

Wed. Mar 23, 2022

B302

Symposium | Co-Innovation Program (CIP) | Informatics for every chemist:
Fundamentals of machine/deep learning for predictive data analytics

[B302-1am] Informatics for every chemist:

Fundamentals of machine/deep
learning for predictive data analytics

Chair, Symposium organizer: Hironobu Iyama, Hikaru Takaya,
Kazuhiko Sato, Kazuhiro Matsumoto

9:00 AM - 11:40 AM B302 (Online Meeting)

[B302-1am-01] 21st Century Literacy required in the age
of Digital Transformation

○Noriko Arai¹ (1. National Institute of
Informatics)

9:10 AM - 10:10 AM

[B302-1am-02] The future of DX organic synthesis

○Takashi Ohshima¹ (1. Kyushu University)

10:20 AM - 10:50 AM

[B302-1am-03] Frontier of Catalyst Informatics

○Takashi Toyao^{1,2} (1. Hokkaido University, 2.
Kyoto University)

11:00 AM - 11:30 AM

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Fundamentals of machine/deep learning for predictive data analytics

[B302-1pm] Informatics for every chemist:

Fundamentals of machine/deep
learning for predictive data analytics

Chair, Symposium organizer: Hironobu Iyama, Hikaru Takaya,
Kazuhiko Sato, Kazuhiro Matsumoto

1:00 PM - 3:40 PM B302 (Online Meeting)

[B302-1pm-01] Statistical machine learning for inverse
problems in materials research

○Ryo Yoshida Yoshida¹ (1. The Institute of
Statistical Mathematics)

1:00 PM - 2:00 PM

[B302-1pm-02] Fundamentals of molecular descriptors in
materials informatics

○Yoshihiro Hayashi¹ (1. The Institute of
Statistical Mathematics)

2:10 PM - 2:40 PM

[B302-1pm-03] How can synthetic chemists perform
Artificial Intelligence in synthetic
chemistry?

○Akira Yada¹ (1. National Institute of
Advanced Industrial Science and Technology
(AIST))

2:50 PM - 3:20 PM

B301

Symposium | Co-Innovation Program (CIP) | Innovative rechargeable
battery toward realizing carbon neutrality

[B301-1am] Innovative rechargeable battery toward
realizing carbon neutrality

Chair, Symposium organizer: Nagatoshi Koumura, Eiji Hosono,
Masashi Okubo, Keigo Hoshina

9:00 AM - 11:10 AM B301 (Online Meeting)

[B301-1am-01] Electrolyte design to suppress hydrogen
evolution

○Seongjae Seongjae Ko¹, Atsuo Yamada¹ (1.
The Univ. of Tokyo)

9:10 AM - 9:40 AM

[B301-1am-02] The properties of the zinc secondary
batteries using the organic/inorganic
hybrid separator

○Satoshi Ogawa¹, Mitsuzo Nogami¹ (1.
NIPPON SHOKUBAI Co., LTD.)

9:40 AM - 10:10 AM

[B301-1am-03] Vertically aligned nanosheet electrodes
for fast charge storage

○Wataru Sugimoto¹ (1. Shinshu University)

10:10 AM - 10:40 AM

[B301-1am-04] Development of the next-generation
capacitors for future society

○Shuichi Ishimoto¹ (1. Nippon Chemi-Con
Corp.)

10:40 AM - 11:10 AM

Symposium | Co-Innovation Program (CIP) | Innovative rechargeable
battery toward realizing carbon neutrality

[B301-1pm] Innovative rechargeable battery toward
realizing carbon neutrality

Chair, Symposium organizer: Nagatoshi Koumura, Eiji Hosono,
Masashi Okubo, Keigo Hoshina

1:00 PM - 2:50 PM B301 (Online Meeting)

[B301-1pm-01] Interfacial Ion Dynamics for Advanced All
Solid State Batteries

○Yasutoshi Iriyama¹ (1. Nagoya Univ.)

1:00 PM - 1:50 PM

[B301-1pm-02] Development of Argyrodite Type Sulfide
Solid Electrolytes and Materials for All-
Solid-State Batteries.

○Tsukasa Takahashi¹, Yuki Nakayama¹,
Daisuke Inoue¹ (1. Mitsui Mining & Smelting

Co., Ltd.)

1:50 PM - 2:20 PM

[B301-1pm-03] Materials design of solid ionic conductors toward the next-generation solid-state batteries

○Saneyuki Ohno¹ (1. Kyushu University)

2:20 PM - 2:50 PM

B303

Symposium | Co-Innovation Program (CIP) | Smart chemistry for future medical and life science

[B303-1am] Smart chemistry for future medical and life science

Chair, Symposium organizer: Atsushi Sugasaki, Akira Chiba, Takeshi Nagasaki, Masaru Tanaka

9:00 AM - 11:40 AM B303 (Online Meeting)

[B303-1am-01] Decellularized/inactivated tissue in regenerative therapy: the way for clinical trials

○Tetsuji Yamaoka¹ (1. National Cerebral and Cardiovascular Center Research Institute)

9:05 AM - 9:55 AM

[B303-1am-02] Biomedical applications of hydrogel with precisely controlled structure

○Takamasa Sakai¹ (1. The Univ. of Tokyo)

9:55 AM - 10:25 AM

[B303-1am-03] Antithrombogenic polymer "SEC ONE SURFACE_{TM}" and its application on medical devices

○Yuta Kawakatsu¹, Koryu Den², Atsushi Iwai², Shohei Nakayama², Tomoya Ohashi³, Fumihiko Kajii³ (1. TOYOBO CO., LTD. Medical Equipment & Devices Department, 2. TOYOBO CO., LTD. Medical Equipment & Devices Development Center, 3. TOYOBO CO., LTD. Medical Equipment & Devices Production Center)

10:35 AM - 11:05 AM

[B303-1am-04] Research on skin irritation by high concentration ethanol and mitigating agents

○Masao Hara¹, Rina Hattori¹, Kei Sato¹, Shunsuke Sakurai¹, Misaki Ishida¹, Yumiko Yamawaki², Yuri Okano², Hitoshi Masaki² (1. NOF Corporation, 2. CIEL Corporation)

11:05 AM - 11:35 AM

Symposium | Co-Innovation Program (CIP) | Smart chemistry for future medical and life science

[B303-1pm] Smart chemistry for future medical and life science

Chair, Symposium organizer: Atsushi Sugasaki, Akira Chiba, Takeshi Nagasaki, Masaru Tanaka

1:00 PM - 3:40 PM B303 (Online Meeting)

[B303-1pm-01] *Post-antibody drugs*: Generation of a novel class of drug modalities based on molecular-targeting helix-loop-helix (HLH) peptides

○Ikuko Fujii¹ (1. Osaka Prefecture University)

1:00 PM - 1:50 PM

[B303-1pm-02] Metabolism-Based Production of Cardiomyocytes from Human Pluripotent Stem Cells for Cardiac Regenerative Therapy

○Shugo Tohyama¹ (1. Keio University School of Medicine)

1:50 PM - 2:20 PM

[B303-1pm-03] Towards the industrialisation of regenerative medicine through cell fibre technology

○Hidetoshi Hoshiya¹ (1. CellFiber Co., Ltd.)

2:30 PM - 3:00 PM

[B303-1pm-04] Understanding In-body molecular communication networks for future medicine

○Tadashi Nakano¹ (1. Osaka City University)

3:00 PM - 3:30 PM

B204

Symposium | Medium and Long-Term Program | Condensed Electronic Conjugation of Molecular Materials: Revisiting Electronic Conjugation

[B204-1pm] Condensed Electronic Conjugation of Molecular Materials: Revisiting Electronic Conjugation

Chair, Symposium organizer: Shu Seki, Hiroshi Shinokubo

1:00 PM - 3:40 PM B204 (Online Meeting)

[B204-1pm-01] Condensed Conjugation Molecular Physics and Chemistry: Revisiting Electronic Conjugation Leading to Innovative Physical Properties of Molecular Materials

○Shu Seki¹ (1. Kyoto University)

1:00 PM - 1:15 PM

[B204-1pm-02] Electron transport and crystal structure prediction of layered molecular system
 ○Tatsuo Hasegawa¹ (1. The University of Tokyo)

1:15 PM - 1:45 PM

[B204-1pm-03] Physical properties controlled by hydrostatic pressure and uniaxial strain
 ○Taishi Takenobu¹ (1. Nagoya University)

1:45 PM - 2:00 PM

[B204-1pm-04] Creation of Novel Spin-polarization Materials utilizing Molecular Chirality
 ○Masayuki Suda^{1,2,3} (1. Kyoto Univ., 2. JST PRESTO, 3. RIKEN)

2:10 PM - 2:25 PM

[B204-1pm-05] Excellent device performance from higher-density organic films
 ○Toshinori Matsushima¹, Yu Esaki¹, Aoyama Tetsuya², Chihaya Adachi¹ (1. Kyushu University, 2. RIKEN)

2:25 PM - 2:55 PM

[B204-1pm-06] Charge injection and electronic phase transition in molecular solids
 ○Shun Watanabe¹ (1. The University of Tokyo)

2:55 PM - 3:10 PM

[B204-1pm-07] Materials and Device Structures in Organic LEDs
 ○Junji Kido¹ (1. Yamagata University)

3:10 PM - 3:40 PM

Symposium | Medium and Long-Term Program | Chemistry of curious biological phenomena

[B204-1am] Chemistry of curious biological phenomena

Chair, Symposium organizer: Masaki Kita, Hirokazu Arimoto
 9:00 AM - 11:40 AM B204 (Online Meeting)

[B204-1am-01] Search for the therapeutic seeds for infectious diseases from microbial secondary metabolites
 ○Masato Iwatsuki¹ (1. Kitasato University)

9:10 AM - 9:35 AM

[B204-1am-02] Toward making unique bioactive molecules
 ○Kenichiro Itami¹ (1. Nagoya University)

9:35 AM - 10:05 AM

[B204-1am-03] Key compounds for cell death regulation
 ○Mikiko Sodeoka¹ (1. RIKEN)

10:05 AM - 10:35 AM

[B204-1am-04] Membrane-active key natural products interacting with lipid layers
 ○MICHIO MURATA MURATA¹ (1. Osaka University)

10:35 AM - 11:05 AM

[B204-1am-05] Challenge of mysteries of Manatabi reaction of cats, a classic but still fascinating issue of natural product chemistry
 ○Toshio Nishikawa¹ (1. Nagoya University)

11:05 AM - 11:35 AM

B202

Symposium | Medium and Long-Term Program | Tasks and prospects for social implementation of artificial photosynthesis technologies

[B202-1am] Tasks and prospects for social implementation of artificial photosynthesis technologies

Chair, Symposium organizer: Ryu Abe, Akihiko Kudo, Hiroaki Misawa

9:00 AM - 11:40 AM B202 (Online Meeting)

[B202-1am-01] Established output of Artificial photo synthesis project granted by NEDO and perspective view for its industrialization
 ○Tohru Setoyama¹ (1. Mitsubishi Chemical Corporation)

9:05 AM - 10:05 AM

[B202-1am-02] Hydrogen and selective production of valuable chemicals for economical artificial photosynthesis
 ○Kazuhiro Sayama¹ (1. National Institute of Advanced Industrial Science and Technology (AIST))

10:10 AM - 10:40 AM

[B202-1am-03] Development of energy supply to houses by artificial photosynthesis technology
 ○Yutaka Amao¹ (1. Osaka City University)

10:40 AM - 11:10 AM

[B202-1am-04] Recent progress in Solar-driven CO₂ Reduction Reaction Systems Utilizing Molecular Catalysts and Semiconductors
 ○Takeshi Morikawa¹ (1. Toyota Central R&D Labs., Inc.)

11:10 AM - 11:40 AM

Symposium | Medium and Long-Term Program | Frontier of new paradigm of molecular systems chemistry – Design and measurement of concerted molecular functions

[B202-1pm] Frontier of new paradigm of molecular systems chemistry – Design and measurement of concerted molecular functions

Chair, Symposium organizer: Kunihiro Ishii, Shun-Ichi Ishiuchi
1:00 PM - 3:40 PM B202 (Online Meeting)

[B202-1pm-01] Chem-Bio Hybrid, a Chemically Engineered Enzyme Encapsulated in a Molecular Cage

○Daishi Fujita¹ (1. Kyoto University)
1:05 PM - 1:30 PM

[B202-1pm-02] Structures and functions of supramolecules investigated by cold gas-phase spectroscopy

○Satoru Muramatsu¹ (1. Hiroshima Univ.)
1:30 PM - 1:55 PM

[B202-1pm-03] Signal-Amplification Sensing with Functional Chemosensors

○Gaku Fukuhara¹ (1. Tokyo Institute of Technology)
1:55 PM - 2:20 PM

[B202-1pm-04] Efficient and robust photoreaction regulated by multiple molecules in pigment protein complexes

○Toru Kondo¹ (1. Tokyo Tech.)
2:20 PM - 2:45 PM

[B202-1pm-05] Toward rational control of concerted functions exerted by protein complexes

○Takahiro Kosugi^{1,2,3,4} (1. Institute for Molecular Science, 2. ExCELLS, 3. SOKENDAI, 4. JST PRESTO)
2:45 PM - 3:10 PM

[B202-1pm-06] Coordination of 5,000 cells produces swimming and phototactic behavior in the multicellular green alga Volvox

○Noriko Ueki¹ (1. Hosei University)
3:10 PM - 3:35 PM

W1

Symposium | Asian International Symposium | International Symposium on Molecular Science - Physical Chemistry / Theoretical Chemistry, Chemoinformatics, Computational Chemistry - Cosponsored by Japan Society for Molecular Science

[W1-1am] International Symposium on Molecular

Science - Physical Chemistry / Theoretical Chemistry, Chemoinformatics, Computational Chemistry - Cosponsored by Japan Society for Molecular Science

Chair, Symposium organizer: Yasuhiro Ohshima, Miho Hatanaka, Akiyoshi Hishikawa

9:00 AM - 11:40 AM W1 (Online Meeting)

[W1-1am-01] Light-induced dynamics of molecules probed by an ultrafast stopwatch

○Jian Wu¹ (1. East China Normal University)
9:05 AM - 9:40 AM

[W1-1am-02] Air lasing by population inversion in N₂⁺ induced by strong-field coherent coupling of the X, A and B states

○Erik Loetstedt¹, Youyuan Zhang¹, Toshiaki Ando¹, Atsushi Iwasaki¹, Huailiang Xu², Kaoru Yamanouchi¹ (1. The University of Tokyo, 2. Jilin University)
9:40 AM - 10:00 AM

[W1-1am-03] Simulations of strong laser-driven multielectron dynamics using classical and quantum computers

○Takeshi Sato¹ (1. The Univ. of Tokyo)
10:00 AM - 10:20 AM

[W1-1am-04] Putting the ‘Chemistry’ back in to Chemical Vapour Deposition Nanomaterial Synthesis: Insight from Quantum Simulations

○Alister Page¹ (1. University of Newcastle)
10:25 AM - 11:00 AM

[W1-1am-05] Ionic Liquid Kinetics on Polarizable Electrode Surface

○Taichi Inagaki¹ (1. Keio University)
11:00 AM - 11:20 AM

[W1-1am-06] Multi-Scale Theoretical/Computational Approach to Heterogeneous Catalysis

○Atsushi Ishikawa¹ (1. National Institute for Materials Science)
11:20 AM - 11:40 AM

Symposium | Asian International Symposium | International Symposium on Molecular Science - Physical Chemistry / Theoretical Chemistry, Chemoinformatics, Computational Chemistry - Cosponsored by Japan Society for Molecular Science

[W1-1pm] International Symposium on Molecular Science - Physical Chemistry / Theoretical Chemistry, Chemoinformatics, Computational

Chemistry - Cosponsored by Japan
Society for Molecular Science

Chair, Symposium organizer: Satoshi Takahashi, Yasuteru Shigeta
1:00 PM - 3:40 PM W1 (Online Meeting)

[W1-1pm-01] Computer-aided drug design and screening
of potential compounds to combat COVID-
19

○THANYADA RUNGROTMONKOL¹, Bodee
Nutho², Panupong Mahalapbutr³, Kamonpan
Sanachai¹, Supot Hannongbua¹, Kittikhun
Wangkanont¹, Supakarn Chamni¹, Warinthorn
Chavasiri¹, Tuanjai Somboon¹, Siwaporn
Boonyasuppayakorn¹, Wanchai De-eknamkul¹,
Tanatorn Khotavivattana¹ (1. Chulalongkorn
University, 2. Mahidol University, 3. Khon Kaen
University)

1:00 PM - 1:35 PM

[W1-1pm-02] Theoretical study of copper-catalyzed atom
transfer radical addition reactions

○Megumi Kayanuma¹ (1. AIST)

1:35 PM - 1:55 PM

[W1-1pm-03] Role of dynamics in conformational
transitions and functions of biomolecules

○Toshifumi Mori¹ (1. Kyushu Univ.)

1:55 PM - 2:15 PM

[W1-1pm-04] Liquid-liquid phase separation in the tales
of intrinsically disordered proteins

○Jie-rong Huang¹ (1. Institute of Biochemistry
and Molecular Biology, National Yang Ming Chiao
Tung University, Taiwan)

2:20 PM - 2:55 PM

[W1-1pm-05] The Stickers-and-Spacers Framework for
Describing Biomolecular Phase Separation

○Jeong-Mo Choi¹ (1. Pusan National
University)

2:55 PM - 3:15 PM

[W1-1pm-06] Label-free observation of liquid-liquid phase
separation in vitro and in a living cell using
Raman microscopy

○Shinji Kajimoto^{1,2} (1. Tohoku University, 2. JST
PRESTO)

3:15 PM - 3:35 PM

Symposium | Asian International Symposium | International Symposium on
Molecular Science - Physical Chemistry / Theoretical Chemistry,
Chemoinformatics, Computational Chemistry - Cosponsored by Japan
Society for Molecular Science

[W1-1vn] International Symposium on Molecular
Science - Physical Chemistry / Theoretical
Chemistry, Chemoinformatics,
Computational Chemistry - Cosponsored
by Japan Society for Molecular Science

Chair, Symposium organizer: Tatsuya Ishiyama, Akiyoshi
Hishikawa

4:10 PM - 5:30 PM W1 (Online Meeting)

[W1-1vn-01] Ion transport in concentrated aqueous
electrolytes for Li-ion batteries

○Jonggu Jeon¹ (1. Institute for Basic Science)

4:10 PM - 4:45 PM

[W1-1vn-02] Theoretical Investigation of Dielectric
Constant at Monolayer Interfaces by
Polarizable Molecular Dynamics Simulation

○Lin Wang^{1,2} (1. Department of Chemistry,
Tohoku Univ., 2. ESICB, Kyoto Univ.)

4:45 PM - 5:05 PM

[W1-1vn-03] Understanding Charge-Transfer Reactions by
Constrained Density Functional Theory

○Tatsuya Joutsuka^{1,2} (1. Ibaraki University, 2.

Frontier Research Center for Applied Atomic
Sciences)

5:05 PM - 5:25 PM

W2

Symposium | Asian International Symposium | Asian International
Symposium - Coordination Chemistry and Organometallic Chemistry -

[W2-1am] Asian International Symposium -
Coordination Chemistry and
Organometallic Chemistry -

Chair, Symposium organizer: Hisako Hashimoto, Teppei Yamada,
Takahiko Kojima, Ryotaro Matsuda, Aiko Fukazawa, Shigeyuki
Masaoka, Yoshiaki Nishibayashi, Hisashi Shimakoshi

9:00 AM - 11:40 AM W2 (Online Meeting)

[W2-1am-01] Stimuli-Responsive Porous Crystals

○Hiroshi Sato¹ (1. RIKEN)

9:05 AM - 9:25 AM

[W2-1am-02] Ion-Conductive Porous Crystals

○Masaaki Sadakiyo¹ (1. Tokyo Univ. Sci.)

9:25 AM - 9:45 AM

[W2-1am-03] Electrically Conductive Metal-Organic
Frameworks

○Sarah Sunah Park¹ (1. Pohang University of
Science and Technology (POSTECH))

9:45 AM - 10:15 AM

[W2-1am-04] Photocatalysis Utilizing Photoinduced
Electron Transfer Coupled Phase Migration
○Akinobu Nakada^{1,2} (1. Chuo University, 2.
PRESTO/JST)
10:30 AM - 10:50 AM

[W2-1am-05] Organorhodate and -Iridate — Structure and
Reactivity—
○Takanori Iwasaki¹ (1. Grad. Sch. of Eng., The
University of Tokyo)
10:50 AM - 11:10 AM

[W2-1am-06] Recent Advance in the Chemistry of Low-
Coordinate Low-Valent Transition-Metal
Complexes
○Liang Deng¹ (1. Shanghai Insitute of Organic
Chemistry, CAS)
11:10 AM - 11:40 AM

B103

Symposium | Special Program | Photo and electric functions of low
dimensional material

[B103-1am] Photo and electric functions of low
dimensional material

Chair, Symposium organizer: Takuya Fujimura, Yasutaka Suzuki
9:00 AM - 11:40 AM B103 (Online Meeting)

[B103-1am-01] Stabilizing and aligning Aqua-Fe
Complexes for Replaceing TiO₂
Nanoparticles
○Yusuke Ide¹ (1. National Institute for
Materials Science)
9:05 AM - 9:28 AM

[B103-1am-02] Magnetic Property of Heterostructured
Nanosheets Film
○Takashi Yamamoto¹ (1. Keio Univ.)
9:28 AM - 9:51 AM

[B103-1am-03] Self-Repairing Electrocatalysts for Alkaline
Water Electrolysis Using Hybrid Metal
Hydroxides
○Yoshiyuki Kuroda¹ (1. Yokohama National
University)
9:51 AM - 10:14 AM

[B103-1am-04] Enhanced Photochemical Reactions on
Low-dimensional Materials
○Tatsuto Yui¹ (1. Niigata University)
10:26 AM - 10:49 AM

[B103-1am-05] Structural colors of inorganic nanosheets
○Nobuyoshi Miyamoto¹ (1. Fukuoka Institute

of Technology)

10:49 AM - 11:12 AM

[B103-1am-06] Speculation of formation pathway of
zeolite using ESI-MS and NMR
○Nao Tsunoji¹ (1. Hiroshima University)
11:12 AM - 11:35 AM

B203

Symposium | Special Program | Chemistry for Mobility Batteries

[B203-1am] Chemistry for Mobility Batteries
Chair, Symposium organizer: Nobuyuki Imanishi
9:00 AM - 11:40 AM B203 (Online Meeting)

[B203-1am-01] Innovative Batteries for Sustainable
Mobility
○Hideki Iba¹ (1. Toyota Motor Corporation)
9:05 AM - 9:30 AM

[B203-1am-02] Development of all-solid-state batteries
with inorganic amorphous materials
○Akitoshi Hayashi¹ (1. Osaka Prefecture
University)
9:30 AM - 9:55 AM

[B203-1am-03] New developments in solid electrolytes
for all-solid-state battery applications
○Ryoji Kanno¹ (1. Tokyo Institute of
Technology)
9:55 AM - 10:20 AM

[B203-1am-04] Challenges and Perspective in Developing
Fuel Cell Materials for Vehicles
○Kensaku Kodama¹, Seiji Sano², Shintaro
Tanaka³ (1. Toyota Central R&D Labs., Inc. , 2.
Toyota Motor Corporation, 3. Honda R&D
Co.,Ltd.)
10:20 AM - 10:45 AM

[B203-1am-05] Progress of research on perfluorinated
electrolyte polymer for fuel cells
○satoru hommura¹ (1. AGC Inc.)
10:45 AM - 11:10 AM

[B203-1am-06] Current Status and Issues of
Electrocatalysts for Polymer Electrolyte
Fuel Cells
○Hiroyuki UCHIDA¹ (1. University of
Yamanashi)
11:10 AM - 11:35 AM

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[B302-1am-01] 21st Century Literacy required in the age of Digital Transformation

○Noriko Arai¹ (1. National Institute of Informatics)

9:10 AM - 10:10 AM

[B302-1am-02] The future of DX organic synthesis

○Takashi Ohshima¹ (1. Kyushu University)

10:20 AM - 10:50 AM

[B302-1am-03] Frontier of Catalyst Informatics

○Takashi Toyao^{1,2} (1. Hokkaido University, 2. Kyoto University)

11:00 AM - 11:30 AM

DX 時代の教育に求められること

(国立情報学研究所¹, 一般社団法人教育のための科学研究所²) ○新井紀子
(National Institute of Informatics¹, Institute of Science for Education²) ○Noriko Arai

Keywords : Reading Skill, 21st Century Literacy, Artificial Intelligence

人類の歴史は、技術革新とそれに伴う社会変化の連続と見做すことができる。文字の発明は時空を超えた正確な情報伝達を可能にしたし、蒸気機関の発明は人々を重労働から解放した一方で、機械の下で単純労働に従事する労働と、高賃金だが教育投資を必要とする知的労働に分断した。1960年代に実用化されたコンピュータは、「半導体回路の集積密度は1年半~2年で2倍となる」とするムーアの経験則に従って処理速度を伸ばしてきた。それに伴い、アナログな形式で共有されていた情報のデジタル化が進んだ。21世紀に入ると、膨大なデジタルデータを「人間を真似て」処理する統計的なデータ処理の技術(人工知能技術)が発達した。その適用範囲は、それまで極めて知的で専門的スキルを要すると考えられてきた分野(翻訳、画像診断、新しい化学物質の発見等)に及ぶ。また、一定のプロトコルの下で、コンピュータ同士が情報を共有、自動処理するデジタルトランスフォーメーション(DX)が進むことで、帳票処理や会計処理などホワイトカラーが担ってきた仕事の機械代替が進んでいる。このような技術革新を背景として、どのような能力を備えた人材を育成すべきなのかについては、「(AIが労働を担うのだから)アートなどよりクリエイティブな教育を進めるべき」「むしろAIに教育を支援させるべき」など百家争鳴の状況にある。

我々の研究グループでは、「ロボットは東大に入れるか」(2011年~2020年)というAIプロジェクトを通じ、現状のAI技術でも有名私大を含む大半の大学は入学可能なレベルにあることを実証した上で、そのエラー解析から「少ないデータから、常識と論理をもって正確に文章を読解すること」や「統計的外れ値にあるサンプルではAIは想定外の誤った判断をすること」等を示した。一方で、AI同様に短文を正確に読解することや、誤ったヒューリスティックを使わずに論理的に判断することを、人間も苦手としていることを、我々が開発した「リーディングスキルテスト」を受検した2万5千人の中高校生のデータから明らかにした。

リーディングスキルテスト(RST)は、①係り受け解析、②照応解決、③同義文判定、④推論、⑤イメージ同定、⑥具体例同定、の6つの観点から、教科書・新聞・辞書など事実について書かれた200字程度の短文を正確に読み解く力を問う診断テストで、小学5年生から社会人まで受検できるように設計されている。図1, 2はそれぞれ係り受け解析、具体例同定の問題例である。問題は項目応答理論に基づき受検者の学年や能力に合わせて出題され、6つの観点と総合評価で能力値が診断結果としてフィードバックされる。これまで20万人以上がRSTを受検し、そこから次のような結果が得られた。

- (1) 6つの観点のどれについても小学生から中学3年生まで平均能力値が向上する。
ただし、高校1年生以上では平均能力値は向上していない。
- (2) 6つの観点のどれについても学年内分散が極めて大きい。
- (3) 中学3年生のRSTの平均能力値と全国学力状況調査(学テ)点数の間には、国語・理科・数学のいずれにおいても0.6以上の正の相関がある。
- (3) 高校1年生では、RSTの平均能力値と入学した高校の偏差値の間には0.8以上の正の相関がある。

このことからRSTで測れるような事実について書かれた短文を正確に読解する力は、義務教育時代に自然に向上しながら格差が広がり、その能力で入学し得る高校の偏差値がほぼ決定され、その後は少なくとも現状の教育では能力が向上せず、格差が固定化していることが示唆される。

以下の文を読みなさい。

アミラーゼという酵素はグルコースがつながってできたデンプンを分解するが、同じグルコースからできていても、形が違うセルロースは分解できない。

この文脈において、以下の文中の空欄にあてはまる最も適当なものを選択肢のうちから1つ選びなさい。

セルロースは()と形が違う。

- ☐ デンプン ☐ アミラーゼ
☐ グルコース ☐ 酵素

図1. 係り受け解析問題例

以下の文を読みなさい。

2で割り切れる整数を偶数という。そうでない整数を奇数という。

偶数をすべて選びなさい。

- ☐ 8
☐ 110
☐ 65
☐ 0

図2. 具体例同定問題例

DX 有機合成の拓く未来

(九大院薬¹) ○大嶋 孝志¹

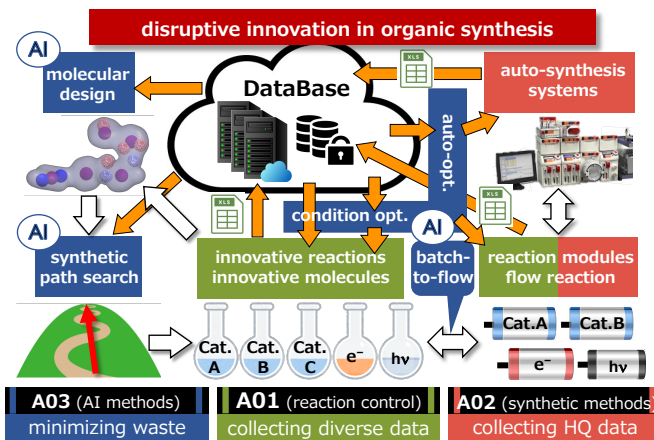
The future of DX organic synthesis (¹Graduate School of Pharmaceutical Sciences, Kyushu University)○Takashi Ohshima¹

Grant-in-Aid for Transformative Research Areas (A) “Digitalization-driven Transformative Organic Synthesis” was launched. This Research Area aims to build our own digitization platform (PF) for digital organic synthesis (interdisciplinary fusion of experimental and information science) that leads to disruptive innovation in organic synthesis. Three Research Groups A01 (deepening reaction control with AI support), A02 (deepening synthetic methods with AI support), and A03 (deepening AI methods to support organic synthesis) will work together to conduct this research. We will develop three automated systems for (1) reaction conditions optimization, (2) synthetic pathway search, and (3) molecular design of highly complex molecules to demonstrate their effectiveness in discovering innovative basic reactions. We will also demonstrate the industrial utility of this PF by (4) developing batch-to-flow conversion methods, (5) constructing automated synthesis systems, and (6) applying it in multi-step molecular conversion reactions.

Keywords : Digi-TOS; Artificial Intelligence; Machine Learning; Flow Reaction; Auto-Synthesis

有機合成 (実験科学) とデータサイエンス (情報科学) の異分野融合によって、有機合成に破壊的イノベーションを起こすことを目的とする、学術変革領域研究 (A) 「デジタル有機合成」が2021年9月に発足しました。本領域は、A01 班 (AI 支援による反応制御の深化)、A02 班 (AI 支援による合成手法の深化)、A03 班 (有機合成を支援する AI 手法

の深化) の3班体制で、①反応条件最適化、②合成経路探索、③高次複雑系分子設計の3つの自動化システムを開発し、革新的な基礎反応の発掘や開発効率の超加速化を実証するとともに、④バッチ→フロー変換法の開発、⑤自動合成システムを構築し、⑥多段階分子変換反応に展開することで産業的実用性を示すことを計画しています。本講演では、本領域研究の概要と研究計画、半年間の活動内容、そして将来的に目指しているものなどを紹介したいと思います。



キャタリストインフォマティクスの最前線

(北大触媒研¹・京大触媒電池²) ○鳥屋尾 隆^{1,2}

Frontier of Catalyst Informatics

(¹*Institute for Catalysis, Hokkaido University*, ²*ESICB, Kyoto University*) Takashi Toyao,^{1,2}

Recent revolutions made in data science could have a great impact on traditional catalysis research in both industry and academia and could accelerate the development of catalysts. Machine learning (ML), a subfield of data science, can play a central role in this paradigm shift away from the use of traditional approaches. In this talk, recent progress that has been made in utilizing ML to create homogeneous and heterogeneous catalysts will be presented. The focus of the talk is on the design, synthesis, and characterization of catalytic materials/compounds as well as their applications to catalyzed processes.

Keywords : *Catalyst informatics, Catalyst, Machine learning*

触媒研究者は膨大な文献情報を統合して作業仮説をたてるが、触媒関連情報は膨大で多岐にわたるため、実験を行わずに仮説構築・触媒特性予測をすることは困難である。最近、理論・実験材料科学とデータ科学の融合領域が注目されているが、固体触媒のような複合的・化学的現象への展開は萌芽的段階にあり、他の材料分野に遅れをとっている。¹⁻⁵ 本発表では、触媒化学とデータ科学の境界領域研究に関する現状を我々の取り組み⁶⁻¹⁰とともに紹介する。

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Symposium | Co-Innovation Program (CIP) | Informatics for every chemist: Fundamentals of machine/deep learning for predictive data analytics

[B302-1pm] Informatics for every chemist: Fundamentals of machine/deep learning for predictive data analytics

Chair, Symposium organizer: Hironobu Iyama, Hikaru Takaya, Kazuhiko Sato, Kazuhiro Matsumoto

Wed. Mar 23, 2022 1:00 PM - 3:40 PM B302 (Online Meeting)

[B302-1pm-01] Statistical machine learning for inverse problems in materials research

○Ryo Yoshida Yoshida¹ (1. The Institute of Statistical Mathematics)

1:00 PM - 2:00 PM

[B302-1pm-02] Fundamentals of molecular descriptors in materials informatics

○Yoshihiro Hayashi¹ (1. The Institute of Statistical Mathematics)

2:10 PM - 2:40 PM

[B302-1pm-03] How can synthetic chemists perform Artificial Intelligence in synthetic chemistry?

○Akira Yada¹ (1. National Institute of Advanced Industrial Science and Technology (AIST))

2:50 PM - 3:20 PM

材料研究における逆問題と統計的機械学習

(情報・システム研究機構 統計数理研究所¹・物質・材料研究機構²) ○吉田 亮^{1,2}
Statistical Machine Learning for Inverse Problems in Materials Research (¹*The Institute of Statistical Mathematics, Research Organization of Information and Systems*, ²*National Institute for Materials Science*) ○Ryo Yoshida^{1,2}

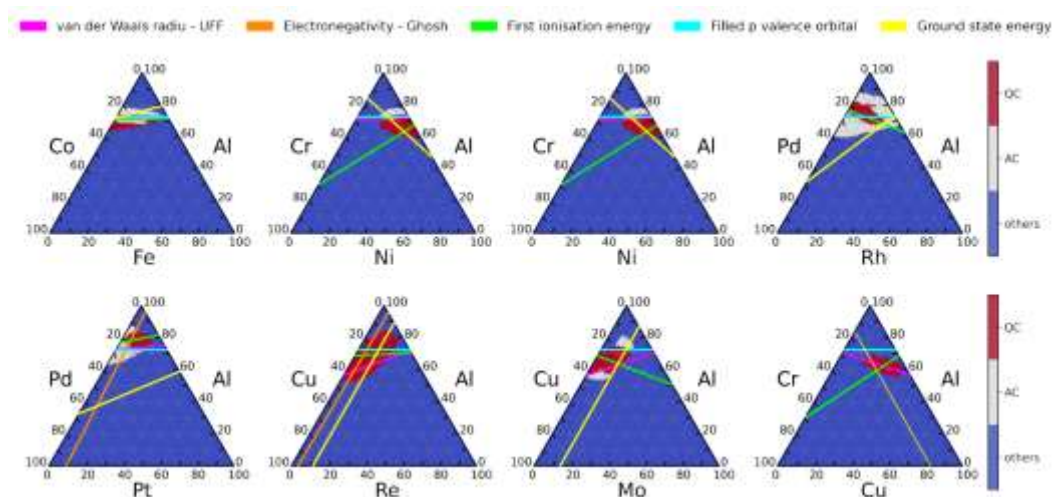
Data-driven science is advancing rapidly and transform the world around us. As such, machine learning has received considerable attention as a key driver to the next frontier of materials science, enabling us to reap substantial time and cost savings in the discovery and development of innovative materials. The objective of designing materials is to identify a set of design variables that exhibits desired properties. Here, we conduct a two-stage workflow that consists of forward and backward predictions. The objective of the forward problem is to predict the properties of any given design variable. The task of the inverse problem is to identify promising design candidates that exhibit desired properties by solving the inverse mapping of the forward model. This talk describes a basic concept and key technologies of machine learning for the inverse materials design, such as, probabilistic inference using generative machine learning models, explainable machine learning, and adaptive design of experiments. Without going into technical details, the essence of these machine learning techniques is illustrated with various applications taken from polymer design [1, 2, 3], computational design of synthetic reaction routes [4], prediction and discovery of new quasicrystals [5], integration of computational chemistry and machine learning based on adaptive design of experiments, transition learning [6, 7, 8, 9], microstructure prediction for composite materials using deep generative models [10]. In particular, I discuss use cases and strategies for obtaining human-interpretable knowledge from black-box models of machine learning.

Keywords :Materials Informatics; Inverse Design; Explainable Machine Learning; Ammonium Iodide

マテリアルズインフォマティクスの問題の多くは、順問題と逆問題の形式に帰着する。順問題の目的は、系の入力に対する出力の予測である。物性探索の文脈では、入力物質（分子、組成、結晶等）、出力は物性に相当する。これに対し、逆問題では、出力の目標値を設定した上で、それを達成する入力の状態を予測する。データ科学の観点において、これらの計算は、物質・材料の“表現・学習・生成”というタスクに相当する。記述子と呼ばれる特徴ベクトルを用いて物質の構造を“表現”し、データのパターンから構造から物性の数値的写像を“学習”する。さらに、計算で所望の物性値を有する物質を“生成”し、有望な候補物質や設計パラメータを炙り出す。対象となる入力は、分子、組成、結晶、混合物、プロセス、合成経路など、問題に応じて多様な形式をとりうる。本講演では、物質・材料の表現・学習・生成というコンセプトに基づいてマテリアルズインフォマティクスの諸問題と要素技術を概説する。特に、様々な適用例（ポリマー設計[1, 2, 3]、機械学習による合成経路探索[4]、機械学習による新しい準結晶の予測と発見[5]、適応的実験計画に基づく計算化学と機械学習の融合、転

移学習[6,7,8,9], 深層生成モデルによる複合材料の微細組織の予測と設計[10]など ※時間の制約上, 一部を抜粋) を紹介しながら, 順問題と逆問題, 表現と生成, 転移学習, 内挿と外挿などの話題を取り上げる. 特に、機械学習のブラックボックスモデルから人間が解釈可能な知識を得るための戦略を議論する.

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機械学習による準結晶の組成予測 (三元系相図). 逆問題を解くことで, 機械学習のブラックボックスモデルに内在する入出力のルールを抽出し, 熱力学的に安定な準結晶相の形成する五つのルール法則を明らかにした. 発見されたルールは, 人間が解釈可能な五つの数式で表現される.

マテリアルズインフォマティクスにおける分子記述子の基礎

(統計数理研究所 ものづくりデータ科学研究センター) ○林 慶浩
Fundamentals of molecular descriptors in materials informatics (*Data Science Center for Creative Design and Manufacturing, Institute of Statistical Mathematics*) ○ Yoshihiro Hayashi

This talk presents an outline of molecular descriptors used in the field of materials informatics. Molecular descriptors are numerical vectors that represent the characteristics of a molecule based on its chemical structure and physicochemical properties. Representative molecular descriptors are explained in an overview of their algorithms, features, and points to note when using them.

Predefined fingerprints quantify the pattern of chemical structures based on the presence/absence or frequency of predefined fragments. Some of the most famous examples are MACCS Keys [1]. While intuitive for chemists, if the defined fragment set is redundant for the target group of compounds, it results in a sparse vector representation where most elements are zero.

Enumerative fingerprints, such as Extended Connectivity Fingerprint (ECFP) [2], are a descriptor that solves this problem. ECFP counts all substructures up to the N-th proximity atoms. In ECFP, all substructures up to the N-th proximity atoms are counted, so that the fragment set is defined according to the input compound group. In addition, the atomic features are propagated to neighboring atoms during the counting process, resulting in a condensed representation of the local environment of the atoms.

In machine learning using these descriptors, features are first created, and then machine learning is applied using the features as input. On the other hand, in recent years, an approach to predict physical properties using graph-based neural networks such as Graph Convolutional neural network (GCNN), which considers chemical structures as graphs and uses the graph data as input for machine learning, has been developed [3,4]. In GCNN, a vector representation of the local environment of an atom is created by repeatedly performing convolution operations on nearby nodes (atoms) in the input graph, as shown in Figure 1. The weights for this convolution are estimated from the data. The output layer is then constructed through a neural network. In other words, the process of creating a vector of descriptors in conventional approaches is replaced by a neural network with an architecture that reflects the graph structure of the molecule, enabling learning of physical properties from chemical structures.

Detailed description will be presented in the talk on the day.

