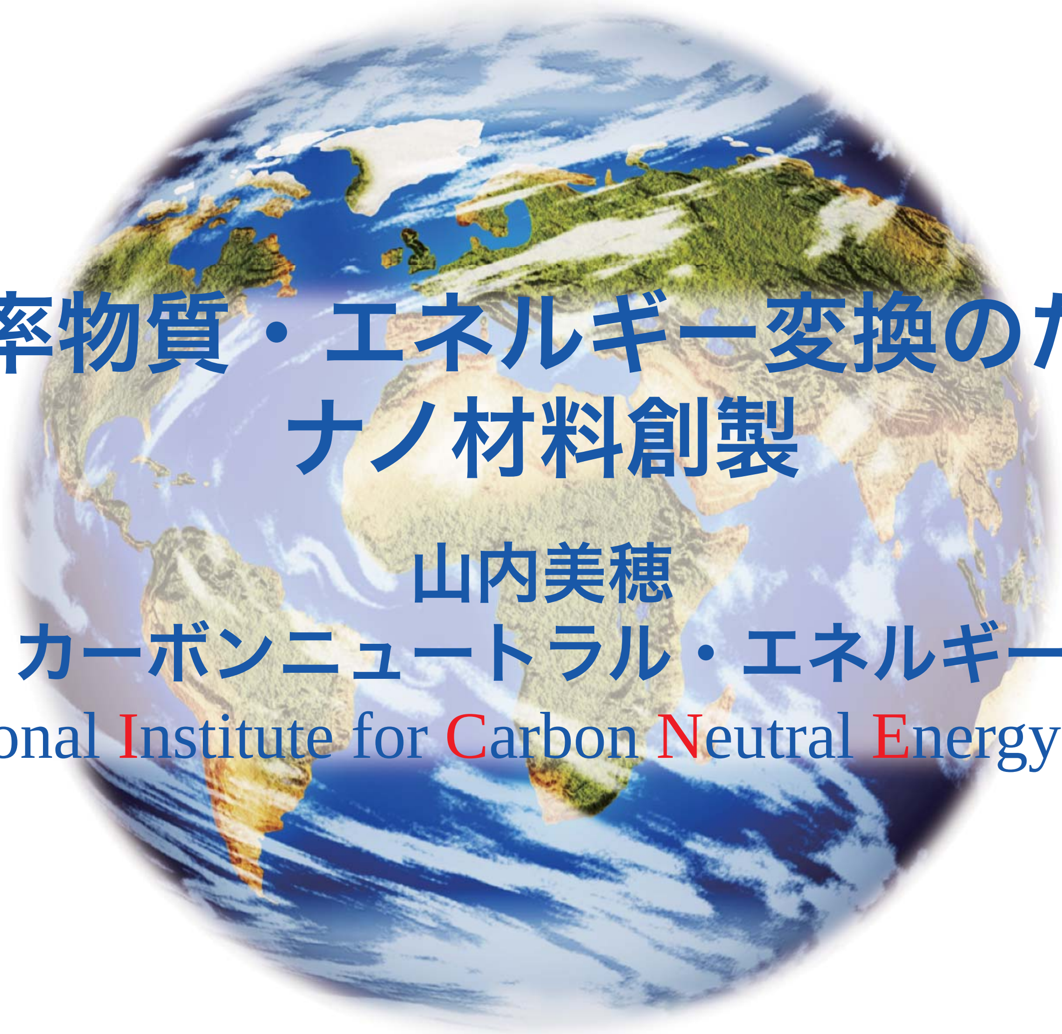
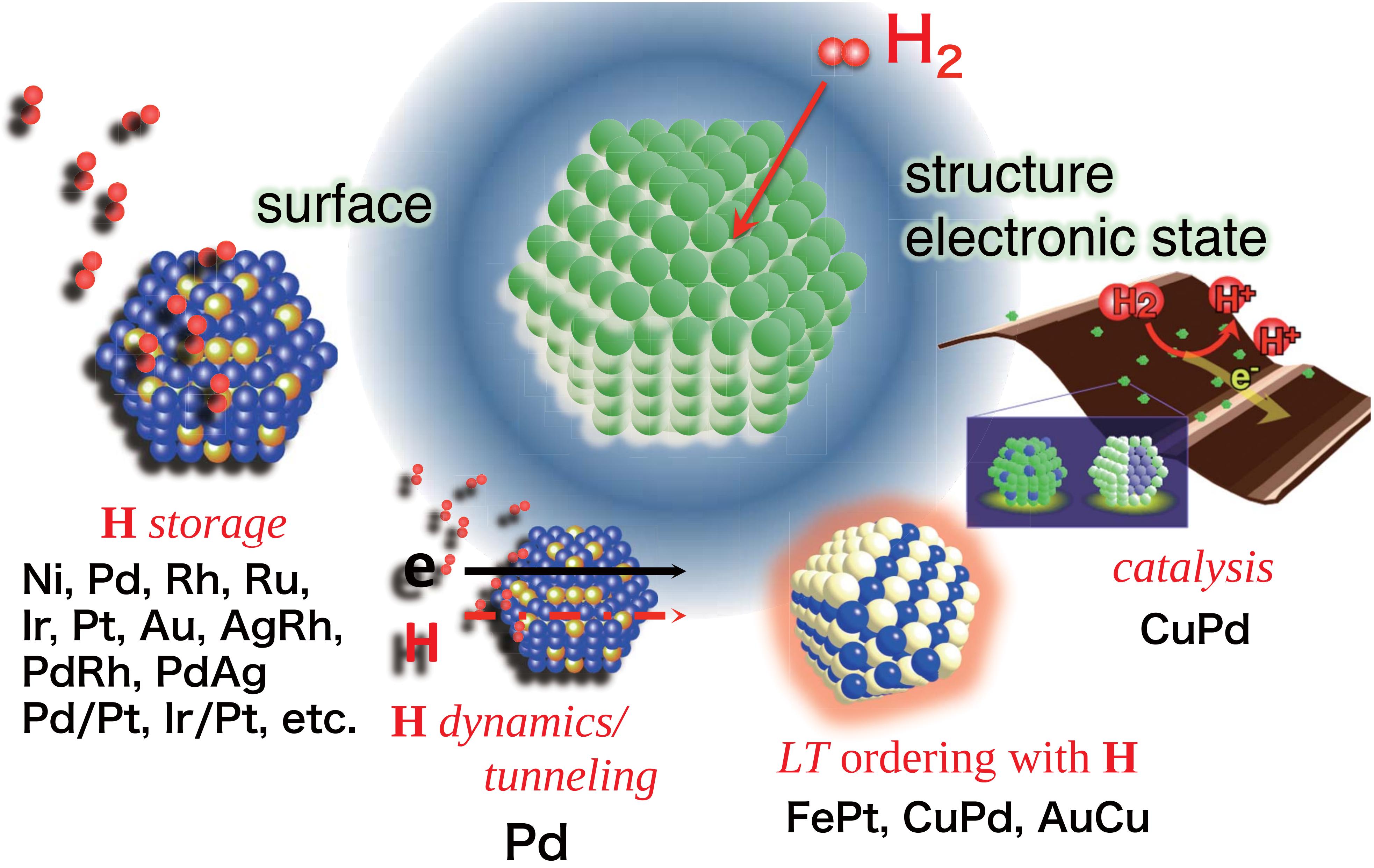
PF研究会「次世代放射光光源を用いた構造物性研究への期待

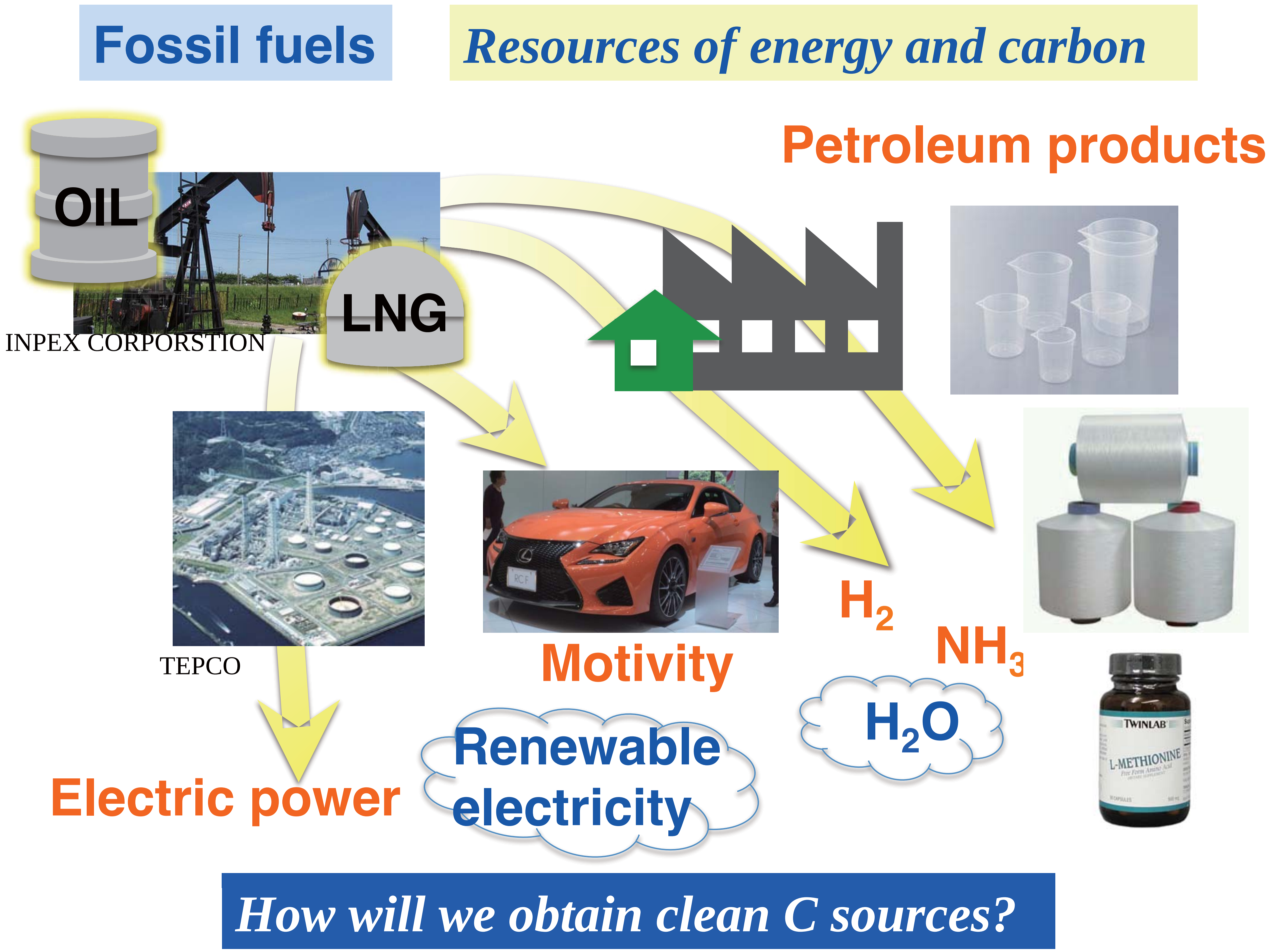


高効率物質・エネルギー変換のための ナノ材料創製

山内美穂
九州大学　カーボンニュートラル・エネルギー国際研究所
(International Institute for Carbon Neutral Energy Research)

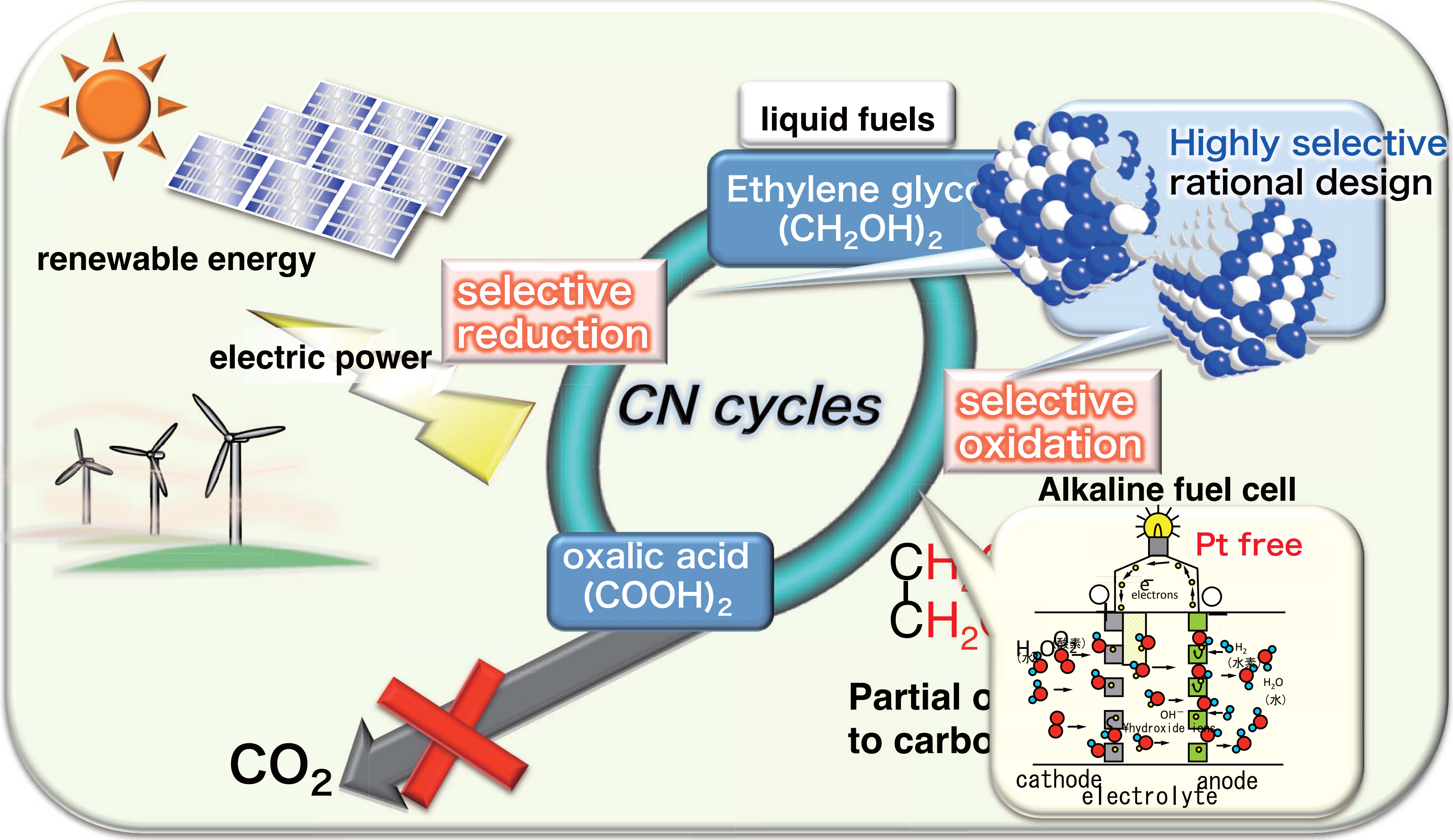
Nano-materials science created by interaction between metals and H




Fossil fuels
Resources of energy and carbon
Petroleum products
OIL
LNG
INPEX CORPORSTION
TEPCO
Electric power
Motivity
Renewable electricity
H_2
NH_3
H_2O
TWINLAB
L-METHIONINE
How will we obtain clean C sources?

Proposed energy cycles using liquid fuels without CO_2 emission

~Carbon Neutral energy (CN) cycles~



Novelty and problem

１. Development of highly selective catalysts

・<u>**Selective EG oxidation to oxalic acid**</u>

・<u>**Non-Pt electrode catalysts**</u>

２. Development of fuel-cell devices

・**Alkaline fuel cells**

(<u>**Hydroxide ionic conductor**</u>, <u>**mechanism**</u>)

３. Development of fuel reproduction systems

・<u>**Carboxylic acid reduction catalysts**</u>

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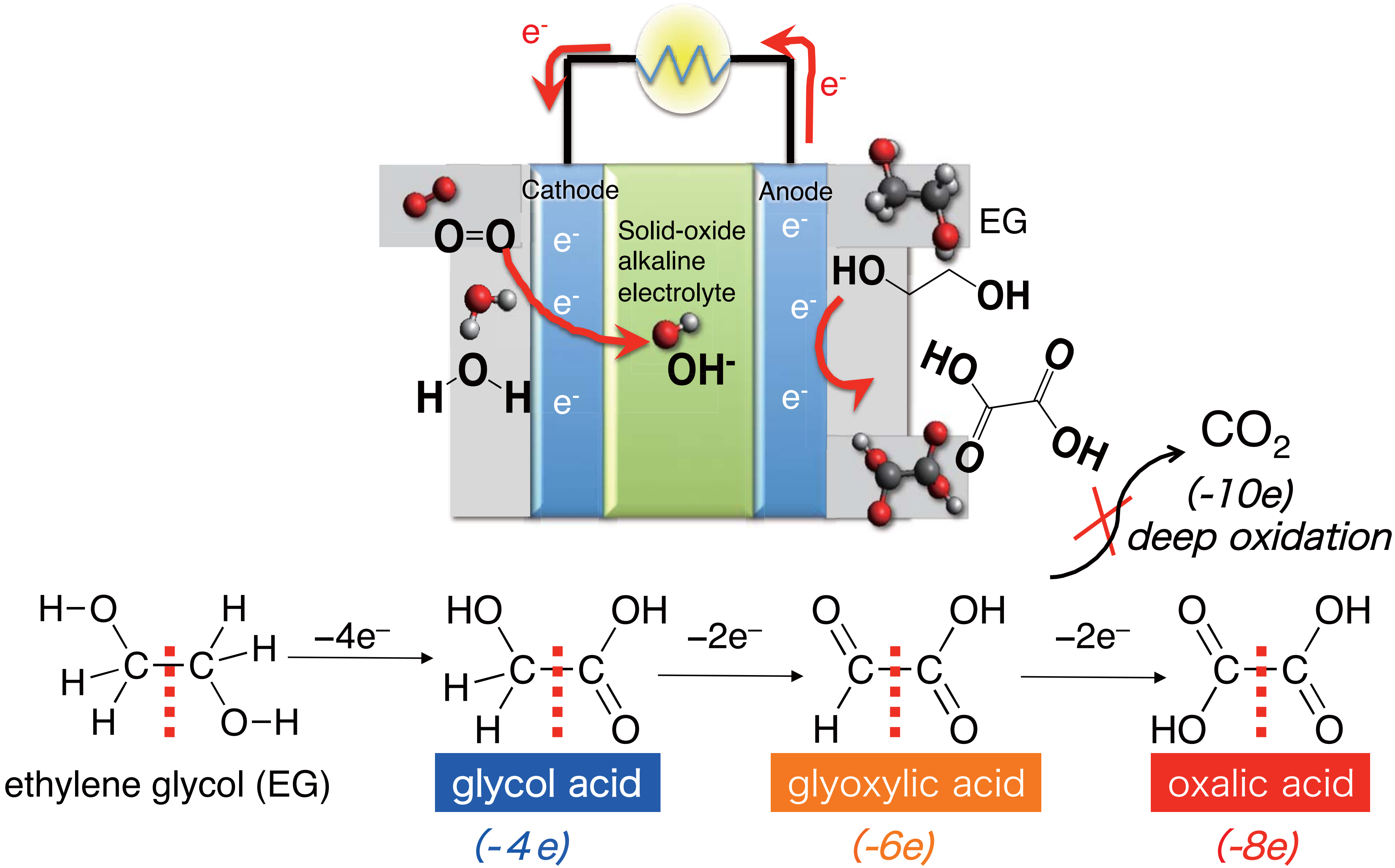
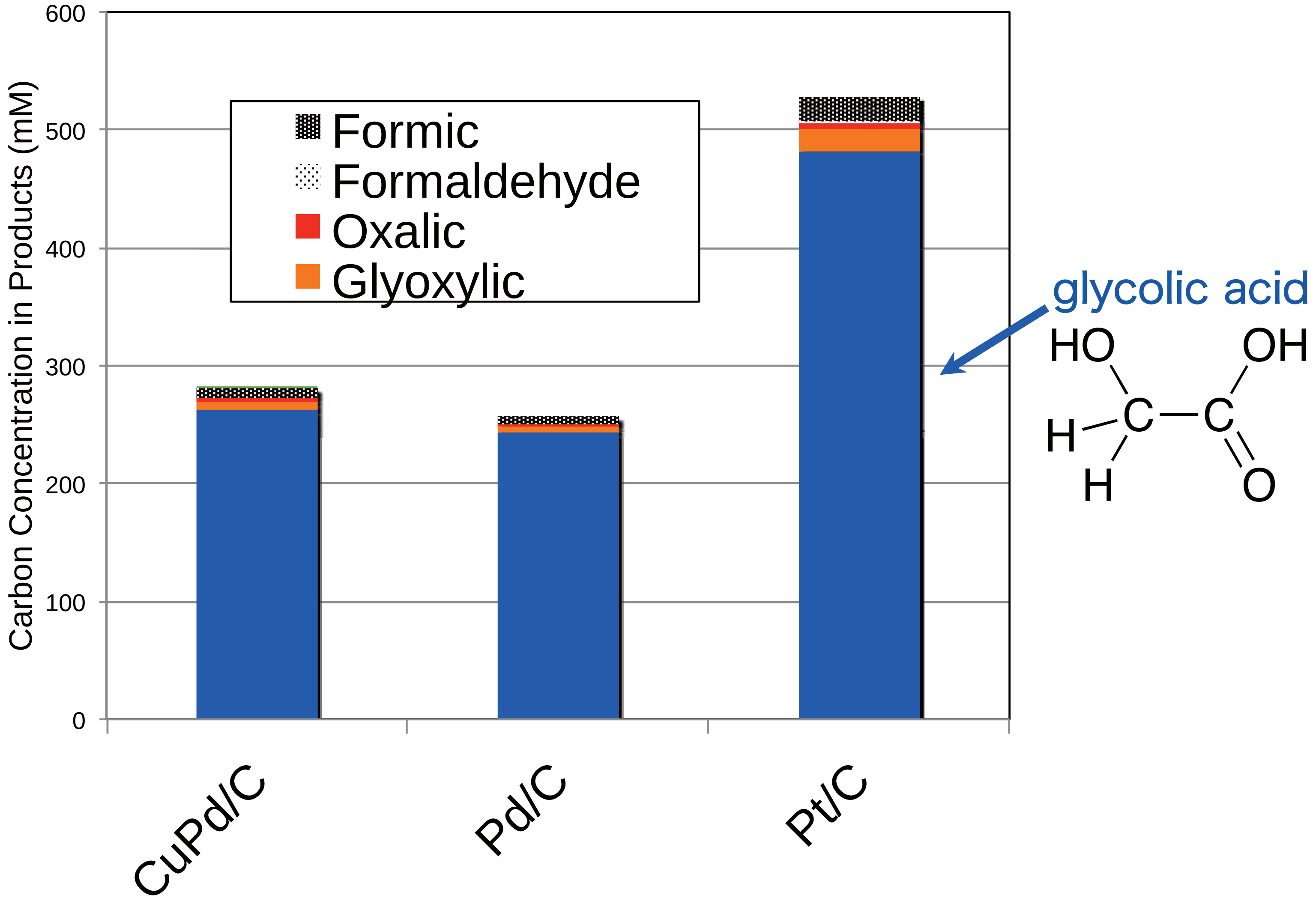
・**Carboxylic acid reduction catalysts**

