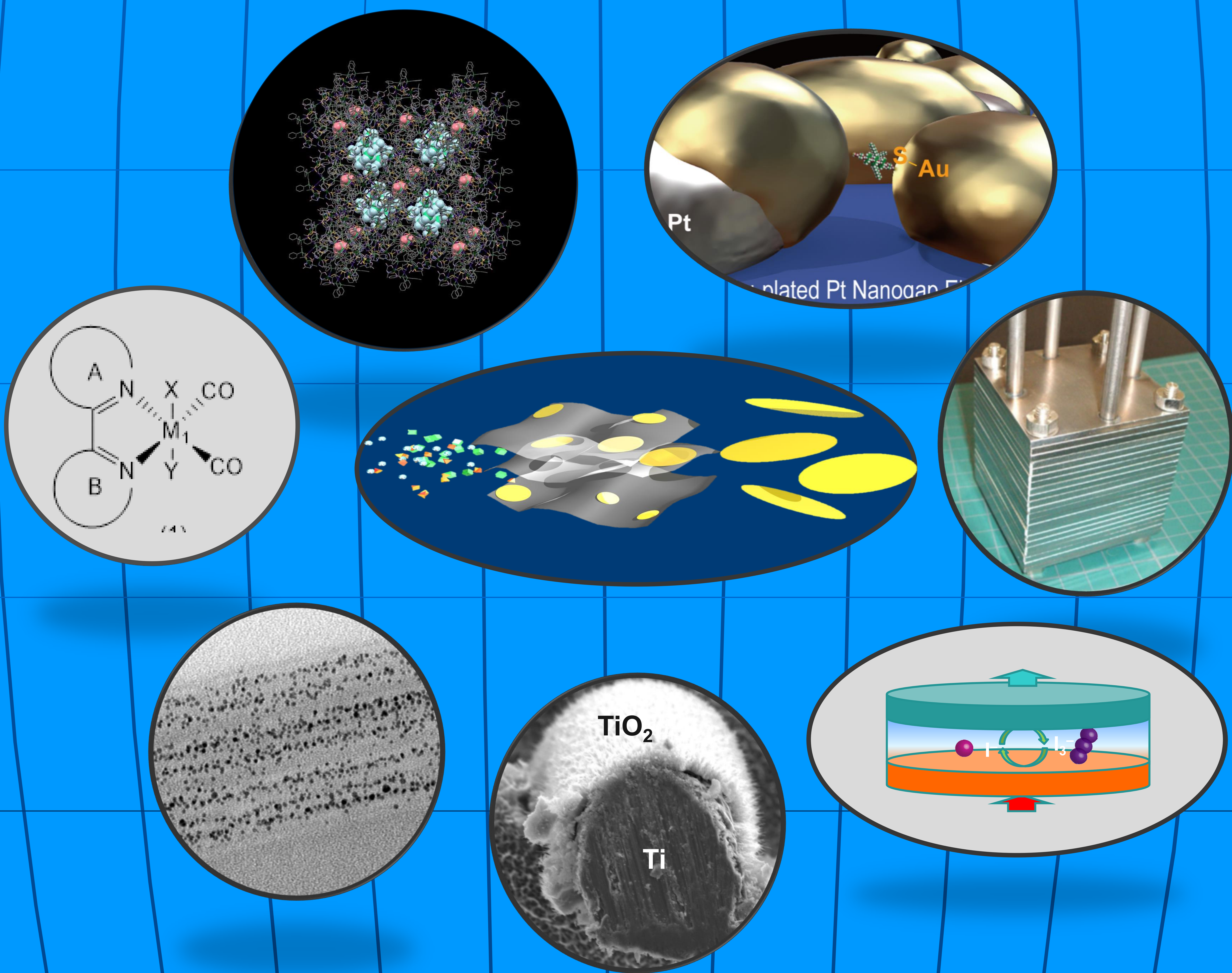
Selected Novel Technologies for Licensing

2018 MRS Fall

Innovative Technologies for Your Products



Japan Science and Technology Agency

Simple "Nanosheets" synthesis

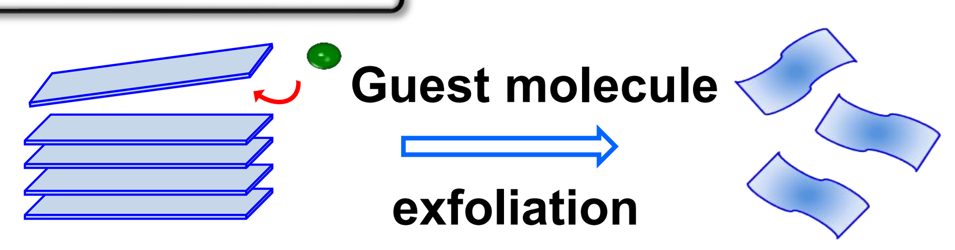
New method to synthesize thin "Nanosheets" for various materials

Associate Prof. Yoshiaki UCHIDA (Osaka University)

1. Background

Conventional Method to synthesize "Nanosheets"

Top-down method



Bottom-up method

- Chemical Vapor Deposition
- Hydrothermal method

(Disadvantages and Limitations)

- Applicable materials are limited.
- Large energy is required.

- Not suitable for tens of nanometer sheets production
- Large-scale equipment is required.

"New Simple Method" has been strongly awaited

The method can;

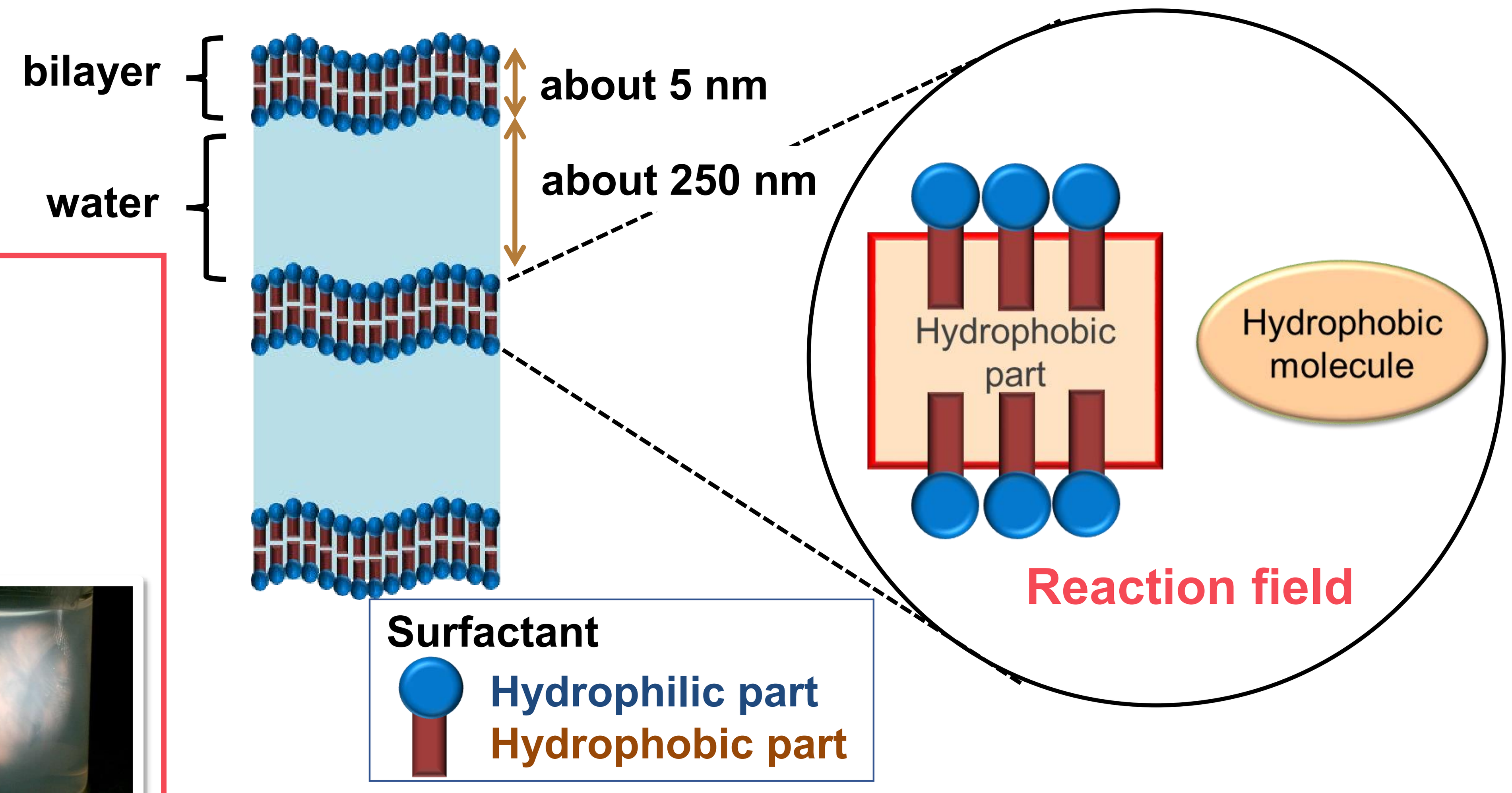
- be applied to various materials
- realize very thin (less than10nm) nanosheets

2. Principle of the Invention

We developed and invented "New Simple Method", which use "Hyperswollen Lamellar Phase(HL phase)" for synthesis of the very thin nanosheets.

HL phase has bilayers highly-separated (ex. ~200nm) by solvent.

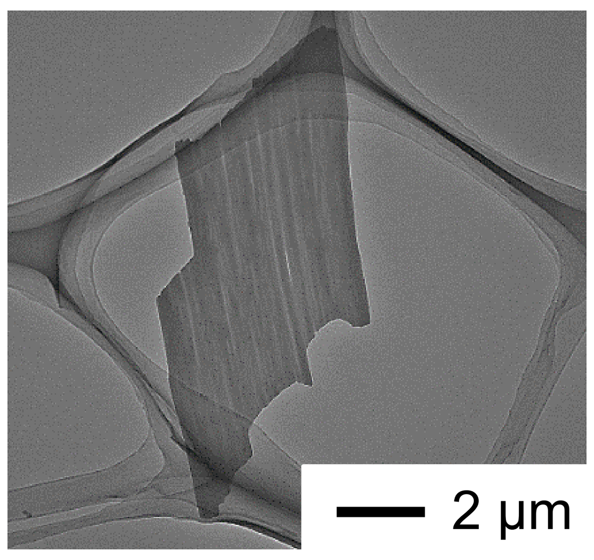
- The materials for forming nanosheets, the solvent (H_2O and/or organic solvent) and the surfactant will be mixed together.
- The HL phase will be formed after being heated and stirred.
- When the HL phase is suitably formed, an iridescent color due to the Bragg reflection of visible light can be observed.

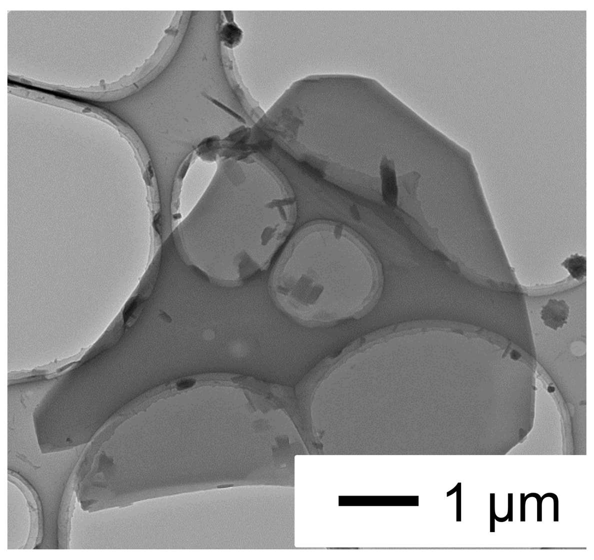


3. Experiment and Result

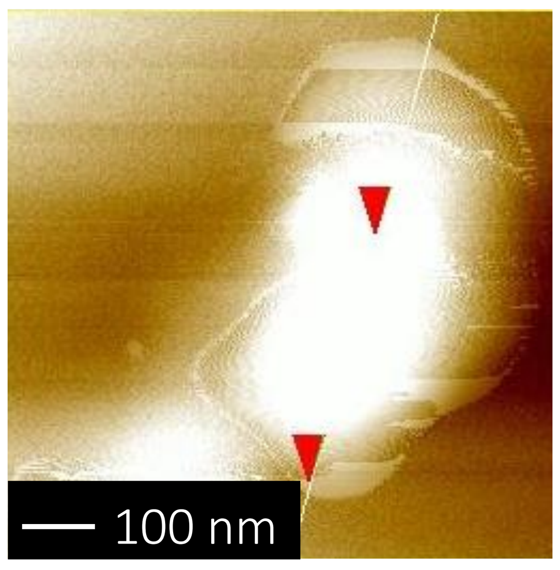
Nanosheets example: Metal Organic Framework (MOF)