Keywords : *Materials Informatics; Molecular Descriptor; Machine Learning*

本講演では、マテリアルズインフォマティクス(MI)の分野で用いられる分子記述子について概説する。分子記述子は、その分子の特徴を化学構造や物理化学的性質に基づく数値ベクトルとして表現したものである。いくつかの代表的な分子記述子について、アルゴリズムの概要やそれぞれの特徴、使用時の注意点などを解説する。

事前定義型のフィンガープリントは、あらかじめ定義されたフラグメントの有無や頻度に基づき化学構造のパターンを数値化する。有名なものとして、MACCS Keys [1]

などがある。化学者にとって直感的である一方で、定義されたフラグメント集合が解析対象の化合物群に対して冗長な場合、ほとんどの要素が0である疎なベクトル表現となる。

この問題を解決する記述子として、ECFP (Extended Connectivity Fingerprint) [2] を代表とする、列挙型のフィンガープリントが挙げられる。ECFP では第 N 近接までの全ての部分構造を数え上げる。このため、入力された化合物群に応じてフラグメント集合が定義される。また、数え上げの際に、原子特徴量を隣接原子へ伝播させることで、原子の局所的な環境を縮約した表現となる。

これらの記述子を用いた機械学習では、まず特徴量を作り、その後それを入力とした機械学習を適用する。一方で、近年では化学構造をグラフと捉えて、このグラフデータをそのまま機械学習の入力とする、GCNN (Graph Convolutional neural network) といったグラフ系ニューラルネットワークを用いて物性を予測するアプローチが開発されている[3,4]。GCNN では、Figure 1 に示したように入力されたグラフ上で近いノード (原子) に対する畳み込み演算を繰り返し行うことで、原子の局所的な環境のベクトル表現とする。この畳み込みの重みはデータから推定される。その後ニューラルネットワークを通して出力層を構築する。つまり、既存アプローチにおける記述子というベクトルを作る過程を、分子のグラフ構造を反映したアーキテクチャを持つニューラルネットワークに置き換えることで、化学構造から物性の学習を可能とする。

詳細な解説は当日の講演で発表する。

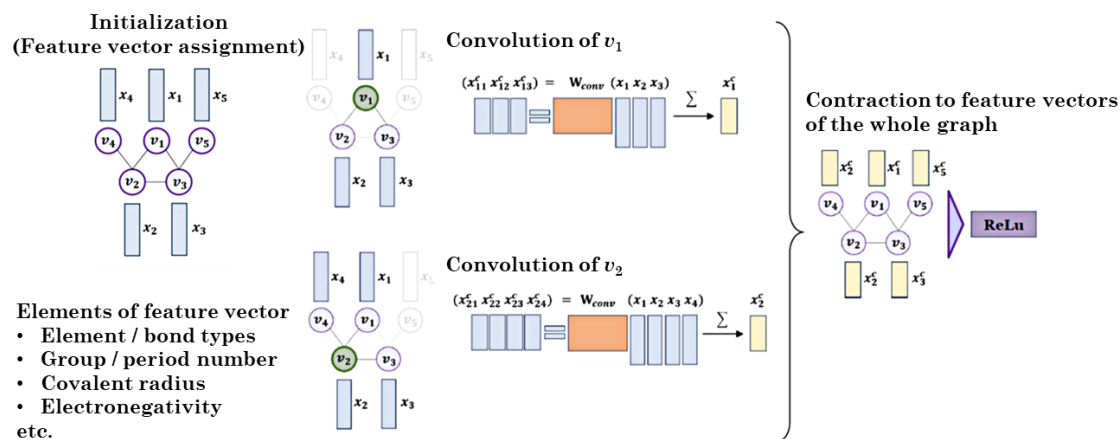


Figure 1. Computation of convolutional layer of graph neural network.

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合成化学者が合成化学に AI を活用するためには？

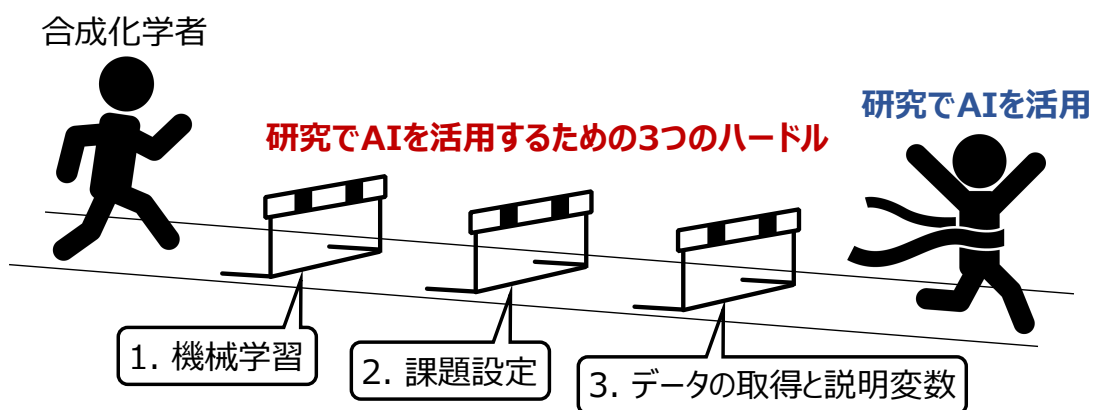
(産総研 触媒化学融合研究セ) ○矢田 陽

How can synthetic chemists perform Artificial Intelligence in synthetic chemistry? (Interdisciplinary Research Center for Catalytic Chemistry (IRC3), National Institute of Advanced Industrial Science and Technology (AIST))○Akira Yada

Considering the future of synthetic chemistry, the use of artificial intelligence (AI) technologies such as machine learning in synthetic chemistry research is becoming essential. However, many researchers still have questions about using AI in their chemistry, how many hurdles there are, and how big they are to introducing AI in the first step. This lecture will present what is necessary for synthetic chemists to utilize AI technologies for their research based on the speaker's experience.

Keywords : Machine learning; Artificial intelligence; Organic synthesis; Catalyst; Chemist

合成化学の将来を考えた時、合成化学研究に機械学習等の人工知能(AI)技術を活用することは必要不可欠となりつつある。しかし、どのように研究に活用すれば良いのか、そもそも AI 導入にどれくらいのハードルがありそれを乗り越えるのがどれくらい困難なのか、などの疑問を持っている研究者が未だに多い。講演者は、合成化学者が AI 技術を活用していく上で 3 つの超えるべきハードルがあると考えている。1 つ目は機械学習のハードル、2 つ目は課題設定のハードル、3 つ目はデータの取得と説明変数である。本講演では、これら 3 つのハードルを超えて合成化学者が自らの研究に機械学習等の AI 技術を活用していくために必要なことについて、講演者の体験に基づいて紹介する¹⁻²⁾。



1) Machine Learning Approach for Prediction of Reaction Yield with Simulated Catalyst Parameters, A. Yada, K. Nagata, Y. Ando, T. Matsumura, S. Ichinoseki, K. Sato, *Chem. Lett.* **2018**, 47, 284.

2) Ensemble Learning Approach with LASSO for Predicting Catalytic Reaction Rates, A. Yada, T. Matsumura, Y. Ando, K. Nagata, S. Ichinoseki, K. Sato, *Synlett* **2021**, 32, 1843.

Symposium | Co-Innovation Program (CIP) | Innovative rechargeable battery toward realizing carbon neutrality

[B301-1am] Innovative rechargeable battery toward realizing carbon neutrality

Chair, Symposium organizer: Nagatoshi Koumura, Eiji Hosono, Masashi Okubo, Keigo Hoshina

Wed. Mar 23, 2022 9:00 AM - 11:10 AM B301 (Online Meeting)

[B301-1am-01] Electrolyte design to suppress hydrogen evolution

○Seongjae Seongjae Ko¹, Atsuo Yamada¹ (1. The Univ. of Tokyo)

9:10 AM - 9:40 AM

[B301-1am-02] The properties of the zinc secondary batteries using the organic/inorganic hybrid separator

○Satoshi Ogawa¹, Mitsuzo Nogami¹ (1. NIPPON SHOKUBAI Co., LTD.)

9:40 AM - 10:10 AM

[B301-1am-03] Vertically aligned nanosheet electrodes for fast charge storage

○Wataru Sugimoto¹ (1. Shinshu University)

10:10 AM - 10:40 AM

[B301-1am-04] Development of the next-generation capacitors for future society

○Shuichi Ishimoto¹ (1. Nippon Chemi-Con Corp.)

10:40 AM - 11:10 AM

水素発生を抑制する水系電解液の設計

(東大院工¹) ○高 晟齊¹・山田 淳夫¹

Electrolyte design to suppress hydrogen evolution (¹*Department of Chemical System Engineering, The University of Tokyo*) ○Seongjae Ko,¹ Atsuo Yamada¹

As an ultra-safe energy storage system, aqueous electrolyte-based batteries have been developed over the past decades. However, the reductive decomposition of electrolyte (hydrogen evolution reaction) has hampered the utilization of low-potential anode materials, which is essential to increase the energy density of batteries. In this presentation, the thermodynamic and kinetic mechanisms to suppress the hydrogen evolution reaction will be discussed based on the salt concentration, liquid structure, cation, and anion dependency of the electrolyte.

Keywords : Aqueous electrolytes; Aqueous batteries; Hydrate melt; Concentrated electrolytes

水を電解液の溶媒として用いる水系二次イオン電池は、火災・爆発の危険性が極めて低く安価であることから、過去 30 年間活発に研究されてきた¹⁾。しかし、純水の熱力学的電位窓は 1.23 V しかないため、3.7 V 程度の作動電圧を示す市販電池に比べ低エネルギー密度であることが問題となっていた²⁾。当研究室ではこの問題を解決するため、極端に高い塩濃度により個々の水分子を孤立させた新たなカテゴリーのイオン伝導性液体「常温熔融水和物 (ハイドレートメルト)」を開発し、高度な安全性と高エネルギー密度化の両立が可能なシステムの構築に挑んできた。この常温熔融水和物が熱力学的・速度論的に高い酸化・還元耐性を有していることに注目し、3V 級の水系二次イン電池を実現した。

常温熔融水和物の開発において、対アニオン種を選択が重要である。高溶解性、高可塑性、高表面保護被膜(SEI)形成能を持ちながらも、加水分解しにくいアニオン(CF₃SO₃⁻ (OTf), N(SO₂F)₂⁻ (FSI), N(SO₂CF₃)₂⁻ (TFSI), N(SO₂C₂F₅)₂⁻ (BETI))に加え、末端

基に非対称性をもたせることで高い振動自由度と低格子エネルギーにより、より高塩濃度化を可能にするアニオン((SO₂CF₃)(SO₂C₂F₅) (PTFSI), (SO₂CF₃)(SO₂C₃F₇) (HTFSI))を活用しつつ、共晶組成を探索することで、新規な常温熔融水和物群の開発に成功した(図1)³⁾。

ラマン分光測定とDFT-MD計算により、これら常温熔融水和物においては、ほぼ全ての水分子がキャリアイオン(Li⁺, Na⁺, K⁺)に電子供与し

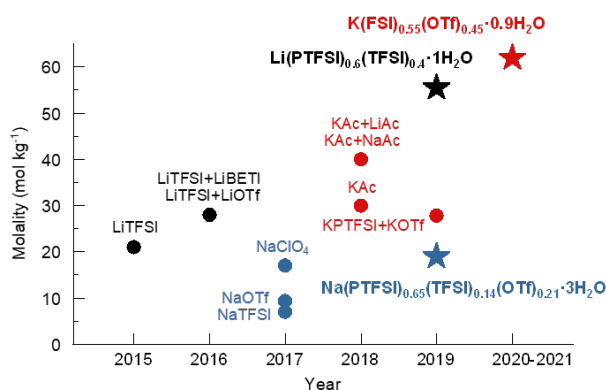


図 1. 常温熔融水和物の位置づけ。対アニオン種の戦略的選択によって超高塩濃度化に成功した。

ながら配位していることにより、水分子間の水素結合ネットワークが切断され、フリーな水分子(クラスター)が存在しない独特な溶液構造を持っていることが明らかになった。

種々の電極における電解液の酸化・還元安定性を Linear sweep voltammetry (LSV)を用い調べた結果、従来の低濃度(1.0 mol L⁻¹)水溶液より 1 V 以上広い電位窓を示した(図 2)。特に、Li 系常温熔融水和物においては、非水系電解液に匹敵する還元耐性を示し、水系電解液中では一切報告例のない Al 電極の Li 合金化・脱合金化反応を初めて観察することに成功した。

一方、電位窓はキャリアイオン依存性を示す。これは、SEI 形成とその維持能に大きなキャリアイオン依存性があることを示唆する。一定電位で還元され、電極表面に塩由来 SEI を形成するものの、イミド塩の還元分解生成物が水に溶けやすい、あるいは、水と反応しやすいことにより SEI の機能性が低下することが知られている⁴⁾。例えば、代表的な還元生成物である LiF の水への溶解度は KF より数百倍低い。また、キャリアイオンのルイス酸性が強いほどキャリアイオンが水分子とより強く配位し、水分子をより効率的に孤立させる。従って、Li 系熔融水和物においては、SEI 形成とその維持に有利な環境が形成されることにより、SEI による水の還元反応(水素発生)が大きく抑制され、非水系電解液に匹敵する高い還元耐性を示すと考えられる。

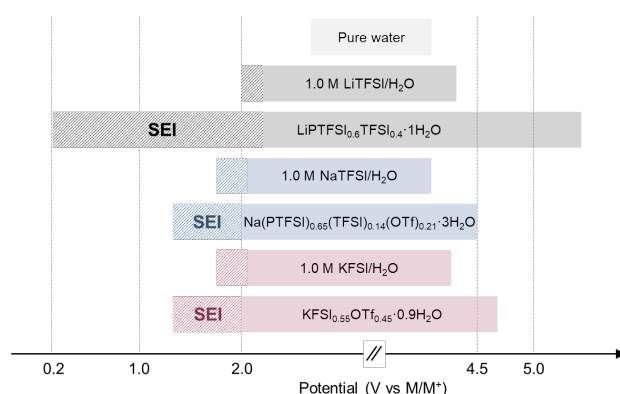


図 2. 常温熔融水和物によって 1 V 以上拡張された電位窓。常温熔融水和物の電位窓はカチオン依存性を示す。

本講演においては、「水分子の孤立」と「高機能性表面保護被膜(SEI)形成」を同時に実現するための熱力学的・速度論的要因を考慮した材料設計指針をより詳細に議論する。

- 1) W. Li et al., *Science*, 264, 5162, 1115-1118 (1994)
L. Suo et al., *Science*, 350, 6263, 938-943 (2015)
- 2) Y. Yamada et al., *Nat. Energy*, 1, 16129 (2016)
- 3) Y. Yamada et al., *Nat. Energy*, 1, 16129 (2016), Q. Zheng et al., *Angew. Chem. Int.*, 58, 1-7 (2019)
S. Ko et al., *Electrochem. Commun.*, 104, 106488 (2019)
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- 4) L. Suo et al., *J. Am. Chem. Soc.*, 139, 51, 18670-18680 (2017)
S. Ko et al., *ACS Appl. Mater. Interfaces*, 11, 49, 45554-45560 (2019)
R. Bouchal et al., *Angew. Chem. Int.*, 132, 16047-16051 (2020)

有機/無機複合セパレータを用いた亜鉛二次電池の諸特性

((株)日本触媒¹⁾ ○小川 賢¹・野上 光造¹

The development of the zinc secondary battery using the organic/inorganic hybrid separator
(¹NIPPON SHOKUBAI CO., LTD. ○Satoshi Ogawa,¹ Mitsuzo Nogami,¹

The problem of dendrite growth remains unresolved in secondary zinc batteries. In order to improve the cycle life of zinc-secondary batteries, we developed an organic/inorganic composite separator that exhibits an inhibitory effect on short circuits caused by zinc dendrite growth. This separator is designed to have a sufficient ionic conductivity as well as suppression properties for preventing a short circuit. To obtain these performances, inorganic particles and hydrophobic particles are utilized which provide no extra space and no extra electrolyte for dendrite growth. Additionally, this material exhibits a good ionic conductivity. It was also confirmed that the separator we developed provided the carbon-zinc hybrid capacitor with a long life. It was also found that the carbon-zinc hybrid capacitor systems are preferable for evaluating the cyclability of separators used for zinc secondary batteries because the system has a good reproducibility. Consequently, the cycle life using the organic/inorganic composite separator was more than 10 times longer than that of conventional microporous membranes.

Keywords : Zinc Battery, Dendrite, Separator, Hybrid Capacitor

リチウムイオン電池を中心に生活の様々な場面で蓄電池が用いられる中で、SDGs 目標の達成への機運から鉛蓄電池など従来型の蓄電池に対しても代替が求められるようになってきた。限定された用途でリチウムイオン電池に代替される検討が進んでいるものの、安全性確保の観点から煩雑な制御回路を付加しなければならず、従来の蓄電池とできるだけ近い形で入れ替えられる新規な水系蓄電池が求められている。

そのような背景の中、亜鉛を用いた二次電池開発が注目されている。亜鉛は、資源的に豊富であり、電気化学的な利用が簡便なためマンガン乾電池など一次電池負極として一般的に用いられてきた。従って、亜鉛を用いた電池を充電可能にすることができれば、既存のシステムとの整合性が高く、かつ資源や安全面において SDGs 要求を十分に満たせることが期待できる。

しかしながら、亜鉛の充電利用には課題があった。それは充電生成される亜鉛が、初期の形状には戻らず、対極へ向けて樹状析出してしまうことである。これによって、電池内部で短絡を引き起こしやすく、電池材料として古くから使われつつも、放電だけに特化した一次電池利用に留まっていたのである。

我々はそのような課題に対し、有機/無機ハイブリッド構造を利用した新規セパレータを開発し、電池の内部短絡を抑制できることを見出した。講演では、このセパレータを用いて検討した様々な亜鉛蓄電池に関する検討と、そこで見出したカーボン亜鉛ハイブリッド電池について紹介したい。

1) S. Ogawa, Y. Takazawa, H. Harada, M. Nogami, *Electrochemistry*. 2022, IN PRESS

高速電荷蓄積を目指したナノシートの配向制御

(信州大繊維¹・信州大先鋭材料研究所²) 杉本 渉^{1,2}

Vertically Aligned Nanosheet Electrodes for Fast Charge Storage (¹*Faculty of Textile Science and Engineering, Shinshu University*, ²*Research Initiative for Supra-Materials, Shinshu University*) Wataru Sugimoto^{1,2}

Nanosheet materials are promising electrode materials for various applications where high surface area is a determinant factor, for example electrochemical supercapacitors. However, the high aspect ratio of nanosheets may be disadvantageous in terms of mass transfer. Synthesis of porous nanosheet electrodes is thus vital to achieve high capacity at high rates. Vertical alignment of nanosheets can provide the necessary high surface area and the rapid diffusion of ions. A simple and scalable method to synthesize vertically aligned graphene and TiO₂ nanosheet electrodes will be presented and its high-rate performance as electrode materials for electrochemical energy storage will be briefly described.

Keywords : Nanosheet; Vertical alignment; Supercapacitors; Li-ion batteries; Porous electrodes

剥離ナノシートコロイドからナノシート薄膜電極を成膜する方法としては、キャストやスピンコート法、ラングミュアプロジェクト法、交互積層法、電気泳動堆積法などがよく用いられる。いずれの成膜法でも支持体である基板に対してナノシートは平行に堆積するため、膜厚方向に対する物質移動はナノシートのアスペクト比に依存する。そのため、膜内の物質移動が実際の膜厚の数百～数千倍も長くなることもある。小型化ナノシートや穴あきナノシートの利用や、ナノシート間にピラーを導入するなど物質移動を促進する試みもなされている。我々は、ナノシートの積層形態を制御することで、物質移動を促進できなかいかと考え、ナノシートを垂直に配向させる手法を開発し、電極反応の高速化に成功した¹。

負に帯電したナノシートを含むコロイドに直流電場を印加すると、ナノシートは正極に電気泳動堆積される^{2,3}。この泳動堆積膜を風乾するとナノシートが基板に対して平行に堆積したナノシート膜が得られる。膜厚はコロイド濃度、泳動時間や電場により制御可能である、配向性を高い厚膜電極を成膜するのに適している。一方で、泳動浴から取り出しそのまま乾燥させるのではなく、凍結乾燥するとナノシートが基板に対して垂直に堆積した垂直配向ナノシート膜が得られる。ナノシートは電場に対して平行に泳動され、電極上に析出するので、凍結乾燥することで、ナノシートが基板に対して垂直配向を維持した膜が得られる。凍結時に形成された氷晶がテンプレートとなり、細孔を形成する。氷晶の大きさは凍結速度で決まり、細孔は数十 μm から数百 μm の範囲で制御できる。

例として、Fig. 1 に垂直配向酸化グラフェン電極の断面像を示す。酸化グラフェンナノシートコロイドを泳動浴とし、凍結乾燥後することで垂直配向酸化グラフェンナノシート電極が得られ、続いて水素還元し、還元型酸化グラフェンに変換する。こ

のような垂直配向膜を用いると拡散距離が膜厚と同程度になるため、高速電荷蓄積が可能になる。垂直配向ナノシートと水平配向ナノシートを比較すると、高走査速度での比静電容量維持率が圧倒的に高い。

Figure 2 に垂直配向グラフェンと水平配向グラフェン電極を用いて電気二重層キャパシタとしての蓄電能の性能を比較している。サイクリックボルタンメトリーの電位掃引速度が速い場合でも垂直配向ナノシート電極は低掃引速度での比静電容量と比べてあまり変化せず、急速な電荷蓄積が可能であることを示している。

なお、この成膜法は酸化グラフェンに限らず、コロイドナノシートであれば適用可能であり、例えば垂直配向 TiO_2 ナノシートにも適用でき、乾燥プロセスの制御により、水平配向、ランダム配向、垂直配向の $\text{TiO}_2(\text{B})$ 電極を創り分けることができる⁴。

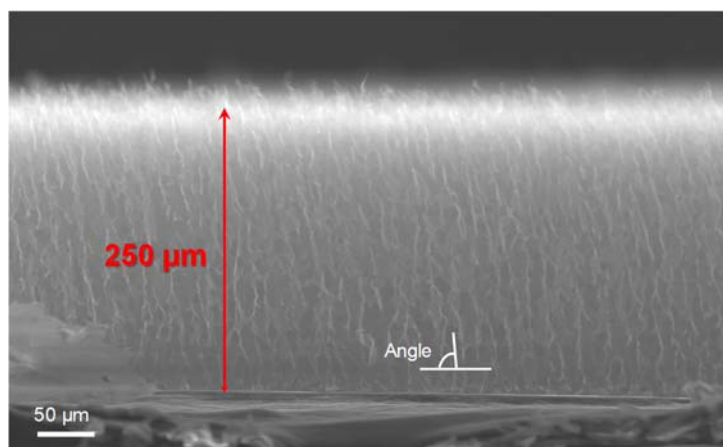


Figure 1. SEM image of graphene oxide film obtained by electrophoretic deposition and freeze-drying.

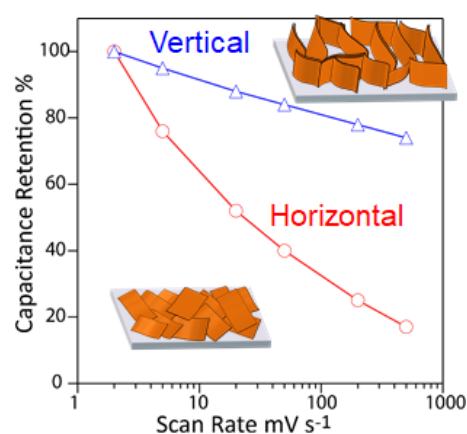


Figure 2. Retention of specific capacitance as a function of the scan rate of vertically and horizontally aligned reduced graphene oxide electrodes in 0.5 M H_2SO_4 .

- 1) D. Mochizuki, R. Tanaka, S. Makino, Y. Ayato and W. Sugimoto, *ACS Appl. Energy Mater.*, **2**(2), 1033 (2019).
- 2) W. Sugimoto, O. Terabayashi, Y. Murakami and Y. Takasu, *J. Mater. Chem.*, **12**, 3814 (2002).
- 3) W. Sugimoto, K. Yokoshima, K. Ohuchi, Y. Murakami and Y. Takasu, *J. Electrochem. Soc.*, **153**, A255 (2006).
- 4) T. Yoshida, D. Takimoto, D. Mochizuki and W. Sugimoto, *Electrochemistry*, **88**(4), 305 (2020).

未来社会に向けた次世代キャパシタの開発

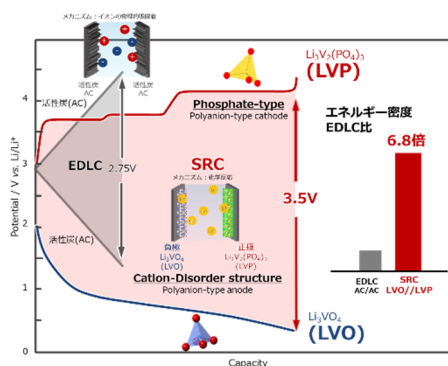
(日本ケミコン) 石本修一

Development of Next Generation Capacitors for Future Society (¹Basic Research Center, Nippon Chemi-Con Corp.) ○Shuichi Ishimoto,¹

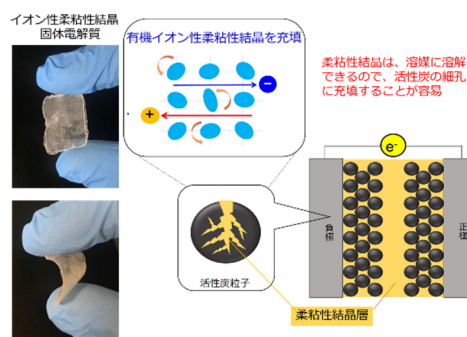
In order to achieve a sustainable and well-being future society, the energy storage devices should play an increasingly important role. Supercapacitors are one of the energy storage devices, which have excellent characteristics in terms of output performance and stability. They currently have been used in the applications such as current peak assistance and energy regeneration for construction equipment and automotive. As the next markets of supercapacitors in the future society, efficient renewable energy storage and power sources for IoT sensor nodes are especially expected because supercapacitors possess desirable characteristics in their applications. So, we have been working on development of next generation capacitors to meet their applications. In this presentation, we will introduce two types of our next generation capacitors, called Super Redox Capacitor with high energy density and Solid-State Supercapacitor with superior reliability, and discuss the future markets of supercapacitors.

Keywords : Energy Storage Device; Supercapacitor; High Power Density; Carbon-Neutral

豊かで持続可能な未来社会を実現するために、蓄電デバイスの役割は、近年ますます重要となってきた。蓄電デバイスの中で、スーパーキャパシタは、電池と比べて、出力性能や安定性の点で優れた特徴を持った蓄電デバイスであり、これまでに電流ピークアシストやエネルギー回生の用途において活用されてきた。これからのカーボンニュートラルや情報社会といった未来社会においてもスーパーキャパシタの活用される分野は広がっていくことが期待されている。特に再生可能エネルギーの蓄電やIoTにおけるセンシングノードの電源としての活用は、スーパーキャパシタの特徴に合った使い方であり、このようなアプリケーションに適用できるような次世代キャパシタの開発が求められている。本講演では、このような未来社会の用途に向けて当社で取り組んでいる2種類の次世代キャパシタである高エネルギー密度スーパーレドックスキャパシタと高信頼性固体型電気二重層キャパシタを紹介するとともに、未来社会でのキャパシタの可能性について議論する。



スーパーレドックスキャパシタ(SRC)



固体型電気二重層キャパシタ

Symposium | Co-Innovation Program (CIP) | Innovative rechargeable battery toward realizing carbon neutrality

[B301-1pm] Innovative rechargeable battery toward realizing carbon neutrality

Chair, Symposium organizer: Nagatoshi Koumura, Eiji Hosono, Masashi Okubo, Keigo Hoshina

Wed. Mar 23, 2022 1:00 PM - 2:50 PM B301 (Online Meeting)

[B301-1pm-01] Interfacial Ion Dynamics for Advanced All Solid State Batteries

○Yasutoshi Iriyama¹ (1. Nagoya Univ.)

1:00 PM - 1:50 PM

[B301-1pm-02] Development of Argyrodite Type Sulfide Solid Electrolytes and Materials for All-Solid-State Batteries.

○Tsukasa Takahashi¹, Yuki Nakayama¹, Daisuke Inoue¹ (1. Mitsui Mining & Smelting Co., Ltd.)

1:50 PM - 2:20 PM

[B301-1pm-03] Materials design of solid ionic conductors toward the next-generation solid-state batteries

○Saneyuki Ohno¹ (1. Kyushu University)

2:20 PM - 2:50 PM

全固体電池の高性能化に向けた界面イオンダイナミクス

(名大院工) ○入山 恭寿

Interfacial Ion Dynamics for Advanced All Solid State Batteries

(¹Graduate School of Engineering, Nagoya University) ○Yasutoshi Iriyama

All-solid-state rechargeable lithium batteries (SSBs) have expected as a candidate for next-generation batteries. Formation of low-resistive electrode-solid electrolyte interface and its stabilization within wide operating voltages are indispensable to improve the battery performance. In this presentation, our research works in addition to recent research topics in “Interface IONCS” focusing on interface of SSBs will be introduced.

Keywords : all solid state battery, interface

カーボンニュートラルの実現に貢献する次世代蓄電池の一つとして、全固体リチウム二次電池 (SSB) が注目されている。最近ではバルク型 SSB を搭載した電気自動車が発行ナンバープレートをつけて走行し、積層セラミックコンデンサのプロセス技術を活用した積層型 SSB も開発されるなど、実用化の取り組みが加速している。SSB の更なる高性能化には、コア材料となる電極活物質の高容量化と高イオン伝導固体電解質の開発とともに、界面でのイオン移動抵抗の低減とその安定化が必要である。

全固体電池の高エネルギー密度化にむけて高容量な Li 金属負極の利用が期待されている。一方、固体電解質上で Li 金属の析出溶解を高電流密度で行う、あるいは析出溶解厚みを増やすと固体電解質が短絡するという問題点がある。この短絡要因には化学的・電氣的・機械的要因などの諸説があるが、LLZ の場合には Li 析出溶解に伴う界面での空隙形成とその後の電流集中が短絡トリガーになっていると考えられる。この空隙形成を緩和する手法として、演者らは LLZ 上で起こる Li 金属の析出・溶解反応が表面洗浄や高温 (~100 °C) での充放電反応が有効であることを見出している。25 °C での Li 析出溶解反応の安定化には依然課題が多いが、固体電解質の比表面積を増やして電流密度を低減し課題克服を目指す取り組みもある。

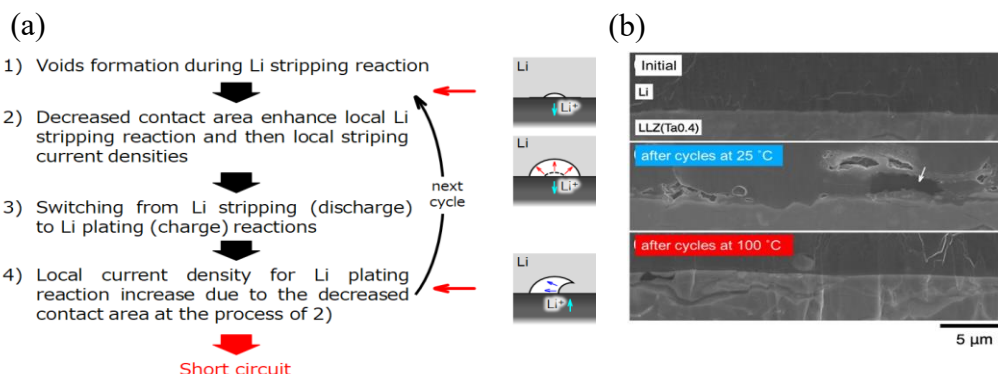


Fig. 1 (a) A plausible short-circuit process of LLZ. (b) Cross-sectional SEM image of Li/LLZ interface of pristine (top) and after Li plating-stripping reactions at 25 °C (middle) and 100 °C (bottom).

高エネルギー密度化に向けて、電池の作動電圧の向上も期待される。その際、固体電解質の電位窓と界面で起こる不定比性、空間電荷層形成の様相を明らかにすることは重要である。従来、固体電解質の電位窓は例えば CV を用いた電気化学的な評価を元に見積もられてきた。一方、計算科学による熱力学的安定性の観点からは、実験から予想される値より電位窓がかなり狭い可能性が指摘されている。この熱力学的安定性は分解生成物の生成を想定して見積もられているが、分解生成物の生成とは別に、準安定的な Li 組成変化が固体電解質の酸化還元を通じて生じるという指摘もある。実験的には、固体電解質の界面近傍で Li 濃度変化が生じることが EELS や ERD 法等を用いて確認されている。また、酸化還元とは異なり、空間電荷層が形成される材料が存在することも報告されており、用いる固体電解質の種類と電位に応じて界面の様相は変化すると考えられる。

硫化物系固体電解質は高いイオン伝導率を備えるとともに成形性にも優れ、加圧することで動作可能な SSB が構築できる。この硫化物系 SSB は車載用 SSB の第一世代に位置づけられているが、その次の候補の一つに酸化物系 SSB が挙げられている。酸化物系固体電解質のイオン伝導率は硫化物系に比べて現状では低い。また、一般に硬い材料であるため、硫化物系のように加圧するのみで動作する電池を構築することが難しい。従って、電池の大型化にも資する界面接合プロセスの開発も重要な課題である。更にその次の世代には、全固体フッ化物イオン二次電池などの革新型電池の開発も期待されている。新学術「蓄電固体界面科学」では、こうした“蓄電池の固体化”を支える界面イオンダイナミクスの基礎学理構築に向けた研究を進めている。領域で得られた成果のいくつかを当日の講演で紹介する。

謝辞

本発表の一部の内容は 19H05813、19H05814、19H05815、20H05288 新学術領域研究「蓄電固体界面科学」、JST ALCA-SPRING の助成を受けて行ないました。関係各位にお礼申し上げます。

アルジロダイト型硫化物固体電解質を中心とした全固体電池用材料開発

(三井金属鉱業株式会社) ○高橋 司・中山 祐輝・井上 大輔

Development of Argyrodite Sulfide Solid Electrolytes and Materials for All-Solid-State Batteries (MITSUI MINING & SMELTING CO. LTD.,) ○Tsukasa Takahashi, Yuki Nakayama, Daisuke Inoue

We have been developing argyrodite-type sulfide solid electrolytes. Argyrodite-type sulfide solid electrolytes have many excellent properties, such as high ionic conductivity, electrochemical stability, and formability, and are expected to be the main electrolytes for next-generation all-solid-state batteries. This solid electrolyte is a crystalline solid electrolyte with a cubic argyrodite-type crystal structure. We have developed a high-performance electrolyte by optimizing the composition, crystal structure and powder properties.

In this presentation, we will discuss argyrodite type sulfide solid electrolytes. In this talk, I will explain the characteristics and potential of all-solid-state batteries using data from a prototype all-solid-state battery.

Keywords : All-Solid-State Battery; Solid Electrolyte; Sulfide; Argyrodite

地球温暖化抑制の観点から、世界的にカーボンニュートラルへ向けた活動が行われている。EV、ESS といった蓄電デバイスの進化は重要なポイントであり、次世代蓄電池の候補として全固体電池が有望視されている。様々な全固体電池が検討されているが、硫化物系の全固体電池は、イオン伝導率、成形性等のメリットから実用化に最も近い電池系として期待され、一部は実用化段階を迎えている。

我々はこれまでアルジロダイト型硫化物固体電解質に着目して開発を行ってきた。アルジロダイト型硫化物固体電解質は、高イオン伝導性や電気化学的な安定性、高成形性など多くの優れた性能を有し、次世代全固体電池の主要電解質として注目されている。本固体電解質は結晶性の固体電解質であり、我々は組成、構造、粉体特性の最適化により実用可能なレベルで高性能な固体電解質を開発した。

本講演ではアルジロダイト型硫化物固体電解質について説明すると共に、実際に作成した全固体電池のデータから全固体電池の特徴と可能性について説明する。

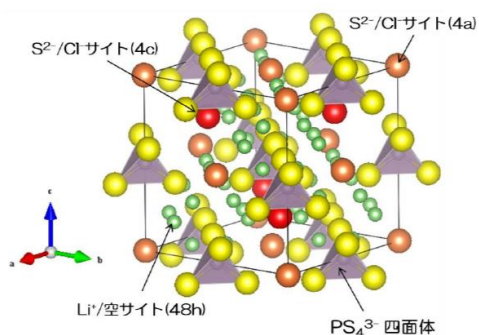


図 1. アルジロダイト型結晶構造

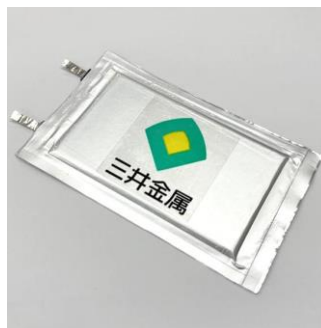


図 2. 全固体電池試作品

次世代固体電池へ向けたイオン伝導固体の設計と応用そして展望

(九大院工) ○大野 真之

Materials design of solid ionic conductors toward the next-generation solid-state batteries
(¹Graduate School of Engineering, Kyushu University) ○Saneyuki Ohno

Solid-state batteries are attracting attention as the next-generation energy storage devices that realize safety and high energy density. The first part of this talk will present the design strategies of ion-conducting inorganic solids.¹ As mobile ions travel through their lattice sites via a hopping conduction mechanism, any modification of the crystal structure of the material of interest greatly impacts the resulting ion transport.² In addition to this “static-lattice” effect, recent studies revealed that “lattice dynamics” contribute further changes in the ionic conductivity of inorganic superionic conductors. For instance, whereas the conventional oxides have high electrochemical stability, more polarizable sulfides tend to possess faster ion transport. Followed by a brief overview of materials design, challenges and perspectives of their applications toward the next-generation solid-state batteries will be discussed with a particular emphasis on the current issues in composite cathodes with a substantially high interfacial area density.^{3,4}

Keywords : Solid-state batteries, Solid electrolytes, Structure-composition-transport relationship, Li-ion conducting sulfides, sulfur cathodes

高いエネルギー密度と安全性を持つ次世代蓄電デバイスとして注目される全固体電池だが、その実現と更なる向上へ取り組むべき課題は数多く存在する。本講演の前半では、その要となる固体電解質の性能向上への取り組みを、最新の研究成果を基に紹介する¹。ホッピング伝導機構に依拠する固体中のイオン伝導は、ごく僅かな結晶構造や組成の変化によりその値を大きく変える²。また、例えば“硬い”酸化物材料と比較して“柔らかな”硫化物固体電解質が高いイオン伝導度を保持するように、結晶構造の静的な変化のみならず、その“動的な”変化も構造中のイオン輸送に大きく影響を与えることも明らかになってきている。後半では、次々世代型大容量複合正極の全固体化へ向けた取り組みに焦点を当てる。複合化に伴う界面濃度の上昇により、電解質の界面での劣化が電池性能へ及ぼす影響が顕在化する³。今後固体電解質に求められる特性や乗り越えるべき障壁、そしてその展望を議論する⁴。

- (1) Ohno, S.; Banik, A.; Dewald, G. F.; Kraft, M. A.; Krauskopf, T.; Minafra, N.; Till, P.; Weiss, M.; Zeier, W. G. Materials Design of Ionic Conductors for Solid State Batteries. *Prog. Energy* **2020**, 2 (2), 022001.
- (2) Ohno, S.; Helm, B.; Fuchs, T.; Dewald, G.; Kraft, M. A.; Culver, S. P.; Senyshyn, A.; Zeier, W. G. Further Evidence for Energy Landscape Flattening in the Superionic Argyrodites $\text{Li}_{6+x}\text{P}_{1-x}\text{M}_x\text{S}_5\text{I}$ (M = Si, Ge, Sn). *Chem. Mater.* **2019**, 31 (13), 4936–4944.
- (3) Ohno, S.; Rosenbach, C.; Dewald, G. F.; Janek, J.; Zeier, W. G. Linking Solid Electrolyte Degradation to Charge Carrier Transport in the Thiophosphate-Based Composite Cathode toward Solid-State Lithium-Sulfur Batteries. *Adv. Funct. Mater.* **2021**, 31 (18), 2010620.
- (4) Ohno, S.; Zeier, W. G. Toward Practical Solid-State Lithium-Sulfur Batteries: Challenges and Perspectives. *Accounts Mater. Res.* **2021**, 2 (10), 869–880.

Symposium | Co-Innovation Program (CIP) | Smart chemistry for future medical and life science

[B303-1am] Smart chemistry for future medical and life science

Chair, Symposium organizer: Atsushi Sugasaki, Akira Chiba, Takeshi Nagasaki, Masaru Tanaka

Wed. Mar 23, 2022 9:00 AM - 11:40 AM B303 (Online Meeting)

[B303-1am-01] Decellularized/inactivated tissue in regenerative therapy: the way for clinical trials

○Tetsuji Yamaoka¹ (1. National Cerebral and Cardiovascular Center Research Institute)

9:05 AM - 9:55 AM

[B303-1am-02] Biomedical applications of hydrogel with precisely controlled structure

○Takamasa Sakai¹ (1. The Univ. of Tokyo)

9:55 AM - 10:25 AM

[B303-1am-03] Antithrombogenic polymer "SEC ONE SURFACE_{TM}" and its application on medical devices

○Yuta Kawakatsu¹, Koryu Den², Atsushi Iwai², Shohei Nakayama², Tomoya Ohashi³, Fumihiko Kajii³ (1. TOYOBO CO., LTD. Medical Equipment & Devices Department, 2. TOYOBO CO., LTD. Medical Equipment & Devices Development Center, 3. TOYOBO CO., LTD. Medical Equipment & Devices Production Center)

10:35 AM - 11:05 AM

[B303-1am-04] Research on skin irritation by high concentration ethanol and mitigating agents

○Masao Hara¹, Rina Hattori¹, Kei Sato¹, Shunsuke Sakurai¹, Misaki Ishida¹, Yumiko Yamawaki², Yuri Okano², Hitoshi Masaki² (1. NOF Corporation, 2. CIEL Corporation)

11:05 AM - 11:35 AM

脱細胞化/殺細胞化組織をスキャホールドとする再生医療の臨床化

(国循研究センター) 山岡 哲二

Decellularized/inactivated tissue in regenerative therapy: the way for clinical trials
(National Cerebral and Cardiovascular Center Research Institute) ○Tetsuji Yamaoka

Acellular biological scaffolds made of human or animal tissues have been attracting attentions as biological scaffolds in regenerative medicine. We have been studying high hydrostatic pressure (HHP) to treat cells and/or tissues. We decellularized or killed (inactivated) cells in the tissue at 1000 or 200MPa, respectively for the purpose of two major regenerative medicine applications. First, we have been developing ostrich carotid artery-derived acellular vascular grafts with very thin inner diameter of 2mm and length of 30cm and evaluated in large animals. Another application is to treat giant congenital melanocytic nevi (GCMN). GCMN is light brown to black patch or plaque that appears at birth which has the risk to result in malignant melanoma. We newly developed clinically-applicable HHP instrument, treated the GCMN tissue extracorporeally to kill the nevus cells, and assess if the treated skin tissue can be used as the autologous transplantable epidermal substitute.