Direct EG alkaline fuel cell



EG oxidation to oxalic acid without C-C cleavage

EG electrooxidation on CuPd, Pd, Pt

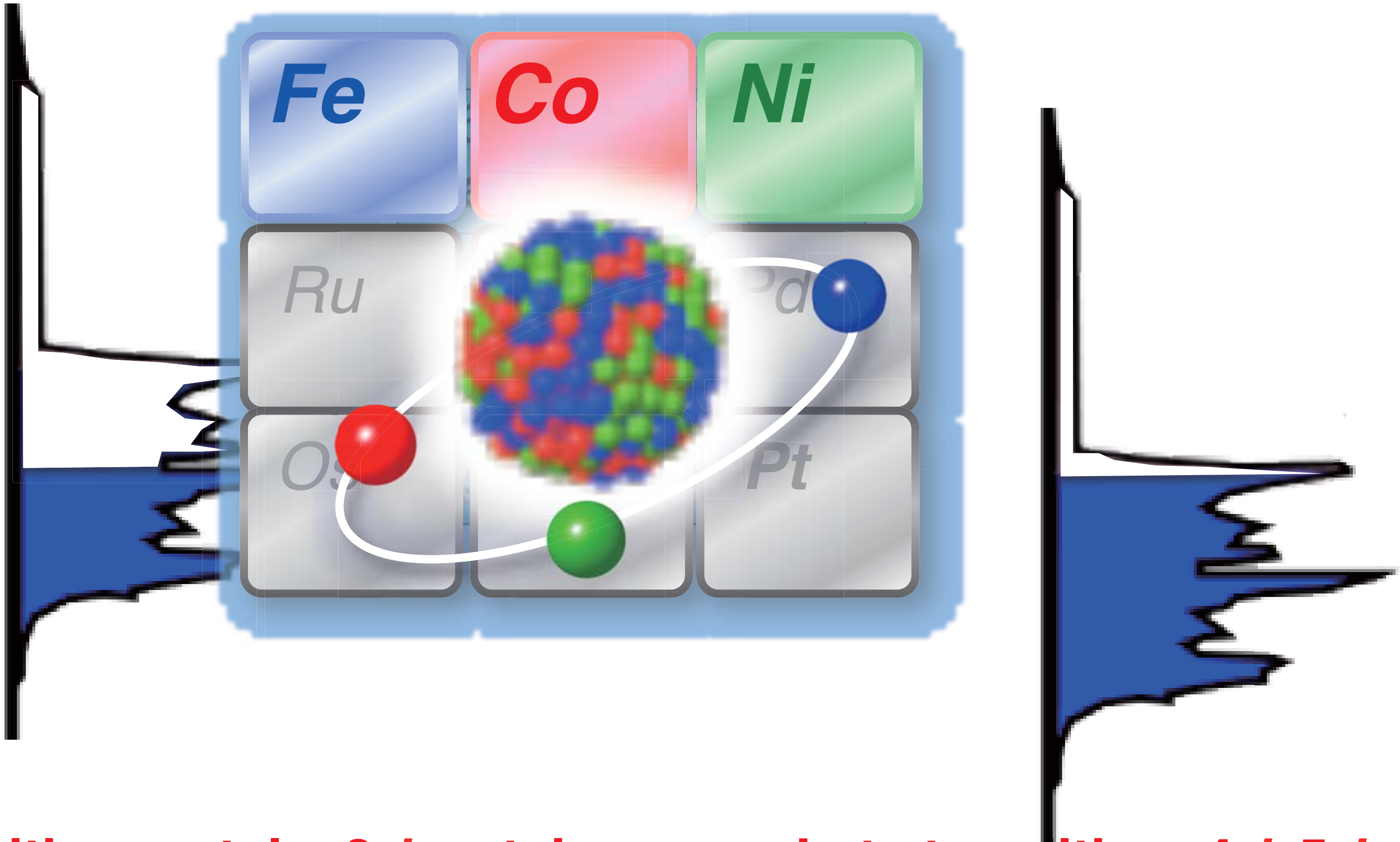


EG can be oxidized to glycolic acid (4e-oxidation) on Pt-group catalysts.

Elemental strategy for materials transformations

✔Interaction with lone pair
(CO, -OH, N_2)

✔Interaction with H

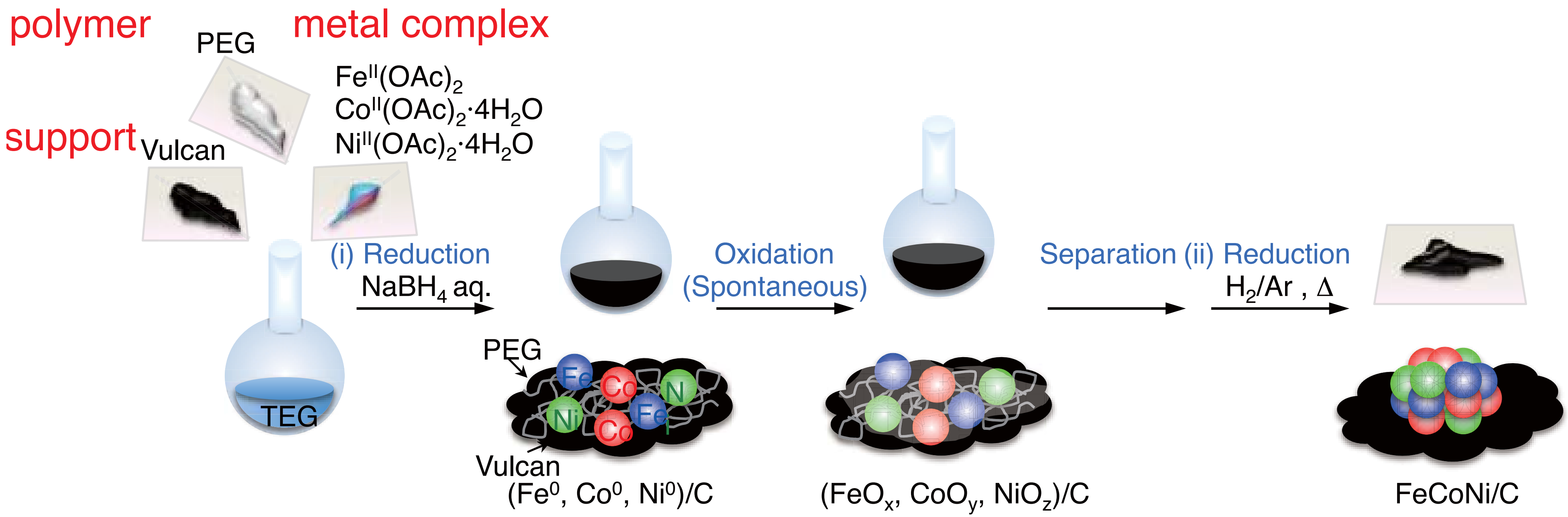


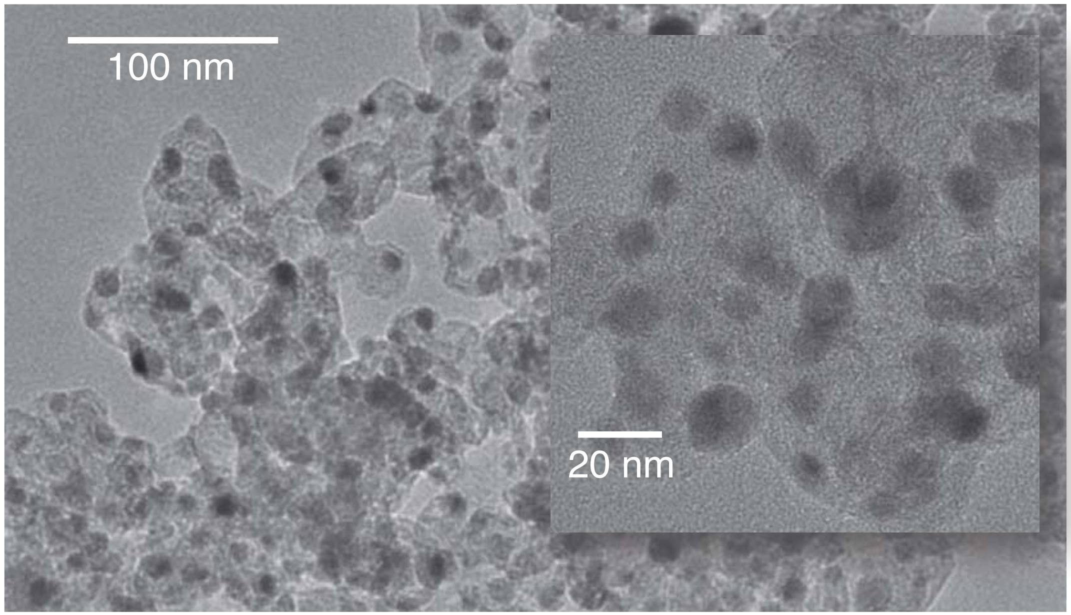
Early transition metals, 3*d* metals
Fe, Co

Late transition, 4*d*, 5*d* metals
Pd, Pt

Phys. Chem. Chem. Phys., 17, 11359 - 11366 (2015).

Novel synthetic method for Fe-group NAs : 2 step reduction

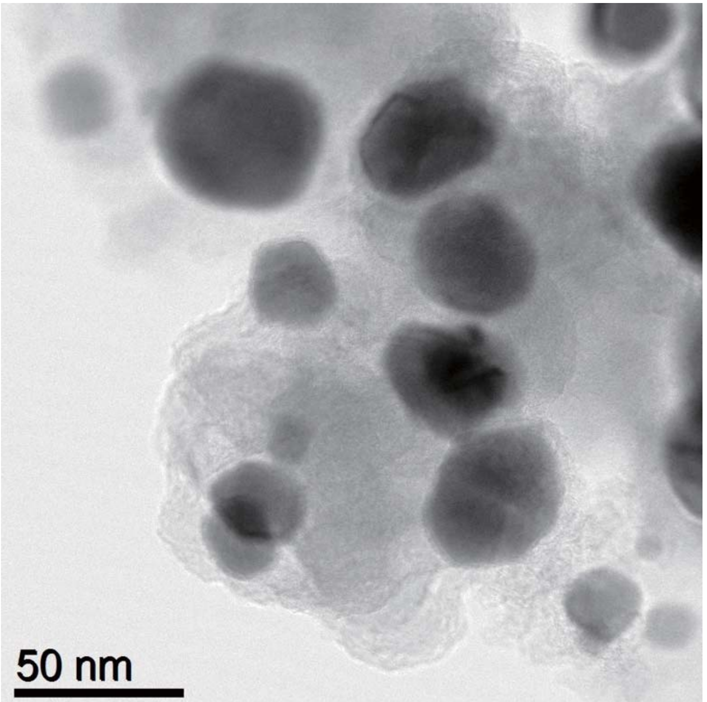




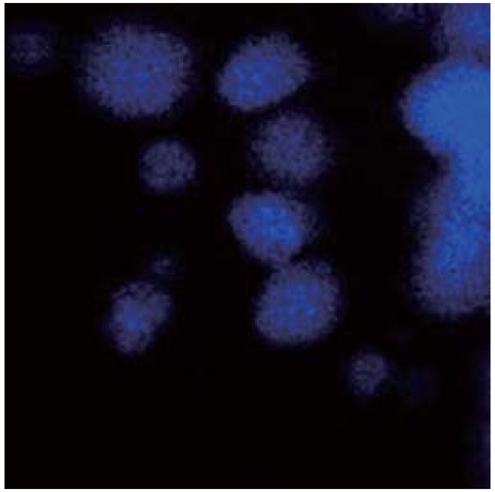
Phys. Chem. Chem. Phys., 17, 11359 - 11366 (2015).

STEM image & elemental map for FeCoNi/C

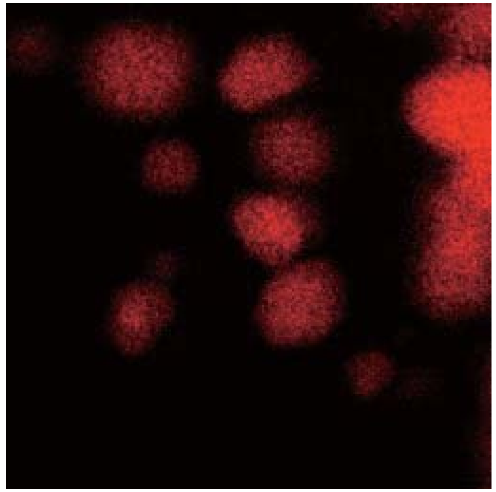
STEM-BF



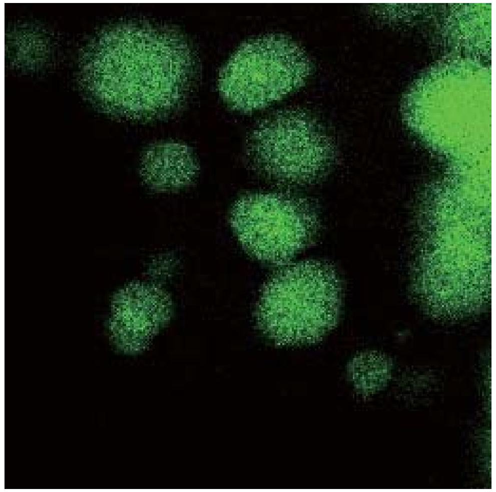
Fe-K$_{\alpha}$



Co-K$_{\alpha}$



Ni-K$_{\alpha}$



Identification by ICP-MS & TEM

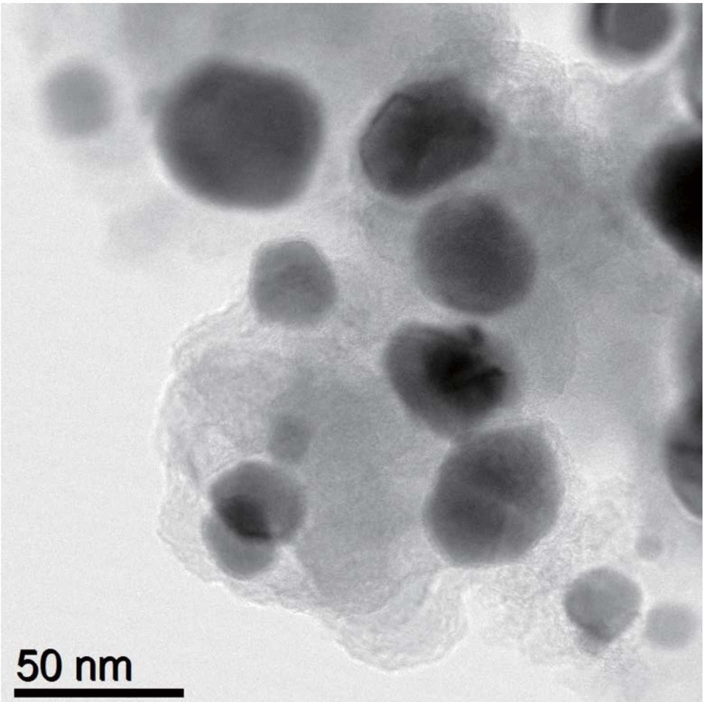
diameter	: 32.8 nm
loading	: 38.1 wt%
Fe : Co : Ni	= 33.4 : 36.9 : 29.7

Collaboration with Prof. Matsumura and Mr. Yamamoto

Phys. Chem. Chem. Phys., 17, 11359 - 11366 (2015).

STEM image & elemental map for FeCoNi/C

STEM-BF



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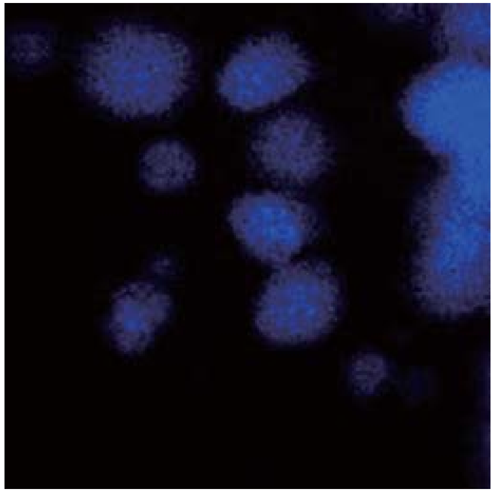
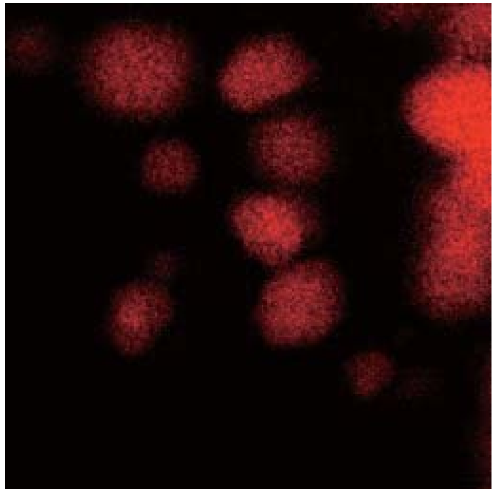
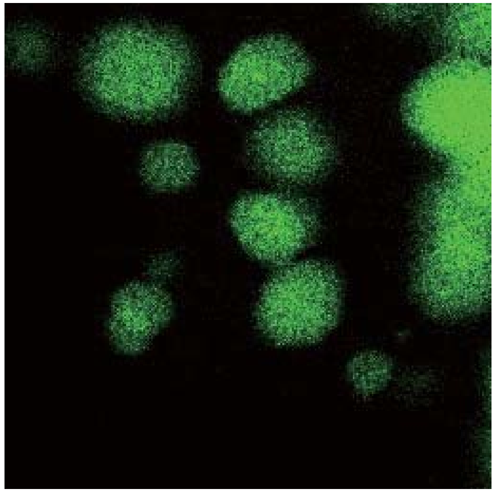
$Fe\text{-}K_\alpha$



