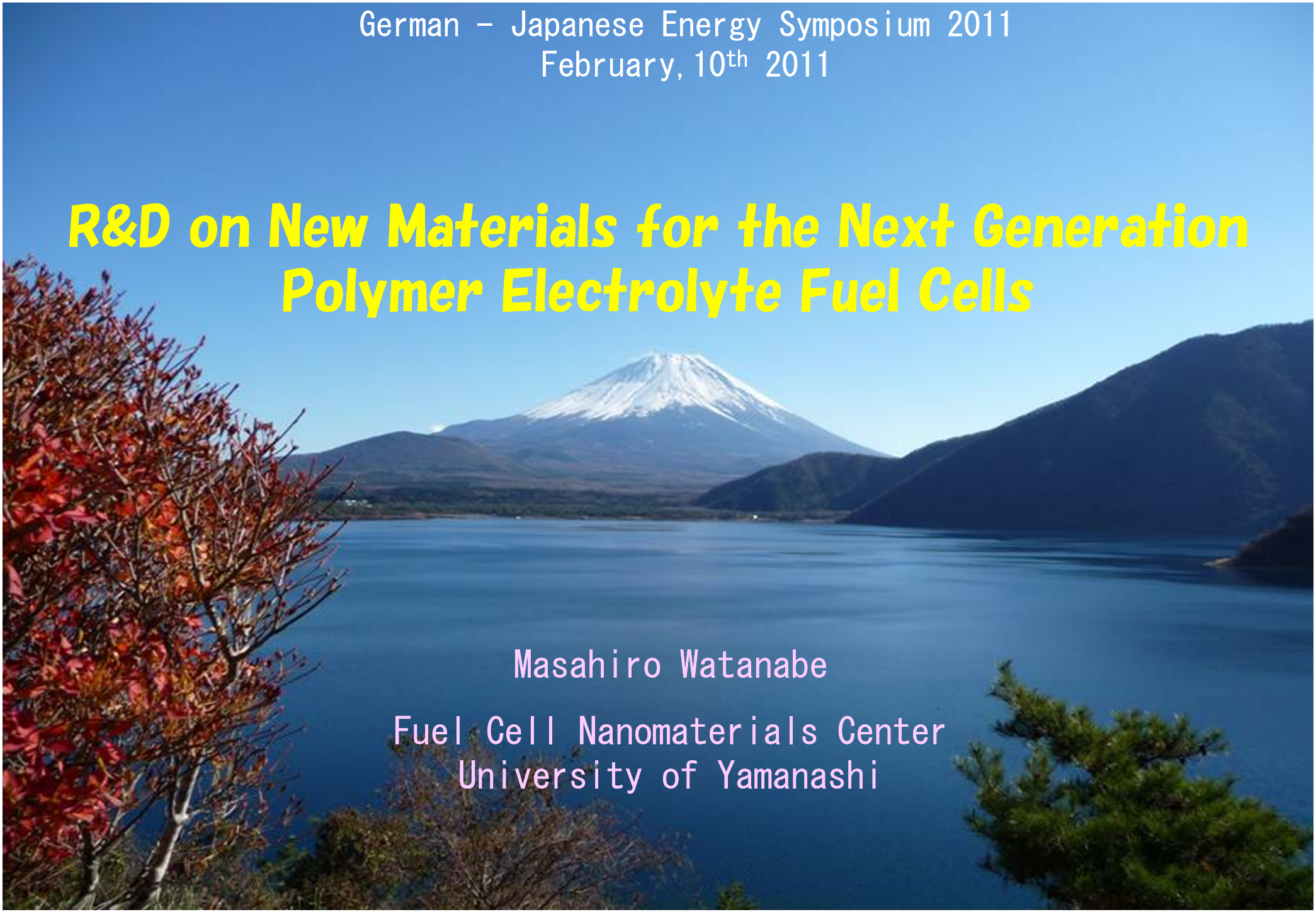
German - Japanese Energy Symposium 2011
February, 10th 2011

R&D on New Materials for the Next Generation Polymer Electrolyte Fuel Cells



Masahiro Watanabe

Fuel Cell Nanomaterials Center
University of Yamanashi

Outline

- ✓History of our research group
- ✓Problems to the PEFC wide applications
- ✓Some results at "HiPer-FC Project" R&D
  - ✓Analysis of degradation mechanisms
  - ✓Preparation of catalysts with high performance and high durability
  - ✓Preparation of HC-type membranes
  - ✓MEA for FCV applications; new evaluation method proposal
- ✓Conclusion

Research Laboratory for Fuel Cells

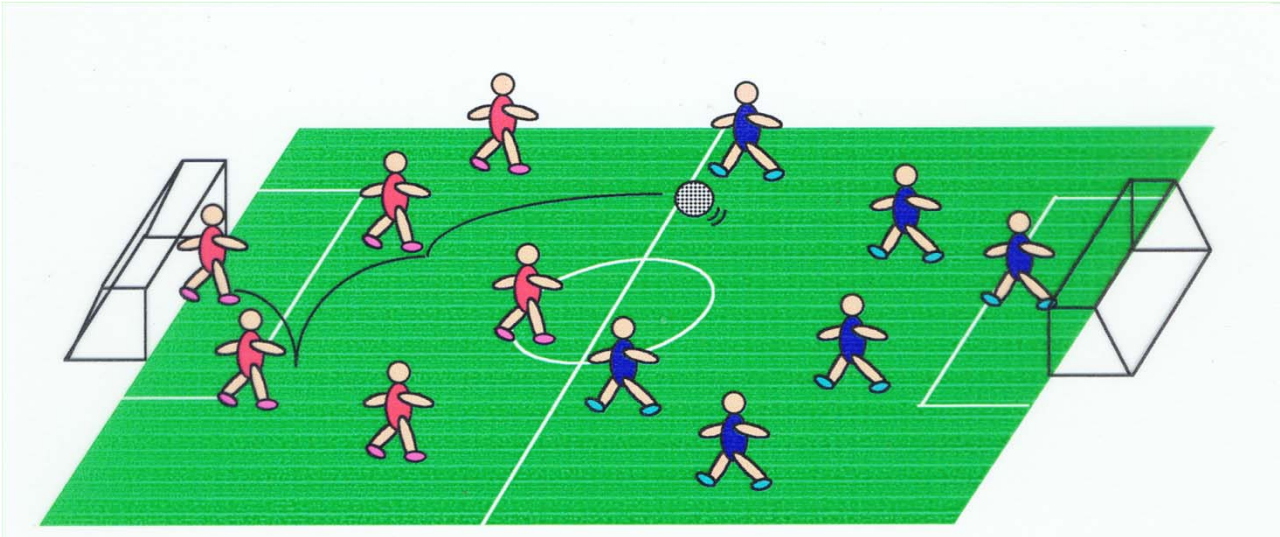
constructed in 1978

University of Yamanashi

Clean Energy Research Center (Re-structured at 2001.4)

High Performance Fuel Cells

High Voltage (Efficiency)
High Current Density (Power)
Long Life

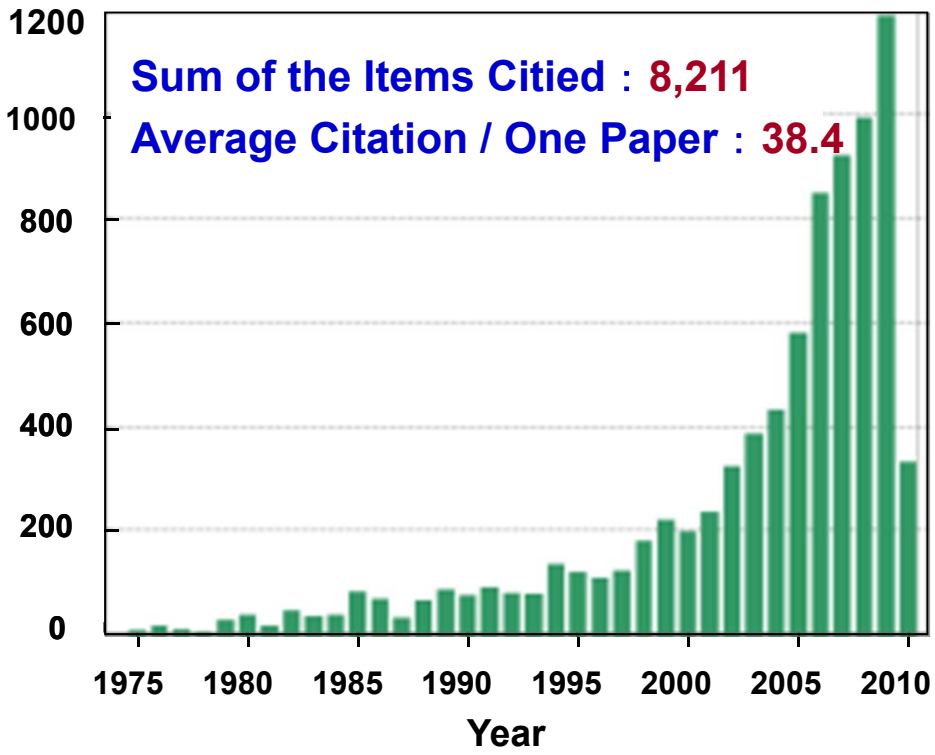


Controlling Factors

Reactants & Products	=	Boll
Electrocatalysts	=	Players
Electrode Structures	=	Formations
Electrolyte	=	Field
	&	
Promoters	=	Supporters

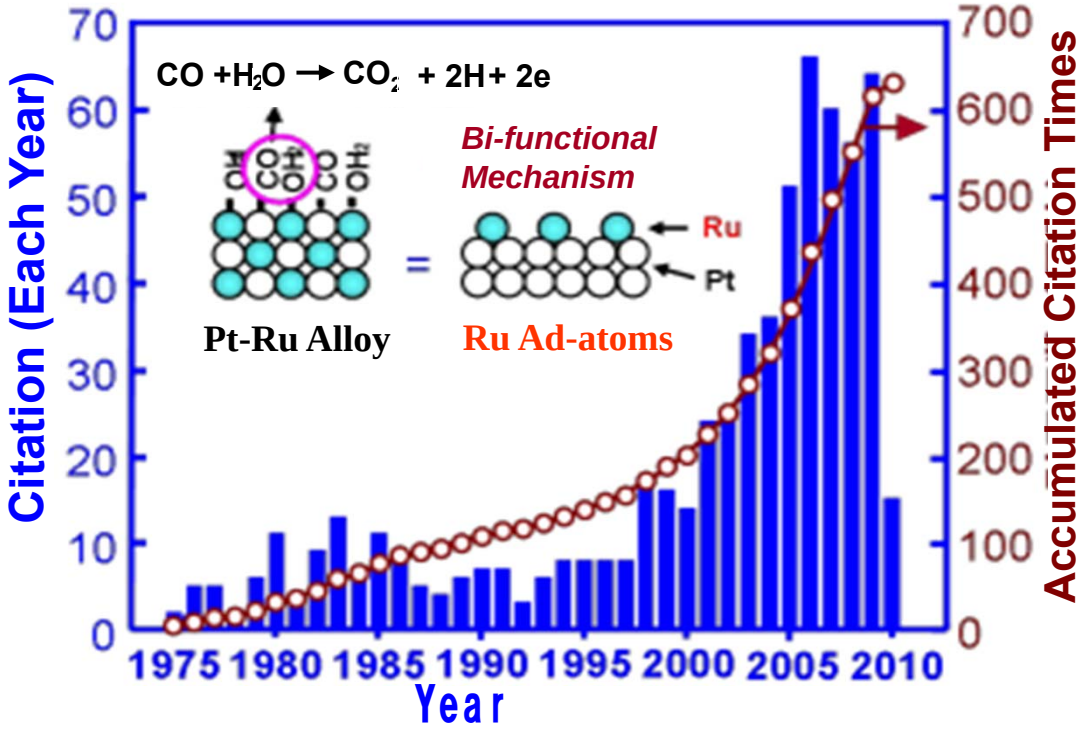
Citation of Watanabe's Works Relating to Fuel Cells

Citations/Year on All Papers



- Total number of original papers published : > 250
- Most of the papers have been published in top-ranked international journals
- More than 50 filed patents

An Example of Citation on One Paper



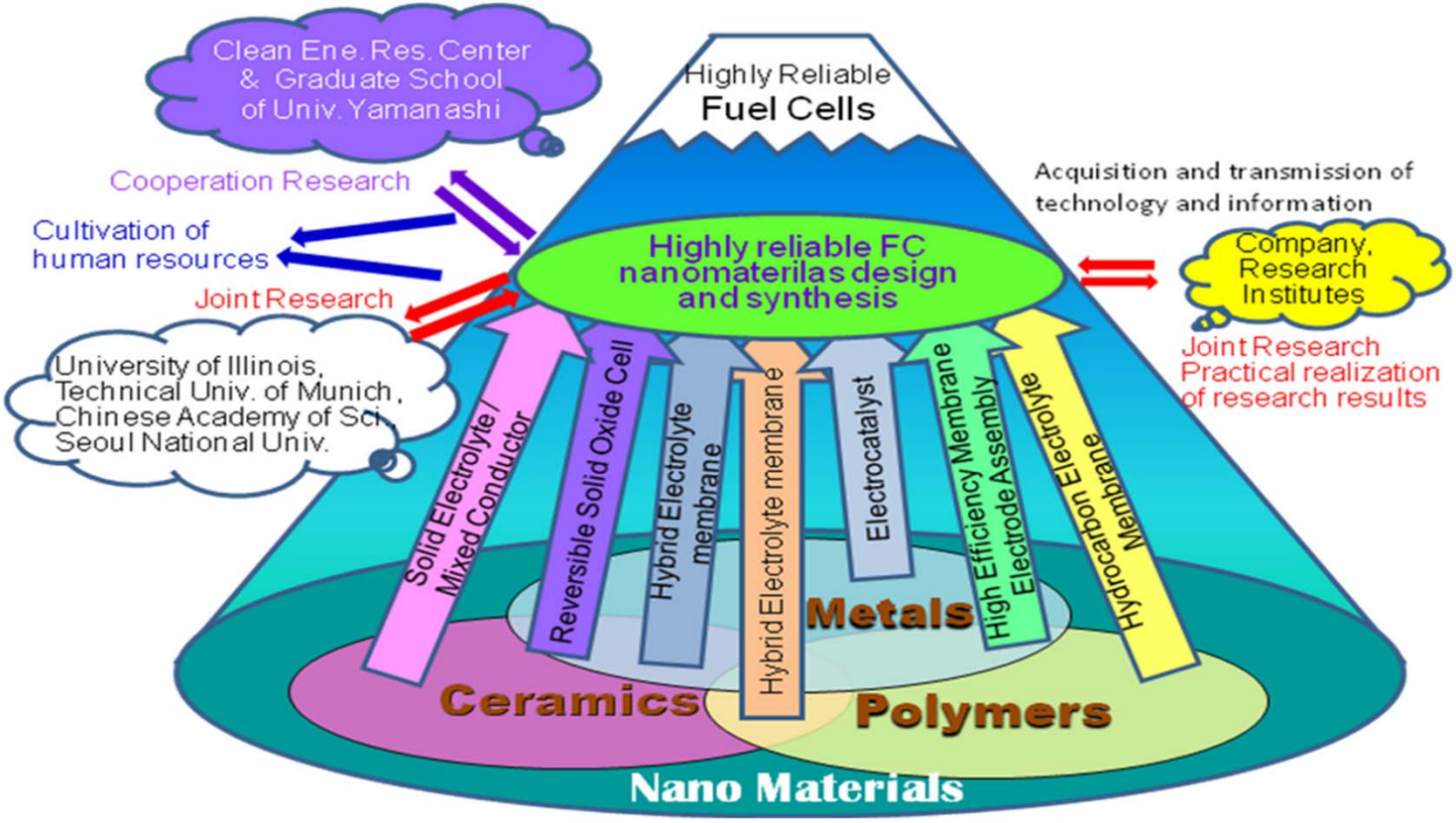
M. Watanate and S. Motoo, J. Electroanal. Chem., 60, 267(1975)

Electrocatalysis by Ad-atoms Part Ⅱ. Enhancement of the Oxidation of Methanol on Platinum by Ruthenium Ad-atoms

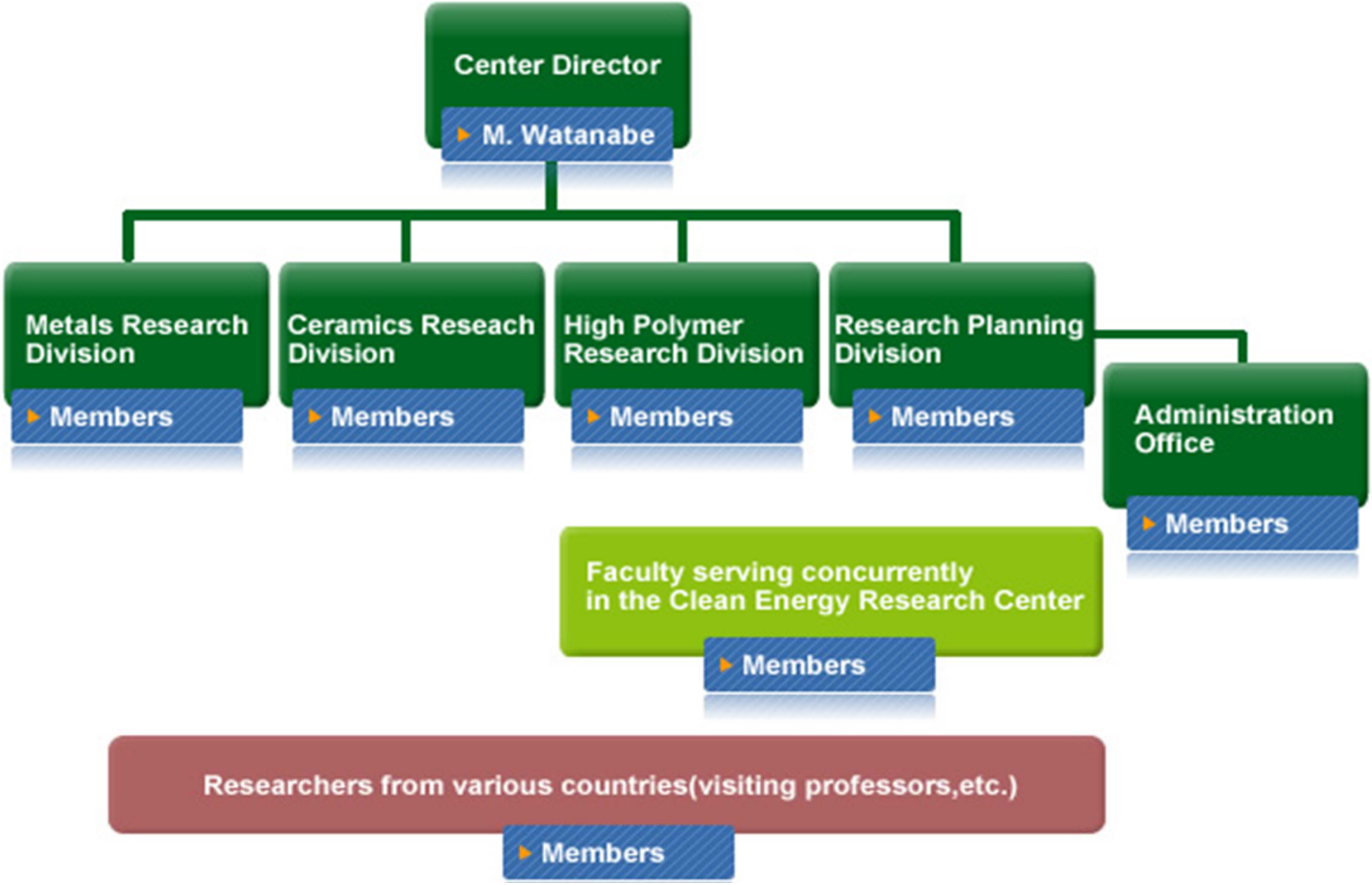
- Cited 630 times by 43 coutries and 376 institutions
- Discovery of "Bi-functional Mechanism" & "Catalysis by Ad-atoms"
- The Pt-Ru is only one alloy catalyst used commercially in "EneFarm" and "DMFC"

Started in April, 2008

Currently promoting
"HiPer-FC project"
From 2008 for 7 years funded
> 90 million US dollars by NEDO



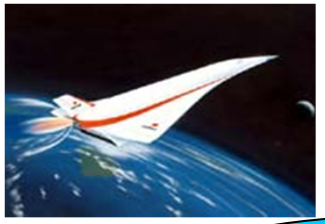
Organization of Fuel Cell Nanomaterials Center

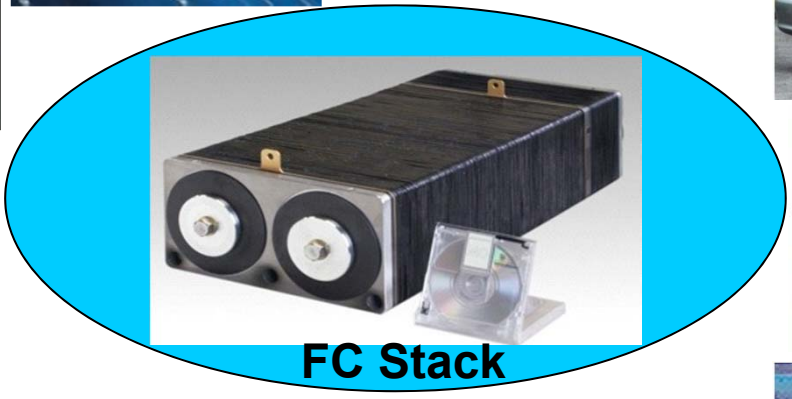


Members in FC Team (April, 2010)

Position	Clean Energy Research Center	Fuel Cell Nanomaterials Center
Profs.	2	8
Associate Profs	1	4
Full Time Guest Profs	—	4
Assistant Profs	—	5
Post-Doc Researches	2	1
PhD course Students	14（Inc. 2 engs. from FC companies）	
Mr. course Students	16	
B. Students（4th year）	12	—
Administrative Staffs	4	10
Total	83	

Various Applications of Polymer Electrolyte Fuel Cells(PEFC)





Essential Problems but Soluble

1. Cost Reduction
   - Reduction of Pt loading to ca.1/10
   - Reduction of PEM cost to ca. 1/20
   - Improving MEA performance
   - Reduction of separator cost to ca. 1/20
2. Reliability Improvement
   - Elucidation of mechanisms & Technical polishing
3. Infrastructure Construction
   - New process for the production and storage of H_2 as well as the production processes of clean gasoline and GTL
   - Easing official restrictions

HiPer-FC Project

- Research on Nanomaterials for **Hi**gh **Per**formance **F**uel **C**ells -

The **Fuel Cell Nanomaterials Center** was established in April, 2008. The University of Yamanashi was adopted as the lead organization for a 7-year project by the New Energy and Industrial Technology Development Organization (NEDO) in 2008. The Center is the core institution of this huge project, and the total budget of the project is more than US$ 90 M.

