for Electrodeposition of Metal and Metal Alloys ...........................................................................................................43
Measurement of Adhesion Strength of Al Electroplating Film for AZ31, AZ61, and AZ91 Substrates ...........................................................................................................43
Electrodeposition of Al-W Alloys in AlCl₃-NaCl-KCl Molten Salt Containing WCl₄ ..................................................................................................................................................43
Evidence of Nitrogen Incorporation During Anodizing Sputtering - Deposited Al-Ta Alloys ..................................................................................................................................................44
Photoelectrochemical Evidence of Inhomogeneous Composition at nm Length Scale of Anodic Films on Valve Metals Alloys ..........................................................44
Highly Active Ni/Y-Doped ZrO₂ Catalysts for CO₂ Methanation .......................45
Effect of Current Density and Behaviour of Second Phases in Anodizing of a Mg-Zn-RE Alloy In a Fluoride/Glycerol/Water Electrolyte ..................................................................45
Growth of Barrier Type Anodic Film on Magnesium in Ethylene Glycol-Water Mixed Electrolytes Containing Fluoride and Phosphate ..................................................46
Effect of Pb-Underpotential Deposition on Anodic Dissolution and Passivation of Pure Fe and Fe-Ni Alloys in Acidic Perchlorate Solution ........................................46
Film Growth and Alloy Enrichment during Anodizing AZ31 Magnesium Alloy in Fluoride/Glycerol Electrolytes of a Range of Water Contents ...........................................47

Control of Surface Wettability of Aluminum Mesh with Hierarchical Surface Morphology by Monolayer Coating: From Superoleophobic to Superhydrophilic 48

Fabrication of a Resistive Switching Gallium Oxide Thin Film with a Tailored Gallium Valence State and Oxygen Deficiency by rf Cosputtering Process ..........48

Formation of Porous Anodic Films on Carbon Steels and Their Application to Corrosion Protection Composite Coatings Formed with Polypyrrole .....................49

Characterization of Corrosion-Resistant, Nanometer-Thick, Layer-By-Layer Aluminosilicate Coatings Prepared on Stainless Steel .......................................50

Redox-Induced Proton Insertion and Desertion of Zircon-Type Neodymium Chromate(V) ........................................................................................................50

Electrochemical Impedance Spectroscopy of High-Efficiency Hydrogen Membrane Fuel Cells Based on Sputter-Deposited BaCe0.8Y0.2O3−δ Thin Films ....................51

Outline of the 5th International Round Table on Titanium Production in Molten Salt (I) .............................................................................................................52

Capturing the Non-Spherical Shape of Granular Media and Its Trickle Flow Characteristics Using Fully-Lagrangian Method .............................................52

Reduction of TiS2 by OS Process In CaCl2 Melt ..................................................53

Superhydrophilicity of a Nanofiber-Covered Aluminum Surface Fabricated via Pyrophosphoric Acid Anodizing .................................................................53

Performance Simulation of Flat Plate Thermoelectric Module Consisting of Square Truncated Pyramid Elements .................................................................54

CO Gas Production by CO2 Gas Decomposition in Molten Salt Electrolysis ......54

Fabrication of Self-ordered Porous Alumina via Anodizing in Sulfate Solutions ..55

Exploration for the Self-ordering of Porous Alumina Fabricated via Anodizing in Etidronic Acid .................................................................55

Influence of Gas Injection Pipe on CO2 Decomposition by CaCl2-CaO Molten Salt and ZrO2 Solid Electrolysis .................................................................56

Helical Configuration for Thermoelectric Generation ............................................57

Structural Investigation and Indium Substitution in the Thermoelectric Mn2.7Cr0.3Si4/Al2-XInx Series .................................................................57

Self-ordered Porous Alumina Fabricated via Phosphonic Acid Anodizing ........58
Temperature Dependence of Behavior of Interface Between Molten Sn and LiCl-KCl Eutectic Melt due to Rising Gas Bubble ................................................................. 59

SPH Simulations of the Behavior of the Interface between Two Immiscible Liquid Stirred by the Movement of a Gas Bubble ................................................................. 59

Analysis of the Performance of Thermoelectric Module under Concentrated Radiation Heat Flux ............................................................................................................. 60

Influence of Gas Injection Pipe on CO₂ Decomposition by CaCl₂-CaO Molten Salt and ZrO₂ Solid Electrolysis .............................................................................. 60

Numerical Optimization of Trapezoidal Thermoelectric Elements for Double-Pipe-Shaped Module ......................................................................................... 61

Al-Zn Co-Electrodeposition by a Double Counter Electrode Electrodeposition System From an AlCl₃-1-Ethyl-3-Methylimidazolium Chloride Ionic Liquid Bath ........ 62

Electrochemical CO₂ Reduction in Ionic Liquid Using Two Compartment Cell Separated with Proton-Conducting Membrane .............................................. 62

Development of Aluminum Air Battery Using An Ionic Liquid Electrolyte Solution. .................................................................................................................... 63

Hydrogen Permeation into a Carbon Steel Sheet Observed by a Micro-Capillary Combined with a Devanathan-Stachurski Cell ........................................ 64

FEM Analysis for Sinusoidal Perturbation of Hydrogen Permeation into a Steel Sheet .............................................................................................................. 64

Optical Characterization of Passive Oxides on Metals ........................................... 65

Passivation Behavior of Type-316L Stainless Steel in the Presence of Hydrogen Sulfide Ions Generated from Local Anion Generating System ................. 65

Heterogeneity of a Thermal Oxide Film Formed on Polycrystalline Iron Observed by Two-Dimensional Ellipsometry ................................................................. 66

Effect of Surface Conditions and Relative Humidity on Hydrogen Permeation Behavior of Zinc Coated Steels During Wet and Dry Corrosion ...................... 67

Development of an Area-Selective Technique for Electrochemical Hydrogen Detection with Laser Local Activation ................................................................. 67

Effect of Surface Conditions and Specimen Composition on Hydrogen Permeation Behavior of Coated and Uncoated Steels during Wet and Dry Corrosion at a Constant Dew Point ......................................................... 68

Formation of Layered Structure Porous Type Anodic Alumina Films Locally with a Solution Flow Type Micro-Droplet Cell ................................................. 68
Formation of Oxide Films for High-Capacitance Aluminum Electrolytic Capacitor by Liquid Phase Deposition and Anodizing

Effect of a Kind of Metal Cation on Corrosion Mechanism of A3003 Aluminum Alloy in Tap Water

Improvement of Corrosion Resistance of Aluminum Alloy with Wettability Controlled Porous Oxide Films

Effects of Metal Cations on Corrosion of Mild Steel in Model Fresh Water

Effect of Metal Cations in Solutions on Surface Film Structure of Aluminum Alloys

SYMPOSIUM REPORT

Symposium of "Oxide Films: A Symposium In Honor of Masahiro Seo"

Symposium to Celebrate The 90th Birthday of Professor Norio Sato
CURRENT ACTIVITIES and PRESENTATIONS
LAbORATORY OF MATERIALS FOR SUSTAINABLE ENGINEERING

Prof. Dr. Mikito Ueda
TEL / FAX: +81-11-706-6813
E-mail: mikito@eng.hokudai.ac.jp

Assoc. Prof. Dr. Hisayoshi Matsushima
TEL / FAX: +81-11-706-6352
E-mail: matsushima@eng.hokudai.ac.jp

Academic Researcher Dr. Toshiaki Ohtsuka
TEL / FAX: +81-11-706-6351
E-mail: ohtsuka@eng.hokudai.ac.jp

Secretary Mrs. Mari Takagi
TEL/FAX: +81-11-706-7813
E-mail: mtakagi@eng.hokudai.ac.jp

Students

K. Sato, Y. Kohno, M. Onishi, R. Ogawa, H. Takahashi, S. Mizukami,

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

Current topics on research are in the following:

(1) Production of high purity Na by electrorefining reaction in ionic liquid

To produce high purity Na from the used Na-S battery, electrorefining process was developed. We were investigated NaFSI-TEATFSI or NaTFSI-TEATFSI ionic liquid as candidate of the electrolyte. 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-W alloys in chloride molten salt

To improve the pitting corrosion resistance of Al in chloride solutions, electrodeposition of Al-W alloys of various compositions was carried out at 423 K by constant potential control in AlCl$_3$-NaCl-KCl molten salt containing WCl$_4$. The electrodeposited 95 at%W-Al alloy was obtained by constant potential electrolysis at 0.4 V vs. Al/Al(III).

(3) Adhesion strength of Al electroplating film on Mg alloys

To investigate the relationship between adhesion strength of Al electroplated film and Al concentration in Mg alloy substrates and the grain size of the Mg alloy, Al electroplating was carried out with AZ31, AZ61, AZ91, and of AZ31 with different grain sizes in an ionic liquid of a mixture of AlCl$_3$ and 1-ethyle-3-methyl-imidazolium chloride at 283 K. Dense Al electrodeposits were formed on all the substrates. The adhesion strength increased with increases in the Al content of the Mg alloys. Increasing the average grain size also resulted in increases in the adhesive strength.

(4) 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 Au single crystal substrate has been investigated in aqueous sulfuric acid solution. We will analyze the growth or dissolution late from one nuclei.

(5) Deuterium isotope separate

We are exploring the possibility of hydrogen isotope separation by using several types of fuel cells and alkaline water splitting. The separation factor of D/H during polymer electrolyte and alkaline fuel cells is measured by quadrupole mass spectroscopy (Q-mass). We try to build novel separation system where the electrolysis is combined with several fuel cells.

(6) 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. We find the water molecules confined in Nafion membrane take super-cooling state down to -140℃.

(7) Electrochemical metal hydride formation in ionic liquid
We try to create metal hydride as one of candidates for hydrogen storage media. The electrochemical sodium hydride formation is investigated by using NaTFSI-TEATFSI ionic liquid. Several electrochemical methods such as cyclic voltammetry, open circuit potential measurement are applied to confirm NaH formation.

Other Activities

Prof. M. Ueda was invited in 98\textsuperscript{th} meeting of the Committee of the Electrolytic Science and Technology, and present paper entitled by "Production of high purity sodium by electrorefining process", Tokyo, February 1, 2016 and was also invited annual meeting of the Ionic Liquid Research Association, and present paper entitled by "Electrodeposition of Al alloys in low-temperature chloroaluminate molten salts", Osaka University, Osaka, June 3, 2016. Prof. M. Ueda organized the session of "Molten Salts and Ionic Liquids 20" in PRiME 2016, Hawaii convention center, Honolulu, USA, October 2-7, 2016. Prof. M. Ueda attended 2016 Euchem conference on Molten Salts and Ionic Liquids, and present paper entitled by "Electrodeposition of Al-Zr alloys in low-temperature chloroaluminate molten salts", Vienna, Austria, July 3-8, 2016.

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.

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.

Electrochemical AC Impedance: Solartron 1260

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).
Rotating Disc Electrode (RDE) system.
Near Infrared Spectrometer: Ocean optics NIR256-2.1

**Presentations**


Production of high purity sodium by electrorefining process; M. Ueda: 98\textsuperscript{th} meeting of the Committee of the Electrolytic Sience and Technology, Tokyo, February 1, 2016.


Electrodeposition of Al alloys in low-temperature chloroaluminate molten salts; M. Ueda: Annual meeting of the Ionic Liquid Research Association, Osaka University, Osaka, June 3, 2016.

NIR study of conductive mechanism of Nafion membrane below freezing point; Y. Kohno, H. Matsushima, T. Ohtsuka, M. Ueda: Summer Meeting of Hokkaido branch of Japan Chemical Society, Muroran institute of technology, Muroran, July 23, 2016.

Electrochemical formation of NaH by NaTFSI-TEATFSI ionic liquid; H. Matsushima, M. Ueda, M. Ante, A. Bund: Summer Meeting of Hokkaido branch of Japan Chemical Society, Muroran institute of technology, Muroran, July 23, 2016.

Dissolution rate of Ti in H₂O₂-NH₃ mixture solution; M. Fujii, M. Ueda, O. Seri: Summer Meeting of Hokkaido branch of Japan Chemical Society, Muroran institute of technology, Muroran, July 23, 2016.


Study of Nafion membrane below freezing temperature by using near infrared spectroscopy and electrochemical impedance spectroscopy; Y. Kouno, H. Matsushima, T. Ohtsuka, M. Ueda: PRiME2016, Honolulu, USA, October 2-7,


In-situ observation of electrochemical phenomena by fast scanning probe microscopy; H. Matsushima: The joint meeting of the Hokkaido and Tokai branch of ECSJ, Hokkaido University, Sapporo, November 23-24, 2016.

INTERFACIAL ELECTROCHEMISTRY LABORATORY

Prof. Dr. Hiroki Habazaki
TEL./FAX: +81-11-706-6575
E-mail: habazaki@eng.hokudai.ac.jp

Assoc. Prof. Dr. Yoshitaka Aoki
TEL./FAX: +81-11-706-6752
E-mail: y-aoki@eng.hokudai.ac.jp

Specially Appointed Assist. Prof. Dr. Chunyu Zhu
TEL./FAX: +81-11-706-6736
chunyu6zhu@eng.hokudai.ac.jp

Visiting Professor
Prof. Emeritus Dr. Masahiro Seo
TEL./FAX: +81-11-706-6735
E-mail: masaseo@eng.hokudai.ac.jp

Foreign Researchers
Dr. Damian Kowalski

Students

In January Dr. Chunyu Zhu joined our laboratory as an Assistant Professor and in October Dr. Damian Kowalski as a post-doctoral researcher. In December, Mr. Khurram Shahzad received a Ph.D. degree and returned to Pakistan. Mr. Andrea Zaffora, an internship student from Palermo University, returned to Italy in February with fruitful experimental results.