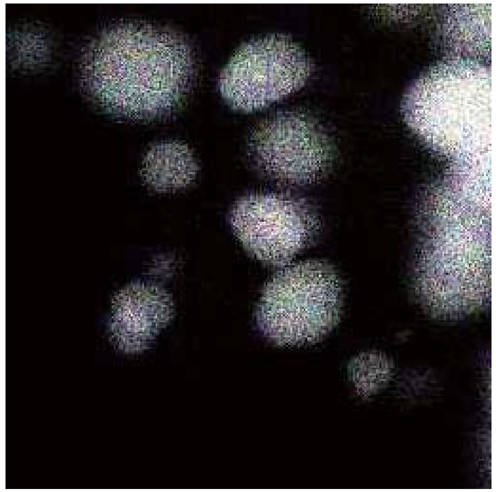
$Co\text{-}K_\alpha$



$Ni\text{-}K_\alpha$



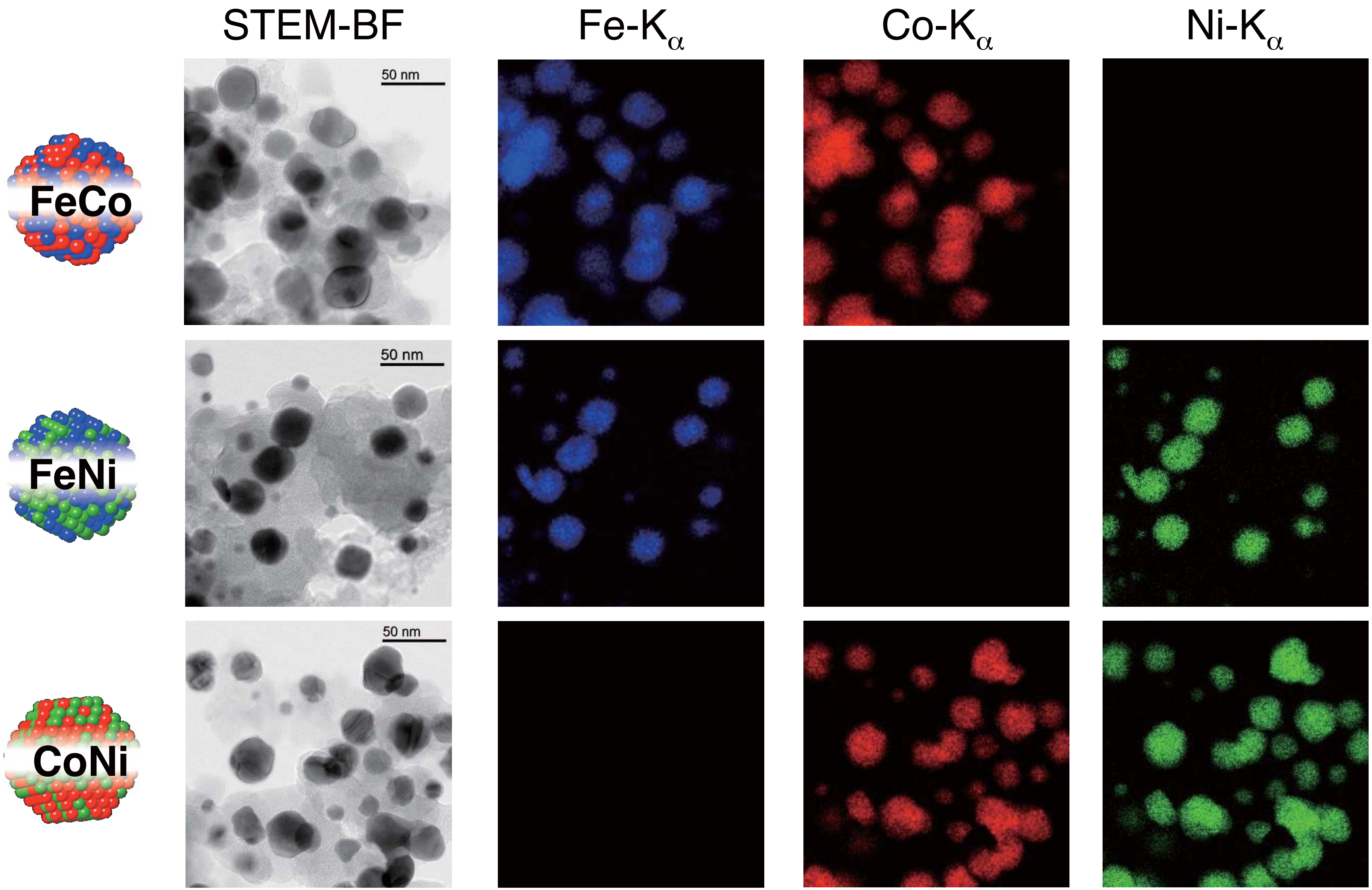
Overlay



Collaboration with Prof. Matsumura and Mr. Yamamoto

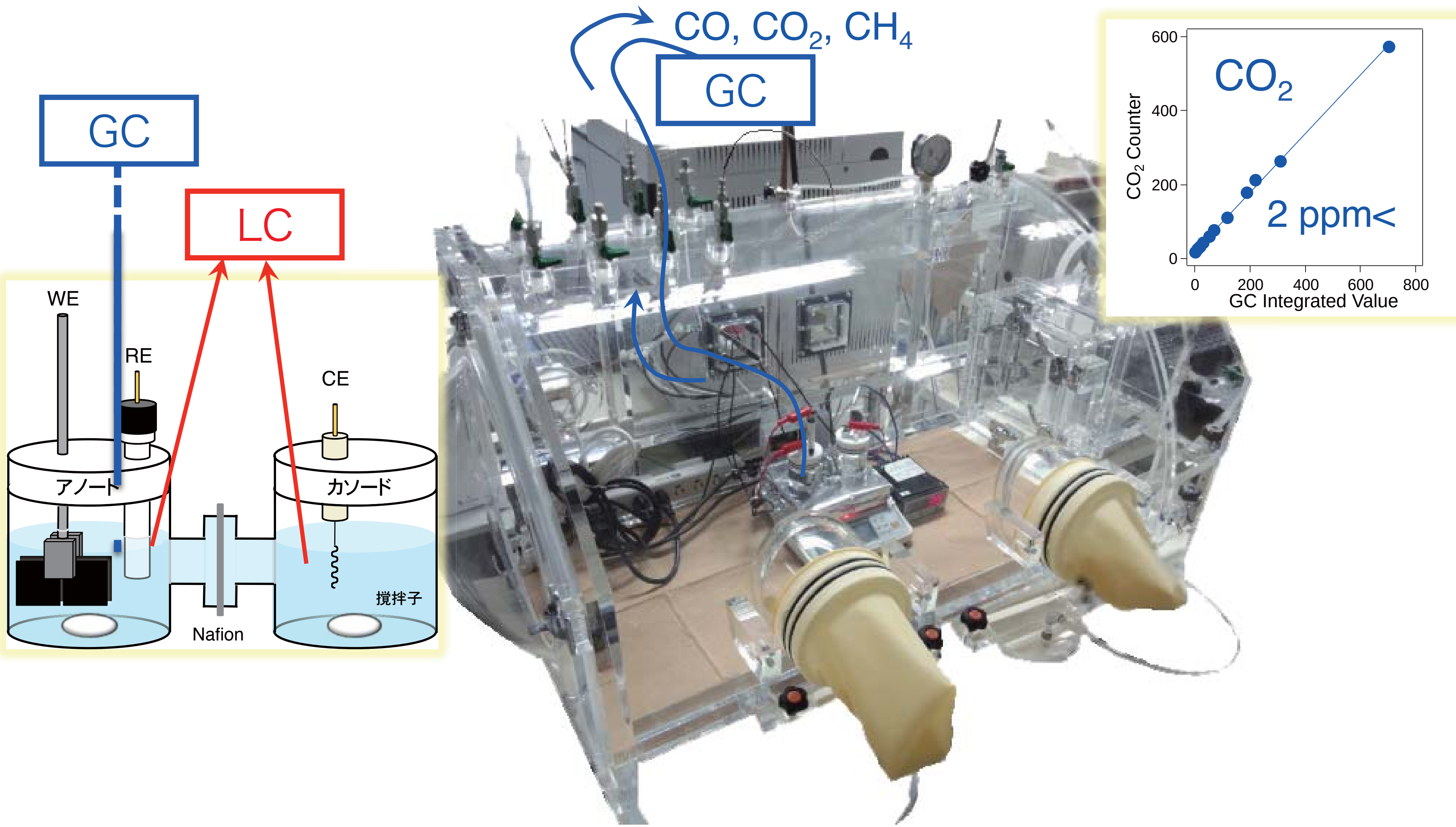
Phys. Chem. Chem. Phys., 17, 11359 - 11366 (2015).

Elemental distribution of FeCo/C, FeNi/C, CoNi/C

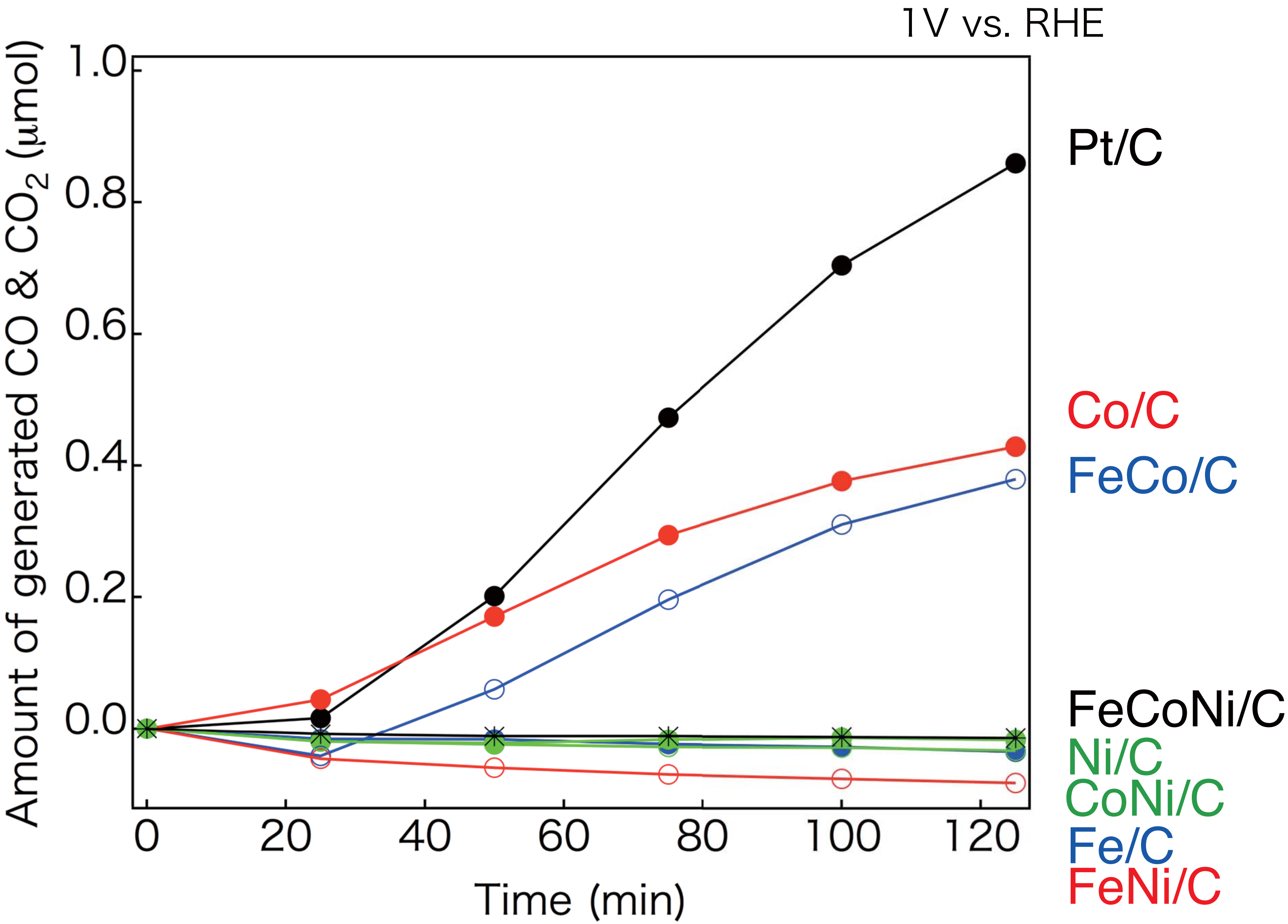


Collaboration with Prof. Matsumura and Mr. Yamamoto

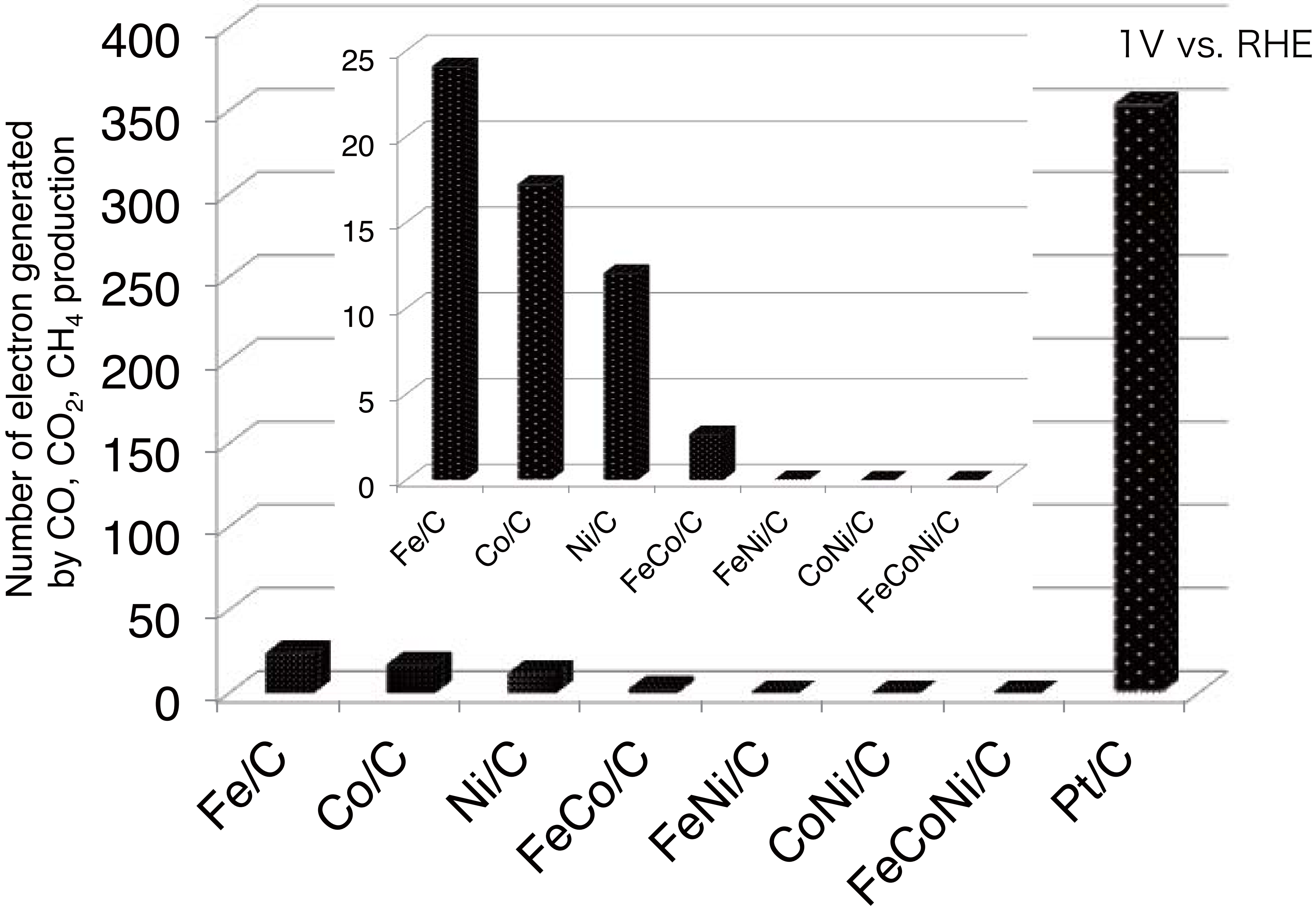
Completely-anaerobic electrochemical reactor



Time courses of CO_2 productions (gas phase)

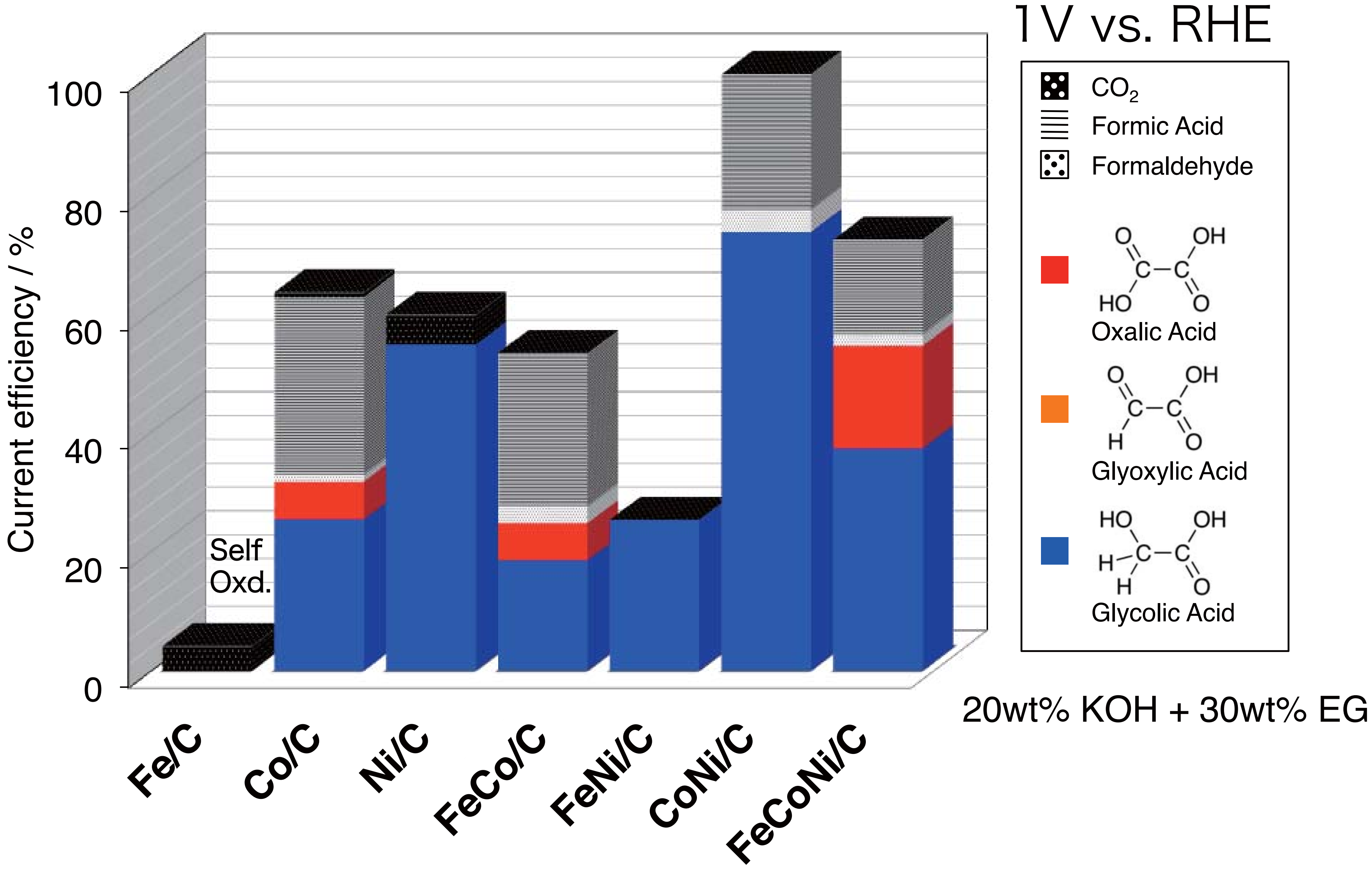


Time courses of CO_2 productions (total)



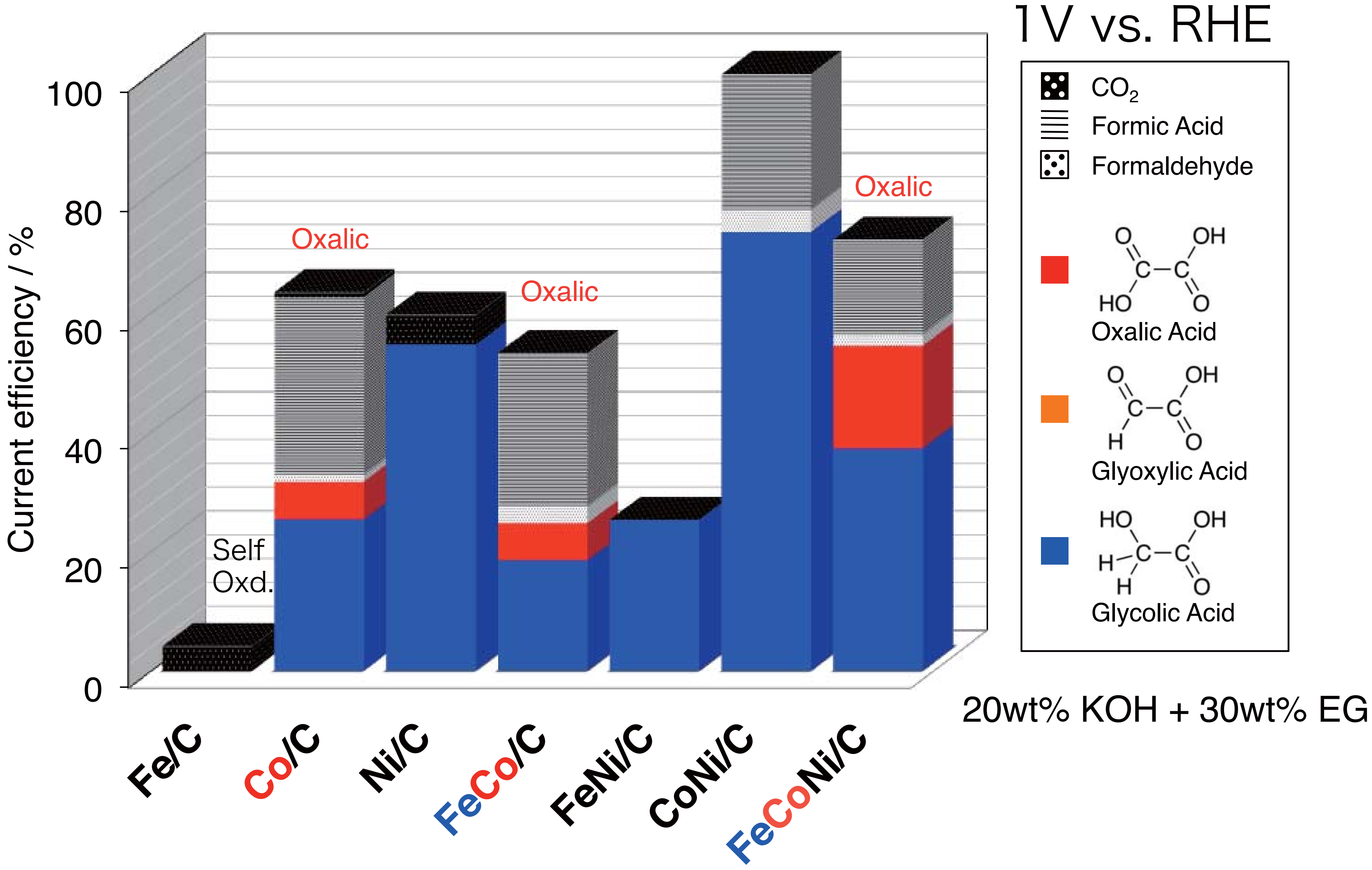
***Phys. Chem. Chem. Phys.*, 17, 11359 - 11366 (2015).**

Product distribution over Fe-group catalysts



Phys. Chem. Chem. Phys., 17, 11359 - 11366 (2015).