Research Items

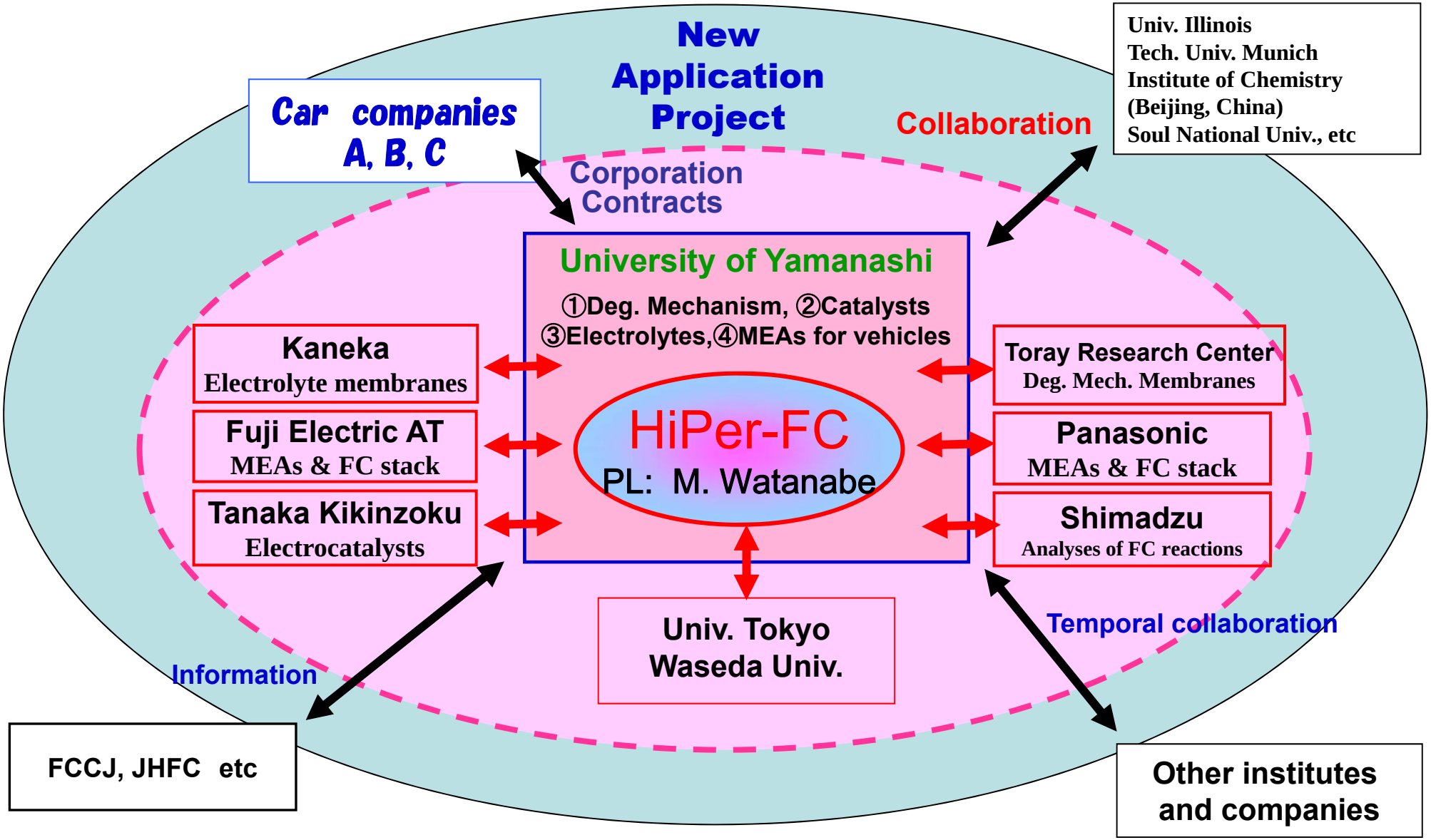
1. **Analysis of degradation mechanisms**
2. **Research and development of catalysts with high activity and high durability**
3. **Development of electrolyte membranes for operation over a wide temperature range and low humidity conditions**
4. **Research for high performance, high reliability MEAs for automobile use**

Final Targets of the Project (FY2008~FY2014)

1. To develop MEAs that can start at -30℃ and operate at temperatures up to 100 ℃ and a relative humidity (RH) of 30%.
2. The catalyst should be decreased to 1/10 of the conventionally used amount.
3. These materials installed in fuel cells are expected to demonstrate prospective performances, e.g. cell efficiencies up to 64% LHV (lower heating value) at 25% of the rated load and durability of 5,000 operating hours and a couple of 10,000 on-off operations.

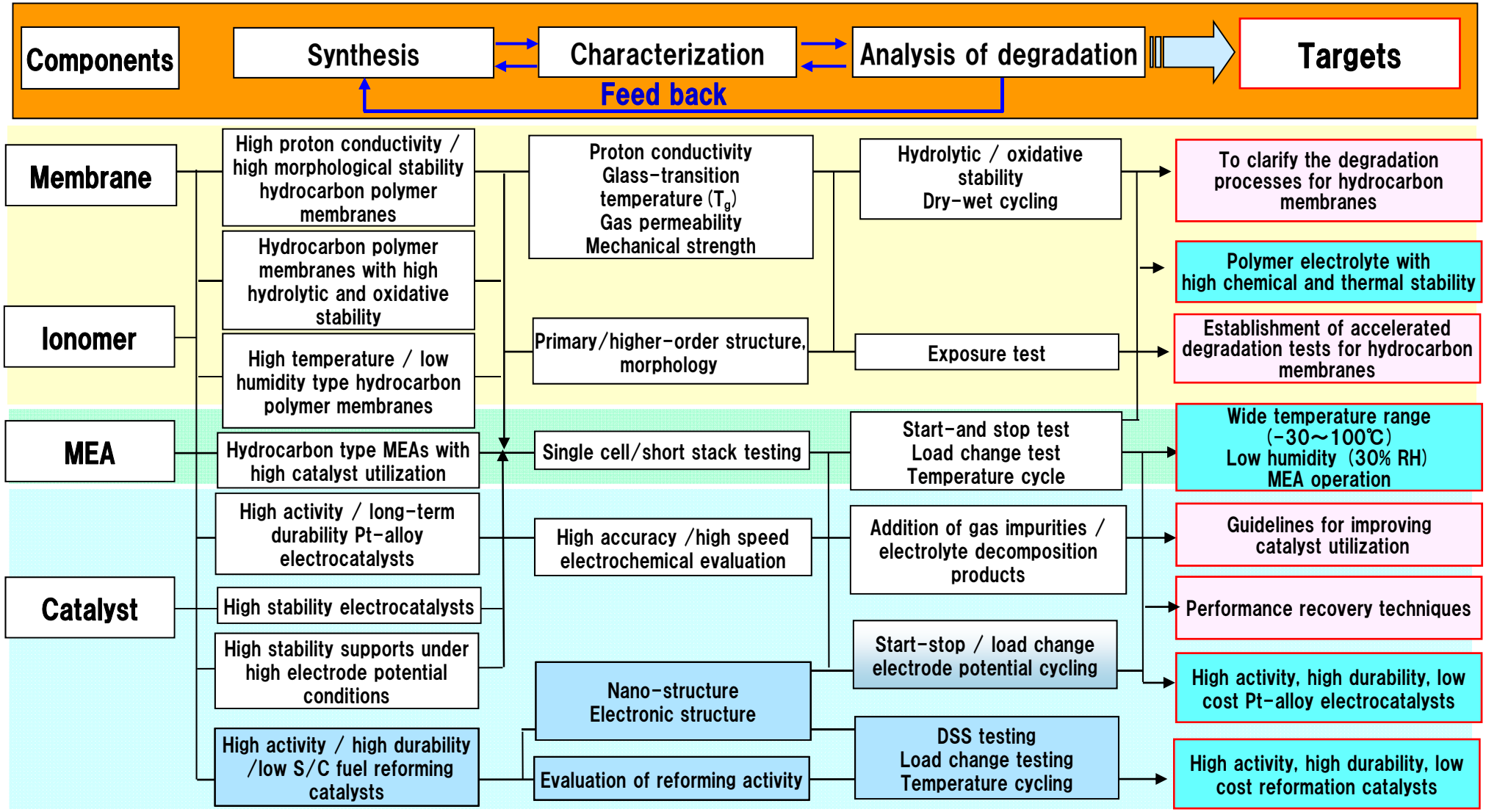
HiPer-FC Project Organization

(NEDO, 2008～2014FY)



Research and Development Map of the Project

Feeding back of degradation analyses to the developments of electrocatalysts and electrolyte membranes and to their Integrated MEAs



High Performance, High Durability & Low Cost for The Wide Penetration of PEFCs into the Market

Developments of Innovative New Materials & Cells/System Designs
Such as
Catalysts, Electrolytes, MEA, Separators & Fuel Processers

Lack for the Guiding Principles for Such Developments &
For the Standard Evaluation Methods,
Resulting in Huge Wastes of "Men, Time & Money"

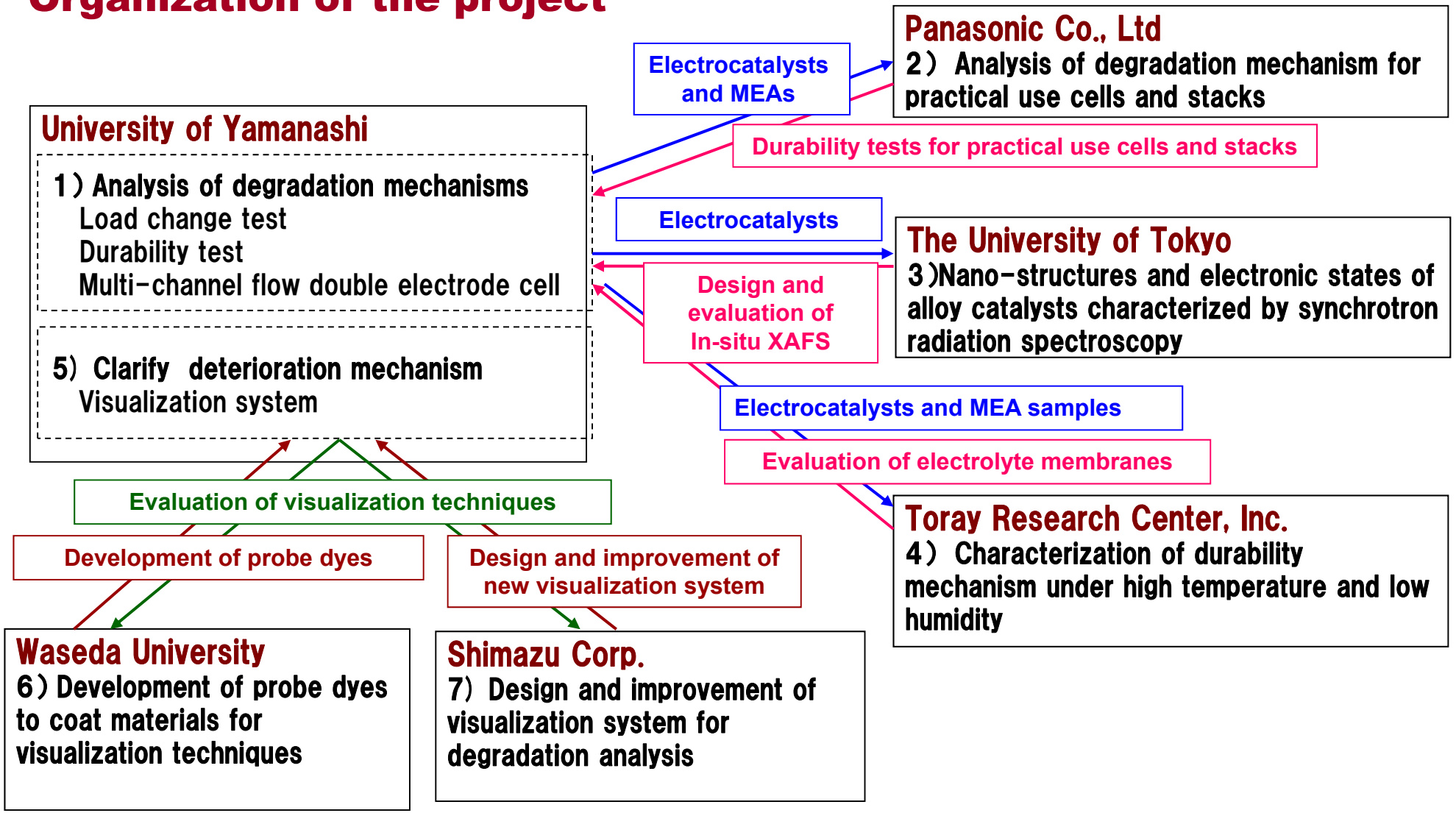
(1) Development of Simple, Precise & Standard Evaluation Methods

(2) Development of New Materials etc. using the above Methods

(3) Analyses of the Materials, and Studies of the Mechanisms on the Processes & Degradations relating to them

1. Analysis of degradation mechanisms

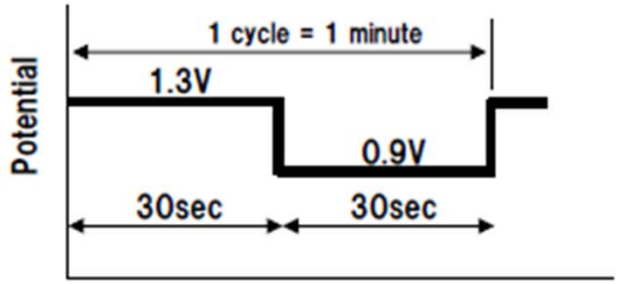
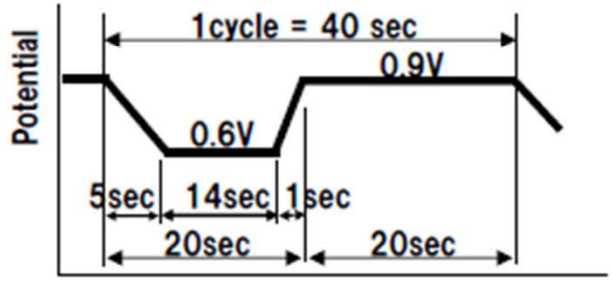
Organization of the project



III-2 Electrode Catalyst Durability Evaluation

III-2-2 Single Cell Potential Cycle conditions and Evaluation Test (Cathode side Evaluation)

proposed by FCCJ

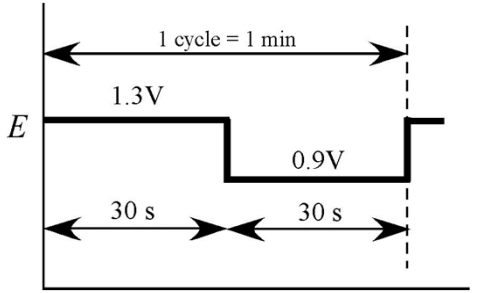
	Evaluation Test Mode	Measurement/Inspection Items
Cathode side Evaluation	【Start/Stop Test】 Cathode : N2 Anode (Counter/Ref. Electrode): H2  【Load Cycle Test】 Cathode :N2 Anode (Counter/Ref.Electrode) : H2  	Diagnosis during Test (a) Current change (Continuous Monitoring) (b) CO_2 concentration change in Cathode exit (Continuous Monitoring) Diagnosis at periodical stop during Test (c) IV Measurement ①Supply humidified air into cathode and humidified H2 into anode. ②Change current under constant gas stoichiometry. (d) CV (Measure ECA change). ①Supply humidified N2 into cathode and humidified H2 into anode. ②Potential cycle (0.05V⇔1.2V vs Anode potential @ 20 mV/s) ・ECA change analysis/evaluation by Hydrogen absorption Evaluation Points at after the Test ・Corrosion of catalyst support ・Precious metal dissolution/oxidation ・Catalyst particle growth

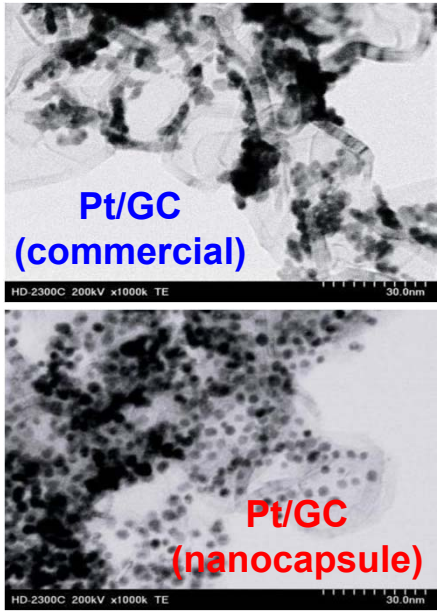
Effect of factors on the degradation rates and mechanism