Keywords : *High Pressure, Acellular Scaffold, Small-diameter Blood vessel, Nevus*

組織工学（再生医療）の一要素であるスキャホールドとして、動物や人の組織から細胞成分を除去して作製される脱細胞化組織が提案されている。生体吸収性合成高分子製スキャホールドと同様に生体吸収性であるが分解のメカニズムや速度は異なる。また、「細胞外マトリックスに類似しているからスキャホールドして優れている」というような表記も散見されるが、具体的な対象が特定されておらず曖昧で誤解を生じる表現なので望ましくない。スキャホールドとしての機能を特定して議論すべきである。我々は、一般的な界面活性剤による脱細胞化法では無く、超高静水圧処理を一過程とする脱細胞化異種脱細胞化法を採用し、この手法が組織の変化に与える影響検討するとともに、そのスキャホールドとしての真の機能を、できるだけ適応部位に近い *in vivo* 環境で評価してきた結果、国内外で開存報告が無い臨床的意義を有する内径 2mm の脱細胞化血管の開存化に成功したので報告する。さらに、高静水圧処理で細胞を確実に殺滅化させられる条件を見だし、この条件にもとづいて、腫瘍に対する新しい腫瘍治療法を確立した。すなわち、腫瘍組織を摘出して体外で加圧することで全ての細胞を殺滅（殺細胞化）し、その組織を自己由来殺細胞化スキャホールドとして患者に再移植するという新治療法の非臨床 POC を確立した。京都大学形成外科森本尚樹教授とともにその医師主導治験を開始したので報告する。

- 1) Tissue-engineered submillimeter-diameter vascular grafts for free flap survival in rat model. H. Yamanaka, T. Yamaoka, et al., *Biomaterials*, **2018**, 179 156-163
- 2) Complete cell killing by applying high hydrostatic pressure for acellular vascular graft preparation, A. Mahara, N. Morimoto, T. Sakuma, T. Fujisato, and T. Yamaoka, **2014**, *Biomed Res Int*, 379607
- 3) An Exploratory Clinical Trial of a Novel Treatment for Giant Congenital Melanocytic Nevi Combining Inactivated Autologous Nevus Tissue by High Hydrostatic Pressure and a Cultured Epidermal Autograft: Study Protocol. N. Morimoto et al, **2016**, *JMIR Res Protoc*, 5(3) e162

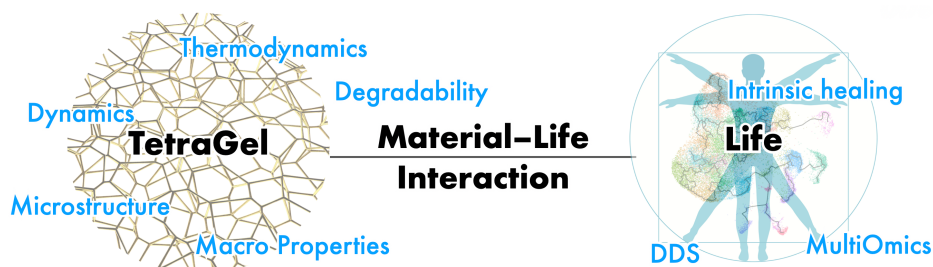
Biomedical applications of hydrogel with precisely controlled structure

(¹Graduate School of Engineering, University of Tokyo) ○Takamasa Sakai¹

Keywords: Hydrogels; Tetra-PEG gel; Elastic modulus; Osmotic pressure; Tendon fracture

Hydrogel is a material in which the polymeric network is swollen with a large amount of water. It is possible to exchange substances with the surrounding environment through the water. Because their composition and properties are similar to biological soft tissue, hydrogels are helpful as biomaterials. When used as biomaterials, hydrogels deteriorate in vivo due to various factors and dissolve with swelling. The swelling pressure of hydrogels is defined as the difference between the osmotic pressure that drives the swelling, and the elastic pressure that resists the swelling. Therefore, it is essential to understand and control the elastic and osmotic pressures of hydrogels.

The various physical properties of polymer gels were extrapolated from those of the single polymer chains, polymer solutions, and rubbers. However, our recent research has revealed that the existing theories cannot explain the elastic and osmotic pressures, which are elementary properties of polymer gels. In the presentation, we first discuss the elastic and osmotic pressures, and will introduce hydrogels for hemostat and anti-adhesion agent.

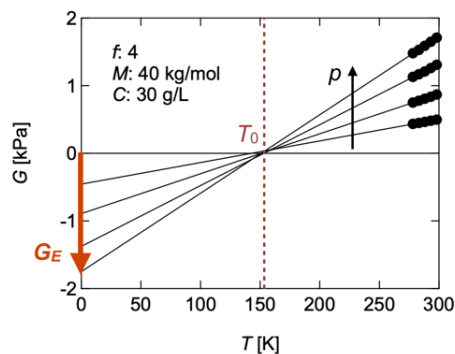


Elastic modulus of Polymer Gels [1]

Materials consisting of a polymeric network structure, such as rubbers and polymer gels, are soft and stretch well. The entropy force explains the elastic property based on the second law of thermodynamics. To confirm this experimentally, we can measure the shear modulus's (G) temperature dependence. Using the relation $G_S = T\partial G/\partial T$, we can separate G into $G = G_S + G_E$, the entropy contribution G_S and the energy contribution G_E . For rubber, experiments have confirmed that $G \approx G_S$ and theories describing rubber elasticity have been developed, focusing only on entropy elasticity (G_S).

On the other hand, the theory of rubber elasticity has been conventionally ($G \approx G_S$) used without any experimental verification for polymer gels, which are rubber swollen by solvents. However, our recent study revealed a non-negligible negative G_E in polymer gels (G -axis intercept of an extrapolated straight line in Fig. 1). This study investigated the physical laws governing the negative G_E using various samples with systematically modulated microscopic structural parameters (prepolymer binding ratio p , branching number f , molar mass M , and concentration C) to elucidate its origin.

We measured the T -dependence of G for all samples and found that the extrapolated line passes through a point (T_0) on the T -axis, independent of p (Figure 1). Thus, the elastic modulus can be written as $G = a(T - T_0)$, where the first and second terms represent the entropy contribution G_S and the energy contribution G_E , respectively. When the C^* specified by f and M was appropriately chosen and normalized, C -dependence of T_0 , which governs the energy elasticity, fell on one master curve. This suggests that T_0 is a universal function of C/C^* . Analysis of the C/C^* dependence of T_0 indicates that the physical origin of the energy elasticity is most likely the interaction of the polymer chain with the solvent.

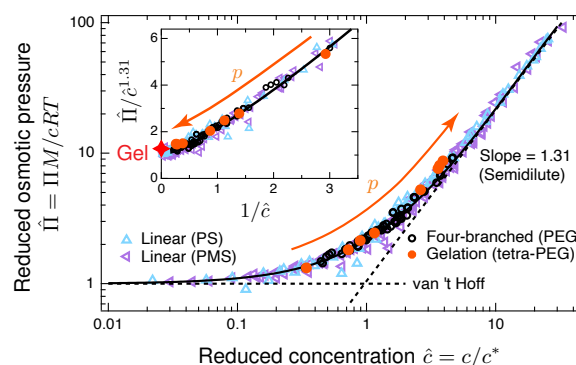


Osmotic Pressure of Polymer Gels [2]

A standard theory and experiments show that the osmotic pressure of a linear polymer solution in a good solvent is described by a universal equation of state $\hat{\Pi} = f(\hat{c})$ (solid black line in Fig. 2), independent of the length of the polymer chains and the type of solvent. Here, $\hat{c} = c/c^*$ is a dimensionless quantity in which the polymer concentration c is normalized by the overlapping concentration c^* , and $\hat{\Pi} = \Pi M/(cRT)$ is a dimensionless quantity in which the osmotic pressure Π is normalized by the molar mass M of the polymer, the gas constant R , and the absolute temperature T . In the semi-dilute region where polymer chains penetrate each other, the osmotic pressure approaches asymptotically to the scaling law:

$$\hat{\Pi} = f(\hat{c}) = K\hat{c}^{1/(3\nu-1)} \quad (\text{for } \hat{c} \gg 1) \quad (1)$$

, where $K \simeq 1.1$ and $\nu \simeq 0.588$ is the excluded volume index giving $1/(3\nu-1) = 1.31$. In this study, we measured the osmotic pressure during the gelation process, from the sol state to the gel state, as the end reaction of the polymer chain progresses. It was found that the osmotic pressure can be described by the universal equation of state (1) for linear polymer solutions, even though the polymers form large clusters and a polymer network as the end reaction progresses.



- 1) Y. Yoshikawa, N. Sakumichi, U. Chung, and T. Sakai, *Physical Review X* **2021**, 11, 11045.
- 2) T. Yasuda, N. Sakumichi, U. Chung, T. Sakai, *Physical Review Letters* **2020**, 125, 267801.

合成系コーティング材料「セックワン®」の医療機器への応用

(¹東洋紡株式会社 医療機器事業部、²東洋紡株式会社 医療機器開発センター、³東洋紡株式会社 医療機器製造センター) ○川勝 雄太¹、田 光龍²、岩井 敦史²、中山 翔平²、大橋智哉³、梶井 文彦³

Antithrombogenic polymer "SEC ONE SURFACE™" and its application on medical devices
(¹TOYOBO CO., LTD. Medical Equipment & Devices Department, ²TOYOBO CO., LTD. Medical Equipment & Devices Development Center, ³TOYOBO CO., LTD. Medical Equipment & Devices Production Center) ○Yuta Kawakatsu¹, Koryu Den², Atsushi Iwai², Shohei Nakayama², Tomoya Ohashi³, Fumihiko Kajii³

SEC ONE SURFACE™ is a terpolymer which has Hydrophilic, Hydrophobic and Water repellent groups and also colorless viscous liquid. The three units, Hydrophilic, Hydrophobic and Water repellent units on its side chains contribute not only to prevent foreign body recognitions when contact with blood but also its antithrombogenicities.

Platelet adhesion test and Blood clot formation test were conducted to confirm the antithrombogenicities on SEC ONE SURFACE™. As shown in Figure 1 as Platelet adhesion test, the platelet adhesion was suppressed on coated surface. Then, the blood clot formation was prevented on coated surface as presented in Figure 2 as blood clot formation test.

Keywords : Antithrombogenic; Hydrophilic; Hydrophobic; Water repellent

セックワン® は親水基、疎水性基、撥水性基からなる三元共重合体であって無色透明な粘性液体である。ポリマーの側鎖に「親水性」、「疎水性」、「撥水性」の3成分を有することにより、血液が異物に接触する際に発生する反応を抑制することができ、抗血栓性を発揮する。

セックワン®の抗血栓性を確認するため血小板粘着評価及び血液接触評価を実施した。血小板粘着評価において、図1のように材料表面における血小板の粘着が抑制された。また、血液接触評価において図2のように血栓形成が抑制された。



図1 血小板粘着評価結果

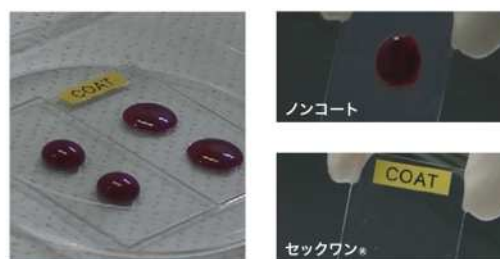


図2 血液接触評価結果

高濃度エタノールの皮膚刺激性とその緩和剤に関する研究

(日油株式会社¹・株式会社 CIEL²) ○原 真佐夫¹・服部 莉奈¹・佐藤 圭¹・櫻井 俊輔¹・石田 実咲¹・山脇 裕美子²・岡野 由利²・正木 仁²

Research on skin irritation by high concentration ethanol and mitigating agents (¹NOF Corporation, ²CIEL Corporation) ○Masao Hara,¹ Rina Hattori,¹ Kei Sato,¹ Shunsuke Sakurai,¹ Misaki Ishida,¹ Yumiko Yamawaki,² Yuri Okano,² Hitoshi Masaki²

The global COVID-19 infection has increased the opportunities for hand sanitizer with high concentration ethanol. Although the sanitizer is effective in inactivating the envelope virus, the frequent use cause a higher risk of skin irritation.

In order to estimate the irritating potential of high concentration ethanol on skin, we established an evaluation system using a secretion of proinflammatory cytokine in a reconstructed human epidermal model. In the presentation, we will report on the irritation caused by high concentration ethanol and the effects of mitigating agents using this evaluation system.

Keywords : high concentration ethanol; hand disinfection; hand sanitizer; skin protection; MPC polymer

COVID-19 の感染拡大により、エタノール製剤による手指消毒の頻度が増加している。該製剤は、エンベロープウイルス不活化には有効である。しかしながら、該製剤を頻回使用した場合は皮膚を刺激し、肌荒れを発症させる。

そこで、再生皮膚モデルの炎症性サイトカイン分泌を利用したエタノールの皮膚刺激性を予測するための評価系を確立した。発表では、本評価系を用いたエタノールの皮膚刺激性とその緩和剤の効果を報告する。

Symposium | Co-Innovation Program (CIP) | Smart chemistry for future medical and life science

[B303-1pm] Smart chemistry for future medical and life science

Chair, Symposium organizer: Atsushi Sugasaki, Akira Chiba, Takeshi Nagasaki, Masaru Tanaka

Wed. Mar 23, 2022 1:00 PM - 3:40 PM B303 (Online Meeting)

[B303-1pm-01] *Post-antibody drugs*: Generation of a novel class of drug modalities based on molecular-targeting helix-loop-helix (HLH) peptides

○Ikuro Fujii¹ (1. Osaka Prefecture University)

1:00 PM - 1:50 PM

[B303-1pm-02] Metabolism-Based Production of Cardiomyocytes from Human Pluripotent Stem Cells for Cardiac Regenerative Therapy

○Shugo Tohyama¹ (1. Keio University School of Medicine)

1:50 PM - 2:20 PM

[B303-1pm-03] Towards the industrialisation of regenerative medicine through cell fibre technology

○Hidetoshi Hoshiya¹ (1. CellFiber Co., Ltd.)

2:30 PM - 3:00 PM

[B303-1pm-04] Understanding In-body molecular communication networks for future medicine

○Tadashi Nakano¹ (1. Osaka City University)

3:00 PM - 3:30 PM

ポスト抗体医薬： Helix-loop-helix (HLH)を土台分子した新しい創薬モダリティー

(大阪府大院・理) ○藤井 郁雄

Post-antibody drugs: Generation of a novel class of drug modalities based on molecular-targeting helix-loop-helix (HLH) peptides

(Department of Biological Science, Graduate School of Science, Osaka Prefecture University)

○ Ikuo Fujii

Antibodies are indisputably the most successful reagents in molecular-targeting therapy. However, use of antibodies has been limited due to the biophysical properties and the cost to manufacture. To enable new applications where antibodies show some limitations, we have developed an alternative-binding molecule with non-immunoglobulin domain. The molecule is a helix-loop-helix (HLH) peptide, which is stable against enzyme degradations *in vivo* and is too small to show immunogenicity. Here, we introduce our HLH molecular-targeting peptides, termed “*microAntibodies*”, that show antibody-like functions, high affinity and high specificity for the targeted proteins.

Keywords : *Molecular-targeting Drug; Peptide; Directed Evolution; Drug Modality; Mid-size Molecule*

現在、タンパク質相互作用に対する分子標的ツールとして抗体が注目されており、また分子標的医薬品としても汎用されるようになってきている。しかし、抗体（抗体医薬）には、以下のような問題点が指摘されている。①細胞内の疾患関連タンパク質をターゲットとすることができない。②ヒト化等が必要である。③生産に膨大なコストを必要とする。その結果として薬剤治療費が高騰し社会問題になっている。これらの問題点は全て、抗体の基本構造に起因するものである。そこで、イムノグロブリン構造を利用せず、目的の標的タンパク質に対して特異的に結合する抗体様物質の開発研究が始まっている。演者らは、抗体様物質として、ヘリックス・ループ・ヘリックス (HLH) 構造をもつペプチドの開発を行っている。この分子標的 HLH ペプチドは、天然アミノ酸からなる比較的小さなペプチド（分子量：4,000）であるにもかかわらず s 抗体と同等の結合活性（ K_d : 数 nM 以下）と安定性（血清中半減期：14 日以上）を持ち、免疫システムに対して寛容であり抗原性を示さない。これらのことから、上記の抗体（抗体医薬）の問題点を一挙に解決し、抗体に代わる新しい分子標的物質として期待される。そこで、この分子標的 HLH ペプチドとそれに関わる基盤技術を開発し、新しい創薬モダリティーの確立を目指している。本講演では、作用メカニズムの異なる 3 つの分子標的 HLH ペプチド（1. 分子標的ペプチド, 2. 分子標的ペプチド-CPP 複合体, 3. 分子標的 HLH ペプチド-薬物複合体 PDC）について紹介し、分子標的 HLH ペプチドの設計およびその生物機能について議論する。

代謝機構に基づく心筋細胞の大量製造と再生医療への応用

(慶大医¹) 遠山 周吾¹

Metabolism-Based Production of Cardiomyocytes from Human iPSCs for Regenerative Therapy

(¹Keio University School of Medicine) Shugo Tohyama¹

Cardiac regenerative therapy using human induced pluripotent stem cells (hiPSCs) is a potentially promising strategy for patients with heart failure, but the inability to eliminate residual hiPSCs and generate a massive amount of purified hiPSC-derived cardiomyocytes (hiPSC-CMs) has been a barrier to realizing this potential.

We previously developed an innovative method for efficiently eliminating residual undifferentiated pluripotent stem cells (PSCs) and non-cardiac cells and producing a large number of highly purified cardiomyocytes based on metabolic profiles in hiPSCs and hiPSC-CMs (1-5). Moreover, we revealed that tryptophan supplementation promoted the proliferation of hiPSCs for large-scale culture (6).

We also developed an efficient transplantation system using pure hiPSC-CM spheroids (7-8). Transplanted pure hiPSC-CM spheroids also improved cardiac function in rat, pig, and monkey models (9). These technologies will facilitate the clinical application of purified hiPSC-CM spheroids-mediated regenerative therapy for heart failure patients.

Keywords : iPSCs; Cardiomyocytes; Regenerative Therapy; Metabolism; Heart Failure

ヒト iPS 細胞を用いた心臓再生医療は、心臓移植治療における極度のドナー不足を補う新たな治療法として注目を集めているが、分化後に未分化幹細胞が混入し腫瘍化を引き起こすリスクを抱えているため、安全性の高い心筋細胞を効率よく作製する手法の確立が求められていた。

そこで、我々はヒト iPS 細胞および分化心筋細胞における代謝プロファイルの差異を明らかにし、その性質を利用した革新的培養法を開発することにより、ヒト iPS 細胞から安価かつ簡便に心室筋細胞を大量選別する方法を確立することに成功した (1-5)。また、トリプトファン代謝を理解することで簡便にヒト iPS 細胞の増殖を促進させる培養環境を同定した (6)。

さらに、我々は移植後の生着率を高めるためにスフェロイド移植法を開発した (7-8)。非臨床試験において安全性および有効性を確認し (9)、現在は臨床グレードのヒト iPS 細胞を用いて心室筋細胞の大量作製を行っている。本シンポジウムでは臨床応用目前に迫ったヒト iPS 細胞を用いた心臓再生医療の現状を紹介したい。

1. **Tohyama S**, et al. Distinct Metabolic Flow Enable Large-Scale Purification of Mouse and Human Pluripotent Stem Cell-Derived Cardiomyocytes. **Cell Stem Cell** 12:127-137, 2013.
2. **Tohyama S**, et al. Glutamine Oxidation is Indispensable for Survival of Human Pluripotent Stem Cells. **Cell Metabolism** 23:663-674, 2016.
3. **Tohyama S†** & Fukuda K†. Safe and Effective Cardiac Regenerative Therapy with Human Induced Pluripotent Stem Cells. How Should We Prepare Pure Cardiac Myocytes? **Circulation Research** 120:1558-1560, 2017. (†Corresponding author)
4. **Tohyama S**, et al. Efficient Large-Scale 2D Culture System for Human Induced Pluripotent Stem Cells and Differentiated Cardiomyocytes. **Stem Cell Reports** 9:1406-1414, 2017.
5. Tanosaki S, **Tohyama S†**, et al. Fatty Acid Synthesis is Indispensable for Survival of Human Pluripotent Stem Cells. **iScience** 2020:23:101535. (†Corresponding author)
6. Someya S, **Tohyama S†**, et al. Tryptophan Metabolism Regulates Proliferative Capacity of Human Pluripotent Stem Cells. **iScience** 2021:24:102090. (†Corresponding author)
7. Hattori F, Chen H, **Tohyama S**, et al. Nongenetic method for purifying stem cell-derived cardiomyocytes. **Nature methods** 7: 61-66, 2010.
8. Tabei R*, Kawaguchi S, **Tohyama S**, et al. Development of a transplant injection device for optimal distribution and retention of human induced pluripotent stem cell-derived cardiomyocytes. **J Heart Lung Transplant**. 38:203-214, 2019.
9. Kawaguchi S, Soma Y, **Tohyama S**, et al. Intramyocardial Transplantation of Human iPS Cell-Derived Cardiac Spheroids Improves Cardiac Function in Heart Failure Animals. **J Am Coll Cardiol. Basic Trans Science** 2021:6:239-254.

細胞ファイバ技術による再生医療の産業化を目指して

星谷 英寿

Towards the industrialisation of regenerative medicine through cell fiber technology

CellFiber is a startup company that commercializes cell fiber technology developed in the Takeuchi Laboratory of the University of Tokyo. A cell fiber is a structure in which cells are encapsulated in a gel tube about the thickness of a hair. The cell fiber technology has the potential to rapidly manufacture high-quality regenerative medicine products in large quantities at low cost. Cell fiber technology can be used not only for cell proliferation and differentiation, but also for various processes such as recovery, storage, distribution, and transplantation. *Keywords: Regenerative medicine; Cell therapy; Gene therapy; Manufacturing; Process development*

株式会社セルファイバは、東京大学竹内研究室で開発された、細胞ファイバ技術を事業化するスタートアップです。細胞ファイバは髪の毛程の太さのゲルチューブに細胞を封入した構造物です。細胞ファイバ技術は、高品質な再生医療等製品を安価かつ大量に迅速に製造する可能性を持っています。細胞の増殖・分化だけでなく、回収・保存・流通・移植等、様々な工程に実績があります。

生体内分子通信ネットワークの理解と医療応用

(大阪市大・工) 中野 賢

Understanding in-body molecular communication networks for future medicine
(Graduate School of Engineering, Osaka City University) Tadashi Nakano

Molecular communication is an emerging research field in information and communications engineering. In molecular communication, molecules are used as a carrier of information. A key research issue in molecular communication is to understand how biological entities communicate using molecules. In this talk, I will give an overview of molecular communication research. I will also talk about our recent research to understand how cancer cells communicate and migrate to collectively form a network structure.

Keywords : Molecular Communication; Network Formation; Cancer

分子通信とは、生体分子や生化学反応に基づくバイオナノマシンのための新しい情報通信パラダイムである。分子通信で想定するバイオナノマシンは、生体分子で構成される微小デバイスであり、遺伝子改変細胞や人工細胞などを指す。分子通信は、電気信号もしくは光信号に基づく現在の通信とは異なり、生体分子を情報伝達のキャリアとして利用する。分子通信では、通信の送り手と受け手の間で生起する一連の生化学反応を通信と捉える。分子通信に関する研究は、情報工学的な視点から細胞間の相互作用を理解することを一つの目標としており、生物学や医学への貢献が期待される。

本講演ではまず、これまでの分子通信研究を概観する。次に、分子通信研究の一環として我々の研究グループで取り組んでいる、がん細胞集団が作る分子通信ネットワークを理解するための研究を紹介する。

- 1) T. Nakano, A. Eckford, T. Haraguchi, *Molecular Communication*, Cambridge University Press (2013).
- 2) T. Nakano, Y. Okaie, S. Kobayashi, T. Hara, Y. Hiraoka, T. Haraguchi, "Methods and Applications of Mobile Molecular Communication," *Proceedings of IEEE*, 107(7):1442-1456 (2019).
- 3) T. Nakano, "Molecular Communication: A 10 Year Retrospective," *IEEE Transactions on Molecular, Biological and Multi-Scale Communications*, 3(2):71-78 (2017).
- 4) T. Nakano, Y. Okaie, Y. Kinugasa, T. Koujin, T. Suda, Y. Hiraoka, T. Haraguchi., "Roles of Remote and Contact Forces in Epithelial Cell Structure Formation," *Biophysical Journal*, 118(6):1466-1478 (2020).

Symposium | Medium and Long-Term Program | Condensed Electronic Conjugation of Molecular Materials: Revisiting Electronic Conjugation

[B204-1pm] Condensed Electronic Conjugation of Molecular Materials: Revisiting Electronic Conjugation

Chair, Symposium organizer: Shu Seki, Hiroshi Shinokubo

Wed. Mar 23, 2022 1:00 PM - 3:40 PM B204 (Online Meeting)

[B204-1pm-01] Condensed Conjugation Molecular Physics and Chemistry: Revisiting Electronic Conjugation Leading to Innovative Physical Properties of Molecular Materials

○Shu Seki¹ (1. Kyoto University)

1:00 PM - 1:15 PM

[B204-1pm-02] Electron transport and crystal structure prediction of layered molecular system

○Tatsuo Hasegawa¹ (1. The University of Tokyo)

1:15 PM - 1:45 PM

[B204-1pm-03] Physical properties controlled by hydrostatic pressure and uniaxial strain

○Taishi Takenobu¹ (1. Nagoya University)

1:45 PM - 2:00 PM

[B204-1pm-04] Creation of Novel Spin-polarization Materials utilizing Molecular Chirality

○Masayuki Suda^{1,2,3} (1. Kyoto Univ., 2. JST PRESTO, 3. RIKEN)

2:10 PM - 2:25 PM

[B204-1pm-05] Excellent device performance from higher-density organic films

○Toshinori Matsushima¹, Yu Esaki¹, Aoyama Tetsuya², Chihaya Adachi¹ (1. Kyushu University, 2. RIKEN)

2:25 PM - 2:55 PM

[B204-1pm-06] Charge injection and electronic phase transition in molecular solids

○Shun Watanabe¹ (1. The University of Tokyo)

2:55 PM - 3:10 PM

[B204-1pm-07] Materials and Device Structures in Organic LEDs

○Junji Kido¹ (1. Yamagata University)

3:10 PM - 3:40 PM

高密度共役の科学：電子共役概念の変革と電子物性をつなぐ

(京大院工) 関 修平

Condensed Conjugation Molecular Physics and Chemistry: Revisiting Electronic Conjugation Leading to Innovative Physical Properties of Molecular Materials (*Graduate School of Engineering, Kyoto University*) Shu Seki

Herein, we will establish a novel concept of intermolecular electronic conjugation, referred to as “X”-conjugation, by revisiting thoroughly the longitude and latitude in the development of “conjugation” in chemistry. Starting from the precise design of organic molecules with well-confined intermolecular spaces, thermal fluctuations in the condensed phases of molecular systems will be controlled perfectly by the wide-range/spatial alignment of intermolecular interactions as well as the leading-edge energy dissipation theory. Such control will result in extraordinarily high density-of-states (DOS) in the molecular substances. A series of unique assessment techniques of opto- and magneto-electronic properties of molecular materials is presently the central complex of the current research project, pioneering the unprecedented properties of molecular systems with “X”-conjugation.

Keywords : *Condensed Conjugation; aromaticity; antiaromaticity; X-conjugation*

さまざまな物質の性質～物性について見つめてみれば、electron/電子に関係のない物性が世の中にはほとんど存在しないことに気づく。すぐに思い浮かべることができるのは、原子核反応くらいだが、原子“核”の寄与が極めて大きい質量（とそれにまつわる性質）ですら、物質の密度（とそれにまつわる熱容量などの性質）など、電子の介在になしに議論することはできない。電子共役概念は、単純に電子の（空間的な）非局在性に伴うエネルギー利得として 1899 年、Thiele によってすでに定義されている。この定義に則った電子共役は果たしてこれまで物質として具現化され、検証されてきた $\pi \cdot \sigma \cdot \delta$ 共役などの電子の原子軌道角運動量をもとに定義されたもののみののだろうか？ 体積を有する 3 次元空間中の自由粒子の状態数を量子統計力学において数え上げれば、

$$\Omega(\varepsilon) = (2m)^{3/2} (6\pi^2 \hbar^3) \cdot V \varepsilon^{3/2} \quad (1)$$

という誰もが学部で固体物理学の講義で学ぶ、極めてシンプルな量子理想気体を理解するための状態数モデルに思い至る。体積ひいては電子非局在性を直接反映する L の拡張は、高い準位密度： $d\Omega(\varepsilon)/d\varepsilon$ の達成に直結することから、なるべく多くの電子を空間に充填しつつ高い非局在性を維持するという考え方に矛盾は無い。“分子空隙の電子”非局在性は、例えば溶媒和電子のような過渡的なモデル¹⁾、あるいは分子間電子対生成のような静的なモデル²⁾によってすでに議論がなされているが、高度に組織化して充填しつつ、高い $\Omega(\varepsilon) \cdot d\Omega(\varepsilon)/d\varepsilon$ を達成することは可能であろうか？ 物質の秩序性と空間充填に対するアプローチとしてまず思い浮かぶのは Wallach 則³⁾で、分子対称性とその物性という、化学における根源的な問いの一つとして現在も興味を引き続けている⁴⁾。分子対称性と物質状態密度に関する高密度共役からのアプローチについても紹介する。

1) J. Ma, S. Seki, *et al.*, *Nat. Commun.* **2019**, *10*, 102; 2) H. Shinokubo *et al.*, *Nat. Commun.* **2016**, *7*, 13620; D. Sakamaki, S. Seki *et al.*, *Angew. Chem. Int. Ed.* **2017**, *56*, 16597; T. Kubo *et al.*, *J. Am. Chem. Soc.* **2016**, *138*, 4665; 3) O. Wallach, *Ann. Chem.* **1887**, *238*, 78; 4) C. P. Brock, B. Schweizer, J. D. Dunitz, *J. Am. Chem. Soc.* **1991**, *113*, 9811.

層状分子系の電子輸送と結晶構造予測

(東大院工¹) 長谷川 達生¹

Electron Transport and Crystal Structure Prediction of Layered Molecular System (¹Graduate School of Engineering, The University of Tokyo) ○Tatsuo Hasegawa¹

Layered molecular system composed of rod-like π -conjugated organic molecules is quite attractive and promising to realize the condensed π -electronic conjugation system. Herein, we present and discuss our recent studies to develop layered organic semiconductors, with focusing on the concept of high layered crystallinity that is obtainable with unsymmetric rod-like organic molecules composed of extended π -electron cores linked with long alkyl chains, which are found to provide high-performance printed organic thin-film transistors. We also argue the possibility of step-by-step crystal structure prediction of these materials.

Keywords : Organic semiconductors, Layered crystallinity, Thin-film transistors, Crystal structure prediction

π 共役分子の 2 次元配列により得られる層状結晶構造は、分子間の空隙を最小化した高密度 π 共役系を実現する舞台として有力である。実際、チエノアセン類による縮合多環系に長鎖アルキル基を連結した有機分子 (図1に例) は、単純な構成でありながら、近年、優れた層状有機半導体を多数与えることが明らかになりつつある。本講演では、これら分子が共通して示す高い層状結晶性をキーワードに、分子配列構造と π 電子機能について議論したい。

長軸に沿って非対称なこれら棒状分子は横繋がり分子層を形成し易く、かつ長軸の向きが互いに相対する分子層の対が、細胞膜に似た 2 分子膜構造を形成することで、層状性 (層の独立性) を著しく増強させる^{1,2)}。実際これら分子は、分子層レベルの厚みの極薄結晶を形成し易く、また単層 2 分子膜構造の構築も可能である³⁾。そこでは、アルキル鎖間の層状秩序化が、 π 共役骨格による層状ヘリンボーン (layered herringbone ; LHB) 構造 (図1a) の形成を促し、補強する役割を担う。これらの特徴は、半導体-絶縁層界面からなる薄膜トランジスタ (TFT) を構築する上では理想的であり、実際に層内に形成された 2 次元 π 共役系にもとづく優れたデバイス特性を得ることができる^{4,5)}。またこれら層状有機半導体は、塗布 (溶液プロセス) により容易に高均質な結晶性薄膜を形成できる顕著な特長がある。そこでは、溶液の気液界面近傍で生じる液晶性の前駆膜を介して逐次的に単結晶薄膜化が進行することが、

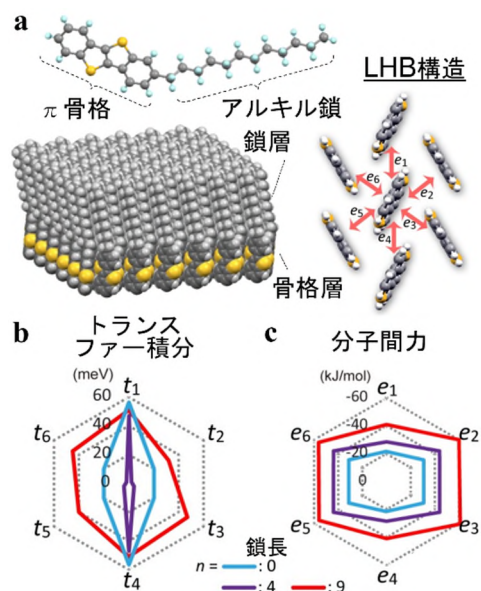


図1 (a)有機半導体 mono-C₆₀-BTBT の層状ヘリンボーン構造、(b)分子間トランスファー積分、(c)分子間力。

分子動力学計算により示されている⁶⁾。これらの特長を駆使することで、撥液性のきわめて高いゲート絶縁層とのクリーンな半導体界面を塗布形成することも可能であり (図2a)、これにより理論限界に迫る超高急峻なスイッチングを示す塗布型 TFT 構築が実現している (図2b)⁷⁾。さらに、各種 π 共役骨格への適用や、これらに付与する置換基の位置や種類により多種多彩な積層様式が発現し競合することが明らかになりつつある⁸⁻¹³⁾。

これら層状有機半導体の基本的な電子構造・ π 電子機能は、分子配列構造 (結晶構造) がいったん分かれば、最高占有分子軌道間の重なりなどをもとに、ある程度の見通しを立てることができる (図1b)。一方、分子間に働く分子間力についても、近年、高精度量子化学計算を用いた詳細な解析が可能になってきており¹⁴⁾、アルキル基の役割を含めた層状結晶構造の起源に関する理解が大幅に進んできている (図1c)。ただここで問題となるのが、結晶内での詳しい分子配列構造を、分子の設計段階では知り得ないことである。結晶構造予測は計算科学上の難問であることが古くから指摘されており、結晶内の多数の分子の配置や方位を正しく予測することは未だ困難である¹⁵⁾。このため、高性能な半導体が得られるかどうかは、実際に分子を合成し、デバイスを作ってみるまでは分からないというギャンブル的要素が色濃く残っている。これこそが実験家にとっての醍醐味ではあるものの、材料開発の足枷となっていることも事実である。単なる結果の解析から予測への進化が今後の材料開発において強く希求されるなか、本稿で紹介した層状性有機半導体は、比較的単純な分子構造、稠密なパッキング構造、支配的な分子間相互作用が明瞭なことを活かして、段階的な構造最適化による結晶構造予測が可能になりつつある。これらを含めた研究の現状について紹介したい。

本研究は井上悟・都築誠二・荒井俊人・松岡悟志・浜井貴将・北原暁・東野寿樹・堀内佐智雄・熊井玲児・峯廻洋美・米谷慎の各氏を含む方々との共同研究によります。また本研究は CREST 革新材料開発 (JPMJCR18J2) による支援を受け行われました。

1) S. Inoue et al., *Chem. Mater.* **2015**, 27, 3809. 2) H. Minemawari et al., *Chem. Mater.* **2017**, 29, 1245. 3) S. Arai et al., *Adv. Mater.* **2018**, 30, 1707256. 4) T. Hamai et al., *Phys. Rev. Appl.*, **2017**, 8, 054011. 5) T. Hamai et al., *Phys. Rev. Mater.* **2020**, 4, 074601. 6) M. Yoneya et al., *J. Phys. Chem. C*, **2017**, 121, 8796. 7) G. Kitahara et al., *Sci. Adv.* **2020**, 6, eabc8847. 8) S. Inoue et al., *Chem. Mater.* **2018**, 30, 5050. 9) S. Inoue et al., *Chem. Sci.* **2020**, 11, 12493. 10) T. Higashino et al., *CrystEngComm* **2020**, 22, 3618. 11) S. Arai et al., *Adv. Funct. Mater.* **2020**, 30, 1906406. 12) T. Higashino et al., *Chem. Mater.* **2021**, 33, 7379. 13) S. Inoue et al., *Chem. Mater.* **2022**, 34, 72. 14) 都築誠二「有機分子の分子間力」(東京大学出版会) **2015**. 15) 例えば, A. R. Oganov et al. *Nat. Rev. Mater.* **2019**, 4, 331.

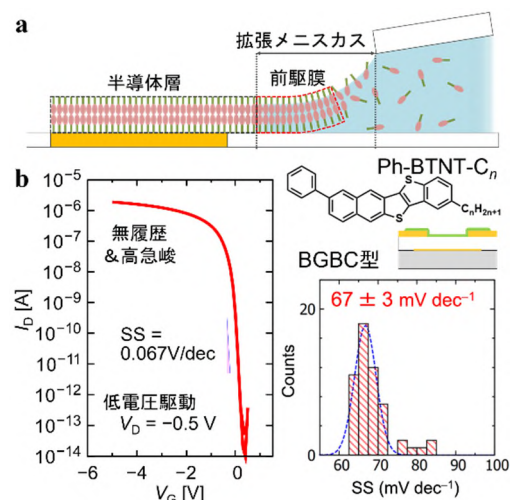


図2 (a)溶液法による層状有機半導体の製膜過程の模式図、(b)有機TFTの伝達特性とスイッチング特性。

圧力と歪みを用いた物性制御

(名大院工) ○竹延 大志

Physical properties controlled by hydrostatic pressure and uniaxial strain (¹Graduate School of Engineering, Nagoya University) ○Taishi Takenobu

“Hydrostatic pressure” and “uniaxial strain” can be powerful tool to control lattice parameter and crystal symmetry of materials. Particularly, organic materials are one of the most suitable materials to apply these methods due to their intrinsic flexibility. Here, I will introduce our recent progress of physical properties controlled by hydrostatic pressure and uniaxial strain.

Keywords : Hydrostatic pressure; Strain; Physical properties

『圧力』や『歪み』は、物質の格子定数や結晶構造の対称性を変化させる強力な手法である。例えば、静水圧を用いた格子定数制御は物性物理において一般的な研究手法であり、シリコン膜に歪みを加えた歪みシリコンは LSI の性能を引き上げる半導体プロセス技術として知られている。特に、有機材料に代表させるような本質的な柔軟さを有する材料は、圧力や歪みにより物理的な性質を自在に制御できる可能性があり、既に多くの研究が行われている。一方で、物性物理におけるもう一つの一般的な研究手法として、物質中の電荷数を制御するキャリアドーピングが知られているが、『圧力』や『歪み』とキャリアドーピングを組み合わせた物性制御は極めて限定されている。そこで我々は、キャリアドーピング手法として電解質を用いた電気二重層ドーピングおよび電気化学ドーピングを駆使し、『圧力』や『歪み』とキャリアドーピングを両立させた。より具体的には、プラスチック基板上の極薄膜への歪み導入(図1)と、圧力媒体に電解質を用いた静水圧印加(図2)の二手法について紹介する¹⁻³⁾。

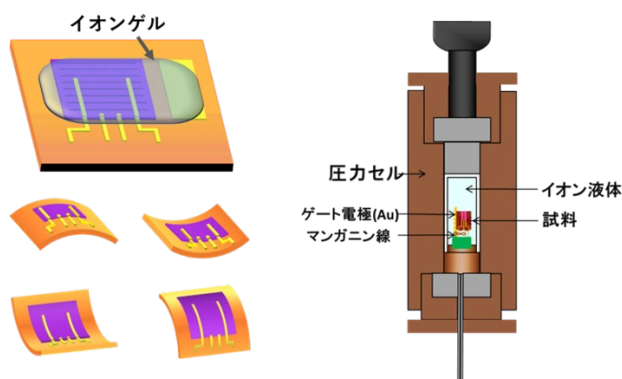


図1 素子構造と歪み実験 図2 静水圧印加実験

- 1) Room-Temperature Chiral Light-Emitting Diode Based on Strained Monolayer Semiconductors. J. Pu et al., *Adv. Mater.* **2021**, 33, 2100601.
- 2) Two-dimensional ground-state mapping of a Mott-Hubbard system in a flexible field-effect device. Y. Kawasaki et al., *Sci. Adv.* **2019**, 5, eaav7282.
- 3) Electrolyte-Gating-Induced Metal-Like Conduction in Nonstoichiometric Organic Crystalline Semiconductors under Simultaneous Bandwidth Control. H. Ito et al., *Phys. Status Solidi RRL* **2019**, 1900162.