Product distribution over Fe-group catalysts



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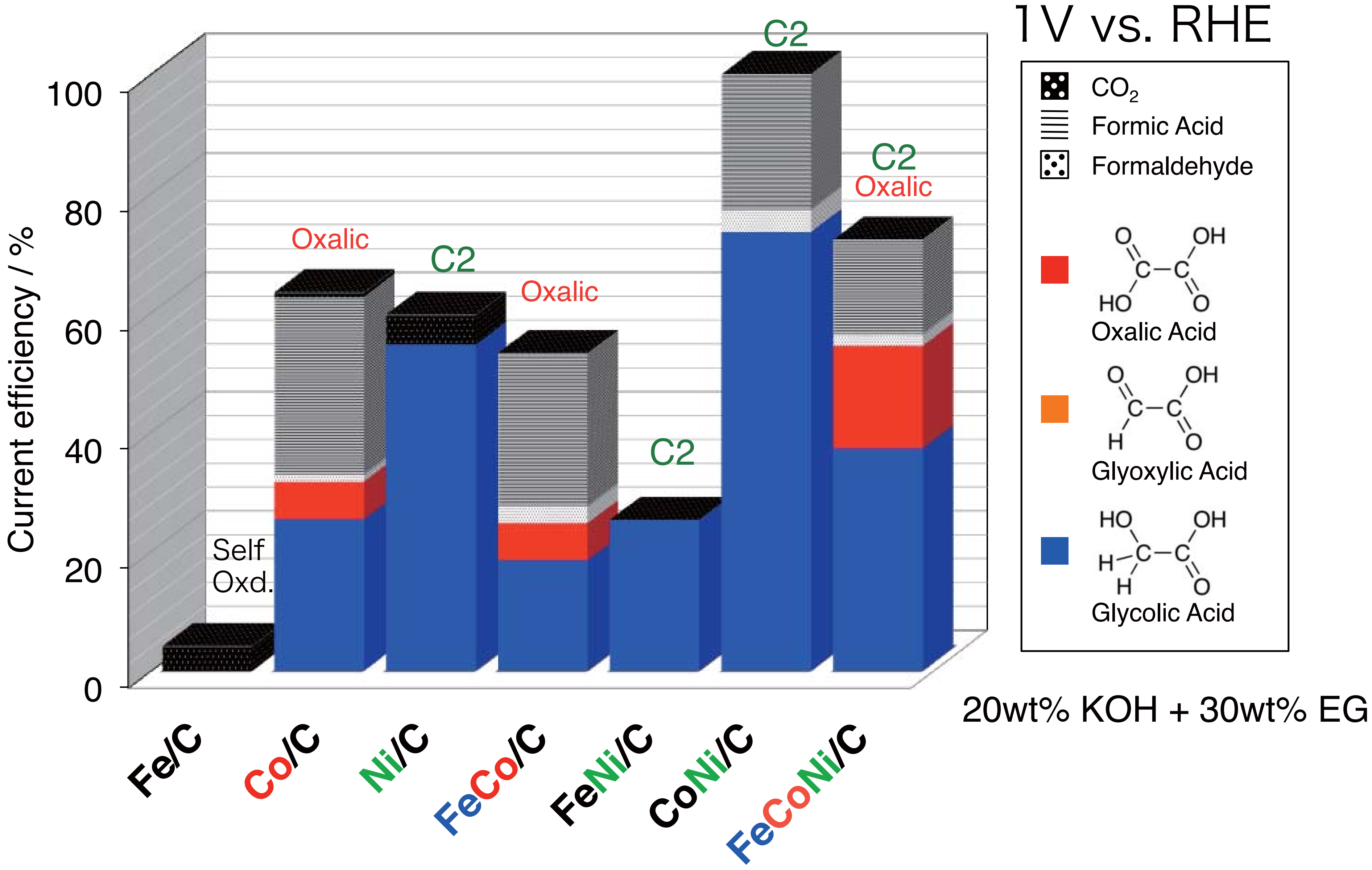

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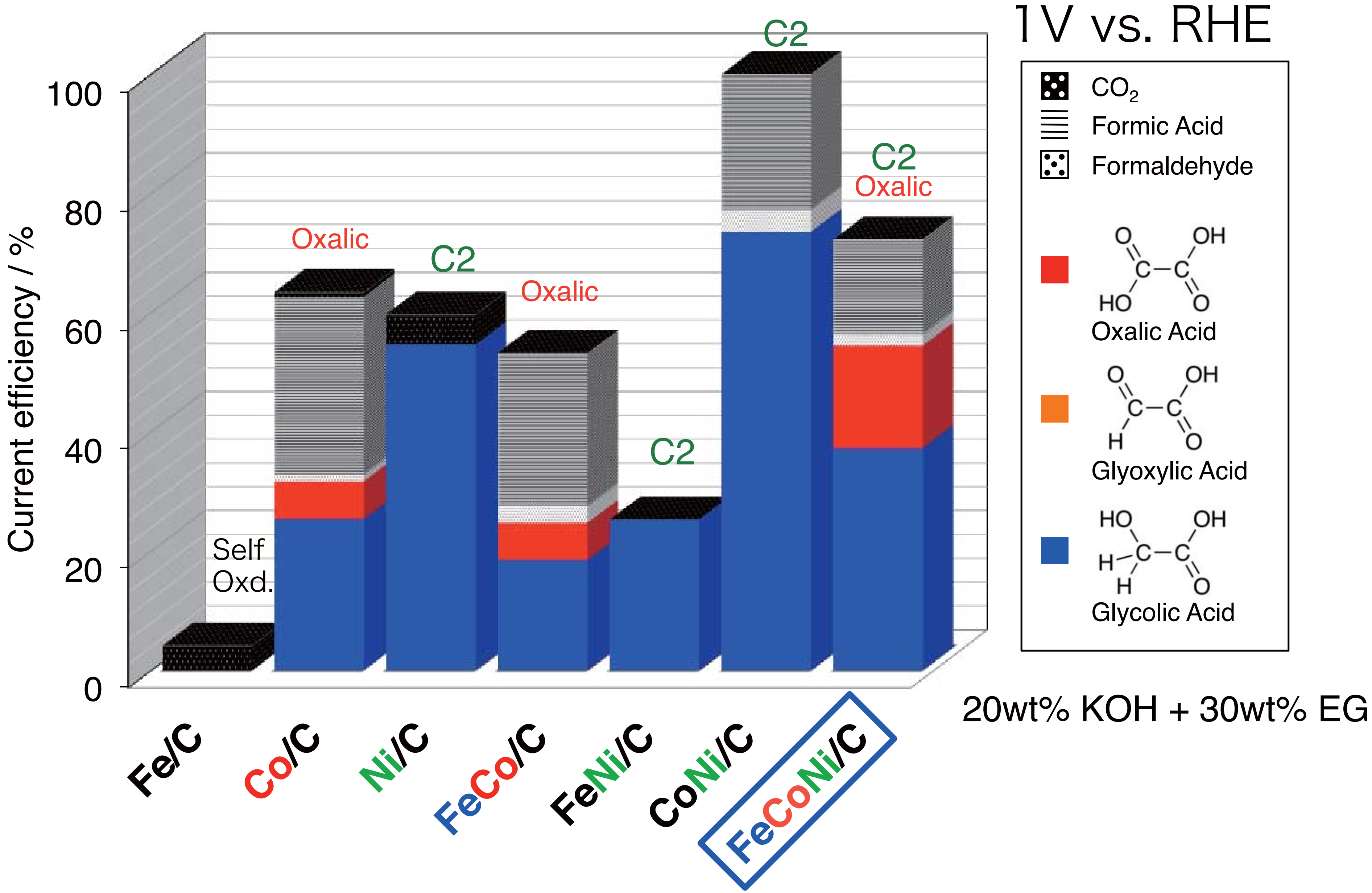
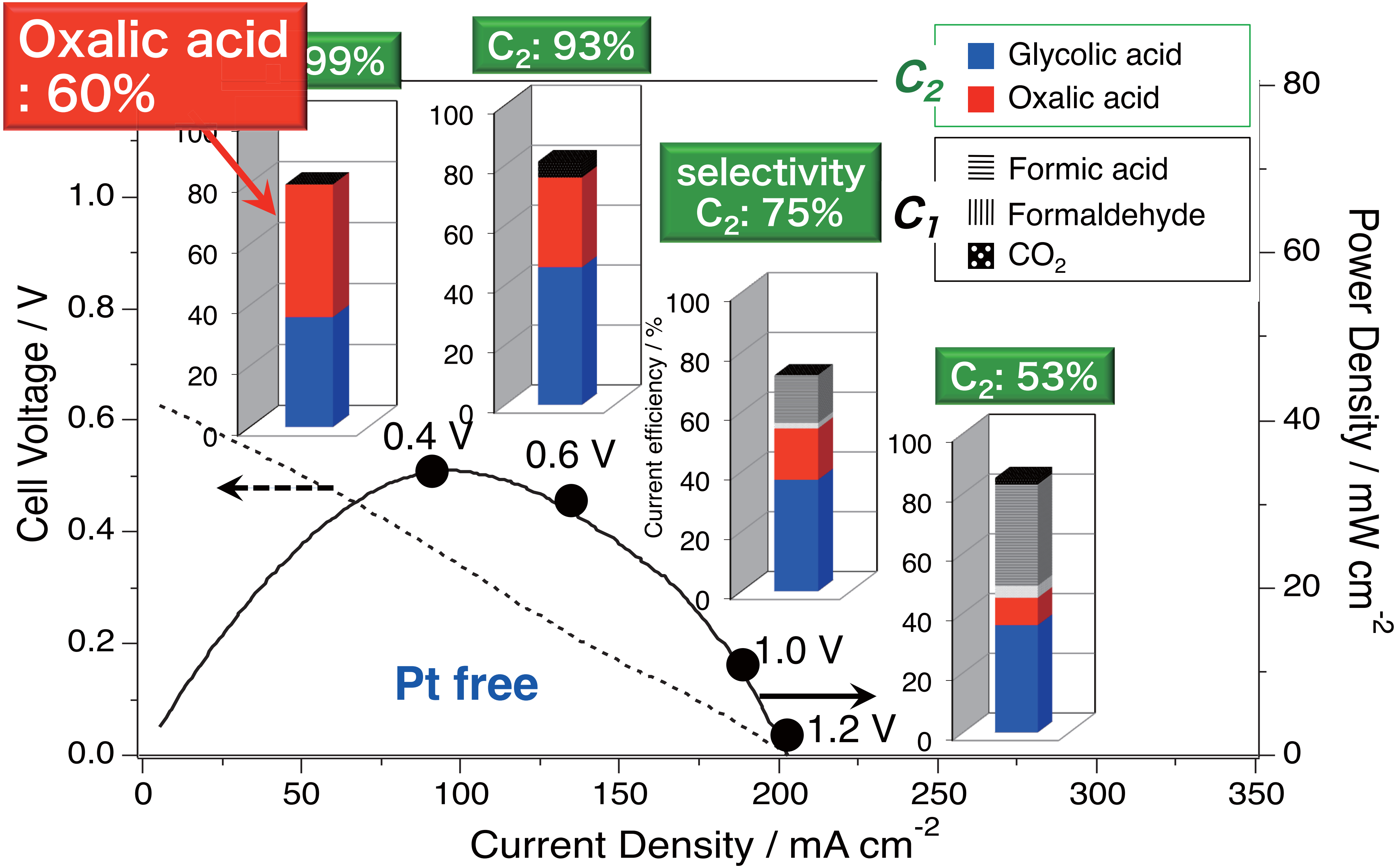


Sci. Rep., 4, 5620 (2014).

Power generation from EG on FeCoNi/C



Novelty and problem

1. Development of highly selective catalysts

・**Selective EG oxidation to oxalic acid**

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・**Solid alkaline fuel cells**
(**Solid hydroxide ionic conductor**, **mechanism**)

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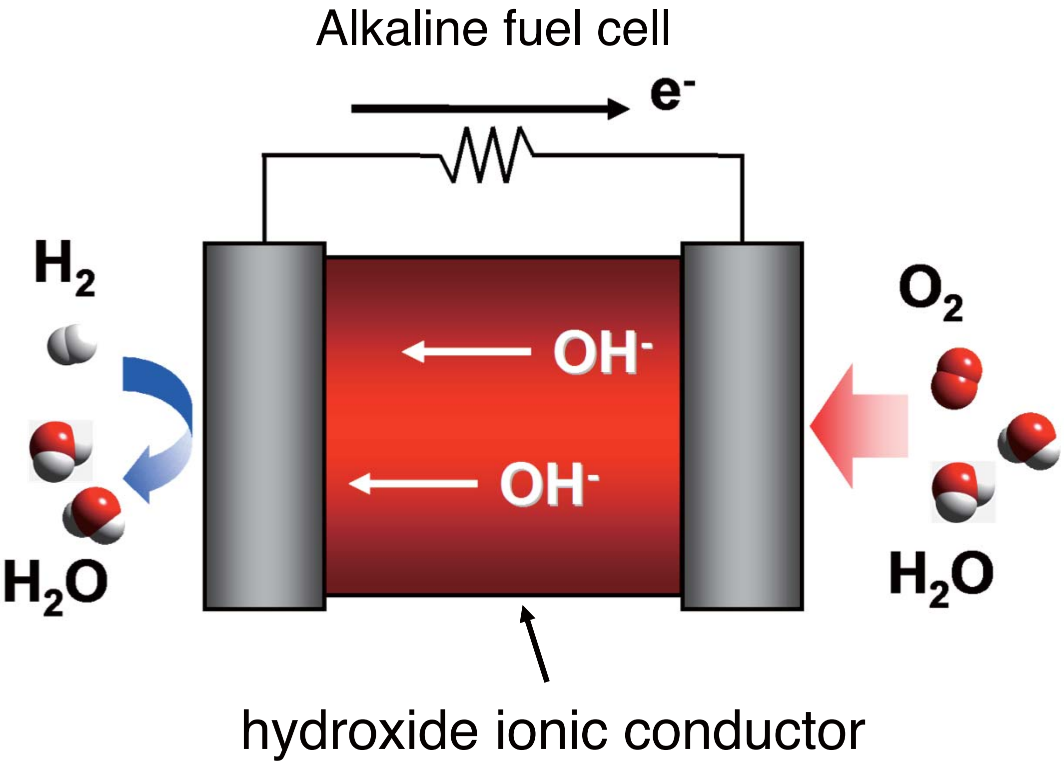
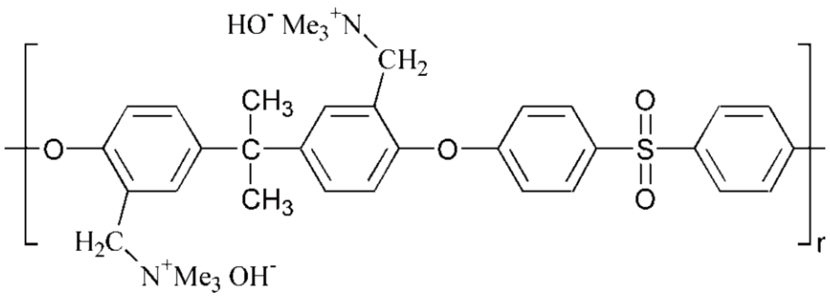
Hydroxide ionic conductor

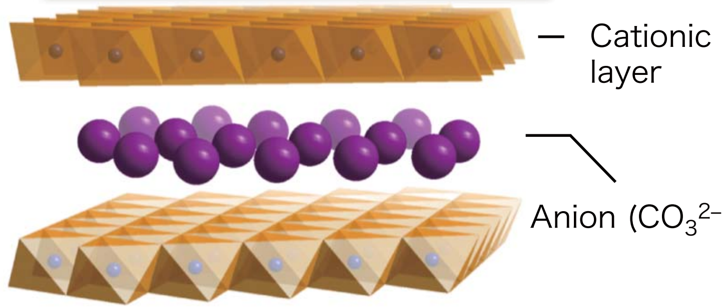


Development of novel hydroxide ionic conductor is indispensable for practical use of alkaline fuel cells.

Organic polymer[1]

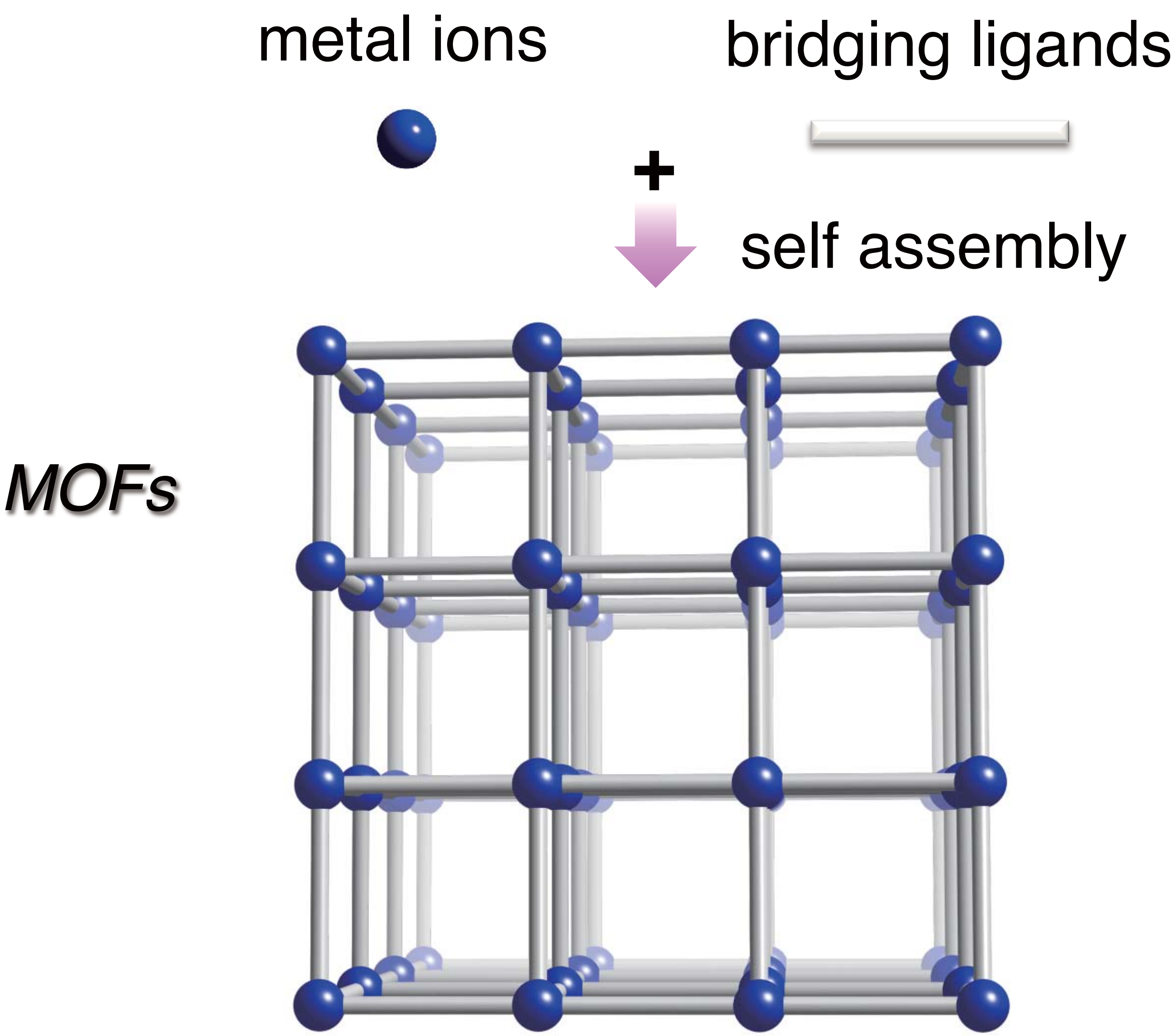


layered minerals[2]

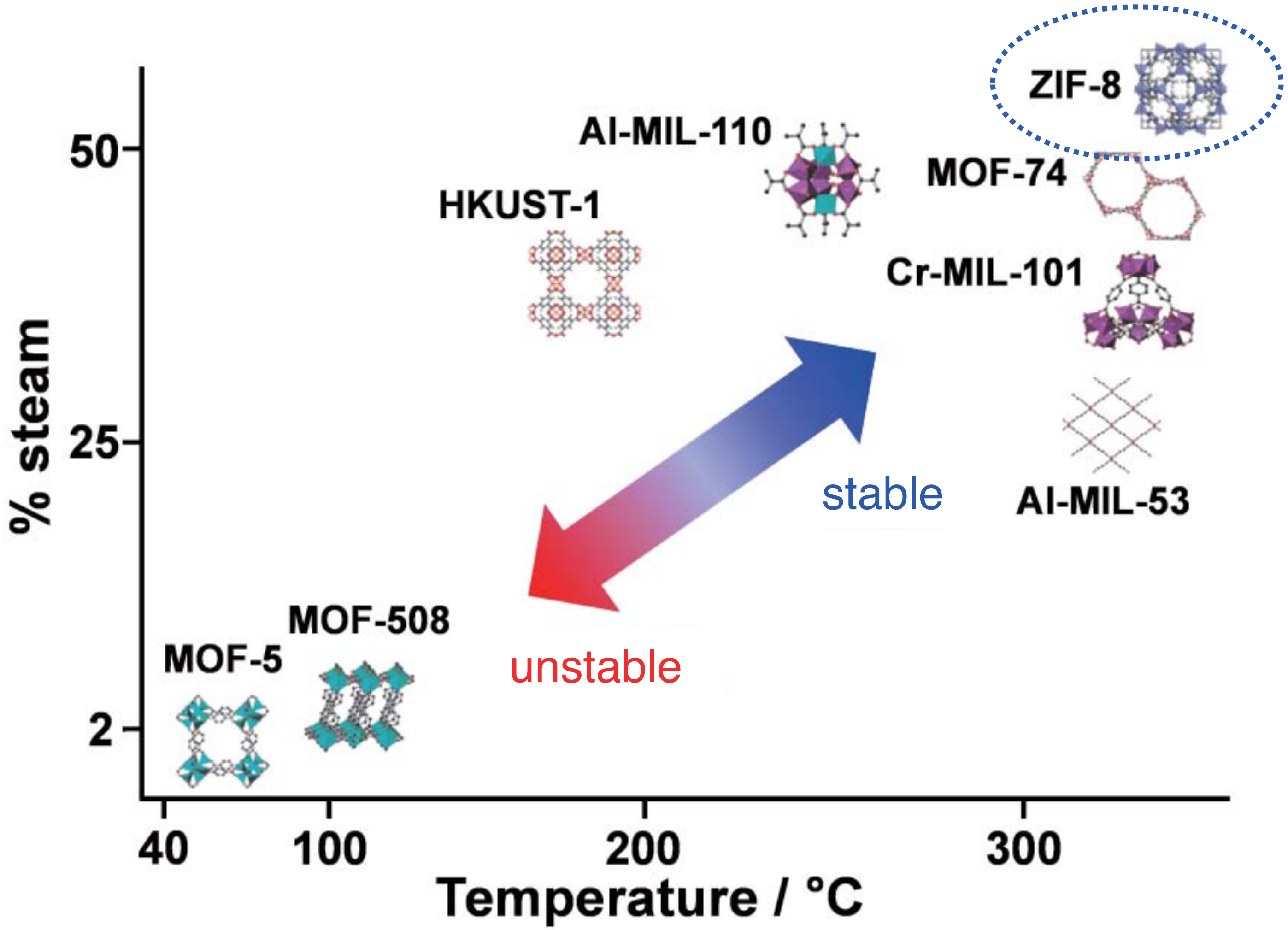


1) J. R. Varcoe, R. C. T. Slade, Fuel cells 2005, 5, 187. 2) K. Tadanaga et. al., Solid State Ionics 2011, 192, 185.