<Start-stop test>

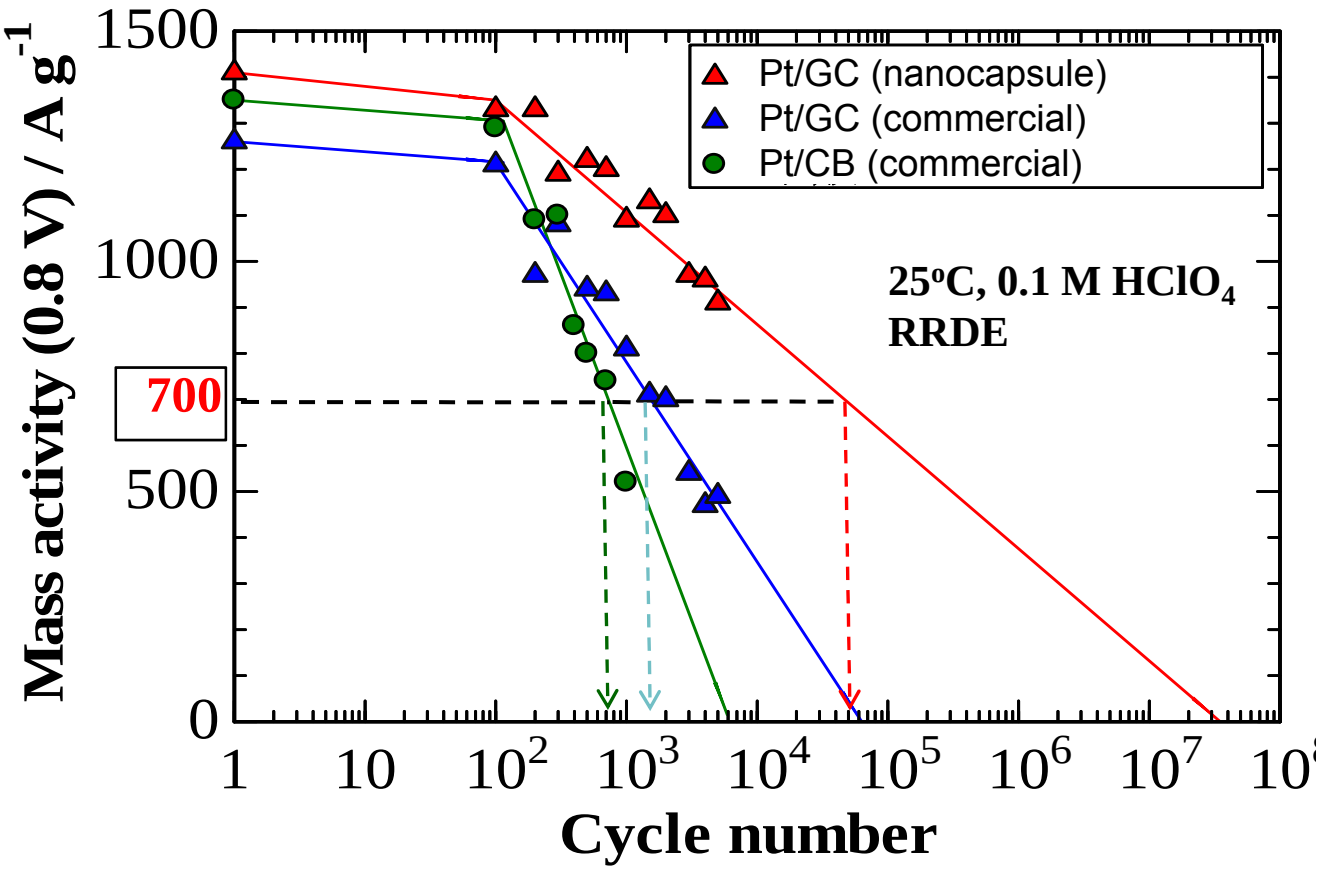
Cathode: N_2

Anode (counter/reference): H_2





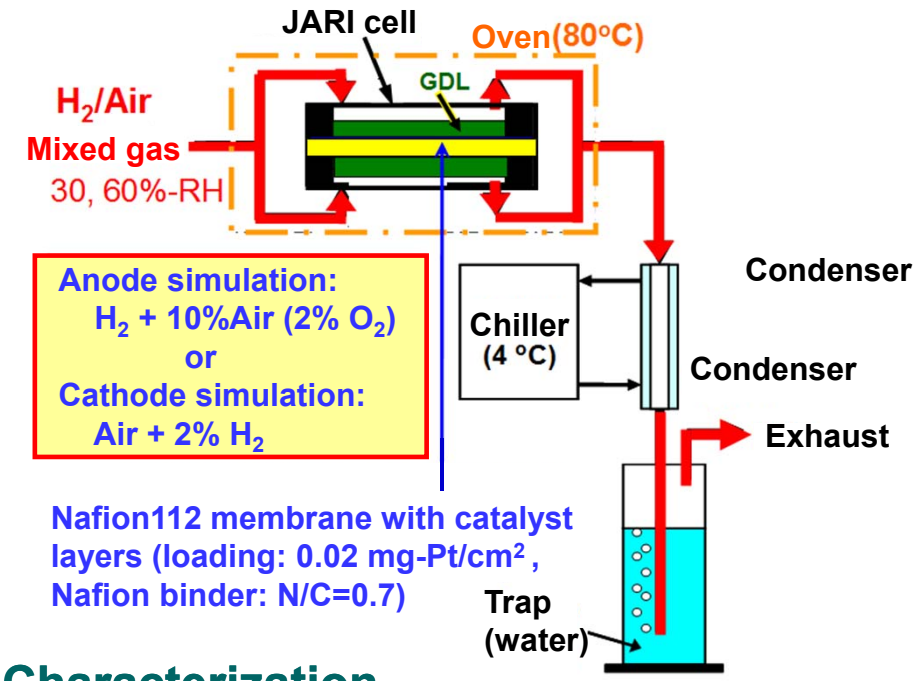
Corrosion rates of prepared and commercial catalysts during durability testing

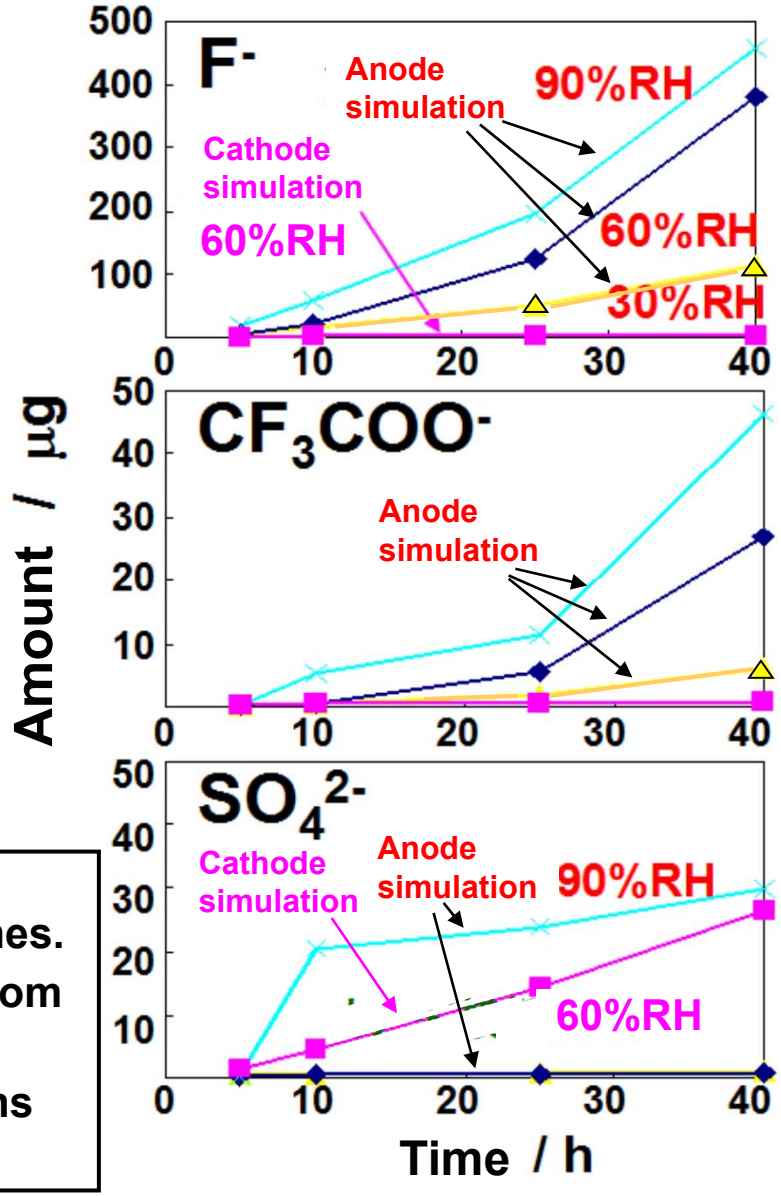


- Linier relationship between MA and log*N* was found, predictable a long term operation behavior.
- The cycle life of n-Pt/GC was 30 times longer than that for the commercial Pt/GC.
- The nanocapsule Pt/GC exhibited the lowest value of H_2O_2 production.

Mechanism & Durability on Electrolyte Membrane Degradation

Toray Research Center, Univ. of Yamanashi





Characterization

- Trapping water : Ion chromatography
- MEA : Cross-section SEM/EPMA, TEM, IR, Raman, Solid F-NMR
- MEA extracts: F-NMR, FAB-MS, LC/MS

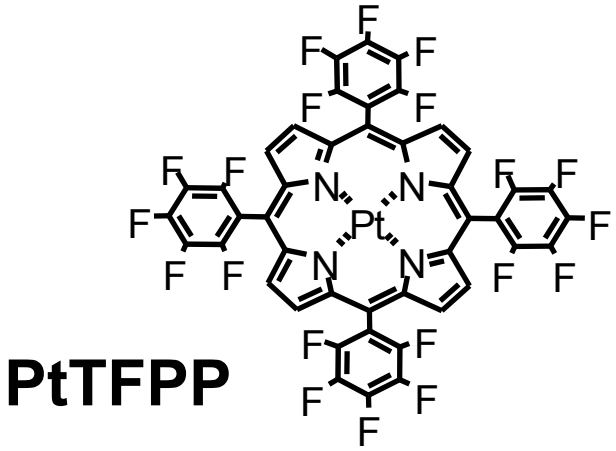
◆We have revealed the humidity dependence of the degradation of commercial perfluorosulfonic acid membranes.

◆The formation mechanism of SO_4^{2-} presumably differed from those of other decomposed ions.

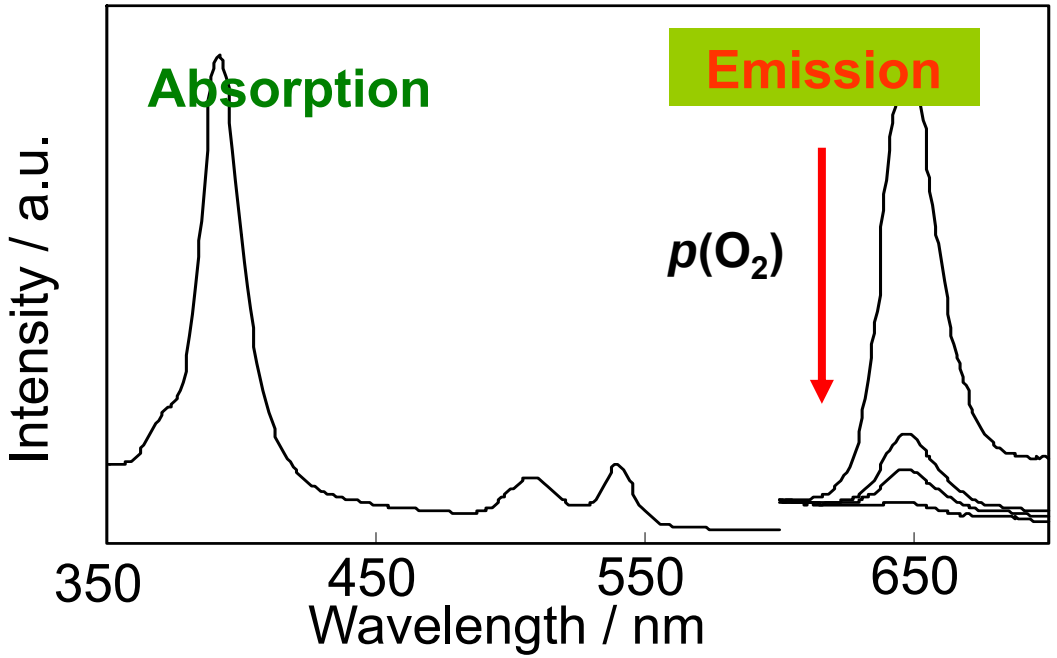
◆The water extraction method clarified that long side-chains decomposed from the MEA.

Partial Pressure Measurement of Oxygen Using a Dye Molecule

Pt porphyrins emit light upon irradiation.
The emission is quenched by O_2.



PtTFPP

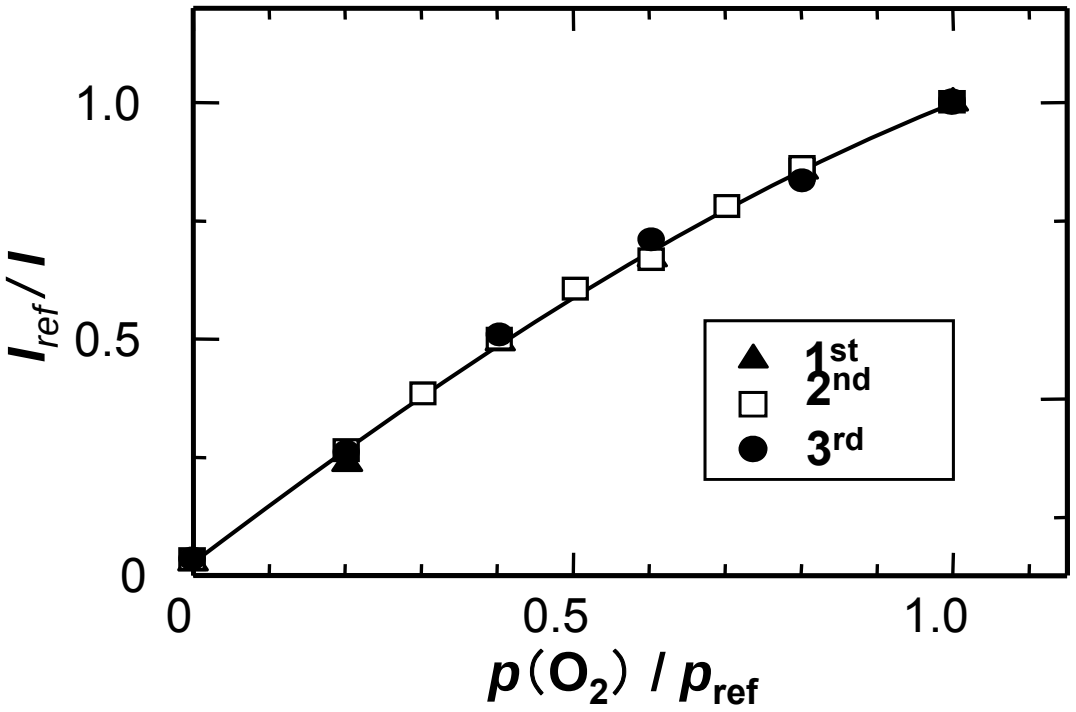


0.65 wt% 65 wt%

Physically and Chemically Stable.

O_2 partial pressure can be probed by Emission from Dye.

Stern-Volmer Plots



$p(O_2)$: O_2 partial pressure

I : Emission intensity

p_{ref} and I_{ref} : The values for air as the reference

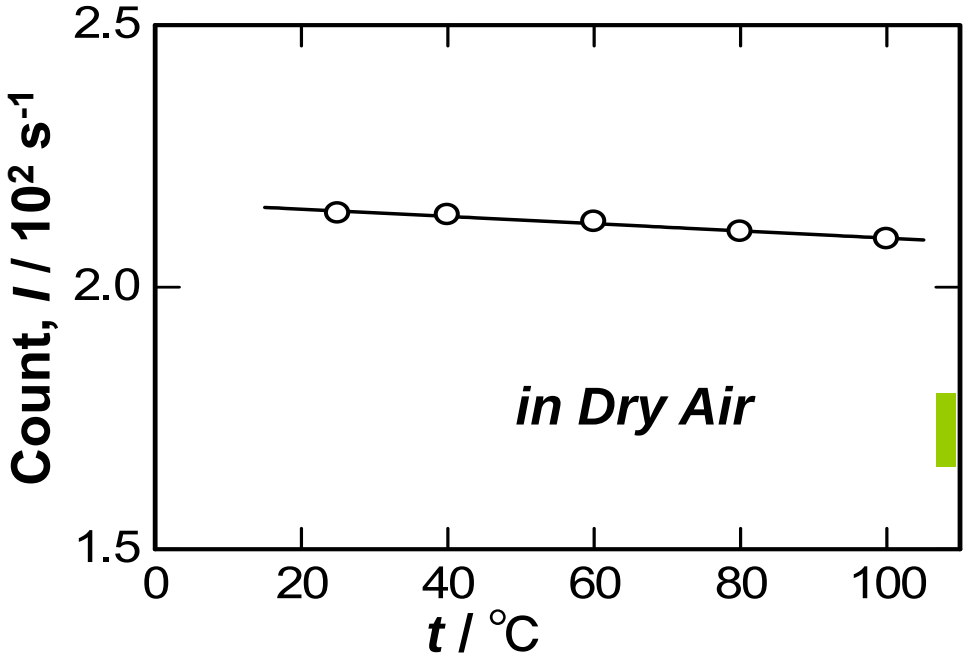
***Stern-Volmer* Plots were well expressed with third order fitting.**

$$I_{ref}/I = A_0 + A_1(p/p_{ref}) + A_2(p/p_{ref})^2 + A_3(p/p_{ref})^3$$

This third-order equation was used to calibrate the oxygen partial pressure.