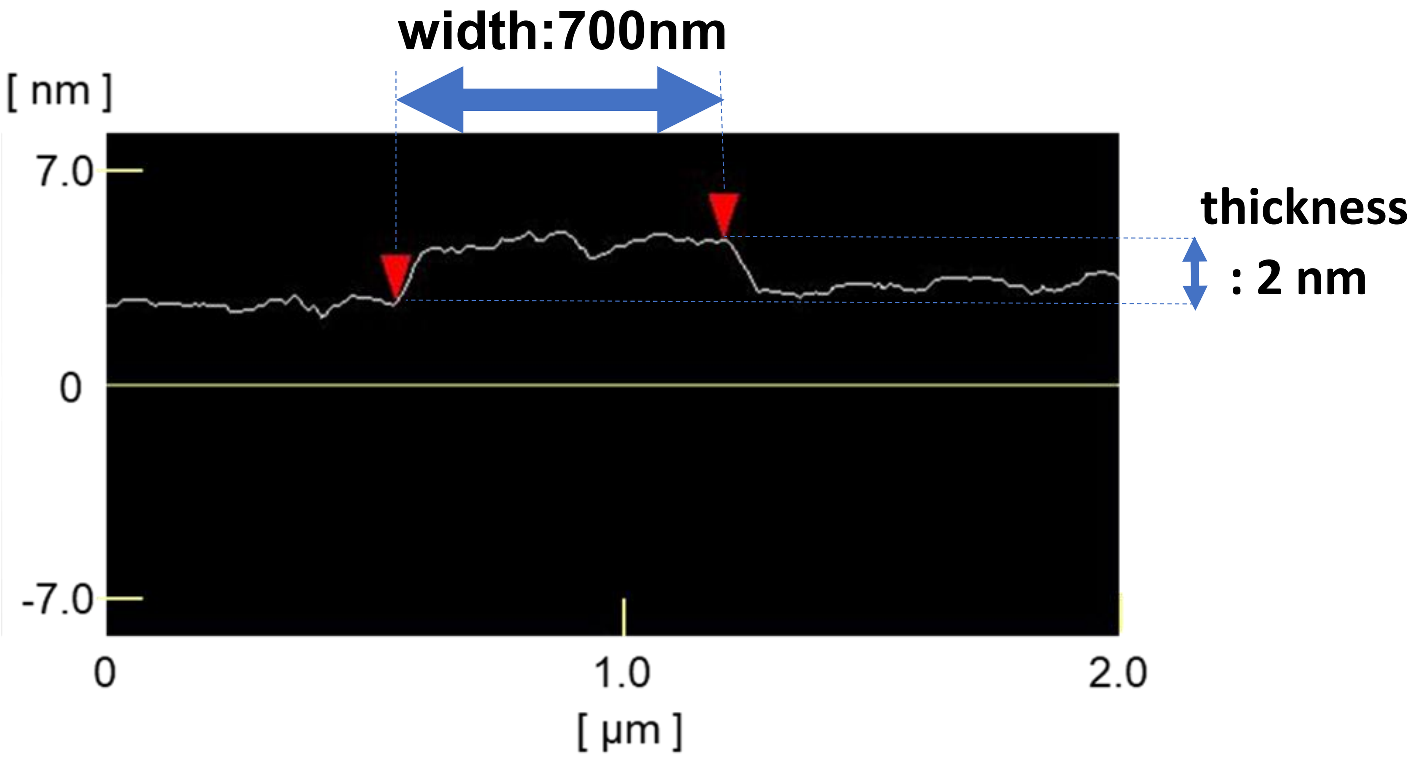
◆TEM



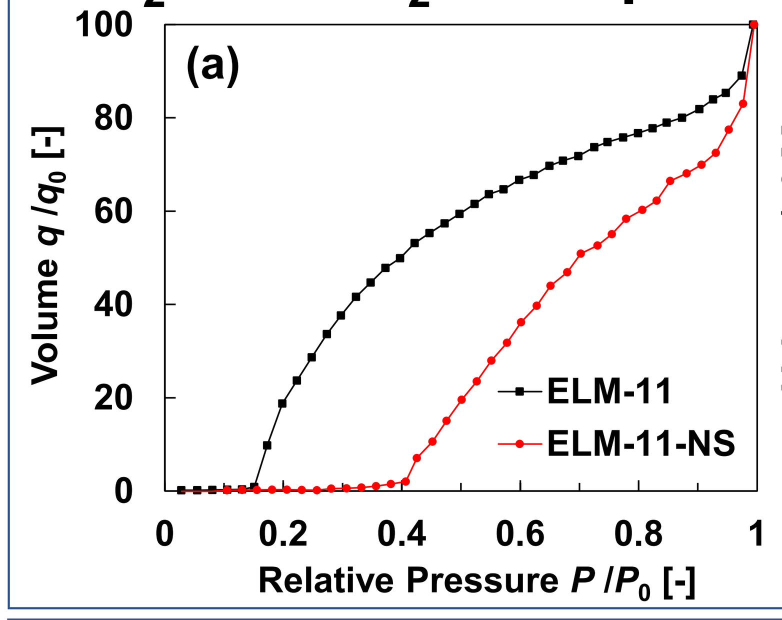


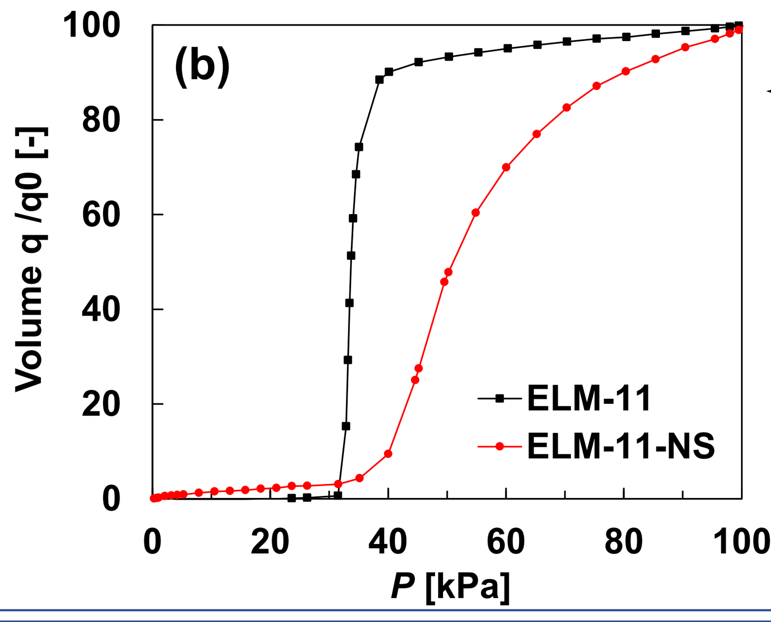
◆AFM



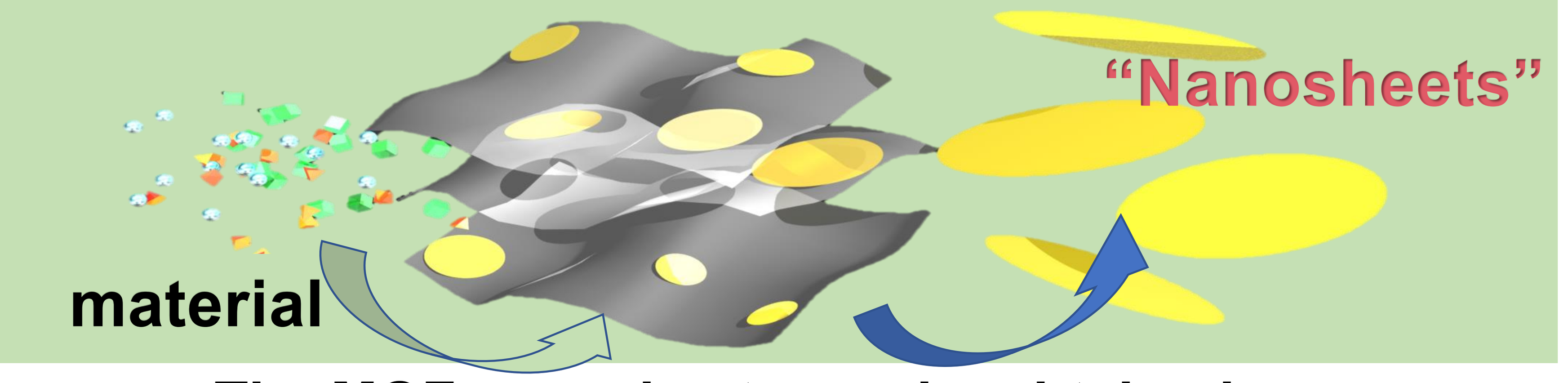


◆N_2 and CO_2 adsorption





◀ (a) when increasing the relative pressure of N_2 at 77 K and
(b) when increasing the absolute pressure of CO_2 at 273 K
adsorption isotherms of bulk sample and Nanosheets of MOF (ELM-11)
※ELM-11 : $[Cu (bpy)_2(BF_4)_2]$



The MOF nanosheets can be obtained by large gate-opening pressure.

4. Application Examples

・Porous material ・Adsorbent ・Catalyst
・Surface modification material etc.

5. Patent Licensing Available

Patent No.: WO2018/016650 (JP, US)

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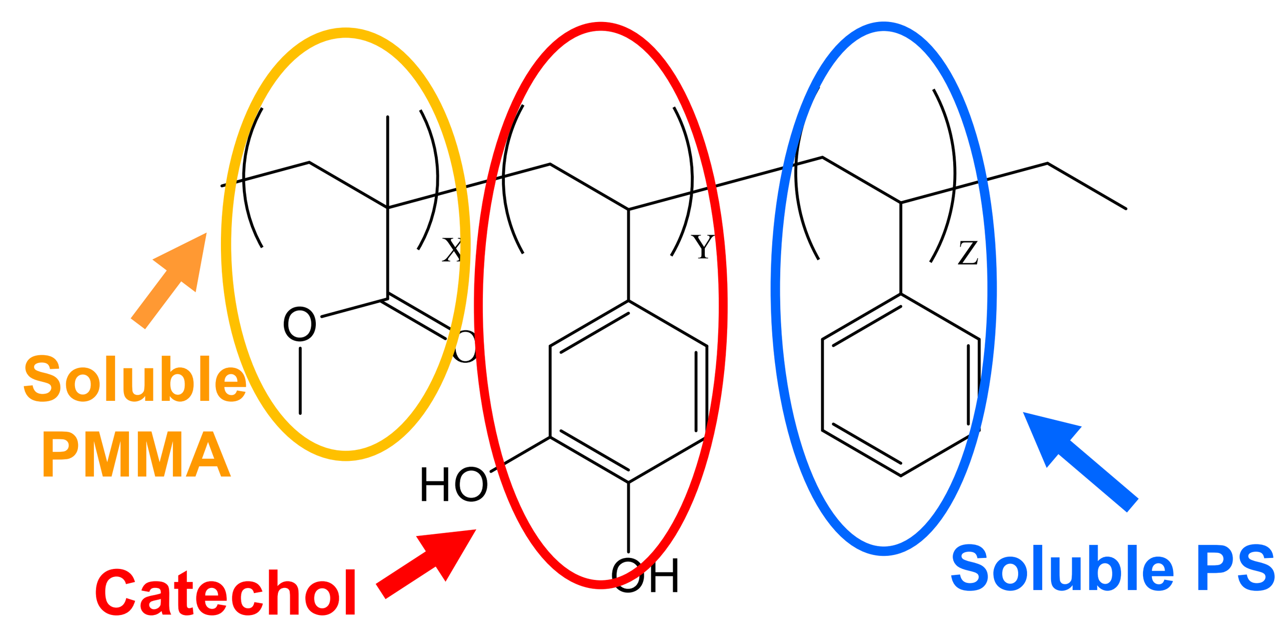
Unique Block Copolymers

New block copolymers containing catechol segments capable of supporting inorganic nanoparticles

Associate Prof. Hiroshi YABU (Tohoku University)

1. Abstract

We invented new unique block copolymers containing Catechol segments.



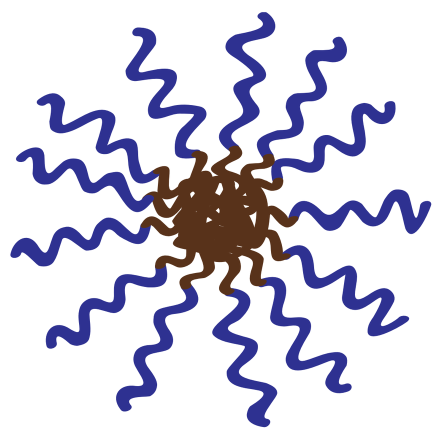
Our block copolymers

1. This block copolymer is adhesive to solid substrates.
2. This polymer is capable of forming inorganic nanoparticles from metal ions.
3. No reducing agent is required to form the particles.
4. This polymer containing inorganic nanoparticles has further electrical conductivity.

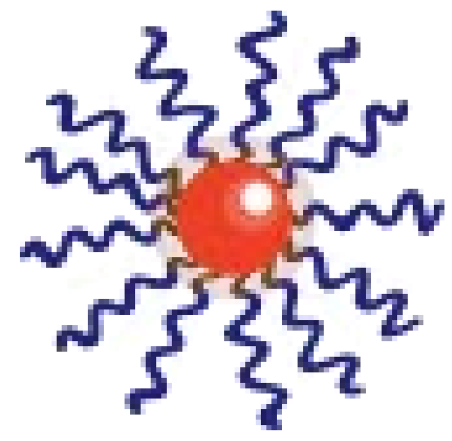
2. Key Features

Our block copolymers

(i) cast solution onto a substrate
(ii) evaporate solvent



Inorganic material (eg. metal salt) solution



This block copolymer has adhesion to the substrate.

Each segment aggregates to microphase separated phase.

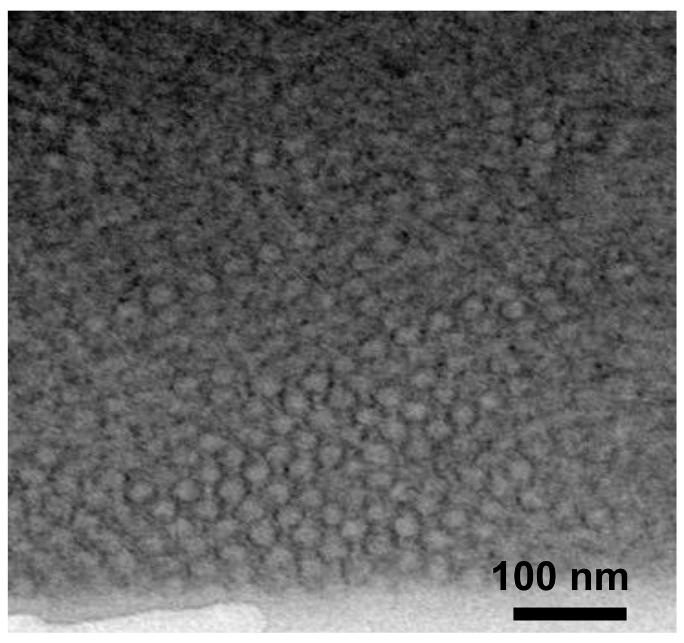
The Catechol segments reduce metal ions without any reducing agent.

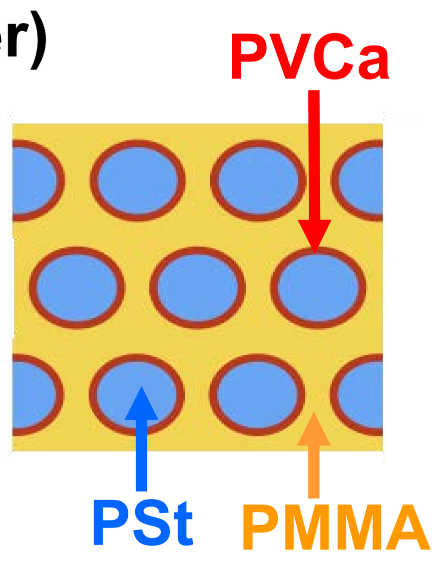
Inorganic nanoparticles are supported with block copolymers

3. Experimental Data

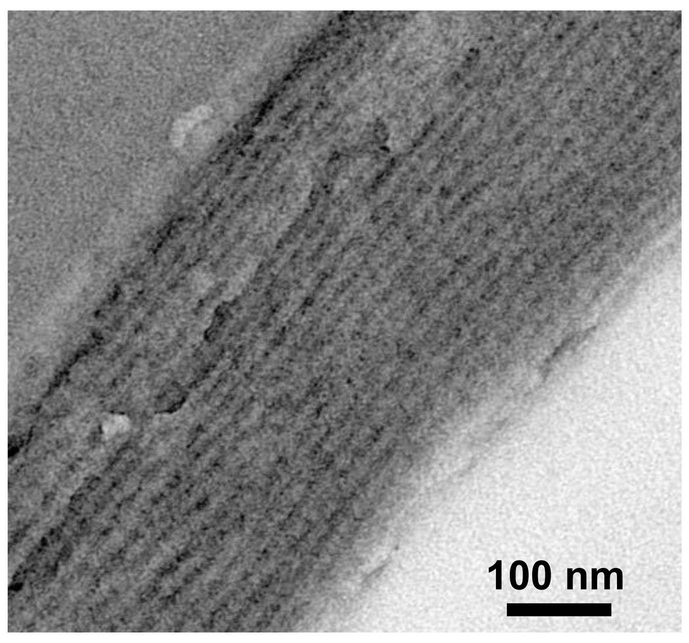
Eg. Triblock polymer (PMMA / PSt / PVCa)

◆TEM (Block copolymer)



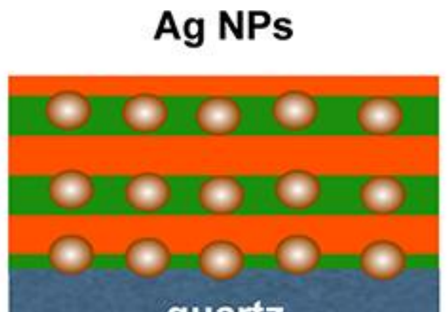


Core-Shell Cylinder (CSC) Microphase Separation

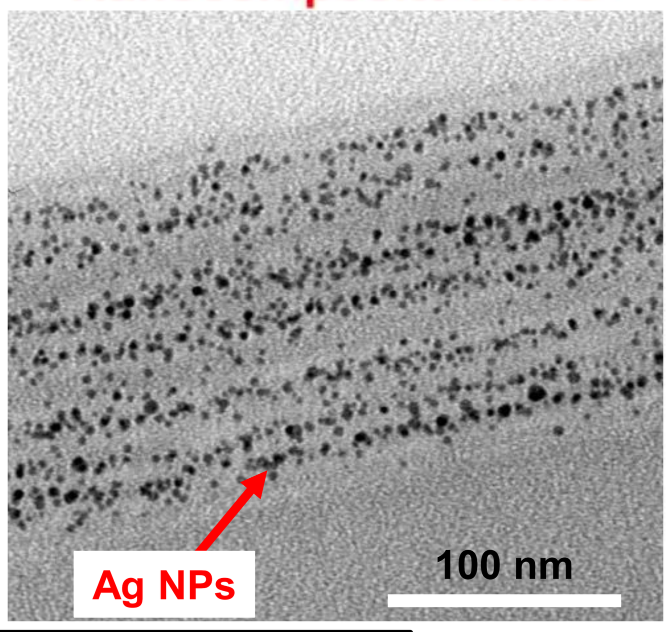


Layered structure is formed.

◆Block Copolymer + Nano particle (Ag)

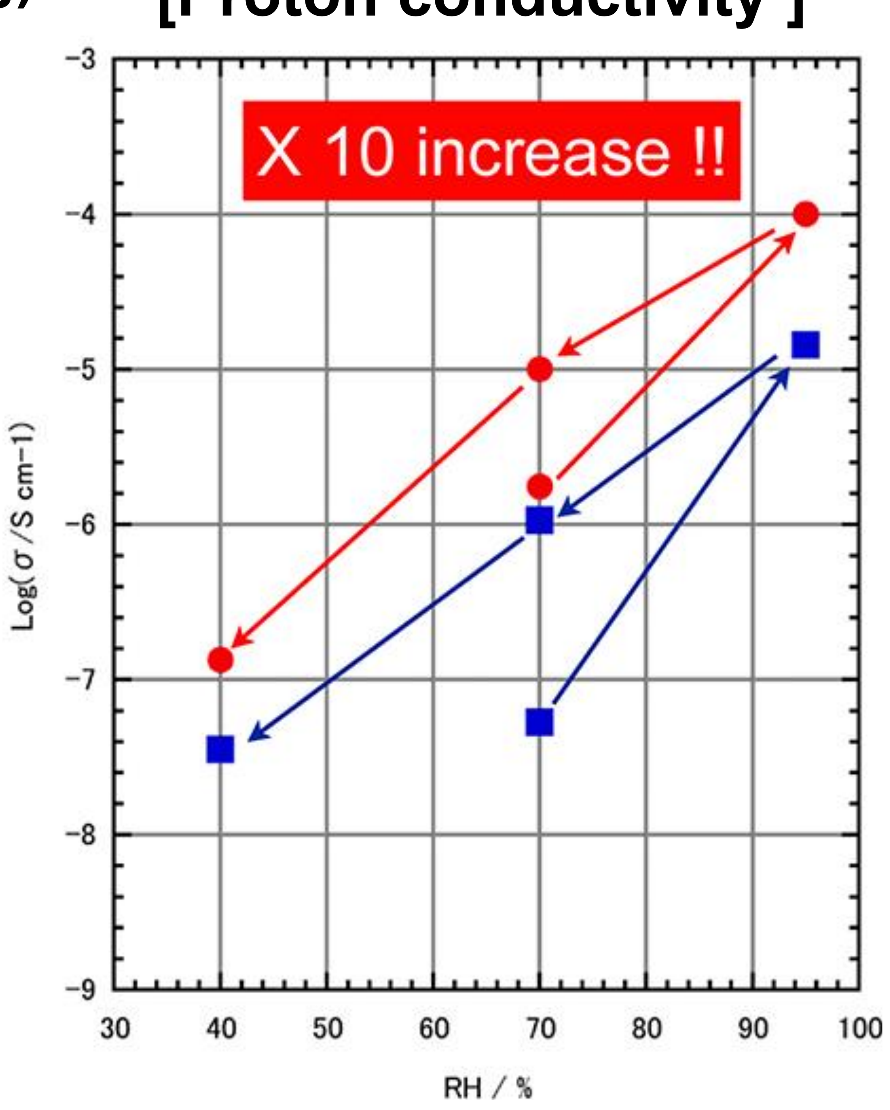


Nanocomposite Films



Nanocomposite film with anisotropic proton conductivity is realized by nanoparticle precipitation in the layered structure.