The research activities of the laboratory are directed towards the development of advanced oxide films and nanomaterials utilizing electrochemical processes, PVD and combustion synthesis methods for possible applications including novel fuel cells, air batteries, photocatalysis, capacitors, corrosion protection and self-cleaning surfaces. 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 as follows:

1) Formation of self-ordered nanoporous nanotubular anodic films on iron and iron-base alloys

We successfully fabricated self-ordered nanoporous and nanotubular anodic films on iron and stainless steels in fluoride-containing ethylene glycol electrolytes. Critical factors controlling the composition and morphology of the anodic films were investigated in detail. Further, we succeeded to fabricate corrosion-protection composite coatings consisting of a polypyrrole conducting polymer layer and a porous anodic iron oxide layer. The composite coating showed highly improved corrosion protection and adhesion to iron substrate in comparison with a single polypyrrole layer.

2) Efficient formation of anodic films on magnesium

Magnesium is the lightest practical structural metal with superior mechanical properties, but poor corrosion resistance limits its practical applications. Corrosion of magnesium occurs even in water, forming a rather thick, highly cracked oxide film. In our laboratory, we found that a barrier-type anodic film is formed at ~100% efficiency on magnesium in fluoride-containing organic electrolyte. The efficiency is reduced in aqueous electrolyte, but still uniform barrier film is formed when fluoride and phosphate are added simultaneously in aqueous electrolyte. Uniform film growth on magnesium is discussed in terms of Pilling-Bedworth ratio and transport numbers of cations and anions during film growth.

3) Tailoring of mesoporous anodic TiO$_2$ films in novel hot phosphate-glycerol electrolytes

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. Using this novel electrolyte, we obtained mesoporous anatase films without heat treatment. Such films will be suitable for various applications.

4) 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 its alloys and stainless steel, and obtained superoleophobic surfaces after coating with a fluoroalkyl monolayer, which had the lowest surface energy. To improve the durability, self-healing superhydrophobic and superoleophobic surfaces have been designed.

(5) 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. Oxygen incorporation into the Zr alloy is also useful to improve the dielectric properties and thermal stability.

(6) Intermediate temperature fuel cells using a proton-conducting thin film electrolytes

Proton-conducting oxide thin films were fabricated by RF sputtering, and used for proton ceramic fuel cells (PCFCs). In the PCFCs we used a hydrogen-permeable metal anode, which acts as a blocking electrode for oxide ions. Research interest was also directed towards how to reduce the charge-transfer resistance at the proton-conducting electrolyte/cathode interface. PCFCs can be applied for ammonia fuel.

Other Activities

Prof. H. Habazaki presented keynote lectures entitled “Dielectric properties of anodic oxides on Zr alloys: towards development of an alternative of Ta capacitor” at 5th International Conference on Advanced Capacitors (ICAC2016), which was held on 23-27 May at Otsu, “Oxide films on metals and alloys: growth mechanism and application to corrosion protection” at EUROCORR2016, which was held on 11-16 September at Montpellier, France and “Self-Organized Formation of Porous Anodic Films on Iron and Their Application” at PRiME2016, which was held on 2-7 October at Honolulu, USA. He also attended Gordon Research Conference–Corrosion Aqueous on 10-15 July at New London, USA and delivered an invited lecture entitled “Efficient formation of barrier and nanoporous anodic films on metals”.

9
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.

Low-voltage field-emission scanning electron microscope: Zeiss Sigma500 system.

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, measureable in the frequency range of 10 µHz to 32 MHz.

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

Presentation at International Symposia

Efficient hydride ion conduction of highly-nonstoichiometric TiNx thin films and its application to hydrogen permeation, C. Kura, Y. Aoki, E. Tsuji, H. Habazaki, HU-UCB Joint Symposium, 7 January, Hokkaido University, Sapporo (2016)

Self-healing Hydrophobic CeO₂ Film by Anodic Deposition, K. Nakayama, Y. Aoki, H. Habazaki, HU-UCB Joint Symposium, 7 January, Hokkaido University, Sapporo (2016)

Formation behaviour of nanostructured anodic films on iron, K. Shahzad, E. Tsuji, Y. Aoki, H. Habazaki, HU-UCB Joint Symposium, 7 January, Hokkaido University, Sapporo (2016)

Self-healing superhydrophobic CeO₂ coating on stainless steel, H. Habazaki, K. Nakayama, C. Zhu, Y. Aoki, 11th International Symposium on Electrochemical
Micro and Nanosystem Technology (EMNT2016), 17-19 August, Royal Belgium Institute of Natural Science Brussels (2016)


Formation of Nanoporous NiFe$_2$O$_4$ Oxide Films By Anodizing of Fe-Ni Alloy, R. Tomizawa, C. Zhu, E. Tsuji, Y. Aoki, and H. Habazaki, PRiME2016, 2-7 October, Hawaii Convention Center, Honolulu (2016) (Poster)


Design of High Performance Intermediate Temperature Fuel Cells Based on BaCe$_{0.8}$Y$_{0.2}$O$_3$/Pd Heterointerfaces, Y. Aoki, T. Yamaguchi, E. Tsuji, and H. Habazaki, PRiME2016, 2-7 October, Hawaii Convention Center, Honolulu (2016)


Characterization of Proton-Conducting Y(CrO$_4$)$_{1-x}$(PO$_4$)$_x$ As a Cathode Material of Proton-Conducting Ceramic Fuel Cells, K. Kuroda, Y. Aoki, C. Zhu, and H. Habazaki, PRiME2016, 2-7 October, Hawaii Convention Center, Honolulu (2016)

Characterization of Proton-Conducting Solid Oxide Electrolysis Cells Using High Valence State Manganate(V) Ba$_3$(MnO$_4$)$_2$ as an Oxygen Evolution Reaction Electrocatalys”, T. Kobayashi, Y. Aoki, C. Zhu, and H. Habazaki, PRiME2016, 2-7 October, Hawaii Convention Center, Honolulu (2016)
ECO-PROCESSING LABORATORY

Prof. Dr. R. O. Suzuki  
Tel.:+81-11-706-6339 Fax.:+81-11-706-7882  
E-mail:rsuzuki@eng.hokudai.ac.jp

Assoc. Prof. Dr. T. Kikuchi  
Tel.:+81-11-706-6340 Fax.:+81-11-706-6341  
E-mail:kiku@eng.hokudai.ac.jp

Assist. Prof. Dr. S. Natsui  
Tel.:+81-11-706-6340 Fax.:+81-11-706-6342

Technical Staffs

M. Kitamura, H. Noguchi, A. Yamase

Students

S. Akiya, S. Oki, N. Suzuki, A. Takenaga, R. Nashimoto,  
H. Ikeda, R. Kondo, T. Sakaguchi, T. Sudo, T. Matsuzaki  
K. Kawahara, K. Kunimoto, T. Sakaguchi, A. Sawada, Y. Yashima

Prof. Ryosuke O. Suzuki merged as the professor of Eco-processing laboratory 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 CaCl₂ is applied.

Dr. Kikuchi joined as an associate professor from the laboratory of interface microstructure analysis on May 2010, and he began to study the micro- and nano-structure fabrication by anodizing science and technology. He has now been working on the fabrication of various novel materials such as superhydrophilic and superhydrophobic aluminum, highly ordered dimple arrays, and photoluminescence porous alumina.

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 liquid metal emulsified molten salt at high temperature.

Current topics on research are in the following:

(1) Molten salt electrolysis of CaCl$_2$

Reduction of the oxides is studied, when the CaO dissolved in the molten CaCl$_2$ is decomposed to form metallic calcium. A low oxygen potential produces the metallic powders at the cathode. The mechanism of this proposal is examined from the electrochemistry and thermodynamics.

(2) Nanostructure fabrication by anodizing

Anodic porous alumina has been widely investigated as a nanostructure template in various nano-applications. The nanomorphology 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 the novel anodizing processes using phosphonic acid, etidronic acid, and pyrophosphoric acid.

(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 seeking for the highest output. This work links with energy harvesting to conduct the electrolysis.
(5) Morphology of droplets electrolytic deposition in molten salt

The droplets behavior of electrochemically deposited liquid metal in molten chloride is investigated. To understand the kinematic morphology between cathode and electrolyte, an in-situ observation of the behavior of the interface between electro-deposited molten metal phase and the molten salt system was carried out.

Prof. Suzuki made the awarded lecture on “Oxide reduction using molten salt electrolysis” at the 159th Annual Meeting of Japan Institute of Metals held at Osaka University. As a chairman he conducted “5th International Round Table on Titanium Production in Molten Salts (Ti-RT2016), at Hokkaido Univ., Sapporo and Toya Culture Center, Toya, Hokkaido, during 10-14 July 2016. Totally 65 participants got together to discuss the common topics on molten salt. Its proceedings will be published as a special issue of Materials Transactions, March 2017.

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$_2$O$_3$ 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$_2$ gas with RF heating and they are detected by the infrared absorption method.

CO/CO$_2$ Gas Analyzer IR-400: 4 sets. Yokogawa (0.1 vol%-100 %)

Gas Chromatography, Shimazu

NO/SO$_2$ Gas Analyzer IR-400: Yokogawa. In the range of 0.1 vol% and 1 vol%.

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.

Laser Diffraction Particle Analyzer: MicrotracBEL, MT3000II:

Contact Angle Meter: Kyowa Interface Science, DM-501.


Presentations


Electrolytic reduction of $V_2S_3$ in molten CaCl$_2$; T. Matsuzaki, S. Natsui, T. Kikuchi and R. O. Suzuki: *ibid*.


Reduction of CaTiO$_3$ by electrolysis in the molten salt (CaCl$_2$-CaO); H. Noguchi, S. Natsui, T. Kikuchi and R. O. Suzuki: *ibid*.


Anodizing of aluminum in an acetylenedicarboxylic acid solution; S. Akiya, T. Kikuchi, S. Natsui, R. O. Suzuki: *ibid*.

Effect of anodizing conditions on the Vickers hardness of anodic oxide films formed by etidronic acid anodizing; A. Takenaga, T. Kikuchi, S. Natsui, R. O. Suzuki: *ibid*.

Fabrication of superhydrophobic aluminum surface via pyrophosphoric acid


Growth behavior of anodic alumina nanofibers fabricated by pyrophosphoric acid anodizing and their hydrophilicity; D. Nakajima, T. Kikuchi, S. Natsui, R. O. Suzuki: ibid.


Electrolysis of fluidized TiO$_2$ particles in LiCl-KCl-Li$_2$O melt; T. Sudo, S. Natsui, T. Kikuchi, R. O. Suzuki: 159th Annual Meeting of Japan Institute of Metals (Fall session), Toyonaka Campus, Osaka Univ., Toyonaka, Osaka, Japan, 21-23 Sept., 2016.

Reduction of metallic oxides using CaCl$_2$ melt; R.O. Suzuki: ibid.

Fabrication of ordered porous alumina by anodizing in a sodium hydrogen sulfate solution; R. Kondo, T. Kikuchi, S. Natsui, R. O. Suzuki: ibid.


Performance simulation of flat plate TE module consisting of frustum shape elements; S. Oki and R.O. Suzuki : The 13th Annual Meeting of the Thermoelectrics Society of Japan (TSJ2016), Katsushika Campus, Tokyo Univ. of Sci., Tokyo, Japan, 5-7 Sept., 2016.


Development of fully-Lagrangian numerical simulation for multi-phase flow in metallurgical processes; S. Natsui : The Eleventh Korea-Japan Workshop on Science and Technology in Ironmaking and Steelmaking, Zao, Miyagi, Japan, 6 Aug., 2016.


Calcium reduction of TiS₂ in CaCl₂ melt; N. Suzuki, H. Noguchi, M. Tanaka, S. Natsui, T. Kikuchi and R.O. Suzuki : 5th International Round Table on Titanium
Production in Molten Salts (Ti-RT2016), Hokkaido Univ., Sapporo and Toya Culture Center, Toya, Hokkaido, 10-14 July 2016.

Reduction of CaTiO$_3$ in molten CaCl$_2$ - As basic understanding of electrolysis; R.O. Suzuki, H. Hada, H. Noguchi, M. Kitamura, S. Natsui and T. Kikuchi : *ibid*.

Observation of gas bubbles and spark flashing during electrolysis of CaO-CaCl$_2$ melt; M. Kitamura, H. Noguchi, S. Natsui, T. Kikuchi and R.O. Suzuki : *ibid*.

Reduction of VS$_x$ in CaCl$_2$ melt; T. Matsuzaki, N. Suzuki, A. Nange, S. Natsui, T. Kikuchi and R.O. Suzuki : *ibid*.

OS Reactor Test; K. Ono and R.O. Suzuki : *ibid*.


Controlling of wettability on the nanofiber-covered aluminum surface; D. Nakajima, T. Kikuchi, S. Natsui and R. O. Suzuki : *ibid*.

Fabrication of ordered porous alumina using metal salt solutions; R. Kondo, T. Kikuchi, S. Natsui and R. O. Suzuki : *ibid*.

High voltage anodizing of aluminum in an ethylene glycol solution; H. Ikeda, T. Kikuchi, S. Natsui and R. O. Suzuki : *ibid*.

Electrochemical reduction of fluid oxide particles in LiCl - KCl molten salt; T. Sudo, S. Natsui, T. Kikuchi, R. O. Suzuki: *ibid*.

Numerical analysis of high-temperature material processing by using discrete element type simulation method; S. Natsui: The 2nd Material Process Special Lecture Meeting, Ito Campus, Kyushu University, Fukuoka, May 12, 2016.

Performance simulation of flat plate thermoelectric module consisting of square truncated pyramid elements; S. Oki, S. Natsui, T. Kikuchi and R.O. Suzuki : The 35th International Conference on Thermoelectrics (ICT-2016) & The 1st Asian Conference on Thermoelectrics (ACT-2016), Wuhan, China, 29 May-2 June 2016.

SPH analysis of interfacial flow of the two immiscible melts; S. Natsui, R.


Fabrication of ordered porous alumina by anodizing in a phosphonic acid solution; 158th Annual Meeting of Japan Institute of Metals (Spring session), Katsushika Campus, Tokyo Univ. of Sci., Tokyo, Japan, 23-25 March, 2016.