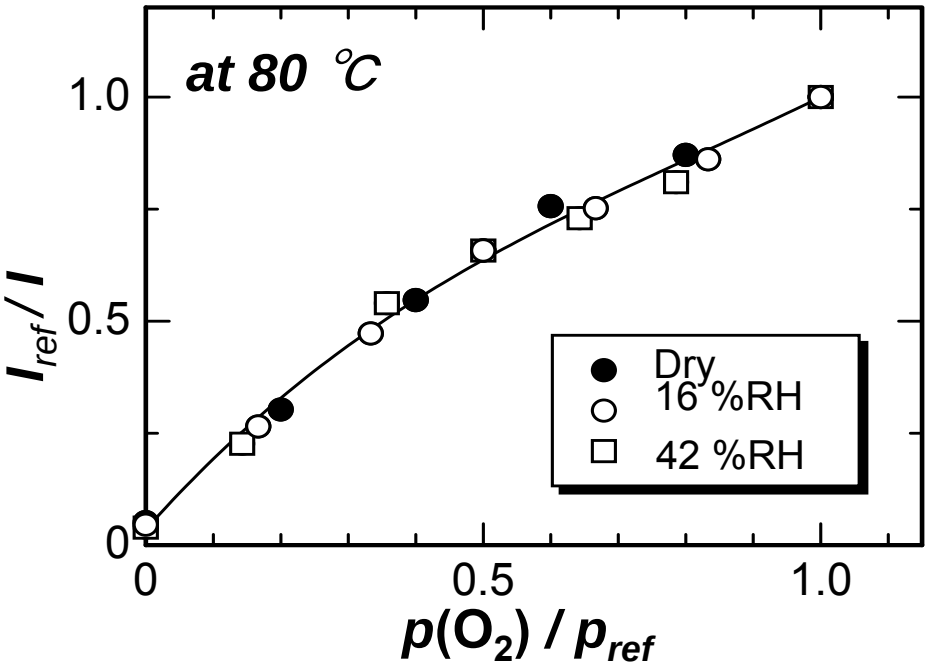
Dependency on Temperature and Humidity

Effect of Temperature



Very Small Influence of Temperature（0.5 % / ℃）

Effect of Relative Humidity

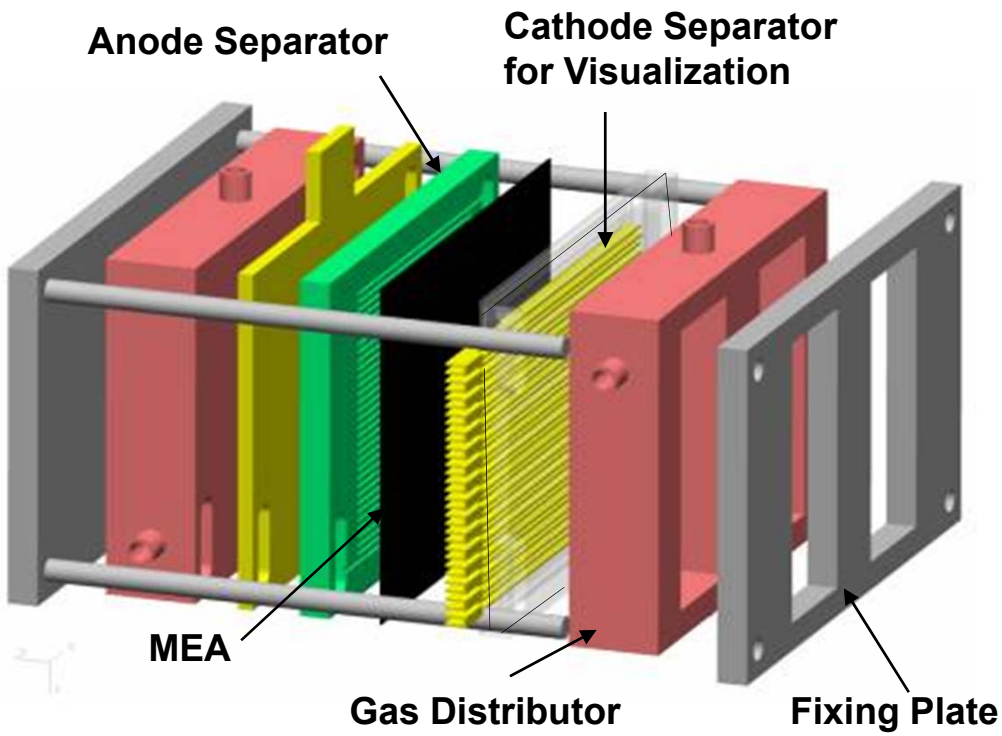


$p(O_2) = p(\text{total}) - p(N_2) - p(H_2O)$

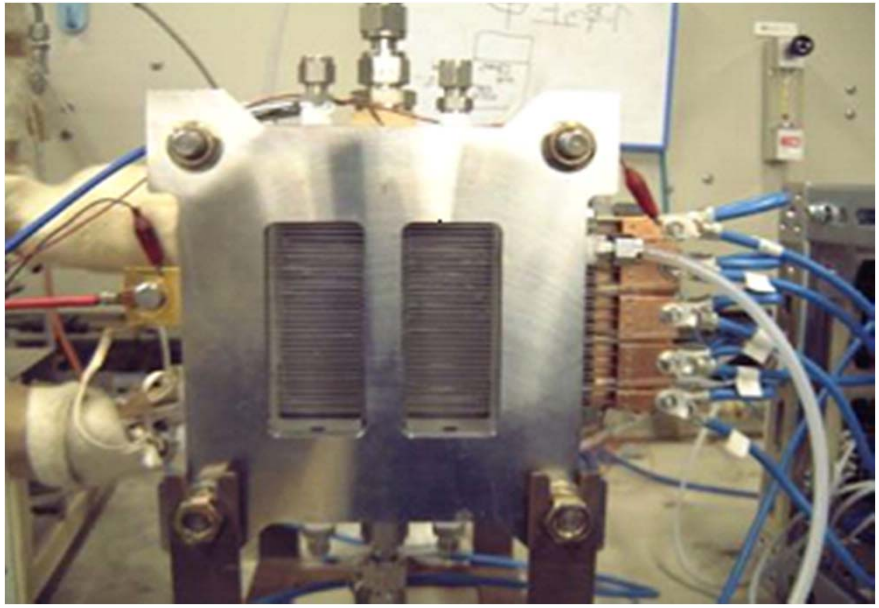
No Influence of Humidity

PEFC for Visualization

Visualization of O_2 under Power Generation!



Visualization Cell



Cell Temp: 70 ℃
Humidifier Temp: 55 ℃
(RH=50 %)
Air Flow: 500 mL min^{-1}
H_2 Flow: 500 mL min^{-1}

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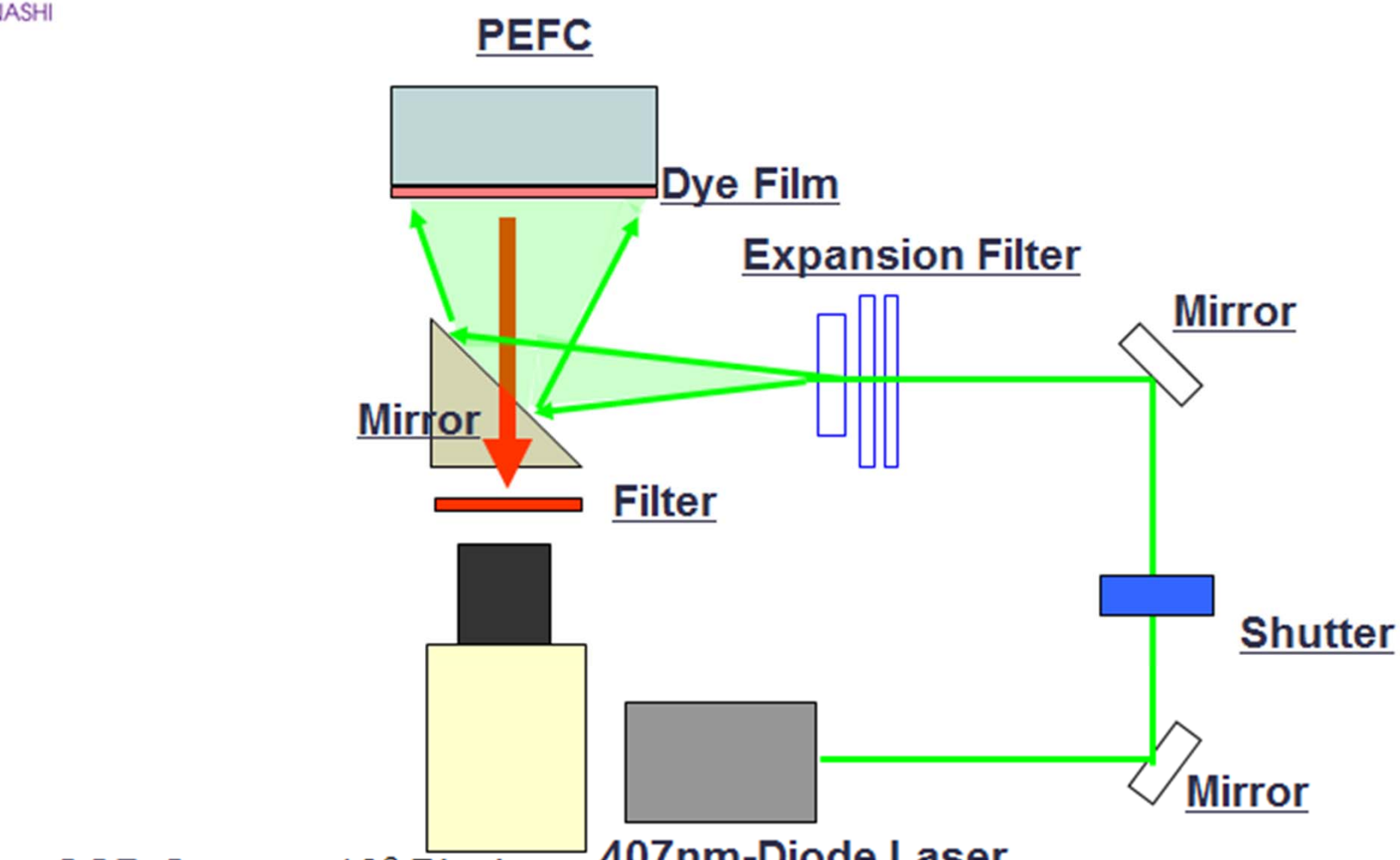
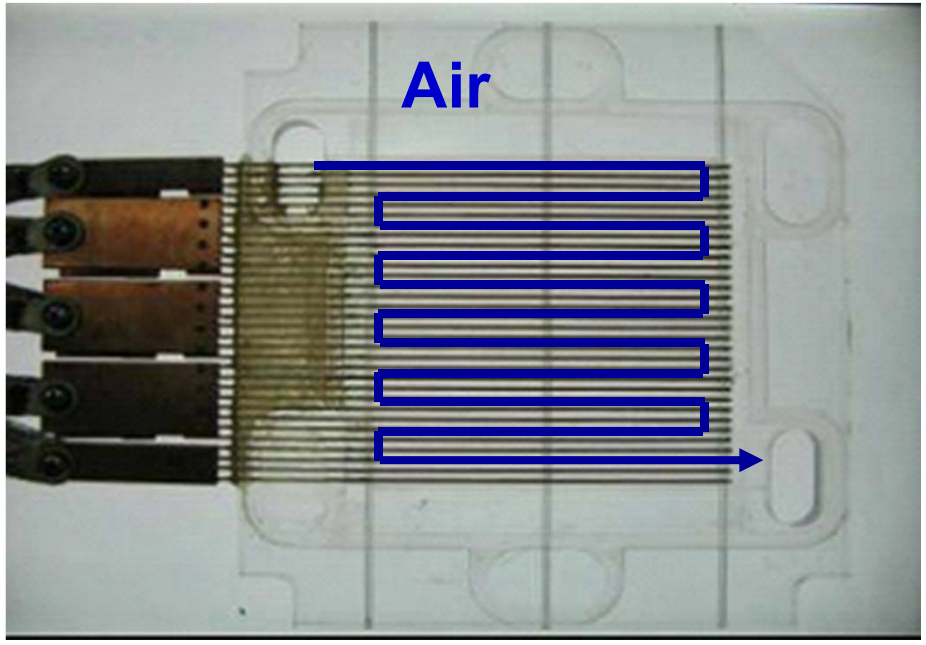
Optical Settings for O_2 Visualization

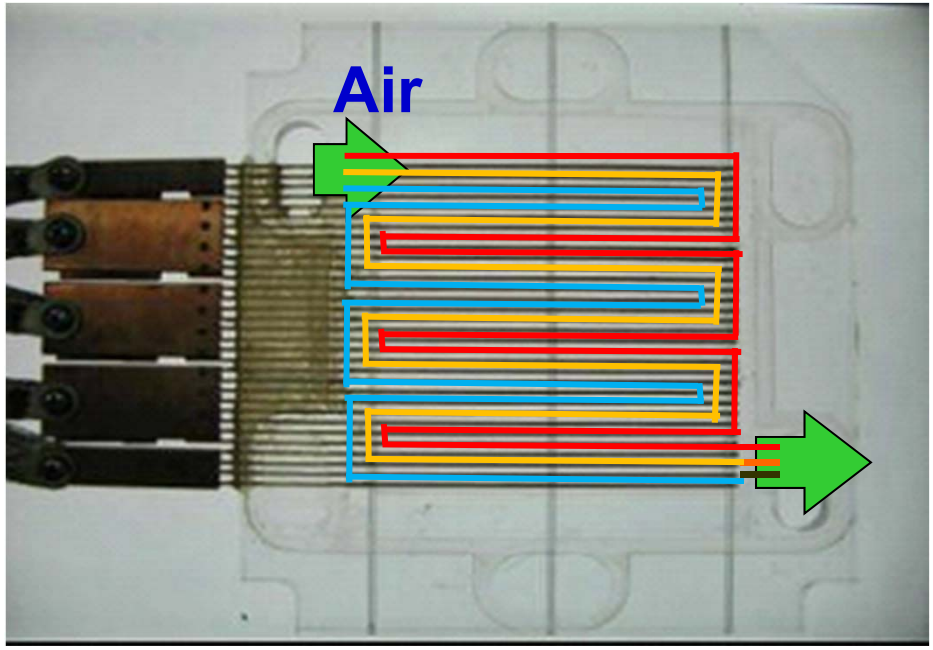


Separators

Single-Serpentine Channel



Triple-Serpentine Channels



Cathode separator of acrylic acid resin having metallic ribs.
Dye Film is coated on the flow channel.
Visualization Area: 10 cm x 10 cm,
Rib Width: 1 mm, Channel Width: 2 mm,
Channel Depth: 1 mm.

Calibration Curve at *Each Pixel*

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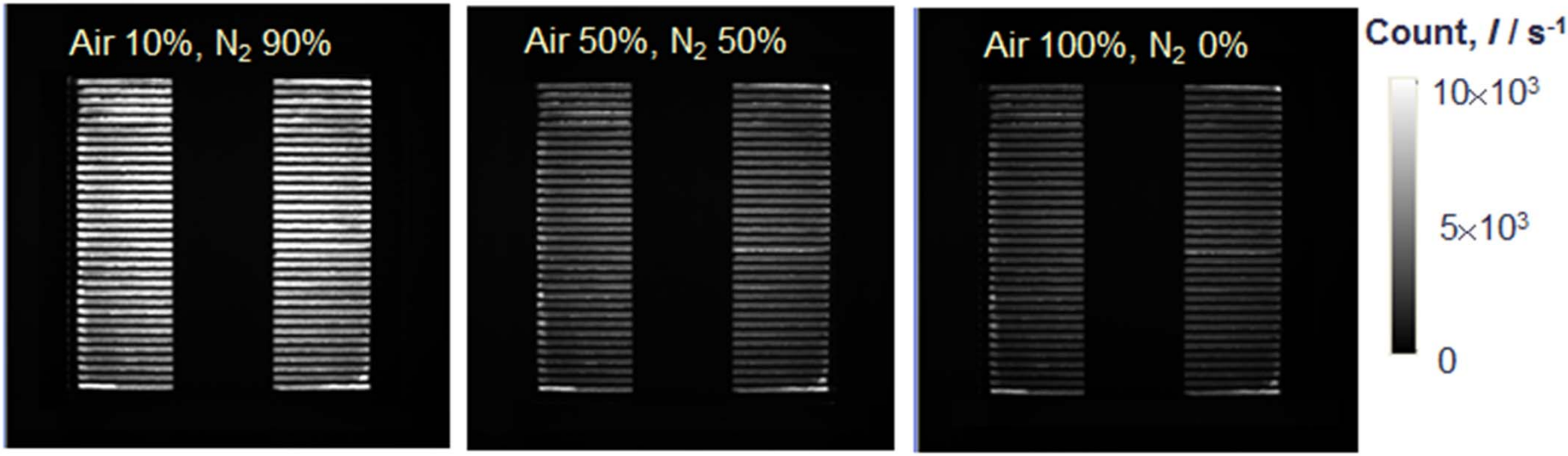
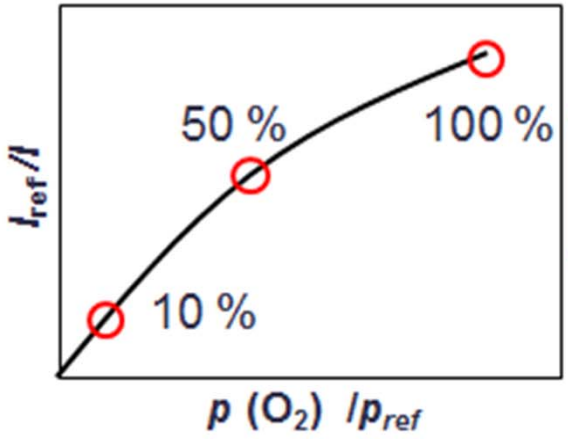
Before operation, *Stern-Volmer* plots were obtained at each pixel.

Air in N_2 = 0～100%. $P(O_2)$ content was changed by 10%.



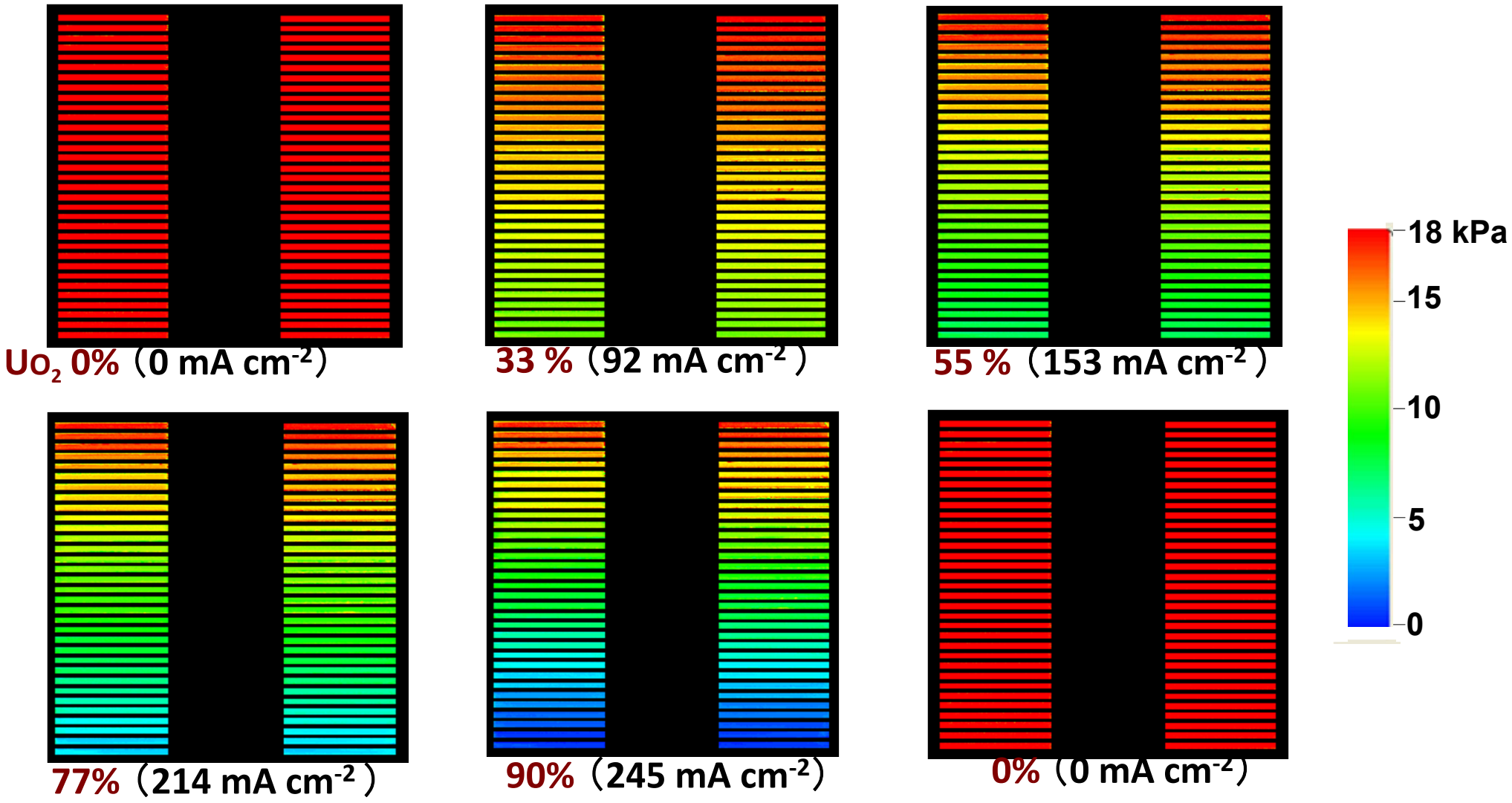
***Stern-Volmer* Plots**

500 x 500-pixel images



Calibration curves at all 250,000 pixels are prepared for visualization.

O_2 Partial Pressure at Different O_2 Utilizations



Change in O_2 utilization produced different patterns.