[Proton conductivity]



■ Block Copolymer
● Block Copolymer + Ag Nano particles

4. Application Examples

◆Adhesive material
◆Electrical conductivity material (with Metal nano particle) : Electrode, Electrolytes for Fuel Cell etc
◆Magnetic material (with Magnetic particle)

5. Patent Licensing Available

Patent No.: WO2015/129846 (JP, US, EP)

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SUSTAINABLE DEVELOPMENT GOALS

A New Conceptual Ionic Crystal

NCIS: Non-Coulombic Ionic Solid
Formation of Crystals from a Multinuclear Metal Complex

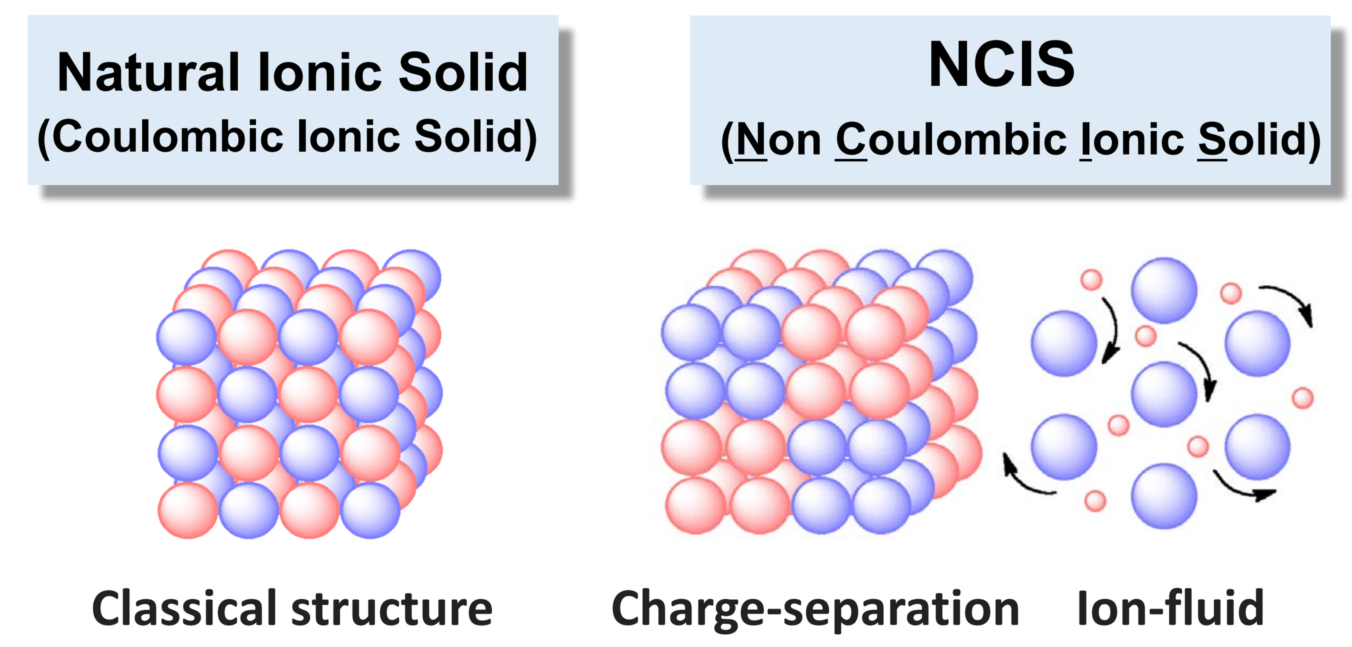
Prof. Takumi KONNO (Osaka University)

1. Introduction

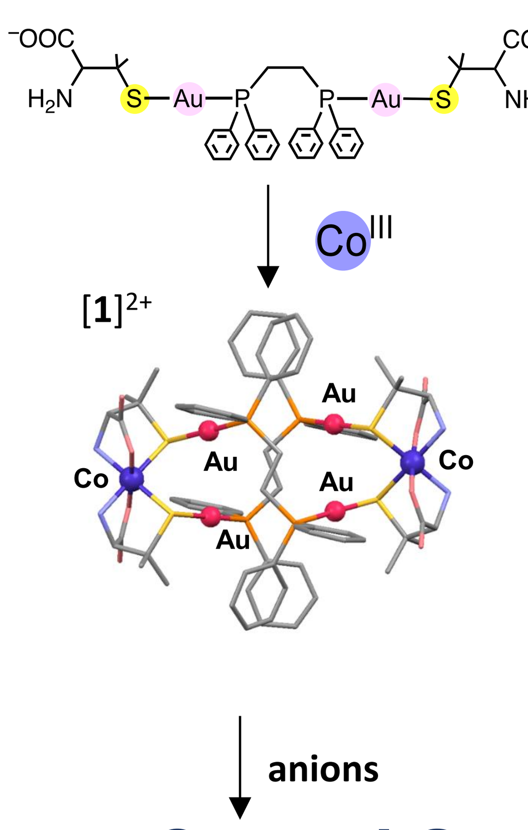
In natural ionic solids, the spatial arrangement of cations and anions is strictly ruled by Coulombic force, and that their positions are tightly fixed.

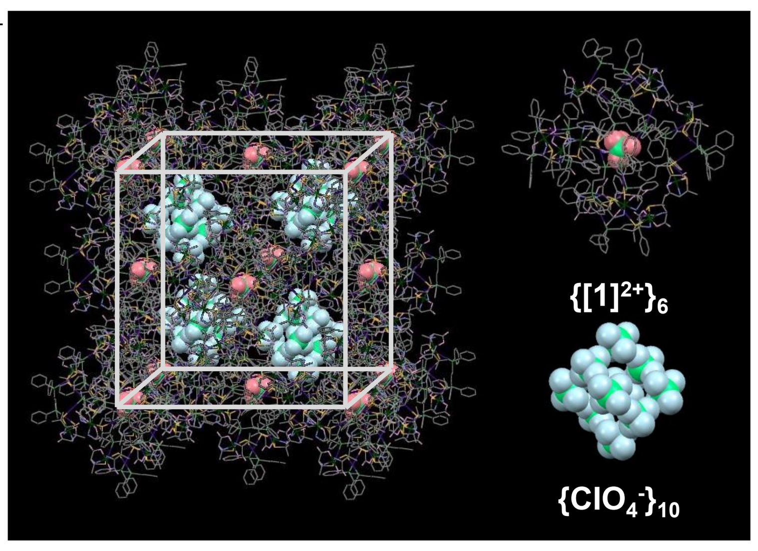
A species of ionic solids we synthesized are ruled by non-Coulombic interactions. The unique structures lead to some novel phenomena and various sorts of functionalities.

We named the new conceptual ionic solid species as Non-Coulombic Ionic Solids (NCIS).



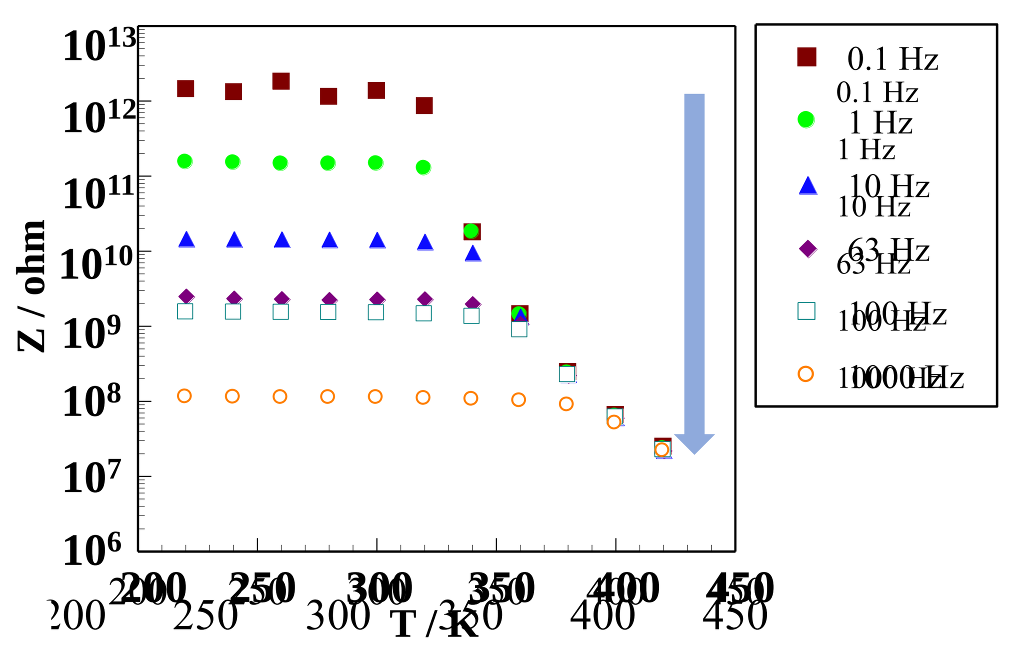
2. Dieletric Response of Charge-Separation-type NCIS





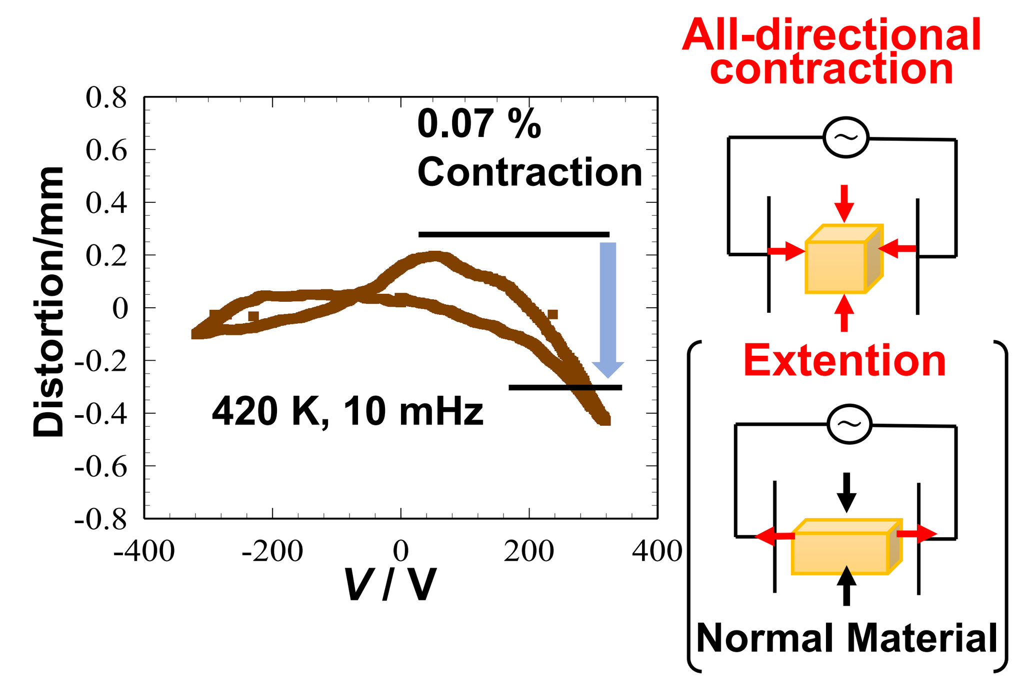
The structure is formed by non-Coulombic interactions from polynuclear metal complex cations and anion clusters

Crystal Structure of $[1]X_2 \cdot nH_2O$



It can be used for the resistance thermometer because the impedance decreases as the temperature rises.

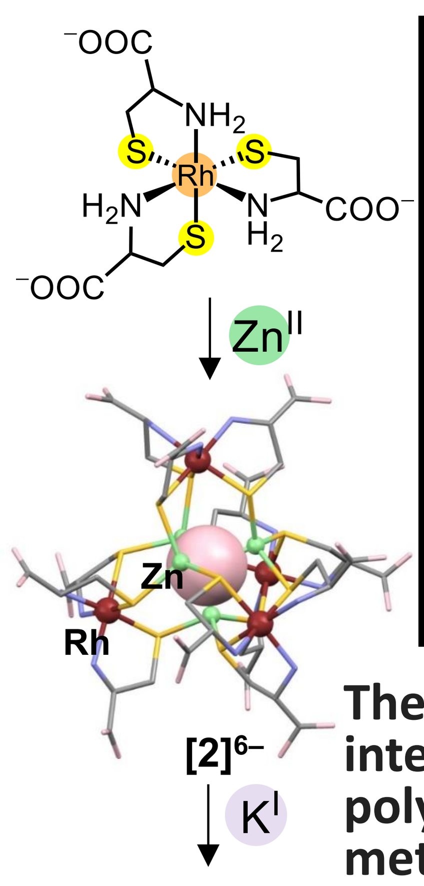
Thermal Resistance Change

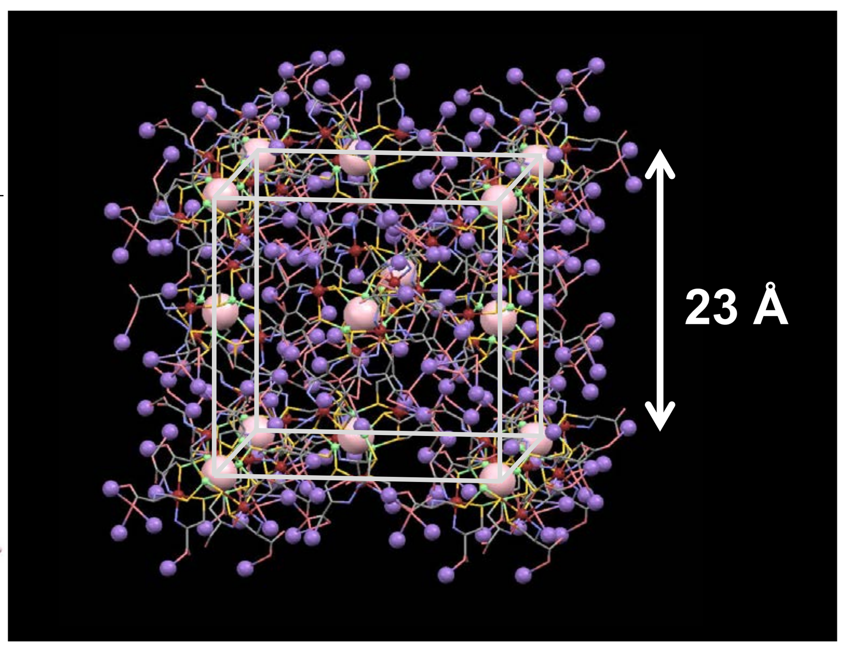


The Isotropic volume shrinkage is caused by the changes in position and orientation of anion clusters and water molecules in response to electric fields.