分子キラリティを利用した新奇スピン偏極材料の創製

(京大院工・JST さきがけ・理研) 須田 理行

Creation of Novel Spin-polarization Materials utilizing Molecular Chirality

(Graduate School of Engineering, Kyoto University, JST PRESTO, RIKEN)

○Masayuki Suda

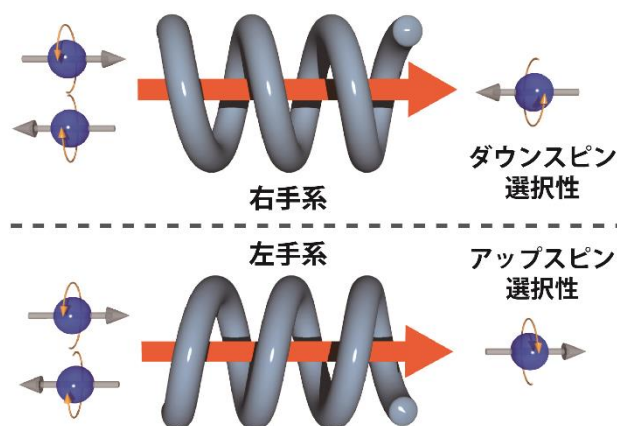
Recently, the chiral-induced spin-selectivity effect was discovered in which chiral molecules act as spin filters. This effect opens new possibility not only for future molecular spintronics but also for spin-electrochemistry. In this talk, novel chiral materials which shows high spin-polarization will be introduced and the possibility for developing new molecular spintronics and spin-electrochemistry utilizing these materials will be discussed.

Keywords : Aziridine; Chirality; Spintronics; Chiral-induced spin-selectivity effect

分子のキラリティと物理現象のキラリティを統合する“真のキラリティ”は「空間反転対称性 P は破るが、純粋回転 R と時間反転対称性 T との組み合わせ RT は破らない」と定義される。すなわち、(非スピン偏極)電流はアキラルな現象と定義されるのに対し、スピン偏極電流はキラルな現象と定義することが出来る。この事実は、電流からスピン偏極電流へのキラル分子による新たな変換原理の可能性を示唆する。

実際に近年、R. Naaman らによりキラル分子によるスピン選択性: "Chiral-induced Spin Selectivity (CISS) effect"が報告され、外部磁場や磁性体を用いない新たなスピン偏極電流の生成法として注目を集めつつある。

本講演では、低次元ナノ構造にキラル分子を組み込むという新戦略によって創製した高スピン偏極材料を紹介すると共に、これらの材料のスピン트로ニクス並びに電気化学分野への応用の可能性などについても議論する。



- 1) M. Suda et al., *Nat. Commun.* 2019, 10, 2455., 2) A. Inui et al., *Phys. Rev. Lett.* 2020, 124, 166602.

有機膜の密度制御とデバイス応用

(九大 I²CNER¹・理研 RAP²) ○松島 敏則¹・江崎 有¹・青山 哲也²・安達 千波矢¹
 Excellent device performance from higher-density organic films (¹I²CNER, Kyushu Univ.,
²RIKEN RAP) ○Toshinori Matsushima,¹ Yu Esaki,¹ Tetsuya Aoyama,² Chihaya Adachi¹

The influences of film density and molecular orientation on the carrier conduction and air stability of vacuum-deposited amorphous organic films of *N,N'*-di(1-naphthyl)-*N,N'*-diphenyl-(1,1'-biphenyl)-4,4'-diamine (α -NPD) were investigated.¹⁾ The substrate temperature (T_{sub}) during vacuum deposition had different effects on the film density and molecular orientation of α -NPD. Film density was a concave function of T_{sub} ; maximum density was attained at $T_{\text{sub}} = 270\text{--}300\text{ K}$ [Fig. 1(a)]. α -NPD molecules were randomly oriented at $T_{\text{sub}} = 342\text{ K}$, and their horizontal orientation on the substrate became dominant as T_{sub} decreased. Hole current and air stability were clearly raised by increasing the film density by 1–2% [Fig. 1(b) and 1(c)]; these effects were, respectively, attributed to enhanced carrier hopping between neighboring α -NPD molecules and suppressed penetration of oxygen and water. These results imply that increasing film density is more effective to enhance the electrical performance of organic thin-film devices with α -NPD films than control of molecular orientation. Additionally, we demonstrated that performance of organic light-emitting diodes is greatly influenced by T_{sub} ²⁾.

Keywords : Film density; Molecular orientation; Organic film; Carrier transport; Air stability

有機膜の密度がデバイス特性に及ぼす影響を検討するためのモデル材料として α -NPD を用いた¹⁾。様々な基板温度において α -NPD を成膜した結果、その膜密度と分子配向は基板温度に大きく依存した。基板温度が 270–300 K の時に膜密度が最大となることを見出した[Fig. 1(a)]。分子配向に関しては、高い基板温度を用いるほど、面内配向からランダムに変化した。分子配向がデバイス特性に及ぼす影響は明確には観測されなかった。しかし、膜密度の増加は 1–2% であるが、 α -NPD 膜に流れる電流と大気安定性が大幅に向上することを見出した[Fig. 1(b) and 1(c)]。膜中の空隙が圧縮されることによって、分子間のキャリアホッピングが改善されたことや、水や酸素が膜中に侵入しづらくなったことが考えられる。また本研究では、有機 EL 特性が基板温度に大きく依存することも見出したので報告する²⁾。

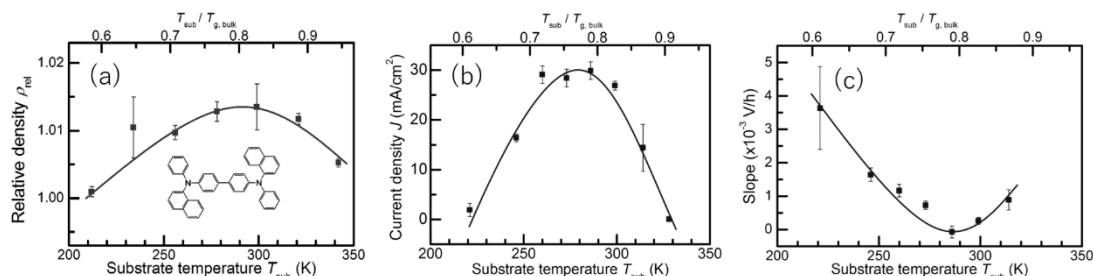


Fig. 1. Plots of (a) film density, (b) current density, and (c) air stability as a function of T_{sub} .

- 1) Y. Esaki et al., *J. Phys. Chem. Lett.* **2017**, 8, 5891–5897.
- 2) Y. Esaki et al., *Adv. Electron. Mater.* **2021**, 7, 2100486.

分子性固体への高密度電子注入と電子相転移

(東大新領域¹⁾) ○渡邊 峻一郎¹

Charge Injection and Electronic Phase Transition in Molecular Solids

(¹*Graduate School of Advanced Materials Science, The University of Tokyo*)

○Shun Watanabe¹

When high-density charge carriers are injected into a crystal, its electronic state changes from an insulator to a metal. “Insulator—metal transition (IMT)” is a natural consequence of the band picture based on the periodic lattice of atoms in crystals particularly with noninteracting electrons, and can be triggered predominantly by a precise control of band filling. During the past half century, no apparent IMT signature has been observed in organic semiconductors, presumably because the presence of unavoidable structural disorders in organic semiconductors is likely a limiting factor. In contrast, we successfully demonstrated a perfect single crystal of solution-processed organic semiconductors, and realize the first experimental observation of IMT in organic semiconductors.

Keywords : *Organic Semiconductors; Insulator—Metal Transition; Single Crystals*

不純物のない絶縁性の固体物質に電子や正孔を高密度に注入することで、電気を流さない絶縁体から電気を流す金属へと変化する。この絶縁体—金属転移 (Insulator—Metal Transition; IMT)は固体物質における電子相転移であり、電子相関を無視した場合のバンド伝導電子系において当然の帰結であるいえる。有機半導体についても、過去半世紀に渡り IMT の研究が進められてきたが、実験的に実証されていない。これは、欠陥のない極めて高純度な有機半導体薄膜を製造することが困難であったためである。有機半導体の結晶は分子間力のみの弱い相互作用で構成されているため外界からのかく乱に弱く、高密度に電荷を注入することも困難であった。

我々はこれまで、厚さが数分子層の有機半導体単結晶薄膜を印刷プロセスによって作製する手法/技術を開発して^{1,2)}。本手法で得られた有機半導体単結晶薄膜の表面には、わずかな欠陥もなく、薄膜中の分子層数までも精密に制御されている。このような高品質な薄膜表面を用いて、4 分子あたり 1 電荷に相当する高密度のキャリアを注入した結果、有機半導体の IMT を初めて実験的に観測することに成功した³⁾。このとき、電子は層状分子の一分子層厚みのみに電荷が閉じ込められた二次元ホールガスが形成されていることも明らかとなった。講演では、ある程度の構造乱れを有する高分子半導体における電子相転移の可能性についても議論する⁴⁾。

1) J. Tsurumi, S. Watanabe, J. Takeya, *Nat. Phys.* **2017**, *13*, 994.

2) A. Yamamura, S. Watanabe, J. Takeya, *Sci. Adv.* **2018**, *4*, aao5758

3) N. Kasuya, S. Watanabe, J. Takeya, *Nat. Mater.* **2021**, *20*, 1401.

2) Y. Yamashita, J. Takeya, S. Watanabe, *Nature* **2019**, *572*, 634.

有機 EL のおける分子設計とデバイス設計

(山形大院工) 城戸 淳二

Materials and Device Structures in Organic LEDs (*Graduate School of Organic Materials Science, Yamagata University*) Junji Kido

The performance of organic LEDs has been steadily improved and, today, OLEDs have been widely used for smart phones and televisions. In this talk, the recent development of high-performance OLEDs and the future prospects will be discussed. High quantum efficiencies have been achieved by using phosphorescent emitters such as iridium complexes. In this case, it is important to use organic materials with high triplet excited energy levels as the host and carrier transport materials to confine the triplet excited energy of the phosphorescent emitter. Internal quantum efficiency of 100% have achieved for phosphorescent OLEDs. Recent years, solution-processable OLEDs with phosphorescent emitters have received attentions to lower the production cost. In solution process, emitter materials are deposited by inkjet printing and red, green, blue layers are patterned, and such displays have been commercialized. Recent progress in the development of fully solution processed OLEDs will be introduced.

Keywords : OLED; phosphorescence; solution process

有機 EL 素子は、この 20 年、着実に高性能化し、現在ではスマホや大型テレビにまで使用されている。そこで、本講演では、高性能有機 EL の開発に関して、最近の状況について解説し、今後の展望について述べる。量子効率に関してはイリジウム錯体などのリン光材料を用いることにより高効率化が可能である。この際、励起三重項準位の高いホスト材料や輸送材料などの周辺材料を使用する必要があり、リン光素子においてはすでに内部量子効率 100%が達成されている。近年では、さらなる低コスト化を目指して、製造プロセスにおいて、真空蒸着から塗布による成膜、製造技術への移行が検討されている。この場合、赤、緑、青の発光層材料はインクジェット印刷により成膜されるが、このようなディスプレイは一部製品化され始めている。本稿では、さらに進んだ究極のオール塗布型有機 EL ディスプレイの開発について、材料からデバイス構造まで紹介する。

Symposium | Medium and Long-Term Program | Chemistry of curious biological phenomena

[B204-1am] Chemistry of curious biological phenomena

Chair, Symposium organizer: Masaki Kita, Hirokazu Arimoto

Wed. Mar 23, 2022 9:00 AM - 11:40 AM B204 (Online Meeting)

[B204-1am-01] Search for the therapeutic seeds for infectious diseases from microbial secondary metabolites

○Masato Iwatsuki¹ (1. Kitasato University)

9:10 AM - 9:35 AM

[B204-1am-02] Toward making unique bioactive molecules

○Kenichiro Itami¹ (1. Nagoya University)

9:35 AM - 10:05 AM

[B204-1am-03] Key compounds for cell death regulation

○Mikiko Sodeoka¹ (1. RIKEN)

10:05 AM - 10:35 AM

[B204-1am-04] Membrane-active key natural products interacting with lipid layers

○MICHIO MURATA MURATA¹ (1. Osaka University)

10:35 AM - 11:05 AM

[B204-1am-05] Challenge of misteries of Manatabi reaction of cats, a classic but still facinating issue of natural product chemsitry

○Toshio Nishikawa¹ (1. Nagoya University)

11:05 AM - 11:35 AM

微生物代謝産物からの抗感染症シードの探索

(北里大 大村研¹・北里大 感染制御科学府²) ○岩月正人^{1,2}

Search for the therapeutic seeds for infectious diseases from microbial secondary metabolites (¹*Ōmura Satoshi Memorial Institute, Kitasato University*, ²*Graduate School of Infection Control Sciences, Kitasato University*)○Masato Iwatsuki^{1,2}

Since joining The Kitasato Institute in 2002, the speaker has been consistently engaged in discovering seed compounds for anti-infective drugs from microbial metabolites in the “Ōmura Drug Discovery Group” under the guidance of Distinguished Emeritus Professor Satoshi Ōmura. In this symposium, the speaker would like to introduce the anti-infective seed compounds derived from microorganisms that I have been able to discover with many co-workers and the efforts of students.

After joining the institute, we first conducted screening targeting bacteria and discovered lariatins¹⁾ (anti-tuberculosis agents), guadinomines²⁾ (type III secretion mechanism inhibitors of Gram-negative pathogenic bacteria), and aogacillin³⁾ (Circumventors of arbekacin resistance in MRSA). Since 2009, we have also screened for parasites and fungi and discovered clonocoprogens⁴⁾ (anti-malarial agents) and actinoallolides⁵⁾ (anti-trypanosomal agents).

After the discovering some of these seed compounds, the “Ōmura Drug Discovery Group” has been conducting drug discovery research (hit-to-lead, optimization, and mechanism of action analysis).

Keywords : *Microbial second metabolites; drug development, Infectious disease*

講演者は北里研究所へ 2002 年に入所して以来、大村智先生の御指導のもと大村創薬グループで微生物代謝産物から抗感染症薬の創薬シード化合物の探索に一貫して従事してきた。本講演ではこれまで多くの先生方のご指導、学生の皆様の努力により発見に携わることができた微生物由来の抗感染症シード化合物について紹介したい。

入所後はまず細菌を標的としたスクリーニングを行い、lariatins 類¹⁾ (抗結核活性)、guadinomine 類²⁾ (グラム陰性病原細菌の三型分泌機構阻害活性)、aogacillin 類³⁾ (MRSA に対するアルベカシン耐性克服活性) を発見することができた。2009 年以降は寄生虫、真菌を標的としたスクリーニングも行い、clonocoprogen 類⁴⁾ (抗マラリア原虫活性)、actinoallolide 類⁵⁾ (抗トリパノソーマ原虫活性) などを発見することができた。

これらの創薬リードのうち幾つかは発見後に大村創薬グループ内で創薬研究 (誘導体合成、全合成および作用機序解析) を展開している。

1) M. Iwatsuki, *et al.*, *J. Am. Chem. Soc.* **2006**, *128*, 7486.

2) M. Iwatsuki, *et al.*, *J. Antibiot.* **2008**, *61*, 222.

3) K. Takata, *et al.*, *Org. Lett.* **2013**, *15*, 4678.

4) T. Ouchi, *et al.*, *J. Antibiot.* **2020**, *73*, 365.

5) Y. Inahashi, *et al.*, *Org. Lett.* **2015**, *17*, 864.

ユニークな生物活性分子の創製を目指して

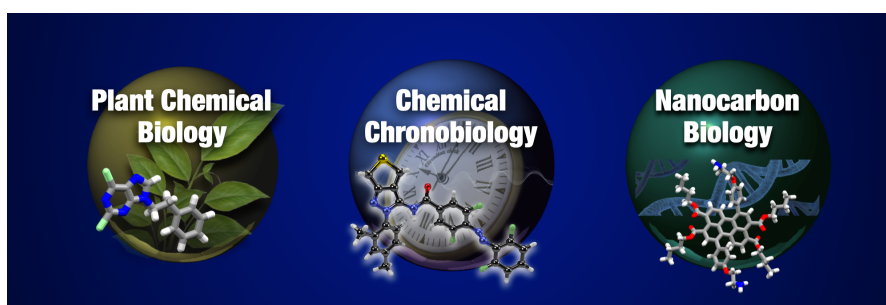
(名大 WPI-ITbM・名大院理) 伊丹健一郎

Toward making unique bioactive molecules (*Institute of Transformative Bio-Molecules (WPI-ITbM), Nagoya University; Graduate School of Science, Nagoya University*) Kenichiro Itami

Our group has focused on catalyst-enabling synthetic chemistry with broad directions, including applications in molecular nanocarbons, pharmaceuticals, and plant/animal chemical biology. In this talk, I will describe about our exciting interdisciplinary research conducted at the Institute of Transformative Bio-Molecules (ITbM) in Nagoya University, where we aim at developing unique molecules and molecular technology for plant biology, chronobiology, live imaging, and theoretical science.

Keywords: Synthetic chemistry; bioactive molecules; plant biology; chronobiology; nanocarbon biology

分子には無限のチカラがあります。この地球上にはエネルギー問題、食糧問題、環境問題、医療問題など実に多くの「問題」がありますが、それらの問題の多くに対して「分子で答えを出す」ことが原理的に可能です。我々の研究のゴールは、問題を解決するような画期的な機能をもつ分子や構造的に美しい分子（美しい分子には機能が宿る）を開発し、世に送り出すことです。これまで我々は名大 ITbM を主な舞台として合成化学と植物科学、時間生物学（体内時計）、ライブイメージング、理論科学の融合研究を展開してきました。本講演では、これらの取り組みで見出してきたユニークな生物活性分子やナノカーボンバイオロジーという新領域の開拓研究について述べたい。



細胞死制御鍵化合物

(理研開拓研究本部¹・理研環境資源化学センター²) 袖岡 幹子^{1,2}

Key compounds for cell death regulation (¹*RIKEN Cluster for Pioneering Research*, ²*RIKEN Center for Sustainable Resource Science*) Mikiko Sodeoka,^{1,2}

We developed IM-54 (currently commercially available as a reagent for biochemical experiments) as a compound that selectively inhibits necrosis-like cell death induced by oxidative stress such as peroxides, but not apoptosis, and reported it in 2005.¹⁻³ At that time, necrosis was still considered to be a passive cell death with no control mechanism that occurs when cells are severely injured. Recently, however, the existence of various types of "controlled necrosis" such as necroptosis, pyroptosis, NETosis, and ferroptosis has been revealed. We also developed NT compounds that selectively induce lipid peroxidation-associated necrosis at low concentrations, which can be inhibited by IM compounds. In addition, water-soluble derivatives of IM showed remarkable effects in a rat cardiac ischemia-reperfusion injury model, indicating that IM-sensitive necrosis is closely related to ischemia-reperfusion injury.⁴ On the other hand, cell death induced by erastin, a compound found by Stockwell *et al.* as an anticancer compound, was named ferroptosis in 2012 because iron plays critical role. Ferroptosis has many similarities with necrosis induced by peroxides or NT compound, which we have been focusing on, and IM-54 also inhibited erastin-induced ferroptosis. Furthermore, IM-54 was found to inhibit NETosis of neutrophils, but not necroptosis or pyroptosis.⁵ Recently, it has been reported that lipid peroxidation plays an important role also in NETosis, and IM was found to be highly selective for lipid peroxidation-mediated necrosis.⁶ We are currently investigating the regulatory mechanisms of lipid peroxidation-mediated necrosis by elucidating mechanisms of action of IM and NT compounds. In this talk, I would like to introduce some aspects of our research.

Keywords : *Cell Death; Ferroptosis; NETosis; Lipid Peroxidation; Indolylmaleimide*

我々は、アポトーシスは抑制せず、過酸化物質などの酸化ストレスによって誘導されるネクローシス様の細胞死を選択的に抑制する化合物として IM-54 を開発し(現在生化学実験用試薬として市販)、2005 年に報告した¹⁻³)。当時はまだネクローシスは細胞が強い傷害を受けたときに起こる制御機構をもたない受動的な細胞死であると考えられていたが、現在ではネクロトーシス、パイロトーシス、ネトローシス、フェロトーシスなど様々なタイプの“制御されたネクローシス”の存在が明らかになっている。また我々は、IM 化合物で抑制しうるネクローシスを選択的に誘導する化合物の探索と最適化も行い、脂質過酸化を伴うネクローシスを低濃度で誘導する NT 化合物の開発にも成功した。また、IM の水溶性誘導体がラット心虚血再灌流障害モデルにも顕著な効果を示したことから、IM 化合物が抑制しうるネクローシスは、虚血再灌流障害に深く関わっていることが示された⁴)。一方、Stockwell らによって抗癌化合物として見出された化合物エラスチンによって誘導される細胞死は、鉄が関与することから、2012 年にフェロトーシスと名付けられた。フェロトーシスは、我々が着目してきた

過酸化物質や NT 化合物によって誘導されるネクロトーシスと共通点が多く、IM-54 はエラスチンによって誘導されるフェロトーシスも抑制した。さらに IM-54 は、好中球のネトーシスも抑制することが明らかになる一方、ネクロトーシス、パイロトーシスは抑制しなかった⁵⁾。最近ネトーシスにも脂質過酸化が重要な働きをしていることが報告され⁶⁾、IM は脂質過酸化が関与するネクロトーシスに高い選択性を示すことがわかった。現在 IM 化合物や NT 化合物の作用機序解明を通じて、これら脂質過酸化が関与するネクロトーシスの制御機構の解明することをめざす研究を行っている。本講演では、その研究の一端についてご紹介したい。

- 1) M. Katoh, K. Dodo, M. Fujita, M. Sodeoka, *Bioorg. Med. Chem. Lett.* **2005**, *15*, 3109.
- 2) K. Dodo, M. Katoh, T. Shimizu, M. Takahashi, M. Sodeoka, *Bioorg. Med. Chem. Lett.* **2005**, *15*, 3114.
- 3) M. Sodeoka, K. Dodo, *Chem. Rec.* **2010**, *10*, 308.
- 4) K. Dodo, T. Shimizu, J. Sasamori, K. Aihara, N. Terayama, S. Nakao, K. Iuchi, M. Takahashi, M. Sodeoka, *ACS Med. Chem. Lett.* **2018**, *9*, 182.
- 5) K. Dodo, E. Kuboki, T. Shimizu, R. Imamura, M. Magarisawa, M. Takahashi, T. Tokuhiro, S. Yotsumoto, K. Asano, T. Suda, M. Tanaka, M. Sodeoka, *ACS Med. Chem. Lett.* **2019**, *10*, 1272.
- 6) S. Yotsumoto, Y. Muroi, T. Chiba, R. Ohmura, M. Yoneyama, M. Magarisawa, K. Dodo, N. Terayama, M. Sodeoka, R. Aoyagi, M. Arita, S. Arakawa, S. Shimizu, M. Tanaka, *Sci. Rep.* **2017**, *7*, 16026.

生物現象を司る天然物と膜脂質

(阪大院理) ○村田 道雄

Interactions of natural products with membrane lipids are highly important for the expression of biological functions. (*Graduate School of Science, Osaka University*) ○Michio Murata

Molecular behavior under bilayer membrane environments is one of the important research topics concerning how organic molecules exert their biological activities when interacting with cellular membranes. However, chemistry-based approaches to this property have not been successful when compared with the structural biological strategy on ligand-receptor interactions. Here, we have investigated the molecular behavior of natural products such as saponins and antibiotics, and revealed that there are significant differences in membrane affinity and dynamics among ligands having different biological activities, suggesting the specific contribution of ligand-membrane interactions to their biological activity.

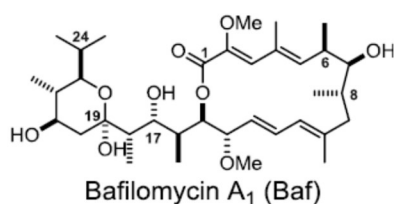
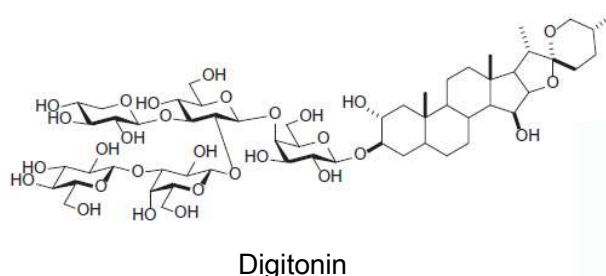
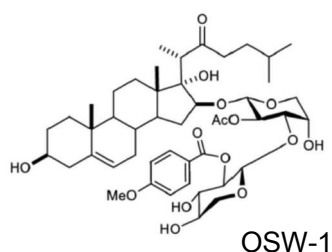
Keywords : *Natural product chemistry; solid-state NMR; saponin*

天然物の生物作用を考えるうえで細胞膜との相互作用は、標的分子への結合の親和性と同様に重要な研究対象である。脂質二重膜環境下での分子挙動は、有機分子が細胞膜と相互作用する際の生物学的活性を大きく左右する。しかし、この特性に対する化学的アプローチは、標的分子への結合に関する構造生物学的手法と比較して成功していない。近年、天然物のわずかな構造の違いが膜脂質との相互作用に大きな影響を与えることが明らかとなり、膜結合過程が天然物の疎水性以外の構造的要因の重要が広く認識されるようになった。本講演では、天然物と生体膜の相互作用が生物活性に特異的に寄与している事例を、天然物のなかでもサポニンや抗生物質に焦点を当てて紹介する。

ユリ科植物球根由来の OSW-1 は、コレステロールとの相互作用によって効率的に膜に結合し、二重膜構造をほとんど改変することなくイオン透過性を有する会合体を形成する¹⁾。この OSW-1 の活性の強さは、代表的な膜破壊性サポニン・digitonin とほぼ同等であり、かつ、類似のステロール依存性を示すが、両者のメカニズムは膜破壊の程度において明確に異なっている¹⁻²⁾。

膜タンパク質 ATPase の阻害剤である bafilomycin A₁ (Baf) は、高い膜結合性を示す。一方、そのメチル基を除去した誘導体(desFBaf)は膜結合性が大幅に低下するが³⁾、その違いが分子の柔軟性に起因することが、フッ化体の固体 NMR 測定によって明らかになった⁴⁾。すなわち、Baf のマクロラクトン環と 16 位以降の側鎖は比較的安定した立体配座を取るが、desFBaf の場合は、環部分の安定配座の違いによって側鎖との水素結合が弱くなり、分子全体の剛直性が低下することによって、脂質二重膜に結合しにくくなっていることが示唆された。

なお、OSW-1 については、東京農工大学・櫻井香里博士、本研究室の花島慎弥博士との、bafilomycin については、大分大学・土川博史博士との共同研究成果である。



- 1) Sterol-Recognition Ability and Membrane-Disrupting Activity of Ornithogalum Saponin OSW-1 and Usual 3-O-Glycosyl Saponins. Malabed, R., Hanashima, S., Murata, M., Sakurai, K. *Biochim. Biophys. Acta*, 1859, 2516-2515 (2017).
- 2) Interactions of OSW-1 with lipid bilayers in comparison with digitonin and soyasaponin. Malabed, R., Hanashima, S., Murata, M., Sakurai, K. *Langmuir* 36, 3600-3610 (2020).
- 3) Modification of bafilomycin structure to efficiently synthesize solid-state NMR probes that selectively bind to vacuolar-type ATPase. Shibata, H., Tsuchikawa, H., Hayashi, T., Matsumori, N., Murata, M. and Usui, T. *Chem. Asia. J.* 10(4), 915-924 (2015).
- 4) Diosgenin-induced physicochemical effects on phospholipid bilayers in comparison with cholesterol. Ondevilla, J. C., Hanashima, S., Mukogawa, A., Umegawa, Y., Murata, M. *Bioorg. Med. Chem. Lett.* 36, 127816 (2021).

古くて新しい天然物化学の課題：ネコのマタタビ反応の謎に挑戦する

(名大院生命農学¹⁾ ○西川俊夫¹

Challenge of mysteries of the Matatabi reaction of cats, old but still fascinating issue of natural product chemistry (¹ Graduate School of Bioagricultural Sciences, Nagoya University)

○Toshio Nishikawa¹

When a domestic cat (*Felis silvestris catus*) encounters a plant Matatabi (*Actinidia polygama*), it behaves like euphoric rubbing and rolling, thus this phenomenon is called the Matatabi reaction of cats. In the 1950s to 1960s, matatabilactones were isolated as the active ingredients that evoke this reaction. However, many mysteries associated to the matatabi reaction, such as why only felines react to matatabi and what the behavioral significance is, had not been clarified yet. Several years ago, we initiated to investigate molecular mechanism of the Matatabi reaction of cats and found that the matatabilactones are not enough for induction of the Matatabi reaction in cats. Re-investigation of active component from matatabi leaves revealed nepetalactol as new and more active compound inducing the reaction. Behavioral analysis of cats using synthetic nepetalactol and finding of potent repellent activity of nepetalactol against mosquitoes led us to conclude that the matatabi reaction is not simple euphoric behavior but for chemical defense against mosquito bites. In this symposium, the details of these studies and the latest results on the matatabi reaction will be discussed.

Keywords : cats, Matatabi reaction; iridoids, nepetalactol; repellent activity

ネコ科動物にマタタビを与えると、陶酔したようにゴロゴロ転がる特有な行動、マタタビ反応を示す。1950-60年代、この反応を引き起こす活性成分として通称「マタタビラクトン」が単離された。しかし、その後長い間なぜネコ科動物だけがマタタビラクトンに反応し、その行動の意義は何なのかなど、数多くの謎が解明されずに残されていた。我々は、数年前マタタビ反応の分子機構解明を目指して研究を始め、化学合成したマタタビラクトンにマタタビ反応を誘導する十分な活性がないことに気づき、改めてマタタビ葉から活性物質の抽出を試み、強力な活性を示すネペタラクトールを同定した。次いで、合成したネペタラクトールを使ったネコの行動解析から、マタタビ反応はネコがネペタラクトールを体に擦り付ける行動であることを明らかにした。ネペタラクトールの生物活性を調べるなか、ネペタラクトールに蚊に対する忌避活性があることを発見し、実際にマタタビ反応したネコも蚊に刺されにくくなることを見出した。以上の結果より、ネコのマタタビ反応は、単にネコが陶酔して転がっているのではなく、昆虫忌避活性を示すマタタビの成分を体に付着させ、害虫から身を守るための防御行動だったと結論した¹⁾。本講演では、以上の研究の詳細とともに、ネコがマタタビ葉に障害を与えた時のイリドイド成分の変化とそれに対するネコの反応など最新の研究成果について紹介する。

1) R. Uenoyama et al. *Science Advances* **2021**, eabd9135.

Symposium | Medium and Long-Term Program | Tasks and prospects for social implementation of artificial photosynthesis technologies

[B202-1am] Tasks and prospects for social implementation of artificial photosynthesis technologies

Chair, Symposium organizer: Ryu Abe, Akihiko Kudo, Hiroaki Misawa

Wed. Mar 23, 2022 9:00 AM - 11:40 AM B202 (Online Meeting)

[B202-1am-01] Established output of Artificial photo synthesis project granted by NEDO and perspective view for its industrialization

○Tohru Setoyama¹ (1. Mitsubishi Chemical Corporation)

9:05 AM - 10:05 AM

[B202-1am-02] Hydrogen and selective production of valuable chemicals for economical artificial photosynthesis

○Kazuhiro Sayama¹ (1. National Institute of Advanced Industrial Science and Technology (AIST))

10:10 AM - 10:40 AM

[B202-1am-03] Development of energy supply to houses by artificial photosynthesis technology

○Yutaka Amao¹ (1. Osaka City University)

10:40 AM - 11:10 AM

[B202-1am-04] Recent progress in Solar-driven CO₂ Reduction Reaction Systems Utilizing Molecular Catalysts and Semiconductors

○Takeshi Morikawa¹ (1. Toyota Central R&D Labs., Inc.)

11:10 AM - 11:40 AM

Established output of Artificial photo synthesis project granted by NEDO and perspective view for its industrialization

(Mitsubishi Chemical Corp. Science & Innovation Center) ○Tohru Setoyama

Keywords: Artificial Photosynthesis, Photo catalyst, water splitting, CO₂ utilization, Reactive separation

It has passed 10 years since the start of ARPCChem project at 2012. We have conducted four subjects as shown in Figure 1.

Development of photo catalyst for water splitting under visible light is the most important subject. Sun light conversion to hydrogen(STH) is the key index of catalytic activity. By the simulation study of economic feasibility of obtained green hydrogen, we concluded that 5% or more as STH is required. Furthermore, photo catalyst sheet by coating of powder catalyst on support is useful for the realization of cheap module of hydrogen production combined with safe & selective separation membrane. In order to compare the scalability by photocatalytic system, Figure 2 shows the comparison of output of photo electrode systems and photo catalyst sheet. While photo electrode system has trade-off relationship between activity and scalability, photo catalyst sheet could exceed its limit easily. 10% as STH and 1ha installation of photo catalyst sheet is the threshold of commercialization.

AS a CCU technology, reactive separation of methanol synthesis is very attractive from LCA view point. By introducing zeolite membrane, Equilibrium limit can break easily, resulting in the very small recycle. Very selective conversion of methanol to requested olefin will be useful for realistic application of CO₂ as a differentiation from cracker process.

We will show many results of four subjects in ARPCChem project and argue their economic feasibilities. We think that the economic feasibility is the key for the commercialization of artificial photo synthesis even it shows enough LCA improvement.

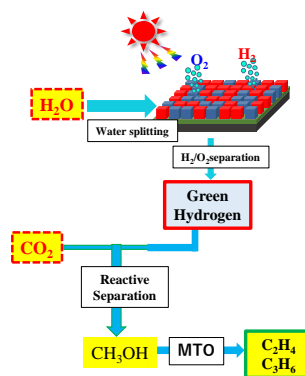


Figure 1 Four subjects of Artificial photo synthesis

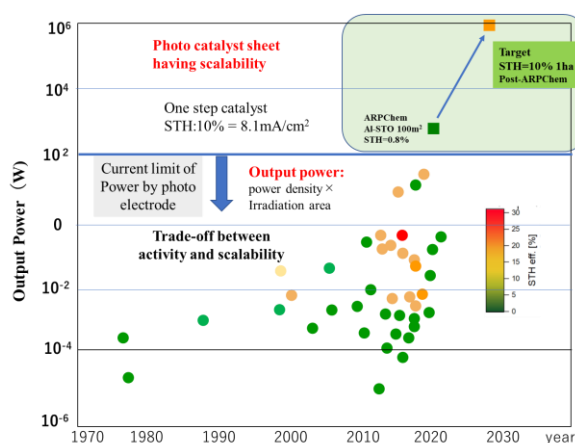


Figure 2 Scalability of photo catalyst sheet as a comparison with photo electrode for water splitting

経済性のある人工光合成のための水素および選択的有用化学品製造

(産総研・ゼロエミッション国際共同研究) ○佐山和弘

Hydrogen and selective production of valuable chemicals for economical artificial photosynthesis (National Institute of Advanced Industrial Science and Technology (AIST))
Kazuhiro Sayama

This presentation reviews the recent progresses on the oxidative production of various high-value-added chemicals using simple and inexpensive oxide semiconductor photoanodes for the technology associated with solar-to-chemical conversion processes. The photoelectrochemical production of oxidizing reagents can be highly economical and contribute to global warming by replacing the conventional processes. Various oxidizing reagents and useful chemicals, such as H_2O_2 , HClO , persulfates and organic compounds, can be produced photoelectrochemically with excellent faradaic efficiencies. These photoelectrochemical processes are key technologies enabling the expansion of solar energy utilization toward a sustainable and low-carbon society.

Keywords : Artificial photosynthesis; H_2 ; solar-to-chemical; photoelectrochemical production

経済合理性のある人工光合成技術として、湿式の空気焼成で調製でき、単位面積当たりのコストが低い酸化物系光電極による有用化学品製造の研究は近年盛んに検討されている。酸素発生以外のアップヒルの酸化反応は単発的に論文が報告されていたが、その報告例は非常に少なく、その意義は単に学術的な立場であった。我々は、太陽エネルギーで水素と同時に様々な酸化剤などの有用化学品を製造できる新規光電気化学システムの可能性を検討してきた。その研究の中での注目すべき成果 (HClO や H_2O_2 生成等) をいくつか報告する。

例えば、 HClO は漂白剤や消毒薬、上水道殺菌剤として広く使われている。最近では抗ウイルス作用も注目されている。世界中で膨大な量が利用され、電子当たりの価格や CO_2 排出係数が酸素に比べて格段に大きく、経済性や環境性のインパクトは非常に大きい。我々は $\text{BiVO}_4/\text{WO}_3$ 光電極を用いて、 NaClO 生成の電流効率が約 80% になること、および反応初期においては 97% と非常に高いことを報告した。小さな分散システムでは、 O_2 還元と組み合わせれば非常にシンプルな自立システムが構築できる。このような光電極や光触媒技術を用いれば、将来的には外部電力無しで、 NaCl から NaClO を効率良く製造できる。また最近我々は海水電解の選択性が表面に担持する助触媒で制御できることを見いだした¹⁾。 NaCl 水溶液中の $\text{BiVO}_4/\text{WO}_3$ 光電極上での助触媒修飾の検討を行ったところ、マンガン酸化物 (MnO_x) を担持すると特異的に幅広い条件下で HClO を生成せずに酸素のみ生成することが分かった。マンガン以外の金属元素を修飾した光電極を用いた場合には、 HClO と酸素が生成した。マンガンを修飾した光電極において HClO 生成が著しく抑制される挙動は、用いた NaCl 水溶液の pH や Cl^- 濃度、マンガン前駆体やマンガン酸化物の結晶構造の違い、異種元

素との複合 ($\text{Mn}/\text{Ca}=4$ のカルシウム複合など) によってもほとんど変化せず、マンガンは非常に広範な条件下で選択的に HClO 生成を抑制しながら酸素を発生できる非常に特異な元素であることを明らかにした。この挙動は多種多様な共存イオンを含む人工海水でも再現されることを確認した。今回の成果は海水や塩水を用いた太陽光水素製造技術の実用化に貢献するだけでなく、天然光合成の理解の深化にも貢献する可能性がある。天然光合成の酸素発生中心は、マンガンの酸化物集合体で構成されているが、マンガンという元素が使われる理由は不明であった。これまで、天然で Mn 以外の O_2 発生中心は見つかっておらず、 O_2 発生過電圧の低く賦存量の大きい他の元素 ($\text{Fe}, \text{Ni}, \text{Co}$ 等) が使われなかった理由は不明確であった。今回の光電極を用いた実験結果から、「生物にとって有害な HClO 生成を幅広い条件下で抑制できるというマンガンの特異的な性質が酸素発生中心の進化に関与している」という新たな仮説を提唱できた。殺菌性の高い HClO が生成しないという希有な特徴を持った MnOx は天然光合成にとって唯一の選択肢だったと推察できる。天然光合成と人工光合成研究の相互理解と融合が進むことで、革新的なシステム構築に寄与すると考えられ、この成果はまさにその本質的な異分野融合の好例と言える。

また、我々は光電気化学的な選択有機変換の研究にも注力している。KA オイルなどポリマー材料の酸化的な有機変換はシステム全体の経済性を大きく高める可能性がある。人工光合成研究は水素や CO_2 還元の研究にとどまらずに、様々な展開の可能性を秘めている。新しい言葉が生まれながら異分野融合が進んでいくと考えられる。これらの研究の動向についても紹介する。

1) AIST プレス (2020.10.9)。S. Okunaka, Y. Miseki K. Sayama, iScience, 23, 101540 (2020).

人工光合成技術による住宅へのエネルギー供給の実現性

(阪市大人工光合成セ) ○天尾 豊

Development of energy supply to houses by artificial photosynthesis technology (*Research Center for Artificial Photosynthesis, Osaka City University*) ○Yutaka Amao

Although artificial photosynthesis has been expected for the long time, it has not been realized yet. Artificial photosynthesis technology requires solar energy and lacks the decisive means of climate change or nighttime energy supply. In addition, although artificial photosynthesis technology is promising in terms of renewable energy utilization, it is still difficult to cover large-scale energy such as the entire city. In this lecture, the demonstration of artificial photosynthesis technology for supplying energy to house is introduced. The energy supply system for houses consists of the reduction of carbon dioxide to formic acid by solar energy (artificial photosynthesis technology) and hydrogen production based on catalytic decomposition of formic acid.