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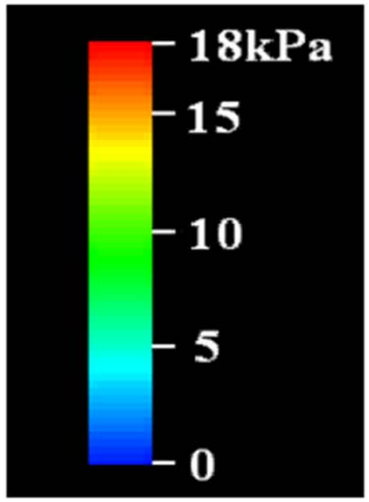
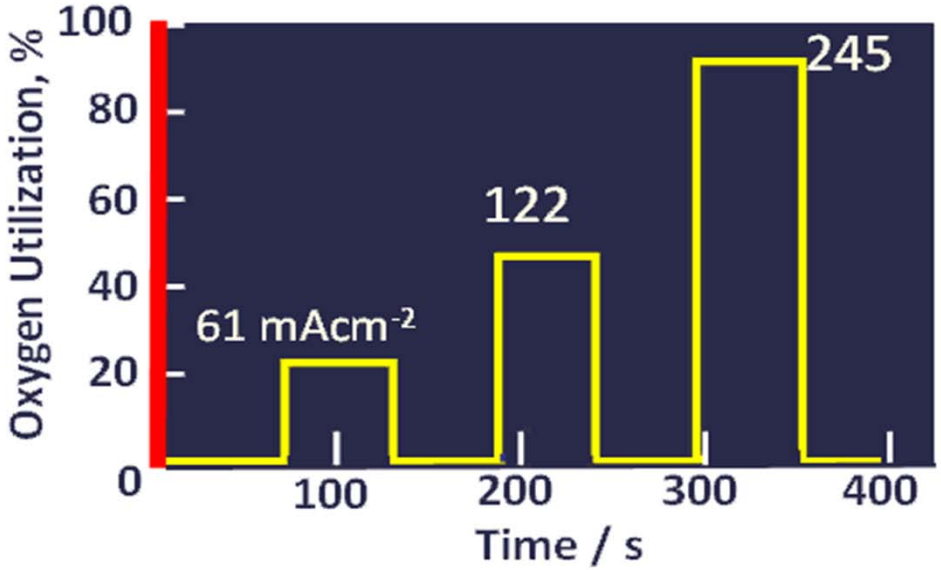
Real-Time Imaging

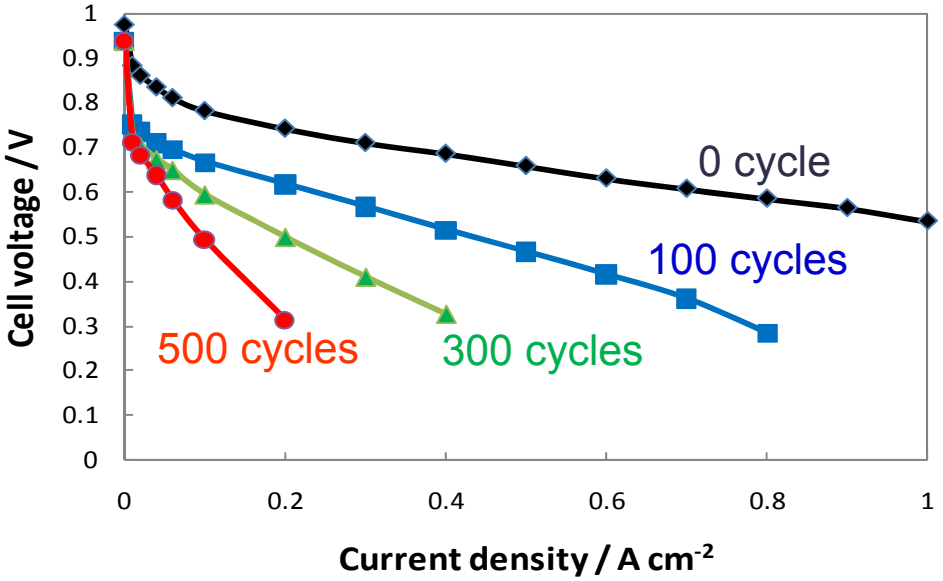




Visualization of CO_2 at the Cathode during the Degradation of Carbon Support

Degradation during Start-up/Shut-down Cycles of FCs

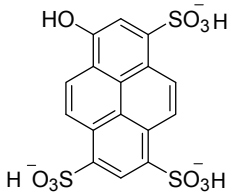
The anode flow channel was alternately filled with H_2 and Air in 30 s. Gas flow rate was 100 $mLmin^{-1}$.



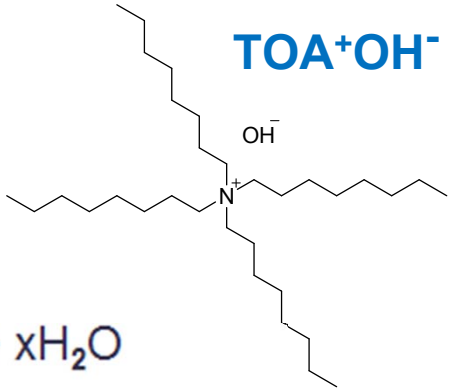
As the cycles increased, the degradation rapidly proceeded.
It is now known to be caused by corrosion at the cathode.

CO_2 formation

HPTS

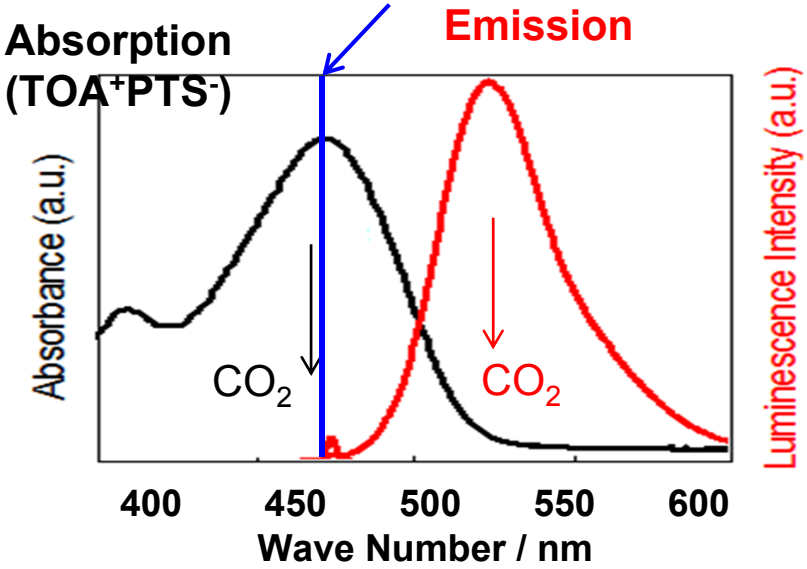


TOA^+OH^-



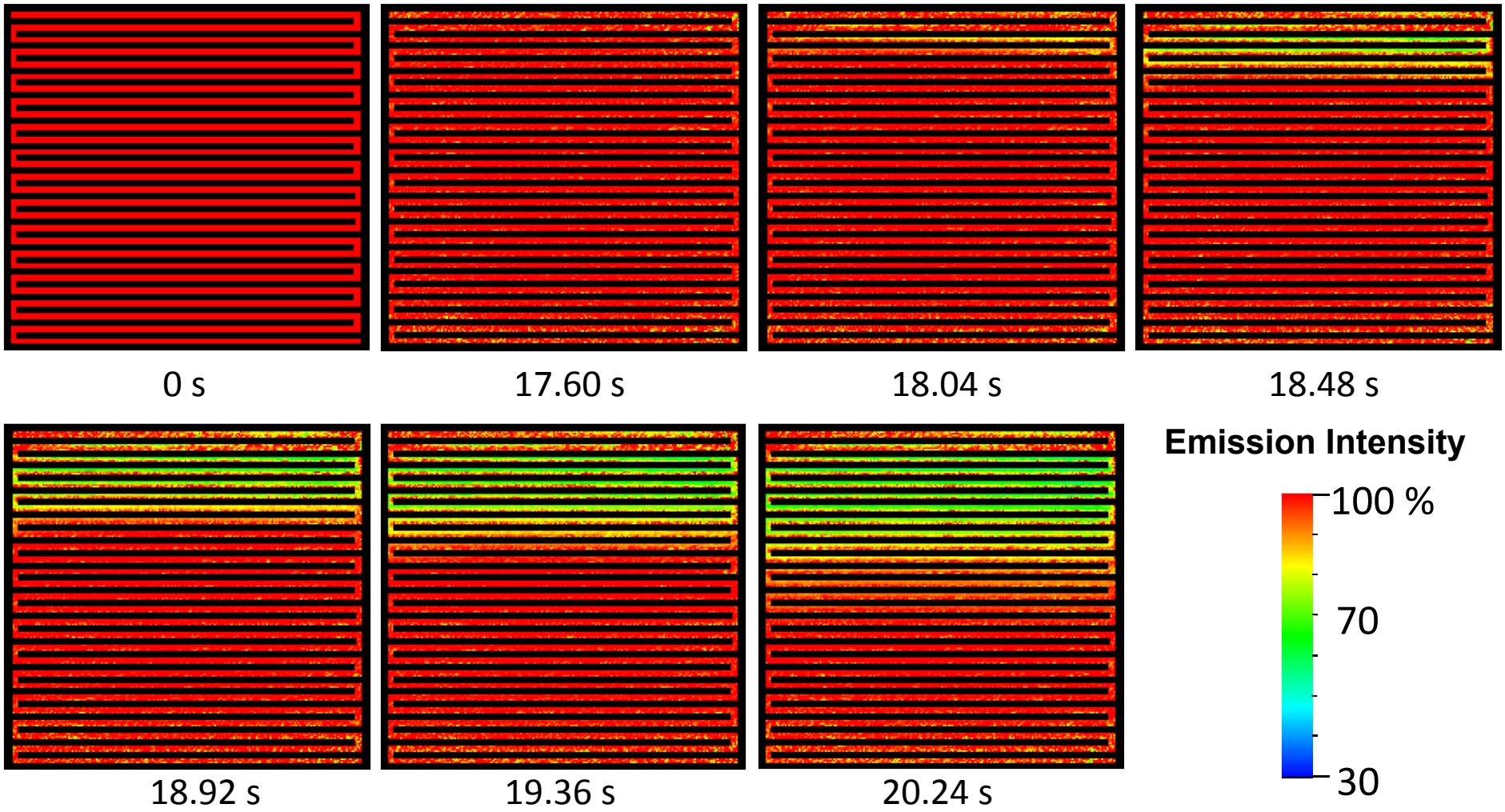
$$TOA^+PTS^- + xH_2O \rightleftharpoons CO_2 \rightleftharpoons TOA^+HCO_3^- + (x-1)H_2O + HPTS$$

Excitation (**473nm**)



Emission change at *cathode*
With change of anode atmosphere from H_2 to Air

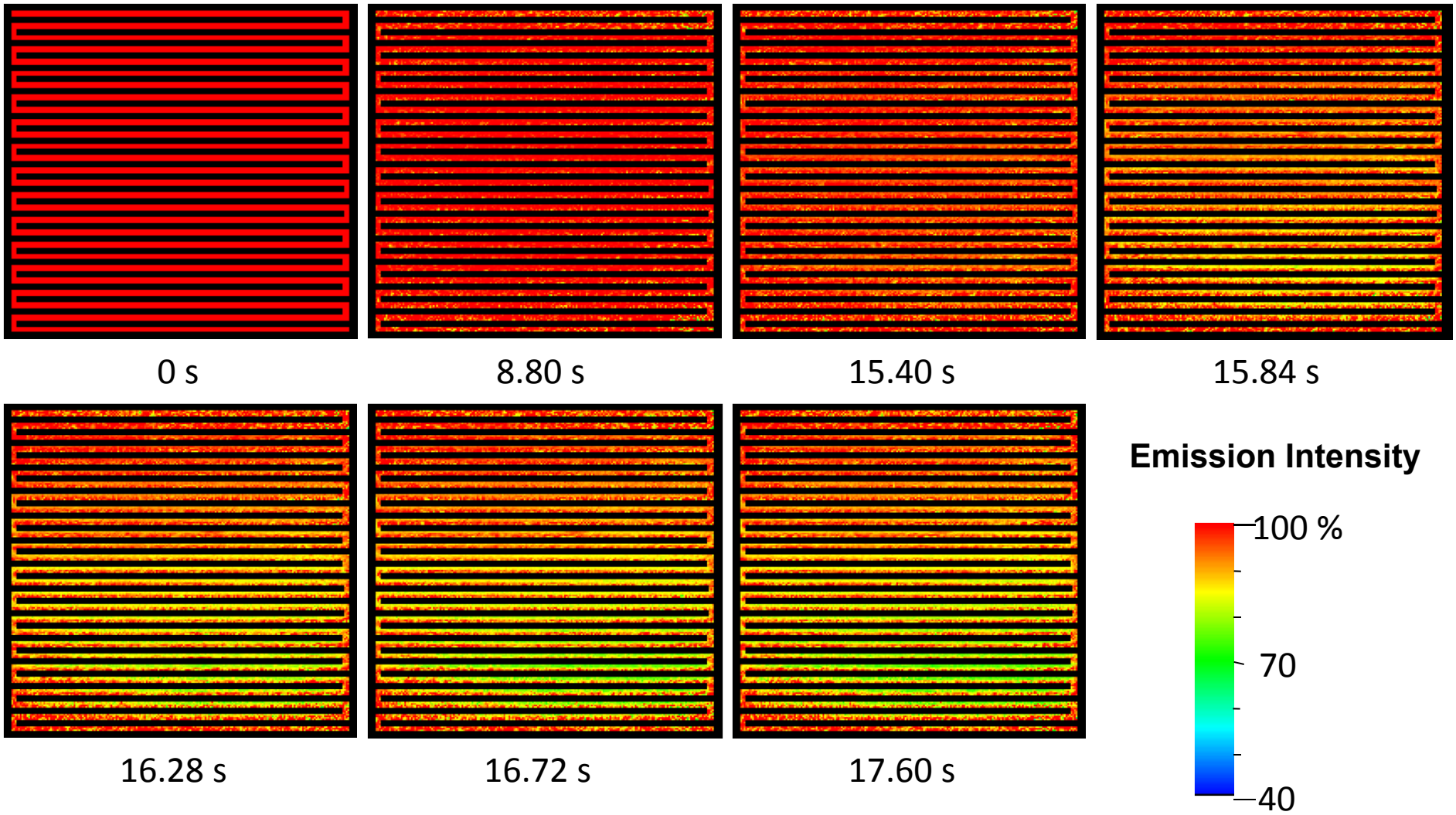
Stop simulation



- **CO_2 formation was detected in milliseconds at the cathode.**
- **Degradation proceeded in the upper part of the cathode.**

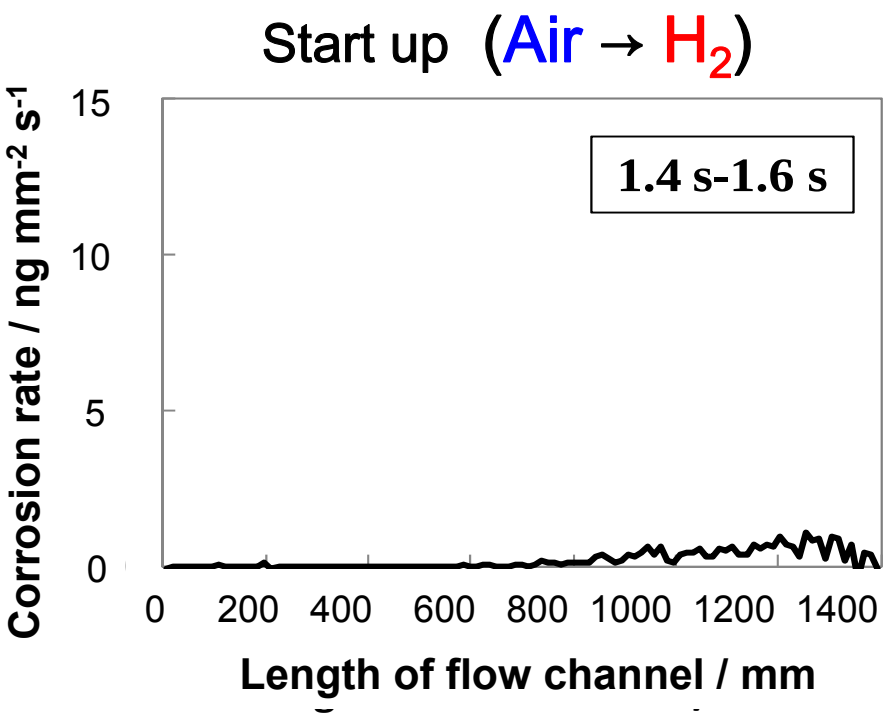
Emission change at cathode
With change of anode atmosphere from Air to H_2

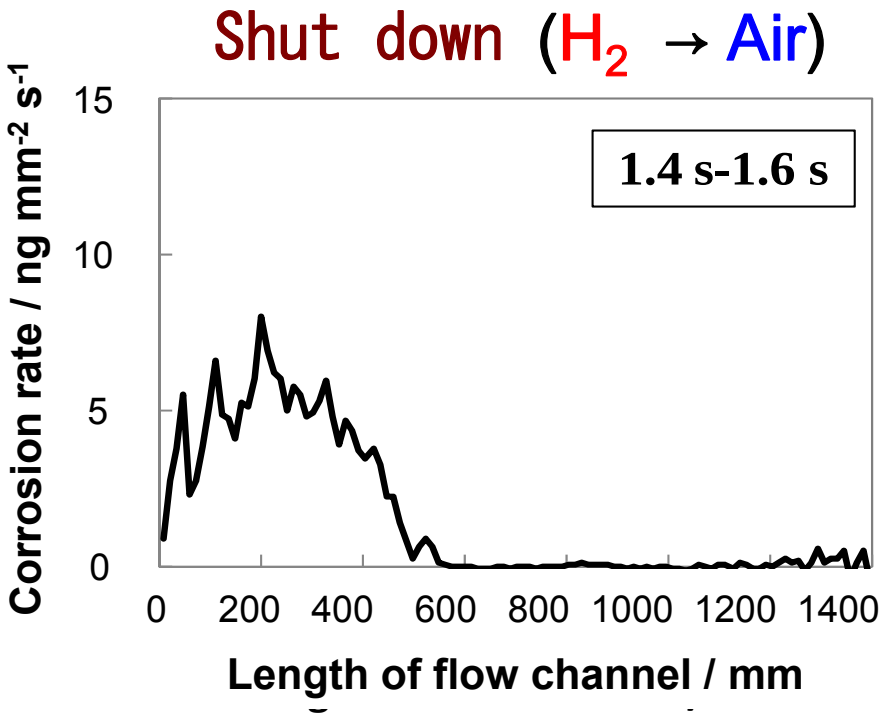
Start-up simulation



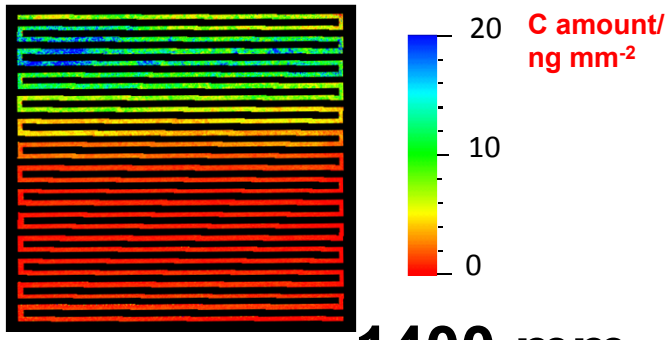
- **Degradation proceeded in the lower part of the MEA.**