Negative Electrostriction

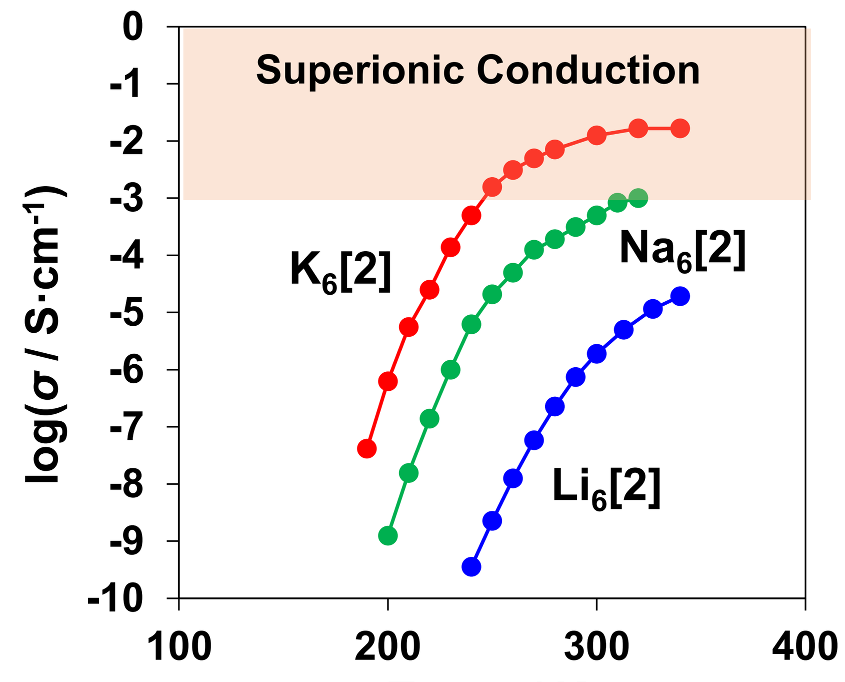
3. Fast Ionic Conduction of Ion-fluid-type NCIS





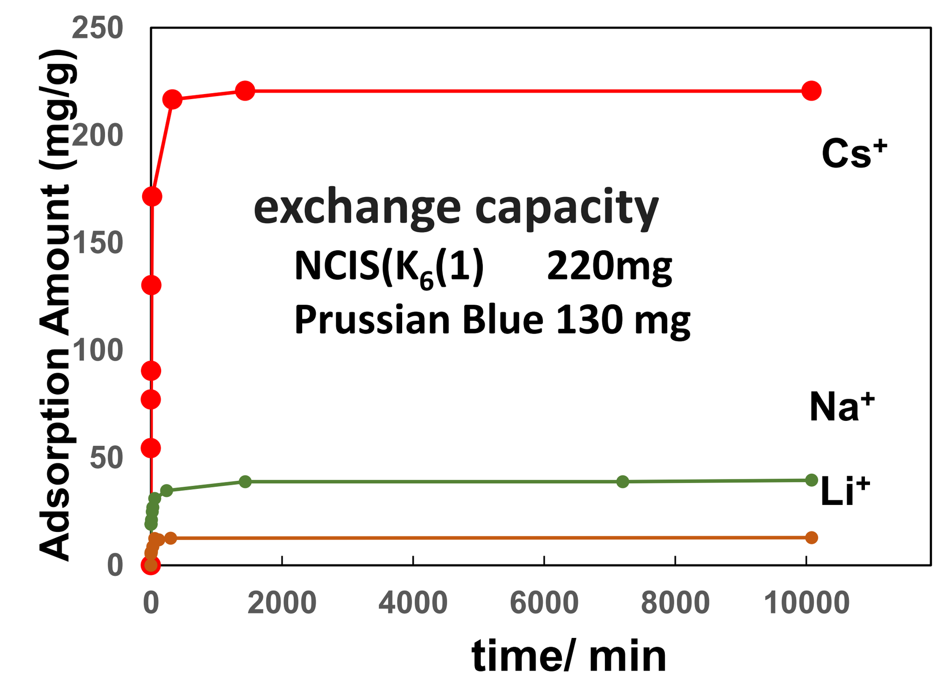
The structure is formed by non-Coulombic interactions from lattice structure of polynuclear metal complex anions, and alkali metal cations capable of moving freely.

Structure of $K_6[2] \cdot nH_2O$



The potassium salt shows superionic conduction above room temperature in Ion-Fluid-type NCIS.

Superionic K^+ Conduction



Alkali metal ions in crystal are quickly, completely exchanged just by soaking crystals in solution.

Quick ion exchange

4. Application Examples

- Actuator for micro devices
- Adsorbent of cesium ion
- All solid-state Battery
- Negative Temperature Coefficient(NTC) Thermistor

5. Patent Licensing Available

Patent No.: WO2018/056237
Patent No.: WO2018/079831

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Electroless Au Plating on Pt

Room temperature operable 0.7nm Au nanogap electrodes by electroless Au plating on Pt

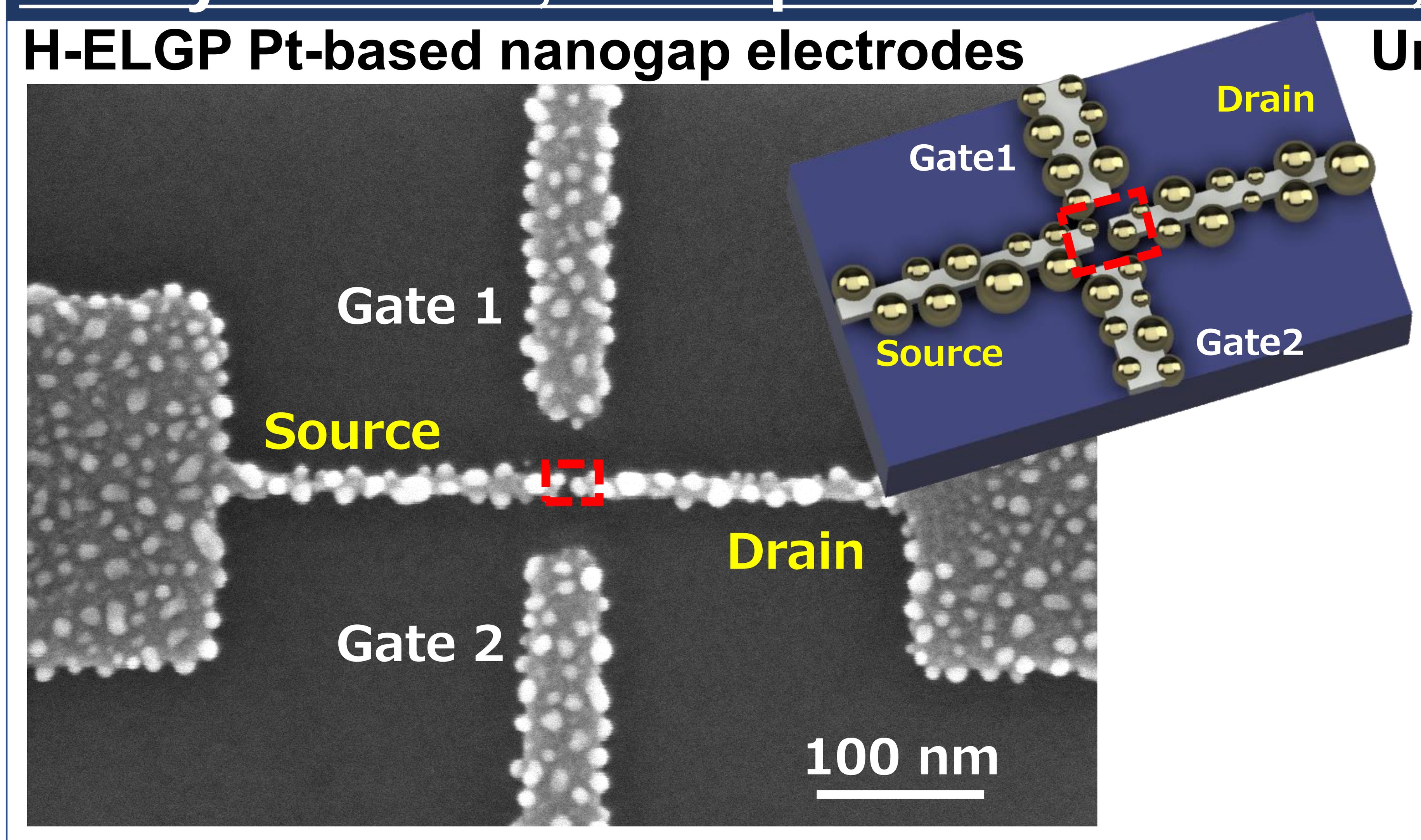
Prof. Yutaka MAJIMA (Tokyo Institute of Technology University)

1. Abstract

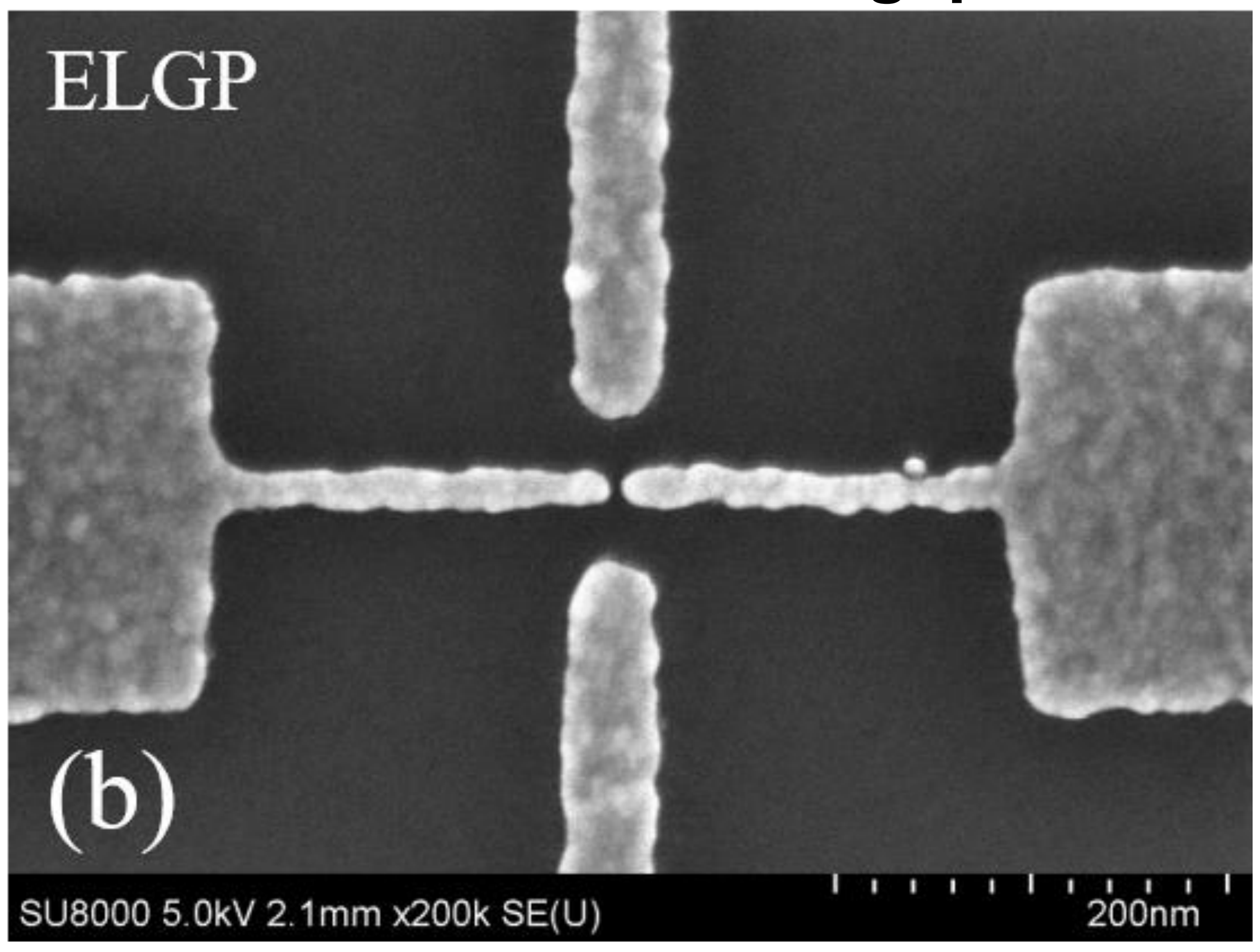
- Au has not been used in several tens of nanometers scaled devices in a room temperature for the reason that it could not maintain its shape due to its surface self-diffusion.
- Our unique Electroless Au plating (ELGP) on Pt technology overcame this problem.
- The nanogap electrodes by Hemispheric ELGP (H-ELGP) on Pt can realize:
  - Gap separation control: self-termination mechanism without short circuit
  - Robustness: thermally stable from room temperature to 573K
  - Ultra-small gap: i.e. 0.7 nm gap

2. Key Features, Principle of the Invention, Structure of the Material

H-ELGP Pt-based nanogap electrodes

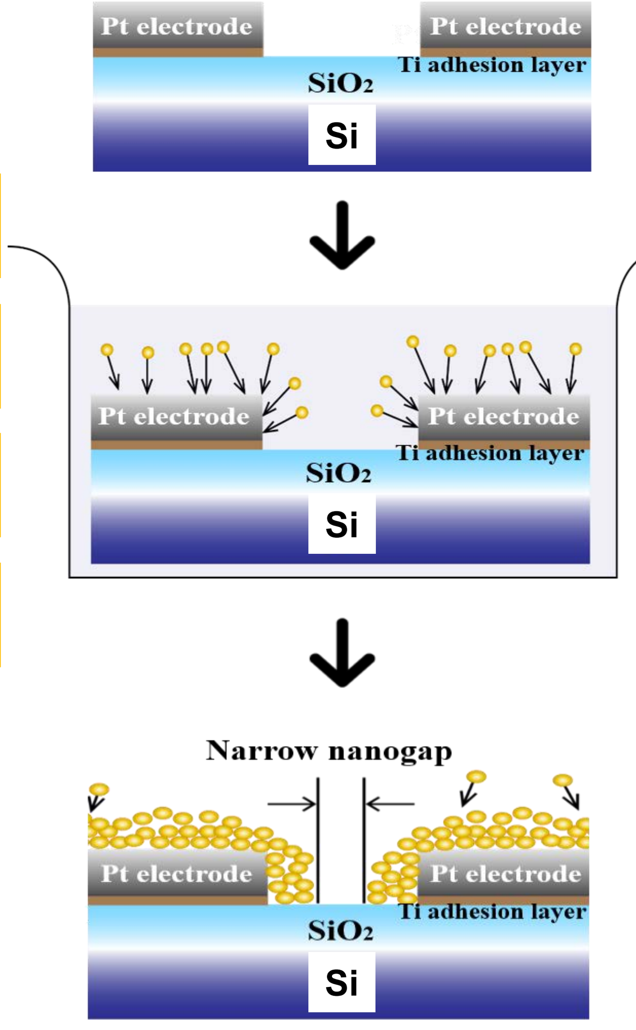


Uniform ELGP Pt-based nanogap electrodes



3. Fabrication Process of H-ELGP

- Pt initial electrodes patterned by EBL
- Chip cleaning
- Pre-treatment solution process
- Electroless Au Plating (ELGP)
- Characterization
  can be checked by
  Scanning Electron Microscope (SEM)



Advantages of Pt electrodes

- High melting point
  T_m(Pt)=1768℃, T_m(Au)=1064℃
- Strong adhesion and durability

Advantages of ELGP

- Simple bottom-up process
- Mass-producibility
- Operable at room temperature
- Non-toxic materials

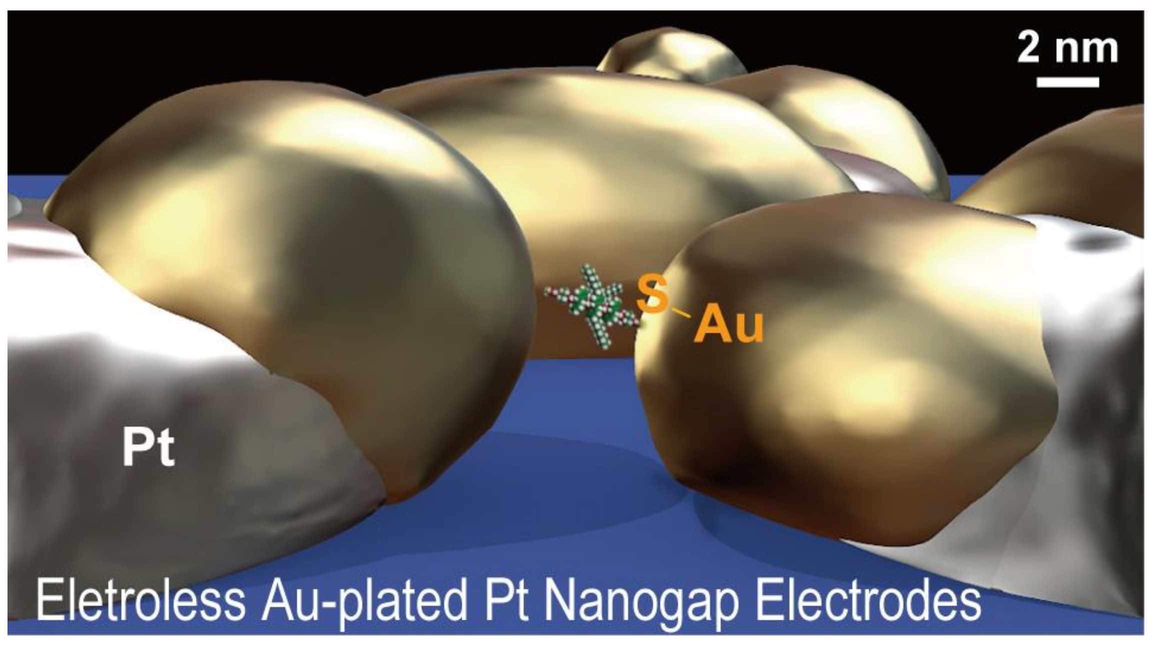
4. Applications

ELGP on Pt

- Biosensor, Power electronics, Automobile
- Advantage: Thermally stable and low contact resistance

H-ELGP nanogap electrodes

- Nanogap sensors, logic transistor beyond 3nm node
- Advantage: Robust nanogap, large gate capacitance



Eletroless Au-plated Pt Nanogap Electrodes

5. Patent Licensing Available

Patent No.: WO2012/121067 (JP, US, KR, CN)
WO2013/129535 (JP, US, EP, CN, KR, TW)
WO2015/033600 (JP, US, EP, CN, KR, TW)

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H_2 Generator

Innovative method to realize both High Energy Efficiency and Facility Miniaturization

Prof. Hiroshi TAKAMURA (Tohoku University)
Prof. Hiroshige MATSUMOTO (Kyushu University)

1. Background

- High efficient and compact "PEFC(Polymer Electrolyte Fuel Cell)" for small and medium-sized offices and homes and high efficient and compact "Hydrogen Fueling Infrastructure" for Hydrogen Vehicles have been required strongly for wide spreading Hydrogen Society.
- Although the conventional "Steam Reforming" method is excellent, there are difficult problems to solve i.e. its slow starting characteristics, very difficult to reduce its size.
- The conventional "POX(Partial Oxidation of Methane)" method, which use the air as an oxidant, has weak points i.e. high cost, easy dilution of Hydrogen.