Keywords : *Artificial photosynthesis; Carbon dioxide utilization; Hydrogen energy*

人工光合成系は、長年にわたって期待されているものの、これまでに実現することはなかった。人工光合成技術には太陽光エネルギーが必要であり、気候変動あるいは夜間のエネルギー供給手段の決め手を欠いていた。また、人工光合成技術は有望であるものの、市街全域などの大規模なエネルギーを賄うことはいまだ困難である。そこで、人工光合成系の実証の場とした住宅一棟の電力を賄うことを目的とした取り組みを紹介する。

具体的には二酸化炭素をギ酸に還元する人工光合成系とギ酸を分解し水素を製造する触媒系を住宅に搭載し、エネルギー供給と二酸化炭素循環とを両立させたシステムである(図1)。

太陽光エネルギーと二酸化炭素から製造したギ酸を水素エネルギーキャリアとして用いる場合、ギ酸を効率的に水素と二酸化炭素へ分解するための触媒が必要である。親水性高分子ポリビニルピロリドン(PVP)を分散剤としたコロイド状白金微粒子(Pt-PVP)を触媒として用いることによってギ酸を選択的に水素と二酸化炭素に分解できることを見出している。これまでに、Pt-PVPのギ酸分解に基づく水素生成機構につ

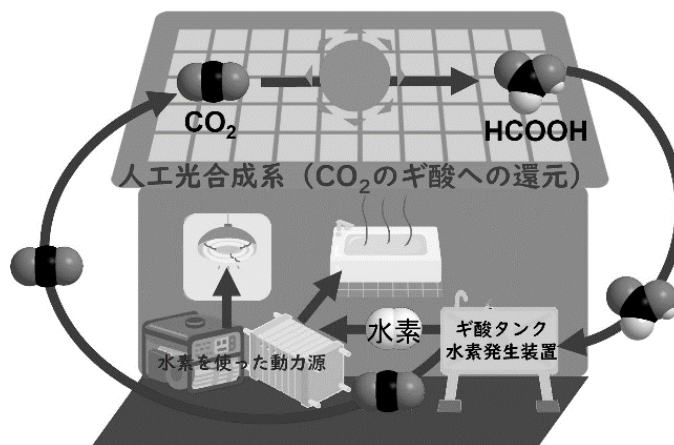


図 1. 二酸化炭素からギ酸を生成する人工光合成系とギ酸から水素生成する触媒系を搭載した住宅の概念図

いて赤外分光法や X 線吸収微細構造解析等により明らかにしてきた。その結果、電子供与性を持つ高分子 PVP をコロイド分散剤として使用することで、白金微粒子のギ酸分解に基づく水素生成活性の向上が可能であることがわかった。また、白金微粒子内の白金原子の価数を 0 価に制御することで、ギ酸分解に基づく水素生成を選択的に触媒し、一酸化炭素を含まない水素生成が可能であることも見出した。これまでの知見を基に Pt-PVP を触媒として用いたギ酸分解に基づく水素生成についてスケールアップ実験の検討結果の一例を示す。pH 3.5 に調整した 3.0 M ギ酸水溶液 30 mL (に Pt-PVP (4 wt%) 3 mL を加え、反応温度 60°C で反応させた。バイアル瓶の全体積は 110 mL であり、気相は約 77 mL である。また、反応と同時に気相に水素と二酸化炭素が放出され平衡圧に達することを防ぐため、バイアル瓶の可動式のシリンダを取り付け、生成した気体の体積を測定した。結果を図 2 に示す。反応時間とともに生成する気体の体積が定常的に増加していることがわかる。反応時間 90 分で生成した気体の体積は 1.4 L にまで増加し、42.6 mmol (1.1 L) の水素生成が観測され、およそ 50% のギ酸が水素に分解できた。

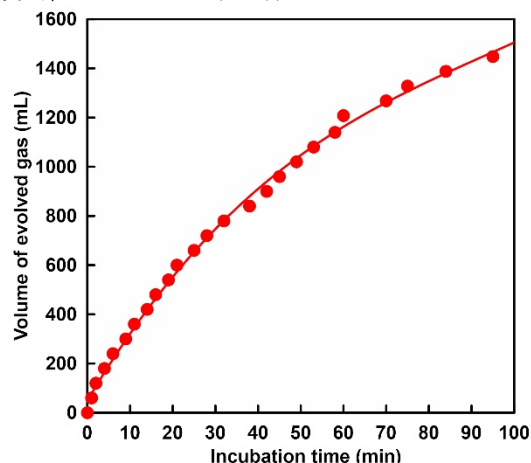


図 2. Pt-PVP が触媒するギ酸分解に基づく生成気体体積の経時変化

二酸化炭素をギ酸に還元する人工光合成系についてはこれまでに、ギ酸脱水素酵素と色素、半導体光触媒とを複合化させた反応系を構築してきた。実用を見据えた場合、これら反応系をデバイス化する必要がある。人工光合成系デバイスの一例として、シリカゲルベースの薄層クロマトグラフ (TLC) プレート上に太陽光捕集・増感分子、電子伝達分子及び酵素を固定化した基板固定型光駆動二酸化炭素 - ギ酸変換デバイスの構築に至っている。このデバイスでは、太陽光捕集・増感分子として緑色植物等から抽出したクロロフィルを加水分解したクロリン e_6 (H_2Chl-e_6)、電子伝達分子として長鎖アルキル基を有するビオローゲン分子 (1-メチル-1'-カルボキシウンデカノイル-4,4'-ビピリジニウム: $CH_3-V-COOH$)、酵素としてギ酸脱水素酵素を用いている。このデバイスに電子供与分子を含む二酸化炭素を飽和した pH7.4 の緩衝液中で可視光照射するとギ酸が定常的に生成することを見出した。現在、このデバイスの構成要素を検討し、ギ酸脱水素酵素の代替えとなる触媒開発や半導体光触媒との複合化等を進め、ギ酸生成効率向上に取り組んでいる。

これら要素技術についてスケールアップ等を進め、住宅一棟へのエネルギー供給の実証実験を開始する予定である。

分子触媒と半導体を活用した太陽光 CO₂ 還元反応系の進展

(豊田中研) ○森川 健志

Advances in Solar-driven CO₂ Reduction Reaction Systems Utilizing Combinations of Molecular Catalysts and Semiconductors (*Toyota Central R&D Labs., Inc.*) Takeshi Morikawa

An artificial photosynthetic reaction, which is solar-driven carbon dioxide (CO₂) reduction using water (H₂O) as an electron donor and proton source, to produce high-value carbon compounds is expected to contribute to a carbon-neutral society in the future. This is also regarded as a technology to create light energy carriers based on CO₂. Our main approach is developing photosystems composed of metal complex molecular catalysts for CO₂ reduction reaction and semiconductor materials for light absorption and charge separation. For H₂O oxidation, semiconductor photocatalysts and inorganic compounds are used. Three typical approaches, (1) photocatalysts, (2) photoelectrodes, and (3) solar-powered electrolyzers (combination of solar cells and electrodes) will be introduced (Figure 1).

Keywords : CO₂ reduction; Water; Solar Energy; Artificial Photosynthesis; Photocatalysis

人工光合成は、植物の光合成の様に太陽光エネルギーで二酸化炭素(CO₂)と水(H₂O)を反応させる事で、活用価値の高い化合物を合成します。この技術は CO₂ 排出量の低減だけでなく CO₂ を基にした光エネルギーキャリアの実現にも繋がる可能性があり、将来におけるカーボンニュートラル社会への貢献が期待されています。

当研究グループが研究開発を進めている人工光合成の主な方式は、CO₂ 還元反応場に金属錯体分子触媒を、そして光の吸収・電荷分離には半導体材料を用いて、これらの優れた機能を連結させるものです。また H₂O の酸化反応には半導体光触媒や無機化合物の触媒を活用します。我々は、主に①光触媒、②光電極、③太陽光電解(太陽電池と電極の組合せ)、の3つの方式に取り組んでいます(図1)¹⁾。講演では、これらの方式における我々の取り組み事例を紹介します。

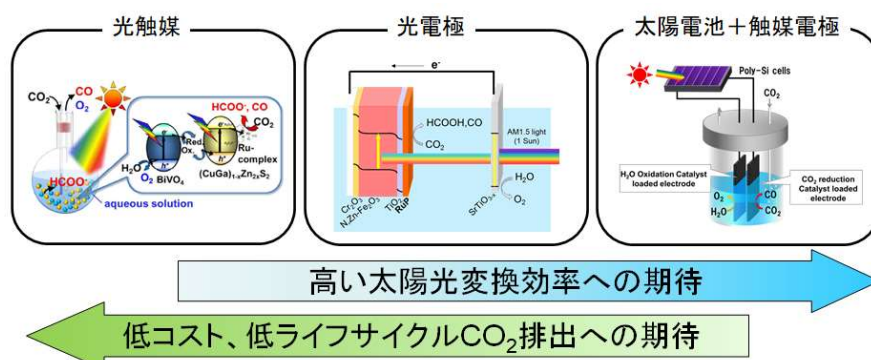


図1 分子触媒と半導体を活用した太陽光 CO₂ 還元反応系

- 1) Solar-Driven CO₂ Reduction Using a Semiconductor/Molecule Hybrid Photosystem: From Photocatalysts to a Monolithic Artificial Leaf, T. Morikawa, S. Sato, K. Sekizawa, T. M. Suzuki, T. Arai., *Acc. Chem. Res.* **2021**, (doi.org/10.1021/acs.accounts.1c00564).

Symposium | Medium and Long-Term Program | Frontier of new paradigm of molecular systems chemistry – Design and measurement of concerted molecular functions

[B202-1pm] Frontier of new paradigm of molecular systems chemistry – Design and measurement of concerted molecular functions

Chair, Symposium organizer: Kunihiko Ishii, Shun-Ichi Ishiuchi

Wed. Mar 23, 2022 1:00 PM - 3:40 PM B202 (Online Meeting)

[B202-1pm-01] Chem-Bio Hybrid, a Chemically Engineered Enzyme Encapsulated in a Molecular Cage

○Daishi Fujita¹ (1. Kyoto University)

1:05 PM - 1:30 PM

[B202-1pm-02] Structures and functions of supramolecules investigated by cold gas-phase spectroscopy

○Satoru Muramatsu¹ (1. Hiroshima Univ.)

1:30 PM - 1:55 PM

[B202-1pm-03] Signal-Amplification Sensing with Functional Chemosensors

○Gaku Fukuhara¹ (1. Tokyo Institute of Technology)

1:55 PM - 2:20 PM

[B202-1pm-04] Efficient and robust photoreaction regulated by multiple molecules in pigment protein complexes

○Toru Kondo¹ (1. Tokyo Tech.)

2:20 PM - 2:45 PM

[B202-1pm-05] Toward rational control of concerted functions exerted by protein complexes

○Takahiro Kosugi^{1,2,3,4} (1. Institute for Molecular Science, 2. ExCELLS, 3. SOKENDAI, 4. JST PRESTO)

2:45 PM - 3:10 PM

[B202-1pm-06] Coordination of 5,000 cells produces swimming and phototactic behavior in the multicellular green alga *Volvox*

○Noriko Ueki¹ (1. Hosei University)

3:10 PM - 3:35 PM

Chem-Bio Hybrid, a Chemically Engineered Enzyme Encapsulated in a Molecular Cage

(¹Institute for Integrated Cell-Material Sciences (iCeMS), Kyoto University) ○Daishi Fujita

Keywords: *self-assembly; protein.*

Spatial isolation of molecules is often a powerful strategy for regulating their molecular behavior. Biological systems well-employ such mechanisms, however, scientists have yet to rival nature, particularly for macromolecular substrates. We demonstrated that a “wireframe” molecular scaffold improves the structural and enzymatic properties of a protein encapsulated within. Particularly, when the three-dimensionally confined enzyme was exposed to an organic solvent, its half-life was prolonged 1000-fold. Kinetic and spectroscopic analysis of the enzymatic reaction revealed that the key to this stability is the isolated space; this is reminiscent of chaperonins, which use their large internal cavities to assist the folding of client proteins. The single-molecule protein-caging affords a new type of protein-based nanobiotechnology that accelerates molecular biology research as well as industrial applications.

Figure 1

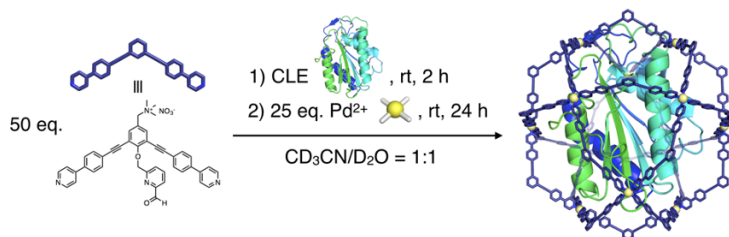
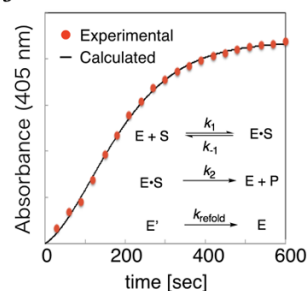


Figure 2



[1] D. Fujita, R. Suzuki, Y. Fujii, M. Yamada, T. Nakama, A. Matsugami, F. Hayashi, J. -K. Weng, M. Yagi-Utsumi, M. Fujita *Chem* **2021**, 7, 2672.

[2] D. Fujita, Y. Ueda, S. Sato, N. Mizuno, T. Kumasaka, M. Fujita *Nature* **2016**, 540, 563.

[3] D. Fujita, Y. Ueda, S. Sato, H. Yokoyama, N. Mizuno, T. Kumasaka, M. Fujita *Chem* **2016**, 1, 91.

[4] D. Fujita, K. Suzuki, S. Sato, M. Yagi-Utsumi, Y. Yamaguchi, N. Mizuno, T. Kumasaka, M. Takata, M. Noda, S. Uchiyama, K. Kato, M. Fujita *Nat. Commun.* **2012**, 3, 1093.

気相極低温分光で見るホストゲスト相互作用：超分子の構造と機能の解明に向けて

(広島大院先進) ○村松 悟

Structures and functions of supramolecules investigated by cold gas-phase spectroscopy

(¹Grad. School of Advanced Science and Engineering, Hiroshima Univ.) Satoru Muramatsu

Gas-phase spectroscopy under cold condition by using a cryogenic (~4 K) ion trap is a powerful tool to investigate host-guest interactions, by visualizing slight conformational change of the host molecule as clear spectral difference. In this talk, I show our recent studies particularly on crown ether complexes with ammonium ion guests; we discuss how the structure of these molecules are determined, and demonstrate the exceptional ability of this method to unveil the host-guest interactions.

Keywords: Host-guest chemistry; Supramolecules; Gas-phase spectroscopy; Cryogenic Ion trap

ホストゲスト相互作用は超分子形成における基本単位であり，その緻密な繰り返しによって，DNA の二重らせん構造やタンパク質の高次構造，種々の超分子ポリマーのような，協奏的機能を発現しうる高秩序なナノ構造体が形成される。一方で，このような超分子を構成する分子の多くは柔軟で様々な構造を取り得るため，たった1箇所相互作用部位だけでもその会合様式を決定することは容易でない。この問題に対し，我々は，極低温イオントラップ中に孤立させたイオンの気相分光手法（図 1a）を活用することで，代表的なゲスト分子（クラウンエーテルやカリックスアレーン）による包接錯体の会合様式を明らかにしてきた。例えば，エチルアンモニウム-ジベンゾ-18-クラウン-6 錯体（EtNH₃⁺·DB18C6）に対して異性体選別赤外分光を行ったところ，2種類の異なる赤外スペクトルを得た（図 1b）^[1]。単結晶中にも現れる既知構造に加えて，クラウンエーテルのジエチルエーテル部位が面外に外れた新規構造を見出し，それが NH···O 間の強い水素結合に起因することを明らかにした。気相極低温分光によって，このような幾何構造的にわずかな違いを捉え，明瞭に異なるスペクトルとして可視化できるのである。講演では，まず，この分光を実現するための装置論および測定原理（図 1a）を概説する。その後，上述の EtNH₃⁺·DB18C6 を含む種々のクラウンエーテル-アンモニウム錯体の構造^[1,2]を紹介し，特に単結晶中などの従来環境では現れないような特異な構造に注目しながら，その起源を議論する。

[1] Kubo, M; et al. *J. Phys. Chem. A* **2020**, *124*, 3228. [2] Goda, R.; et al. *J. Phys. Chem. A* **2021**, *125*, 10410.

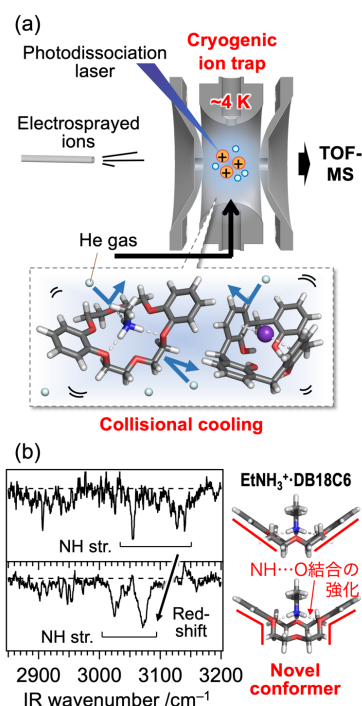


Fig. 1. (a) Schematic image of cold gas-phase spectroscopy by using a cryogenic ion trap. (b) Isomer-selective IR spectra and corresponding structure of EtNH₃⁺·DB18C6 complexes. Red lines are eye-guides to show tilting of a diethyl ether moiety in the bottom structure.

高度に機能化された化学センサーを用いる増幅計測 ～分子、超分子、高分子から細胞に至る広範囲な系の制御に向けて～

(東工大理¹) ○福原 学¹

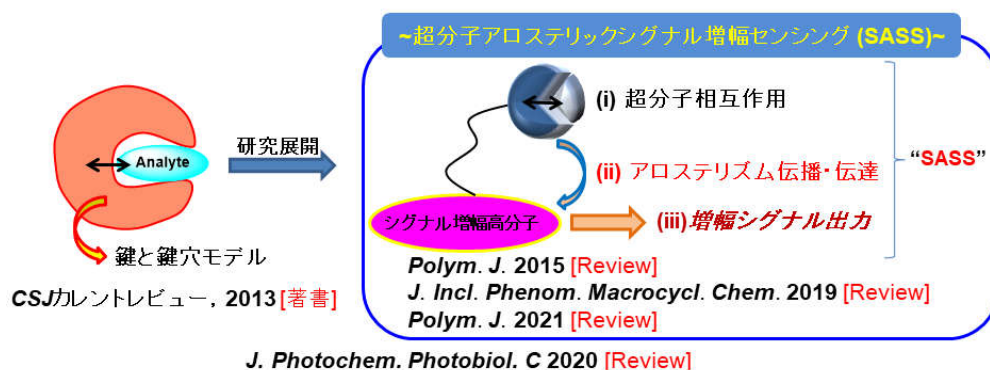
Signal-Amplification Sensing with Functional Chemosensors (¹Department of Chemistry, Tokyo Institute of Technology) ○Gaku Fukuhara¹

Chemical sensing is one of the most challenging topics in current chemistry. Such an analytical approach by using synthetic molecular receptors or chemosensors has attracted a great deal of attention in recent years. In this presentation, a novel sensing method, which is defined as “supramolecular allosteric signal-amplification sensing”, and the related results will be discussed.

Keywords : Amplification Sensing; Chemosensor; Allosterism

現在、医薬系・生体系・環境問題など幅広い分野において、特定の検体を高感度かつ選択的に検知できる化学センサーの開発は、ナノテクノロジーとも密接に関連し社会に対する波及効果は高く、現代化学の最重要テーマである¹。このような分析化学ならびに超分子化学分野の融合領域に跨る学問は、新たな学術領域（Analytical supramolecular chemistry）として統一されつつある^{2a}。

近年では、分子構造的にも物性的にも多様化してきている検体や生体内での夾雑系を標的とした時、もし化学センサーの設計・開発後に検体に対してセンサーの認識サイト（レセプター）の形やサイズが適合しなければ低感度・低選択性といった問題点を抱えている（左図）。我々はこのような背景の基、生体内認識過程で精緻に活用されているアロステリック効果に想を得て、レセプターから分光リポーターへとアロステリックに伝播した情報を増幅して読み取る「Supramolecular Allosteric Signal-amplification Sensing (SASS)」手法を提案した（右図）²。本講演では、この進展著しい **SASS** に基づく結果について議論したい。



1) (a) You, L.; Zha, D.; Anslyn, E. V. *Chem. Rev.* **2015**, *115*, 7840. (b) Schroeder, V.; Savagatrup, S.; He, M.; Lin, S.; Swager, T. M. *Chem. Rev.* **2019**, *119*, 599.

2) (a) Fukuhara, G. *J. Photochem. Photobiol. C* **2020**, *42*, 100340. (b) Fukuhara, G. *Polym. J.* **2015**, *47*, 649. (c) Fukuhara, G. *J. Incl. Phenom. Macrocycl. Chem.* **2019**, *93*, 127. (d) Fukuhara, G. *Polym. J.* **2021**, *53*, 1325.

複数の分子が織りなす安定・高効率な生体光反応

(東工大生命理工・JST さきがけ) ○近藤 徹

Efficient and robust photoreaction regulated by multiple molecules in pigment protein complexes

(Dept. of Life Sci. Tech., Tokyo Tech., JST-PRESTO) ○Toru Kondo

Biological system achieves high-efficiency, robustness, and multi-functionality. The function is mediated by functional molecules embedded in a protein. While the molecular properties are important to drive the system, I emphasize here that the protein serving as a scaffold gives more essential advantages as the following: First, the protein has inhomogeneous molecular binding sites, offering different physical properties even for the same type of molecule. Second, molecular arrangements are highly optimized within the protein. Third is the structural flexibility, leading to robustness and allowing response to environmental perturbations. Thus, by tuning the protein scaffold, the system can obtain a variety of functions with only few types of molecules. A lot of studies using spectroscopies, structural analyses, and theoretical approaches, revealed arrangements and inhomogeneous properties of molecules in proteins. However, the structural flexibility and dynamics of proteins remain poorly understood, because the structural change is so small and often stochastic that it is averaged out and hence not observed by conventional ensemble measurements. To overcome the limitation, I apply the single-molecule spectroscopy. In this talk, I will discuss how the protein dynamics contribute to the photochemical reaction in photosynthetic protein complexes, based on the fluorescence fluctuation, cryogenic spectrum, and time-resolved signal observed at the single-molecule level. *Keywords* : *Single-molecule spectroscopy; Protein dynamics; Photosynthesis; Photochemical reaction*

高効率で安定な光電変換反応を実現するにはどうすればよいだろうか？これは光デバイスを開発する際の共通議題である。反応効率を高いレベルで維持するだけであれば、硬い構造基盤に最適な配置で機能分子を結合すればよい。しかしそれでも、光吸収・光エネルギー輸送・光電変換などの機能に特化した素子を複数組み合わせる必要がある。ここでさらに、入力信号となる光の強度が揺らいでも反応が一定の割合で生じる、という安定性（機能的なロバスト性）まで考慮しようとする、フィードバック制御機構が必要となり系はより複雑になる。このような系を人工的に設計するのは難しく、構築するには多大なコストを伴う。一方、生体光合成系は、タンパク質と数種類の機能分子を組み合わせるだけでこれを実現している。

光合成タンパク質にはクロロフィル (Chl) やカロテノイド (Car) などの色素分子が複数結合し (図 1)、反応を媒介する。しかし、機能発現にとって本質的に重要なのは結合分子よりもむしろ土台となるタンパク質である。特に以下の3つの性質が鍵を握る。1つ目は「不均一な媒質特性」であり、分子結合サイト毎にリガンドとなるアミノ酸分子の種類や配置が最適化され、全く同じ Chl 分子でも異なる物性（エネルギー準位や酸化還元電位など）を示す。これにより、光吸収・光エネルギー輸送・光電変換などの複数機能を、基本的には Chl 分子だけで達成できる。2つ目は「分子配置

の自由度」であり、3次元的な分子位置や配向が最適化されている。3つ目は「構造の柔軟性」であり、pH変化などの外部刺激でタンパク質構造が変化する。分子結合サイトの構造も歪み、ChlやCarの分子特性や相対配置が変化することで、新たな機能が発現する。各サイトの歪み方は不均一であり、分子物性は個別に調整されるため、より複雑な応答が可能となる。生体系は、このようなタンパク質の特性を活かし、たった数種類の部品だけで多機能化に成功している。一方で、その制御機構は解明されておらず、人工系に応用できるまでには至っていない。

タンパク質の3つの特徴のうち「不均一な媒質特性」や「分子配置の自由度」については、分光測定や構造解析、それらを基にした理論計算などから明らかになりつつある。一方で、「構造の柔軟性」に関しては、分子動力学(MD)計算などを用いた理論研究が進む中、実験検証の例がほとんどない。通常の光学測定では数兆～数京(10^{12} ～ 10^{16})個の粒子を一度に観測するため、不規則かつ微小な構造変化は平均化されて観測できない。そこで、タンパク質1粒子の分光解析が威力を発揮する(図1)¹⁾。本講演では、1分子・1タンパク質レベルで測定した蛍光揺らぎ^{2),3)}、極低温スペクトル⁴⁾、時間分解信号^{5),6)}などの解析結果を基に、光合成光捕集アンテナや反応中心などの光受容性タンパク質(図1)における生体光反応とタンパク質構造ダイナミクスの相関関係について議論する。

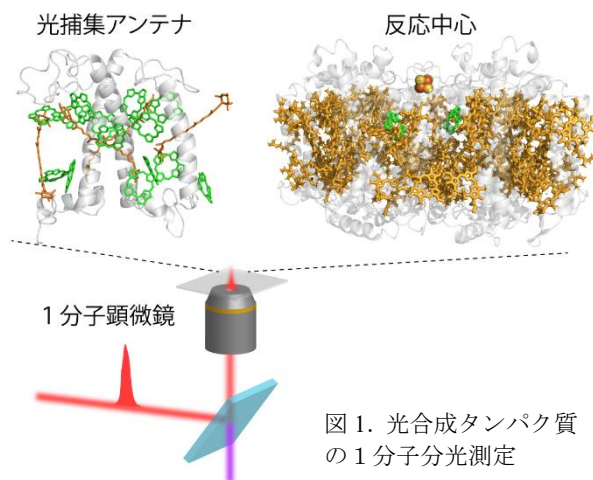


図1. 光合成タンパク質の1分子分光測定

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- 2) Kondo, T., et al., *Nat. Chem.* **2017**, *9*, 772-778.
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タンパク質複合体の協奏的機能を合理的に制御することを目指して

(分子研¹・ExCELLS²・総研大³・JST さきがけ⁴) ○小杉貴洋^{1,2,3,4}

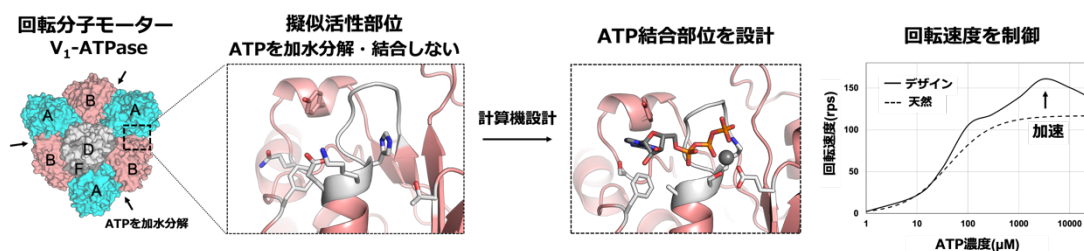
Toward rational control of concerted functions exerted by protein complexes (¹*Institute for Molecular Science*, ²*ExCELLS*, ³*SOKENDAI*, ⁴*JST PRESTO*) ○Takahiro Kosugi^{1,2,3,4}

Concerted functions of protein complexes are exerted by orchestrating the cooperative works between the constituent subunit. No study on rational control of concerted functions have been reported, although recently several protein design methods have been developed and native proteins have been redesigned to regulate or change the functions. Here, we show an approach to designing allosteric site which exerts the orchestration into protein complexes and report, by the approach, concerted function, rotation rate, of a molecular motor V_1 -ATPase was successfully regulated.

Keywords : Protein Complex; Protein Design; Concerted Function; Allostery

タンパク質複合体の協奏的機能は、それぞれのサブユニットが共同的に働くことで生み出される。その多くはアロステリックに制御されているため、新しいアロステリック部位を自由に設計することができれば、それらの協奏的機能を理解し制御することにつながる。しかしながら、これまでにタンパク質複合体に新たにアロステリック部位が設計された例はない。ここで、我々は近年急速に発展しているタンパク質の合理設計技術を用いて、タンパク質複合体にアロステリック部位を設計し、その協奏的機能を制御する方法を考えた。そして、回転分子モーターである V_1 -ATPase の速度を速く、かつ制御することに成功した¹。その成果と今後の展望についてお話しする。

タンパク質複合体の協奏的機能をアロステリック制御する



1) De Novo Design of Allosteric Control into Rotary Motor V_1 -ATPase by Restoring Lost Function. T. Kosugi, T. Iida, M. Tanabe, R. Iino, N. Koga, *bioRxiv* **2020**, 2020.09.09.288571.

緑藻ボルボックスの行動のしくみ—5,000 細胞の集合体が多細胞生物として機能するには

(法政大学¹) ○植木 紀子¹

Coordination of 5,000 cells produces swimming and phototactic behavior in the multicellular green alga *Volvox* (¹Science Research Center, Hosei University) ○Noriko Ueki¹

The spherical green alga *Volvox*, which lives in freshwater, is a simple multicellular organism consisting of ~5,000 cells. Flagella of each cell beat to generate a large water current, allowing the spheroid to swim forward as an individual. A *Volvox* spheroid steers toward light for photosynthesis and moves to the optimal environment. These behaviors are achieved by each cell following simple rules, not a commander or cell-cell communication. The mechanism and its evolutionary process will be discussed.

Keywords : Multicellularity; *Volvox*; Green Algae; Flagella; Behavior

ボルボックスは池や田など淡水に棲む植物プランクトンであり、くるくると回りながら遊泳する様子はまるでミラーボールのように美しい。球形の個体の表面に約 5,000 の体細胞が規則正しく並び、ここから生える鞭毛がその推進力を生み出している (図 1 a)。全ての鞭毛が個体の後端方向に向けて鞭のように打つことで、全体が前進する。この鞭毛の打ち方は「繊毛打」と呼ばれる (図 1 b)。回転遊泳するのは、繊毛打が個体の真後ろでなく、前後軸に対してやや傾いた向きに打つためである。

光合成をするボルボックスにとって、環境の光に素早く反応することが生存に重要である。そのため、急に周囲の光強度が変わると個体は遊泳を一時的に停止し、ブレーキをかけるような動きをする (光驚動反応)。また、一方向から来る光に対しては、光源方向へと向きを変えて移動する (走光性)。たった約 5,000 の細胞が集合した形のボルボックスが、どのようにしてこのような合目的な行動を行うのだろうか。また、そのしくみは単細胞生物から多細胞生物へと進化する過程でどのように獲得され、変化してきたのだろうか。本発表では、我々の研究から見てきたボルボックス光反応行動の自律分散システムとその進化について述べる。

我々は、それらの行動の要素として、ボルボックス細胞が周囲の光強度変化に対して一時的に繊毛打の方向を変化させることを見出した (図 1 c)。その反応性は個体前方の細胞ほど高く、前端では光刺激に反応して繊毛打方向がほぼ 180° 逆転した。光驚動反応の行動は、この繊毛打の方向変化で説明できる。一方、走光性では光の方向を検出する必要があるが、これは個体の回転により各細胞が感知する光が周期的に変動することを利用して。つまり、回転

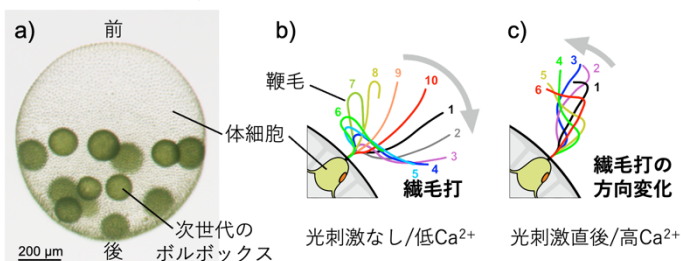


図 1 ボルボックスの体のつくりと体細胞から生える鞭毛の動き

遊泳によって光源側を向いた細胞のみ光強度の増加を感知し、一時的に繊毛打方向が変化してまたすぐ戻る。その結果、個体の光源側のみ推進力が減少し、光源方向へ向きを変える。実際、光の周期変動に反応して繊毛打の方向変化が繰り返し起きることを、実験的に確かめることができた¹⁾。

つまり、それぞれの細胞は「光強度の増加を感知したら繊毛打の方向を変える」という単純なルールに従っているだけであった。これに加えて、個体の前後にかけて光感受性の勾配があるだけで、ボルボックスは光驚動反応・走光性という2種類の光反応行動を見事に実現していることが判明した。

次に我々は、このしくみの進化過程を検証した。ボルボックスの光反応行動システムは細胞一つだけでは機能し得ない。祖先単細胞生物は異なるしくみを持ち、多細胞化進化の過程で変化したはずである。ボルボックスの属する生物群には、多細胞化進化の過程を反映する様々な細胞数の近縁種が現存している(図2)。ボルボックスが一つのルールで2種類の光反応行動を行うのに対し、近縁の単細胞種クラミドモナスは全く別の鞭毛運動で2種類の行動を行う。通常の繊毛打波形を「鞭毛打」波形に変換することで光驚動反応を行い、二本の鞭毛の打つ強さのバランスを変化させることで走光性の方向転換を行う。前者は 10^{-6} M以上、後者は 10^{-7} M程度の鞭毛内 Ca^{2+} で調節されることが報告されている。そこで我々は、ボルボックスにおける繊毛打の方向変化の由来を明らかにするため、界面活性剤で除膜処理した個体にATPを加えて運動を再活性化させる実験(通称ゾンビ・ボルボックス法)により、鞭毛運動に対する Ca^{2+} の影響を調べた。その結果、 10^{-6} M以上の Ca^{2+} で繊毛打方向変化が見られたことから、単細胞祖先生物の波形変換反応に由来すると考えられた²⁾。

さらに、中間的な細胞数を持つ種を含めた鞭毛の光反応様式は「反応なし」「繊毛打の停止」を加えた4パターンに分類できた(図2)。単細胞祖先生物が最初の多細胞化を経たとき光に対する鞭毛の反応が一旦なくなり、その後球形に進化すると繊毛打の停止を素要因とする光反応行動を行うようになったと考えられる。「繊毛打の方向変化」は最大サイズが1 mmを超える種に限られることもわかった。多細胞化進化の過程で、より大きな個体サイズの運動制御に適した様式が獲得されたと思われる。

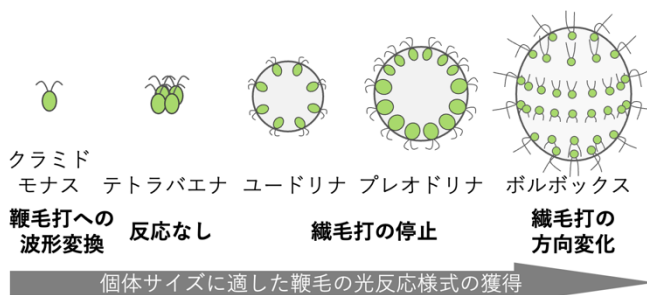


図2 大型化進化に合わせて獲得された鞭毛の光反応様式

- 1) How 5000 independent rowers coordinate their strokes in order to row into the sunlight: Phototaxis in the multicellular green alga *Volvox*. N. Ueki, S. Matsunaga, I. Inouye, A. Hallmann. *BMC biology*. **2010**, 8, 103.
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Symposium | Asian International Symposium | International Symposium on Molecular Science - Physical Chemistry / Theoretical Chemistry, Chemoinformatics, Computational Chemistry - Cosponsored by Japan Society for Molecular Science

[W1-1am] International Symposium on Molecular Science - Physical Chemistry / Theoretical Chemistry, Chemoinformatics, Computational Chemistry - Cosponsored by Japan Society for Molecular Science

Chair, Symposium organizer: Yasuhiro Ohshima, Miho Hatanaka, Akiyoshi Hishikawa

Wed. Mar 23, 2022 9:00 AM - 11:40 AM W1 (Online Meeting)

[W1-1am-01] Light-induced dynamics of molecules probed by an ultrafast stopwatch

○Jian Wu¹ (1. East China Normal University)

9:05 AM - 9:40 AM

[W1-1am-02] Air lasing by population inversion in N₂⁺ induced by strong-field coherent coupling of the X, A and B states

○Erik Loetstedt¹, Youyuan Zhang¹, Toshiaki Ando¹, Atsushi Iwasaki¹, Huailiang Xu², Kaoru Yamanouchi¹ (1. The University of Tokyo, 2. Jilin University)

9:40 AM - 10:00 AM

[W1-1am-03] Simulations of strong laser-driven multielectron dynamics using classical and quantum computers

○Takeshi Sato¹ (1. The Univ. of Tokyo)

10:00 AM - 10:20 AM

[W1-1am-04] Putting the ‘Chemistry’ back in to Chemical Vapour Deposition Nanomaterial Synthesis: Insight from Quantum Simulations

○Alister Page¹ (1. University of Newcastle)

10:25 AM - 11:00 AM

[W1-1am-05] Ionic Liquid Kinetics on Polarizable Electrode Surface

○Taichi Inagaki¹ (1. Keio University)

11:00 AM - 11:20 AM

[W1-1am-06] Multi-Scale Theoretical/Computational Approach to Heterogeneous Catalysis

○Atsushi Ishikawa¹ (1. National Institute for Materials Science)

11:20 AM - 11:40 AM

Light-induced dynamics of molecules probed by an ultrafast stopwatch

(State Key Lab. of Precision Spectroscopy, East China Normal University, Shanghai 200241, China) ○Jian Wu

Keywords: ultrafast molecular dynamics; femtosecond laser pulse;

We introduce an ultrafast stopwatch to probe the light-induced dynamics of molecules by using a polarization-skewed multicycle femtosecond laser pulse, where the starting and stopping arms are constructed by reading the momenta of the ejected electrons and ions measured in coincidence. Pathway-resolved dissociative single and double ionization of the lightest hydrogen molecules are investigated to demonstrate the robust of the stopwatch. The spatiotemporal controlled polarization-skewed pulse is also used to manipulate the parallel and perpendicular transitions in molecules and thus the light-induced reactions.

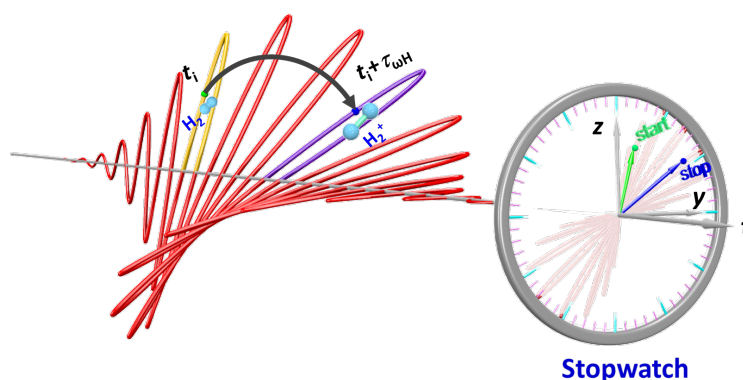


Fig. 1: Schematic illustration a stopwatch to clock the ultrafast dynamics of molecules.

- 1) S. Pan et al, *Phys. Rev. Lett.* **2021**, 126, 063201. 2) Q. Ji et al, *Phys. Rev. Lett.* **2019**, 123, 233202.
- 3) Q. Ji et al, *Phys. Rev. A* **2017**, 96, 053423. 4) H. Li et al., *Phys. Rev. Lett.* **2020**, 125, 053201. 5) H. Li et al, *Opt. Lett.* **2020**, 45, 6591.

Air lasing by population inversion in N_2^+ induced by strong-field coherent coupling of the X, A and B states

(¹*School of Science, The University of Tokyo*, ²*Jilin University*) ○Erik Lötstedt,¹ Youyuan Zhang,¹ Toshiaki Ando,¹ Atsushi Iwasaki,¹ Huailiang Xu,² Kaoru Yamanouchi¹

Keywords: air lasing, strong-field excitation, molecular dynamics, numerical simulation

When an intense, femtosecond near-IR laser pulse is focused in air, a short (~ 1 cm) plasma column called a filament is formed by the interplay between self-focusing and strong-field plasma defocusing. From the filament, unidirectional, coherent, and narrow-bandwidth radiation in the visible and UV wavelength range is emitted, which is referred to as air lasing. The emission at 391 nm, corresponding to the $\text{B}^2\Sigma_u^+(v'=0) \rightarrow \text{X}^2\Sigma_g^+(v''=0)$ transition in N_2^+ (see Fig. 1), has been intensively studied in the past decades, because the air lasing at 391 nm can be produced in a wide range of experimental conditions.

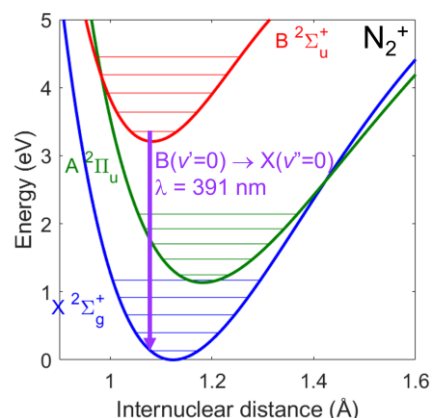


Fig. 1. Potential energy curves of N_2^+ .