Carbon corrosion rate at cathode





0 mm →



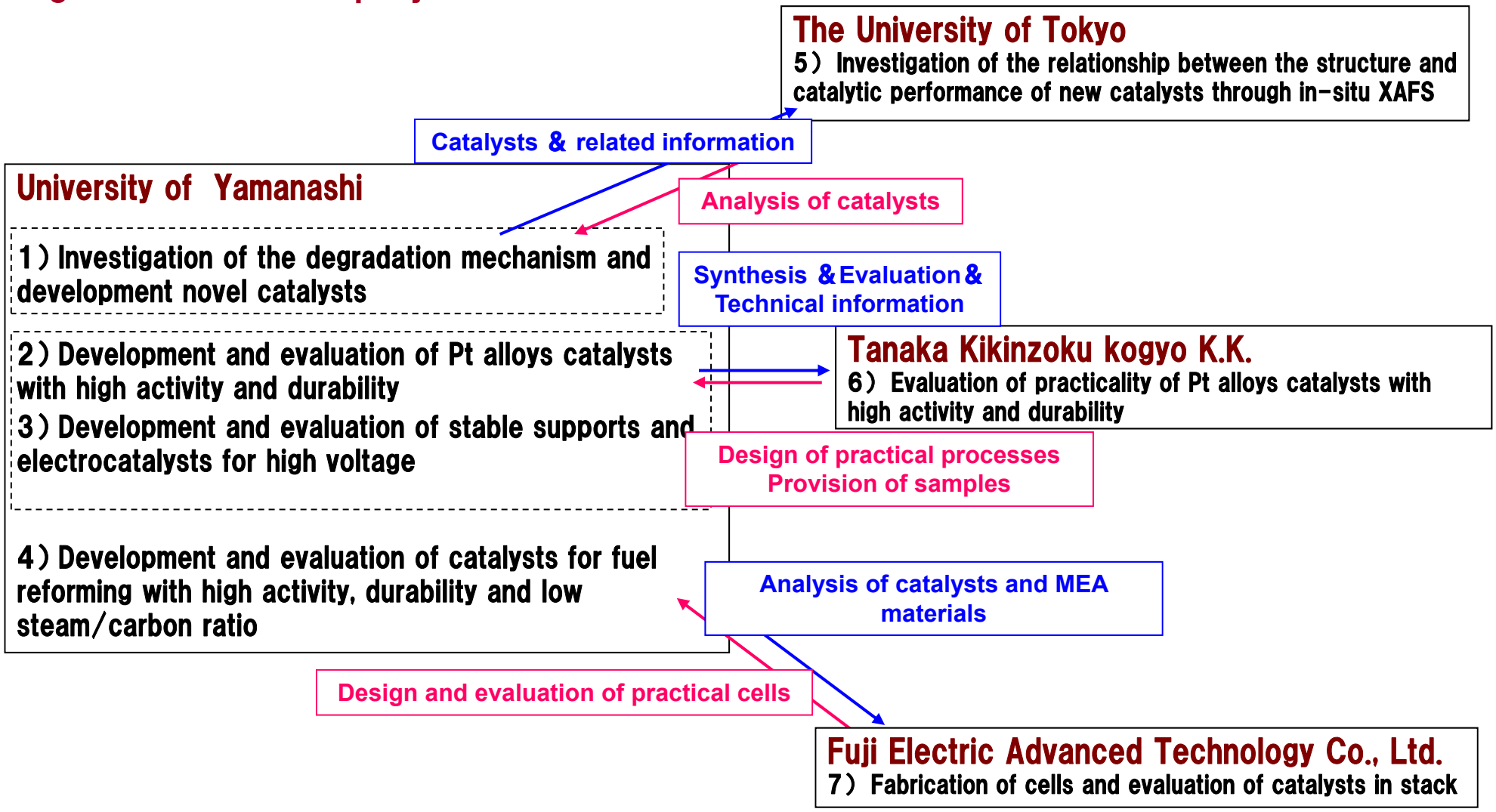
→ 1400 mm

Air → H_2 : 0.4秒まで腐食速度が増加した後、直ちに減少

H_2 → Air : 2.0秒まで腐食速度が増加した後、腐食量一定、腐食速度減少せず

2. Investigation of catalysts with high activity and durability

Organization of the project



Development of High Performance ORR Catalysts

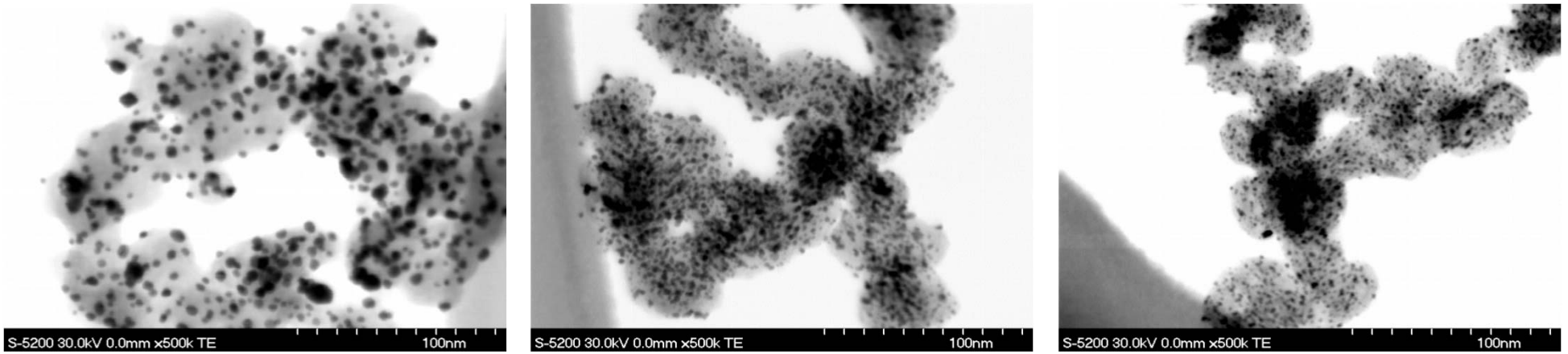
$$J\ (A/g) = I\ (A/cm^2) \times S\ (cm^2/g)$$

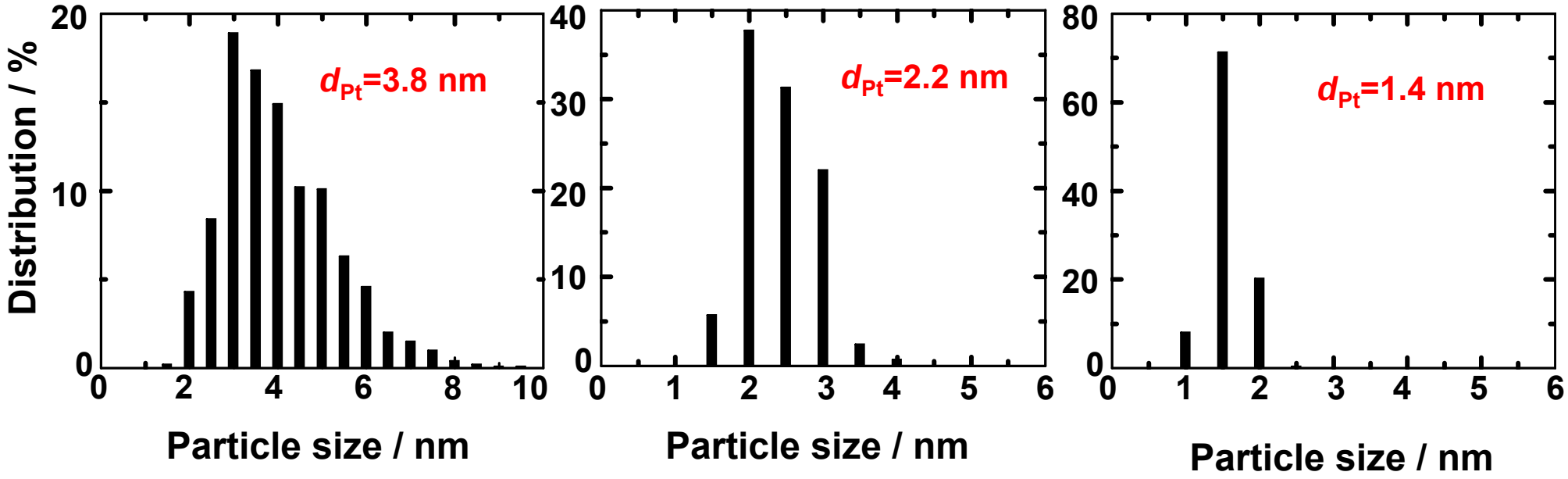
Confirm an enhanced *J* value by increasing the *S* by dispersing Pt on high surface substrates

Needs to answer to the question;

So-called "*Paticle Size Effect*" is true at ORR?

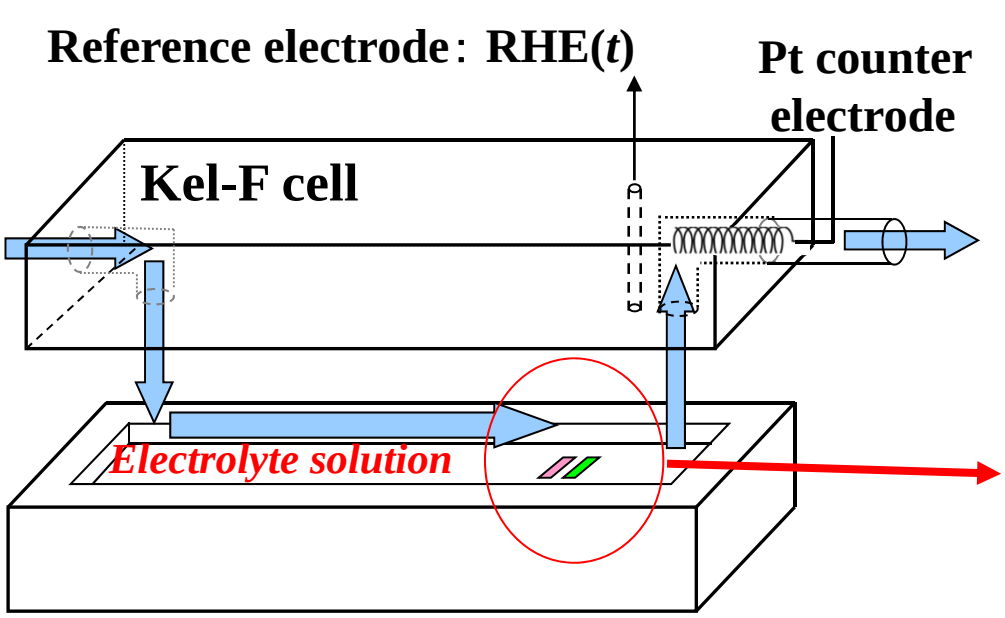
STEM Images & Size Distributionof Pt-CB

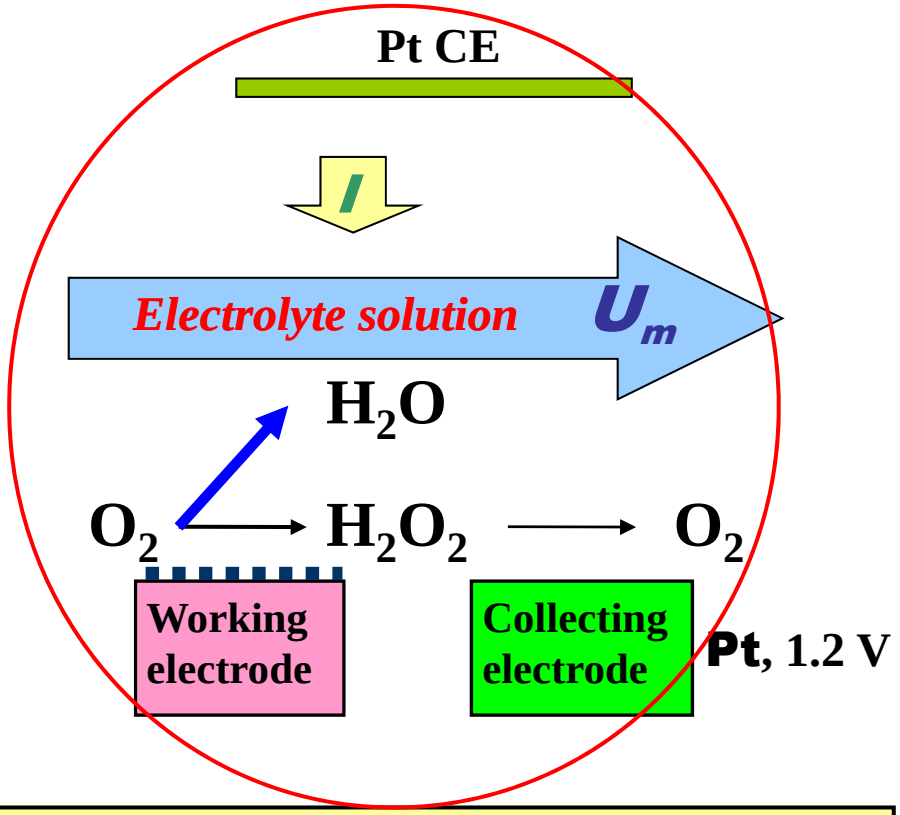




Channel flow double electrode(CFDE) method

Merits: Determination of j_K & yield of bi-products over wide temperature range (r.t. to 110°C) in a closed system under low electric noises





Hydrodynamic voltammograms by laminar flow of O_2-saturated 0.1 M $HClO_4$

Mean flow rate U_m = 10 ~ 50 cm/s

Temperature = 20 ~ 110°C

J. Electroanal. Chem., 574 (2005) 339.
J. Phys. Chem. B, 109 (2005) 5836.
J. Phys. Chem. B, 110 (2006) 16544.

Working electrodes
(Nafion)-bulk Pt
Nafion-sputtered Pt or Pt-M alloys
Nafion-supported Pt or Pt alloy/C

$$\frac{1}{I} = \frac{1}{I_k} + \frac{U_m^{-1/3}}{1.165nF[O_2]w(D^2x_1^2/h)^{1/3}}$$

Determination of Kinetic Current

$$\frac{1}{I} = \frac{1}{I_k} + \frac{U_m^{-1/3}}{1.165nF[O_2]w(D^2x_1^2/h)^{1/3}}$$

U_m: Mean flow rate

n : Electron number

F : Faraday const.

h : A half height of flow channel

D: Diffusion coefficient

x_1: Length of WE

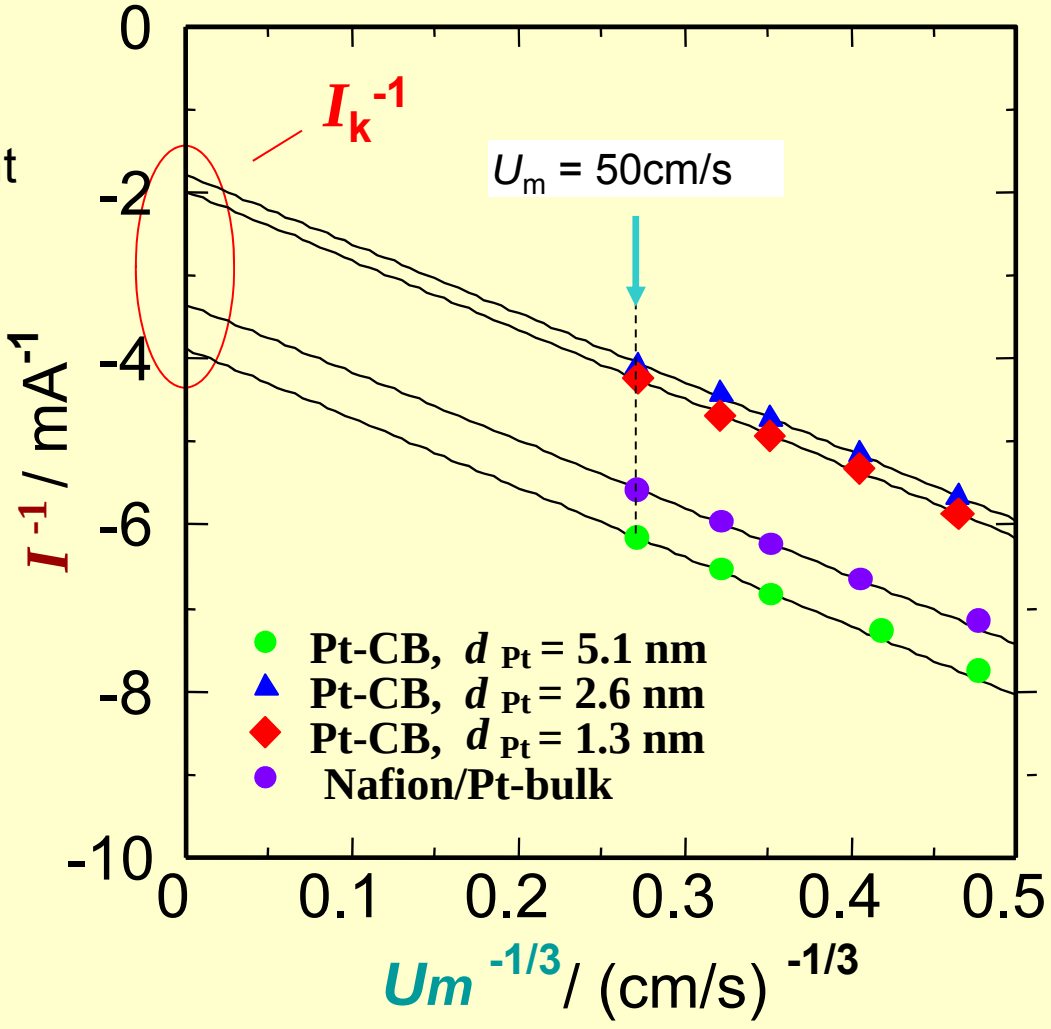
W : Width of WE

O_2 saturated 0.1 M $HClO_4$, 30℃

Scan rate: 0.5 mV/s

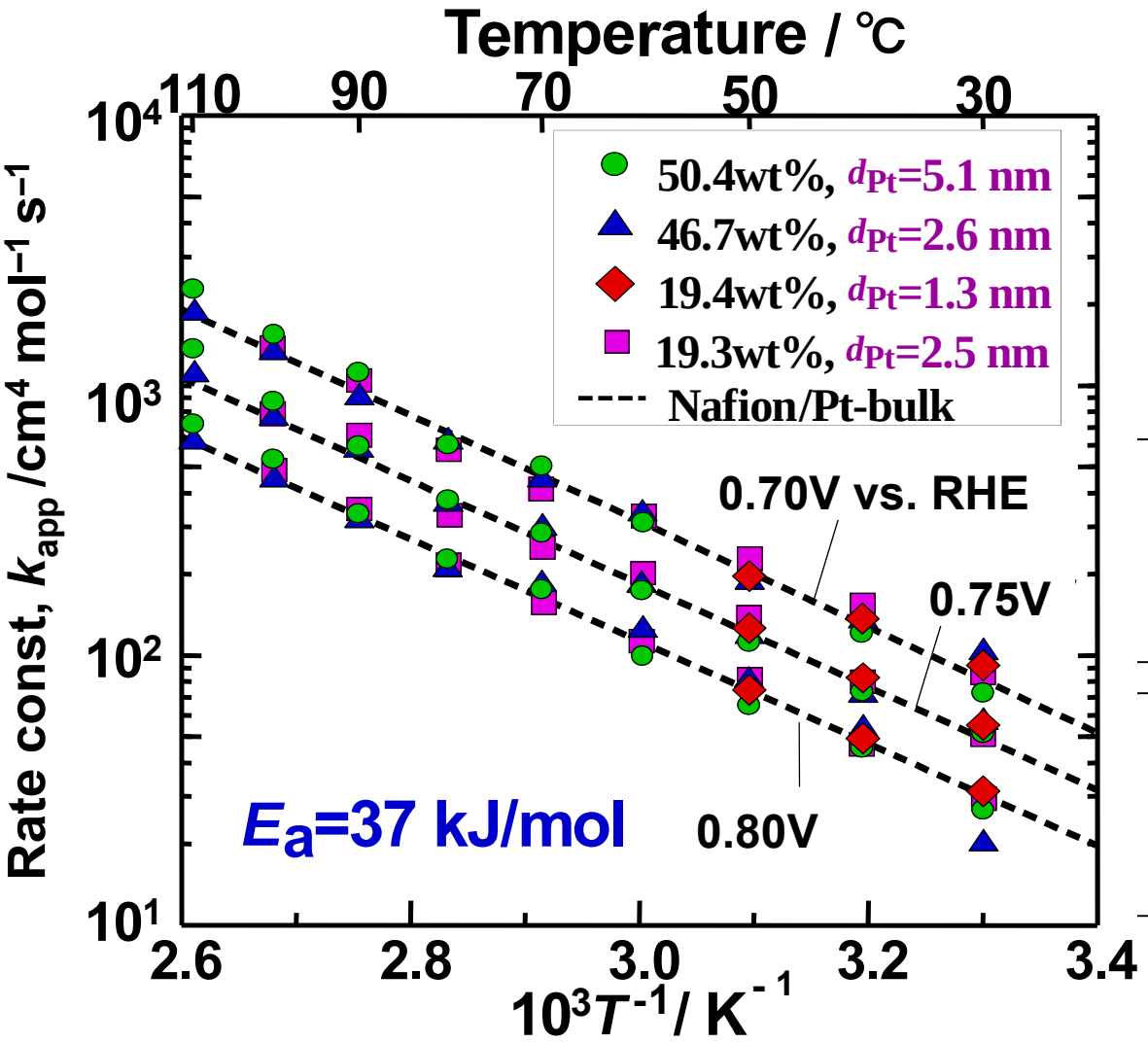
Flow rate: U_m = 10-50 cm/s

Potential: -0.525 V *vs*. E°
(0.760 V *vs*. RHE, 30℃)



Arrhenius Plots of Rate Consts for the ORR

$$I_k / 4FS = -\text{const.} \times k_{ORR}[O_2][H^+] = -k_{app}[O_2][H^+]$$



Electrocatalytic Activity

(1) No particle size effect

⇓

Proportional to S_{Pt}

(2) 80℃ ⇒ 110 ℃

⇓

Activity X3~4

1) *Yano et al., J. Phys. Chem. B,* 110, 16544-16549 (2006) .