Highly designable frameworks: MOF (metal organic framework)



Heat & moisture resistance of MOF



Recently, heat & moisture tolerant MOFs have been synthesized.

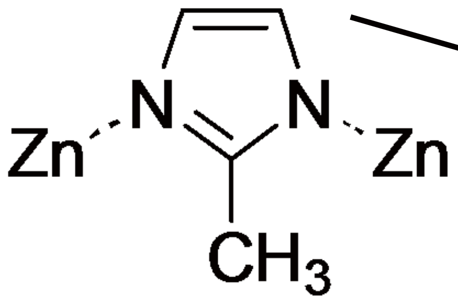
Design for hydroxide ion conducing MOF

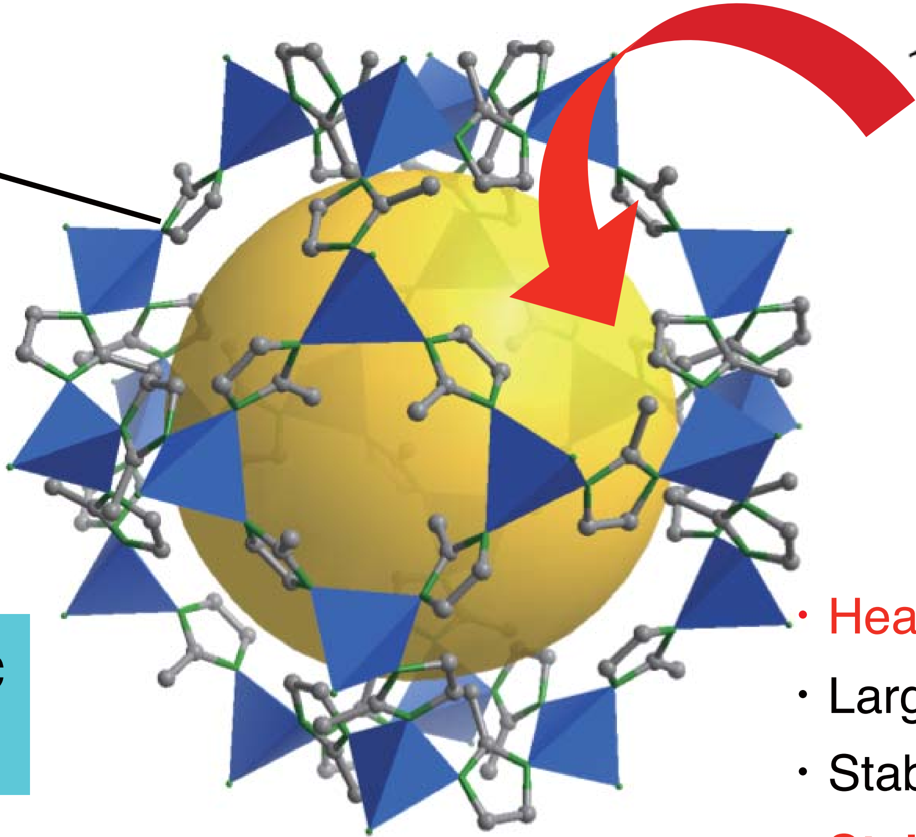
robustness＋designability

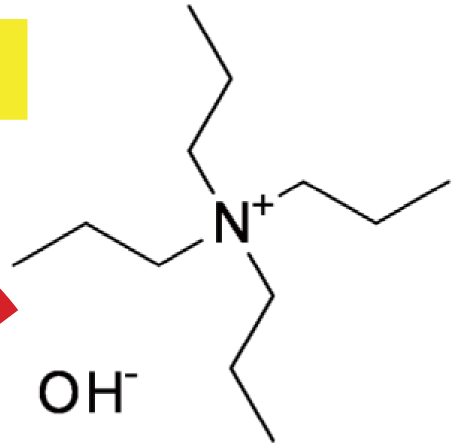
ZIF-8 [1]

ZIF: Zeolitic Imidazol Framework

(2-methyl imidazolate (mIM))







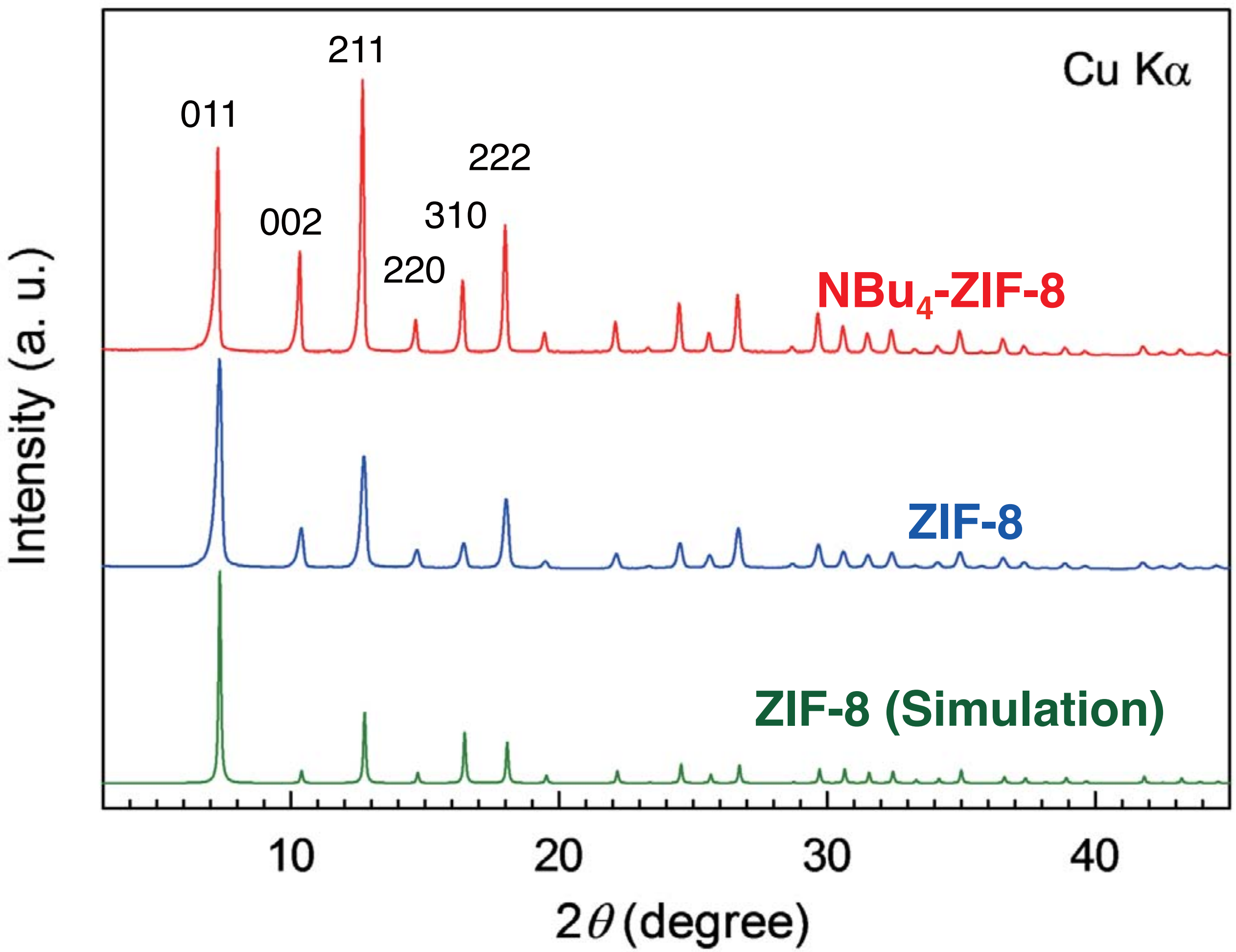
OH^- source

hydrophobic framework

- Heat tolerance （～500°C）
- Large pore（11 Å）
- Stability to air & water
- **Stability to base**
- Insoluble for solvent
- formability to film

1) O. M. Yaghi et al., *PNAS* **2006**, *103*, 10186.

XRD pattern of NBu_4-ZIF-8

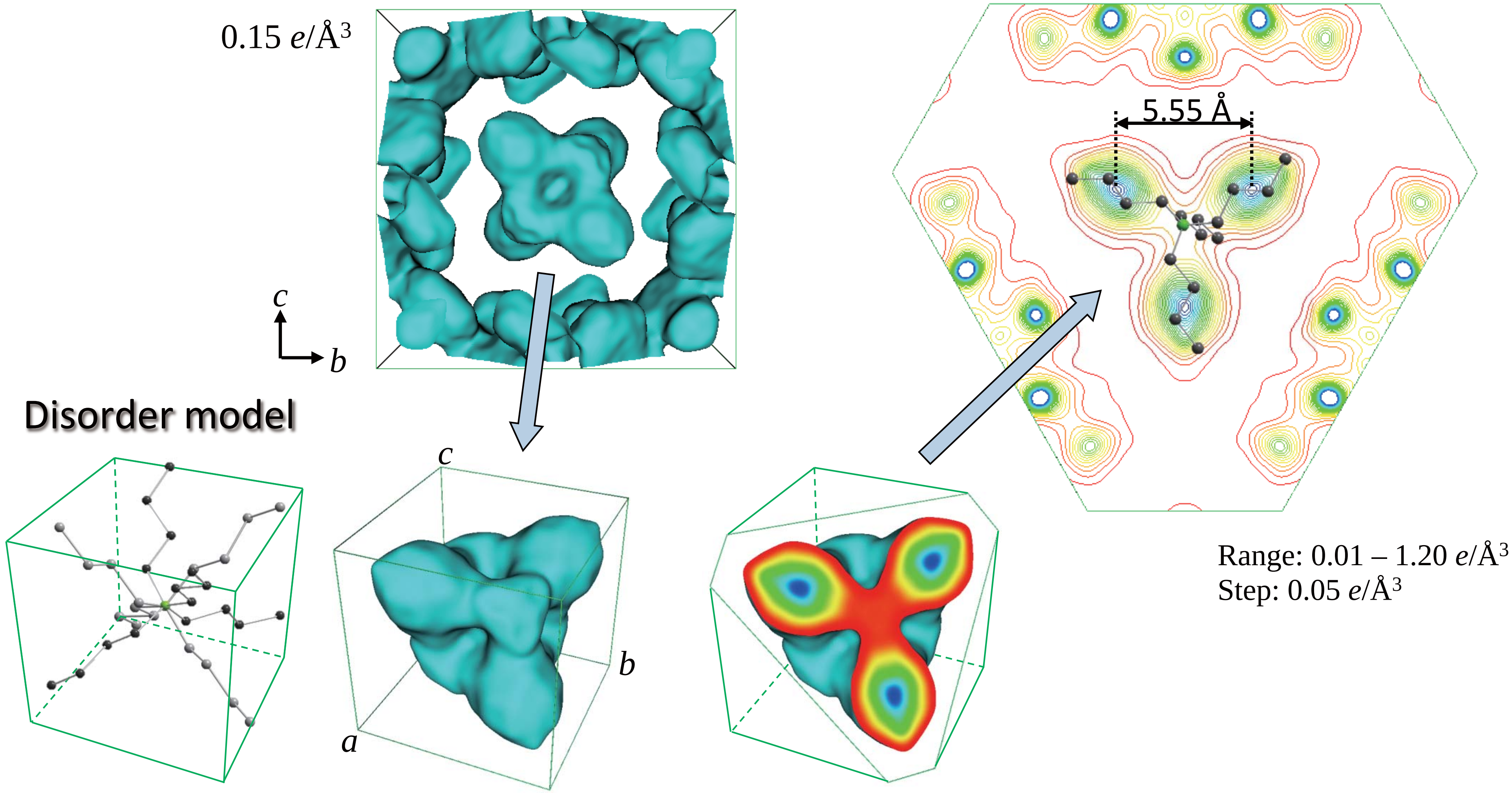


- NBu_4-ZIF-8 shows almost identical XRD pattern of ZIF-8.
- Difference in relative intensity between NBu_4-ZIF-8 & ZIF-8 suggests inclusion of NBu_4 without changing crystalline symmetry of ZIF-8 frameworks.

J. Am. Chem. Soc., 136(5), 1702-1705 (2014).

Visualization of electron density of NBu_4-ZIF-8 by maximum entropy method

BL44B2@SPring-8

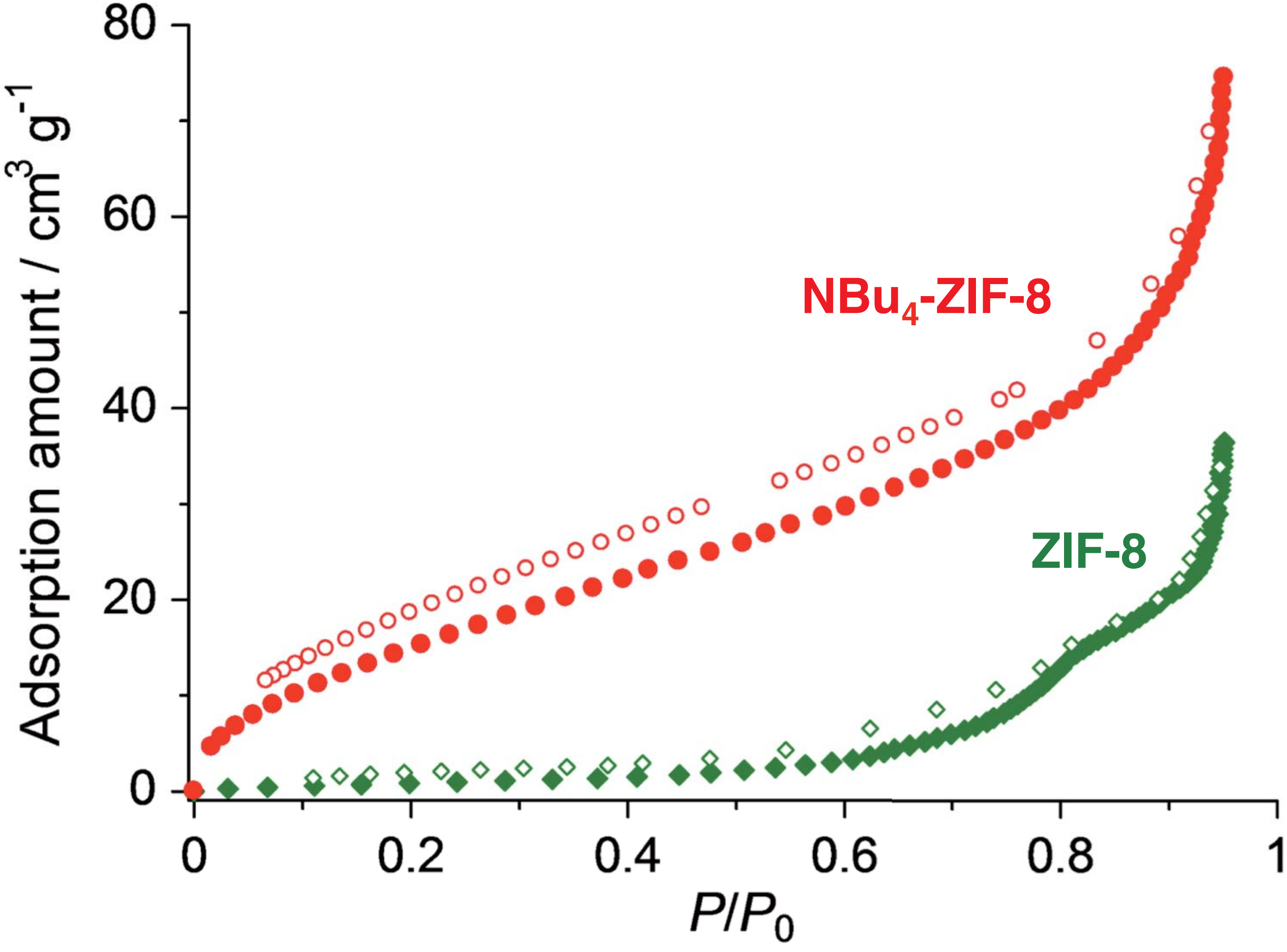


Inclusion of NBu_4^+ molecules are strongly suggested.

→ The first example of ionic molecule including ZIF

J. Am. Chem. Soc., 136(5), 1702-1705 (2014).

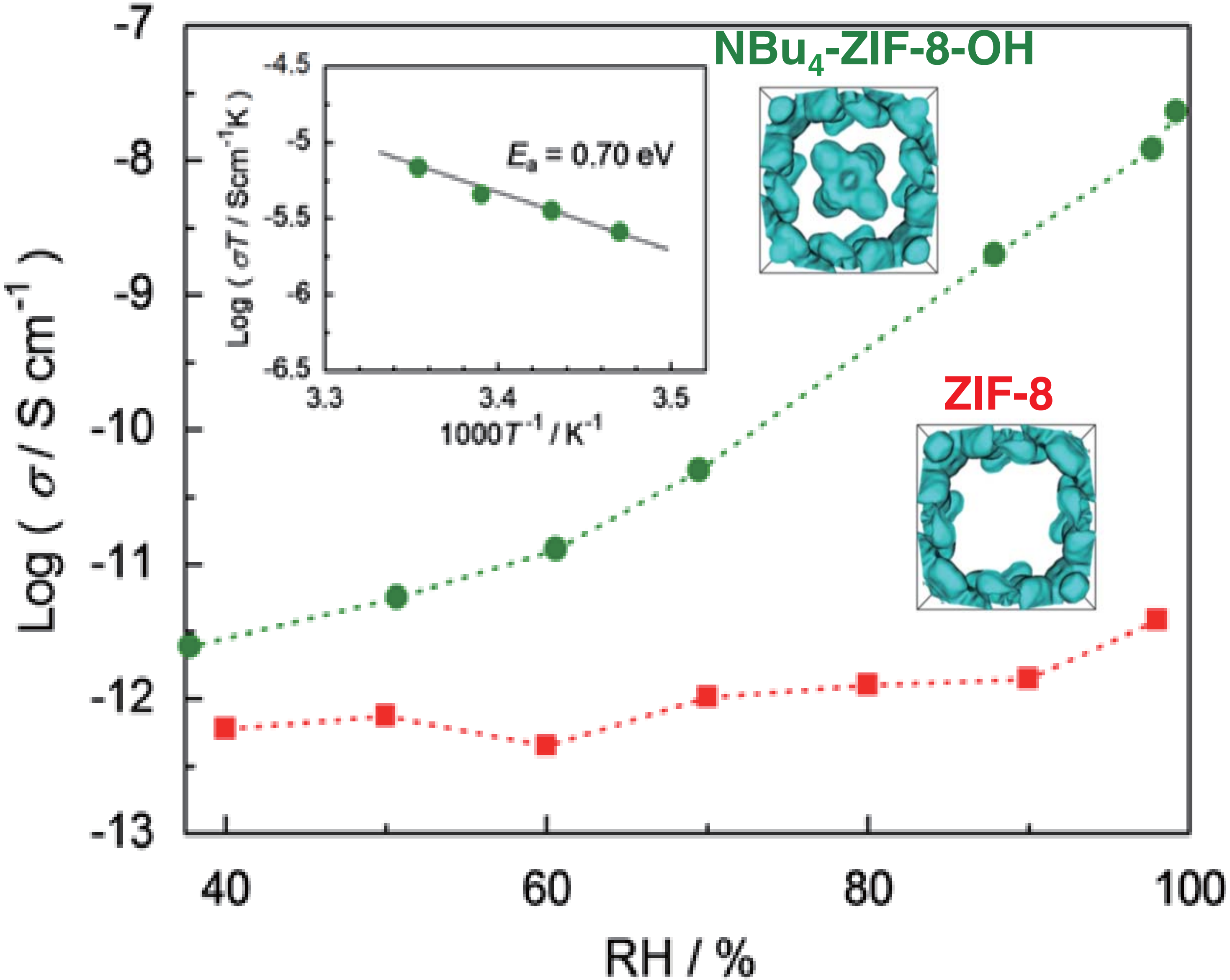
Water vapor absorption isotherm of ZIF-8 & NBu_4-ZIF-8



Ammonia inclusion changes water affinity of ZIF-8.

J. Am. Chem. Soc., 136(5), 1702-1705 (2014).

Humidity dependence of ionic conductivity



Ionic conductivity of NBu_4-ZIF-8 exhibits 4 orders of magnitude higher ionic conductivity than that of the blank ZIF-8 inclusion.