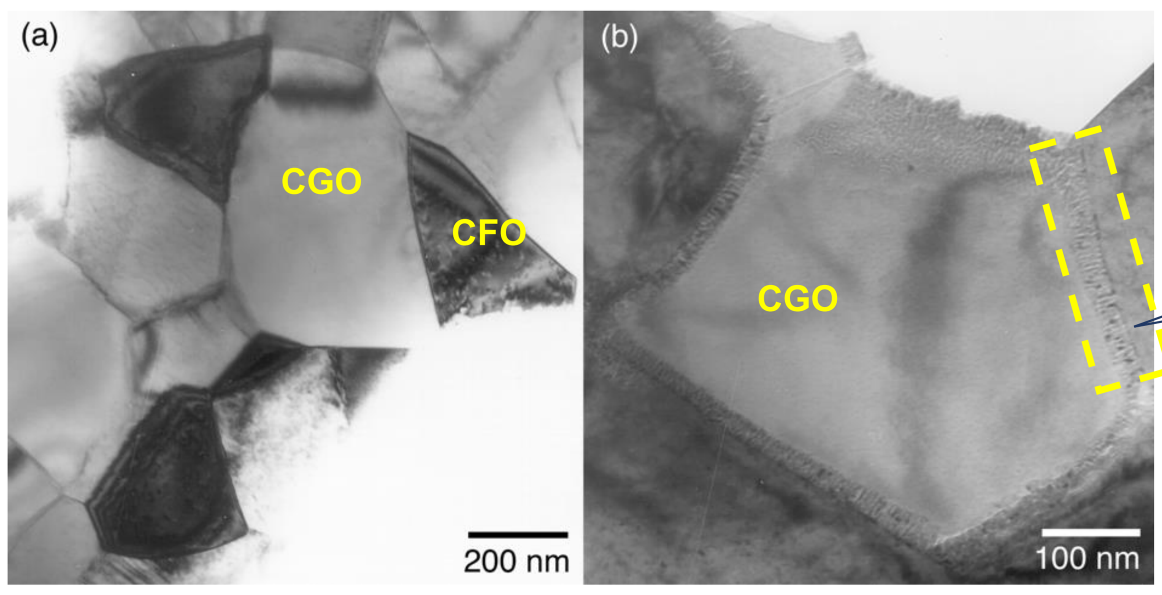
2. An Innovative "MPOX(Membrane separation process+POX)" method

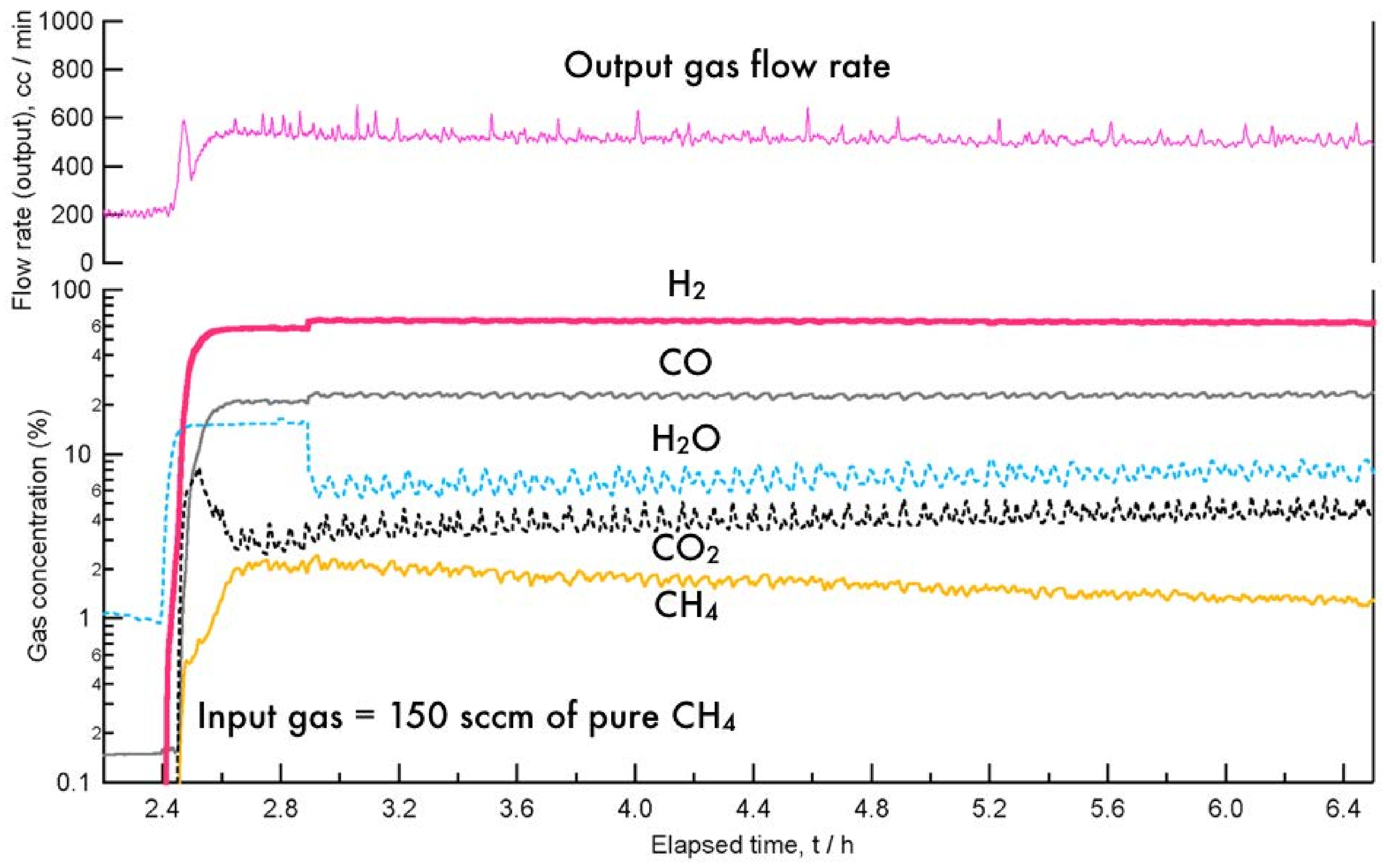
We developed and invented;

- the new hydrocarbon reforming method **"MPOX(Membrane separation process+POX)"** by using Oxygen Permeable Membranes, which can utilize a part of the Joule heat that is generated during the isolation of oxygen.
- the optimal **"Oxygen-Permeable Ceria-based Membrane"** which will realize the MPOX method.

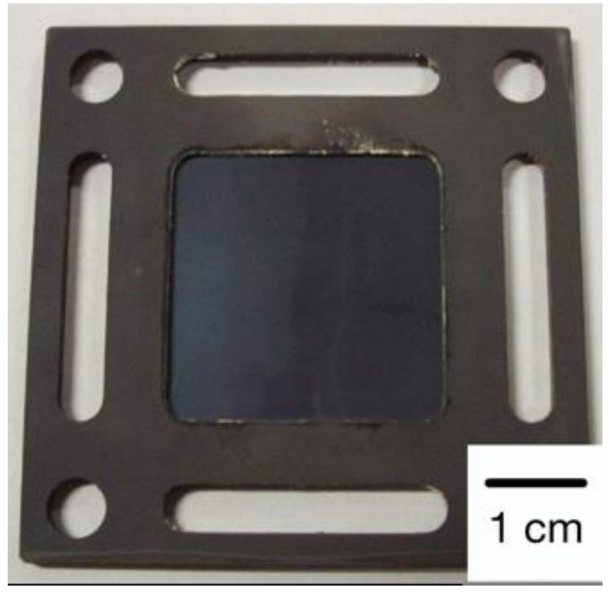
* MPOX effectively utilizes the free energy generated from partial oxidation reaction to oxygen separation.

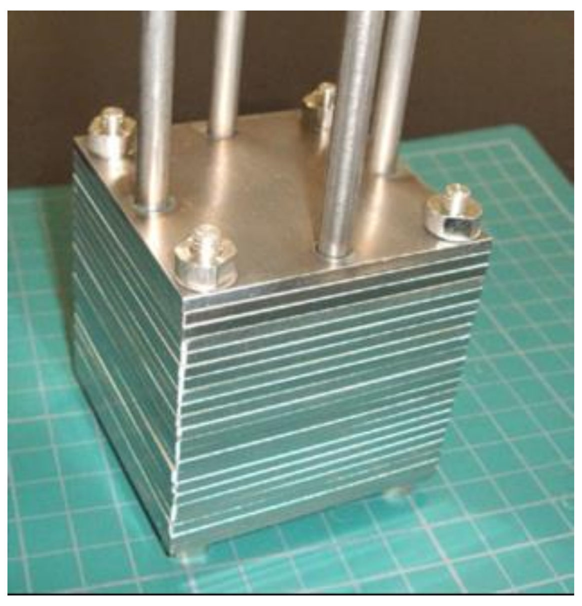
	Composition	Oxygen flux density μmol・cm^{-2}・s^{-1}	Temp ℃	Ref.
BSCF	$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$	8.6	875	Shao et al, 2001
LSGF	$La_{0.7}Sr_{0.3}Ga_{0.6}Fe_{0.4}O_3$	8.2	1000	Ishihara et al, 2002
PSAF	$Pro_{0.7}Sro_{0.3}Fe_{0.8}Al_{0.2}O_3$	8.2	1000	Takamura et al, 2002
Ceria-MFO	$(Ce,Sm_0)O_2$-15vol%$MnFe_2O_4$	10.0	1000	Takamura et al, 2002
LBSFI	$(La_{0.5}Ba_{0.3}Sr_{0.2})(Fe_{0.6}In_{0.4})O_3$	10.6	1000	Aizumi et al, 2004





Flow rate and Compositions of reformate gas





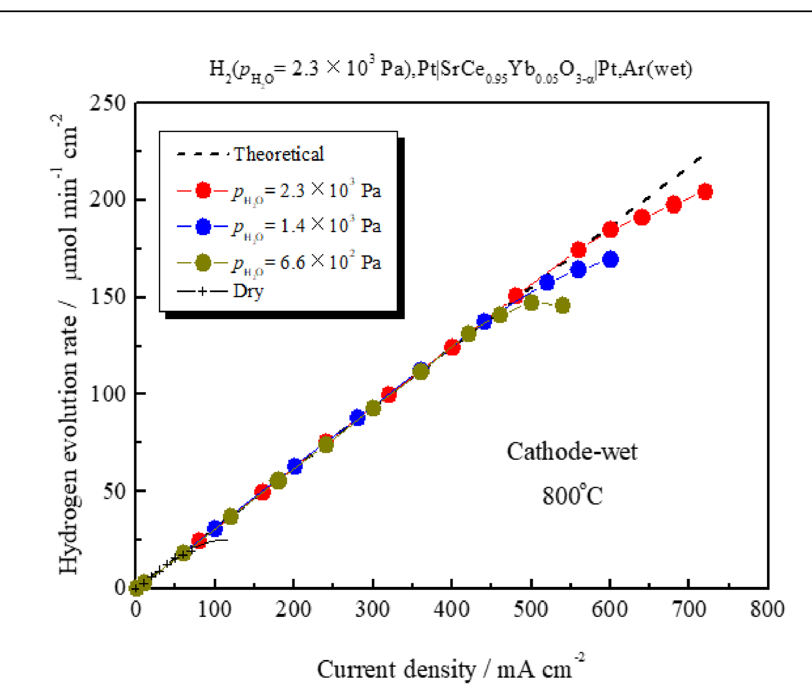
MPOX reformer module comprising of CSO.15MFO and ZMG232R (left) and its 20 stacks (right)

To produce 10 liter/min of hydrogen, 20 stacks module is required.

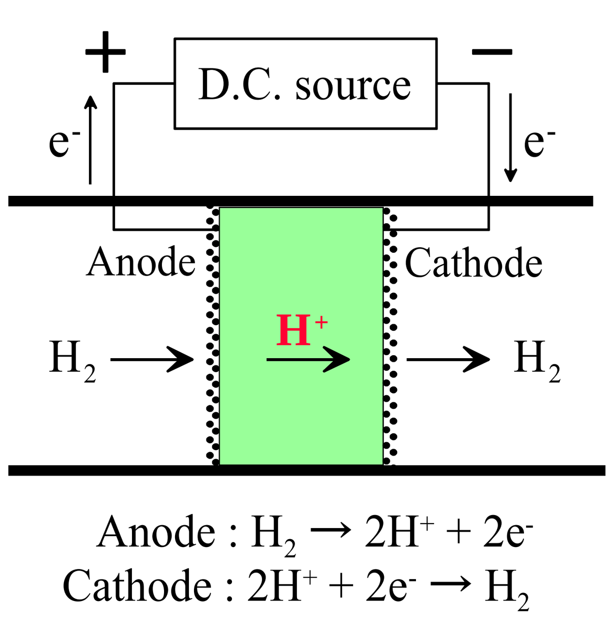
3. New Hydrogen Separation Method by using "Proton"

- We invented a new Hydrogen Separation method by using **"Proton-Conducting Metal Oxide Electrolyte"**.
- **"Electrochemical Hydrogen Pump"**, only applied by DC voltage, leads to hydrogen separation via selective hydrogen transport from the Anode to the Cathode.

* The new method realize superior efficiency and high mobility comparing to the conventional PSA(Pressure Swing Adsorption) method and Pd-Ag alloy membrane separation method.



(Hydrogen pumping rate as a function of current)



(Electrochemical Hydrogen Pump)

4. Patent Licensing Available

Patent No.: WO2007/046314 (JP, US, EP)
WO2003/084894 (JP, US)
WO2007/060925 (JP, EP)

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Energy Harvesting Device

Thermochemical Cell based on Host-Guest Chemistry generating electricity from Room-Temperature Heat

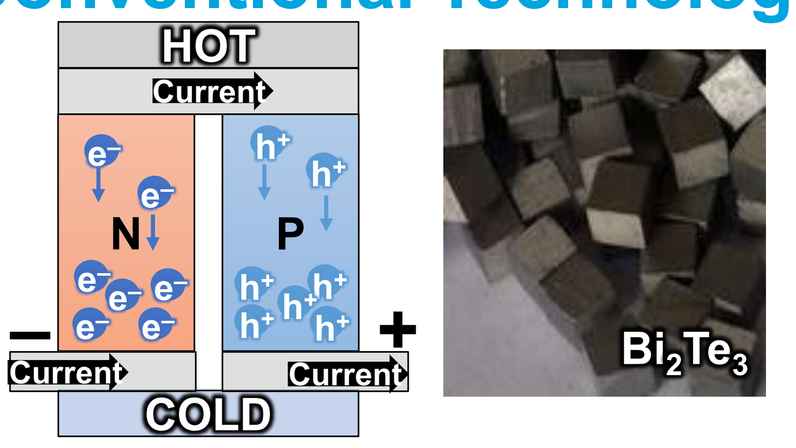
Associate Prof. Teppei YAMADA (Kyushu University)

1. Introduction & Background

Over 60% of energy becomes heat loss without any work at room temperature range and it has been hardly utilized.

"Thermal to Electric" energy harvesting technology at room-temperature range is expected for various wearable micro devices.