CURRENT ACTIVITIES and PRESENTATIONS

AFFILIATE MEMBER

Prof. Dr. Kazuhisa Azumi

Laboratory of Electronic Materials Chemistry
TEL/FAX: +81-11-706-6747
Email: azumi@eng.hokudai.ac.jp

Students

Masaki Aomi, Hiroki Murakoshi, Toshi Oguma, Takumi Kato,
Yuto Yoshikawa, Shu Saito, Hiroki Ito, Yuno Kinugasa,
Yuta Hibino, Kazuki Ikeda, Naoki Kaneko, Shuhei Yamazaki

Our group are investigating 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) Effect of hydrogen absorption on semiconductor properties of the passive films on iron

Hydrogen embrittlement of metals such as high-strength steels used for automobiles and reactors can cause severe accident. Hydrogen absorption to the passive films formed in iron is expected to affect its semiconductor properties and thus be usable as a detection technique of hydrogen. Iron foil sample was put in a Devanathan cell with a capability of photoelectrochemical measurement. Hydrogen was absorbed to iron foil from the backside cell by galvanostatic cathodic polarization and the front surface was illuminated by light to detect the effect of hydrogen absorption on photocurrent under the anodic potentiostatic polarization. Various kind of oxide films as anodic oxide films formed in aqueous or non-aqueous electrolyte solutions and high temperature oxidation films were examined to obtain large photocurrent for sensitive detection of hydrogen absorption. Although a high temperature oxide film showed the largest photocurrent among these oxides, its intensity decreased with time and hydration in the solution. To detect the small difference in photocurrent with and without hydrogen absorption from the backside, a double working electrode system was developed in which iron thin foil electrode was split into two pieces and hydrogen was induced to one of the two foils from the backside. At the front side both foil surfaces were illuminated by light and photocurrent was measured by using a bipotentiostat and two independent lock-in amplifiers. UV or visible laser was also used for pin-point illumination of the surface with scanning across the surfaces of iron foil to detect the location of...
hydrogen absorption. Details are currently under investigation.

(2) Corrosion monitoring of copper foil embedded in swelled bentonite clay

Copper is one of candidate materials used for metal container to reposit high level radioactive nuclear wastes formed in nuclear power plants deep underground around 500 m for over 10000 years. The containers will be exposed to swelled bentonite with underground water and high temperature induced by fission reaction of its contents up to 100 °C in an anaerobic environment. Such condition was simulated in laboratory using a cell containing copper foil of 5µm in thickness embedded in bentonite powder and heater. The cell was put in a glove box filled with nitrogen gas and pure deaerated water was supplied to the cell. Corrosion of copper foil was monitored using temperature compensated resistometry, corrosion potential, impedance spectra and coupling current between two copper foils in a few months. It was confirmed that the corrosion rate of copper foil was as low as in the order of 0.3 µm y⁻¹ at DO level lower than 0.1 mg L⁻¹. Addition of NH₄Cl which accelerated largely the dissolution rate of copper in the solution containing oxygen did not affect the corrosion rate in the current experimental condition. This confirmed that the corrosion rate was controlled mainly by the oxygen but not the ligand such as NH₄⁺.

(3) Corrosion monitoring of reinforced steels in concrete structure

Monitoring system of corrosion environment and corrosion rate of reinforcing steels embedded in concrete have been developed. Many iron wires were embedded in a test cement block in 1D or 3D array arrangements and impedance was measured between two wires properly selected to evaluate the spatial distribution of electric conductivity of cement medium and charge transfer resistance on each wire electrodes. For example, in 3D array arrangement, array of 8 iron wires arranged with x or y direction in 4 layers in depth was embedded in cement block and water was penetrated from the limited area of the top face. Time transition of water penetration and drying process in the cement block was successfully visualized from the impedance data measured between two iron wires selected sequentially from the array. Because of relatively low electric conductivity of cement compared with ordinal electrolyte solution, electric conductivity of cement medium at the crossing area of two iron wires in x and y arrangements could be evaluated to enable spatial distribution mapping of conductivity in a block.

(4) Electrochemical CO₂ reduction in hydrophobic ionic liquid

EMIm-TFSI ionic liquid (IL) which absorbs considerable CO₂ gas was used as an electrolyte medium for electrochemical CO₂ reduction. Two compartments cell was used for electrochemical polarization; one compartment
contained a cathode and IL bath bubbled with CO$_2$ gas, and another compartment contained a Pt anode and KCl aqueous solution. Two compartments were separated by a proton conducting Nafion membrane. This structure was used to suppress sub-reaction such as water decomposition. Gas analysis using a gas chromatography showed that the main product formed on Cu-WE was CH$_4$, CO on Au-WE, and H$_2$ on Ni-WE or Pt-WE. For more efficient and continuous reduction, flow system was constructed in which Cu-mesh WE | Nafion membrane | Pt-mesh CE assembly was placed at the center of two flow cells made of carbon block; top cell had a gas flow channel for CO$_2$ gas and bottom cell had a KCl solution, respectively. Small amount of EMIm-TFSI IL was poured into a top cell to immerse Cu-mesh WE in a thin IL layer. Using this flow cell, however, any improvement in reduction rate was not observed. This result suggested that the bottleneck of electrochemical reduction of CO$_2$ using two compartments cell was not in the transport process of CO$_2$ to Cu-WE surface but in the transport process of H$^+$ from aqueous phase to IL phase.

(6) Patterned growth of polypyrrole using electrochemical technique

Polypyrrole (PPy) is one of the most studied conducting polymers (CPs) and expected to be used for many applications such as solid state electrolytes, electric wiring in flexible devices and actuators. For such purpose, controlling the morphology, orientation, and degree of polymerization of CPs are necessary. In this study, therefore, controlling the morphology of electrochemically polymerized PPy deposits using the pulse polarization technique, from the analogy of morphology control of electrodeposits of metal coating, was investigated. In the experiments PPy was deposited on ITO lass as a working electrode (WE) from an acetonitrile bath containing pyrrole and LiClO$_4$ as supporting electrolyte. Steady anodic polarization and pulse polarization with various pulse conditions were applied and the resultant morphologies of deposited PPy was investigated by SEM observation. Although the PPy morphology was found to be composed of macro-scale undulations probably due to evolution of internal stress and small granular structure in sub-µm scale, variation of polarization condition did not affect such appearance. PPy deposition using porous alumina template was also investigated and PPy nano-tube structure was obtained. PPy nano-tube array with supporting PPy layers at the both sides was fabricated and its properties are under investigated.

Presentation

Development of Al-Air Battery using Ionic Liquid, T.Oguma, K. Azumi; 6th CSJChemistry Festa, 2016.11.14-16, Tokyo. (Best Poster Awarded)
Effect and Control of Minor Elements of Al Alloys on Plating Process, K. Azumi; 33th ARS Conference Atami, 2016.10.27, Izuyama Traning Center. (*Invited*)

Ti electrodeposition from Ionic Liquid Bath; Y. Hibino, K. Azumi; 131th Autumn meeting of Japan Light Metal Society, 11.5-6 (2016) Ibaraki University Mito Campus.


Evaluation of Internal ambient of Concrete using Various Sensors, S. Saito, K. Azumi; *ibid.*


Development of aluminum air battery using an ionic liquid electrolyte solution; T. Oguma and K. Azumi: *ibid.*

Electrochemical CO$_2$ Reduction in Ionic Liquid using Two Compartment Cell Separated with Proton-conducting membrane; H. Yoshikawa and K. Azumi, *ibid.*


Controlling the composition of Zn-Al co-deposit films from EMIC ionic bath using a thin layer cell, K. Azumi and Y. Sato: The 9th Pacific Rim Intern. Conf. Advanced Mat. Processing (PRICM9), August 1-5, 2016, Kyoto International Conference Center, Kyoto, Japan. (*Invited*)


Electrodeposition of titanium from EMIC ionic liquid bath, Y. Hibino and K. Azumi: *ibid.*
Structural control of polypyrrole electrochemically polymerized on template electrodes, Y. Kinugasa, H. Koizumi and K. Azumi: *ibid*.


Corrosion monitoring of reinforced steels in concrete, S. Saito and K. Azumi: *ibid*.


CURRENT ACTIVITIES and PRESENTATIONS

AFFILIATE MEMBER

Assoc. Prof. Dr. K. Fushimi

Tel./FAX:+81-11-706-6737
E-mail:kfushimi@eng.hokudai.ac.jp

Students

Y. Takabatake, Y. Yamamoto, T. Matsuda, M. Goto,
H. Nishimura, T. Kanazawa, R. Nakagawa

Visiting Researcher

J.-S. Lee

In March, Mr. Jun-Seob Lee obtained the degree of Ph.D from Hokkaido University. In April, Ms. Tomomi Kanazawa entered Graduate School of Chemical Sciences and Engineering, Hokkaido University and Mr. Ryogo Nakagawa joined the laboratory. Dr. J-S. Lee stayed in the laboratory as a post-doctoral researcher until September and moved to Bundesanstalt für Materialforschung und –prüfung (BAM), Germany. In October, Mr. Takeshi Matsuda jointed the laboratory.

The research activities of the laboratory are directed to an understanding of the mechanism and kinetics of the heterogeneous interfacial reactions, and to the development of the microelectrochemical techniques for well-understanding the reactions. The research activity is also directed to an understanding of the mechanism and kinetics in wet corrosion of practical materials including steels and titanium alloys.

Current topics on research are in the following:

(1) Application of Liquid-phase Ion-gun for Localized Corrosion of Ferritic Stainless Steel

Liquid-phase ion-gun (LPIG) is a microelectrode technique for studying localized corrosion of metallic materials. The initiation of localized corrosion of types 430 and 443J1 ferritic stainless steels was evaluated in 0.15 M Na₂SO₄ solution by using LPIG. An LPIG, a silver microelectrode covered with a
silver chloride layer, was cathodically polarized to generate $\text{Cl}^-\text{in the vicinity of}$ the stainless steel polarized at 0.4 V$_{\text{SSE}}$. Contact of the stainless steel surface with the Cl$^-\text{concentrated environment by the LPIG operation induced a rapid increase in anodic current flow through the stainless steel electrode. Effects of induction period and cathodic electric charge consumed by the LPIG microelectrode for the current increase were investigated as well as numerical modeling of a critical Cl$^-$ concentration needed for the initiation of localized corrosion. The degradation mechanism of stainless steel surface due to contact with the Cl$^-\text{concentrated solution was discussed from a viewpoint of Cl}^-$ adsorption on the oxide surface.

(2) Grain Dependent of Passive Film Formed on Polycrystalline Iron Surface in pH8.4 Boric-Borate Buffer

Passivating behavior of polycrystalline iron in pH 8.4 boric-borate buffer was investigated by using several micro-electrochemical techniques including two-dimensional (2D) ellipsometry and micro-capillary cell (MCC). Though in situ 2D ellipsometry demonstrated the formation of relatively homogeneous passive film on a polycrystalline iron because of a lack of sensitivity, potentiostatic polarization and electrochemical impedance spectroscopy with the MCC showed that charge transfer resistance and donor density of the passive film depended on the substrate orientation. However, there was no clear grain dependent correlation between the resistance and the density. It was thought that several factors such as anisotropic growth, dissolution, and aging of oxides gave the grain-dependent defect structure of the passive film, depending on the surface crystallographic orientation of the substrate iron.

(3) Made-to-order Photo-electrochemical Treatment of Anodized Titanium Surface under Ellipso-microscopic Observation

A beam of UV-light with a diameter of several tens $\mu$m was irradiated on polycrystalline titanium surface anodized in 0.01 M sulfuric acid solution. Photo-electrochemical current was monitored by the anodic polarization at potentials lower than the oxide formation potential and the irradiated surface was observed by using an ellipso-microscope. A change in optical parameters of the irradiated local surface was affected by power of irradiation light, irradiation period, applied potential, and substrate crystallographic orientation. Though excess conditions induced changing the crystallinity of the oxide film from amorphous to anatase, the change was homogenized by controlling the parameters such as light power and irradiation period. Conditions for a suitable treatment realizing oxide homogenization and corrosion protection were surveyed.

(4) Convection-dependent Hydrogen Permeation into a Carbon Steel Sheet
In order to avoid hydrogen embrittlement of carbon steel sheets, basic research for mechanism and kinetics of hydrogen penetration in the steel is necessary. The Devanathan-Stachurski double electrochemical cell for measurement of hydrogen-permeation into the sheet was extended to an electrolyte-flowing design. Hydrogen-permeation was actualized by a sinusoidal perturbation of the flow rate of the entry cell. The hydrogen-permeation response, i.e., phase shift of the detection current from the entry current, was also analyzed numerically. Dependences of heat-treatment, temperature, and measurement history on hydrogen-permeation response were surveyed by using this technique.

(5) Quantitative Evaluation of Effects of Halide Ions to Corrosion of Iron

Adsorption of halide ions such as chloride ions on steel surface has attracted many attentions in corrosion research because they adsorb on the surface and change a corrosion rate of the steel. In order to evaluate details of the adsorption of halide ions and to investigate the kinetics and mechanism of anion adsorption-to-steel corrosion, a series of studies with an electrochemical quartz crystal microbalance of evaporation-deposited iron was carried out.

(6) Evaluation of Heterogeneity of Passive Film Formed on Carbon Steel in Boric-borate Buffer

Metallographic structure of steels might affect the passivity and corrosion protection. For example, passivity-maintaining current of carbon steel, which is composed of ferrite and perlite, was larger than that of pure iron, which is ferrite. In order to investigate the details of effects of the structure, passive film formed on the carbon steel was evaluated by using scanning electrochemical microscopy (SECM) and imaging Raman spectroscopy. From SECM, passive film formed on perlite allowed flowing a larger electron transfer current of redox mediator than that formed on ferrite. Raman image revealed the heterogeneous distribution of oxides depending on the structure, and a larger amount of magnetite was formed on ferrite than on perlite. It was due to existence of cementite in substrate perlite and difference in the formation of oxide film.

Mr. J.-S. Lee, Mr. Y. Takabatake, and Mr. Y. Yamamoto attended to Hokkaido University-University of California, Berkeley Joint Symposium on Chemical Sciences and Engineering, Sapporo, Japan in January. Dr. K. Fushimi, Mr. Y. Takabatake, Y. Yamamoto, and Ms. T. Kanazawa attended to The 8th Japan-China Joint Seminar on Marine Corrosion and Control, Sapporo, Japan in June. Dr. K. Fushimi and Mr. Y. Takabatake attended to Eurocorr2016, Montpellier, France in September. Dr. K. Fushimi, Mr. Y. Takabatake, and Mr. Y. Yamamoto attended to PRiME2017, Honolulu, HW in October.