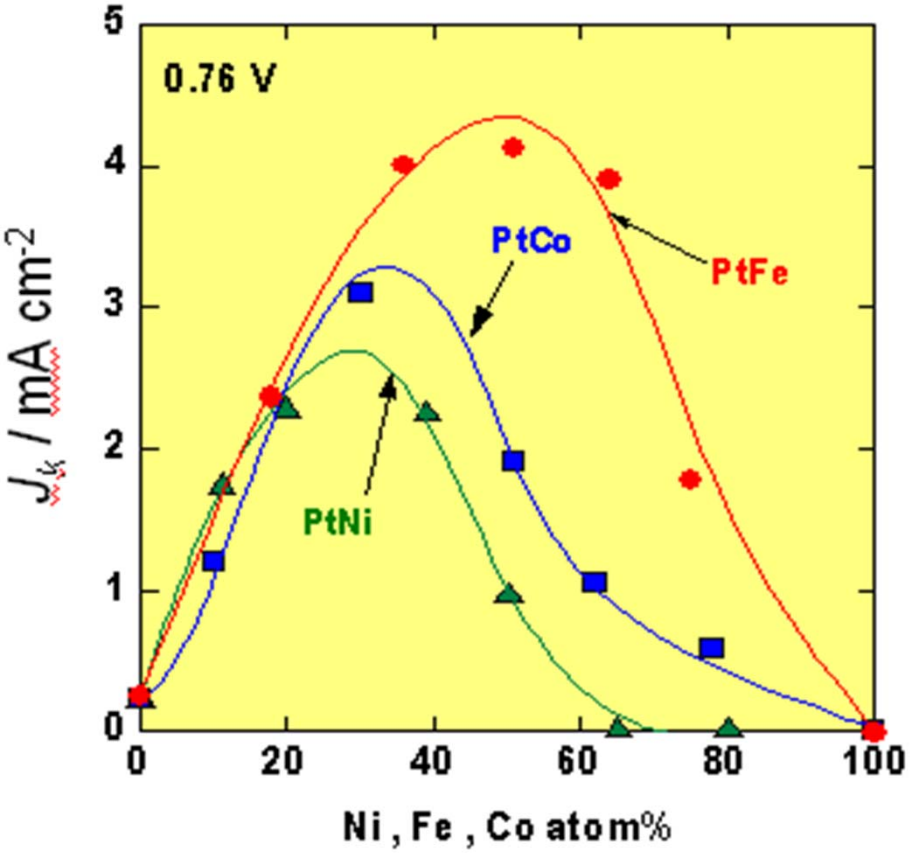
2) *Yano et al., Phys. Chem. Chem. Phys.,* 8, 4932-4939 (2006) .

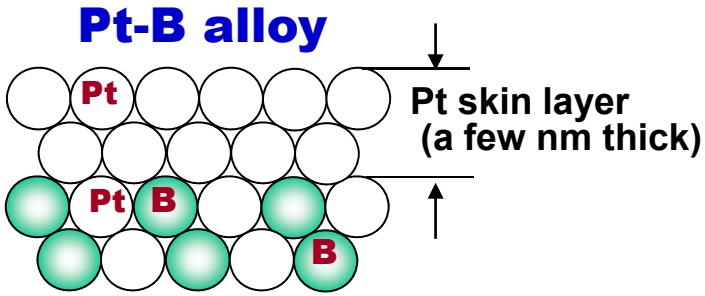
Development of High Performance ORR Catalysts

$$J\ (A/g) = I\ (A/cm^2) \times S\ (cm^2/g)$$

Increase of I by alloying Pt with transient non-precious metals

Enhancement of ORR at Pt-skin/ Pt-(transition)M





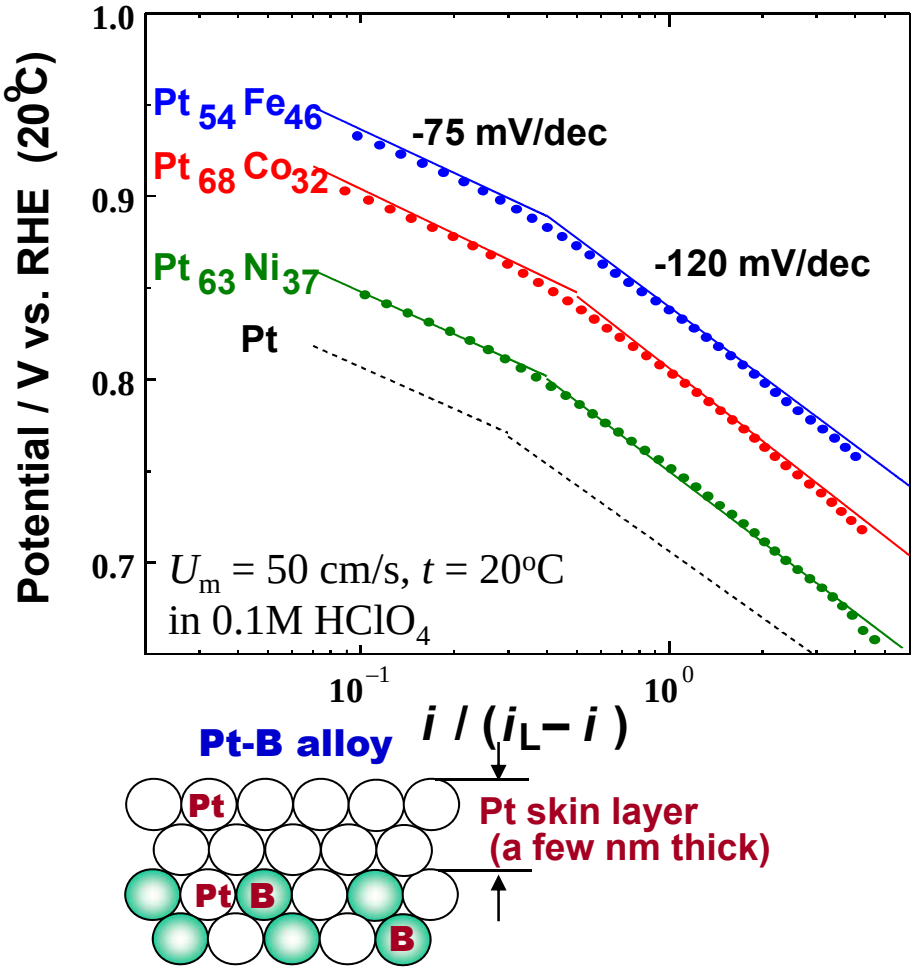
◆ Pt activity was enhanced 10 -20 times by alloying with non-precious metals.

◆ It was also found that Pt skin-layer is formed on the alloys by leaching out of non-precious metals from the surface layer.

◆ This is the first observation of the composition dependent enhancement by Pt-skins underlined with Pt-M alloys.

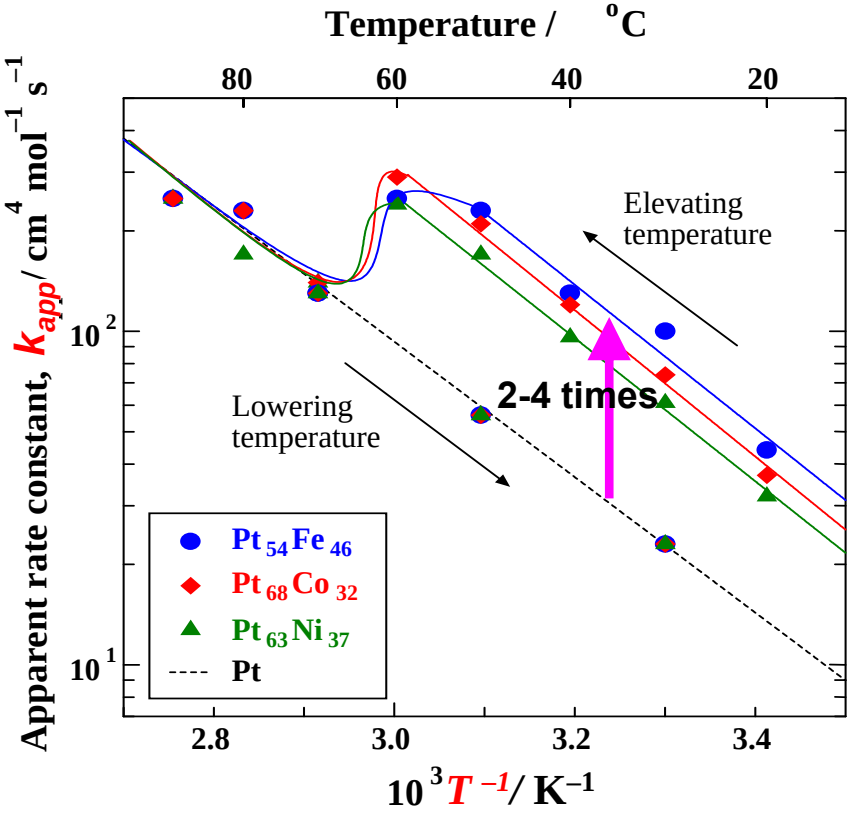
T. Toda, H. Igarashi, M. Watanabe, *J. Electrochem. Soc.*, 145, 4185 (1998) CV, XPS
T. Toda, H. Igarashi, M. Watanabe, *J. Electroanal. Chem.*, 460, 258 (1999) CV, XPS
T. Toda, H. Igarashi, H. Uchida, M. Watanabe, *J. Electrochem. Soc.*, 146, 3750 (1999) CV, XPS ; ←>300times cited, so far.

Enhancement of ORR at Pt Skin-layer Formed on Pt alloys



Enhancement with the same Tafel slopes

The same rate determining step (1e transfer)



$$\log k_{app} = 2.303 \log Z - 2.303 \varepsilon_a / RT$$

ε_a = ca. 38 kJ mol^{-1} (Pt surface)

ε_a = ca. 41 kJ mol^{-1} (Pt alloy surfaces)

Strongly suggesting the following:

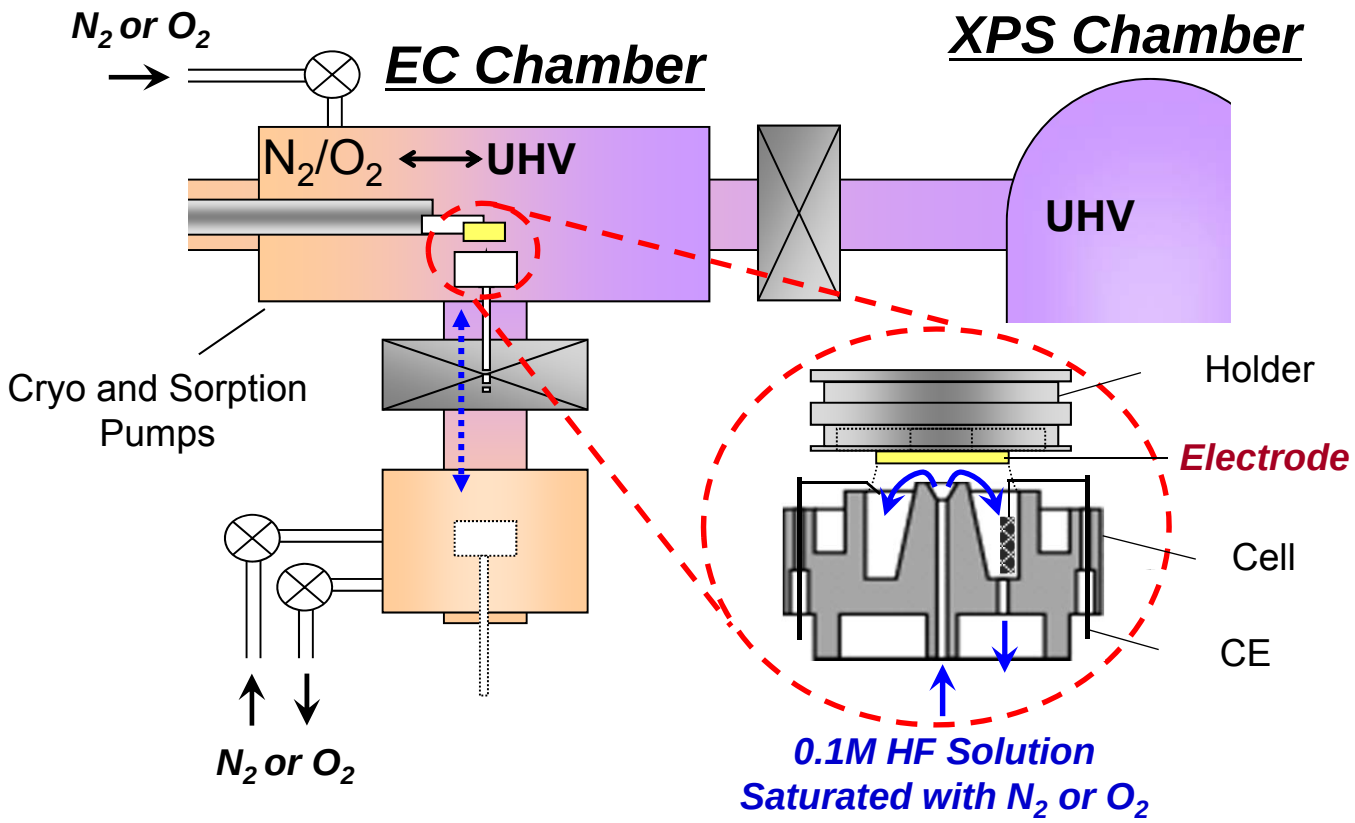
Increase in Z ⇔ Increase in θ_{O2}

T. Toda, et al., *J. Electrochem. Soc.*, **1999**, 146, 3750.

N. Wakabayashi et al. *J. Phys. Chem. B.* **2005**, 109, 5836.

Experimental

EC-XPS apparatus



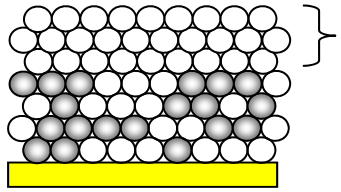
Electrolyte

N_2 or O_2-saturated 0.1 M HF

Test electrode

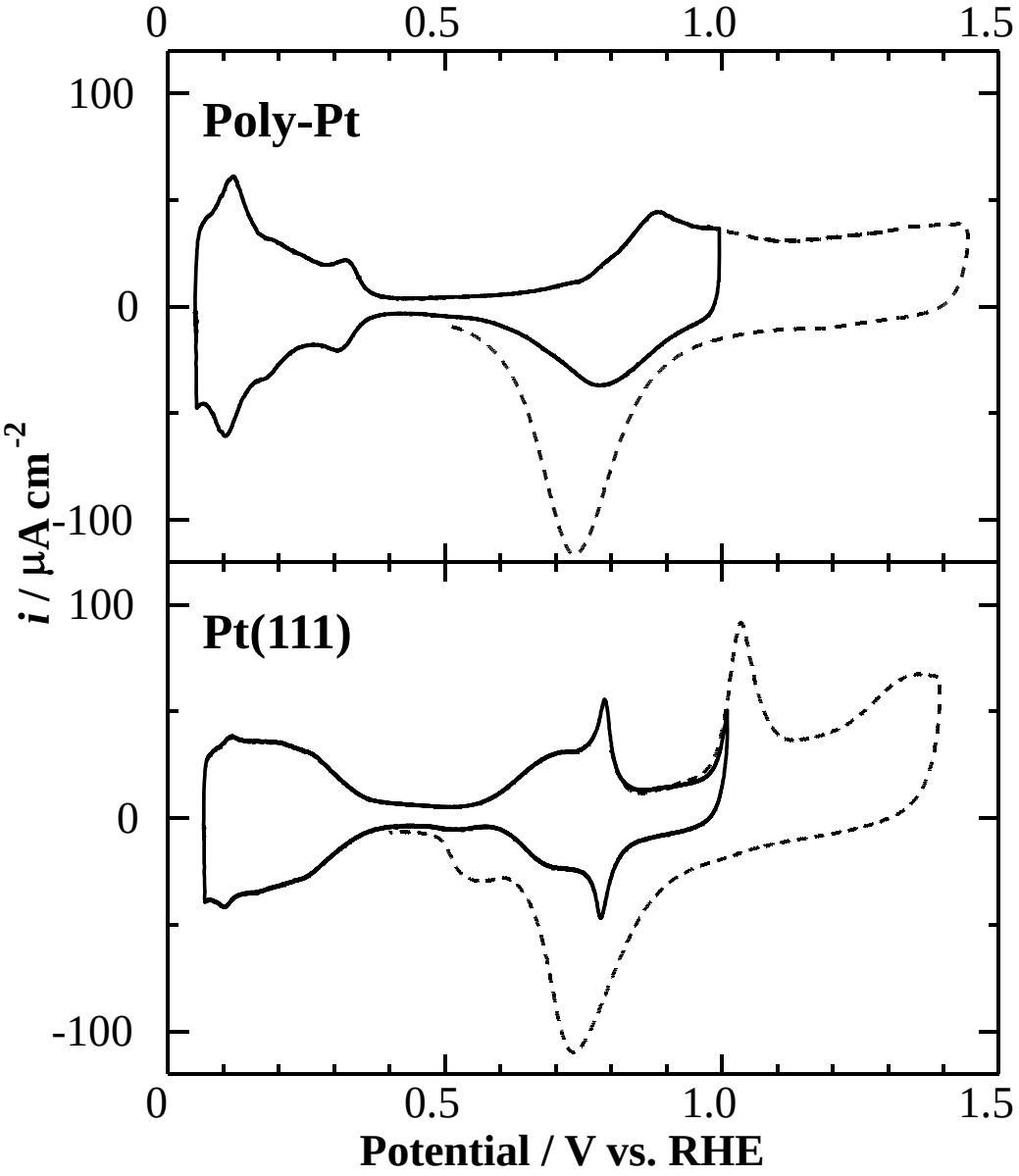
Thin film electrodes sputtered on Au disks.

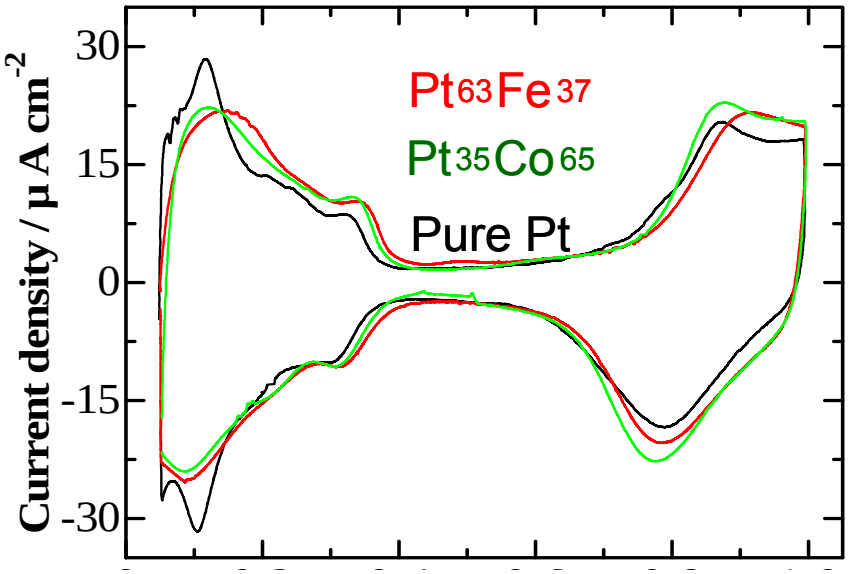
Pure **Pt**, **PtFe** and **PtCo** alloys



Pt skin layer

Each test electrode was polarized at a given potential E for 5 or 15 min in N_2 or O_2 saturated solution, respectively, followed by emersion from solution under potential control. Then, the electrode was transferred to UHV and XPS taken within 5 min.