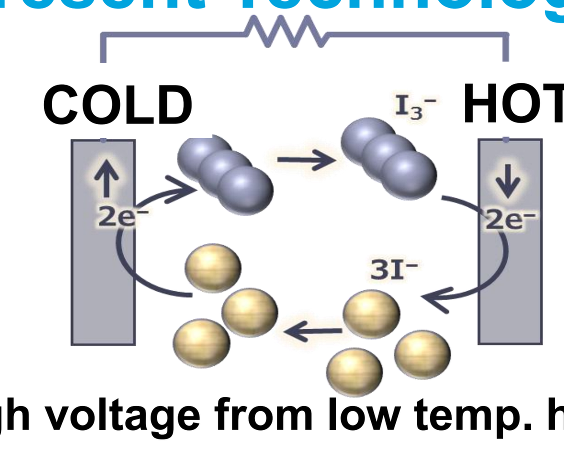
Conventional Technology



× Low performance at room temp.
× Low voltage per cell : complex device
× Toxic and rare atomic elements

Thermoelectric Device

Present Technology Field



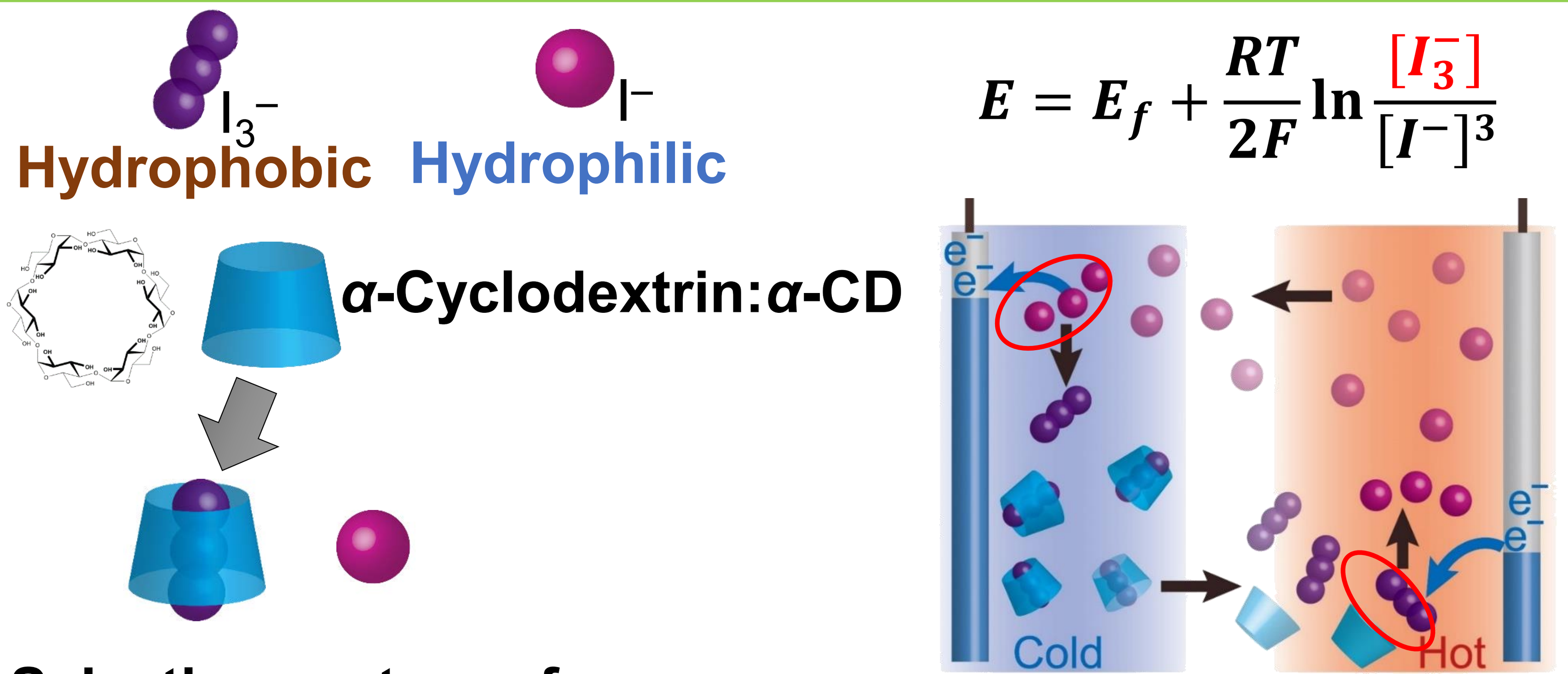
○ High voltage from low temp. heat flow (HighSeebeck coefficient : in order of mV/K)
○ Low cost and non-toxic materials
○ Simple system assembly and easy upsizing

Thermochemical Cell

2. Key Features : Principle of the Invention

Two Strategies to achieve High Concentration Gradient of Redox Species

$$E = E_f + \frac{RT}{2F}\ln\frac{[I_3^-]}{[I^-]^3}$$

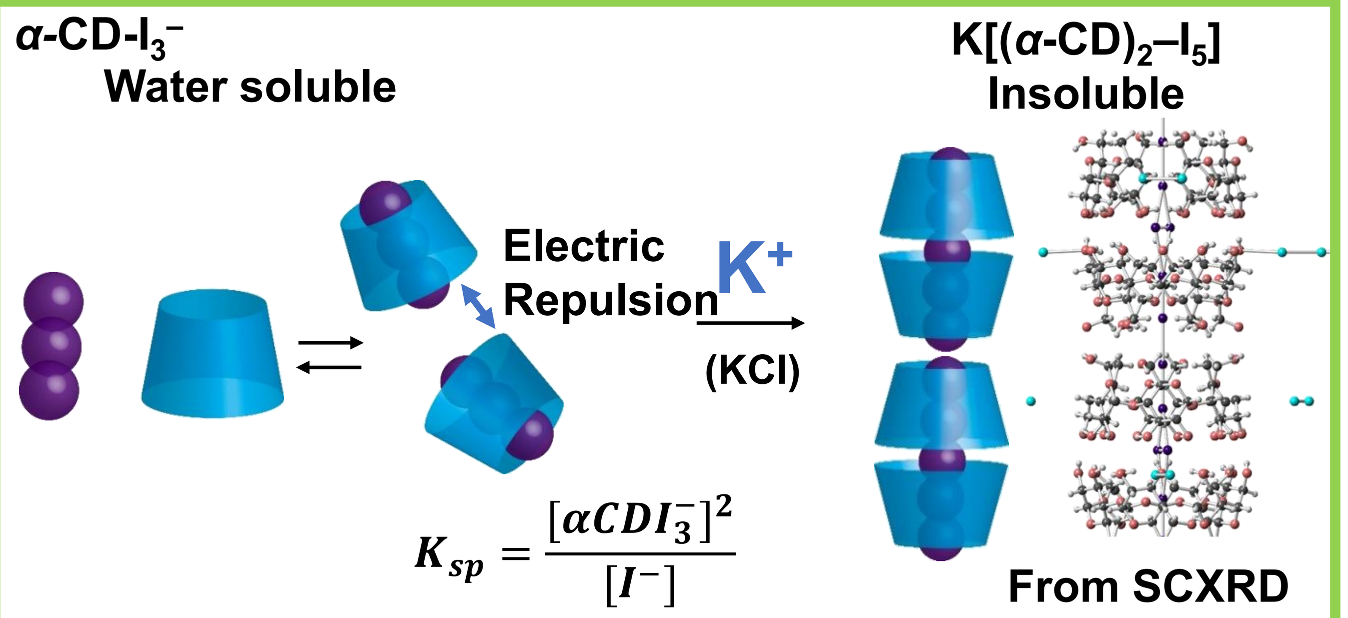


Selective capture of redox species

Low T : I_3^- Captured
Negative potential Shift

High T : I_3^- Released
Positive Potential Shift

Thermocell System based on Supramolecular Chemistry



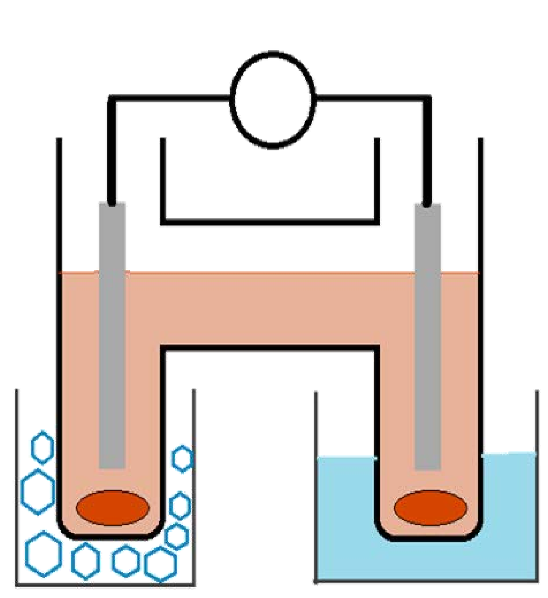
$$K_{sp} = \frac{[\alpha CDI_3^-]^2}{[I^-]}$$

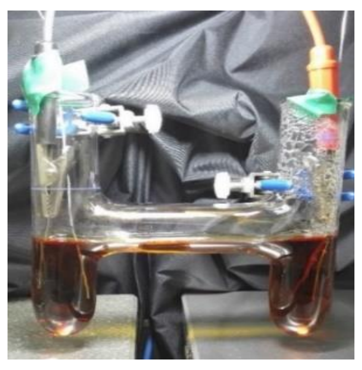
Cold : I_3^- incorporated into precipitation
Hot : I_3^- dissolved and eliminated

Large difference of $[I_3^-]$

Effect of KCl on Precipitation

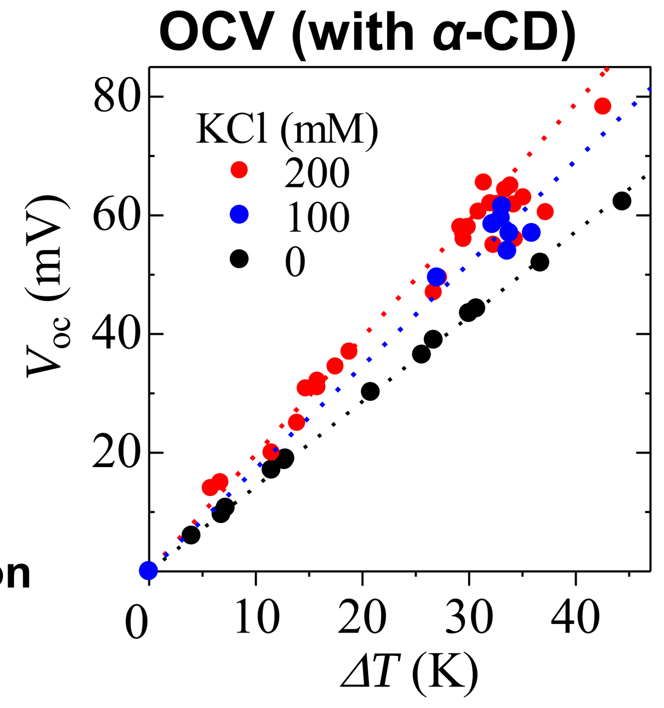
3. Experiment Data and Estimated Characteristics

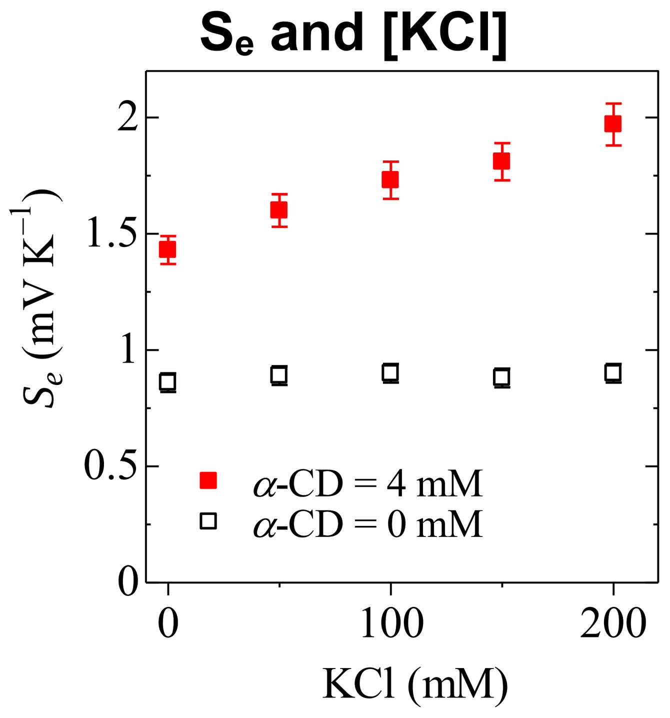




Initial Concentration
$[KI_3]$ = 2.5 mM
[KI] = 10 mM
[α-CD] = 4 mM

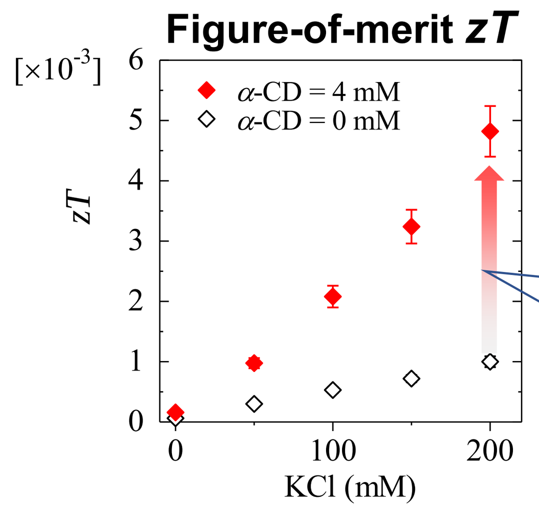
Experimental Cell





KI_3/KI Solution 0.86 mV K^{-1} → (α-CD) Host–Guest 1.43 mV K^{-1} → (KCl) Aggregated 1.97 mV K^{-1}

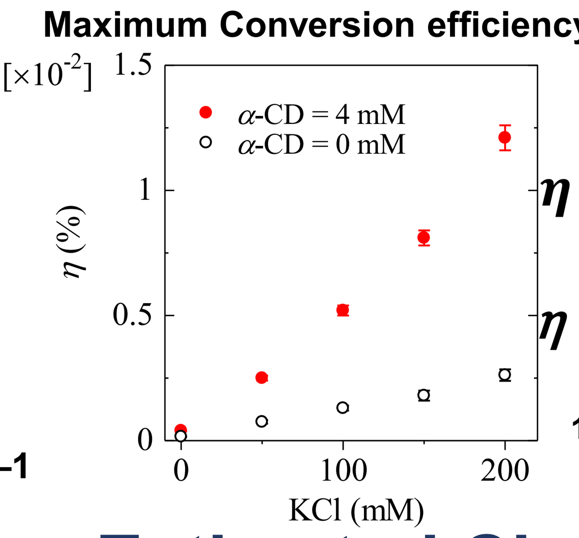
Seebeck Coefficient Enhancement



$$zT = \frac{\sigma S_e^2}{\kappa}T$$

$zT = 5\times10^{-3}$

5 times Enhancement



$$\eta = \frac{\Delta T}{T_h}\frac{\sqrt{1+zT}-1}{\sqrt{1+zT}+\frac{T_c}{T_h}}$$

η = 0.012%

1) Snyder & Toberer, *Nature Mater.*, 2008

Estimated Characteristics

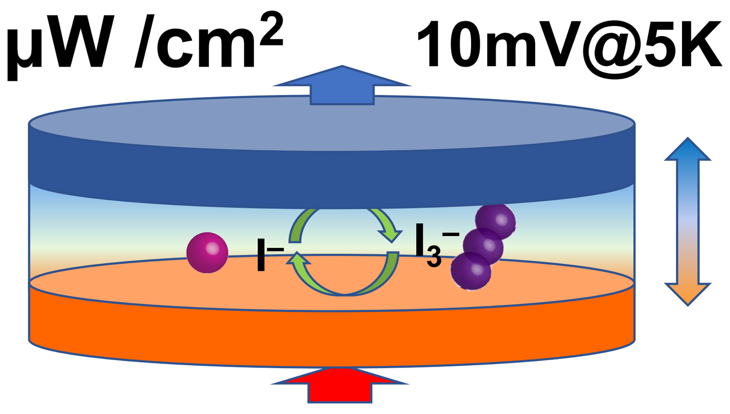
4. Application Examples

○ Wearable Heat Sensor or Energy Source
The sensors or electric power generators are driven by the human body heat.

○ Heat Pump System with Electric Generator
The heat transfer and thermoelectric generation are available at the same time.

○ Energy Harvesting for low-temperature Heat Loss
The energy recovery from underused heat loss in factories, homes, shopping malls is efficiently possible.