Presentations at International Symposia


AFFILIATE MEMBER

Assoc. Prof. Dr. M. Sakairi

Tel.:+81-11-706-7111, Fax.:+81-11-706-7881
E-mail: msakairi@eng.hokudai.ac.jp

Students


Mr. Md. Saiful Islam, Rajshahi University, Bangladesh joined our group as PhD student from 1st October 2016. Research work of our group directs toward (1) effect of metal cations on passive film structure of metals, (2) effect of Mo and CH$_3$COONa on oxide film composition and corrosion behavior of 13 % Cr stainless steel in model oil and gas environments, (3) effect of defects 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 temperature on oxygen transport in thin solution layer formed on metals, (6) hydrogen permeation behavior change with metal cations (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 metals

Based on resent our group research focused on metal cation elucidated the role of the cation on corrosion of metals in aqueous solutions. A new corrosion indicator, “corrosion inhibitory effect of cations, $Y$”, that consists of X and molar volume ratio, $\Delta V$, was proposed and showed the applicability of the proposed This year tow experiments related effect of metal cations were carried out. One is inhibition ability of gluconates for fresh water corrosion of mild steel enhanced by metal cations. The inhibition ability of gluconates for fresh water corrosion of mild steel changed with metal cations were investigated by immersion and electrochemical tests. Metal cations that have large $Y$ can enhance the inhibition ability of gluconates. From EIS, XPS analysis and surface observation, they have large $Y$ may decrease defect sites in the protective film of gluconates on mild steel. Gluconate ligands can adsorb on the oxide film of mild steel, and metal cations that have large $Y$ can bond with the oxide film. The other is investigation of possibility
to reduce corrosion of mild steel in high Cl\(^-\) containing solution by metal cations. From the immersion corrosion test results, Zn\(^{2+}\) showed the lowest corrosion rate and meaning that Zn\(^{2+}\) inclines to deaccelerate the corrosion rate of mild steel in 10 mokm\(^{-1}\) chloride aqueous solution than other cations. After immersion tests in Mg\(^{2+}\), Al\(^{3+}\) and Zr\(^{4+}\) containing solutions, clear grain boundaries were observed on the surface by SEM. From the XPS data analysis, it was found that some protective layer was formed (hydroxide or oxide layer) on the surface except Na\(^+\) and EIS analysis results showed that impedance of the steel surface increases compared with Na\(^+\). These results suggest that corrosion rate is reduced with corrosion inhibition effect of the metal cation, and Zn\(^{2+}\) has the better corrosion inhibition effect on mild steel.

(2) Effect of solution chemistry on corrosion of 13 % Cr-Mo stainless steel in model oil and gas environments

It is well known that Oil and gas environments are severe environment for corrosion. The Mo is added to improve corrosion resistance of 13 % Cr stainless steels. It is, however, not clear the role of Mo in corrosion of 13% Cr in oil and gas environments. The electrochemical tests and surface observation were carried out to elucidate the role of Mo. There was the plateau region of the current density in the anodic polarization curves, and the current density decreased with increasing Mo concentration. Pitting potential shifted to the positive direction as increasing Mo concentration. From GD-OES observation, Mo was enriched at most outer of the passive film. The Mo addition decrease the passive film thickness up to 2 mass %, however, more addition does not influence on the film thickness. From the results, the formation of Mo enriched passive film is the main reason for improving the corrosion resistance.

(3) Effect of defects on hydrogen permeation behavior of Zn coated steels during cyclic wet and dry corrosion.

There are demand for reducing energy consumption and improvement of safety at collisions of automobiles, and the high strength steels are widely studied. It is well known that the high strength steels has high susceptibility to hydrogen embrittlement. From hydrogen embrittlement point of view, the corrosion induced hydrogen is also important. To reduce corrosion of steel, Zn coating is widely applied. Protective coatings are, however, liable to be scratched during use, and as steel is exposed to the environment resulting in the formation of galvanic
couples of the coated layer and steel substrate. The galvanic corrosion may produce larger amount of hydrogen than corrosion of the Zn coating or steel substrate alone. Therefore, the influence of scratch on the hydrogen permeation behavior of Zn coated steel during constant dew point type wet and dry cycle corrosion tests were investigated. The permeated hydrogen through the steels was detected by electrochemically using micro-cell and an area controlled scratch was formed on the coated steels with a laser machining technique. The hydrogen permeation current was observed to be independent of the area of the formed scratches. After the tests, the corrosion products of hydroxychloride (simonkolleite) was observed at initially placement of NaCl solution. The hydrogen permeation current of the coated steels with and without the formed scratches decreased with number of cycles of the wet and dry tests. It was elucidate that the corrosion products play an important role in the hydrogen permeation behavior during wet and dry corrosion. The total amount of permeated current did not proportionally increase with increasing the scratched area. The result suggest that the surroundings of the formed scratch is prone to generate and entry of hydrogen.

(4) Formation of size controlled porous type anodic alumina filters by solution flow type micro-droplet cell and chemical dissolution

Porous-type anodic alumina films have attracted much attention in recent years. To simplify the area selective formation processes of porous-type anodic alumina film, a solution flow-type micro-droplet cell with co-axial dual capillary tubes (Sf-MDC) has been applied. This year experimental purpose is to form porous alumina filter on aluminum with Sf-MDC. The shape of the oxide layer was controlled by controlling the moving direction of the specimen. After the anodizing, the barrier layer of the formed oxide film and remained aluminum under the film was dissolved. From the SEM observation of back sides of anodized specimens after dissolution process, no barrier layer was observed at back side image. Because only back side of the specimen was exposed to the solutions, the pores size at back side was larger than that of front side. The water could permeate the oxide layer after dissolution treatment. This result and the SEM observation results indicated that through-hole membrane can be formed by Sf-MDC anodizing and NaOH dissolution.

(5) Effect of water layer thickness and temperature on oxygen reduction reaction on Zn

Recent exposer tests in cold and heavy snow area like Hokkaido, the corrosion rate in winter is not linearly decreased with temperature. It is important to clarify the unexpected corrosion rate cold district, examination of transport behavior of oxygen in thin water layer formed on the metals at low temperature is required. The effects of electrolyte layer thickness, electrode temperature and
concentration of chloride ions on oxygen limiting current were investigated by electrochemically. The oxygen limiting current increased with decreasing electrolyte thickness independent of electrode temperature and electrolyte concentration. The critical electrolyte thickness of oxygen diffusion at 298K in 1 kmol m$^{-3}$ is expected as 0.6 mm. The oxygen diffusion rate was enhanced by thinning the electrolyte layer and increasing electrolyte concentration.

(6) Effect of metal cation on hydrogen permeation behavior of steels by Laser activation method.

An area-selective technique for electrochemical hydrogen detection with focused pulse YAG laser irradiation was developed. The developed technique was applied to investigate influence of metal cations on hydrogen permeation behavior of iron. Independent of kind of metal cations in the solutions, the hydrogen permeation current was detected after the laser irradiation. The SEM inspection of sample surface after the tests, no different surface morphology was observed. The charge related to amount of permeated hydrogen decreased with metal cation hardness $X$. The time at which hydrogen reached detection side was also delayed by metal cation with large $X$. XPS surface analysis after the each experiments suggest that metal cation with large $X$ was formed protective layer on the iron and inhibit the penetration of corrosion induced hydrogen.

(7) Field exposer test in cold and heavy snow district

The filed exposer test focused on corrosion of steels in cold and heavy snow district has been carrying out in this year. This exposer test is a joint research work with NIMS and exposure site are Sapporo and Akkeshi, Hokkaido, Japan.

Other activities

In June, Assoc. Prof. Sakairi organized The 8th Japan-China Joint Seminar on Marine Corrosion and Control at Hokkaido University, Sapporo, Japan, and also presented paper entitled "Effect of metal cations in solutions on surface film structure of aluminum alloys". Mr. Otani attend the seminar and made poster presentation the title was "Effect of metal cations on corrosion of aluminum alloy in salt water."

In July, Assoc. Porf. Sakairi and Mr. Matsumoto attend HU-AGH joint symposium held in Noboribetsu, Hokkaido, Japan, and Assoc. Prof. Sakairi presented the paper entitled "Analysis of surface film formed on metals in model fresh water with XPS and EIS" and Mr. Matsumoto presented the paper entitled "Formation of porous alumina filter on aluminum with Sf-MDC."
In September Assoc. Prof. Sakairi invited the 66th annual meeting of The Japan Society for Analytical Chemistry, September, Sapporo, (2016) and presented the entitled "Analysis of passive film formed on metals by XPS and EIS".

In October Assoc. Porf. Sakairi and Mr. Otani attend the PRiME 2016/230th ECS Meeting held in Honolulu, Hawaii, and presented the papers entitled "Effect of temperature on behavior of oxygen transport through solution layer formed on metals" and "Effect of Metal Cations in Fresh Water on Surface Film Structure and Initial Corrosion of Mild Steel".

In November, Assoc. Prof. Sakairi invited the 3rd Korea-Japan Joint symposium on ARS & Capacitor held in Jeju, Korea, and presented the paper entitled "Application of solution flow type micro-droplet cell to form shape controlled porous alumina".

In November Mr. Matsumoto attend 5th Hokkaido University - Seoul National University Joint Symposium, Sapporo, Japan, and presented a paper entitled "Area selective anodizing of aluminum by solution slow type micro-droplet cell" Fabrication of shape controlled porous alumina layer on aluminum with Sf-MDC ".

**Presentations**


Effect of specimen temperature on oxygen diffusion in thin solution film on metal, R. Sasaki and M. Sakairi, *ibid*.


Effect of solution chemistry on film structure of porous type anodic alumina formed by Sf-MDC, T. Matsumoto and M. Sakairi, Spring Meeting of Hokkaido branch of The Japan Institute of Light Metals, Sapporo, April, 2016. (Had student presentation prize)


Oxygen diffusion behavior in thin solution layer at low temperature, R. Sakaki and M. Sakairi, *ibid*.


Corrosion inhibition property of metal cation and gluconic acid on mild steel, K. Otani and M. Saakri, *ibid*.


Effect of metal cations on corrosion of aluminum alloy in salt water, K. Otani and M. Sakairi, *ibid*.


Temperature dependency of oxygen diffusion behavior in thin solution layre, R. Sakaki and M. Sakairi, *ibid*. 

T. Matsumoto and M. Saakairi, Formation of porous alumina filter on aluminum with Sf-MDC, 2016 HU-AGH symposium, Noboribetsu, Hokkaido, July, 2016. (Had student presentation prize)

Analysis of surface film formed on metals in model fresh water with XPS and EIS, M. Sakairi and K. Otani, ibid.


Effect of Metal Cations in Fresh Water on Surface Film Structure and Initial Corrosion of Mild Steel, K. Otani and M. Sakairi, ibid.


Effect of scratch size on hydrogen permeation behaviour of Zn-Al coated steel during Wet/Dry cyclic corrosion test, ibid.

Effect of corrosion factors on oxygen diffusion behaviour in thin solution layer, R. Sakaki and M. Sakairi, ibid.


Effect of Zn$^{2+}$ on film structure that formed on Al alloy in fresh water, K. Otani, M. Sakairi and A. Kaneko, ibid.

Application of solution flow type micro-droplet cell to form shape controlled porous alumina, M. Sakairi and T. Matsumoto, the 3rd Korea-Japan Joint symposium on ARS & Capacitor, Jeju, Korea, November, 2016.


Hydrogen permeation behavior of Zn coated steels change with formed scratch area, 2016 Corrosion dream, Tokyo, November, 2016.

ABSTRACT of PUBLICATIONS
**Hydrogen Isotope Separation with an Alkaline Membrane Cell**

R. Ogawa, H. Matsushima and M. Ueda

Electrochemistry Communications, **70**, 5-7 (2016)

The separation of deuterium from a hydrogen-deuterium mixture was carried out using an alkaline membrane fuel cell (AMFC) with a Pt catalyst. This novel use of an AMFC to separate deuterium from a mixture of H\textsubscript{2} and D\textsubscript{2} was demonstrated by the production of deuterium-enriched water during power generation by the AMFC. The deuterium separation factor increased with output current (i) to a maximum value of 1.64 attained at \( i = 30 \text{ mA cm}^{-2} \).

**Study of Deuterium Isotope Separation by PEFC**

S. Shibuya, H. Matsushima and M. Ueda


Hydrogen evolution and oxidation reactions were studied on a polycrystalline platinum electrode in 0.05 M D\textsubscript{2}SO\textsubscript{4} solution at 298 K by using a rotating disk electrode, focusing on the kinetic isotope effect on reactivity. The polarization measurements in the evolution reaction regime, on the one hand, revealed two Tafel regions: at low overpotentials close to the equilibrium potential, the Tafel slope was 0.039 V dec\textsuperscript{-1}, suggesting a Volmer-Tafel mechanism; and at potentials around 0.05 V or lower, a slope of 0.168 V dec\textsuperscript{-1} indicated that a transition to a Heyrovsky-Tafel mechanism occurred. In the oxidation reaction regime, on the other hand, a single Tafel slope of 0.055 V dec\textsuperscript{-1} was observed at potentials of 0.08 V or lower. Comparing between the deuterium and protium data for the kinetic factors supported the presence of an isotope effect, whereby the deuterium was more easily dissociated on the platinum electrode. The present kinetic result supported the deuterium separation of polymer electrolyte fuel cell (PEFC) in which the mixture gases of H\textsubscript{2} and D\textsubscript{2} were purged. The deuterium separation factor increased with increasing in the hydrogen utilization. This suggests a new isotope separation technique and also provides useful data for fuel cells.
Electrodeposition of Al-Ta Alloys in NaCl-KCl-AlCl₃ Molten Salt Containing TaCl₅

K. Sato, H. Matsushima, and M. Ueda


To form Al-Ta alloys for high temperature oxidation resistance components, molten salt electrolysis was carried out in an AlCl₃-NaCl-KCl melt containing TaCl₅ at 423 K. The voltammogram showed two cathodic waves at 0.45 V and 0.7 V vs. Al/Al(III), which may correspond to reduction from Ta(V) to Ta(III) and from Ta(III) to tantalum metal, respectively. Electrodeposits of Al and Ta were obtained in the range from −0.05 to 0.3 V and the highest concentration of Ta in the electrodeposit was 72 at% at 0.3 V. With increasing Ta content in the alloy, the morphology of the electrodeposits became powdery and the particle size smaller.