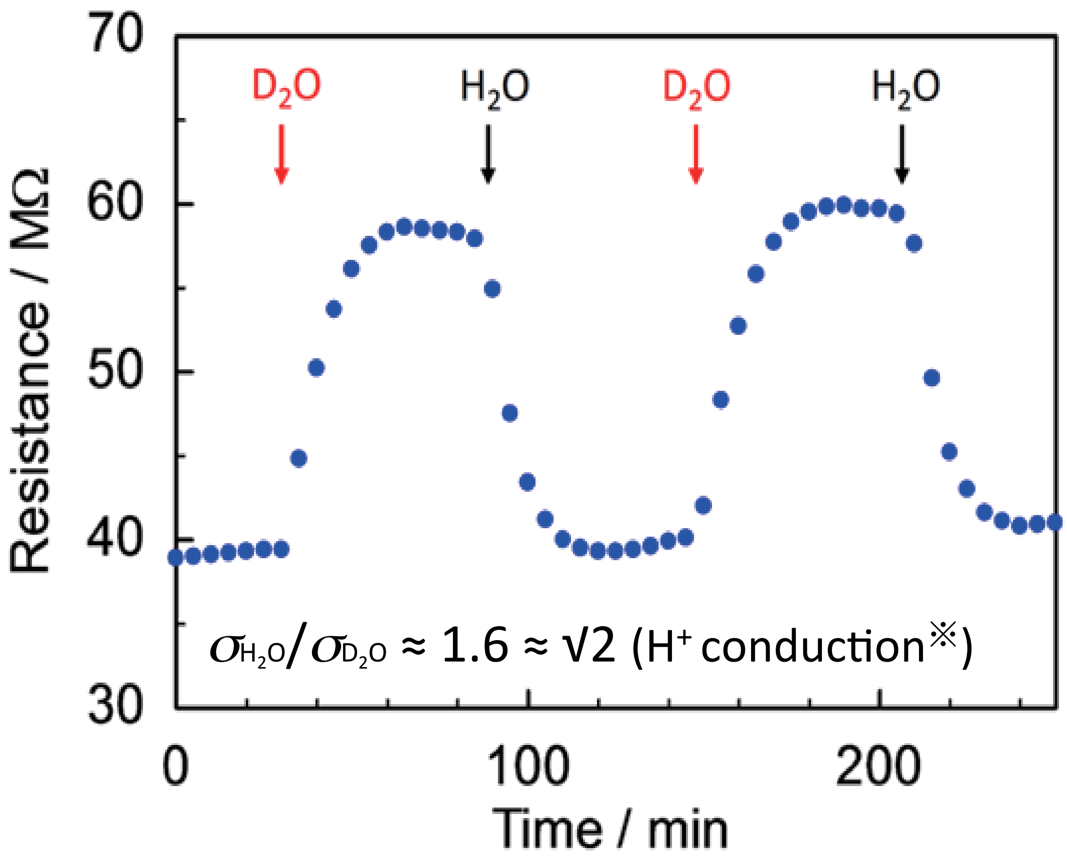
M. Sadakiyo, J. Am. Chem. Soc., 136(5), 1702-1705 (2014).

Conduction mechanism

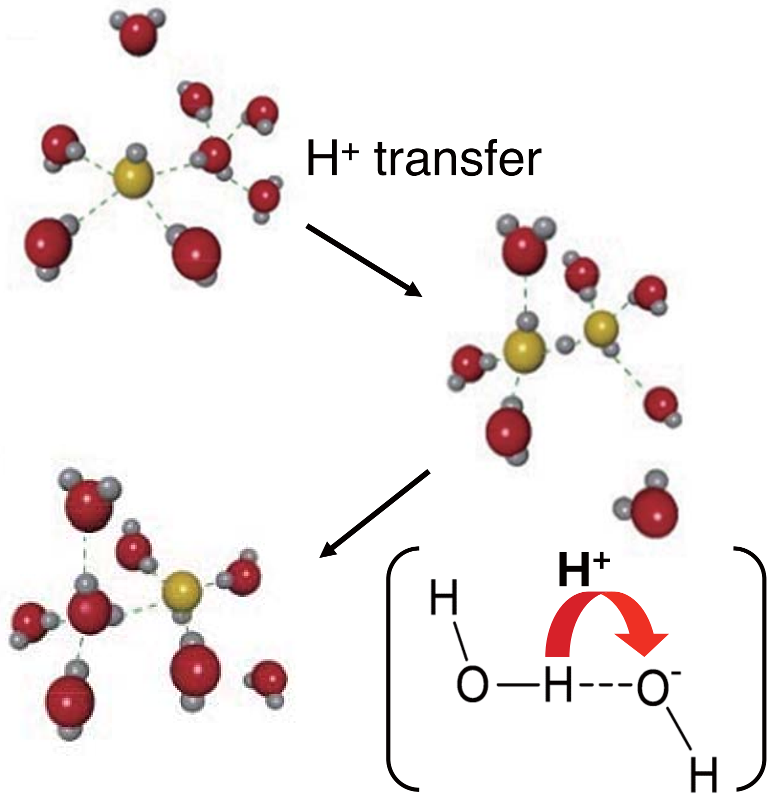
Chemical fomula of NBu_4-ZIF-8-OH

$[Zn(mim)_2]_6(NBu_4(OH)_{0.47}(CO_3)_{0.26})_{0.68}(H_2O)_n$

Ionic conductivity under H_2O or D_2O vapors （25 ˚C）



OH^- conduction model in solution※



H^+ conduction contributes to OH^- conduction → exclusion of NBu_4^+ or CO_3^{2-}conduction

Norby, T.; Friesel, M.; Mellander, B. E. *Solid State Ionics* **1995**, *77*, 105.

M. E. Tuckerman, *Nature* **2002**, *417*, 925.

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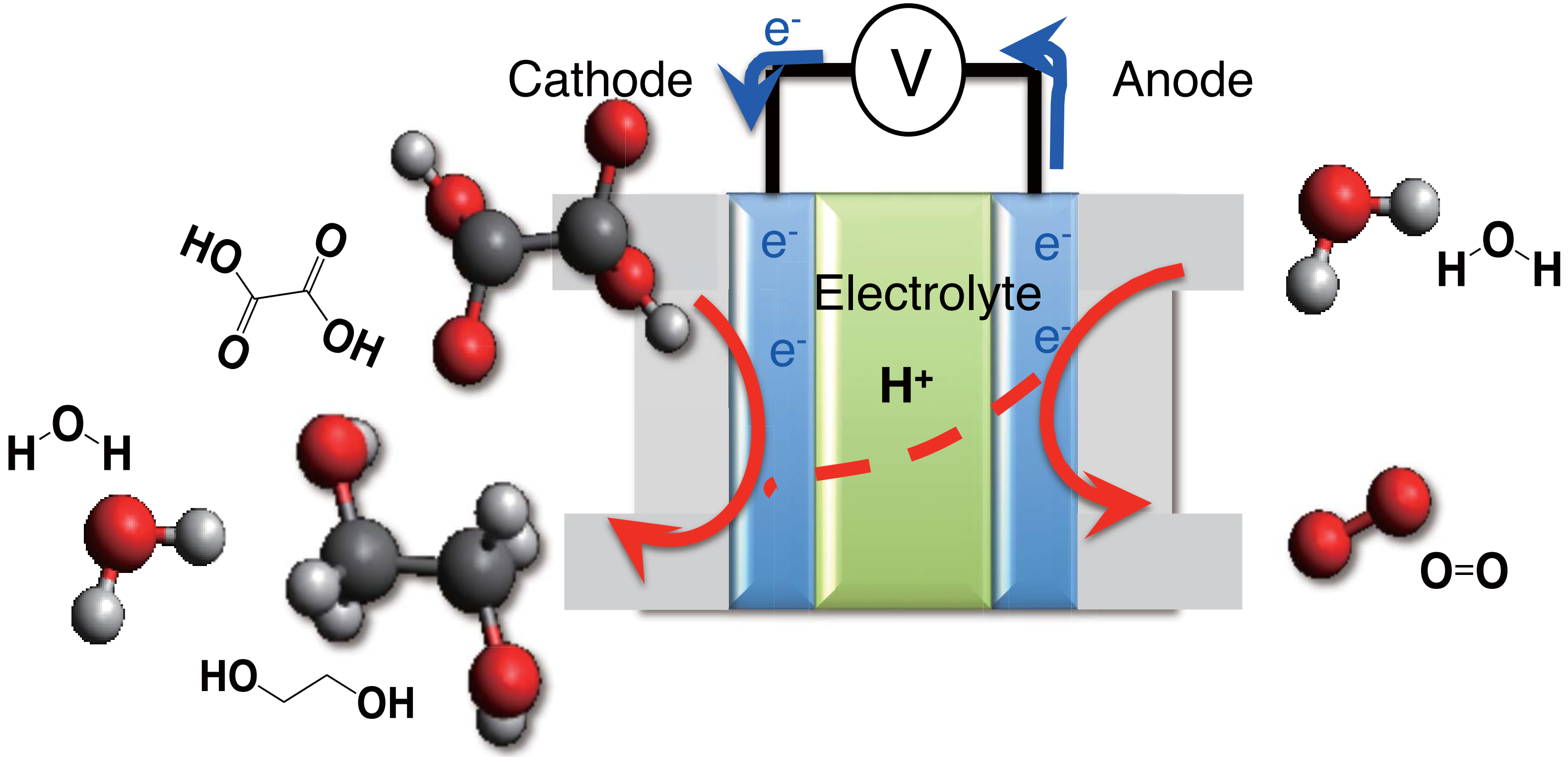
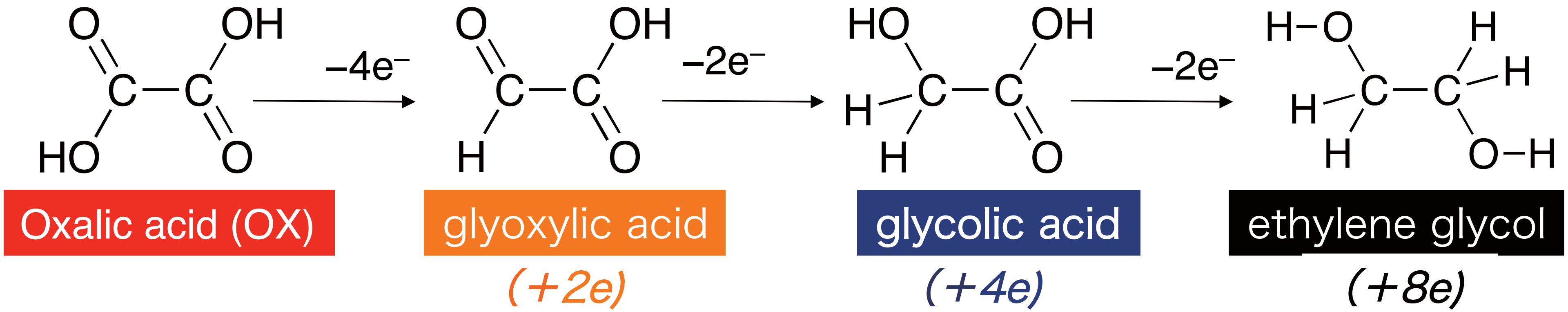
Electrosynthesis of ethylene glycol from oxalic acid



Anode : $4\ H_2O \rightarrow 2\ O_2 + 8\ H^+ + 8\ e^-$

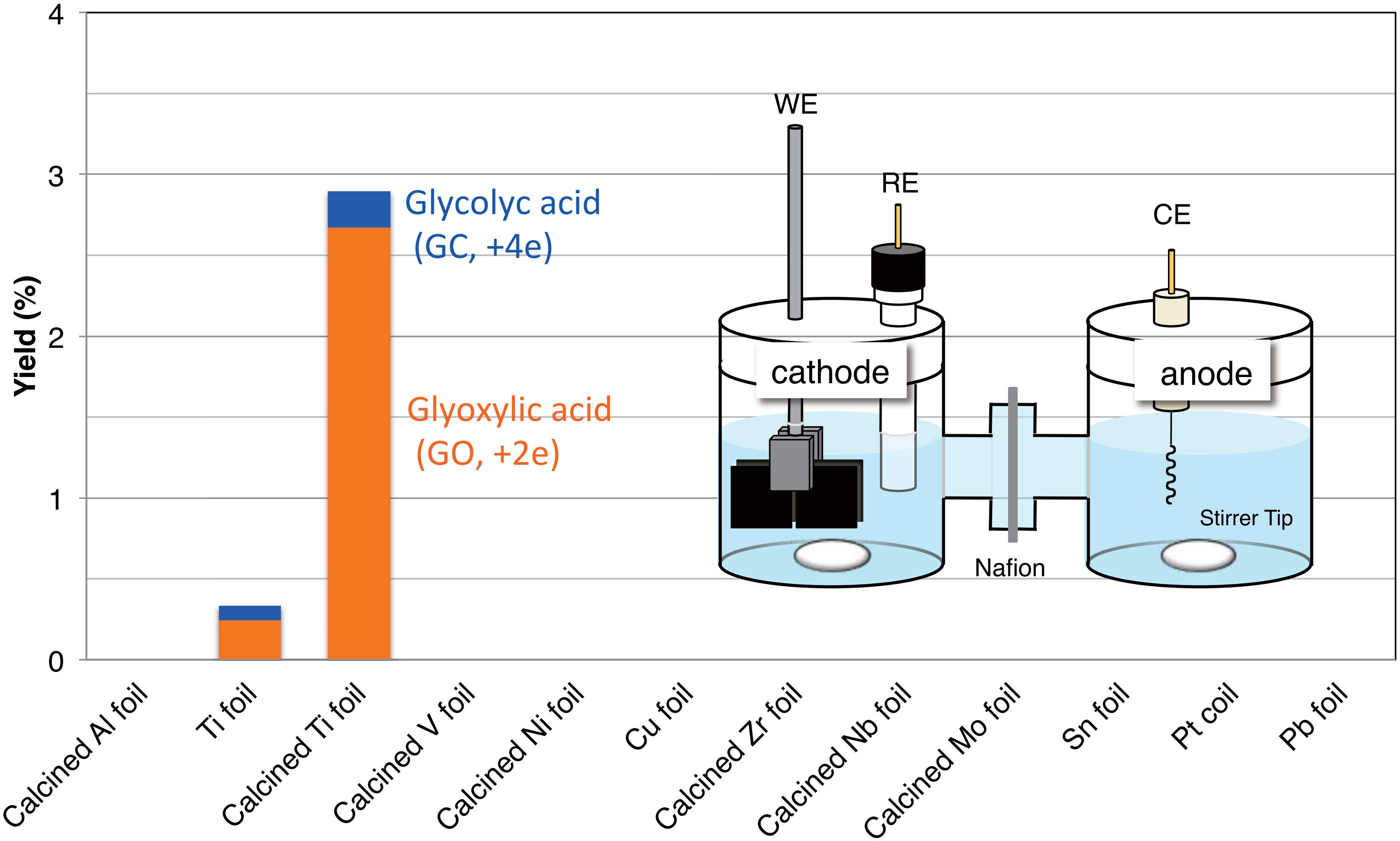
Cathode : $(COOH)_2 + 8\ H^+ + 8\ e- \rightarrow HOCH_2CH_2OH + 2\ H_2O$

Overall : $(COOH)_2 + 2\ H_2O \rightarrow HOCH_2CH_2OH + 2\ O_2$



There are no reports regarding electroreduction of carboxylic acid to alcoholic compounds.

Electroreduction of OX on metal or metal oxide plate



✔Only Ti and TiO_2 plate showed catalytic activities for OX reduction.

✔Reactivities (yields) were quite low.

Preparation of TiO_2 having a high-specific surface area : Porous TiO_2 spheres (PTSs)

H. B. Wu, X. W. Lou, H. H. Hng, *Chem. Eur. J.*, **18**, 2094-2099 (2012).

Tetrabutoxy titane (1 mL)
N,N-dimethyl formamide (10 mL)
isopropyl alcohol (30 mL)

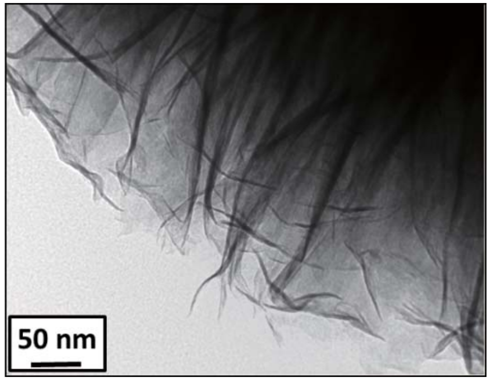
↓ **stirring for 5 min**

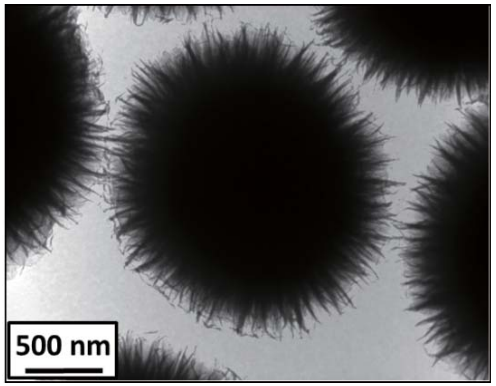
↓ **200 ℃, 20 h in autoclave**

$H_2Ti_2O_5 \cdot H_2O$

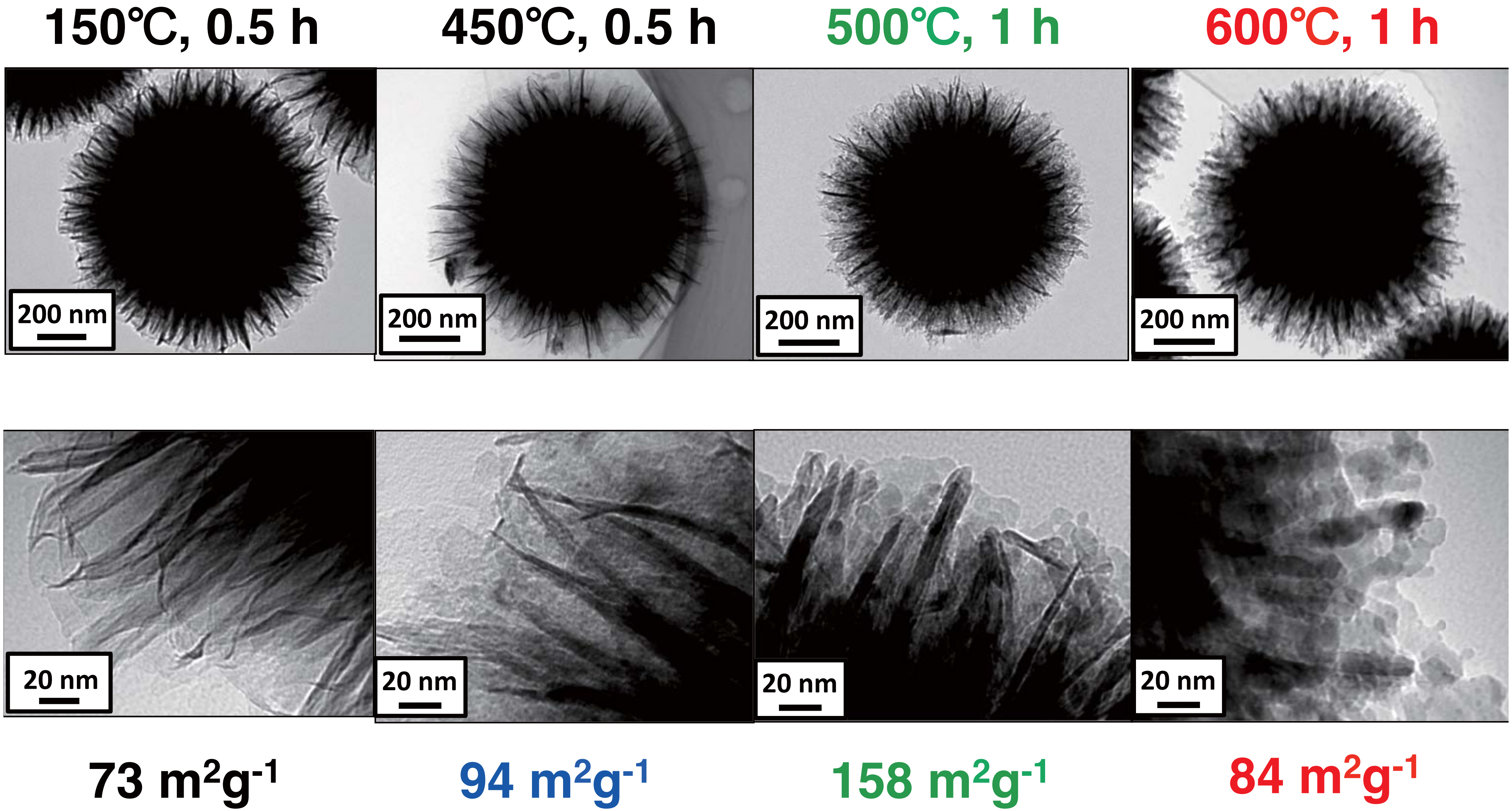
↓ **Calcination under air**

TiO_2

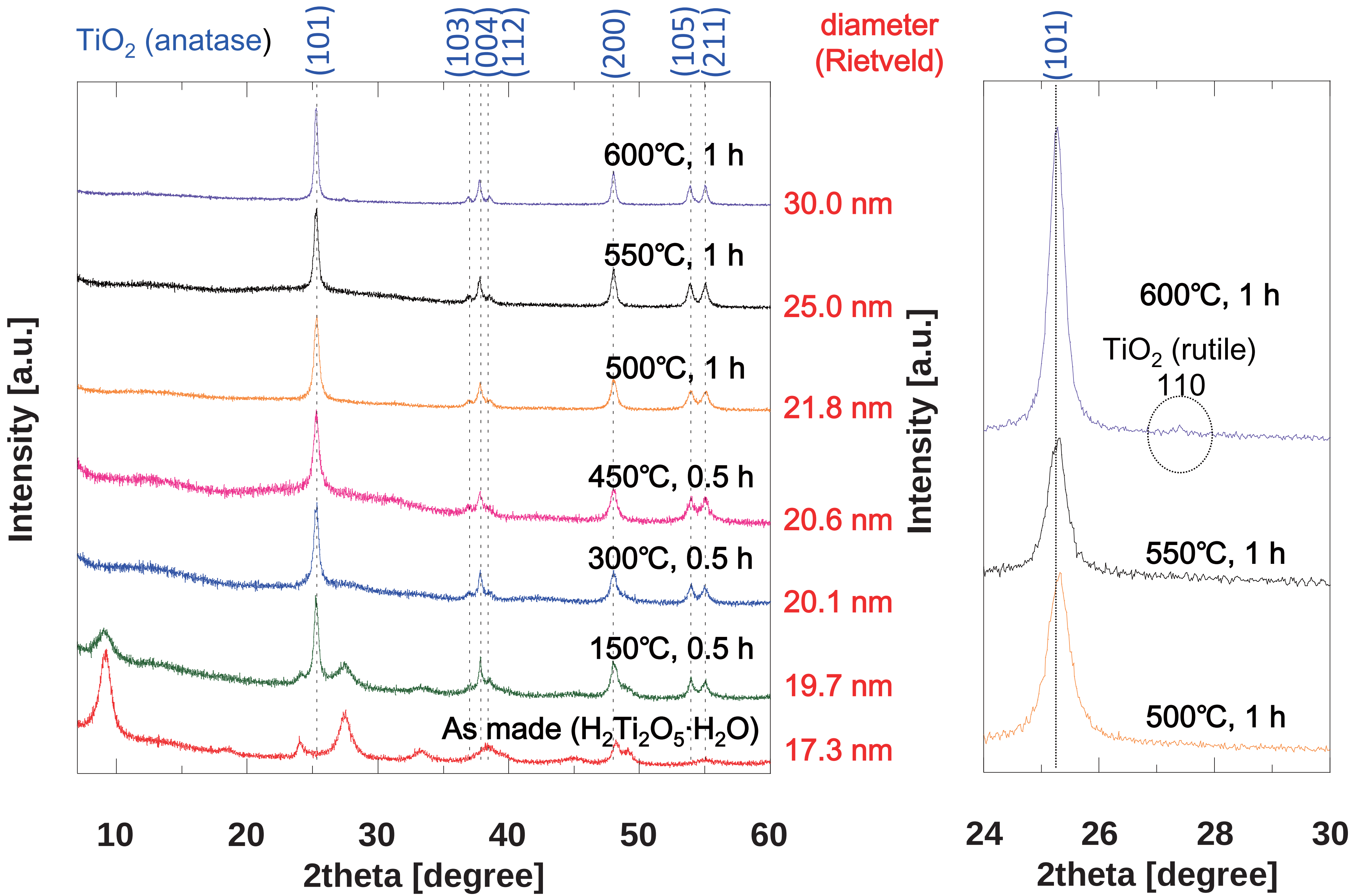




TEM images of prepared porous TiO_2 spheres (PTSs)