~2μW /cm² 10mV@5K



Coin Cell Structure

5. Patent Licensing Available

Patent No.: WO2017/155046 (JP, US, EP, CN)
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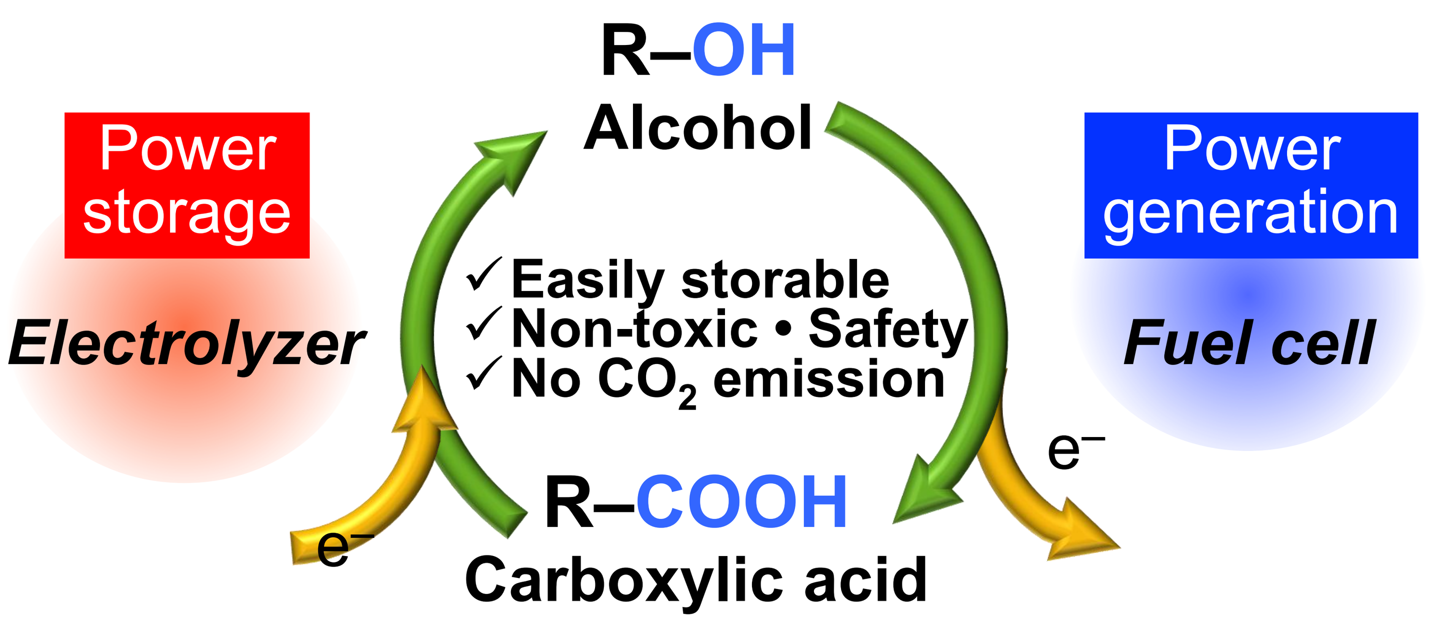
SUSTAINABLE DEVELOPMENT GOALS

Power Storage Facilities

Environmental Friendly Power Storage with Electrochemical Cells Using Natural Carboxylate

Prof. Miho YAMAUCHI (Kyushu University)

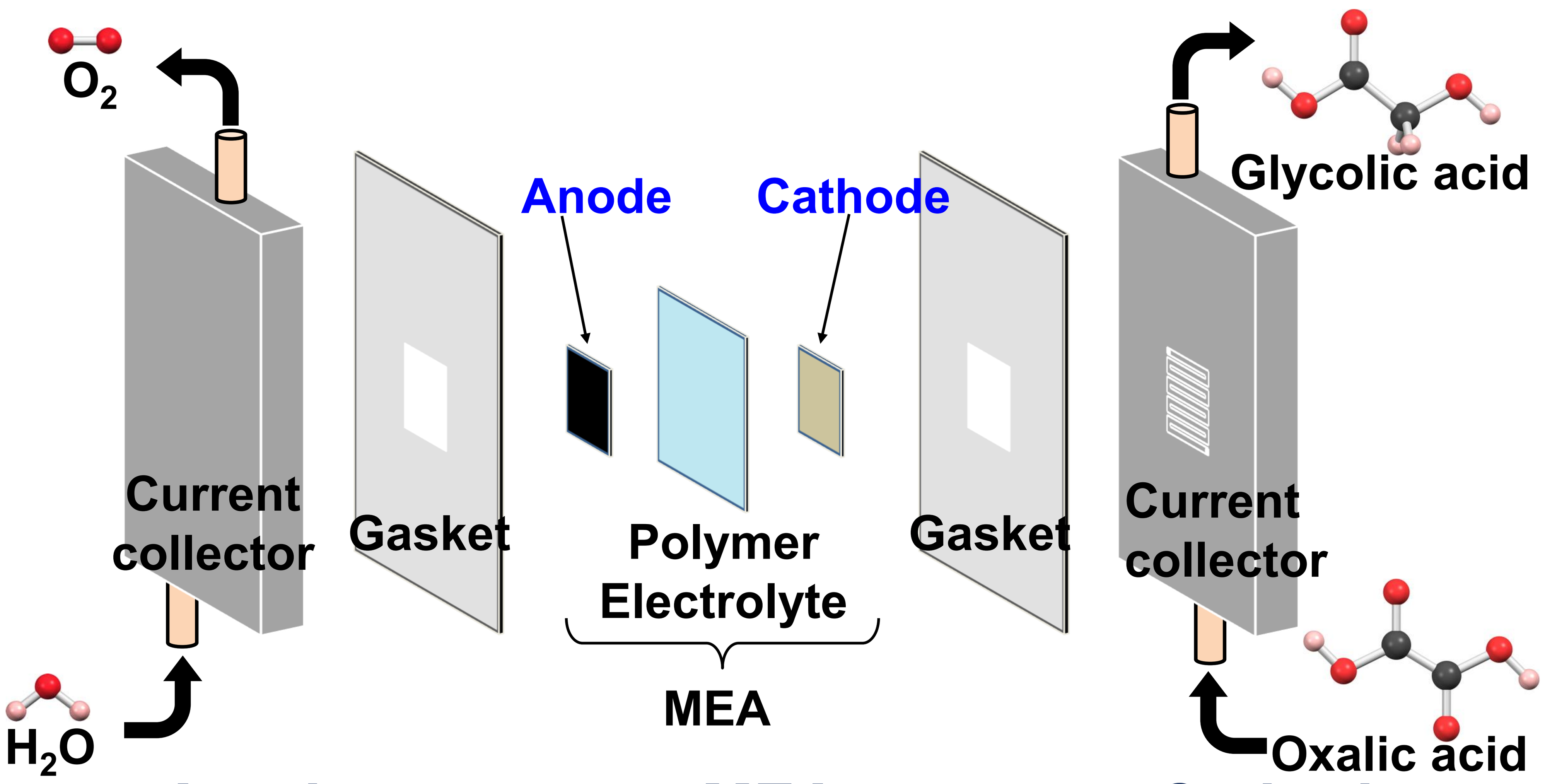
1. Carbon-Neutral Energy Cycle Using Alcohol/Carboxylic Acid Redox Couple



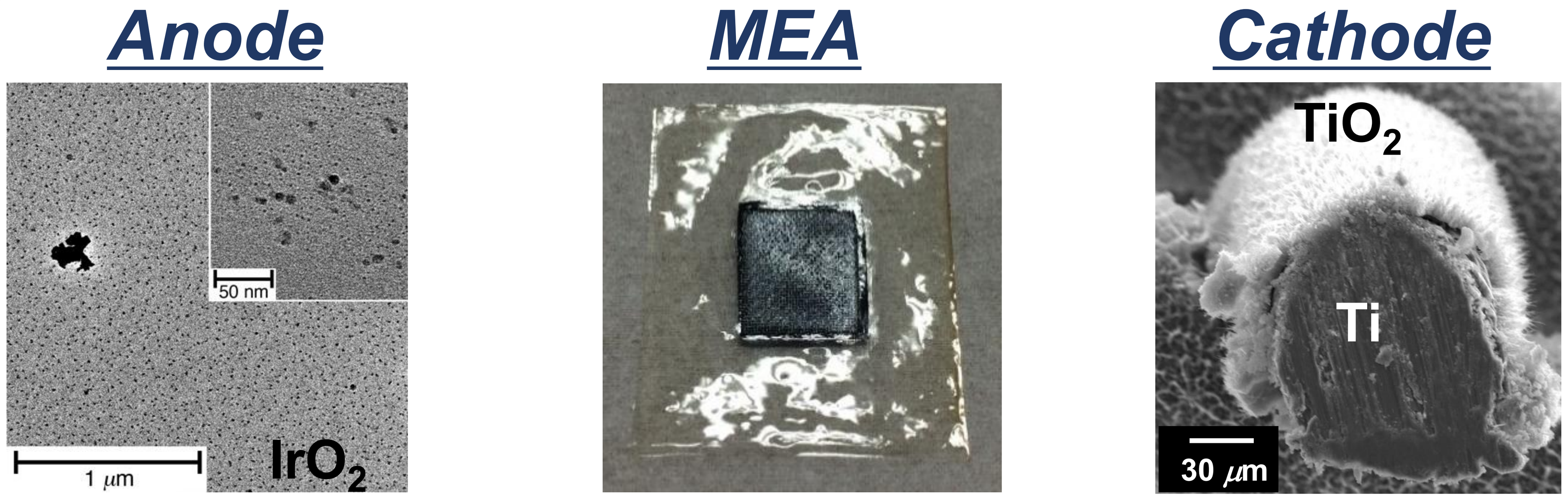
- Alcoholic compounds are attracting much attention as "liquid" energy carrier having "high energy density" and "high chemical stability."
- A flow-type electrolyzer, which enables continuous electro-chemical production of glycolic acid (alcohol) from oxalic acid (carboxylic acid), was newly developed.

$$\underset{\text{Oxalic acid}}{\text{HOOC–COOH}} \xrightarrow{4\,H^+ + 4\,e^-} \underset{\text{Glycolic acid}}{\text{HOOC–CH}_2\text{OH}}$$

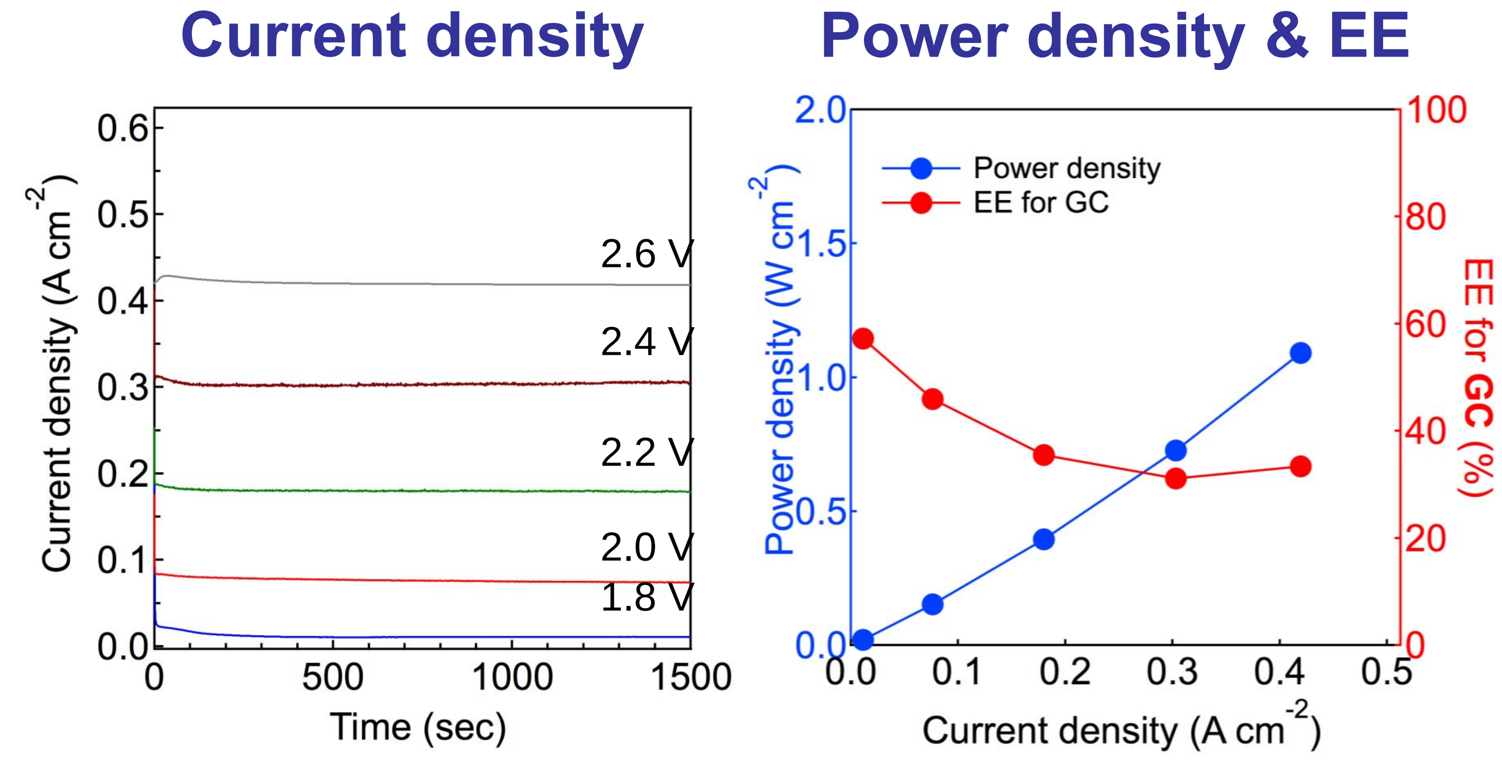
2. Polymer Electrolyte Alcohol Electrosynthesis Cell (PEAEC)



A polymer electrolyte alcohol electro-synthesis cell (PEAEC), which realizes continuous electrochemical reduction of oxalic acid to form glycolic acid without any additives into the reaction solution, has been newly developed.



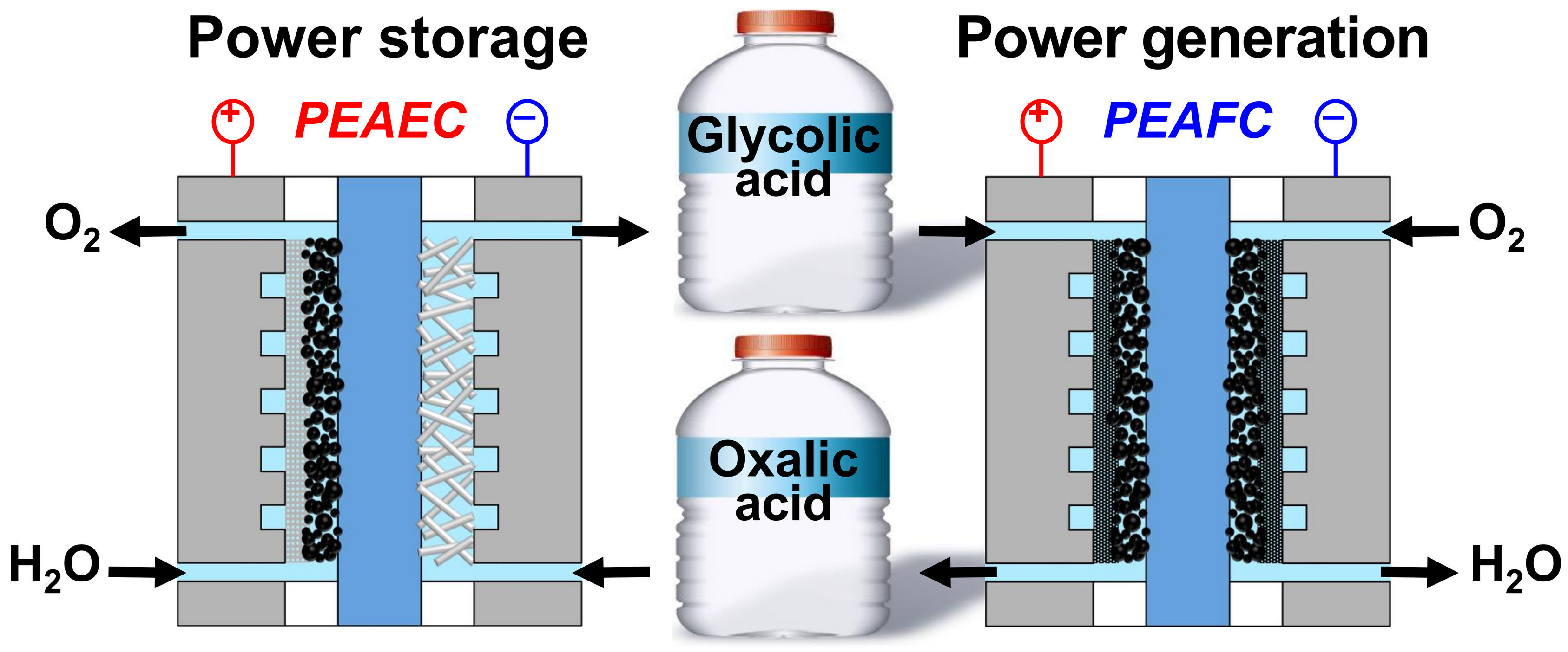
Performance



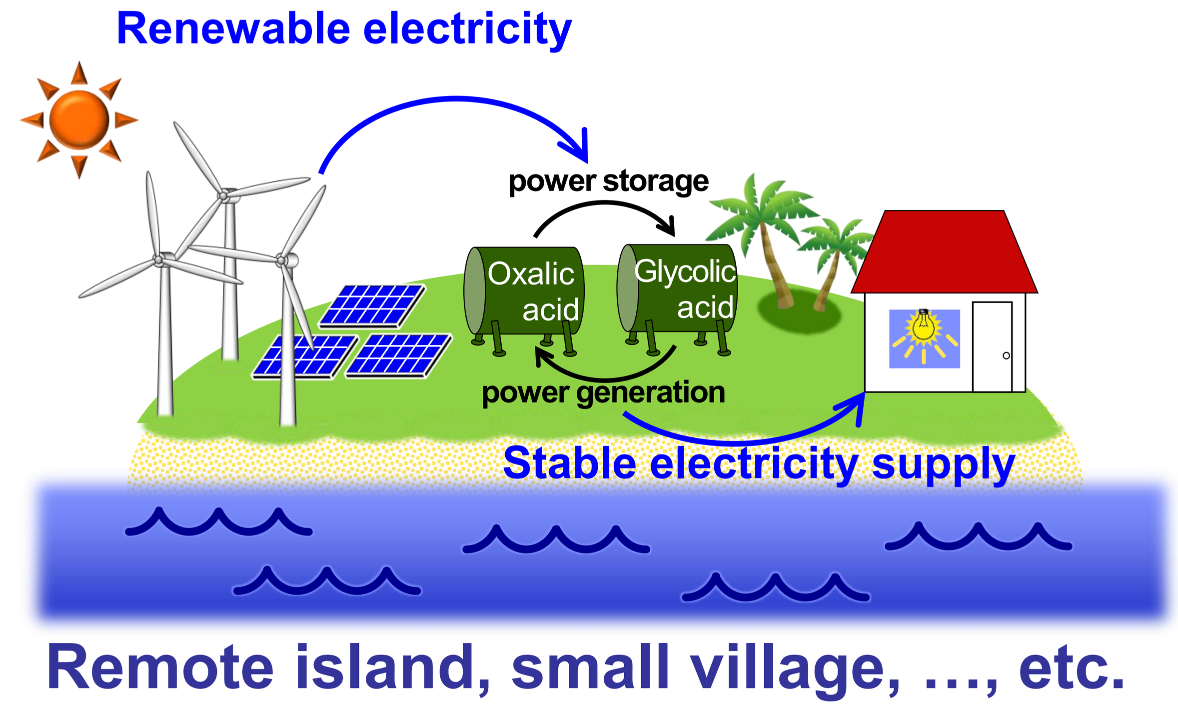
Long-time stability and High energy conversion efficiency (EE) of the PEAEC were demonstrated.