Aging of Passive Oxide on SUS304 Stainless Steel in a Sulfuric Acid Solution

T. Ohtsuka, M. Ueda, and M. Abe


The passive oxide film on SUS 304 stainless steel (SS) was studied in a 0.1 mol dm⁻³ sulfuric acid solution as a function of passivation time. The passive oxide films were measured by ellipsometry and X-ray photoelectron spectroscopy (XPS). A Mott-Schottky plot of the film capacitance was employed to determine the donor density in the n-type semiconducting oxide film, and current measurements of the Fe³⁺/Fe²⁺ redox couple were employed to investigate the electronic transfer process on the passive oxide film. The passive oxide consists of Cr-Fe-Ni oxides in which enrichment of Cr to 57 mol% occurs as the potential increases. During the aging of the passive oxide at 0.6 V vs. Ag/AgCl/saturated KCl (SSC) for 43 ks, the current decreased from 30 μA cm⁻² at 10 s to 0.025 μA cm⁻² at 43 ks, and the Cr ratio in the oxide increased from 49 to 57 mol% with an increase in the O²⁻ ratio. Notably, the film thickness remained nearly constant at 1.3 nm during the aging process. Enrichment of the Cr content resulted in a decrease in the donor density of the n-type semiconducting passive oxide and the inhibition of electronic charge transfer from/to the Fe³⁺/Fe²⁺ redox couple in the electrolyte.
Utilization of Ionic Liquids as an Electrolyte for Electrodeposition of Metal and Metal Alloys

Mikito Ueda

(in Japanese)

Measurement of Adhesion Strength of Al Electroplating Film for AZ31, AZ61, and AZ91 Substrates


ECS Transactions, 75(15), 297-304 (2016)

To investigate the relationship between adhesion strength of Al electroplated film and Al concentration in Mg alloy substrates and the grain size of the Mg alloy, Al electroplating was carried out with AZ31, AZ61, AZ91, and of AZ31 with different grain sizes in an ionic liquid of a mixture of aluminum chloride and 1-ethyle-3-methyl-imidazolium chloride at 283 K. Dense Al electrodeposits were formed on all the substrates. The adhesion strength increased with increases in the Al content of the Mg alloys. Increasing the average grain size also resulted in increases in the adhesive strength.

Electrodeposition of Al-W Alloys in AlCl₃-NaCl-KCl Molten Salt Containing WCl₄

K. Sato, H. Matsushima, M. Ueda

ECS Transactions, 75(15), 305-312 (2016)

To form Al-W alloys for high temperature oxidation resistance components, molten salt electrolysis was carried out in an AlCl₃-NaCl-KCl melt containing WCl₄ at 423 K. The voltammogram showed two cathodic waves at 1.1 V and 0.5 V vs. Al/Al(III), which may correspond to the reduction from W(IV) to W(III) and from W(III) to tungsten metal, respectively. Electrodeposits of Al and W were obtained in the range from -0.05 to 0.4 V and the highest concentration of W in the electrodeposit was 95 at% at 0.4 V. With increasing W content in the alloy, the morphology of the electrodeposits became more powdery and the particle size smaller.
Evidence of Nitrogen Incorporation During Anodizing Sputtering - Deposited Al-Ta Alloys

A. Zaffora, M. Santamaria, F. Di Franco, H. Habazaki and F. Di Quarto

Physical Chemistry Chemical Physics, 18, 351-360 (2016)

Anodic films were grown to 20 V on sputtering-deposited Al-Ta alloys in ammonium biborate and borate buffer solutions. According to glow discharge optical emission spectroscopy, anodizing in ammonium containing solution leads to the formation of N containing anodic layers. Impedance measurements did not evidence significant differences between the dielectric properties of the anodic films as a function of the anodizing electrolyte. Photoelectrochemical investigation allowed evidencing that N incorporation induces a red-shift in the light absorption threshold of the films due to the formation of allowed localized states inside their mobility gap. The estimated Fowler threshold for the internal photoemission processes of electrons resulted to be independent of the anodizing electrolyte confirming that N incorporation does not appreciably affect the density of states distribution close to the conduction band mobility edge. The transport of photogenerated carriers has been rationalized according to the Pai-Enck model of geminate recombination.

Photoelectrochemical Evidence of Inhomogeneous Composition at nm Length Scale of Anodic Films on Valve Metals Alloys

A. Zaffora, M. Santamari, F. Di Franco, H. Habazaki and F. Di Quarto


Anodic films of different thickness (similar to 30 nm and 70 nm) were grown by anodizing sputtering-deposited Ta-19at% Al to different formation voltages. N incorporation into the anodic films was inducing by performing the anodizing process in ammonium containing solutions. Layered anodic films were prepared by a double formation procedure with a first anodizing step in ammonium diborate solution and second anodizing step in borate buffer solution, or vice versa. Glow Discharge Optical Emission Spectroscopy was employed to show the distribution of N across the oxide. Photoelectrochemical measurements evidenced a red shift of the light absorption threshold due to N incorporation. A model was proposed and tested to model the dependence of quantum yield on photon energy and, thus, to estimate the band gap of the layers for both anodized Ta and Ta-19at% Al.
Highly Active Ni/Y-doped ZrO$_2$ Catalysts for CO$_2$ Methanation

H. Takano, Y. Kirihata, K. Izumiya, N. Kumagai, H. Habazaki and K. Hashimoto

Applied Surface Science, 388, 653-663 (2016)

The catalytic methanation of CO$_2$ was carried out on Ni catalysts supported on Y-doped ZrO$_2$ with various Y3+ concentrations and Ni/(Zr + Y) molar ratio = 1. The catalysts were characterized by X-ray diffraction, scanning transmission electron microscopy, specific surface area, temperature-programmed desorption of CO$_2$, and temperature-programmed reaction. In addition, operando diffuse-reflectance infrared Fourier-transform spectroscopy (DRIFT) was used to identify the adsorbed reaction intermediate. Catalysts supported on Y-doped ZrO$_2$ show higher catalytic activity than the catalyst on Y-free ZrO$_2$ with a monoclinic ZrO$_2$ phase. The catalytic activity is also dependent upon the Y$^{3+}$ concentration, and the highest activity was obtained for the catalyst with a Y/(Zr + Y) molar ratio of 0.333, which consists mainly of fcc Ni and cubic ZrO$_2$ phase. Y$^{3+}$ doping into ZrO$_2$ introduces oxygen vacancies, which play an important role in enhancing the catalytic activity. The operando DRIFT study reveals that a CO adsorption intermediate is absent, and bidentate carbonate is an important intermediate for CH$_4$ formation.

Effect of Current Density and Behaviour of Second Phases In Anodizing of a Mg-Zn-RE Alloy in a Fluoride/Glycerol/Water Electrolyte

A. Němcová, I. Kuběna, M. Šmid, H. Habazaki, P. Skeldon and G. E. Thompson


Anodizing of a Mg-Zn-RE alloy was carried out at constant current densities from 0.1 to 10 mA cm$^{-2}$ in a fluoride/glycerol/water electrolyte. Rutherford backscattering spectroscopy, nuclear reaction analysis and analytical transmission electron microscopy revealed barrier-type films composed of oxide and fluoride species. The films were formed by outward migration of cations and inward migration of anions. The transport number of cations in the film above the matrix was in the range ~0.5 to 0.6, and ~0.1 in the film above the grain boundary Mg-Zn-RE phase. From the oxidation behaviour of the Zn-Zr phases, it is suggested that anions and cations migrate through short-circuit paths in the film.
Growth of Barrier Type Anodic Film on Magnesium in Ethylene Glycol-Water Mixed Electrolytes Containing Fluoride and Phosphate


Materials Transactions, 57, 1552-1559 (2016)

In this study, we report the formation of barrier-type anodic films on magnetron-sputtered magnesium films at a constant current density of 10 A m$^{-2}$ in ethylene glycol (EG)-H$_2$O electrolytes containing 0.1 mol dm$^{-3}$ ammonium fluoride and 0.1 mol dm$^{-3}$ dipotassium hydrogen phosphate. The growth efficiency is close to 100% up to 10 vol% H$_2$O, but decreases to 52% in the EG-free aqueous electrolyte. Even at such a low efficiency in the aqueous electrolyte a uniform barrier-type anodic film with flat and parallel metal/film and film/electrolyte interfaces is developed over 100 V. This is contrast to the non-uniform film growth and low breakdown voltage in the phosphate-free aqueous electrolyte containing ammonium fluoride. The anodic films appear to be amorphous regardless of H$_2$O concentration in the phosphate-containing electrolytes, and consist of phosphate-incorporated oxyfluoride. The phosphate incorporation is suppressed by an increase in H$_2$O concentration. In addition, the anodic films consist of two layers with an inner layer containing less amount of phosphate. The outer layer is probably formed at the film/electrolyte interface by the migration of Mg$^{2+}$ ions outwards, while the inner layer is formed at the metal/film interface. The film formation at the former interface even in the aqueous electrolyte at low efficiency is likely to contribute to the formation of barrier films, not porous anodic films.

Effect of Pb-underpotential Deposition on Anodic Dissolution and Passivation of Pure Fe and Fe-Ni Alloys in Acidic Perchlorate Solution

M. Seo, H. Habazaki and T. Nakayama

Journal of Solid State Electrochemistry, 1-10 (2016)

The potentiodynamic polarization curves of pure Fe, Fe-30 Ni, and Fe-70 Ni alloys in acidic perchlorate solutions (pH 1.9) without and with $10^{-3}$ M Pb$^{2+}$ were measured
to investigate the effect of Pb-underpotential deposition (Pb-UPD) on anodic dissolution and passivation in relation to Pb-induced stress corrosion cracking (Pb-SCC) of Ni base alloys. The addition of 10^{-3} M Pb^{2+} shifts the open circuit potentials of pure Fe and Fe-Ni alloys toward noble direction to inhibit the anodic dissolution and promote the passivation, which results from Pb-UPD on substrate metals. The electro-desorption of Pb proceeds with anodic potential sweep and the anodic dissolution is enhanced when the surface coverage of Pb is reduced to a critical level. Tafel slopes ($b^+ = 8.5\sim15$ mV decade$^{-1}$) of anodic dissolution for pure Fe and Fe-Ni alloys in the presence of Pb$^{2+}$ are significantly low as compared with those ($b^+ = 34\sim40$ mV decade$^{-1}$) in the absence of Pb$^{2+}$, which reflects on the rapid enhancement in surface reactivity as a result of electro-desorption of Pb. It is found that the potential region in which anodic dissolution is inhibited by Pb-UPD is located within the potential window of Pb-UPD estimated from the differences in work-function between substrate metals and Pb.

**Film Growth and Alloy Enrichment During Anodizing AZ31 Magnesium Alloy in Fluoride/Glycerol Electrolytes of a Range of Water Contents**

A. Němcová, O. Galal, P. Skeldon, I. Kuběna, M. Šmíd, E. Briand, I. Vickridge, J. J. Ganem and H. Habazaki


The effect of anodizing AZ31 magnesium alloy in a fluoride/glycerol electrolyte containing from 1 to 40 vol.% water on the compositions of the anodic film and the underlying alloy has been investigated. A range of constant current densities and water contents of the electrolyte were employed. Scanning and transmission electron microscopy, with energy-dispersive X-ray spectroscopy, X-ray diffraction and ion beam analyses were used to analyse the anodized alloy. Barrier films, containing fluoride and oxide species, were formed above the matrix, at high current efficiency; a porous film was formed above Al-Mn intermetallic particles. The current density and the water content of the electrolyte affected the O:F atomic ratio and the ionic transport in the films. Significant enrichments of zinc and aluminium were generated in a thin layer of the matrix immediately beneath the film under all conditions of anodizing, with the enrichment of zinc reaching $6.2 \times 10^{15}$ at cm$^{-2}$ in the enriched alloy layer. The cause of the enrichments and the consequences to film growth are discussed.
**Control of Surface Wettability of Aluminum Mesh with Hierarchical Surface Morphology by Monolayer Coating: from Superoleophobic to Superhydrophilic**

K. Nakayama, E. Tsuji, Y. Aoki, S.-G. Park and H. Habazaki

The Journal of Physical Chemistry C, **120**, 15684-15690 (2016)

This paper reports the formation of hierarchically structured aluminum mesh by a combination of simple chemical etching and anodizing. The former introduced micrometer-sized etch pits, and the latter produced nanopores of the order of 10 nm on the mesh with 150 µm mesh openings. Coating the mesh with a monolayer of fluoroalkyl phosphate made the surface superoleophobic to practically any liquid, including hexane with a surface tension as low as 18.4 mN m\(^{-1}\). The hierarchical triple ∼100 µm/∼1 μm/∼10 nm pore surface morphology improved the superoleophobicity compared to the dual ∼100 µm/∼10 nm and ∼1 μm/∼10 nm pore structures. When the aluminum mesh was coated with a fluorine-free alkylphosphate monolayer, the surface was superhydrophobic, but superoleophilic. The noncoated aluminum mesh was superhydrophilic and superoleophilic with a liquid contact angle close to 0°. Using the aluminum mesh with an alkylphosphate coating, a water/oil mixture was successfully separated by allowing only the oil to pass through the mesh. In addition, the mixture was separated using noncoated mesh wetted with water, since oil was not able to pass through the mesh in this case.