However, until 2015, the mechanism and the time scale of the formation of the population inversion between $\text{B}^2\Sigma_u^+(v'=0)$ and $\text{X}^2\Sigma_g^+(v''=0)$ of N_2^+ , resulting in the air lasing at 391 nm, had not been understood well. In 2015¹, we revealed both experimentally and theoretically that the abrupt exposure of N_2^+ to the strong laser field, which is referred to as a sudden turn-on mechanism, combined with the population pumping from $\text{X}^2\Sigma_g^+(v''=0)$ to $\text{A}^2\Pi_u(v'=0)$ of N_2^+ , is responsible for the population inversion and that the population inversion is built up on a femtosecond time scale. In the theoretical model, we consider the time-dependent Schrödinger equation (TDSE) for the nuclear wave packets in the $\text{X}^2\Sigma_g^+$, $\text{A}^2\Pi_u$, and $\text{B}^2\Sigma_u^+$ states,

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} \psi_X(r,t) \\ \psi_A(r,t) \\ \psi_B(r,t) \end{pmatrix} = [T + V - \mathbf{E}(t) \cdot \boldsymbol{\mu}] \begin{pmatrix} \psi_X(r,t) \\ \psi_A(r,t) \\ \psi_B(r,t) \end{pmatrix}, \quad (1)$$

where r is the internuclear distance, $\psi_k(r,t)$ is the nuclear wave packet in the electronic state k , T is the kinetic energy operator, V is a 3×3 matrix having the potential energy curves of the $\text{X}^2\Sigma_g^+$, $\text{A}^2\Pi_u$, and $\text{B}^2\Sigma_u^+$ states on the diagonal, $\mathbf{E}(t)$ is the laser field, and $\boldsymbol{\mu}$ is a 3×3 matrix containing the dipole transition matrix elements. By numerically solving the TDSE, we showed that the population inversion can be explained by the following two mechanisms: (i) after ionization, N_2^+ starts interacting immediately with the intense laser pulse, which efficiently induces the population transfer from the $\text{X}^2\Sigma_g^+$ state to the $\text{B}^2\Sigma_u^+$ state, and (ii) because of the near-resonant $\text{A}^2\Pi_u$ – $\text{X}^2\Sigma_g^+$ coupling, a population is efficiently transferred to the $\text{A}^2\Pi_u$ state, which promotes further the population inversion between the $\text{B}^2\Sigma_u^+$ state and the $\text{X}^2\Sigma_g^+$ state.

In 2019, we conducted pump-probe experiments² and showed that the $B^2\Sigma_u^+(v' = 0) \rightarrow X^2\Sigma_g^+(v'' = 0)$ lasing signal at 391 nm oscillates as a function of the pump-probe delay time at the frequencies corresponding to the energy differences between the vibrational states in the $X^2\Sigma_g^+$ state and those in the $A^2\Pi_u$ state, which can be regarded as direct evidence that the mechanism of the excitation and lasing process of N_2^+ is the coherent V-shaped $A^2\Pi_u - X^2\Sigma_g^+ - B^2\Sigma_u^+$ coupling. Recently, we further showed³ that the rotational coherence created in N_2^+ can be clearly seen in the pump-probe delay-time dependence of the lasing signal at 391 nm. Indeed, the rotational structure of the lasing emission at 391 nm exhibited two maxima in the R-branch emission and the two maxima moved towards the longer wavelength as the delay time increases. By extending our theoretical model by including the rotational degree of freedom of N_2^+ , we showed theoretically that the delay-time dependence of the R-branch emission spectrum can be interpreted as a temporal evolution of a rotational wave packet created in the $B^2\Sigma_u^+$ state.

In order to use the air lasing for practical applications such as stand-off spectroscopic measurements and remote sensing, it is prerequisite to increase further the lasing emission intensity. We demonstrated experimentally⁴ that the air lasing signal at 391 nm can be enhanced by two orders of magnitude by employing a polarization-gated IR laser pulse having a time-dependent polarization direction. At the peak of the pulse, an aligned N_2^+ ensemble is created by the strong-field ionization, and during the latter half of the laser pulse, the polarization direction is changed so that the population transfer from $X^2\Sigma_g^+$ to $A^2\Pi_u$ is promoted efficiently by the $A^2\Pi_u \leftarrow X^2\Sigma_g^+$ transition whose transition dipole moment is perpendicular to the molecular axis, resulting in the significant increase in the air lasing signal. Furthermore, we revealed⁵ that the extent of the population inversion can be increased further by combining the polarization-modulated 800 nm laser pulse with a 1.6 μm IR pulse, which induces vibrational Raman transitions and depletes the population in the $X^2\Sigma_g^+(v = 0)$ state to an almost empty level, leading to a giant enhancement of the lasing signal at 391 nm by 5 orders of magnitude.

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Simulations of strong laser-driven multielectron dynamics using classical and quantum computers

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Keywords: *High-field physics, attosecond science, multielectron dynamics, quantum computer*

High-field physics and attosecond science are rapidly progressing towards world-changing goal of direct measurement and control of the electron motion in matters. To theoretically investigate intense laser-driven multielectron dynamics, the multiconfiguration time-dependent Hartree-Fock method [1-3] has been developed, which, though powerful, suffers from exponential increase of the computational cost with respect to the number of electrons.

To overcome this difficulty, more cost-effective time-dependent multiconfiguration methods have been developed [4-7], which substantially extend the applicability of accurate multielectron simulations. Furthermore, we have succeeded in formulating time-dependent coupled-cluster method using time-dependent orbitals, called TD-OCC method [8,9], which realizes gauge-invariant and size-extensive description of multielectron dynamics.

In this talk, I will summarize theory and implementation of these simulation methods [10-13], both on classical and quantum computers. The efficient implementation enables *ab initio* description, beyond single-active-electron approximation or time-dependent density functional theory, of high-field phenomena directly relevant to experiments, e.g., nonsequential double ionization of noble gas atoms, high-harmonic generation (HHG) enhanced by laser-induced electron recollision [14, 15], and laser polarization-dependent multichannel and multielectron effects on HHG from molecules.

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Putting the 'Chemistry' back into CVD Nanomaterial Growth - Insight from Quantum Simulations

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Keywords: Carbon nanotube; graphene; boron nitride; density functional tight binding; molecular dynamics

Over the last few decades, catalytic chemical vapor deposition (CVD) has matured as a synthetic technique for producing many low-dimensional inorganic nanomaterials, such as carbon nanotubes (CNTs), graphene, boron nitrides and transition metal dichalcogenides. The general mechanism of graphene and CNT formation during CVD is now well established [1]. However, by and large this picture of nucleation has been developed by considering the chemistry of carbon by itself, when, in reality, there are many other chemical species present in a CVD reaction chamber. In this lecture I will discuss our recent quantum chemical simulations that show the influence of such species on the nucleation and growth mechanisms of carbon nanomaterials during CVD (e.g. H_2 [2,3], H_2O [4], NH_3 [5], etc.).

In contrast to carbon nanomaterials, little is known regarding the catalytic pathways underpinning CVD synthesis of boron nitride nanomaterials [1]. I will present the first mechanism explaining the nucleation of boron nitride nanotubes (BNNTs) via CVD of boron oxide and ammonia borane, based on reactive molecular dynamics simulations [6]. Strikingly, BNNTs nucleate via a 'network fusion' mechanism, by which distinct BN fragments first form before 'clicking' together on the nanoparticle surface (Figure 1). We also reveal key roles played by H_2O and H_2 partial pressures and the presence of solid-phase catalytic nanoparticles on this mechanism.

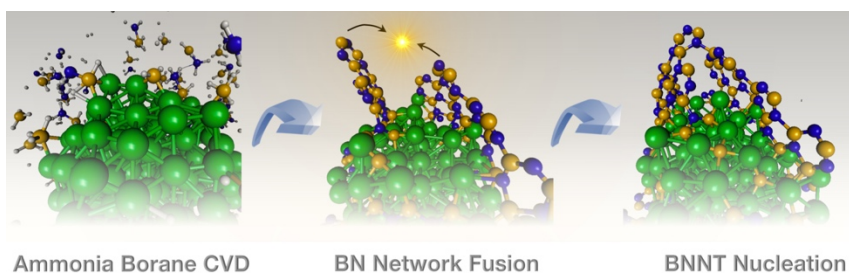


Figure 1. Network fusion nucleation of BNNTs during Ni-catalysed ammonia borane CVD.

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Ionic Liquid Kinetics on Polarizable Electrode Surface

(Department of Chemistry, Faculty of Science and Technology, Keio University)

○Taichi Inagaki

Keywords: electrode surface; interfacial kinetics; ionic liquid; polarization effect; molecular dynamics simulation

The dynamical behavior of electrolyte molecules on an electrode surface is one of the most important factors to determine the performance of electrochemical devices. For example, the charging/discharging rate of the electrical double layer (EDL) capacitors is closely linked to the kinetics of the EDL reconstruction at the electrode surface, and the kinetics is expected to originate from the adsorption (desorption) dynamics of interfacial electrolyte molecules or ions onto (from) the electrode. To improve the device performance, it is quite essential to understand the fundamental interfacial dynamics. These dynamics/kinetics at the molecular level have become an active research field in both experiments and simulations. However, not much is known yet about the dynamics compared to the structural properties.

Here we present a classical molecular dynamics (MD) simulation study on the interfacial ionic liquid kinetics at a graphite electrode surface. In particular, we focus on the nonequilibrium relaxation kinetics of the EDL upon the electrode charge change [1]. The electrochemical cell in this study was constructed with 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF₄] ion pairs sandwiched between two three-layered graphite electrodes (Figure 1). For the computational efficiency, the ion pairs were described by a coarse-grained model [2] which can reproduce the experimental bulk diffusion coefficient. Each cation was modeled by a three-site rigid model, while each anion was represented by one spherical particle. The electrode was represented with a polarizable model to appropriately describe electrostatic interaction between ions and the conductive electrode surface. The electrode atomic charges were determined at each MD time step to satisfy the constant electrostatic potential (ESP) condition inside the electrode according to the constant potential MD method [1,3]. In other words, the ESPs acting on each electrode atom were used as parameters specifying the electrode charge density.

The EDL relaxation process was investigated as follows. An equilibrium state at $t < 0$ was initially prepared under the electrode ESP of -0.75 V and then the ESP was

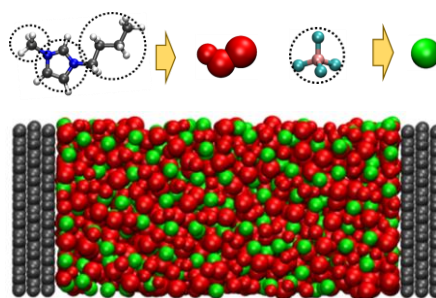


Figure 1. The computational modeling of ions and the electrochemical cell to study the interfacial ionic liquid kinetics.

suddenly dropped to 0 V at $t = 0$. The relaxation to the equilibrium at $t > 0$ was monitored with the change of the electrode charge density reflecting the EDL reconstruction. The relaxation thus simulated was found to occur in the sub-nanosecond timescale in the present case (Figure 2). In comparison with the constant potential simulation, the constant charge simulation, where the electrode charge was completely removed at $t = 0$ and the charge was fixed to zero after that, showed much faster relaxation (several picosecond timescale). The slow relaxation observed in the polarizable electrode originates from the fact that most electrode charges remain as image charges against the interfacial ions. As a result, the small bias (electric field) is imposed on the ions, leading to the quite gradual relaxation. Therefore, the difference in timescale suggests that the electrode polarization effect plays an essential role in the kinetics of nonequilibrium processes like the EDL relaxation.

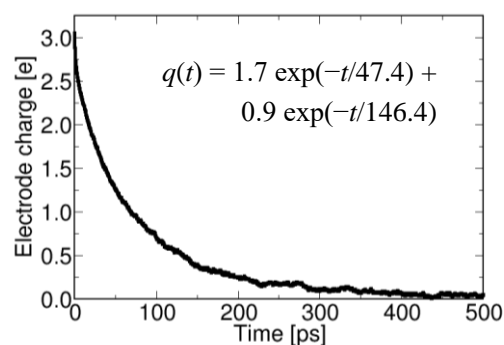


Figure 2. The time evolution of the amount of electrode charge $q(t)$ observed in the relaxation simulation.

The relaxation kinetics observed in the constant potential simulation was further analyzed and found to have approximately two time constants, 47 and 146 ps (Figure 2). This indicates that the relaxation includes two different dynamical processes at least. To obtain molecular insights into the relaxation, we analyzed dynamics of the ions on the basis of the van Hove time-space correlation functions. As a result, we found that the lighter anions contribute largely to the relaxation compared to the cations. In addition, diffusive dynamics of anions were classified into three groups according to initial positions at $t = 0$, that is, the first layer, second layer, and bulk. The analysis showed that the ions in the second layer respond first to the potential drop, which is followed by the ions in the bulk, and the ions in the first layer are most insensitive. This observation suggests that the initial relaxation occurs in the intermediate region between the electrode surface and the bulk due to the delicate balance between the potential drop and the electrode surface interactions. The difference in response rate is expected to be related to the two time constants obtained from the electrode charge reduction curve (Figure 2). Along with the ion dynamics present under the kinetics, the findings gained here are expected to be valuable information to understand interfacial molecular kinetics from computational studies.

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Multi-Scale Theoretical/Computational Approach to Heterogeneous Catalysis

(National Institute for Materials Science (NIMS))

○ Atsushi Ishikawa

Keywords: Density functional theory, microkinetics, chemical kinetics, reaction mechanism

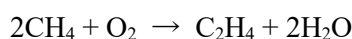
1. Introduction

The oxidative coupling of methane (OCM) has long been studied to provide an efficient way to convert natural gas into high-value chemicals. For the full understanding of its reaction mechanism, the multi-scale theoretical simulation was conducted; the method is based on the density functional theory (DFT), microkinetics, and chemical reactor modeling. Our purpose is to predict the activity (the reactant conversion) and the product selectivity, from atomic or molecular level simulations.[1]

In addition to the above topic, our recent approach that combines the machine-learning with DFT-based microkinetics focusing on the NH_3 synthesis is also introduced.[2]

2. Theoretical method

We investigated the OCM reaction



catalyzed by MgO, first found by Lansford *et al.*[3] We modeled the active site as the stepped MgO surface, based on previously reported experimental results and our theoretical works.[4, 5] The reaction model includes 109 gas-phase and 61 surface reactions. Using DFT, reaction energy (ΔE) was calculated, and activation barrier (E_a) were estimated from ΔE values using the linear free energy relationship. For the DFT calculation, VASP 5.4 program package was used. From ΔE and E_a values, we evaluate the reaction rate constants and constructed reaction rate equations. Reaction rate equations were solved numerically using MATLAB software. The reactant conversion and product selectivity were evaluated from composition of the inlet and outlet gas.

3. Results and discussion

In Figure 1, the transition state (TS) of the H-abstraction from CH_4 obtained from the DFT calculation is shown. The preliminary microkinetic analysis show that this process has the largest contribution to the reactant conversion. The calculated E_a value is 96.5 kJ/mol, which is reasonable agreement with experimental range.

From this E_a value other elementary reactions, the kinetic parameters are obtained and the microkinetic and reactor analysis are performed. In Figure 2, the change of the molar

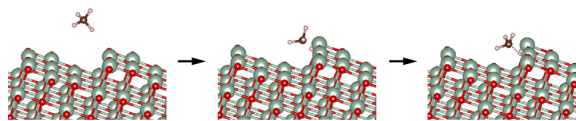


Figure 1. Optimized structures of the CH_4 activation at the stepped MgO. The left, middle, and right correspond to the reactant, TS, and product states.

fraction with reaction time is shown. The reactant i.e. CH_4 and O_2 decreases as the reaction proceeds, while C_2H_6 , H_2O , CO and CO_2 are generated.

In Figure 3, the CH_4 conversion and composition of C-containing compounds were shown. With the increase of temperature, the CH_4 conversion becomes higher but C_2 compounds decreases, which agrees with experimental tendency. Thus, our multi-scale simulation correctly reproduces the activity and selectivity tendency of the OCM catalyst.

4. Conclusions

We theoretically investigated the OCM over MgO , with the DFT calculation, microkinetics, and chemical reactor simulations to evaluate the reactant conversion and product selectivity. What is unique in this study is that both gas-phase and surface-mediated reactions were included, and the kinetic and thermodynamic properties of 170 elementary reactions were all calculated by DFT. Our simulation have found that;

- 1) CH_3 formation from CH_4 is highly endothermic in the gas phase ($\Delta E = 4.73$ eV), while ΔE decreases to 0.33 eV when CH_4 activation occurs on the stepped MgO .
- 2) The mole fraction change along the reaction shows that the C_2 compounds are formed first but CO_x ($x = 1, 2$) are formed later, indicating the overoxidation of C_2 compounds.
- 3) The effects on CH_4 conversion and C_2 selectivity from the temperature and $P_{\text{CH}_4} : P_{\text{O}_2}$ are observed. The CH_4 conversion increases with temperature, while the C_2 selectivity becomes lower. A similar but more moderate dependency was observed for $P_{\text{CH}_4} : P_{\text{O}_2}$. These trends agree well with experimental reports.

Our study strongly suggests that DFT-based microkinetics is a strong approach to analyze the catalysis from the atomic or molecule scale resolution.

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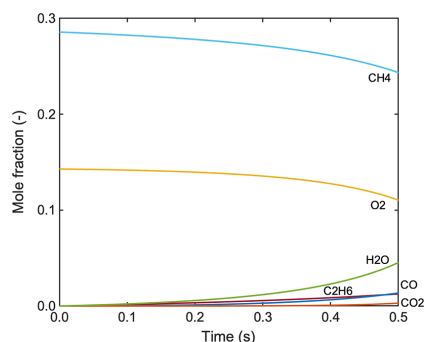


Figure 2. Mole fraction along the reaction time (s) calculated by the reactor simulation.

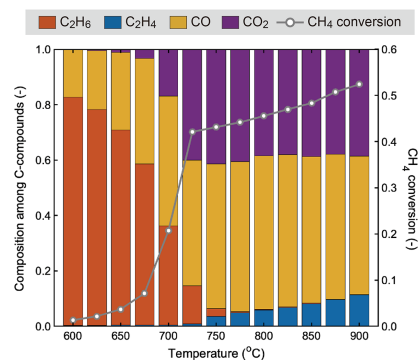


Figure 3. Dependence of the composition of C-containing species (left axis) and CH_4 conversion (right axis) on reaction temperature (in $^{\circ}\text{C}$).

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[W1-1pm] International Symposium on Molecular Science - Physical Chemistry / Theoretical Chemistry, Chemoinformatics, Computational Chemistry - Cosponsored by Japan Society for Molecular Science

Chair, Symposium organizer: Satoshi Takahashi, Yasuteru Shigeta

Wed. Mar 23, 2022 1:00 PM - 3:40 PM W1 (Online Meeting)

[W1-1pm-01] Computer-aided drug design and screening of potential compounds to combat COVID-19

○THANYADA RUNGROTMONGKOL¹, Bodee Nutho², Panupong Mahalapbutr³, Kamonpan Sanachai¹, Supot Hannongbua¹, Kittikhun Wangkanont¹, Supakarn Chamni¹, Warinthorn Chavasiri¹, Tuanjai Somboon¹, Siwaporn Boonyasuppayakorn¹, Wanchai De-eknamkul¹, Tanatorn Khotavivattana¹ (1. Chulalongkorn University, 2. Mahidol University, 3. Khon Kaen University)

1:00 PM - 1:35 PM

[W1-1pm-02] Theoretical study of copper-catalyzed atom transfer radical addition reactions

○Megumi Kayanuma¹ (1. AIST)

1:35 PM - 1:55 PM

[W1-1pm-03] Role of dynamics in conformational transitions and functions of biomolecules

○Toshifumi Mori¹ (1. Kyushu Univ.)

1:55 PM - 2:15 PM

[W1-1pm-04] Liquid-liquid phase separation in the tales of intrinsically disordered proteins

○Jie-rong Huang¹ (1. Institute of Biochemistry and Molecular Biology, National Yang Ming Chiao Tung University, Taiwan)

2:20 PM - 2:55 PM

[W1-1pm-05] The Stickers-and-Spacers Framework for Describing Biomolecular Phase Separation

○Jeong-Mo Choi¹ (1. Pusan National University)

2:55 PM - 3:15 PM

[W1-1pm-06] Label-free observation of liquid-liquid phase separation in vitro and in a living cell using Raman microscopy

○Shinji Kajimoto^{1,2} (1. Tohoku University, 2. JST PRESTO)

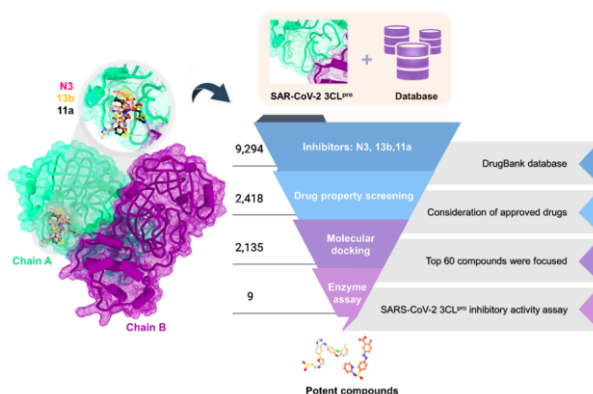
3:15 PM - 3:35 PM

Computer-aided drug design and screening of potential compounds to combat COVID-19

(¹Faculty of Science, Chulalongkorn University, ²Faculty of Pharmaceutical Sciences, Chulalongkorn University, ³Faculty of Medicine, Chulalongkorn University) ○ Thanyada Rungrotmongkol,¹ Bodee Nutho,¹ Panupong Mahalapbutr,¹ Kamonpan Sanachai,¹ Supot Hannongbua,¹ Kittikhun Wangkanont,¹ Supakarn Chamni,² Warinthorn Chavasiri,¹ Tuanjai Somboon,¹ Siwaporn Boonyasuppayakorn,³ Wanchai De-eknamkul,² Tanatorn Khotavivattana¹

Keywords: Antiviral Agents; SARS-CoV-2; 3CL Protease; Drug Design and Screening

SARS-CoV-2 causes the current global pandemic coronavirus disease 2019. Widely-available effective drugs could be a critical factor in halting the pandemic. The main protease (3CL^{pro}) plays a vital role in viral replication; therefore, it is of great interest to find inhibitors for this enzyme. We applied the combination of virtual screening based on molecular docking derived from the crystal structure of the peptidomimetic inhibitors (N3, 13b, and 11a), and experimental verification revealed FDA-approved drugs that could inhibit the 3CL^{pro} of SARS-CoV-2. Three drugs were selected using the binding energy criteria and subsequently performed the 3CL^{pro} inhibition by enzyme-based assay. In addition, six common drugs were also chosen to study the 3CL^{pro} inhibition. Among these compounds, lapatinib showed high efficiency of 3CL^{pro} inhibition (IC₅₀ value of 35 ± 1 μM and K_i of 23 ± 1 μM). The binding behavior of lapatinib against 3CL^{pro} was elucidated by molecular dynamics simulations. This drug could well bind with 3CL^{pro} residues in the five subsites S1', S1, S2, S3, and S4. Moreover, lapatinib's key chemical pharmacophore features toward SAR-CoV-2 3CL^{pro} shared important HBD and HBA with potent peptidomimetic inhibitors. The rational design of lapatinib was subsequently carried out using the obtained results. Our discovery provides an effective repurposed drug and its newly designed analogs to inhibit SARS-CoV-2 3CL^{pro}. Besides the known drugs, biochemical and cell-based assays tested the screened compounds from natural products and synthetic analogs.



Theoretical Study of Copper-Catalyzed Atom Transfer Radical Addition Reactions

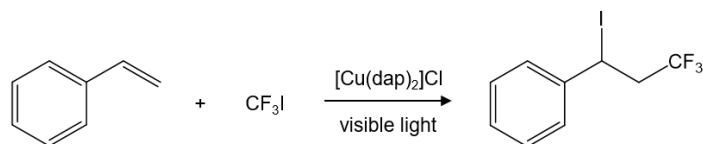
(Research Center for Computational Design of Advanced Functional Materials, National Institute of Advanced Industrial Science and Technology) ○Megumi Kayanuma

Keywords: density functional theory, catalysis, photoredox reaction, copper complex

Photoredox catalysts using copper complexes are recently applied for various reactions, such as atom transfer radical addition (ATRA) reactions. The copper-based photocatalysts provide interesting reactivity, for example, $[\text{Cu}(\text{dap})_2]\text{Cl}$ (dap = 2,9-di(*p*-anisyl)-1,10-phenanthroline) catalyzes ATRA reactions between perfluoroalkyl iodides and styrenes under visible light irradiation, which are not promoted by commonly employed photocatalysts using ruthenium or iridium complexes.¹ It is proposed that these reactions proceed not only by conventional outer-sphere photoredox mechanisms but also by inner-sphere mechanisms.²

In the present study, the mechanism of the visible-light-mediated ATRA reaction of CF_3I with styrene utilizing $[\text{Cu}(\text{dap})_2]\text{Cl}$ is analyzed by means of density functional theory (DFT) using the M06 functional with the D3 version of Grimme's dispersion correction. Stuttgart/Dresden ECP (SDD) is used for Cu and I atoms, and Dunning/Huzinaga full double- ζ basis sets with polarization functions (D95(d,p)) for the others. The solvent effect of acetonitrile is considered with the polarizable continuum model.

The photoexcited Cu(I) complex reduces CF_3I and generates CF_3 radical ($[\text{Cu}(\text{dap})_2]^+ + \text{CF}_3\text{I} \rightarrow [\text{Cu}(\text{dap})_2]^{2+} + \text{CF}_3\cdot + \text{I}^-$). The generated Cu(II) complex was suggested to undergo ligand exchange ($[\text{Cu}(\text{dap})_2]^{2+} + \text{Cl}^- + \text{I}^- \rightarrow [\text{Cu}(\text{dap})(\text{Cl})(\text{I})] + \text{dap}$),¹ which is confirmed by the present calculation. When CF_3 radical binds to styrene, benzyl radical is formed ($\text{CF}_3\cdot + \text{C}_8\text{H}_8 \rightarrow \text{C}_9\text{H}_8\text{F}_3\cdot$). It is shown that the $\text{C}_9\text{H}_8\text{F}_3$ radical does not initiate radical chain process ($\text{C}_9\text{H}_8\text{F}_3\cdot + \text{CF}_3\text{I} \rightarrow \text{C}_9\text{H}_8\text{F}_3\text{I} + \text{CF}_3\cdot$), which is a common mechanism of the ATRA reactions. For the reaction of $\text{C}_9\text{H}_8\text{F}_3$ radical to generate the product, $\text{C}_9\text{H}_8\text{F}_3\text{I}$ ((3,3,3-trifluoro-1-iodopropyl)benzene), two mechanisms were proposed: rebound cycle in which the $\text{C}_9\text{H}_8\text{F}_3$ radical coordinates to Cu ($[\text{Cu}(\text{dap})(\text{Cl})(\text{I})] + \text{C}_9\text{H}_8\text{F}_3\cdot \rightarrow [\text{Cu}(\text{dap})(\text{I})(\text{C}_9\text{H}_8\text{F}_3)]^+ + \text{Cl}^- \rightarrow [\text{Cu}(\text{dap})(\text{Cl})] + \text{C}_9\text{H}_8\text{F}_3\text{I}$) and ligand transfer cycle in which the $\text{C}_9\text{H}_8\text{F}_3$ radical abstracts the iodide atom from $[\text{Cu}(\text{dap})(\text{Cl})(\text{I})]$ ($[\text{Cu}(\text{dap})(\text{Cl})(\text{I})] + \text{C}_9\text{H}_8\text{F}_3\cdot \rightarrow [\text{Cu}(\text{dap})(\text{Cl})] + \text{C}_9\text{H}_8\text{F}_3\text{I}$).¹ The calculations show that ligand transfer cycle is more plausible.



1) T. Rawnner, E. Lutsker, C.A. Kaiser, O. Reiser, *ACS Catal.* **2018**, 8, 3950. 2) T. P. Nicholls, A.C. Bissember, *Tetrahedron Lett.* **2019**, 60, 150883.

生体分子の状態遷移と機能の動力学

(九大先導研¹・九大総理工²) ○森 俊文^{1,2}

Role of dynamics in conformational transitions and functions of biomolecules (¹*Institute for Materials Chemistry and Engineering, Kyushu University*, ²*Interdisciplinary Graduate School of Engineering Sciences, Kyushu University*) ○Toshifumi Mori¹

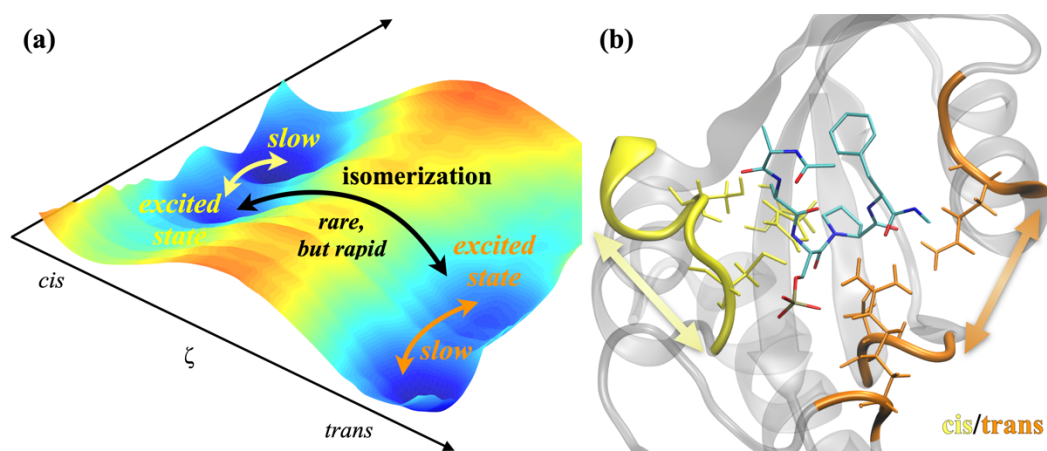
Structural fluctuations and conformational transitions of proteins have been realized to be essential for protein functions. Yet, how these dynamic aspects of proteins contribute to functions often remains elusive. We have been working towards understanding how enzymes adapt to different stages of the catalytic cycle by adjusting their conformations, and have been focusing on unveiling the conformational dynamics of enzymes. In this talk, by mainly focusing on the peptidyl-prolyl isomerization reaction catalyzed by Pin1, we discuss the molecular mechanism of catalytic reaction from two perspectives. Molecular dynamics simulations with replica exchange umbrella sampling and transition path sampling methods are applied to reveal the static and dynamic mechanisms of the reaction, respectively. From a static view, enzyme lowers the free energy barrier of isomerization with rearrangements in ligand-enzyme interactions along the reaction coordinate^{1,2}. From the dynamic view, on the contrary, the isomerization occurs in a short timescale, which turns out to be too rapid for the ligand-enzyme interactions to reorganize to equilibrium². These results indicate that the dynamics of the enzyme plays a role prior to the reaction step by preparing a reactive environment, i.e., as *conformational excited states*. The origin of these slow protein dynamics, which has also been discussed by an NMR experiment³, and how it seemingly couples to the enzymatic reaction cycle will also be discussed.

Keywords : Reaction dynamics; Free energy; Conformational transition; Enzyme catalysis; Molecular dynamics simulation

生体分子の構造揺らぎや状態遷移は生体分子の機能に不可欠であることが、近年の一分子測定をはじめとした実験より明らかになってきた。ところが、このような運動が実際にどのように生体分子機能や酵素反応に寄与するかに関しては、多くの場合あまりよく分かっていない。我々は、特に酵素反応を対象として、分子シミュレーションなど理論化学手法を用いることによって、酵素の構造変化や状態遷移が酵素反応サイクルに沿ってどのように調整され、酵素反応が成り立っているかを、ダイナミクスに特に着目して調べている。本発表では、プロリン異性化酵素の一つである Pin1 を例に、反応機構を静的および動的側面から詳しく調べた。そのために、分子動力学シミュレーションのサンプリング手法である replica exchange umbrella sampling 法および transition path sampling 法を用いた反応経路の探索を行った。

静的側面の解析からは、異性化反応の自由エネルギー面に対する酵素の影響について調べることで、酵素によって反応の自由エネルギー障壁が下がり、反応が促進されている機構が得られた。また、反応座標（異性化の二面角の変化）に沿って、基質-酵素相互作用が徐々に変化していくのが確認された^{1,2}。それに対して、実際に反応

がどのように進行するかを遷移トラジェクトリに基づく反応ダイナミクスの解析から調べたところ、基質の異性化反応自体はごく短時間で進行するため、基質-酵素相互作用がその時間内に追従することはできないことが分かった²⁾。そのため、異性化反応の遷移状態を安定化するのに必要な基質-酵素相互作用は、基質の反応座標の変化が始まる前に、あらかじめ準備されている必要があることが示唆された。以上の結果から、酵素の構造ダイナミクスは、異性化反応そのものが起こる前に、「構造励起状態」として反応が起きやすい環境を準備するために重要であることが示された。本発表ではさらに、酵素の遅い状態遷移の分子起源と、これが NMR 測定などで見られる遅い運動³⁾とどう関係し、さらに酵素反応サイクルと見かけ上どのように相関しているかを議論する。



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Liquid-liquid phase separation in the tales of intrinsically disordered proteins

(¹*Institute of Biochemistry and Molecular Biology, National Yang Ming Chiao Tung University*) ○Jie-rong Huang¹

Keywords: *Intrinsically disordered proteins; liquid-liquid phase separation; nuclear magnetic resonance; RNA-binding proteins; galectin*

Tons of biomolecules react in a cell simultaneously, but how does one biomolecule “know” where and when to react? The prevailing intrinsically disordered proteins (IDPs; >30% in eukaryotic cells) or proteins with intrinsically disordered regions (IDRs; >50% in eukaryotic cells), which do not adopt a defined three-dimension structure, may play a role in the spatiotemporal control of biochemical reactions. Recent studies have demonstrated that some IDPs undergo liquid-liquid phase separation (LLPS) to respond to environmental changes (e.g. temperature, pH) to determine the timing of a reaction (“when”). The increased local concentration within phase-separated droplets also controls the location (“where”) to react. The physicochemical properties of these ID regions probably govern the location and timing for a molecule to react. In this talk, I will use TDP-43 [1,3,4], galectin-3 [2,5], and Musashi protein families [6] as examples to demonstrate how the physicochemical properties of IDRs can relate to their cellular functions and diseases.

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[6] Chiu SH, Ho WL, Sun YC, Kuo JC, and **Huang JR*** *Submitted*

The Stickers-and-Spacers Framework for Describing Biomolecular Phase Separation

(¹*Department of Chemistry, Pusan National University*) ○Jeong-Mo Choi¹

Keywords: Biomolecular Phase Separation; Intrinsically Disordered Proteins; Theoretical Modeling

In the last decade, there has been a growing interest on the phase behavior of biomolecules, especially after demonstration of its biological implications such as reversible formation/dissociation of membrane-less cellular organelles. Several model systems have been discovered and studied, and one of crucial questions in the field is how the phase behavior is encoded in a sequence. Inspired by observations on a subset of disordered proteins that apparently exhibit a rather simple molecular grammar for phase behavior, we developed the *stickers-and-spacers framework* adapted from the field of associative polymers for understanding how multivalent protein and RNA molecules drive phase transitions that give rise to biomolecular condensates. In this talk, I will introduce the framework and discuss its applications in explanation and prediction of biomolecular phase behaviors.

Label-free observation of liquid-liquid phase separation in vitro and in a living cell using Raman microscopy

(¹Graduate School of pharmaceutical Sciences, Tohoku University, ²PRESTO, JST) ○Shinji Kajimoto^{1,2}

Keywords: Raman imaging; LLPS; Liquid droplet; Stress granule; Oxidative stress

We performed Raman imaging of liquid droplets formed via liquid-liquid phase separation (LLPS) in a protein buffer solution, as well as stress granules formed in living cells subjected to oxidative stress. While LLPS plays essential roles in a variety of intracellular events, liquid droplets are also considered to be involved in protein aggregation in neurodegenerative diseases. To elucidate the nature of liquid droplets and reveal the relationship between LLPS and aggregation of proteins, quantification of a single droplet is essential. In this study, for the label-free quantification of LLPS, we obtained Raman spectra of inside and outside of a liquid droplet and estimated the protein concentration of the droplet using the water Raman band as an internal standard. We found that ataxin-3, which has a poly-glutamine chain on its C-terminal portion and is considered as the causative protein of Machado-Joseph disease, exhibits LLPS in buffer solutions containing crowding agents such as polyethylene glycol (PEG) and dextran (DEX)¹. The Raman spectra of liquid droplets of ataxin-3 show that only water and protein existed inside the liquid droplets, while the outside was consisted with water and crowding agents. Based on the intensity of the Amide I band of protein (1660 cm^{-1}) inside a droplet and the O-H stretching band of water ($3100\text{--}3700\text{ cm}^{-1}$) outside droplets, we estimated the concentration of proteins inside a single droplet. The protein concentration varied depending on the concentration of crowding agents; the higher the concentration of PEG was, the higher the concentration of protein inside the droplets. We also performed Raman imaging of liquid droplets of the low-complexity domain of FUS, and found that the concentration of FUS inside a droplets varies depending on the surrounding

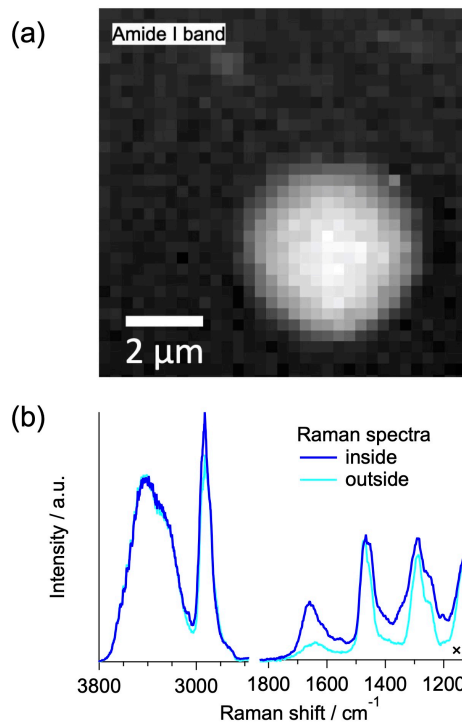


Fig. 1 A Raman image (a) and Raman spectra (b) of a liquid droplet of ataxin-3 formed in buffer solution containing PEG. The Raman image was obtained by mapping the intensity of Amide I band (1660 cm^{-1}).

circumstance, such as salt concentration and pH. These results indicate that the intracellular environments are important for LLPS inside a cell and the nature of liquid droplets varies with the intracellular molecular crowding environments.

As a demonstration of label-free observation of intracellular LLPS, we obtained Raman images of HeLa cells subjected to oxidative stress by addition of sodium arsenite into a medium, which induces stress granule formation. After 30 min. exposure to 0.5 mM sodium arsenite, the intensity of Raman bands assigned to proteins and nucleic acids was increased in some regions of cytoplasm. It is known that proteins and RNAs are the main components of stress granules, so that we concluded that we succeeded in obtaining Raman spectra of stress granules. The hierarchical cluster analysis (HCA) of Raman images consisting of 2500 Raman spectra enables us to visualize the distribution of stress granules. The HCA of Raman images also revealed that the intensity of the C–H stretching band increased not only inside the stress granule regions but also the other cytoplasmic regions. Since the intensity of the C–H Raman band corresponds the concentration of biomolecules having C–H bonds^{2,3}, the increase of the C–H Raman band indicates that the intracellular environments became more crowded in the entire cytoplasmic region after the oxidative stress. The change in the intracellular crowding environments will affect the formation process and change the nature of stress granules.

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Symposium | Asian International Symposium | International Symposium on Molecular Science - Physical Chemistry / Theoretical Chemistry, Chemoinformatics, Computational Chemistry - Cosponsored by Japan Society for Molecular Science

[W1-1vn] International Symposium on Molecular Science - Physical Chemistry / Theoretical Chemistry, Chemoinformatics, Computational Chemistry - Cosponsored by Japan Society for Molecular Science

Chair, Symposium organizer: Tatsuya Ishiyama, Akiyoshi Hishikawa

Wed. Mar 23, 2022 4:10 PM - 5:30 PM W1 (Online Meeting)

[W1-1vn-01] Ion transport in concentrated aqueous electrolytes for Li-ion batteries

○Jonggu Jeon¹ (1. Institute for Basic Science)

4:10 PM - 4:45 PM

[W1-1vn-02] Theoretical Investigation of Dielectric Constant at Monolayer Interfaces by Polarizable Molecular Dynamics Simulation

○Lin Wang^{1,2} (1. Department of Chemistry, Tohoku Univ., 2. ESICB, Kyoto Univ.)

4:45 PM - 5:05 PM

[W1-1vn-03] Understanding Charge-Transfer Reactions by Constrained Density Functional Theory

○Tatsuya Joutsuka^{1,2} (1. Ibaraki University, 2. Frontier Research Center for Applied Atomic Sciences)

5:05 PM - 5:25 PM

Ion Transport in Concentrated Aqueous Electrolytes for Li-Ion Batteries

(¹*Center for Molecular Spectroscopy and Dynamics, Institute for Basic Science (IBS), Seoul 02841, Republic of Korea*, ²*Department of Chemistry, Korea University, Seoul 02841, Republic of Korea*) ○ Jonggu Jeon,¹ Minhaeng Cho^{1,2}

Keywords: Ion Solvation; Ion Transport; Li-ion Batteries; Water-in-Salt Electrolytes; Molecular Dynamics Simulation.

Water-in-salt electrolytes (WiSE) could be a safer alternative to conventional organic electrolytes in battery applications due to their non-flammable nature.¹⁻² The electrochemical performance of these concentrated aqueous solutions of Li electrolytes critically depends on their high electrical conductivity at saturation. Although the solvation structure and dynamics of Li ions in WiSEs have been the subject of numerous studies, even fundamental structural features of the solutions such as the degree of heterogeneity of the electrolyte solutions are not yet agreed upon,³⁻⁶ let alone their dynamics.