3. Prospective Applications

Storage of renewable electricity



Local production for local consumption



Remote island, small village, …, etc.

- ✓ The electric power company can store surplus electricity derived from renewable energy and can stably supply electricity to customers.
- ✓ This application is suitable for usage in small-scale and fixed place.

4. Patent Licensing Available

Patent No.:WO2017/154743 (JP, US, EP, CN, IN)

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Novel CO_2 Reduction Method

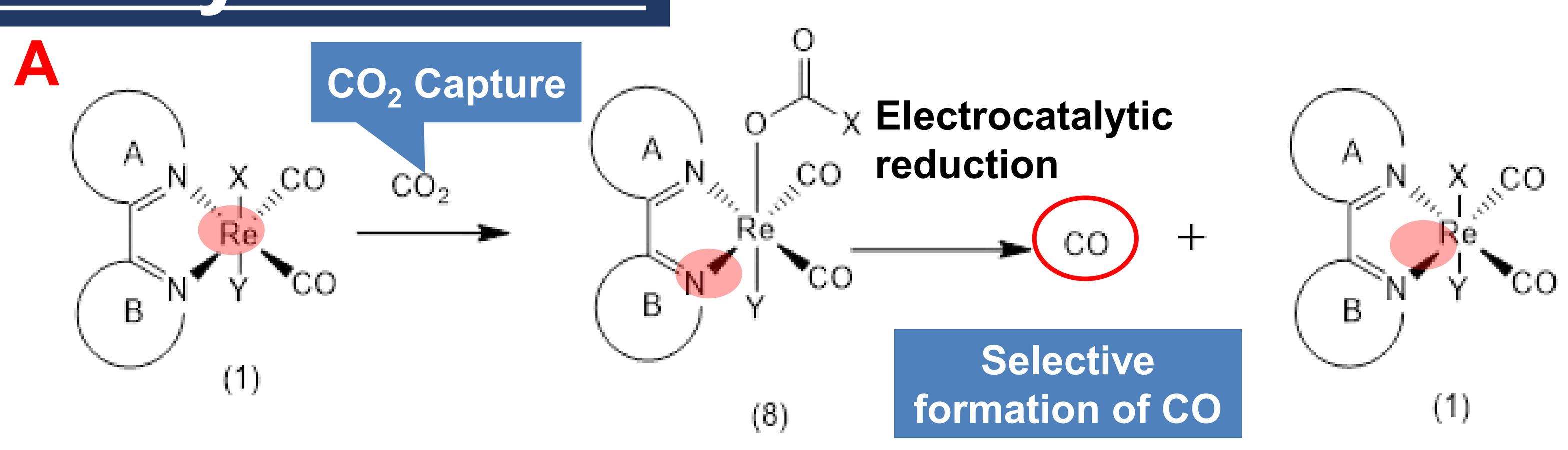
Capturing of CO_2 from low concentration gas by using an Electrocatalysts

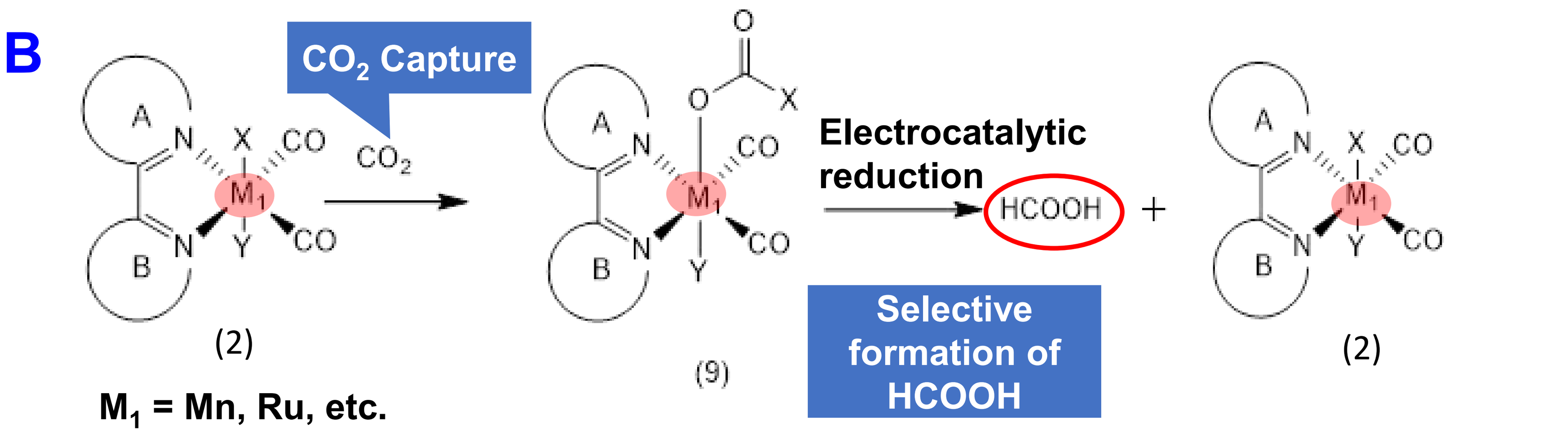
Prof. Osamu ISHITANI (Tokyo Institute of Technology)

1. Background

- Our electocatalysts are useful for removing low concentrations of CO_2 in combustion gases generated from thermal power plants and garbage incineration plants.
- Combustion gas discharged from these plants contains only a small amount (at most a dozen percent) of CO_2. Some extra process is required to apply CO_2 condensation technologies developed by using amines, MOFs, and filters.
- The electrocatalysts are capable of capturing and reducing CO_2 at the same time in the low CO_2 concentration.

2. Key Features





A. Rhenium-complex electrocatalysts

- The complexes can efficiently capture CO_2 from low concentration CO_2 (0.03% – 100%).
- Pressurization is not necessary.
- Electrochemical reduction selectively gives CO.

B. Metal (M1)-complex electrocatalysts (M1 = Mn, Ru, etc.)

- The complexes can efficiently capture CO_2 from low concentration CO_2 (0.03% – 100%).
- Pressurization is not necessary.
- Electrochemical reduction selectively gives HCOOH.

3. Experimental Setup of Electrolysis and Data

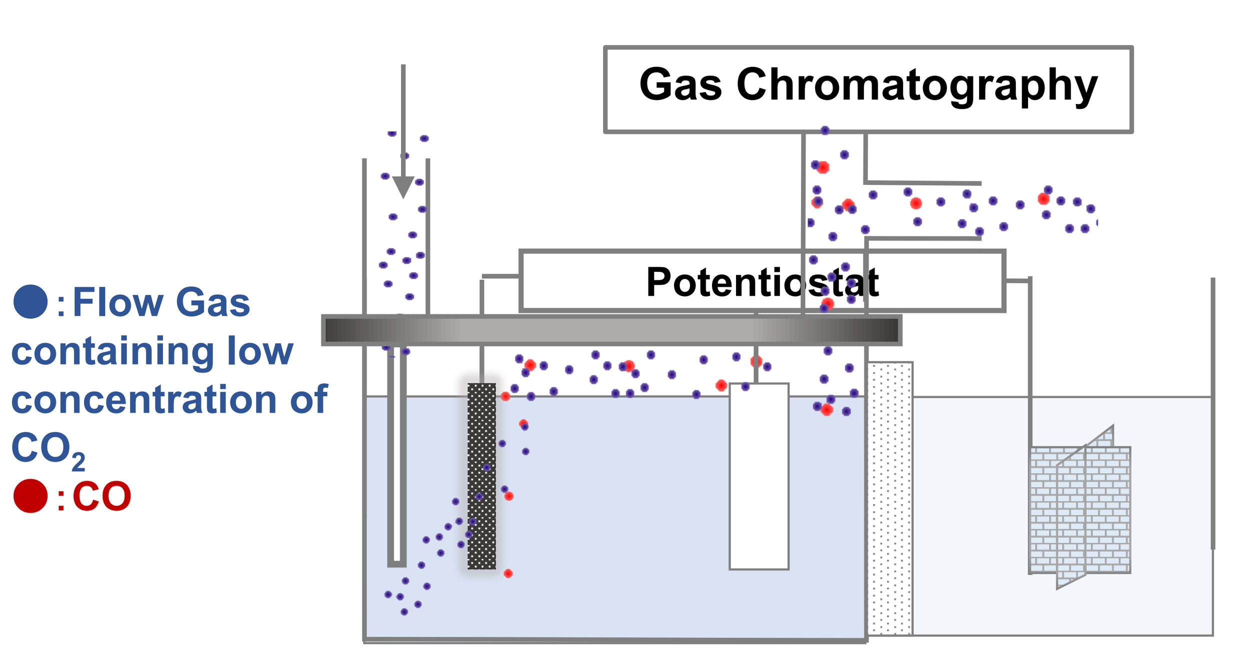
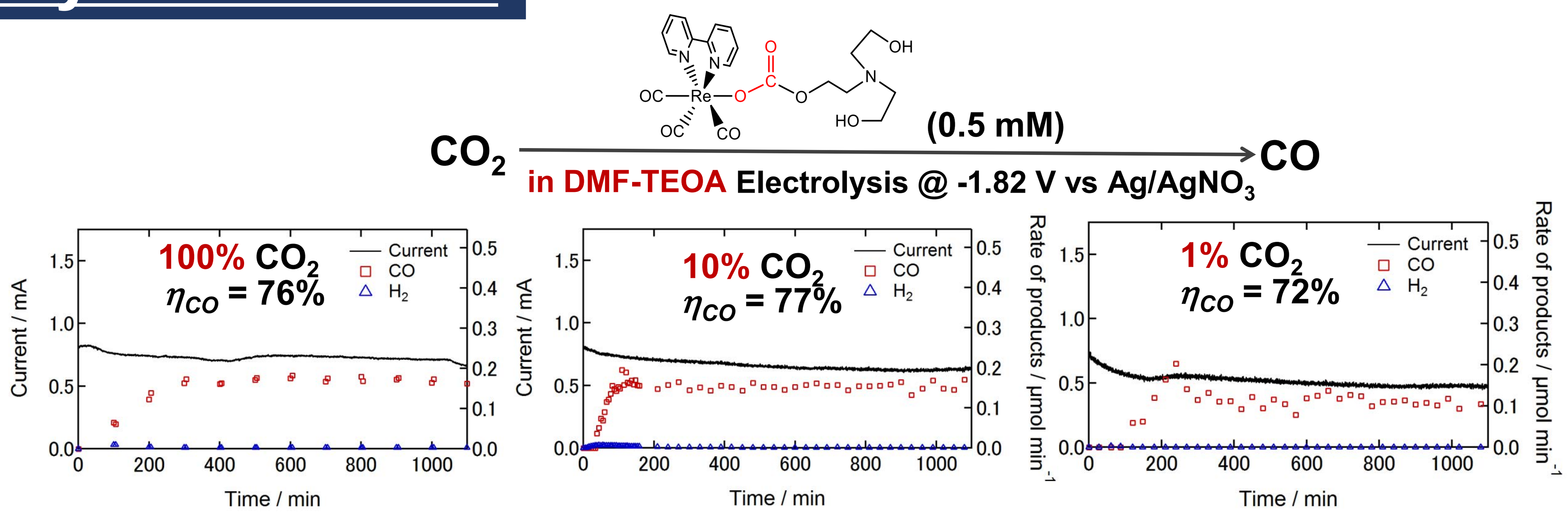


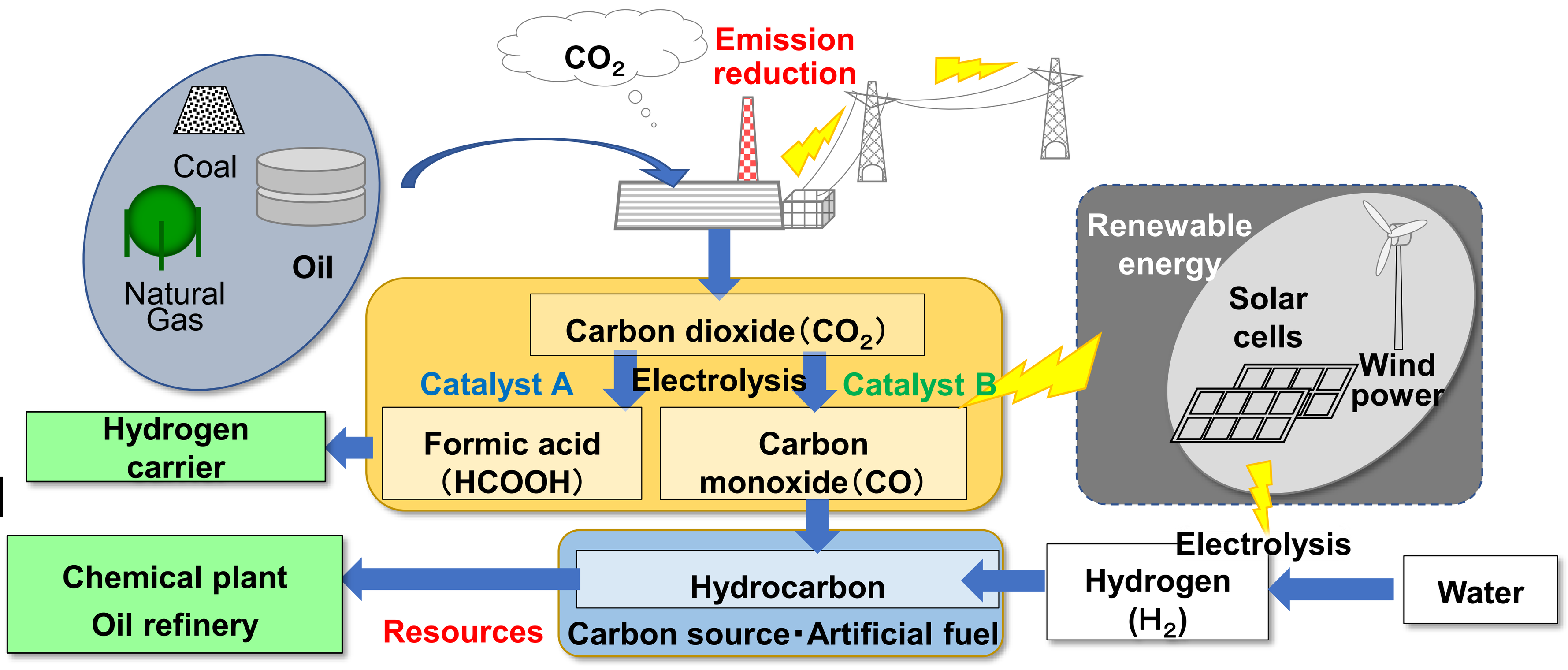
Figure 1. Electrochemical cell for low concentration CO_2



Rhenium(Re)-complex catalyst enhances CO_2 capturing activity.
The result of ηCO_2 under 1% CO_2 was almost comparable to that under 100% CO_2 .
Efficient and selective formation of CO proceeded even under 1% CO_2.

4. Application Examples

① The electrocatalysts convert CO_2 to CO or HCOOH in the low concentration CO_2 atmosphere.
② The obtained CO can be used in the steel industry, or C1 chemistry.
③ The obtained HCOOH can be used as fuel for a fuel batteries.



5. Patent Licensing Available

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Mission :
We contribute to the creation of innovation in science and technology as the core implementing agency of the fourth phase of the Science and Technology Basic Plan.

Visions :
1. To achieve innovation in science and technology through creative research and development.
2. To maximize research outcomes by managing research resources on the virtual network.
3. To develop the nation's infrastructure for science and technology to accelerate innovation in science and technology.

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