**Fabrication of a Resistive Switching Gallium Oxide Thin Film with a Tailored Gallium Valence State and Oxygen Deficiency by rf Cosputtering Process**

C. Kura, Y. Aoki, E. Tsuji, H. Habazaki and M. Martin

RSC Adv., **6**, 8964-8970 (2016)

Resistive switching gallium oxide base thin films with tailored oxygen deficiency were fabricated by rf cosputtering of Ga\(_2\)O\(_3\) and Cr. XPS and STEM-EDX analyses were used to determine that the resultant film was made of a homogeneous oxide glass layer with mixed valance states of Ga(III)-Ga(I). The amount of Ga(I) and the corresponding oxygen deficiency was precisely controlled because the following
redox reaction subsequently progresses within the deposited films: 3Ga(III) + 2Cr(0) → 3Ga(I) + 2Cr(III). The on/off resistance ratio was largely varied by changing the Ga(I) fraction in relation to the oxide ion conductivity, and Ga_{0.82}Cr_{0.18}O_{1.2} thin film was found to exhibit an optimal switching performance. The film resistance state was tunable by 100's of ms pulse biasing and was incrementally changed by increasing the applied pulse numbers. The strongly time-dependent switching events and area dependent current level of Cr-GaO_x films were distinct from the abrupt switching behavior of the filamentary mechanism TiOx thin film devices. It was demonstrated that rf cosputtering of the metal oxides and the corresponding oxygen scavenging metals was a powerful technique to design the bulk state resistive switching devices based on nonstoichiometric metal oxide thin films.

Formation of Porous Anodic Films on Carbon Steels and Their Application to Corrosion Protection Composite Coatings Formed with Polypyrrole

Y. Konno, A. A. Farag, E. Tsuji, Y. Aoki and H. Habazaki

Journal of The Electrochemical Society, 163, C386-C393 (2016)

The growth behavior of nanoporous anodic films on carbon steel containing 0.213 mass% carbon has been examined. The films were grown by anodizing in an ethylene glycol (EG) electrolyte containing 0.1 mol dm^{-3} NH_4F and 0.5 mol dm^{-3} H_2O. The steel contains carbide precipitates with sizes in the range 50–800 nm. The anodic film formed on the carbide phase grew more slowly and was more chemically soluble during anodizing, resulting in submicrometer pits on the anodic film. The nanoporous morphology of the anodic films formed on an α-Fe matrix resembled those formed on iron. Heat treatment of the anodized specimens caused transformation of the chemically soluble fluoride-containing amorphous or poorly crystalline anodic films to crystalline oxide films containing α-Fe_2O_3 and Fe_3O_4. Polypyrrole (PPy) was electropolymerized on the transformed surfaces to form a corrosion-protective composite coating. The resultant specimens coated with the composite coating showed improved durability compared to passivated steel with a PPy coating.
Characterization of Corrosion-Resistant, Nanometer-Thick, Layer-By-Layer Aluminosilicate Coatings Prepared on Stainless Steel


Electrochimica Acta, 201, 311-319 (2016)

Highly corrosion-resistant, ∼65-nm-thick, layer-by-layer aluminosilicate coatings have been prepared by multiple spin casting on Type 430 stainless steel. These coatings have been characterized by field emission scanning electron microscopy, transmission electron microscopy, conductive atomic force microscopy, and micro-electrochemical measurements using a microcapillary cell. The coatings annealed at 400 °C are non-uniform and contain fine iron oxide nodules, which are formed in high densities on the {111} grain surface of the steel. The iron oxide nodules arise from the outward diffusion of the oxidized iron from the substrate through the coating. The coatings annealed at 400 °C are more insulating compared with those before annealing; however, the nodule sites are less insulating owing to the development of more conductive iron oxide channels in the coatings. A microcapillary cell study reveals that the coated specimens prepared from diluted precursor solutions by a layer-by-layer process exhibit higher pitting potential in 3.5 wt% NaCl solution compared with those prepared through a single-layer process. Moreover, the coated specimen obtained from the layer-by-layer process exhibits similarly high pitting potential even at the flaw sites in the coating; in contrast, the pitting potential in the flaw-containing regions of the coated specimen obtained from a single-layer process shifts towards the less noble direction. The layer-by-layer coating is also effective in suppressing the corrosion of the scratched region of the coated specimens, owing possibly to the excellent adhesion between the coating and the substrate.

Redox-Induced Proton Insertion and Desertion of Zircon-Type Neodymium Chromate(V)

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


Redox transformation of NdCrVO₄ involved by insertion/desertion of protons was examined by XRD, XPS, in situ FT-IR and fuel cell tests. It was found that NdCrO₄
caused bulk reduction with H₂ gas at around 400°C, changing to amorphous Nd(III)–Cr(III) hydroxide phase. This hydroxide phase, however, could recover to the original zircon type oxide phase by air oxidation at the same temperature region. Proton-conducting ceramic fuel cells having NdCrO₄ film as an interlayer between cathode and electrolyte was fabricated and the cell was confirmed to exhibit remarkable power generation giving rise to OCV of more than 1.0 V at 500°C. It was speculated that the interlayer facilitates proton transfer from electrolyte to cathode because redox cycling of NdCrO₄ and the corresponding hydroxide was driven by the high proton chemical potential at the interface with electrolyte and plenty of oxygen in cathode gases.

**Electrochemical Impedance Spectroscopy of High-Efficiency Hydrogen Membrane Fuel Cells Based on Sputter-Deposited BaCe₀.₈Y₀.₂O₄₋δ Thin Films**


A hydrogen membrane fuel cell (HMFC) consisting of a Pd solid anode, 1 µm thick BaCe₀.₈Y₀.₂O₄₋δ thin-film electrolyte, and La₀.₆Sr₀.₄Co₀.₂Fe₀.₈O₃ cathode was examined. A single-phase BaCe₀.₈Y₀.₂O₄₋δ thin film was successfully deposited by radio frequency cosputtering with BaCe₀.₈Y₀.₂O₃ and Ce₀.₉Y₀.₁O₂ double targets, as checked by X-ray diffraction, transmission electron microscopy, and wavelength dispersive X-ray analysis. The maximum power density reached 1.05 W cm⁻² at 600°C, and this value was higher than the champion data of the recently reported proton-conducting ceramic fuel cells (PCFCs). Electrochemical impedance analysis was performed to characterize the anode and cathode polarization behavior. The impedance responses of HMFC were explicable with an equivalent circuit built by a series connection of cathode charge-transfer elements and anode mass-transfer elements. The contribution of the mass transfer in Pd bulk was found to be relatively small in comparison to cathode polarization and ohmic loss in normal fuel cell atmosphere. Moreover, the cathodic charge-transfer resistance of HMFC was found to be 25 times smaller than those of the recent PCFC systems. The current results demonstrated that the HMFC retained relatively large gas–proton–electron triple-boundary zones near the interface between the BaCe₀.₈Y₀.₂O₄₋δ electrolyte and porous La₀.₆Sr₀.₄Co₀.₂Fe₀.₈O₃₋δ cathode.
Outline of the 5th International Round Table on Titanium Production in Molten Salt (I)

R.O. Suzuki
Titanium Japan, 64(4), 270-277 (2016)

Chair of 5th International Round Table on Titanium Production in Molten Salt (Ti-RT2016, 10-14 July 2014, Hokkaido, Japan) briefly summarizes its presentations and activities as the first part of three volumes. This article explains the introduction of conference building and successive meetings, and the importance of urgent exchange of technical problems and scientific perspectives. 10 articles are briefly introduced that were given at the morning session of the first day.

Capturing the Non-spherical Shape of Granular Media and Its Trickle Flow Characteristics Using Fully-Lagrangian Method

S. Natsui, H. Takai, R. Nashimoto, K. Ohno, S. Sukenaga, T. Kikuchi, R. O. Suzuki,
AIChE Journal, 63(6), 2257–2271 (2017)
DOI: 10.1002/aic.15538.

We performed a numerical analysis for simulating granular media structures containing non-spherical elements and the liquid trickle flow characteristics of such structures. Fully-Lagrangian numerical simulation methods can track all motion information for solid or liquid elements at each point in time. We introduced suitable compressibility to MPS and performed individual packing behavior calculations for non-spherical elements, based on DEM with expanded functions. RB-DEM is a method using a DEM contact force model that is expanded to handle the motion of freely shaped rigid bodies. It expresses complex shapes to enable low calculation costs and intuitive mounting. We used the boundary for the granular media configured with non-spherical elements to implement a trickle flow simulation based on WC-MPS. Even for elements of equal volume, different shapes changed the liquid passage velocity and hold-up amount. The mean downflow velocity of the liquid phase was not always dependent on the void fraction. For the plane of projection, we obtained a good correlation with the mean downflow velocity in each packed structure, and successfully performed arrangements according to the new liquid-passage shape coefficient.
Reduction of TiS$_2$ by OS Process in CaCl$_2$ Melt

N. Suzuki, S. Natsui, T. Kikuchi and R.O. Suzuki

ECS Transactions, 75(15), 507-515 (2016)

DOI:10.1149/07515.0507ecst

TiS$_2$ was reduced using molten salt electrolysis. At 1173 K in CaCl$_2$-0.5mol% CaS melt, the concentration of sulfur initially decreased significantly. 0.043 mass% S was obtained when the stoichiometric electric charge $Q_0$ was supplied, and 0.01 mass% S was achieved when $Q = 4 Q_0$. Only $\alpha$-Ti was identified by XRD at $Q \geq Q_0$. Metallic Ti and its lower oxides were identified at $Q = Q_0$, but no lower sulfide could be found. It is possible to achieve excellent sulfur removal to a minimum concentration at a larger $Q$, and the use of TiS$_2$ is promising for a new process for titanium refining.

Superhydrophilicity of A Nanofiber-Covered Aluminum Surface Fabricated via Pyrophosphoric Acid Anodizing

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


DOI:10.1016/j.apsusc.2016.06.088

A superhydrophilic aluminum surface covered by numerous alumina nanofibers was fabricated via pyrophosphoric acid anodizing. High-density anodic alumina nanofibers grow on the bottom of a honeycomb oxide via anodizing in concentrated pyrophosphoric acid. The water contact angle on the nanofiber-covered aluminum surface decreased with time after a 4-$\mu$L droplet was placed on the surface, and a superhydrophilic behavior with a contact angle measuring 2.2° was observed within 2 s; this contact angle is considerably lower than those observed for electropolished and porous alumina-covered aluminum surfaces. There was no dependence of the superhydrophilicity on the density of alumina nanofibers fabricated via different constant voltage anodizing conditions. The superhydrophilic property of the surface covered by anodic alumina nanofibers was maintained during an exposure test for 359 h. The quick-drying and snow-sliding behaviors of the superhydrophilic aluminum covered with anodic alumina nanofibers were demonstrated.
Performance Simulation of Flat Plate Thermoelectric Module Consisting of Square Truncated Pyramid Elements

S. Oki and R.O. Suzuki,
DOI:10.1007/s11664-016-4905-7

The performance of a flat-plate thermoelectric (TE) module consisting of square truncated pyramid elements is simulated using commercial software and original TE programs. Assuming that the temperatures of both the hot and cold surfaces are constant, the performance can be varied by changing the element shape and element alignment pattern. When the angle between the edge and the base is 85° and the small square surfaces of all n-type element faces are connected to the low temperature surface, the efficiency becomes the largest among all the 17 examined shapes and patterns. By changing the shape to match the temperature distribution, the performance of the TE module is maximized.

CO Gas Production by CO$_2$ Gas Decomposition in Molten Salt Electrolysis

R. O. Suzuki, F. Matsuura, S. Natsui, T. Kikuchi
ECS Transactions, 75(15), 533-542 (2016)
DOI:10.1149/07515.0533ecst

After complete decomposition of CO$_2$ gas, carbon and oxygen can be used in the steel plant. In addition, CO gas may be used as an effective fuel with easy handling. The preferential decomposition to CO gas is examined by using a combination of CaCl$_2$-CaO melt as a media and ZrO$_2$-8mol% Y$_2$O$_3$ solid-state electrolyte as anode. At a higher electrolysis temperature, CO$_2$ gas is preferentially converted to CO gas. The conversion ratio approached the maximum value of 88.2% at 1273 K. The highest CO concentration was generated at cell voltage of 2.55 V, which is slightly lower than the theoretical decomposition voltage of CaO. Therefore, CO$_2$ decomposes preferentially via the decomposition reaction of carbonate ions. Namely CO$_2$ gas dissolves to form CO$_3^{2-}$ with coexistence of CaO in the melt, CO$_3^{2-}$ precipitates carbon or CO gas bubbles on the cathode, and a part of carbon reacts with the blown CO$_2$ gas to form CO gas.
Fabrication of Self-ordered Porous Alumina via Anodizing in Sulfate Solutions

Ryunosuke Kondo, Tatsuya Kikuchi, Shungo Natsui, and Ryosuke O. Suzuki

DOI:10.1016/j.matlet.2016.07.109

Self-ordered porous alumina was fabricated via anodizing in an acid salt electrolyte solution, sodium hydrogen sulfate (NaHSO₄). High-purity aluminum specimens were anodized in a NaHSO₄ solution under various operating conditions with adjusted concentrations, temperatures, applied voltages, and times. Self-ordering was achieved via NaHSO₄ anodizing at appropriate applied voltages ranging from 20 to 28 V, and ordered cell arrangements with the cell size of 55-77 nm were successfully fabricated. Sulfur atoms originating from the electrolyte anions were incorporated into the ordered porous alumina. A honeycomb distribution consisting of a thick outer layer with a high concentration of sulfur and a very thin inner skeleton with a relatively low concentration sulfur was formed via NaHSO₄ anodizing. Our results suggested that there are now many electrolyte options for the fabrication of self-ordered porous alumina with a wide range of nanosizes.