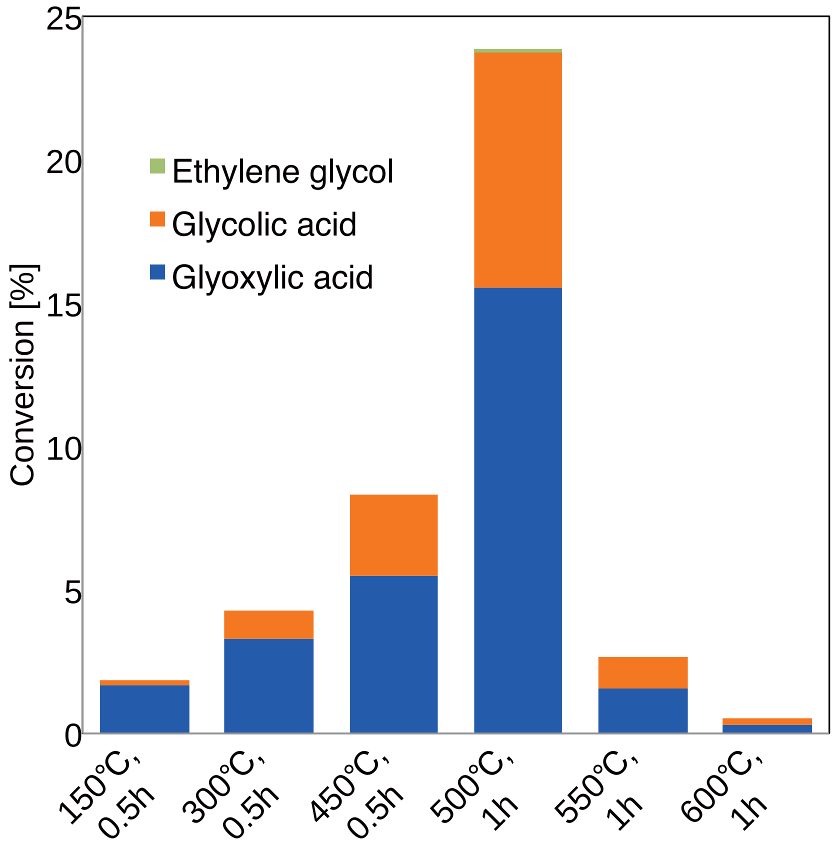
XRD patterns of prepared sample calcined at various temperatures



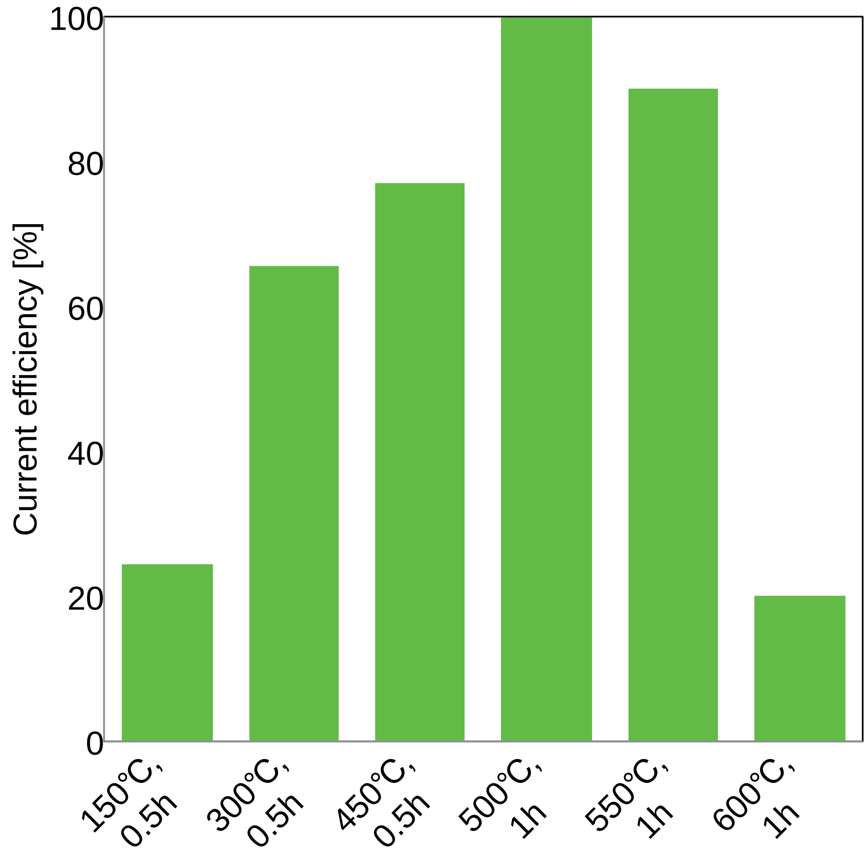
Calcination condition dependence on OX reduction efficiency

(-0.7 V vs. RHE, pH=2.1)

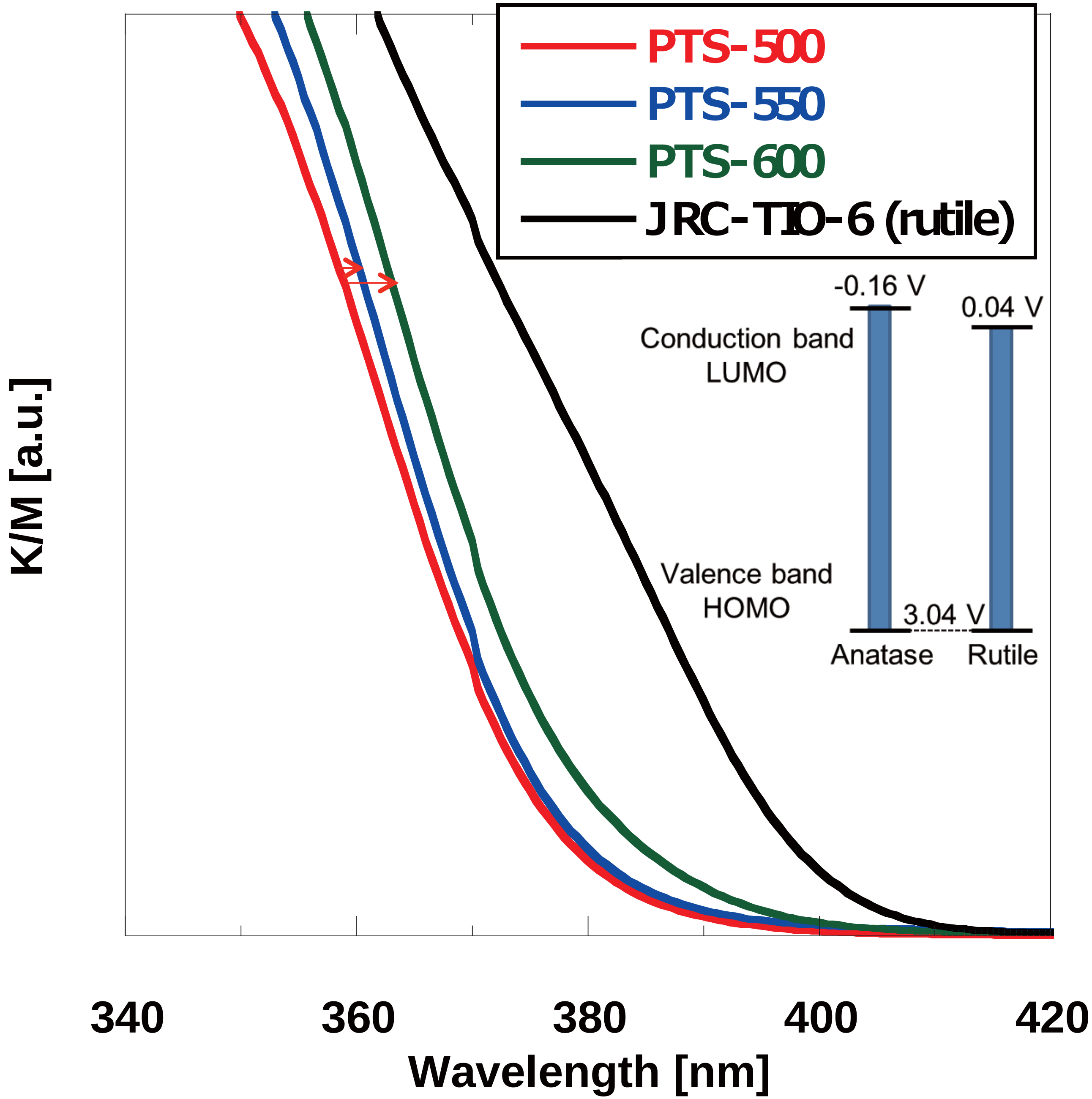
Oxalic acid conversion



Faraday efficiency

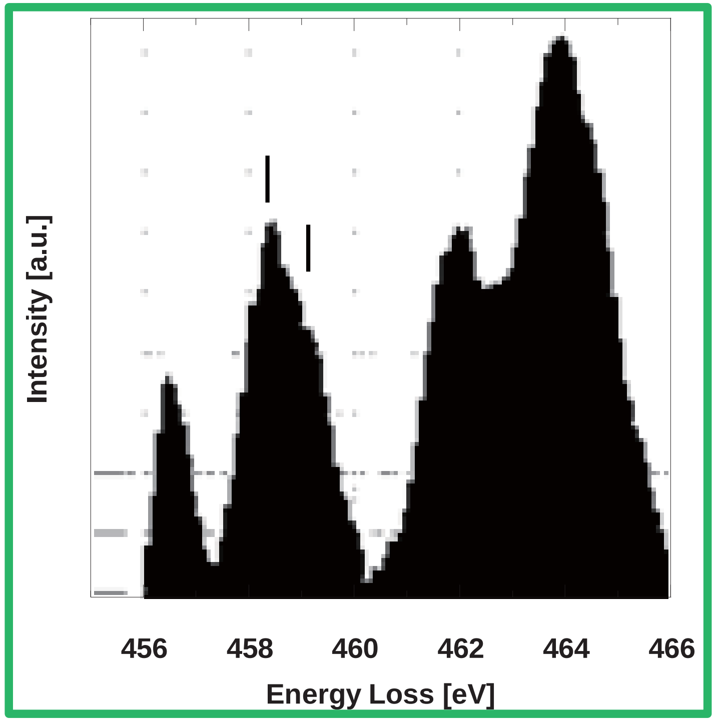


UV-vis spectra of PTSs

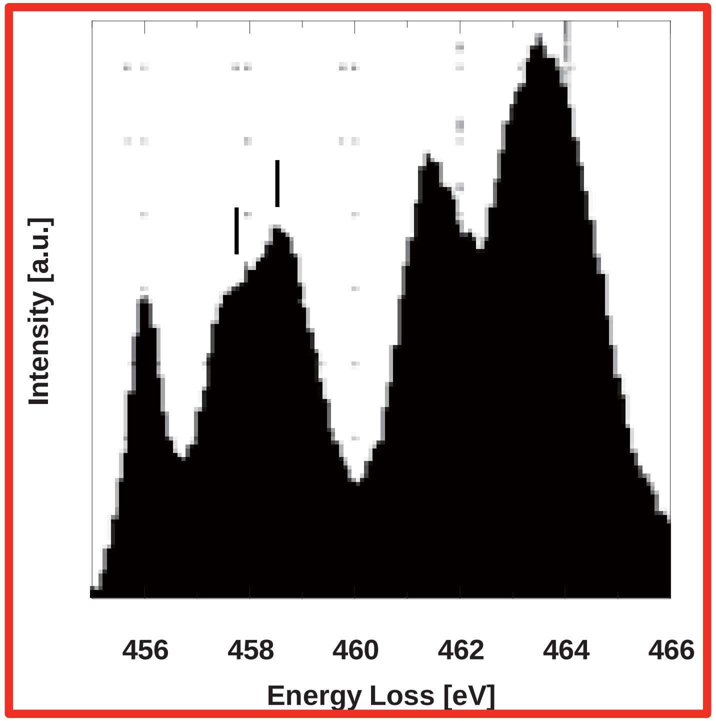


Electron energy-loss spectroscopy (EELS) of TiO_2 (anatase and rutile)

Anatase



Rutile



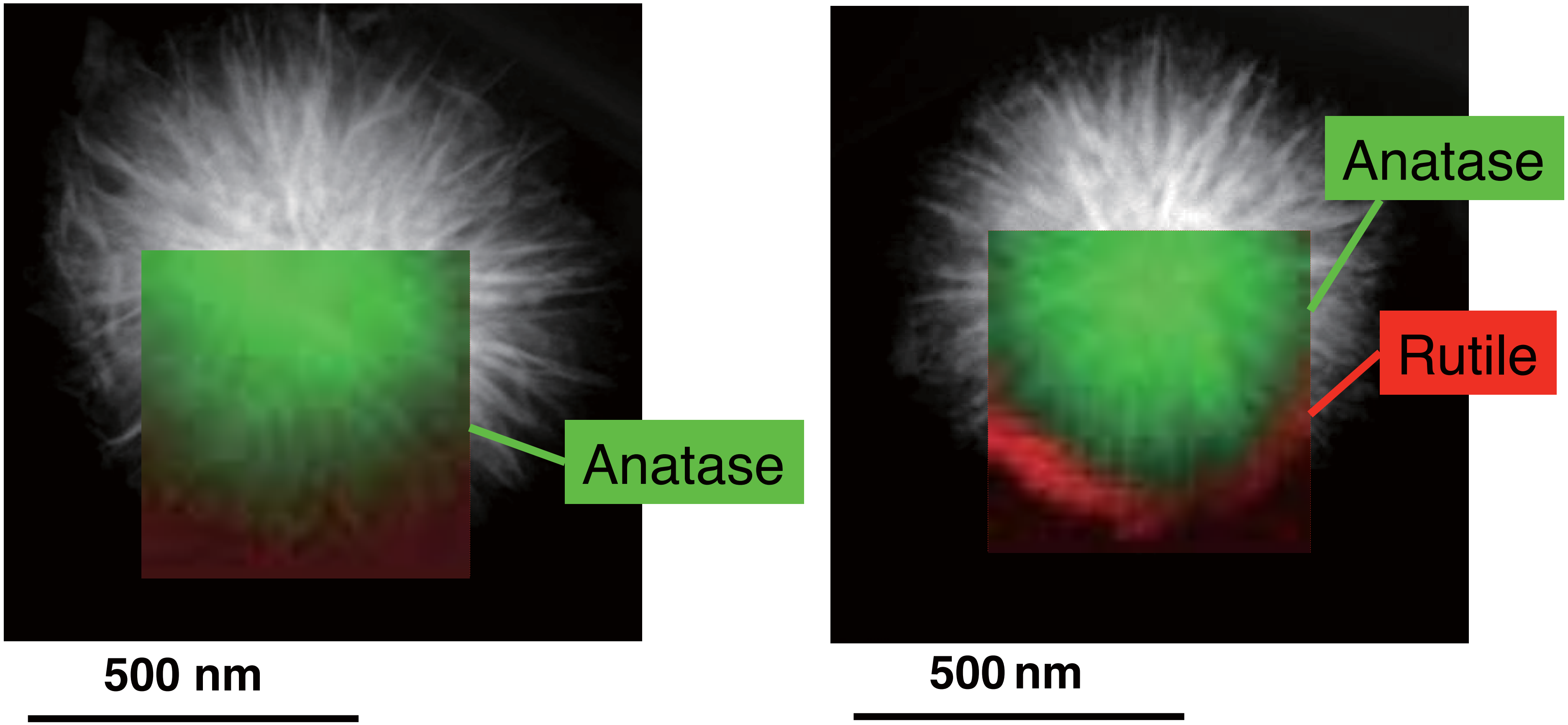
*measured using JSM-ARM200F installed in Next-Generation Fuel Cell Research Center (NEXT-FC), Kyushu University

Energy Environ. Sci., 8, 1456 (2015).

STEM images and EELS maps of PTSs

Calcined at 500 °C

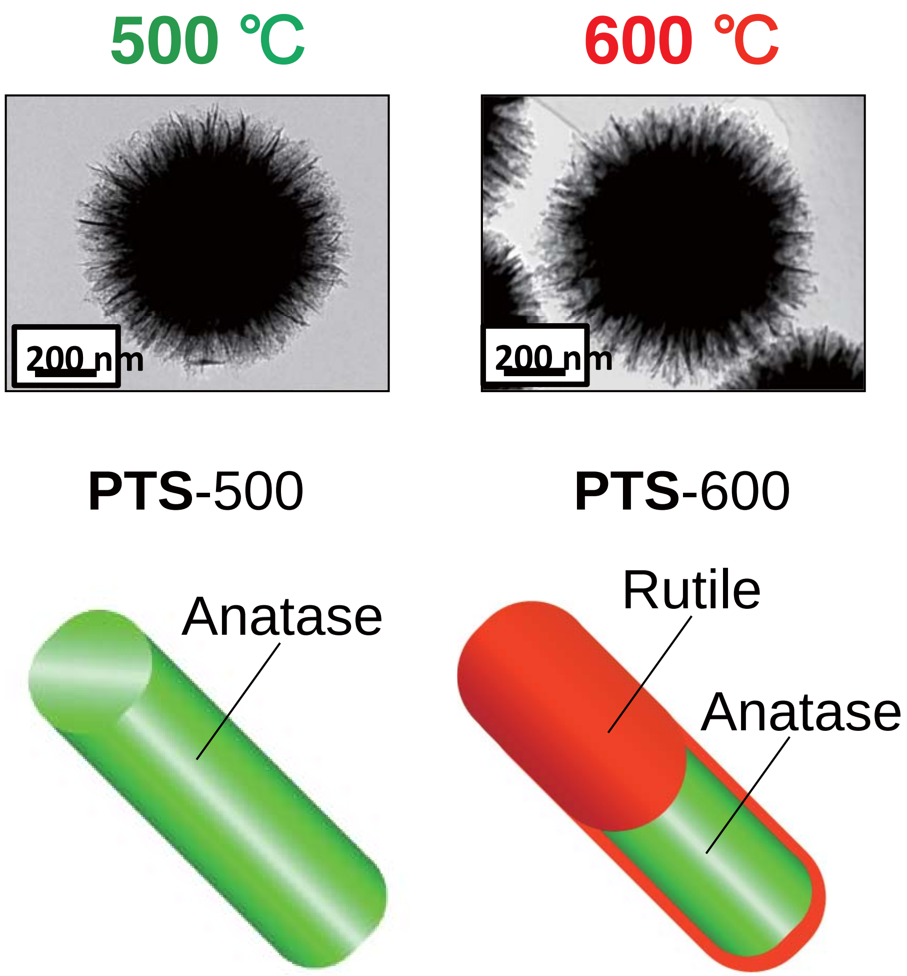
Calcined at 600 °C

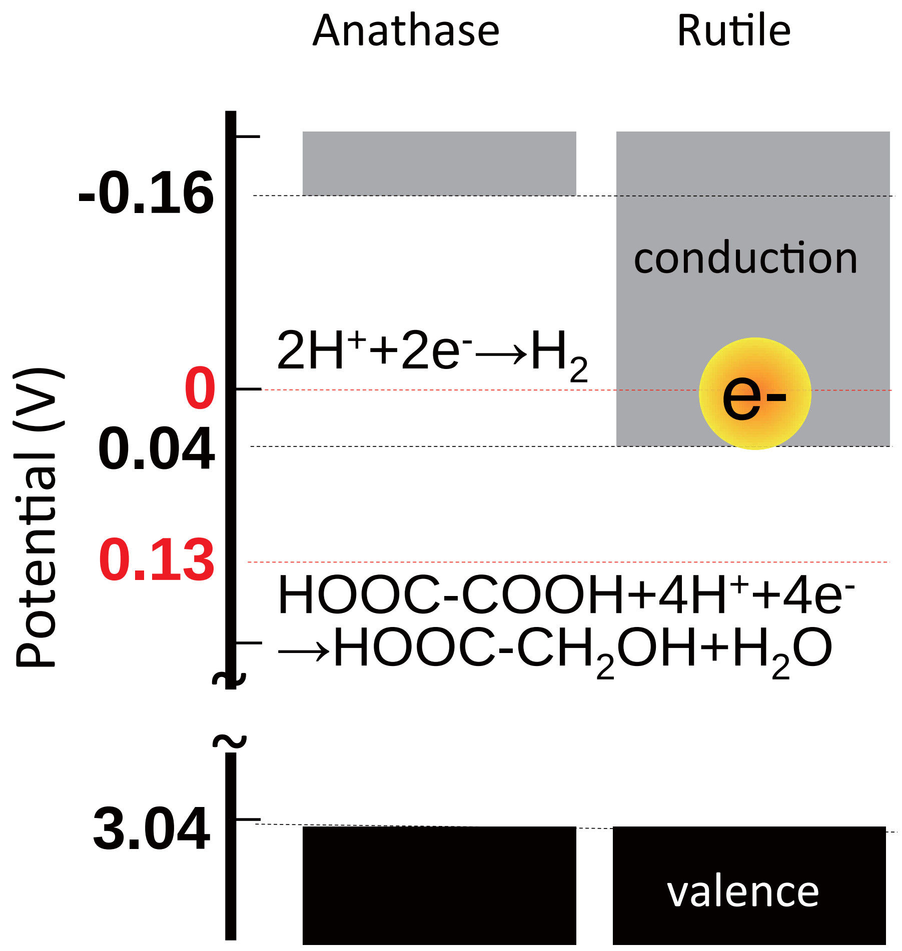


*measured using JSM-ARM200F installed in Next-Generation Fuel Cell Research Center (NEXT-FC), Kyushu University

Energy Environ. Sci., 8, 1456 (2015).