To better understand this with theoretical and computational means, we have developed a non-polarizable molecular mechanics (MM) force field model for concentrated aqueous solutions of LiTFSI ($\text{Li}^+(\text{CF}_3\text{SO}_2)_2\text{N}^-$), which is a representative WiSE. With an eye toward an accurate description of the ion conduction process, the model was designed to accurately reproduce the solution density and ionic and water diffusivities over a wide range of concentrations. In particular, we have applied ionic charge scaling by 80% to account for inter-ionic charge transfer and electronic polarization effects that are usually missing in non-polarizable force field models. This charge scaling turns out to be a crucial measure for the correct prediction of the diffusivity of all three species in the solution.

We investigated four types of predominant atomic interactions and dynamics involving Li ions, anionic oxygens, and atoms of water molecules in the WiSE consisting of LiTFSI with molecular dynamics simulation and theoretical analysis based on the Luzar-Chandler theory.⁷ We thoroughly characterized the atomic compositions in the first solvation shells of the four atom types, Li^+ , $\text{O}(\text{TFSI})$, $\text{H}(\text{H}_2\text{O})$, and $\text{O}(\text{H}_2\text{O})$, calculated thermodynamic stabilities and lifetimes of the contact atom pairs, and identified strong correlation of the Li-ion mobility with the local solvation environment and its dynamics. We conclude that Li ions follow heterogeneous trajectories on the sub-ns time scale consisting of distinctive water-rich and anion-rich segments, switching between a vehicle-type and a hopping-type mechanism in respective regions. The $\text{Li}\cdots\text{O}_\text{W}$ contact pair is slightly more stable than $\text{Li}\cdots\text{O}_\text{T}$ at saturation, and this subtle balance appears responsible for the fast Li-ion transport in this class of WiSE.

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Theoretical Investigation of Dielectric Constant at Monolayer Interfaces by Polarizable Molecular Dynamics Simulation

(¹Graduate School of Science, Tohoku University, ²ESICB, Kyoto University)

○Lin Wang,^{1,2}

Keywords: Sum Frequency Generation Spectroscopy; Interfacial Dielectric Constant; Langmuir Monolayer; Molecular Dynamics Simulation

Due to its highly surface selectivity and sensitivity, sum frequency generation (SFG) spectroscopy has an excellent potential to study interfaces, such as electrode-electrolyte interfaces and monolayer interfaces. It is particularly useful for the *in situ* detection of electrode interfaces in electrochemically working conditions. We have developed the computational analysis of SFG spectroscopy, and calculated microscopic structure and nonlinear susceptibility of various interfaces including electrodes and batteries.^[1-3] However, one of the remaining difficulties to advance our computational analysis is how to deal with uncertainties associated to the interfacial dielectric constant (ϵ'). As an optical probe of interfaces, the dielectric constant of the interface is a critical factor, though it has been treated as an empirical parameter so far. The measurement of ϵ' is not straightforward for a monolayer region. Lack of reliable determination of ϵ' hinders our quantitative analysis of SFG spectra in organic interfaces.

In this work, we extended our theory of SFG to deal with the interfacial dielectric constant besides the nonlinear susceptibility of the interfaces. We propose a general modeling and theory to evaluate the interfacial dielectric constant by *ab initio* polarizable model and molecular dynamics (MD) simulations. The proposed method is able to calculate the frequency-dependent dielectric constant, including the static and optical ones, as a function of the depth position. The present work revealed the local dielectric profile with spatial and frequency decomposition near the interface. To validate our theory of ϵ' , the calculated local dielectric constants of dodecanol-water monolayer are examined. It is noteworthy that the interfacial dielectric constant show anisotropy as well as complicated structure as a function of depth position, which reflects the inhomogeneous structure of the interface. The detailed results of the dielectric profile and its implication to the analysis of SFG spectroscopy will be shown in the presentation. The reliable information of interfacial dielectric profile is necessary to apply the SFG spectroscopy to complex interfaces, such as those at batteries.

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Understanding Charge-Transfer Reactions by Constrained Density Functional Theory

(¹Graduate School of Science and Engineering, Ibaraki University, ²Frontier Research Center for Applied Atomic Sciences, Ibaraki University) ○Tatsuya Joutsuka^{1,2}

Keywords: Proton Transfer; Hole Transfer; Constrained Density Functional Theory; Molecular Dynamics; Electron Transfer

To solve energy problems, photocatalysts have been actively studied for, e.g., decomposing water into hydrogen and oxygen using sunlight.

Developing high-performance photocatalysts requires the molecular-level understanding of charge-transfer reactions in photocatalytic processes. However, even for TiO₂, the mechanism shown in Figure 1 remains unclear. This is partly because photocatalysis involves complex charge-transfer reactions

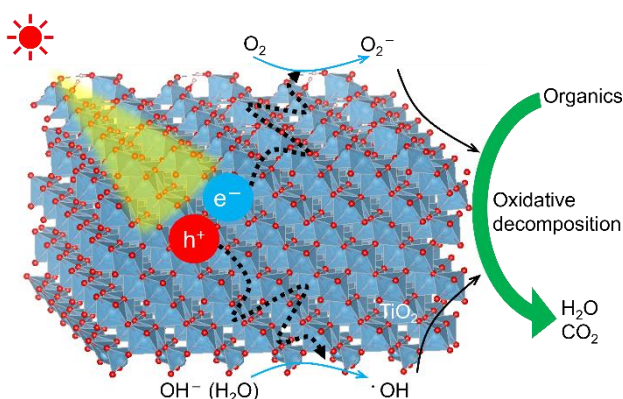


Figure 1. Schematic of charge-transfer reactions in TiO₂ photocatalysis

The aim of this presentation is to understand the charge-transfer reactions in condensed phases *e.g.* TiO₂ photocatalysts by using density functional theory (DFT) calculations. Here, the constrained DFT (CDFT) method is employed to simulate the localized charges. First, we validate the method by molecular dynamics simulations of proton transfer in aqueous silicic acid.^{1,2} In this study, we propose a computational scheme for proton transfer using *ab initio* molecular dynamics (MD) simulations and CDFT. We also plan to talk about another application in aqueous solutions. Next, the facet (directional) dependence by polaron migration is clarified in anatase TiO₂ and compared with the experiment.³ We focus on the discussion of hole migration in bulk anatase TiO₂ and at its surfaces.

In this study, DFT calculations were carried out under three-dimensional periodic boundary conditions using the cp2k program package. For the proton transfer in aqueous solutions, the proposed CDFT method employs the vertical energy-gap coordinate defined by the difference of energies for the reactant and product states, which are defined by different charge constraints to the O atom of proton donor with the Becke density partitioning method. For the polaron transfer in anatase TiO₂, five anatase surfaces were used to study the facet dependence of the stability of surface-trapped holes. To achieve hole formation, the CDFT method was used to optimize all ion coordinates while varying the number of valence electrons on a single O atom.

Figure 2 shows the calculated free energy surface in aqueous silicic acid, and the reaction free energy of deprotonation agrees with the experimental results within a few kcal/mol. There are three main features of the CDFT method: 1. it can be applied not only to homogeneous systems but also to heterogeneous systems; 2. the reaction coordinate is straightforwardly defined; 3. it is easy to perform dynamical analysis⁴ such as transmission coefficients.

Figure 3 shows (a) the potential energy profile of holes (hole trapping energy) and (b) the spin density on an anatase TiO_2 surface with five facets. The profiles are strongly dependent on the crystal facet. For the hydroxylated (112) and (001) surfaces, the holes are most stable on the O atoms of the OH groups on the surface. This is consistent with the best photocatalytic performance on the (112) surface measured experimentally, which is one order of magnitude greater than the well-known Degussa P25 commercially available. It is also found that the hole transfer along the [112] direction in anatase TiO_2 is fastest among all directions, which also supports the experimental findings. These results indicate that, although the

(101) surface is the most thermodynamically stable, the (112) and (001) surfaces provide higher active sites for photocatalytic degradation of organic molecules.

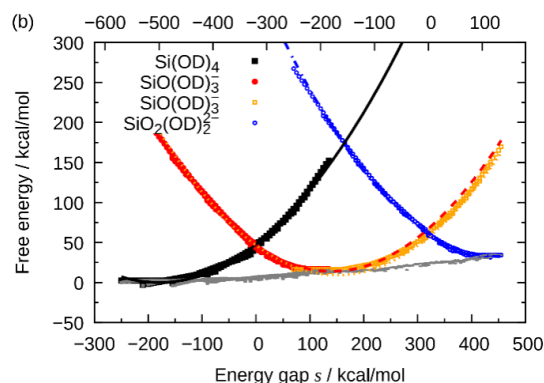


Figure 2. Computed free-energy surfaces of the deprotonation reaction of aqueous orthosilicic acid. The gray points are the adiabatic free-energy surface (FES).

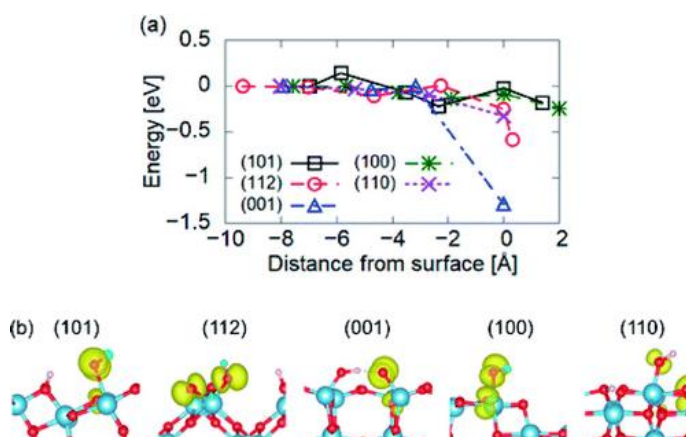


Figure 3. (a) Hole trapping energy at the hydroxylated anatase surfaces. (b) Spin density of a trapped hole (yellow isosurface).

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Symposium | Asian International Symposium | Asian International Symposium - Coordination Chemistry and Organometallic Chemistry -

[W2-1am] Asian International Symposium - Coordination Chemistry and Organometallic Chemistry -

Chair, Symposium organizer: Hisako Hashimoto, Teppei Yamada, Takahiko Kojima, Ryotaro Matsuda, Aiko Fukazawa, Shigeyuki Masaoka, Yoshiaki Nishibayashi, Hisashi Shimakoshi

Wed. Mar 23, 2022 9:00 AM - 11:40 AM W2 (Online Meeting)

[W2-1am-01] Stimuli-Responsive Porous Crystals

○Hiroshi Sato¹ (1. RIKEN)

9:05 AM - 9:25 AM

[W2-1am-02] Ion-Conductive Porous Crystals

○Masaaki Sadakiyo¹ (1. Tokyo Univ. Sci.)

9:25 AM - 9:45 AM

[W2-1am-03] Electrically Conductive Metal-Organic Frameworks

○Sarah Sunah Park¹ (1. Pohang University of Science and Technology (POSTECH))

9:45 AM - 10:15 AM

[W2-1am-04] Photocatalysis Utilizing Photoinduced Electron Transfer Coupled Phase Migration

○Akinobu Nakada^{1,2} (1. Chuo University, 2. PRESTO/JST)

10:30 AM - 10:50 AM

[W2-1am-05] Organorhodate and -Iridate — Structure and Reactivity—

○Takanori Iwasaki¹ (1. Grad. Sch. of Eng., The University of Tokyo)

10:50 AM - 11:10 AM

[W2-1am-06] Recent Advance in the Chemistry of Low-Coordinate Low-Valent Transition-Metal Complexes

○Liang Deng¹ (1. Shanghai Insitute of Organic Chemistry, CAS)

11:10 AM - 11:40 AM

Stimuli-Responsive Porous Crystals

(¹Riken Center for Emergent Matter Science) ○Hiroshi Sato¹

Keywords: Porous Coordination Polymers, Metal–Organic Frameworks, Sorption, Stimuli-Responsive Properties

Porous materials with countless nanometer-sized pores have long been used in our daily lives as functional materials that efficiently separate and remove small molecules such as gaseous molecules. As a new family of porous materials, metal–organic frameworks (MOFs) are synthesized by combining metal ions and organic ligands, and the size, shape, and chemical properties of their pores can be designed and tuned by taking advantage of the combination diversity of the constituents. Compared to conventional porous materials, MOFs are unique in that they can flexibly change their structures in response to the environment, despite their crystalline nature^{1–4}. We are studying the synthesis, function, and mechanism of such unique porous materials in which "hardness" and "softness" operate in concert. In this presentation, I would like to introduce MOF-based porous crystals that respond to external stimuli (Fig. 1). Especially, I will present crystals that respond to guest molecules^{5–7}, light^{8–12}, and mechanical forces¹³. Short summary for each topic is described as follows.

<Guest-responsive porous crystals>

(1) Carbon monoxide (CO)-responsive porous crystal⁵: We successfully developed a porous crystal that changes its porous structure in response to CO, and selectively adsorbs CO. Adsorption of CO molecules in the 1D channels can induce the structural change to accelerate further CO adsorption.

(2) Guest-responsive stepwise expansion in a porous crystal⁶: When a porous crystal was immersed in organic solvents, the crystal swelled and exfoliated. It is interesting to note that layer-number-selective porous nanosheets can be obtained from the crystal suspensions at different stages of interlayer expansion.

(3) Porous crystals with mechanical property change by adsorption¹³: By arranging catenanes in three dimensions, a porous crystal was realized whose Young's modulus changes in response to adsorption (Fig. 2). Crystallographically, it was confirmed that the relative positions of the

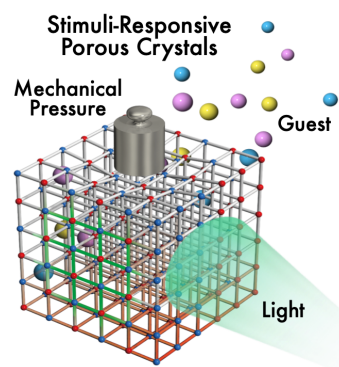


Fig. 1. Stimuli-responsive porous crystals.

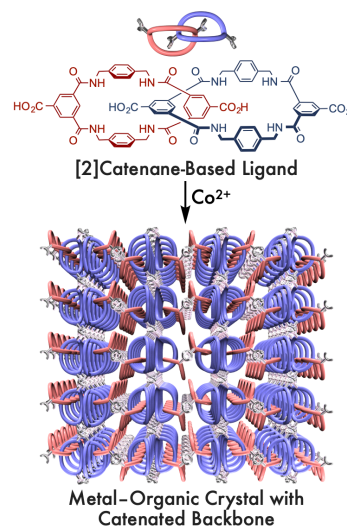


Fig. 2. Catenane-based porous crystal.

macrocycles in the catenated moieties change upon applying mechanical pressure.

<Photo-responsive porous crystals>

(1) [2+2] Photocyclization reaction⁸: A porous crystal containing photoreactive C=C bonds was prepared. When the crystals were irradiated with UV light, [2+2] photocyclization reaction proceeded efficiently, resulting in a formation of cyclobutane rings. The reacted C=C bonds were aligned on the 1D pore surface, and the pore size and shape changed before and after UV light irradiation.

(2) Photochemical generation of highly reactive species⁹: An azide group, which is a nitrene precursor, was successfully introduced on the 1D pore surface of a porous crystal. The pore surface can be photochemically activated and the crystal irreversibly trap gaseous molecules including oxygen and CO.

(3) *cis-trans* isomerization reaction¹⁰: An azobenzene-containing, zirconium-based porous crystal (^{Azo}MOF), upon irradiation with UV light, underwent *trans*-to-*cis* isomerization of its azobenzene pendants to furnish the *cis*-isomer content of 21% (^{Azo}MOF^{21%}) and underwent backward isomerization into ^{Azo}MOF^{1%} upon either irradiation with visible light.

(4) Quantitative and reversible photochemical reaction¹¹: We realized photoresponsive crystalline materials showing quantitative reversible photochemical reactions upon UV and visible light irradiation by introducing structural flexibility into crystalline porous frameworks composed of a diarylethene-based ligand. The structural flexibility of the porous framework enables highly efficient photochemical electrocyclization in a single-crystal-to-single-crystal manner.

(5) Photochemically crushable and regenerative porous crystals¹²: A photochemically crushable and regenerative porous crystal (^{DTE}MOF) was developed by complexation of a diarylethene-based photochromic ligand ^{Py}DTE_{open} with Cd²⁺. When ^{DTE}MOF suspended in DMF/MeOH was exposed to UV light, its crystalline network was readily crushed to afford a homogeneous solution, via ring-closing isomerization of the constituent ^{Py}DTE_{open}. Upon successive exposure of this solution to visible light, colorless crystals identical to those of ^{DTE}MOF were regenerated (Fig. 3).

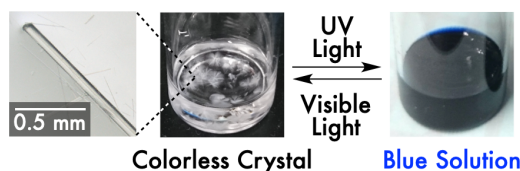


Fig. 3. Photoresponsive porous crystals.

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Ion-Conductive Porous Crystals

(¹*Faculty of Science Division I, Tokyo University of Science*) ○Masaaki Sadakiyo¹

Keywords: Ionic Conduction; Metal–Organic Framework; Covalent Organic Framework; Porous Material

Solid-state ionic conductors are important materials because of their potential applications for energy-related devices such as secondary batteries and fuel cells. Many researchers have investigated to clarify the relationship between structure and ionic conductivity using various solids. The migration of ionic carriers in solids requires some empty spaces or lattice defects for accepting the migrating ions (i.e., ion-conducting pathway). Therefore, the structural features of ionic conductors can be classified into three types.¹ First is the channel (porous) structure or layered structure that allows the included ionic carriers to migrate efficiently in the spaces (e.g. Na- β -alumina). Second is the mean structure, where the ions can migrate to various lattice points, resulting in averaged occupancy of the ions on these sites (e.g. α -AgI). Third is the defect structure, including some defects on the lattice point and the ions located on the neighbouring lattice point can migrate to the next position (e.g. Y-doped ZrO₂).

Metal–organic frameworks (MOFs) have recently emerged as a new class of ionic conductors due to their excellent materials variety and designable pores. The porous structure of MOFs is fundamentally suitable for creating highly ion-conductive materials by constructing efficient ion-conducting pathways in the pores. Many researchers have investigated to create novel ionic conductors using various ionic carriers such as proton (H⁺),² hydroxide ion (OH⁻),³ and lithium ion (Li⁺).⁴ Since the ionic conductivity (σ) is expressed as $\sigma = zen\mu$ (S cm⁻¹), where z is the valence of the ionic carrier, e is the elementary charge, n is the carrier concentration, and μ is the mobility of the charge carrier, it is clear that the introduction of an ionic carrier into the pores of MOFs (high n) and the construction of a suitable environment for the mobile ions in the pores (high μ) are the critical points to achieve high ionic conduction. One of the specific features of MOF-based ionic conductor is the guest inclusion. The guest molecules, namely ‘conducting media’, which enhance the migration of included ionic carrier, can be introduced into the remaining pores of MOFs to achieve high mobility of the ions. For example, H₂O molecules adsorbed in MOFs often enhance the H⁺ conductivity,² which is related to the specific conducting mechanism of H⁺, named as ‘Grotthuss mechanism’.

We have recently focused on the ionic conduction of multivalent ions such as magnesium ion (Mg²⁺) in MOFs. In particular, the Mg²⁺ conductor is one of the key materials for realization of the next-generation secondary battery without the use of rare elements such as Li. However, the number of reports on highly Mg²⁺-conductive solids

is considerably smaller than that of Li ions. In the case of MOFs, there are a few reports on conductivity of Mg^{2+} -included MOFs.^{5,6} However, there is a lack of direct evidence of Mg^{2+} transport and understanding of the role guest molecules for Mg^{2+} conduction in the MOFs. We recently succeeded in demonstrating that efficient Mg^{2+} transport truly occurs in the pores of MOFs and that Mg^{2+} conductivity strongly depends on the types of adsorbed guest molecules.⁷ We prepared a MOF, $\text{Mg-MOF-74} \supset \{\text{Mg}(\text{TFSI})_2\}_x$ ($x \leq 0.15$) ($\text{TFSI}^- = \text{bis}(\text{trifluoromethanesulfonyl})\text{imide}$), including only $\text{Mg}(\text{TFSI})_2$ inside the pores (Fig. 1) and evaluated the ionic conductivity under the presence of various guests vapors (Fig. 2). The ionic conductivity, evaluated by alternating current (ac) impedance measurements, strongly depended on the guest molecules and $\text{Mg-MOF-74} \supset \{\text{Mg}(\text{TFSI})_2\}_{0.15}$ showed superionic

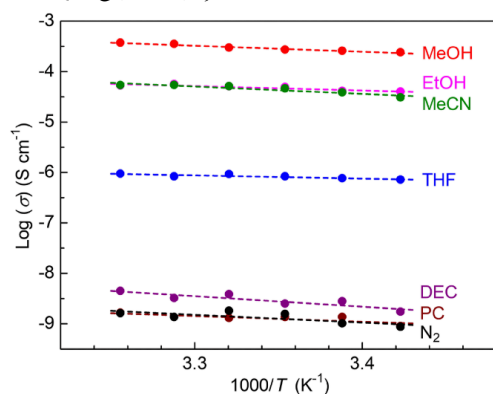


Fig. 2 Temperature dependence of the ionic conductivity of the sample of $x = 0.15$, $\text{Mg-MOF-74} \supset \{\text{Mg}(\text{TFSI})_2\}_{0.15}$.⁷

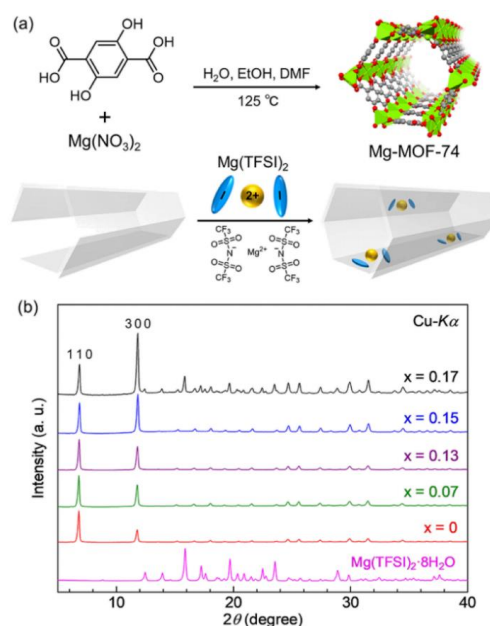


Fig. 1 (a) Schematic illustration of the introduction of only $\text{Mg}(\text{TFSI})_2$ salts inside the pores of Mg-MOF-74 . (b) XRPD patterns of $\text{Mg-MOF-74} \supset \{\text{Mg}(\text{TFSI})_2\}_x$.⁷

conductivity of $2.6 \times 10^{-4} \text{ S cm}^{-1}$ under MeOH vapor at room temperature. Since the ac impedance measurements could not directly evaluate the Mg^{2+} conductivity in this compound because of the presence of anion, TFSI^- , we also estimated the transfer number of Mg^{2+} of the MOF by dc polarization of the cell constructed by non-blocking electrodes and confirmed the efficient Mg^{2+} conduction in the MOF ($t_{\text{Mg}^{2+}} = 0.47$). The tendency that the conductivity deeply depended on the size of guest molecules is indicative that the high Mg^{2+} conduction is derived from the migration of coordinated species of Mg^{2+} .⁷

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Electrically Conductive Metal-Organic Frameworks

(Department of Chemistry, Pohang University of Science and Technology) ○ Sarah S. Park

Keywords: Conductive Metal-Organic Frameworks (MOFs), π interactions

The development of conducting metal–organic frameworks (MOFs) provides an avenue for creating high surface area conductors with potential applications ranging from electrocatalysts and chemiresistive sensors to supercapacitors. Highly ordered and infinite charge/ion transport pathways could be realized in conducting MOF platforms to yield high conductivity. However, it is difficult to engineer electrical conductivity in MOFs because these materials generally have flat bands determined by highly localized organic states and weak hybridization with the inorganic units. Based on using intermolecular π -stacking interactions as topology defining factor of MOFs,¹ strategies for synthesizing and utilizing the conductive and microporous MOFs will be discussed. In addition, four isostructural materials of general formula $M_2(\text{TTFTB})$ ($M = \text{Mn, Co, Zn, and Cd}$; $\text{TTFTB}^{4-} = \text{tetrathiafulvalene tetrabenzoate}$) were synthesized and their single crystal conductivities were studied. $M_2(\text{TTFTB})$ exhibit a striking correlation between their single-crystal conductivities and the shortest $\text{S} \cdots \text{S}$ interaction defined by neighboring TTF cores, which inversely correlates with the ionic radius of the metal ions.² These results provide a systematic blueprint for designing new electrically conductive MOFs based on the through-space charge transport formalism.

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Photocatalysis Utilizing Photoinduced Electron Transfer Coupled Phase Migration

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Keywords: Photocatalysis; Phase migration; Photoinduced electron transfer; Ferrocene; Backward electron transfer

The natural photosynthesis adopts multistep electron and proton transport crossing the interface of Thylakoid membrane for extremely efficient photogenerated charge transport, giving a considerable yield of light-to-chemical conversion.¹ Such redox-directed phase migration can be a rational tool to suppress the backward electron transfer in photocatalysis. We have aimed to construct “photoinduced coupled-electron transfer and phase migration” in two-separable solvent system, where the oxidized form of an electron donor, generated by the photoinduced electron transfer to a photosensitizer in a liquid phase, migrates to another liquid phase. It is expected to suppress the backward electron transfer between charge separated pair due to their spatial separation.

Herein, we report a reductive coupling of benzyl bromide driven by visible-light-induced coupled electron transfer and phase migration of ferrocene in biphasic solutions composed of water and halogenated solvent (Figure).² Visible-light irradiation to the 1,2-dichloroethane/water biphasic solution, where Fc, Ru(II) or Ir(III) complex photosensitizer, and benzyl bromide (Bn-Br) were initially distributed in the DCE phase, facilitated reductive coupling of Bn-Br to dibenzyl (Bn₂) using Fc as an electron donor to form Fc⁺. The key finding is that Fc⁺, generated by photooxidation of Fc in DCE phase, migrated to the aqueous phase following the driving force due to drastic change of partition coefficient compared with Fc. On the other hand, the same photolysis in the absence of aqueous phase failed to afford any product. Thus, the liquid-liquid phase migration is essential for facilitating reduction of Bn-Br in the DCE phase by spatial separation of Fc⁺ to the aqueous phase, suppressing backward charge recombination.

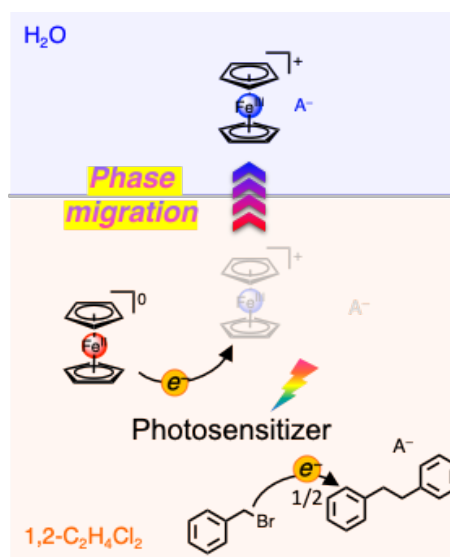


Figure. Photoinduced coupled electron transfer and phase migration developed in this study.

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Organorhodate and -Iridate —Structure and Reactivity—

(Graduate School of Engineering, The University of Tokyo) ○Takanori Iwasaki

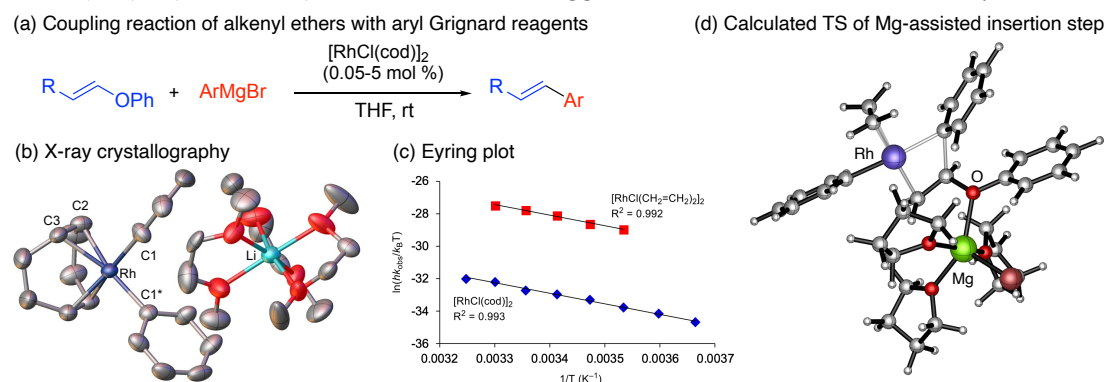
Keywords: Ate Complexes; C–O Bond Cleavage; Homoleptic Complexes; Iridium; Rhodium

Anionic organo transition metal complexes, so-called “ate” complexes, show unique structural feature as well as reactivity. In addition to the classical alkylating reagents such as Gilman reagents, ate complexes have recently been attracting attention as key catalytic active species as useful synthetic tools. In this context, we have developed organo metalates of various late transition metals and employed them to C–C bond formations. In this lecture, I will present our achievements on organo metalates of the group 9 metals, Rh and Ir.

In 2014, we reported that the coupling reaction of alkenyl aryl ethers with aryl Grignard reagents via the vinylic C–O bond cleavage proceeded smoothly in the presence of catalytic amount of $[\text{RhCl}(\text{cod})]_2$ (Scheme 1a).¹ This catalyst showed unique chemoselectivities including selective cleavage of vinylic C–O bond even in the presence of aromatic C–O, C–S, and C–Br bonds.

Mechanistic studies revealed that the treatment of $[\text{RhCl}(\text{cod})]_2$ with an excess ArMgBr yielded $[\text{RhAr}_2(\text{cod})]^-$, which reacted with a vinyl ether to give the coupling product. The corresponding $[\text{Li}(\text{dme})_3][\text{RhPh}_2(\text{cod})]$ (**1**_{Rh}) was successfully isolated and determined its structure by X-ray crystallography (Scheme 1b). Indeed, the isolated **1**_{Rh} catalyzed the coupling reaction, suggesting the intermediacy of the diarylrhodate.

Recently, we conducted further mechanistic studies to gain the insight into the reaction mechanism.² A kinetic study using a flow microreactor revealed that the reaction of diarylrhodate with phenyl vinyl ether is the rate-determining step in the catalytic cycle. In addition, olefinic ligands in the Rh pre-catalysts largely affected catalytic performance, and $[\text{RhCl}(\text{CH}_2=\text{CH}_2)_2]_2$ showed ca. 20 times higher catalytic activity in comparison with $[\text{RhCl}(\text{cod})]_2$ (Scheme 1c). DFT calculations suggest that the reaction between diarylrhodate



Scheme 1. (a) Rh-catalyzed cross-coupling of alkenyl ethers with ArMgBr . (b) ORTEP drawing of **1**_{Rh}. (c) Eyring plot of the reaction using $[\text{RhCl}(\text{cod})]_2$ and $[\text{RhCl}(\text{CH}_2=\text{CH}_2)_2]_2$. (d) Transition state of insertion of vinyl ether.

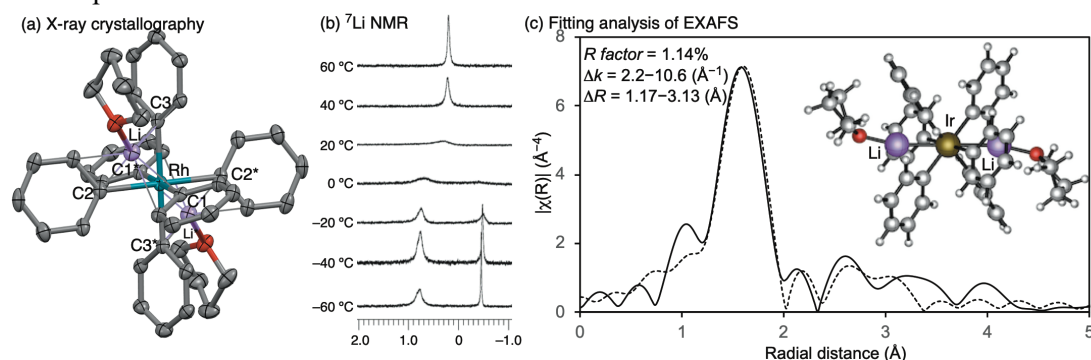
and vinylic ethers proceeds through Mg cation-assisted insertion/*anti*- β -oxygen elimination sequence (Scheme 1d). Based on these mechanistic understanding, we successfully applied the Rh catalyst to the cross-coupling reaction of benzofurans with aryl Grignard reagents.²

Analogous lithium diphenyliridate **1_{Ir}** was synthesized by a similar way to **1_{Rh}**.³ X-ray crystallographic analysis of the complexes showed both contact ion pair (CIP) and solvent-separated ion pair (SSIP) structures depending on the coordination environment around the Li cation.

During the course of the investigation on Rh(I) and Ir(I) organo metalates, we found that Rh(III) and Ir(III) also form ate complexes upon treating aryllithium reagents.⁴ In 1989, Wilkinson and co-workers reported [Li(tmeda)]₃[MMe₆] (M = Rh and Ir) and determined their structure to be a CIP structure.⁵ However, attempts to synthesized homoleptic hexaarylmatalate of Rh and Ir using electron-deficient pentahalophenyllithiums resulted in the formation of pentaarylmatalates, and hexaarylmatalates had not been synthesized for *d*⁶ transition metals.

When MCl₃(tht)₃ (M = Rh and Ir) was treated with 8 equivalents of PhLi, the corresponding [Li(thf)_n]₃[MPh₆] **2** was obtained in 70-76% yields. Crystals suitable for X-ray crystallography were obtained by recrystallization in the presence of 12-crown-4. X-ray crystallography revealed that the crystal structure of **2_{Rh}** contains one Rh bearing six Ph moieties in an ideal octahedral geometry and three Li cations. Two Li cations with one THF molecule contact the Ph moieties on Rh, and the other in the outer sphere is surrounded by two 12-crown-4 molecules (Scheme 2a).

⁷Li NMR and solution-phase EXAFS analyses of **2_{Ir}** indicated that the partially solvent-separated ion pair structure was maintained even in a coordinating solvent, THF (Scheme 2b and c). This may suggested that the coordination of Li cations to the anionic counterpart stabilizes the trianionic iridate.



Scheme 2. (a) ORTEP drawing of anionic part of **2_{Rh}**. (b) VT ⁷Li NMR of **2_{Ir}**. (c) EXAFS spectrum of **2_{Ir}** and 10 equiv. of 12-crown-4 in THF (solid line) and fitting curve of calculated structure (dashed line).

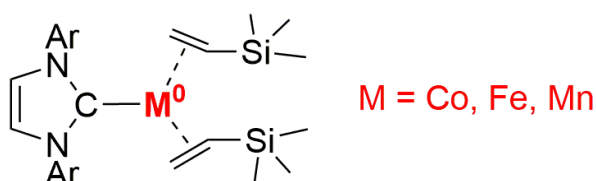
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Recent Advance in the Chemistry of Low-Coordinate Low-Valent Transition-Metal Complexes

(Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai, 200032, People's Republic of China) ○Liang Deng

Keywords: Carbene; Cobalt; Iron; Low Valent; Open-Shell

The knowledge on the formation, structure, and reactivity of low-coordinate 3d metal species forms the basis for the development of new 3d metal-catalyzed organic transformations and also disclosing the mysterious mechanisms of enzymatic catalysis and “single-atom” catalysis.¹⁻³ Aiming to deepen our knowledge on this type of reactive metal species, we have been working on the chemistry of low-coordinate zero-valent cobalt, iron and manganese complexes with N-heterocyclic carbene (NHC) and olefin ligation for years. This ligand set is found effective in stabilizing three-coordinate cobalt(0), iron(0), and manganese(0) complexes in the forms of (NHC)M(olefin)₂. In this presentation, the synthesis, electronic structure, and reactivity of the three-coordinate zero-valent metal complexes will be discussed.⁴



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Symposium | Special Program | Photo and electric functions of low dimensional material

[B103-1am] Photo and electric functions of low dimensional material

Chair, Symposium organizer: Takuya Fujimura, Yasutaka Suzuki

Wed. Mar 23, 2022 9:00 AM - 11:40 AM B103 (Online Meeting)

[B103-1am-01] Stabilizing and aligning Aqua-Fe Complexes for Replacing TiO_2 Nanoparticles

○Yusuke Ide¹ (1. National Institute for Materials Science)

9:05 AM - 9:28 AM

[B103-1am-02] Magnetic Property of Heterostructured Nanosheets Film

○Takashi Yamamoto¹ (1. Keio Univ.)

9:28 AM - 9:51 AM

[B103-1am-03] Self-Repairing Electrocatalysts for Alkaline Water Electrolysis Using Hybrid Metal Hydroxides

○Yoshiyuki Kuroda¹ (1. Yokohama National University)

9:51 AM - 10:14 AM

[B103-1am-04] Enhanced Photochemical Reactions on Low-dimensional Materials

○Tatsuto Yui¹ (1. Niigata University)

10:26 AM - 10:49 AM

[B103-1am-05] Structural colors of inorganic nanosheets

○Nobuyoshi Miyamoto¹ (1. Fukuoka Institute of Technology)

10:49 AM - 11:12 AM

[B103-1am-06] Speculation of formation pathway of zeolite using ESI-MS and NMR

○Nao Tsunoji¹ (1. Hiroshima University)

11:12 AM - 11:35 AM

酸化チタン代替素材開発を指向した鉄アコ錯体の安定化・構造制御

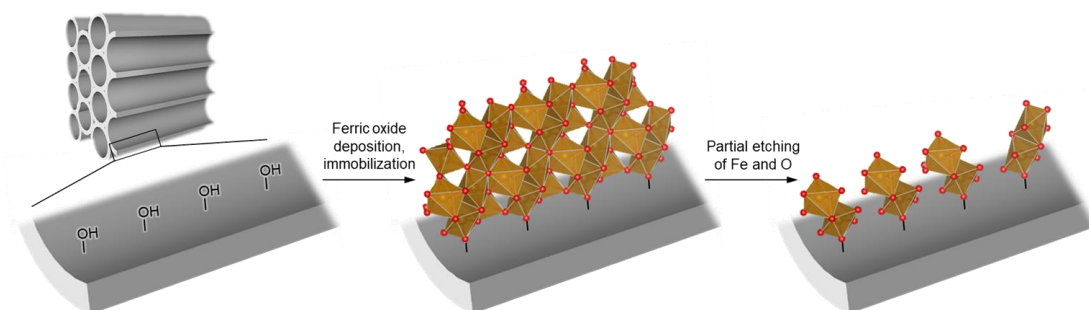
(物材機構 MANA) 井出 裕介

Stabilization and Design of Aqua-Iron Complexes for Replacing TiO_2 (International Center for Materials Nanoarchitectonics, National Institute for Materials Sciences) Yusuke Ide

Despite the ubiquity of aqua-Fe(III) complexes in biological enzymes and their useful properties and cost-effectiveness for many applications, artificially stabilising these fleeting molecules for practical use remains challenging in terms of their stability, the precise control of aqua-Fe(III) complex structures, and the safety of supports. Herein, we demonstrate that dimeric aqua-Fe(III) species can be stabilised/controlled using mesoporous silicas or layered silicates to produce UV absorbers or photocatalysts whose performances exceed to that of commercial TiO_2 nanoparticles. We also report that an exceptional type of green rust, which is a Fe(II)/Fe(III) mixed-valent iron mineral and previously thought to be very instable against oxidation, shows high oxidation stability and good photocatalytic activity higher than that of a benchmark TiO_2 nanoparticle.

Keywords : Iron Oxide; Aqua-Iron Complex; Mesoporous Silica; Layered Silicate; Green Rust

鉄アコ錯体は酵素などの生態系では遍在しているが、通常は不安定で人工的に安定化させることが難しい。担体を使い安定化させた例はあるものの、生成物の安定性や担体の安全性、分子構造の設計性には課題が残っており、鉄ならではの安さと安全性を活かした材料開発には至っていない。我々は、層状珪酸塩や多孔質シリカを巧く用いて酵素で見られるような鉄アコ錯体二量体を設計・安定化させることに成功した^{1,2)}。また、通常は酸化に対して不安定と考えられてきたグリーンラスト ($\text{Fe}^{2+}/\text{Fe}^{3+}$ 系層状複水酸化物、単層はアコ錯体の二次元配向物と見なせる) を酸化に対して安定な状態で合成することにも成功した³⁾。得られた材料は、市販の TiO_2 ナノ粒子を凌駕する光触媒機能、UV 遮蔽機能を示し、人体への安全性が懸念されている TiO_2 ナノ粒子の代替品となる可能性を秘めている。



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異種ナノシート集積膜の磁気特性

(慶大理工) ○山本 崇史

Magnetic Property of Heterostructured Nanosheets Film

(Faculty of Science and Technology, Keio University) ○Takashi Yamamoto

The concept of an “organic-inorganic” hybrid is relatively old but still effective for fabricating functional materials. Recently, in the field of molecule-based magnetism, the approach of an “inorganic-inorganic” heterostructure is growing considerably, where synergistic magnetic properties are emerged. In particular, utilization of two-dimensional materials as a building block is one of the straightforward strategy due to their fascinating electronic properties. Overall, integration of appropriate molecular building blocks leads to develop an innovative functional material. Herein, I would like to introduce our recent examples of heterostructured magnetic materials based on layered double hydroxides (LDH): (i) intercalation compounds exhibiting tunable magnetic properties and (ii) stacked nanosheets assemblies exhibiting a photoamplification of perpendicular magnetic anisotropy.