Exploration for the Self-ordering of Porous Alumina Fabricated via Anodizing in Etidronic Acid

Akimasa Takenaga, Tatsuya Kikuchi, Shungo Natsui, and Ryosuke O. Suzuki

Electrochimica Acta, 211, 515-523 (2016)
DOI:10.1016/j.electacta.2016.06.071

Ordered porous alumina (OPA) with large-scale circular and hexagonal pores was fabricated via etidronic acid anodizing. High-purity aluminum plates were anodized in 0.2-4.2 M etidronic acid solution at 145-310 V and 288-323 K. Self-ordering of porous alumina was observed at 165 V and 313 K in 4.2 M, at 205 V and 303 K in 1.0 M, and at 260 V and 298 K in 0.2 M, and the cell diameter was measured to be 400-640 nm. The ordering potential difference decreased with the electrolyte concentration increasing. OPA without an intercrossing nanostructure could be
fabricated on a nanostructured aluminum surface via two-step anodizing. Subsequent pore-widening in etidronic acid solution caused the circular dissolution of anodic oxide and the expansion of pore diameters to 470 nm. The shape of the pores was subsequently changed to a hexagon from a circle via long-term pore-widening, and a honeycomb structure with narrow alumina walls and hexagonal pores measuring 590 nm in its long-axis was formed in the porous alumina. Transition of the nanostructure configuration during pore-widening corresponded to differences in the incorporated phosphorus distribution originating from the etidronic acid anions.

### Influence of Gas Injection Pipe on CO₂ Decomposition by CaCl₂-CaO Molten Salt and ZrO₂ Solid Electrolysis


*ISIJ Intern.*, **56** (11), 2093-2099 (2016)

DOI:10.2355/isijinternational.ISIJINT-2016-179

The electrochemical decomposition of carbon dioxide to form carbon and oxygen gas in CaCl₂–CaO molten salt was studied. A water model experiment was carried out to study the influence of the tip shape of the pipe, the pipe diameter and the wettability of the gas injection pipe on the bubble shape in the molten salt. Bubbles were formed with both a horizontal tip and an oblique tip when the wettability of the gas injection pipe was good. The specific surface area of the bubbles when using the oblique tip was smaller than when using the horizontal tip. On the other hand, slug flows appeared when wettability was poor. In a hot model experiment, the current density was measured, and it was found that the CO₂ gas concentration decreased. Precipitated carbon was detected from the sample after the experiment. With the same pipe, the decrease of the CO₂ gas concentration when using the oblique tip was more remarkable than when using the horizontal tip. It is likely that the form of the CO₂ gas in the molten salt was bubble-shaped.
Helical Configuration for Thermoelectric Generation

X.N. Meng and R.O. Suzuki

DOI:10.1016/j.applthermaleng.2016.01.061

Performance of thermoelectric (TE) generator (TEG) depends on its physical structure in addition to the properties of TE materials. This study numerically simulated the characteristic performances of a three-dimensional (3-D) helical TE module using finite-volume method, and compared them with those of a conventional straight module. The effect of geometric parameters of helical TE module on the characteristic performances was analyzed, and an optimal helical design was proposed to obtain higher performance. The simulation results show that the helical module can harvest more heat than the straight module, and thus generate higher output power because the conversion efficiencies of two modules are approximately equal. The increase in pitch of the helical module has a positive influence on the characteristic performances, including more heat harvesting and output power, as well as higher conversion efficiency. However, the radial expansion of helical module brings an opposite effect on the unit performances, which is defined by dividing the characteristic performances by the number of p–n pairs, and unit input heat, unit output power, and unit heating area of helical module are decreased with module diameter. Higher performance can be generated by the use of helical module with longer pitch and shorter diameter.

Structural Investigation and Indium Substitution in the Thermoelectric Mn$_{2.7}$Cr$_{0.3}$Si$_4$Al$_2$-xIn$_x$ Series

T. Barbier, E. Combe, R. Funahashi, T. Takeuchi, M. Kubouchi, Y. Miyazaki, E. Guilmeau and R.O. Suzuki

DOI:10.1007/s11664-016-4365-0

Following the recent discovery of the promising Mn$_{2.7}$Cr$_{0.3}$Si$_4$Al$_2$ thermoelectric compound (having, e.g., automotive, industrial, and solar conversion applications), structural characterization by X-ray single-crystal diffraction analysis has been
performed. This layered material is composed of two distinct crystallographic sites where both (Mn, Cr) and (Al, Si) are randomly distributed. The deduced crystallographic parameters were then confirmed by powder x-ray diffraction analysis through a temperature dependence of the phase stability, showing at the same time chemical stability up to 873K. Taking into account the two distinct crystallographic sites highlighted, samples possessing two guest elements, one on each site, were then synthesized to improve the thermoelectric properties. A solid solution is found in the system Mn$_{2.7}$Cr$_{0.3}$Si$_4$Al$_2$-xIn$_x$ with x varying from 0 to 0.2. Thus, double-substituted samples were studied by x-ray diffraction, electrical, and thermal measurements. The present paper describes and discusses the experimental results obtained.

**Self-ordered Porous Alumina Fabricated via Phosphonic Acid Anodizing**

S. Akiya, T. Kikuchi, S. Natsui, N. Sakaguchi and R. O. Suzuki

*Electrochimica Acta, 190, 471-479 (2016)*

DOI:10.1016/j.electacta.2015.12.162

Self-ordered periodic porous alumina with an undiscovered cell diameter was fabricated via electrochemical anodizing in a new electrolyte, phosphonic acid (H$_3$PO$_3$). High-purity aluminum plates were anodized in phosphonic acid solution under various operating conditions of voltage, temperature, concentration, and anodizing time. Phosphonic acid anodizing at 150-180 V caused the self-ordering behavior of porous alumina, and an ideal honeycomb nanostructure measuring 370-440 nm in cell diameter was successfully fabricated on the aluminum substrate. Conversely, disordered porous alumina grew at below 140 V, and anodizing at above 190 V caused local thickening due to oxide burning. Two-step phosphonic acid anodizing allows the fabrication of high aspect ratio ordered porous alumina. HPO$_2$$^-$$^2$ anions originated from the electrolyte were incorporated into the porous oxide during anodizing. Consequently, a double-layered porous alumina consisting of a thick outer layer containing incorporated HPO$_2$$^-$$^2$ anions, and a thin inner layer without anions was constructed via phosphonic acid anodizing.
Temperature Dependence of Behavior of Interface between Molten Sn and LiCl-KCl Eutectic Melt due to Rising Gas Bubble

S. Natsui, R. Nashimoto, H. Takai, T. Kumagai, T. Kikuchi, R. O. Suzuki

DOI:10.1007/s11663-016-0618-9

The interfacial behavior between molten Sn and the LiCl–KCl eutectic melt system was directly observed. We found that the transient behavior of the interface has considerable temperature dependence through a change in the physical properties. The “metal film” generated in the upper molten salt phase dramatically influences the interface shape. Although the lifetime of the metal film depends on the gas flow rate, it is not affected by buoyancy if interface tension is dominant.

SPH Simulations of the Behavior of the Interface between Two Immiscible Liquid Stirred by the Movement of a Gas Bubble

S. Natsui, R. Nashimoto, H. Takai, T. Kumagai, T. Kikuchi, R. O Suzuki

DOI:10.1016/j.ces.2015.11.018

The transient behavior of the immiscible two liquids interface, which is initiated by the rising gas bubble was investigated using Smoothed Particle Hydrodynamics (SPH) model. This developed numerical method is using fully Lagrangian particle-based model, which can track the movement of both the gas and the liquid phase directly. Numerical simulations have been performed for different conditions corresponding to different values of surface tension, viscosity and density, and the predicted topological changes as well as the theoretical pressure and interfacial shape of bubbles are validated. In the case of immiscible two liquids, the column of a lower liquid phase penetrating into the upper liquid phase influences interface area, whose shape strongly depends on the wake flow pattern of a bubble. Thus, the dynamic balance between the buoyancy and the liquid-liquid interfacial tension determines an interface area. Under higher surface tension condition, such as molten metal-slag system, the liquid-liquid interface shape is greatly influenced by the fluctuation of a bubble. Then, linearly changed interface shape can be observed, indicating that this shape becomes easily unstable by slight change of the curvature.
Analysis of The Performance of Thermoelectric Module under Concentrated Radiation Heat Flux

R.O. Suzuki, K.O. Ito and S. Oki,
DOI:10.1007/s11664-015-4237-z

The concentration of solar radiation by either the lens or the mirror is one of the options for practical utilization of light to obtain higher temperature. However, it is difficult to maintain high temperature on the hot side of the module due to solar diurnal motion. This study evaluates the influence of the TE output by the optical light concentration. Three-dimensional partial differential equations describing heat balance and TE phenomena were simultaneously solved by applying the numerical method, and the temperature distribution in the whole TE module as well as the current density were simulated. It was shown that the three models of light concentration on a single TE module (BiTe based, 4 legs having dimensions of 10*10*10 mm) generate a similar output at the external load. This happens because the long leg becomes a large thermal resistance, and because the alumina plate (1mm thick) with a high thermal conductivity covers the top of TE modules. The homogenized temperature at the hot junctions generates the similar output at all three models, when the cold terminals were kept at constant temperature.

Influence of Gas Injection Pipe on CO₂ Decomposition by CaCl₂-CaO Molten Salt and ZrO₂ Solid Electrolysis

Tetsu-to-Hagané, 102(4) 217-223 (2016)
DOI:10.2355/tetsutohagane.TETSU-2015-025

The electrochemical decomposition of carbon dioxide to form carbon and oxygen gas was studied in CaCl₂-CaO molten salt. The water model experiment was carried out to study on the influence of the tip shape of the pipe, the pipe diameter and wettability to the gas injection pipe for the bubble shape in molten salt. Bubbles were formed in both conditions of horizontal and oblique tip with good
wettability of the gas injection pipe. The specific surface area of bubble using oblique tip of the pipe was smaller than horizontal tip. On the other hand, slug flows appeared with poor wettability. In the hot mode experiment, the current density was measured, and the carbon dioxide gas concentration decreased. The carbons were detected from the sample after the experiment. The decrease of carbon dioxide gas concentration using oblique tip were more remarkable than the case using horizontal tip with the same pipe. It is likely that the form of carbon dioxide gases in the molten salt were bubbles shape.

**Numerical Optimization of Trapezoidal Thermoelectric Elements for Double-Pipe-Shaped Module**

S. Oki, K.O. Ito, S. Natsui and R.O. Suzuki


DOI:10.1007/s11664-015-4034-8

Electric power and efficiency are numerically evaluated for the thermoelectric (TE) module designs, by assuming that the hot fluid is carried in the pipe with a hexagonal cross-sectional shape, and that the trapezoidal columnar TE elements are attached to the external surface of the pipe. The thermal heat balance and successive TE phenomena are studied by combining the commercial software and our original TE program. The upper length, the height, and the thickness of the trapezoidal TE elements are assumed to be constant. By varying the base length, the maximum power and the maximum efficiency were evaluated for the case when the radiation heat ratio is minimized. It was demonstrated that the choice of hexagonal cross-section for TE module is the best one under the assumed material properties and in the allowed space between two pipes.
Al-Zn Co-electrodeposition by a Double Counter Electrode Electrodeposition System from an AlCl3-1-ethyl-3-methylimidazolium Chloride Ionic Liquid Bath

Y. Sato and K. Azumi
doi.org/10.1016/j.surfcoat.2015.10.080

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–AlCl3-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.

Electrochemical CO₂ Reduction in Ionic Liquid Using Two Compartment Cell Separated with Proton-Conducting Membrane

H. Yoshikawa, K. Azumi
ECS Transactions, 75 (3) 1-5 (2016).
doi: 10.1149/07503.0001ecst

Electrochemical conversion of CO₂ to CH₄ using EMIM-TFSI ionic liquid bath was investigated. EMIM-TFSI can absorb much CO₂ gas and thus used as an
electrolyte solution. To maximize conversion efficiency, two compartment cell was developed in which ionic liquid bath containing Cu mesh working electrode bubbled with CO₂ gas and KCl aqueous solution bath containing counter electrode were separated by proton conducting Nafion membrane. Suitable condition of water content in the ionic liquid bath and polarization potential for efficient conversion was investigated by using gas chromatography. Spatial arrangement working electrode and membrane was also shown to be an important factor for efficient conversion from CO₂ to CH₄.

Development of Aluminum Air Battery Using an Ionic Liquid Electrolyte Solution.

T. Oguma, K. Azumi;
ECS Transactions, 75 (18) 83-90 (2017).
doi: 10.1149/07518.0083ecst

Prototype Al-air primary battery was constructed to avoid self-discharging due to chemical dissolution of Al in a concentrated alkaline electrolyte during non-operation condition. The battery was composed of two compartments; one of which contained hydrophobic ionic liquid (EMIIM-TFSI) and KOH pellets, and the other contained alkaline KOH aqueous solution and air electrode. Two compartments were separated with an anion exchange membrane. Although EMIIM-TFSI had hydrophobic property, it could contain a little amount of water to enable Al dissolution. Results of current-voltage curve measured in various conditions indicated that the internal resistance of the battery was rather high to limit the battery performance. Impedance analysis using proper arrangement of a pseudo-reference electrode of Ag wire in the battery enabled to estimate resistance of each component of the battery to clarify the bottleneck of this system.
Hydrogen Permeation into a Carbon Steel Sheet Observed by a Micro-capillary Combined with a Devanathan-Stachurski Cell

K. Fushimi, M. Jin, Y. Kitagawa, T. Nakanishi, Y. Hasegawa
ISIJ Int., 56(3), 431-435 (2016)

A micro-capillary technique was applied to a Devanathan-Stachurski electrochemical cell for local measurement of hydrogen permeation into a steel sheet. An electrolyte-flowing design for the hydrogen entry side of the Devanathan-Stachurski cell successfully allowed the detection of hydrogen permeation response on hydrogen exit side electrode in a micro-capillary cell with a diameter of 250 μm. Phase shift of the detected permeation current from a sinusoidal perturbation of the electrolyte flow rate in the hydrogen entry cell was strongly dependent on the metallographic structure of the steel sheet. A local structure, in which two single grains form grain boundaries, led to hydrogen permeation more frequently than did a local structure of single grains. The results suggested that the diffusion coefficient of the boundaries was at least two-times larger than that of the grains.