Detailed structures of PTSs

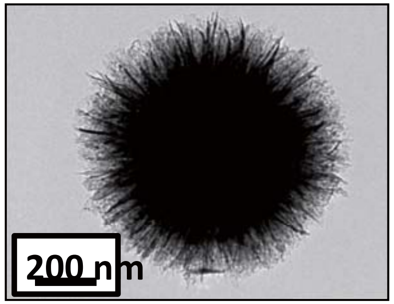




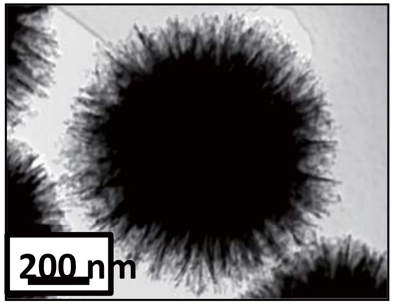
Energy Environ. Sci., 8, 1456 (2015).

Detailed structures of PTSs

500 ℃

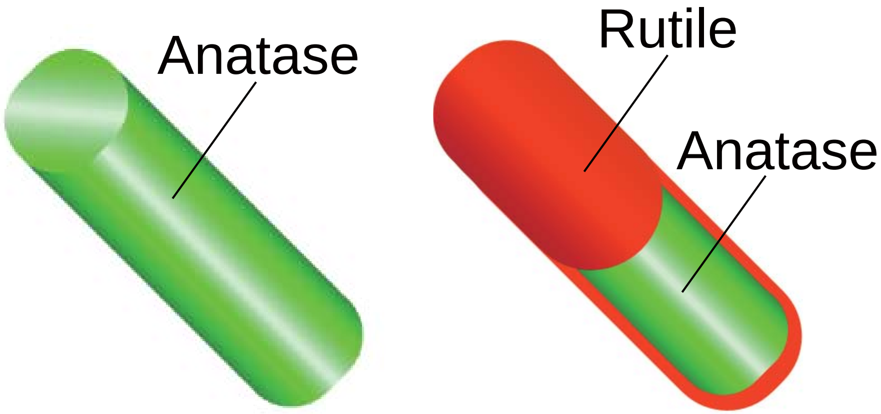


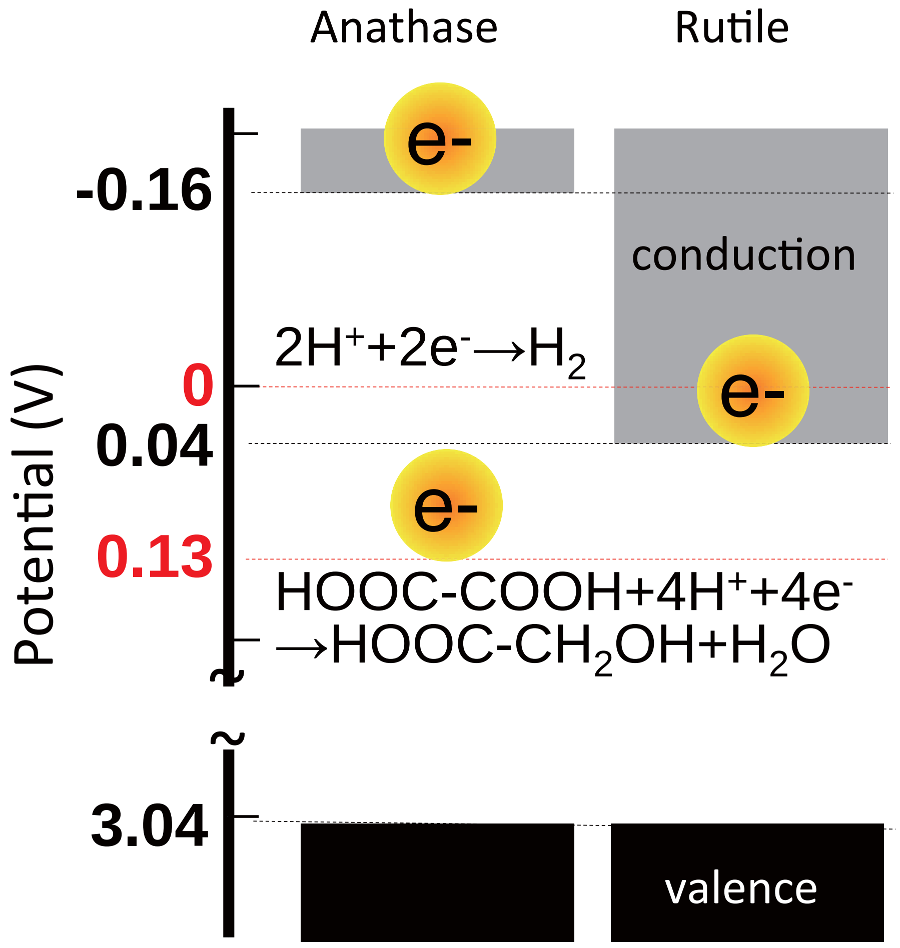
600 ℃



PTS-500

PTS-600

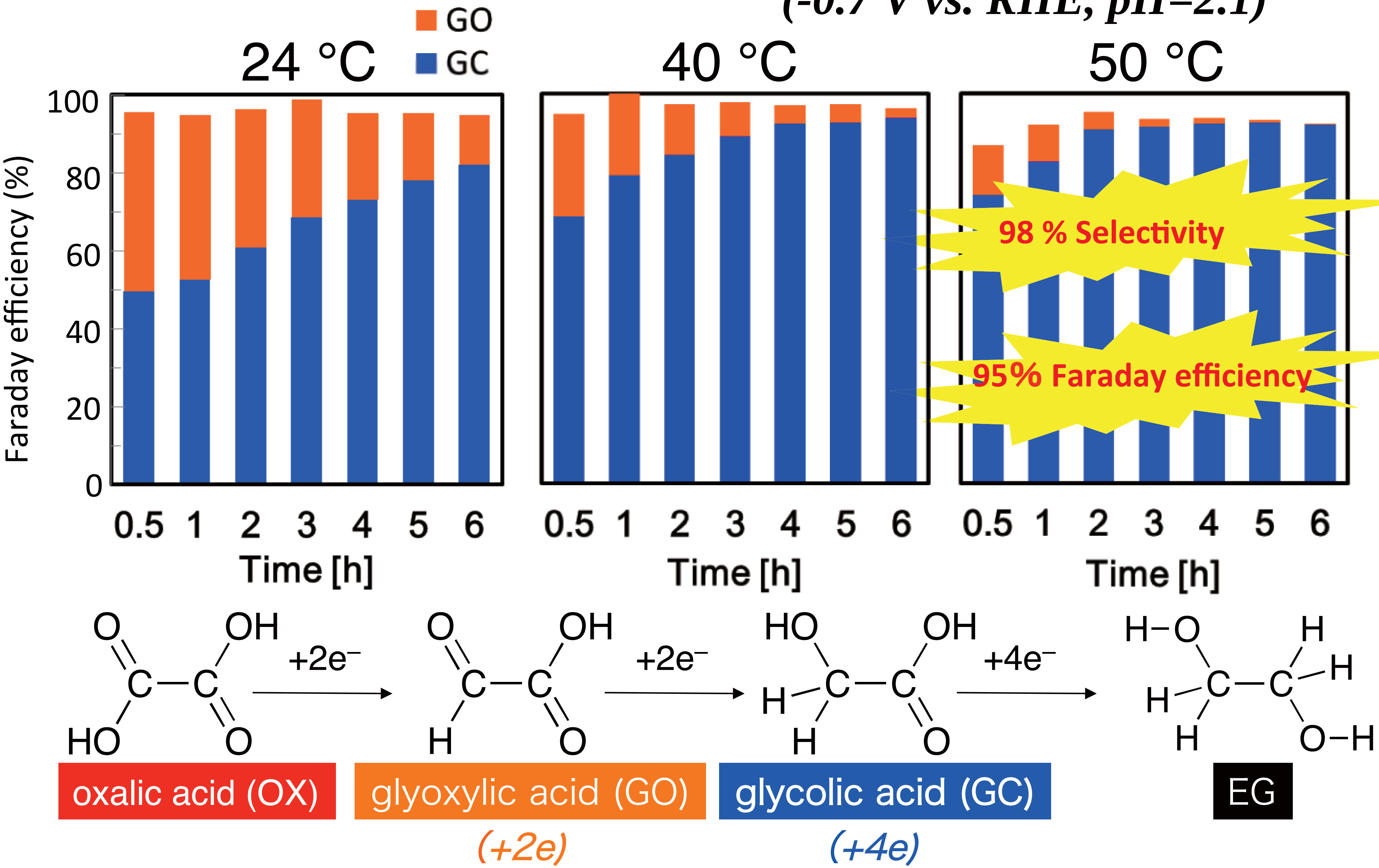




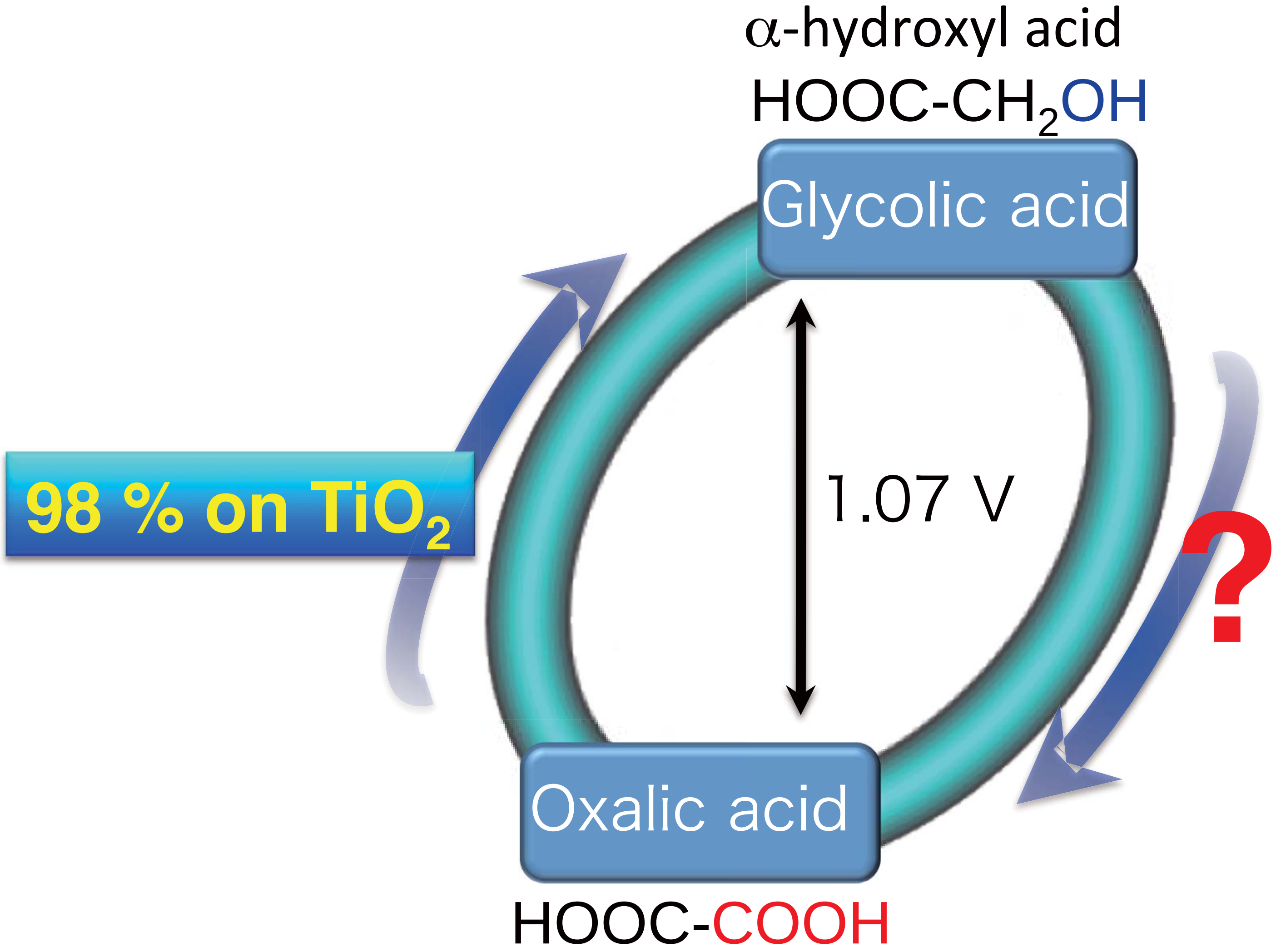
Energy Environ. Sci., **8**, 1456 (2015).

Product distribution on PTS-500

(-0.7 V vs. RHE, pH=2.1)

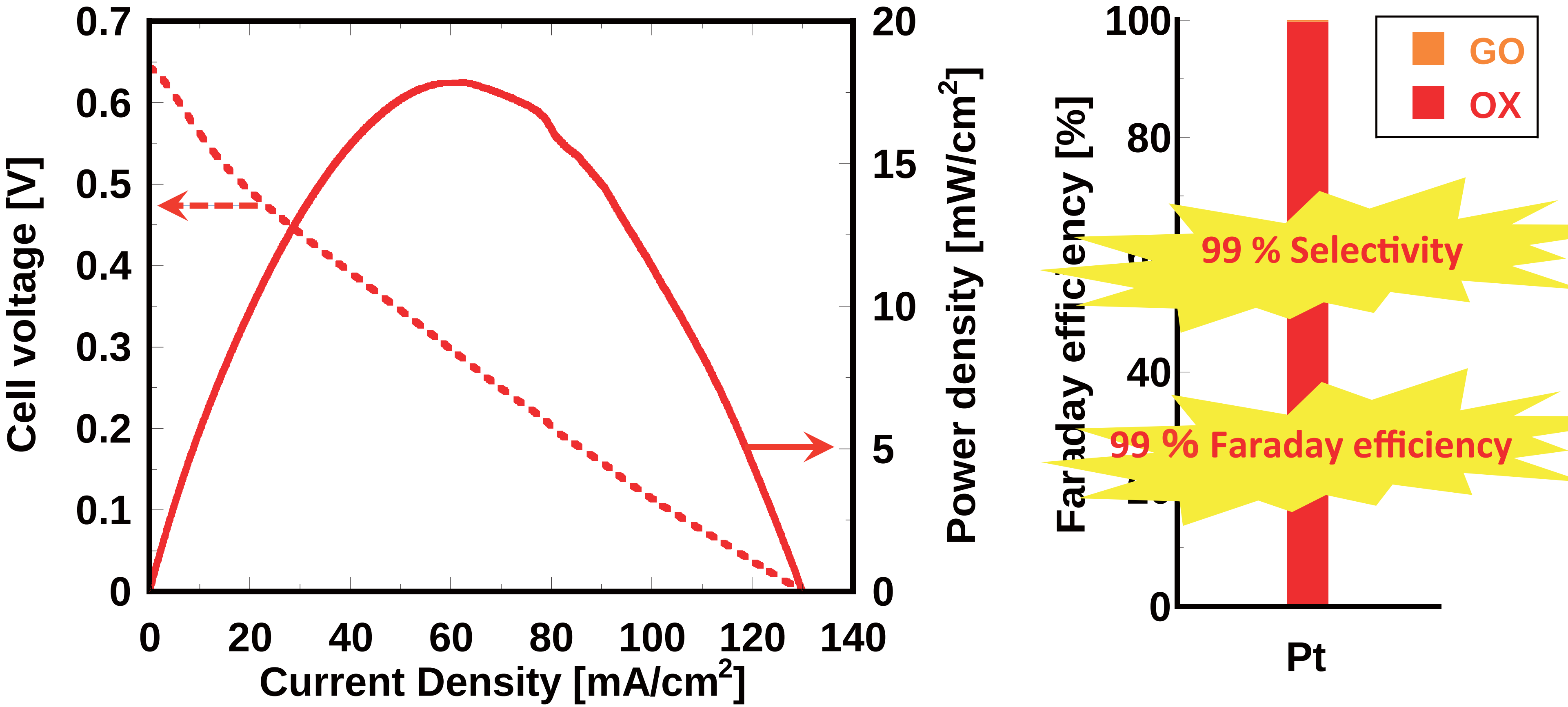


CN cycle using the glycolic acid/oxalic acid redox couple



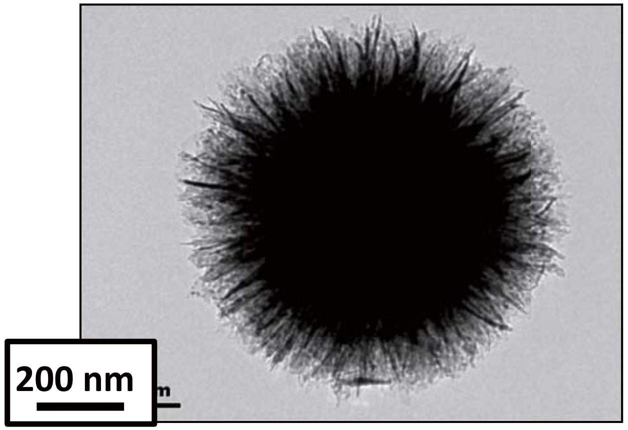
Energy Environ. Sci., 8, 1456 (2015).

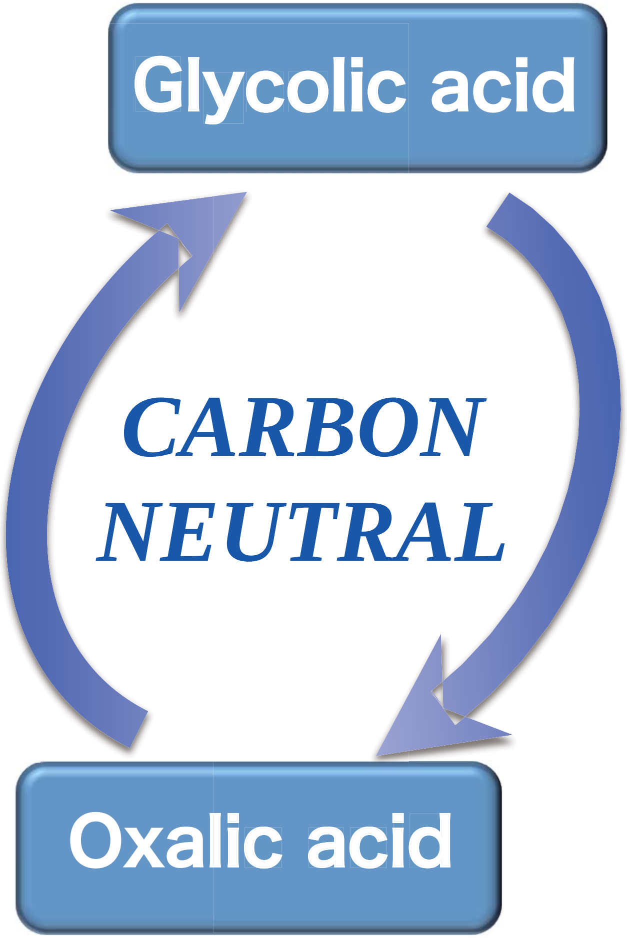
Power generation using direct GC alkaline fuel cell



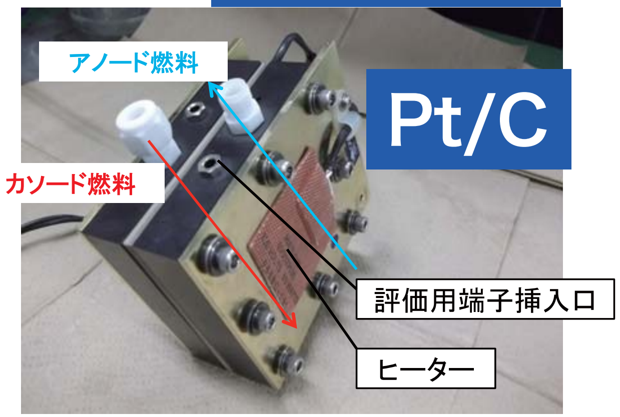
We succeeded in carbon-neutral energy circulation using the glycolic acid/oxalic acid with high selectivities and efficiencies.

glycolic acid selectivity
98%





Cu-Pd/C



oxalic acid selectivity
99%

The first report of power circulation without CO_2 emission.