Keywords: Two-Dimensional Material; Layered Double Hydroxides; Molecule-Based Magnet; Photochemical Reaction; Layer-by-Layer Assembly

機能性材料の創出において、「有機－無機」ハイブリッドと呼ばれる概念は比較的古いものの、依然として有効なアプローチである¹⁾。近年、分子磁性の分野において、「無機－無機」ヘテロ構造の創出によって協奏的な磁気特性を発現させる試みが盛んに行われている²⁾。特に、多彩な電子物性を示す2次元材料をヘテロ構造のビルディングブロックとして利用することは、直截的なアプローチのひとつとして位置づけられる。以上を踏まえると、適切なビルディングブロックを集積することが革新的な機能性材料の創出につながると言える。本講演では、層状複水酸化物 (LDH) をビルディングブロックとした磁性ヘテロ構造の創出に関する我々の研究例を紹介する。

[1] 磁性 LDH をホストとした層間化合物における磁気特性の変調³⁾

インターカレーションによって、Co イオンと Ni イオンを含む LDH (Co-Ni LDH) の層間にアルキル鎖長の異なるスルホン酸アニオンを導入 (Co-Ni- C_n SO₃ LDH) した。粉末 X 線回折による構造評価から、Co-Ni- C_n SO₃ LDH の面間隔が n に対して直線的に増加していることが確認され、Co-Ni LDH の層間距離が系統的に変化した磁性体を揃えることができた。2 K における磁化の磁場依存性では、 n 、すなわち層間距離に応じて保磁力が変化した。これは、Co-Ni LDH の層内に働く超交換相互作用と層間に働く磁気双極子相互作用の競合によって説明できる。層間距離が十分に大きい磁性体においては反強磁性の磁気双極子相互作用による寄与が無視できるほど小さくなる結果、強磁性の超交換相互作用が支配的となり、保磁力が強められたと考えられる。

[2] Co-Ni LDH ナノシート積層体における垂直磁気異方性の光増強^{4,5)}

ナノシートの層電荷を駆動力とした layer-by-layer 法によって、Co-Ni LDH ナノシートとスメクタイト (SSA) ナノシートの集積膜 ([Co-Ni LDH / SSA]) を作製した。原子間力顕微鏡 (AFM) および斜入射 X 線回折 (GIXD) により、Co-Ni LDH と SSA の単一ナノシートの厚みの和を反映した構造周期が確認されたことから、それぞれのナノシートが交互に積層されていることが示唆された。2 K における磁化の磁場依存性では、面直方向に磁場を印加した場合 (H_{\perp}) が面内方向のそれ (H_{\parallel}) よりも磁化されやすく、保磁力は H_{\perp} で 270 Oe であったのに対して H_{\parallel} では 140 Oe であったことから、[Co-Ni LDH / SSA] は垂直磁気異方性を示した (**Figure 1a**)。

ナノシートの層電荷を駆動力とした layer-by-layer 法によって、Co-Ni LDH ナノシートとチタン酸 (TO) ナノシートの集積膜 ([Co-Ni LDH / TO]) を作製した。GIXD により、Co-Ni LDH と TO の単一ナノシートの厚みの和を反映した構造周期が確認されたことから、それぞれのナノシートが交互に積層されていることが示唆された。2 K における磁化の磁場依存性では、磁化の立ち上がりが H_{\perp} の場合が H_{\parallel} よりも鋭く、[Co-Ni LDH / TO] は垂直磁気異方性を示した (**Figure 1b**)。次に、TO ナノシートバンドギャップ励起を行い、2 K における磁化の磁場依存性を測定したところ、磁化率が著しく減少した。減少した磁化率は大気中に放置することによって回復した。X 線光電子分光 (XPS) 測定から、光照射によって Co-Ni LDH 中の Co(III) イオンの一部が還元されていることが確認された。すなわち、[Co-Ni LDH / TO] における垂直磁気異方性の光変調は TO の励起電子が Co-Ni LDH に注入されたことに起因し、実際に光照射前後で垂直磁気異方性の度合いは約 300% 増幅された。

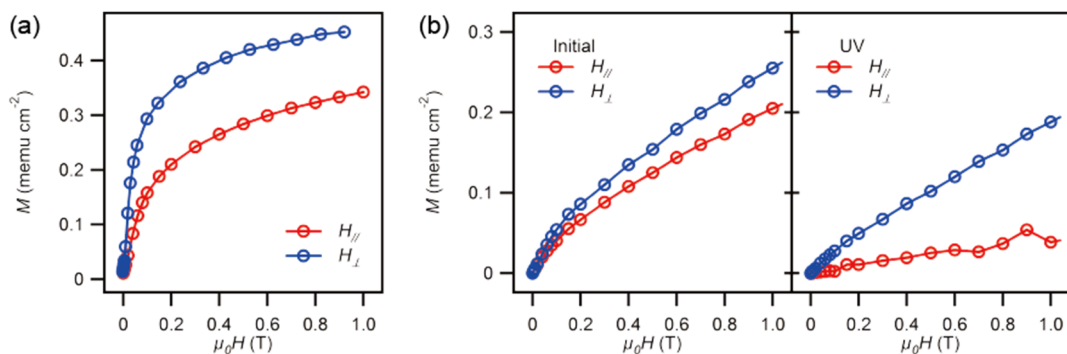


Figure 1. Field-Dependent magnetization at 2 K: (a) [Co-Ni LDH / SSA] and (b) [Co-Ni LDH / TO]

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ハイブリッド水酸化物による水電解用自己修復電極触媒

(横浜国立大学¹⁾) ○黒田義之¹

Self-Repairing Electrocatalyst Consisting of Hybrid Metal Hydroxides for Alkaline Water Electrolysis (¹*Graduate School of Engineering Science, Yokohama National University*)

○Yoshiyuki Kuroda¹

Production of H₂ from renewable energy is highly demanded to solve global warming. Alkaline water electrolysis is promising because of its low cost and scalability; however, degradation of electrocatalysts due to suspension of an electrolyzer is problematic. In this study, self-repairing electrocatalyst by the electrodeposition of hybrid cobalt hydroxide nanosheets (Co-ns) with the 2-D morphology is demonstrated. Deposition of Co-ns on a Ni substrate by electrolysis is applicable for in-situ repair of degraded catalyst film. The accelerated durability test of a Ni electrode coated with Co-ns exhibited quite high durability with the help of short electrolysis to repair electrode. Consequently, the self-repairing catalyst is useful to improve lifetime of alkaline water electrolysis powered by renewable energy.

Keywords : alkaline water electrolysis, oxygen evolution reaction, metal hydroxides, hybrid materials

地球温暖化問題の解決に向け、再生可能エネルギーの普及が急務である。再生可能エネルギーを有効利用するため、水電解による水素製造が注目されている。アルカリ水電解は低コストで大規模製造に適した方法だが、停止時に逆電流が発生し、電極が劣化してしまう。逆電流は電解により充電された電極が、停止時に放電する現象であり、電極触媒や Ni 基材のレドックスが繰り返すことで触媒の剥離、溶出、変質等が進行する。電極基材を導電性酸化物で被覆することで劣化を抑制することができるが、安定な酸化物は触媒活性が低い傾向にあり、活性と耐久性の両立に課題がある。

アルカリ水電解用アノードは主に Ni や Fe からなる金属がアノード酸化して生じた金属水酸化物が酸素発生反応 (OER) 触媒となる。これらは二次元の層状化合物であり、剥離し、電解液に分散させれば、外部から電極表面に輸送可能な電極触媒としての利用が期待できる。すなわち、逆電流により劣化した電極を、電解液に分散させた触媒を用いて修復する自己修復的システムが構築できる。特に二次元構造体は電解液に分散する様々な微粒子の中でも、特に基材の保護に適した構造と考えられる。

本研究では、有機修飾により表面積、分散性を高めたハイブリッド水酸化コバルトナノシート (Co-ns) を用いた、自己修復電極触媒システムについて紹介する。¹⁾ 遷移金属水酸化物を高濃度のアルカリ電解液に分散させることは難しいが、水酸化物層を三脚型配位子により選択的に修飾することで、剥離能、分散能を向上させた。これを用い、アルカリ水電解の起動停止を模した加速劣化試験により、耐久性を評価した。

Co-ns は CoCl₂·6H₂O の水溶液と tris(hydroxymethyl)aminomethane (Tris-NH₂, 図 1(a)) との反応により容易に合成することができる。²⁾ Tris-NH₂ は 3 つのアルコール部位 (CH₂OH) を有し、これが水酸化コバルトのブルーサイト層表面の水酸基と三重の強

固なアルコキシドを結合する。Tris-NH₂は水酸化物を生ずるための塩基兼修飾剤として働き、層の両面が修飾されたハイブリッド構造（図 1(b)）を one-pot で形成する。

次に、1 M KOH 中で Co-ns を触媒とした OER 試験および耐久試験を行った。試験は作用極に金属 Ni を用いたハーフセルで行い、電解液に約 40 ppm の Co-ns を分散させた。参照極には可逆水素電極（RHE）を用いた。このセルで 800 mA cm⁻² の定電流電解を行うと、作用極上に Co-ns が体積し、活性な触媒層を形成した。電気化学的に触媒層を形成できるということは、電極劣化時に電解液から触媒成分を補充し、再形成できることを意味している。また興味深いことに、通常の多孔体であれば、電流密度の増大により内部の活性点は利用不可能となるが、Co-ns からなる多孔質触媒層では層内部まで活性点として機能していることがわかった。

アルカリ水電解の起動停止を模した加速劣化試験は、高速 CV により行った。CV の上限電位は電解状態を模した 1.8 V vs. RHE とし、下限電位は逆電流による放電後を模した 0.5 V vs. RHE とした。これを 500 mV s⁻¹ で繰り返し、2000 サイクル毎に OER 活性を測定した。また、触媒の修復のため、2000 サイクル毎に 800 mA cm⁻² で電解を 30 min 行った。Fig. x に示す様に、触媒を被覆していない Ni 電極では、10000 サイクルまでに大幅な過電圧の増加が認められたが、Co-ns を被覆した電極では過電圧の増加が約 9 mV と軽微であった（図 1(c)）。さらに、修復プロセスを加えた加速劣化試験では、過電圧の増加は認められず、半永久的な活性を示すことがわかった。また、より高活性な OER 触媒として知られる NiFe LDH など、遷移金属を複合したハイブリッド水酸化物触媒では、さらに高い活性を維持することができた。

以上より、二次元ナノシート構造を有するハイブリッド水酸化コバルトナノシートにより、再生可能エネルギーを用いたアルカリ水電解において高耐久性を実現できる可能性が示された。

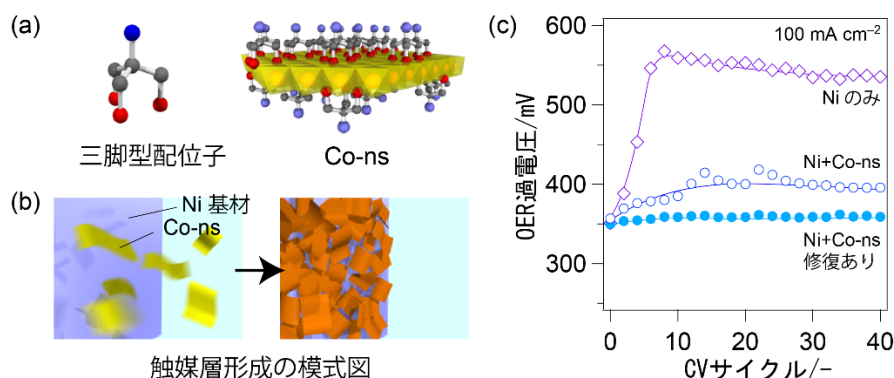


図 1. (a) 三脚型配位子、Co-ns の構造モデル、(b) 触媒層形成プロセスの模式図、(c) 耐久試験における OER 過電圧と CV サイクル数の関係。

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低次元材料の光反応促進現象

(新潟大自然¹) ○由井 樹人¹

Enhanced Photochemical Reactions on Low-dimensional Materials (¹ *Department of Materials Science and Technology, Faculty of Engineering, Niigata University*) ○Tatsuto YUI,¹

The chemical reaction in homogeneous solution proceeds via diffusion and collision processes. In many cases, chemical reactions do not proceed the diffusion and collision processes. Especially, photoreactions strongly affects the diffusion processes, due to the photoreaction starts the electrically excited state having very short lifetime. Thus, this is a one of the important factors in lowering the efficiency and selectivity of photochemical reactions. On the other hand, selective and highly efficient reactions proceed in the bio systems, due to the nano-ordered fixation of reactant within the systems. We have reported that the molecular fixation techniques of dyes on the low-dimensional materials, such as clay minerals, and found that unique photochemical reactions. We will present here the nano-ordered molecular orientation and enhancement the photochemical reactions on the surface of the low dimensional materials.

Keywords : Photoreaction; Low-dimensional Materials; Clay; Dyes; Molecular Orientation

均一溶液の化学反応は、溶質の自由拡散に支配されるため、基本的には拡散速度以上の化学反応は進行しない。特に光化学反応は、短寿命な光励起状態からその反応が進行するため拡散の影響を顕著に受ける。一方、生体における化学反応は、反応基質をナノレベルで精密に配置することで、高効率かつ高選択的な化学反応を進行させている。我々は、分子のナノ配列技術として粘土鉱物をはじめとする様々な低次元材料と光機能性分子との複合化をおこなってきた。本発表では、低次元材料への分子の固定・配列化技術および配列・固定化に伴う光反応の促進現象に関して論ずる予定である。

Liquid Crystalline Nanosheets/Polymer Composite Gels with Structural Colors

(Graduate School of Engineering, Fukuoka Institute of Technology) ○ Nobuyoshi Miyamoto

Keywords: *Structural Colors; Inorganic Nanosheets; Liquid Crystals; Nanocomposite Gels*

Inorganic nanosheets obtained by exfoliation of layered crystals have been investigated as intriguing nanomaterials for various functional materials. Under a certain condition, nanosheets dispersed in a solvent are spontaneously ordered to form crystal phase with regulated superstructures¹. In this study, we prepared the layered perovskite nanosheet liquid crystals with lamellar-like periodic structure that show structural colors and immobilized them in polymer gel by in-situ polymerization technique,² in view of applications as stimuli-responsive soft materials.

The perovskite nanosheets colloids were synthesized using the method reported previously.¹ To obtain the composite gels, monomers (e.g., *N*-isopropylacrylamide), crosslinker and photoinitiator were dissolved into the nanosheet colloid and the mixture was irradiated with UV-light to proceed photo polymerization.

The nanosheet colloid (3 wt%) showed pearl-like structural color, giving the maximum reflectance wavelength (λ_{max}) of 450 nm in the visible reflectance spectrum. As the monomer was added, λ_{max} shifted to 439 nm, indicating the slight change of the interactions between nanosheets. Even after polymerization and swelling to equilibrium state, the structural color was retained ($\lambda_{\text{max}} = 567$ nm), indicating successful immobilization of the superstructure of the liquid crystalline nanosheets. The color of the gel was reversibly changed by mechanically compressing the gel.

Acknowledgment: This research was supported by KAKENHI (#24104005 and #15K05657) and Network Joint Research Center for Materials and Devices (#20191350).

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ESI-MS および NMR によるゼオライト形成過程の調査

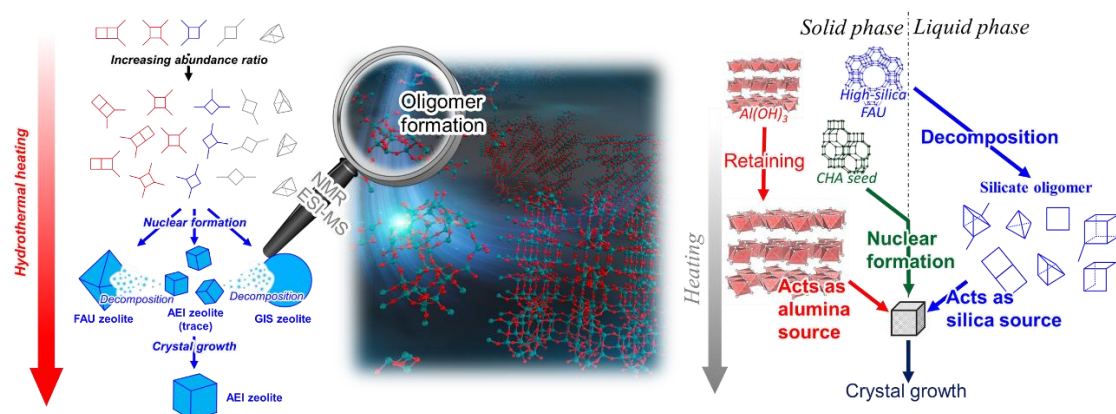
(広島大¹⁾) ○津野地 直¹

Speculation of formation pathway of zeolite using ESI-MS and NMR (¹Graduate School of Advanced Science and Engineering, Hiroshima University)○Nao Tsunoji,¹

Zeolite is porous material used in the industry as a catalyst and adsorbent. Despite of the various application fields of zeolite, because of the complicated formation scheme of the framework, to control the synthesis system of zeolite is still difficult, limiting the rational development of the new function and property. Numerous efforts using various analytical methods have been paid to speculate the crystallization mechanism of zeolite. However, the molecular level insight of synthesis intermediate and their relation to zeolite formation is still not clear completely. Herein, we show the analytical method to investigate the formation pathway of AEI and CHA zeolites combining the electrospray ionization mass and NMR spectroscopies to get molecular level insight for more precise zeolite synthesis^{1,2)}.

Keywords : Zeolite; Electrospray Ionization Mass Spectroscopy; Intermediate Oligomer; Hydrothermal Synthesis; Crystallization mechanism

ゼオライトは、触媒や吸着材として様々な産業で利用されている多孔質材料である。しかし、ゼオライトの応用用途が様々な存在するにもかかわらず、その骨格形成過程が複雑であるため合成系の制御が難しく、合理的な機能・特性開拓が妨げられている。これまでに、様々な分析法を用いたゼオライトの結晶化メカニズムの提唱が行われてきたが、合成中間体の分子レベルの構造知見とその構造と結晶化現象のかかわりに関しては未だに全容が明らかになっていない。本講演では、分子レベルの構造知見に基づくより精密なゼオライト合成の確立を目標として、AEI および CHA ゼオライトの合成過程をエレクトロスプレーイオン化質量分析およびNMRを組み合わせて調査した内容を紹介する^{1,2)}。



- 1) Formation pathway of AEI zeolites as a basis for a streamlined synthesis. N. Tsunoji, D. Shimono, K. Tsuchiya, M. Sadakane, T. Sano, *Chem. Mater.* **2020**, 32, 60.
- 2) High-quality synthesis of nanosized CHA zeolite by combination of starting FAU zeolite and aluminum sources. T. Tanigawa, N. Tsunoji, M. Sadakane, T. Sano, *Dalton. Trans.* **2020**, 49, 9972.

Symposium | Special Program | Chemistry for Mobility Batteries

[B203-1am] Chemistry for Mobility Batteries

Chair, Symposium organizer: Nobuyuki Imanishi

Wed. Mar 23, 2022 9:00 AM - 11:40 AM B203 (Online Meeting)

[B203-1am-01] Innovative Batteries for Sustainable Mobility

○Hideki Iba¹ (1. Toyota Motor Corporation)

9:05 AM - 9:30 AM

[B203-1am-02] Development of all-solid-state batteries with inorganic amorphous materials

○Akitoshi Hayashi¹ (1. Osaka Prefecture University)

9:30 AM - 9:55 AM

[B203-1am-03] New developments in solid electrolytes for all-solid-state battery applications

○Ryoji Kanno¹ (1. Tokyo Institute of Technology)

9:55 AM - 10:20 AM

[B203-1am-04] Challenges and Perspective in Developing Fuel Cell Materials for Vehicles

○Kensaku Kodama¹, Seiji Sano², Shintaro Tanaka³ (1. Toyota Central R&D Labs., Inc. ,
2. Toyota Motor Corporation, 3. Honda R&D Co.,Ltd.)

10:20 AM - 10:45 AM

[B203-1am-05] Progress of research on perfluorinated electrolyte polymer for fuel cells

○satoru hommura¹ (1. AGC Inc.)

10:45 AM - 11:10 AM

[B203-1am-06] Current Status and Issues of Electrocatalysts for Polymer Electrolyte Fuel Cells

○Hiroyuki UCHIDA¹ (1. University of Yamanashi)

11:10 AM - 11:35 AM

サステナブルモビリティ実現のための革新電池への期待

(トヨタ自動車株式会社) 射場英紀

Innovative Batteries for Sustainable Mobility (*Toyota Motor Corporation*) Hideki Iba

Electric vehicles (Fig. 1) are expected to become widespread in order to realize a sustainable society. Since electric vehicles emit less carbon dioxide during driving, reducing the amount of carbon dioxide generated during the production of electric power and vehicles can contribute to carbon neutrality. Therefore, there are great expectations for innovative batteries, and many studies have been conducted so far.

This time, I would like to introduce research examples of these innovative batteries for each carrier ion shown in the periodic table of Fig. 2 and discuss their current status and issues.

Keywords : All Solid-state Battery; Metal Air Battery; Sodium Ion Battery; Magnesium Ion Battery; Metal Hydride

持続可能な社会実現のために、電動車 (Fig.1) の普及が期待されている。電動車は、走行時の二酸化炭素の排出は少ないので、電力や車両の生産時に発生する二酸化炭素を低減すれば、カーボンニュートラルに貢献できる。そのために、革新電池への期待が大きく、これまでに数多くの研究がなされてきた。



Fig. 1 Example of electric vehicles

今回は、これらの革新電池に関連して、Fig.2の周期表¹⁾に示されるキャリアイオンごとに、研究事例を紹介し、その現状と課題について議論したい。



Fig.2 Periodic table (excerpt) and carrier ions for next-generation batteries

Li イオンをキャリアとして用いる電池は、携帯電話、パソコン、電気自動車用として広く普及している。これに固体電解質を用いた全固体電池は、次世代電池の本命として期待されている。また、負極に金属 Li、正極に炭素を用いた Li 空気電池は、次世代電池では、最もエネルギー密度が得られる電池系と位置付けられる。

Na イオン電池は、資源やコストの面で期待が大きく、電極材料の研究の進展により、室温でも駆動できる電池系が実現している。

Mg イオン電池では、種々の電解液の研究が進んでいるが、高エネルギー密度を実現するためには、新しい正極材料の発見が必須である。

水素関連では、多くのハイブリッド車に適用されている Ni-MH 電池には水素吸蔵合金が用いられており、その性能の向上や電池の設計の革新によりさらなる適用拡大が期待できる。

アニオン駆動の電池の一例として、フッ素イオン電池があげられる。RISING プロジェクトにおいて、原理実証がなされ、新しい要素材料の探索により、画期的な性能向上が期待できる

- 1) 一家に一枚周期表, Kohei Tamao, <http://www.pcost.or.jp/index.html>

無機アモルファス材料を用いた全固体電池の開発

(阪府大院工) ○林 晃敏・作田 敦・辰巳砂 昌弘

Development of all-solid-state battery with inorganic amorphous material (*Graduate School of Engineering, Osaka Prefecture University*) ○Akitoshi Hayashi, Atsushi Sakuda, Masahiro Tatsumisago

All-solid-state batteries using inorganic solid electrolytes instead of conventional organic liquid electrolytes have been extensively studied because of their high safety and high energy density. Formation of electrode-electrolyte interfaces using superior solid electrolytes is important to develop solid-state batteries. Amorphous sulfide electrolytes have advantages of high conductivity and appropriate mechanical properties, which are continuously changed by selecting glass composition. Liquid-phase process for synthesizing sulfide electrolytes is effective in having large contact areas with active materials. All-solid-state Li/S batteries with high energy density have been developed by optimizing the electrode-electrolyte interface.

Keywords : All-solid-state Battery; Solid Electrolyte, Amorphous Material; Interface

従来の有機電解液に代えて無機固体電解質を用いた全固体リチウム電池は、安全性と高エネルギー密度を兼ね備えた次世代蓄電池として研究開発が活発化している。この電池を実現するためには、高いリチウムイオン伝導度と適切な機械的性質を備えた固体電解質を用いて電極活物質と広く密着した固体界面を形成し、充放電過程において界面接触を保持することが重要である¹⁾。本講演では主に無機アモルファス材料を用いた全固体電池についての研究の進展について発表する。

Li₃PS₄ ガラスは高い導電率と優れた成形性をもつ優れた固体電解質であり、そのヤング率 (25 GPa) は酸化物ガラスと比べて小さい。また Li₃PS₄ へ LiI を添加することによって成形性が向上し、ヤング率は減少することから、ガラスの組成選択によって電解質の機械的特性を連続的に変化させることができる²⁾。また近年、液相を介した硫化物電解質の合成プロセスの開発が進められている。電解質の前駆溶液を多孔質電極へ含浸して界面形成することによって、従来の電解質粒子を混合する場合と比較して、より少ない電解質割合においても固体界面接触が得られる³⁾。

軽量で高エネルギー密度の全固体リチウム-硫黄電池の開発に向けて、硫黄正極複合体およびリチウム金属負極界面の評価が重要となる。作製プロセスを最適化した硫黄-炭素-電解質複合体を正極に用いた全固体電池は、1 mA cm⁻² 以上の電流密度においても 1000 mAh g⁻¹ 以上の容量を示す⁴⁾。リチウム金属負極の適用に向けては、硫化物ガラス電解質を用いた全固体電池のリチウム短絡メカニズムが明らかになっており、リチウム金属負極と電解質界面の制御が短絡抑制に対して有効である⁵⁾。

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全固体電池の実用化に向けた固体電解質の新展開

(東工大科創研) ○菅野了次

New developments in solid electrolytes for all-solid-state battery applications (Institute of Innovative Research, Tokyo Institute of Technology)○Ryoji Kanno

The key to the commercialization of solid-state batteries is the solid electrolyte. The development of solid electrolytes has a long history. In recent years, materials that meet the requirements of practical batteries have been available and rapidly developed to improve the properties of all solid state batteries: in the Li-based system, many new materials have been developed and optimized to improve the performance of sulfide and oxide batteries. In addition, sodium-based and fluoride-based materials are being developed to realize new solid-state batteries. In this presentation, the current status and future of solid electrolyte development will be reviewed.

Keywords : Solid Electrolyte; Ionic conductor; All-Solid-State Battery

固体電池の実用化の鍵を握る材料が固体電解質である。固体電解質の開発には長い歴史があるが、実用電池の要求に耐える材料がようやく出現し、電池特性の向上にむけて、その開発が急速に進んでいる。リチウム系では硫化物系や酸化物系で多くの新材料が開発された。新規固体電池系を可能にするナトリウム系やフッ化物系なども開発が進んでいる。また、ヒドリドイオンなど既存のイオン導電体の範疇に入らない新たな導電体の開発が進んでいる。図には、代表的なイオン導電体のイオン導電率が研究の進展と共に向上する様子を示した。

イオン導電体の物質開拓には、新規の物質探索がなされた後、特性向上を目指した組成開拓、電池への展開に必要な性能の最適化へと様々な開発過程が存在する。多様な元素系の中でもリチウム系は、全固体電池の電解質として実用化に必要な特性向上がなされている。

講演では進歩が著しいLi系を中心に、固体電解質開発の現状と将来を概観する。

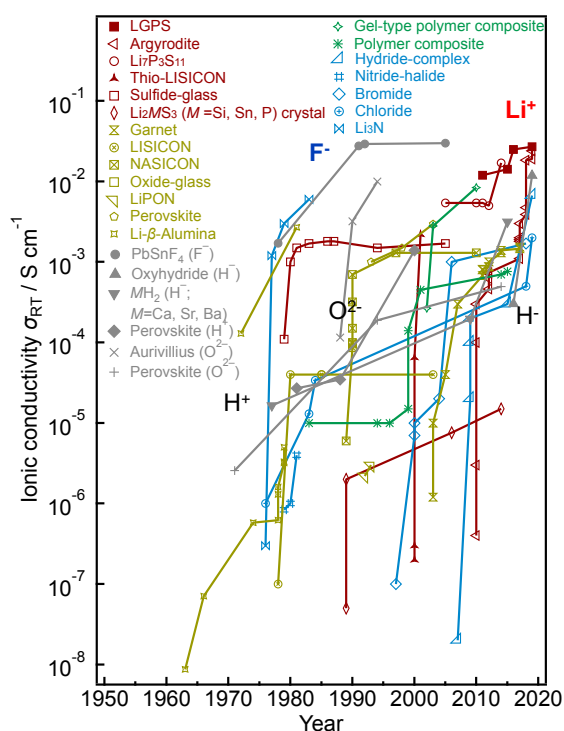


図 イオン導電体の開発の歴史。特に Li^+ , H^+ , H^- , F^- , O^{2-} について物質系の発見後に研究の進展と共にイオン導電率が向上する様子を示す。

自動車向けの燃料電池材料開発における課題と展望

(豊田中研¹・トヨタ自動車²・本田技研³) ○児玉健作¹・佐野誠治²・田中慎太郎³
Challenges and Perspective in Developing Fuel Cell Materials for Vehicles
(¹Toyota Central R&D Labs., Inc., ²Toyota Motor Corporation, ³Honda Motor Co., Ltd.)
○Kensaku Kodama,¹ Seiji Sano,² Shintaro Tanaka³

In the growing concerns for environmental and energy issues, including global warming, air pollution, and energy security, fuel cell vehicle (FCV) is attracting attentions and has been commercialized for passenger vehicle, bus, and forklift. Further improvements in the cell performance and durability are, however, required for the spread of PEFCs in the viewpoint of cost and material reserve. Figure 1 shows the configuration of PEFC, the microstructure of the cathode catalyst layer, and a typical performance curve of a single cell.¹⁾ Various factors, including the catalytic activity, its dependency on the electrode potential, and the transport property of reactants, affect the cell performance and therefore, it is required to adequately control the material properties and microstructures. High durability is also an important issue. These properties are, however, often in a tradeoff relation and technological breakthroughs are required. In this presentation, we review recent PEFC researches mainly focusing on the cathode and identify the origin of the tradeoff relation. Promising development strategies are also discussed.

Keywords : Fuel Cell; Oxygen Reduction Reaction (ORR); Reactant Transport; Activity; Durability

近年の地球温暖化, 大気汚染, エネルギー・セキュリティといった環境・エネルギー問題から, 燃料電池車 (FCV : Fuel Cell Vehicle) への期待が高まっており、固体高分子形燃料電池(PEFC)を搭載した乗用車・フォークリフト・バスが市場投入され始めている。しかし、コスト低減や資源量の観点から、性能・耐久性のさらなる向上が求められている。図1には、PEFCの構成、カソードのミクロ構造、およびセル性能曲線を示す¹⁾。性能には触媒の酸素還元活性、その電位依存性、さらには反応物の輸送が影響し、材料や構造を適切に制御する必要がある。また、耐久性向上も必須課題である。しかし、これらは多くの場合トレードオフの関係にあり、技術的なブレークスルーが必要となっている。本講演では、近年のPEFC研究についてカソード電極を中心にレビューし、技術課題の起源や有望な方策を議論する。

1) K. Kodama, T. Nagai, A. Kuwaki, R. Jinnouchi, Y. Morimoto, *Nat. Nanotechnol.*, **2021**, 16, 140.

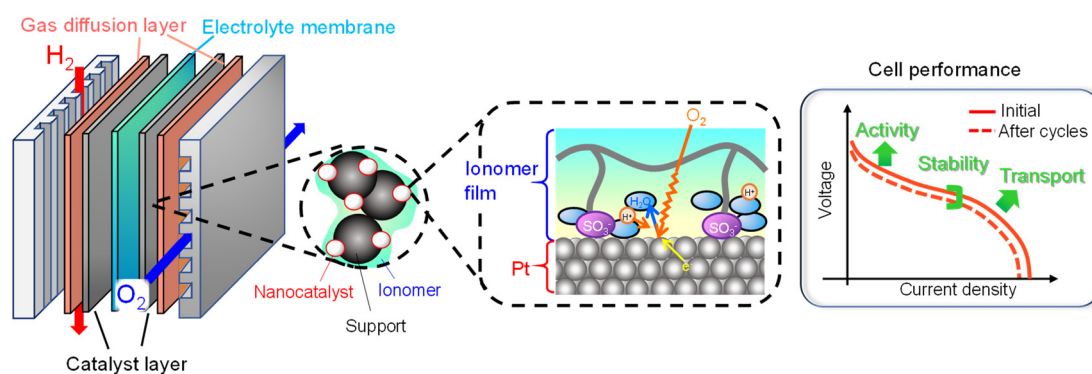


図 1 (左)PEFC の構成、(中)カソード触媒近傍のミクロ構造、(右)セル性能曲線

燃料電池用フッ素系電解質ポリマーの開発動向

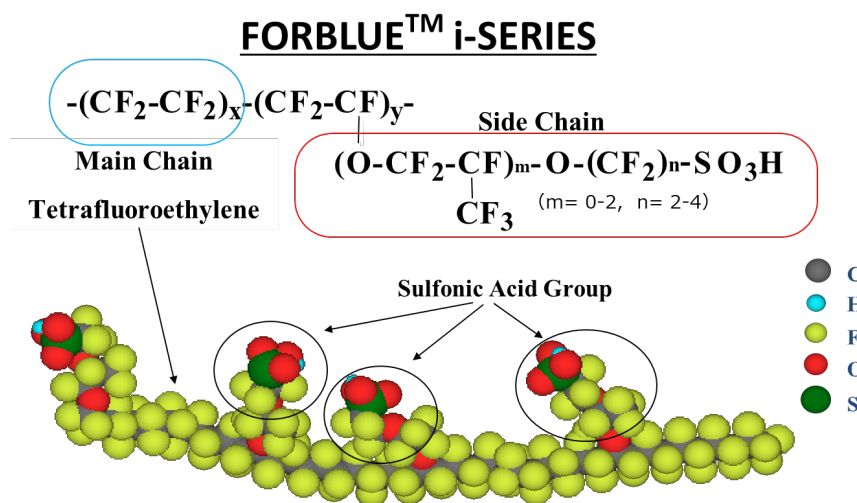
(AGC 株式会社 材料融合研究所) 本村 了

Progress of research on perfluorinated electrolyte polymer for fuel cells (AGC Inc. Materials Integration Laboratories) Satoru Hommura

Fuel cells are attracting attention as environmentally friendly power sources. In particular, polymer electrolyte fuel cells (PEFCs) have short start-up times since they can operate at low temperatures and have high output densities. They have already been commercialized for automotive and stationary applications, and they are becoming more widespread. Perfluorinated electrolyte polymers, such as NafionTM (Chemours) and FORBLUETM i-SERIES (AGC) are used for PEFCs since the electrolyte membranes are required to have chemical durability. Currently it is also expected to be applied to commercial vehicles such as buses and trucks for automobile applications, and electrolyte polymers are required to have characteristics that can be applied in high temperature operation. The development trends of perfluorinated electrolyte polymers for high temperature operation will be discussed in the session.

Keywords : perfluorinated electrolyte polymer, fuel cell

燃料電池は環境に優しい発電源として注目されており、特に固体高分子形燃料電池は低温で作動が可能のため始動時間が短く、また、出力密度が高いという利点を有している。自動車用途、定置用途では、既に商用化されており普及が進んでいる。固体高分子形燃料電池に使われる電解質膜には、化学的な耐久性が求められるため、NafionTM (Chemours) 、FORBLUETM i-SERIES (AGC) に代表されるフッ素系電解質ポリマーが使われている。今後、自動車用途ではバス、トラック等の商用車への展開も期待されており、電解質ポリマーには、高温運転にも適用できる特性が求められている。本講では高温運転に対応した、フッ素系電解質ポリマーの開発動向について紹介する。



燃料電池用電極触媒の現状と課題

(山梨大・クリーンエネルギー研究セ) ○内田裕之

Current Status and Issues of Electrocatalysts for Polymer Electrolyte Fuel Cells (*Clean Energy Research Center, University of Yamanashi*) ○Hiroyuki Uchida

For widespread commercialization of fuel cell vehicles, it is essential to enhance the performance and durability of the electrocatalysts. As the cathode catalysts, Pt-alloy nanoparticles (including core-shell type, shape-controlled type) or nanoframes have been developed. To mitigate the degradation of polymer electrolyte membranes by $\cdot\text{OH}$ radical attack, the anode catalysts with suppressed production rate of H_2O_2 attract attention. In this invited talk, the current status and issues of R & D of electrocatalysts for polymer electrolyte fuel cells will be presented.

Keywords : Fuel Cell; Electrocatalyst; Pt-Alloy; Oxygen Reduction Reaction; Hydrogen Oxidation Reaction

燃料電池自動車 (FCV) や家庭コージェネレーション用の固体高分子形燃料電池 (PEFC) の電極触媒には、強酸性の電解質膜に対する耐食性とカソード酸素還元反応 (ORR) に対して比較的高い活性を有する Pt や Pt-M 合金ナノ粒子を高表面積カーボン担体に高分散した Pt/C や Pt-M/C が用いられてきた。FCV 等のさらに広範な普及には、高性能で高耐久な電極触媒開発が必須である。Pt 質量当たりの活性 MA は面積比活性 j_s と電気化学的比表面積 ECA の積で表される： $MA (\text{A g}_{\text{Pt}}^{-1}) = j_s (\text{A m}^{-2}) \times ECA (\text{m}^2 \text{g}_{\text{Pt}}^{-1})$ 。Pt-Co 等の合金化により j_s が、ナノ粒子化により ECA が増大する。本講演では、我々のこれまでの研究成果と最近の研究動向をまとめて発表する。

1. Pt 合金における ORR 活性向上因子の解明と Pt-M/C 触媒の高活性・高耐久化

Pt 系ナノ粒子表面は、(111), (100), (110)等の基本低指数面から構成されている。そこで任意組成の Pt-Co 合金単結晶電極を作製し、0.1 M HClO_4 電解液中で ORR 比活性 j_s と表面構造を解析した。Pt-Co 単結晶電極の j_s が(100) < (110) << (111)の序列であり $\text{Pt}_{73}\text{Co}_{27}$ (111)で Pt(111)のその 27 倍の最大活性に達すること、電極最表面は原子的に平坦な Pt スキン層であり、その直下の第二層には Co が 98 atom%まで濃縮されて電子的修飾効果をもたらしていることを見出した (図 1) ²⁾。これにより、合金表面層組成制御が高活性化の重要指針となることを明らかにできた。

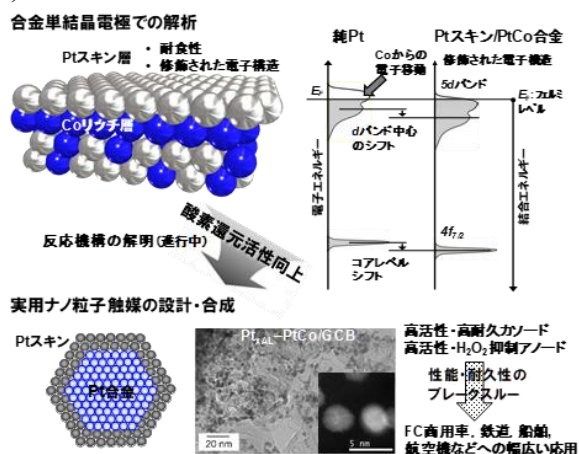


図 1. 高活性・高耐久カソード触媒の開発。CSJ カレントレビュー第 44 号「モビリティ用電池の化学」(2022 年発行)より許可を得て複製。
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ナノカプセル法で組成と粒径を均一に制御した $\text{Pt}_x\text{Co}/\text{C}$ ($x=1\sim3$) 触媒は高い初期 MA を示したが、高温域で脱合金した³⁾。この原因が合金表面に自然に生成する Pt スキン層の不均一性にあると考え、数原子層厚さの Pt スキンを制御析出した $\text{Pt}_{x\text{AL}}\text{-PtCo}/\text{C}$ を合成し、高い質量活性と耐久性の両立に成功した (図 1)⁴⁾。最近の解析により、電気化学的に安定化した $\text{Pt}_{x\text{AL}}\text{-PtCo}$ は不規則構造であった⁵⁾。また、 $\text{Pt}_3\text{Co}/\text{C}$ の熱処理条件はほぼ同じにして組成と粒径分布は同じで構造のみ変えると、規則構造よりも不規則構造合金の耐久性が高いこともわかった⁶⁾。

近年、ORR 高活性触媒としてコア-シェル型、形態制御型やナノフレーム触媒などが研究開発されている⁷⁾。これらは酸性電解液中で極めて高い MA を示すことが確認されたが、実際の単セルの触媒層では期待したような性能が発揮できないというギャップが問題視されている⁸⁾。その原因として、電池作動条件での耐久性が不十分か、あるいは触媒層の作製法が最適化されていない可能性が考えられる。前者に関しては、触媒開発者が高温電解液中での溶解試験等を行って明確にしておく必要がある。FC 商用車、鉄道、船舶等の重負荷用途への拡大に向けて、後者の課題解決を含めたコンソーシアム型プロジェクトが益々重要になっている。

2. 新規アノード触媒の開発

上記の $\text{Pt}_{x\text{AL}}\text{-PtM}/\text{C}$ ($M = \text{Fe}, \text{Co}$) 触媒は都市ガス改質燃料に含まれる CO に対する高い耐性と市販 Pt/C の約 2 倍の水素酸化反応 (HOR) 質量活性を有し、耐酸化性も併せ持つことを初めて見出した⁹⁾。また、電解質膜を分解する $\cdot\text{OH}$ ラジカルの発生源となる H_2O_2 の発生速度を抑制することにより、電解質膜の耐久性を著しく向上させる新しいアノード触媒としても期待できる¹⁰⁾。

謝辞

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