FEM Analysis for Sinusoidal Perturbation of Hydrogen Permeation into a Steel Sheet

Y. Yamamoto, Y. Kitagawa, T. Nakanishi, Y. Hasegawa, K. Fushimi
ISIJ Int., 56(3), 472-477 (2016)

Numerical calculation for the diffusion problem of hydrogen absorbed in a steel sheet during hydrogen permeation measurement using a double electrochemical cell was carried out. The finite element method (FEM) was applied to obtain the concentration distribution of hydrogen expressed by one- or two-dimensional Fick’s laws in the sheet, assuming that hydrogen concentration at the hydrogen entry interface was perturbed sinusoidally and both the hydrogen entry and exit reactions were in a mass-transport controlled process. From a comparison with experimental results reported previously, in which a phase shift from entry current to exit current waves observed on a single grain of the specimen sheet was at least two-times larger than that on two grains, it was estimated that the diffusion coefficient at a grain boundary located between two grains was five orders in magnitude larger than that on a single grain.
Optical characterization of passive oxides on metals

T. Ohtsuka, K. Fushimi

Electrochemistry, 84(11), 826-832 (2016)

In-situ optical detection of the passive oxide films on iron and titanium was reviewed. The optical techniques such as ellipsometry (i.e., reflection of polarized light), Raman spectroscopy, and potential modulation reflectance (PMR) have been successfully applied to the detection in thickness, composition, and semiconducting property, respectively, of the thin passive oxides under the in-situ condition. The growth mechanism of the passive oxide has been discussed from the precise measurement of thickness as a function of potential and time by a three-parameter ellipsometry. From the in-situ Raman spectra, the composition of the passive oxide has been estimated to be Fe$_3$O$_4$-$\gamma$-Fe$_2$O$_3$ for iron and anatase TiO$_2$ for titanium. From PMR, the Mott-Schottky type plot could be drawn in the passive oxide on iron, which indicates that the formation of the space charge layer can be optically seen. From the PMR spectra, one has evaluated light-absorption edge that may correspond to a band-gap energy between the valence and conduction band.

Passivation Behavior of Type-316L Stainless Steel in the Presence of Hydrogen Sulfide Ions Generated from Local Anion Generating System

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


The passivity of type 316L stainless steel was studied in a pH 8.4 boric acid-borate buffer solution containing hydrogen sulfide ions (HS$^-$) by using a local anion-generating system. During potentiostatic polarization of the stainless steel at a primary passive potential of 0.4 V$_{SSE}$ and at a secondary passive potential of 0.9 V$_{SSE}$ in solutions with and without HS$^-$, the current density flowing for passive film formation was increased by the presence of HS$^-$ at both potentials, while 15 Hz impedance at 0.9 V$_{SSE}$ in the solution with HS$^-$ was larger than that in the solution without HS$^-$. It was thought that the presence of HS$^-$ in the solution during film
Heterogeneity of a Thermal Oxide Film Formed on Polycrystalline Iron Observed by Two-Dimensional Ellipsometry

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


Heterogeneity of the thermally oxidized surface of a polycrystalline iron substrate was investigated by using two-dimensional (2D) ellipsometry and a micro-capillary cell (MCC). Thickness mapping of a bi-layered oxide film (inner Fe$_3$O$_4$ layer/outer $\alpha$-Fe$_2$O$_3$ layer) on the iron substrate was performed by 2D ellipsometry, and it was demonstrated that the grain-dependency of the thickness of Fe$_3$O$_4$ determined the heterogeneity of oxide thickness on the polycrystalline iron. Degradation behavior of the thermally oxidized surface during galvanostatic polarization was observed by in situ 2D ellipsometry. The transients of ellipsometric parameters showed different trajectories depending on the substrate orientation, indicating that the magnitude of degradation of the oxide by the cathodic current differed depending on the heterogeneous oxide structure. EIS measurements with the MCC revealed that donor density $N_D$ of the oxide was greater in the order of $\{0 0 1\} > \{1 1 1\} > \{1 0 1\}$. It was concluded that the grain-dependency of the oxide thickness and $N_D$ was attributed to the anisotropic growth of the two oxide layers.
Effect of Surface Conditions and Relative Humidity on Hydrogen Permeation Behavior of Zinc Coated Steels during Wet and Dry Corrosion

M. Sakairi and H. Takagi

ISIJ International, 56 452–458 (2016)

The effects of scratch, surface element composition, and relative humidity on the hydrogen permeation behavior of zinc coated steels during wet and dry cycle corrosion tests were investigated. The permeating hydrogen was measured electrochemically, and a size controlled scratch was formed on zinc coated steels with a laser machining technique. The hydrogen permeation current was observed on the zinc coated steels with a formed scratch (S-coated): no significant hydrogen permeation current was observed on the zinc coated steel without the formed scratch (NS-coated) or on steel with zinc coating removed by mechanical grinding (R-steel). The zinc corrosion products effectively reduced the hydrogen permeation current from the S-coated at low relative humidity. The total amount of permeating hydrogen per unit area of formed scratch was independent of the area of the formed scratch in wet and dry cycling.

Development of an Area-selective Technique for Electrochemical Hydrogen Detection with Laser Local Activation

M. Sakairi, K. Igarashi and A. Nagao

ISIJ International, 56 483-486 (2016)

An area-selective technique for electrochemical hydrogen detection with laser local activation (focused pulse YAG laser irradiation) has been newly developed. The developed technique was applied to measure hydrogen permeation behavior of iron at selected areas of various grain structures. The hydrogen permeation current was detected after the laser irradiation, suggesting that indirect activations of hydrogen generation and entry reactions were produced by the focused pulse YAG laser irradiation, which activated dissolution of metals at the irradiated areas. An obtained hydrogen diffusion coefficient, DH, was in good agreement with previously reported DH of iron, while a clear dependence of DH on grain structure at the entry side was not found.
**Effect of Surface Conditions and Specimen Composition on Hydrogen Permeation Behavior of Coated and Uncoated Steels during Wet and Dry Corrosion at a Constant Dew Point**

K. Igarashi and M. Sakairi  

A wet and dry corrosion test with a constant dew point was applied to investigate the effects of scratches and specimen composition on the hydrogen permeation behavior of Zn and 55 mass% Al–Zn coated steels as well as of uncoated steel. There was an etched size controlled scratch formed on specimens with a laser machining technique. The hydrogen permeation current was observed to be independent of the specimen composition and the area of the formed scratches, the corrosion products were observed after the tests. 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 suggested that the composition, scratch, and corrosion products play an important role in the hydrogen permeation behavior during wet and dry corrosion.

**Formation of Layered Structure Porous Type Anodic Alumina Films Locally with a Solution Flow Type Micro-droplet Cell**

M. Sakairi, F. Nishino, and R. Itzinger  

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 on aluminum. The anodizing process with different repetition numbers, yielding different oxide layer numbers, was performed with the Sf-MDC. 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.
Formation of Oxide Films for High-Capacitance Aluminum Electrolytic Capacitor by Liquid Phase Deposition and Anodizing

M. Sakairi, R. Fujita, and S. Nagata

Surface and Interface Analysis, 48, 899-905 (2016)

Liquid-phase deposition (LPD) treatment and anodizing were used to form oxide layer for a high-capacitance aluminum electrolytic capacitor. Formation of protective oxide layers and modification of LPD conditions make it possible to prolong the LPD duration and lead to the formation of TiO₂ and NaF deposits on aluminum. A titanium oxide/aluminum oxide mixed layer was formed by a combination process of LPD treatment and anodizing. The capacitance of the formed layer was about 300% higher than that of an anodic oxide film formed on electro-polished aluminum. The structures and compositions of the films that were formed were determined by transmission electron microscopy, scanning electron microscopy, and Rutherford backscattering spectroscopy.

Effect of a Kind of Metal Cation on Corrosion Mechanism of A3003 Aluminum Alloy in Tap Water

K. Otani, M. Sakairi, and A. Kaneko

Material Transaction, 57, 1539-1546 (2016)

Effect of a kind of metal cation on corrosion mechanism of A3003 aluminum alloy in tap water was investigated by electrochemical techniques and immersion corrosion tests. Corrosion rate of the aluminum alloy decreased with increase in a hardness of cation, except for Mg²⁺. XPS analyses showed metal cations, classified as a hard acid in tap water were incorporated in hydroxides on the aluminum alloy. The results suggest that the incorporated cations have corrosion inhibitory effect (e.g., Ca²⁺ and Zn²⁺) or corrosion promotive effect (e.g., Mg²⁺). These different effects can be explained by difference in molar volume between hard metal cation’s hydroxide and aluminum hydroxide.
Improvement of Corrosion Resistance of Aluminum Alloy with Wettability Controlled Porous Oxide Films

M. Sakairi and V. Goyal

Corrosion Science and Technology, 15, 166-170 (2016)

The combined process of porous type anodizing and desiccation treatment was applied to improve wettability of A1050 aluminum alloy. The water contact angles of anodized samples were increased considerably with desiccation treatment. However, there was no considerable effect of polishing and anodizing time on water contact angle. The corrosion behavior with the treatments was investigated electrochemically. The corrosion resistance of the samples in 3.5 mass% NaCl solutions increased with higher contact angle. Anodized and desiccated samples showed better corrosion resistance than un-desiccated samples around rest potential region.

Effects of Metal Cations on Corrosion of Mild Steel in Model Fresh Water

K. Otani and M. Sakairi

Corrosion Science, 111, 302-312 (2016)

The effects of metal cations on corrosion of mild steel in model fresh water were investigated by electrochemical techniques and immersion tests. Analysis of X-ray photoelectron spectroscopy showed that metal cations have large hardness of cations, X, are incorporated in passive films. The electrochemical and immersion results showed that X is not suitable as a corrosion indicator of mild steel. A novel corrosion indicator, “corrosion inhibitory effect of cations Y”, that consists of X and molar volume ratio, ∆V, is proposed, and it is shown that the novel indicator can estimate the corrosion rate of mild steel in fresh water.
Effect of Metal Cations in Solutions on Surface Film Structure of Aluminum Alloys

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

Proc. of the 8th Japan-China Joint Seminar on Marine Corrosion and Control, O-12 (2016)

An effect of metal cations in solutions on structure of surface film formed on aluminum alloys were investigated by X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and scanning electron microscopy (SEM). In this study, model fresh water with different kind of metal cations were used. The surface morphology of A5052 alloy after immersion was strongly dependent on contained metal cations, while not significant morphology change of A3003 alloy with immersion was observed. The hard metal cations which reduced the corrosion rate were incorporated into the outer layer portion of the oxide films. From AES analysis, oxide film structure was changed by incorporation of hared metal cations.
SYMPOSIA
Symposium of "Oxide Films: A Symposium in Honor of Masahiro Seo"

Hawaii Convention Center, Honolulu, on October 4, 2016
in PRiME 2016/230th ECS Meeting

This symposium was held at as a part of PRiME 2016/230th ECS Meeting program organized by H. Habazaki, K. Azumi, A. W. Hassel and K. Hebert. The symposium was focused on recent progress on formation, breakdown and properties of various oxide films on metals and alloys. Emphasis will be on fundamental studies using novel physicochemical and electrochemical methods for characterizations of oxide films on practical and advanced materials at macro, micro and nano-scales. The scope of the symposium also includes functional materials based on oxides; oxide films for corrosion protection, including the breakdown of such films; formation and applications of nanostructured oxide layers; and oxide layers for dielectric, electrocatalytic and photocatalytic applications. Invited speakers are: Philippe Marcus (CNRS), Toshiaki Ohtsuka (Hokkaido University), Christofer Leygraf (KTH Royal Institute of Technology), Detlef Diesing (Universität Duisburg-Essen), Hideki Masuda (Tokyo Metropolitan University), Robert G. Kelly (University of Virginia), Francesco di Quarto (Palermo University), Manuel Lohrengel (University of Düsseldorf), Sannakaisa Virtanen (University of Erlangen-Nuremberg), Hidetaka Asoh (Kogakuin University), Koji Fushimi (Hokkaido University) and Shinji Fujimoto (Osaka University). The proceedings of a meeting was published as ECS Transactions Volume 75 No.27, Electrochemical Society (ECS), ISBN:9781607687764. Symposium party was also held at the same building after the symposium with many colleague and attendance. Please enjoy the party Photos!
Symposium to Celebrate the 90th Birthday of Professor Norio Sato

June 30th to July 1st, 2017, Chateraise, Gateaux Kingdom Sapporo

This symposium was organized by our research group to celebrate the 90th birthday of our mentor of corrosion research, Dr. Norio Sato, an emeritus professor of Hokkaido University. His great achievements in and significant contributions to the corrosion science and engineering have been known worldwide by a long list of many honors such as The Corrosion Division Award (1983), Fellow Award (1999), The Olin Palladium Medal Award (2001) from The Electrochemical Society in USA (ECS), The U. R. Evans Award (1985), Honorary Fellow (1998) from The Institution of Corrosion Science and Technology in UK, The W. R. Whitney Award (1989) and Fellow Award (1993) from The National Association of Corrosion Engineers in USA (NACE), etc. He also played an important part in establishment of The Japan Society of Corrosion Engineering.

In the symposium, five lectures were given. (1) "The corrosion research at Norio Sato's laboratory and its subsequent progress" presented by Dr. Toshiaki Ohtsuka, emeritus professor of Hokkaido University, (2) "The 1st 〜 8th International Passivity Symposia" presented by Dr. Norio Sato, emeritus professor of H.U., (3) "High temperature materials developed at and expanded from Hokkaido University" presented by Dr. Toshio Narita, emeritus professor of H.U., (4) "Forefront of molten salts and ionic liquids research" presented by professor Mikito Ueda, and (5) "Micro-electrochemistry for evaluation of passivity perturbation" presented by professor Koji Fushimi. After the symposium, celebration dinner was held. Dr. Toru Tsuru, an emeritus professor of Tokyo Institute of Technology and Dr. Sachiko Ono,
an emeritus professor of Kogakuin University gave their complimentary speeches. Dr. Koji Hashimoto, emeritus professor of Tohoku University, currently a professor of Tohoku Institute of Technology, also read congratulatory addresses sent from Dr. Michael J. Graham and Dr. Barry MacDougall, NRC National Research Council of Canada, and Professor Ronald M. Latanision, Massachusetts Institute of Technology. Many other participants can be found in a group photo.