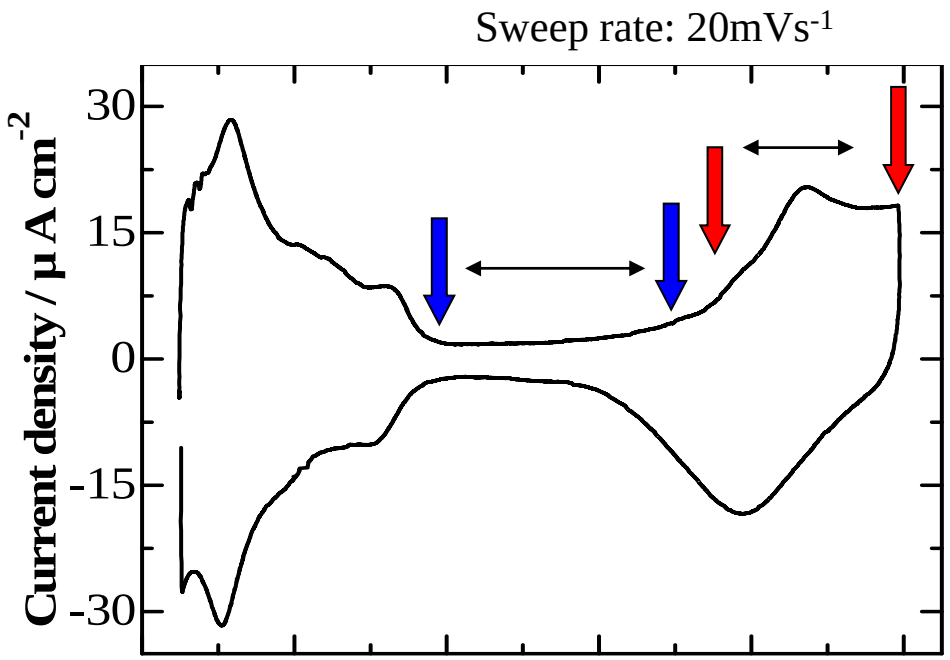


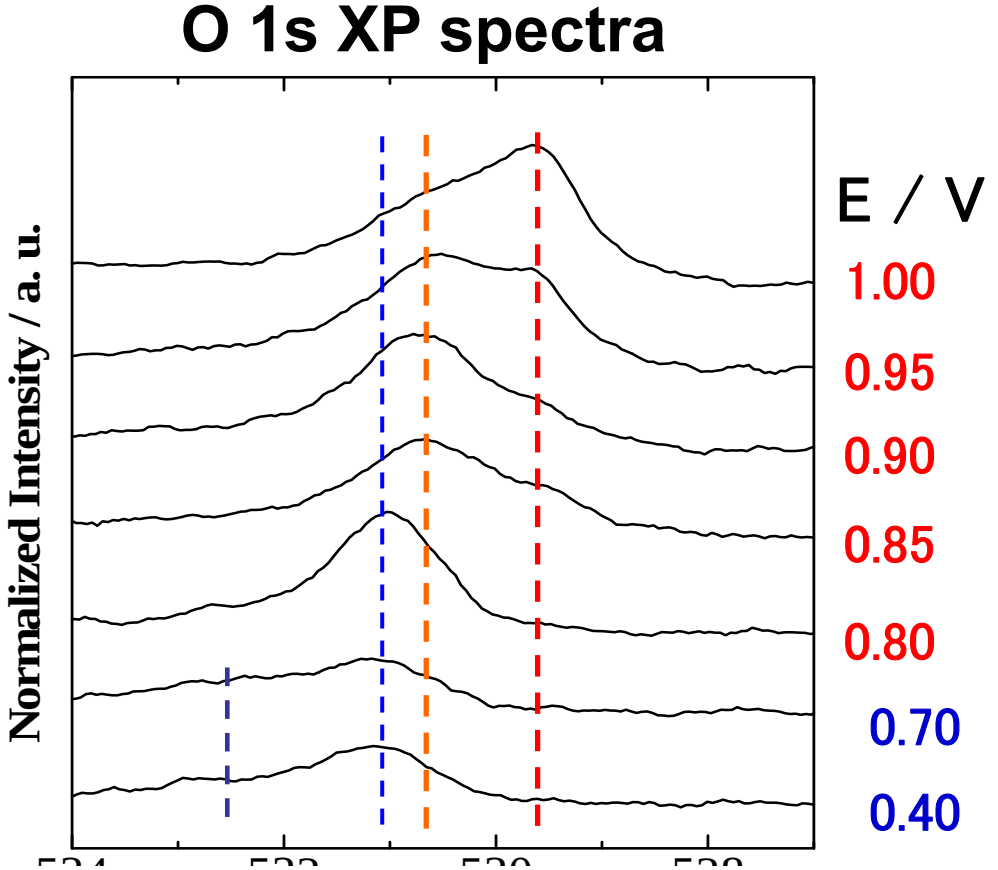


CVs at poly-Pt, Pt(111) and Pt skins in N_2 saturated 0.1N HF electrolyte, 20mVs^{-1}.

No noticeable differences from those in the conventional electrolytes were observed in the CVs.

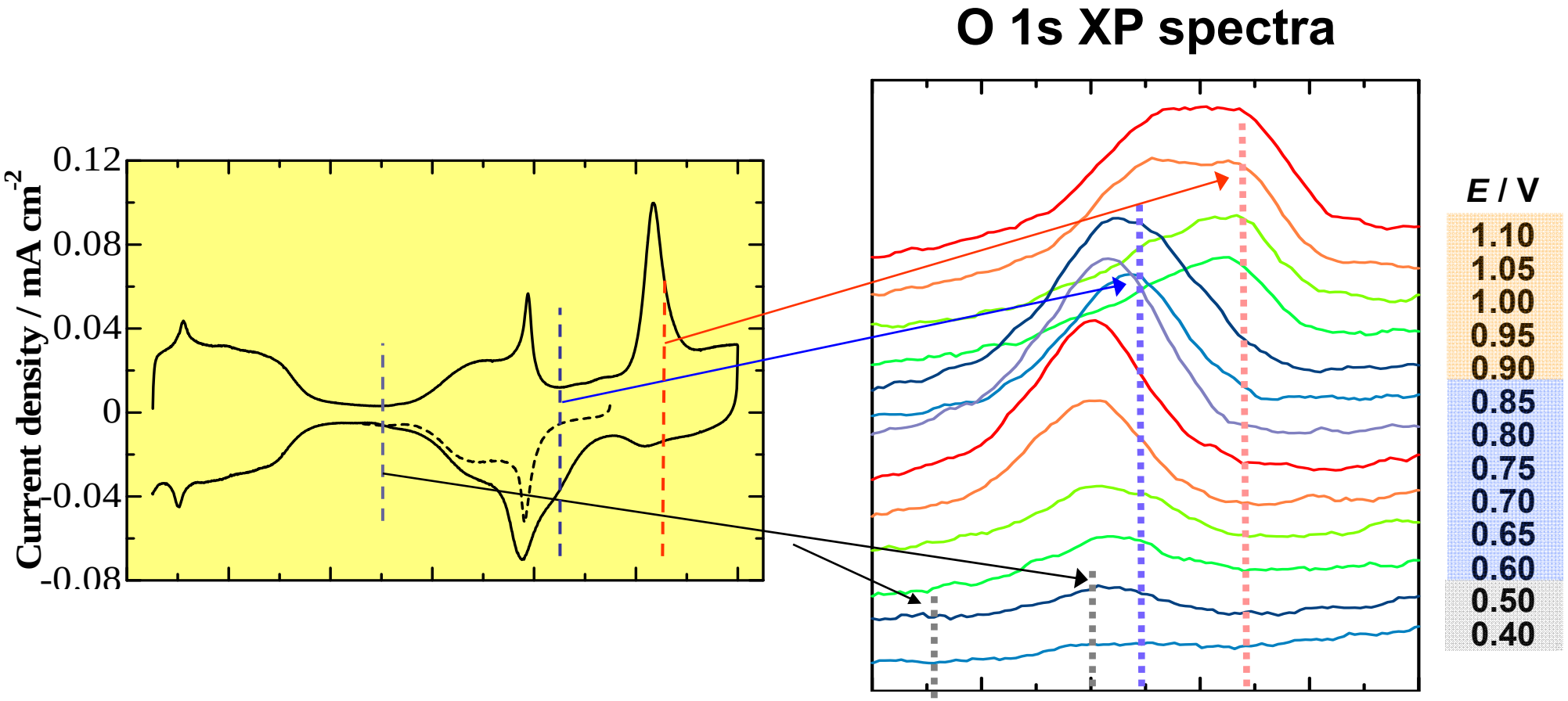
O1s spectra for pure Pt after emersion in N_2-purged solution





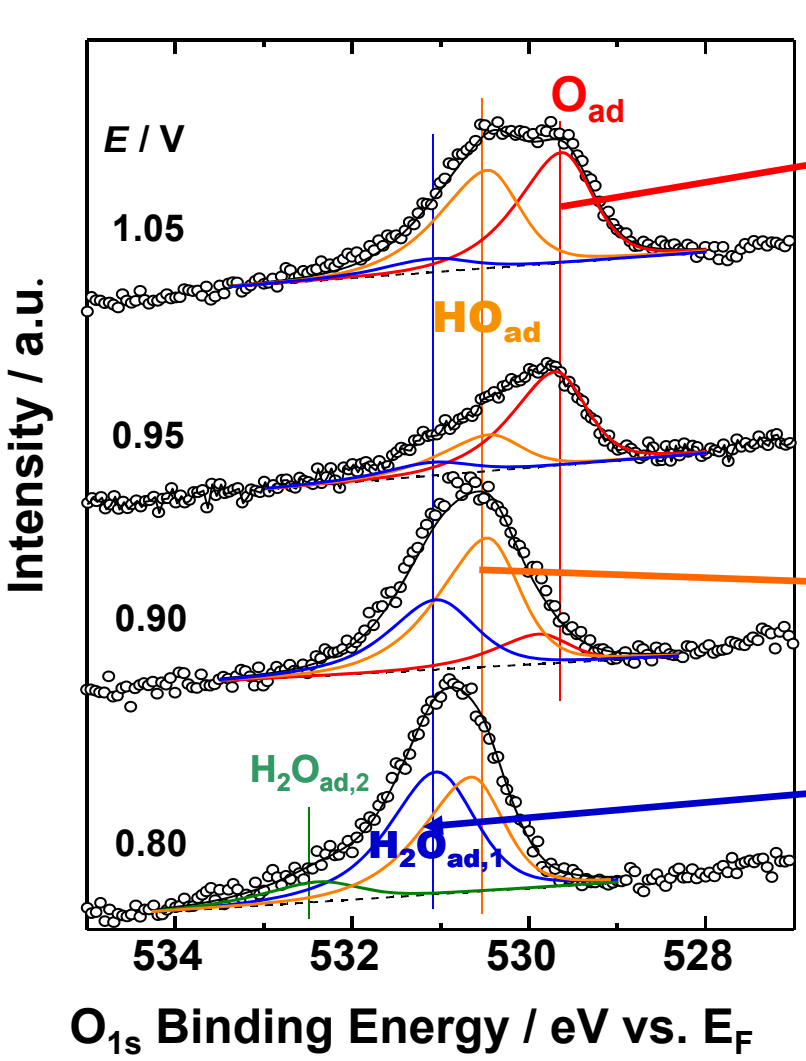
O1s spectra clearly changed with the electrode potential.

O1s spectra for Pt(111) after emersion from N_2-purged solution



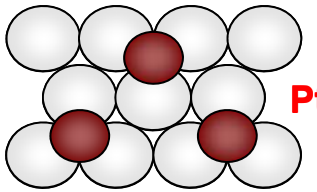
O1s spectra clearly changed with the electrode potential.

O1s spectra for Pt(111) after emersion from N_2-purged solution



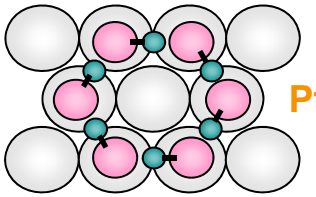
O_{ad} (529.5 eV)

Norton P. R. *Surf. Sci.* **1975**, *47*, 98.



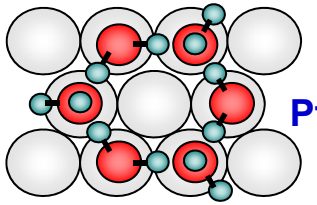
OH_{ad} (530.5 eV)

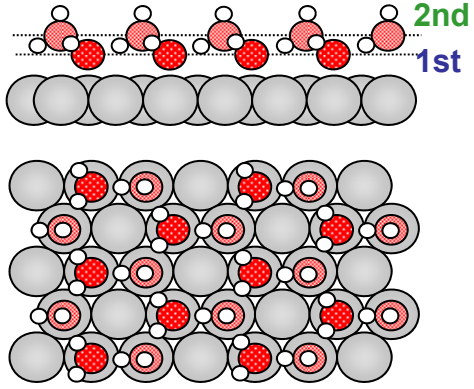
Fisher G.B. et al. *Surf. Sci.* **1980**, *94*, 446.



H_2O_{ad}(532.5 eV)

Fisher G.B. et al. *Surf. Sci.* **1980**, *94*, 446.



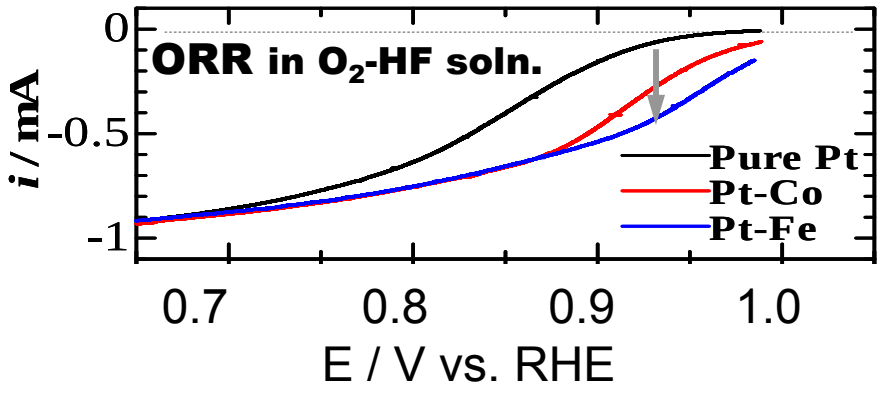


Bi-layer model

$H_2O_{ad,1}$ Pt atom

$H_2O_{ad,2}$ OH_{ad}

Mechanism of the ORR enhancement at Pt-based alloys



$$i_K / (4FS) = - k [H^+][O_{2,bulk}]$$

$$k = Z e^{-Ea/RT}$$

◆ The enhanced O_{ad} coverage at Pt skin-layers, compared to pure Pt, should be ascribed to the electronic structure modified by that of the underlying alloy.

◆ The increased O_{ad} values are clearly correlated with the increased Z values.

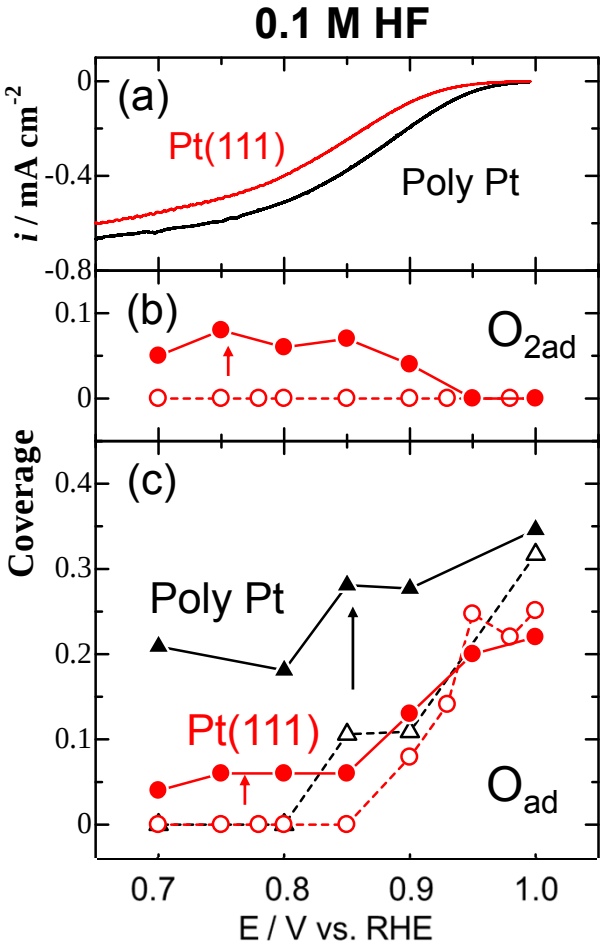
◆ Thus, we propose the enhancement mechanism below for the ORR at the Pt-skin surface, i.e., the enrichment of the limiting reactant O_{ad} for the slowest elementary step, resulting in the higher total reaction rate.

$$\begin{cases} O_2 \rightarrow 2\,O_{ad} & \textit{(enhanced)} \\ O_{ad} + H^+ + e^- \xrightarrow{r.d.s.} OH_{ad} & \textit{(slowest)} \\ OH_{ad} + H^+ + e^- \rightarrow H_2O & \textit{(slow)} \end{cases}$$

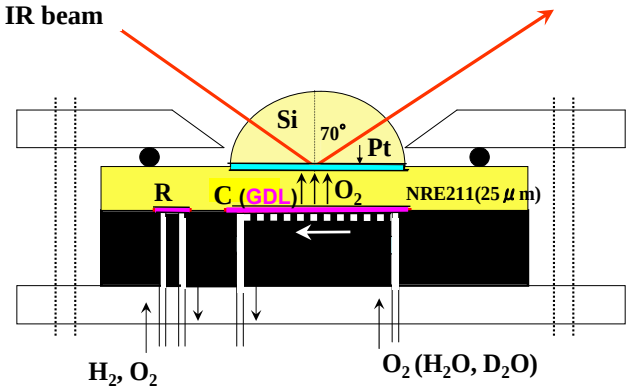
Fundamental Research on Catalytic Reactions in Fuel Cells

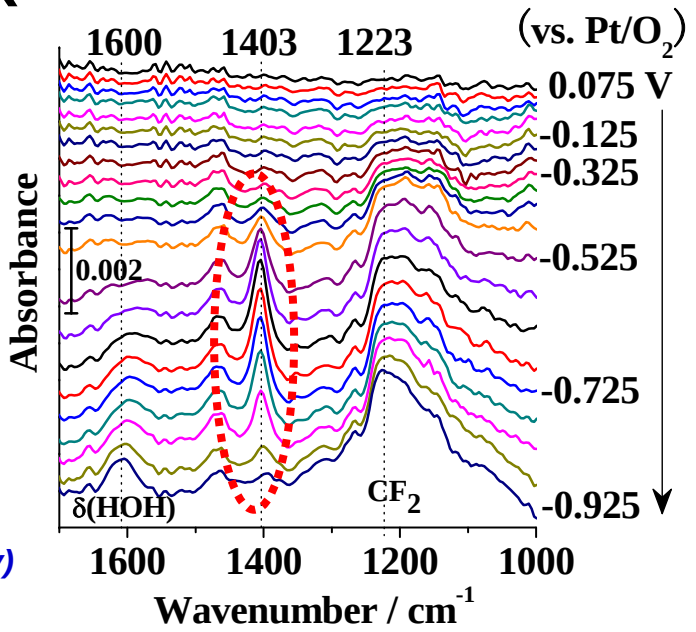
Analysis of oxygen species adsorbed on Pt electrodes during ORR -- Univ. of Yamanashi

EC-XPS



in situ ATR-FTIR



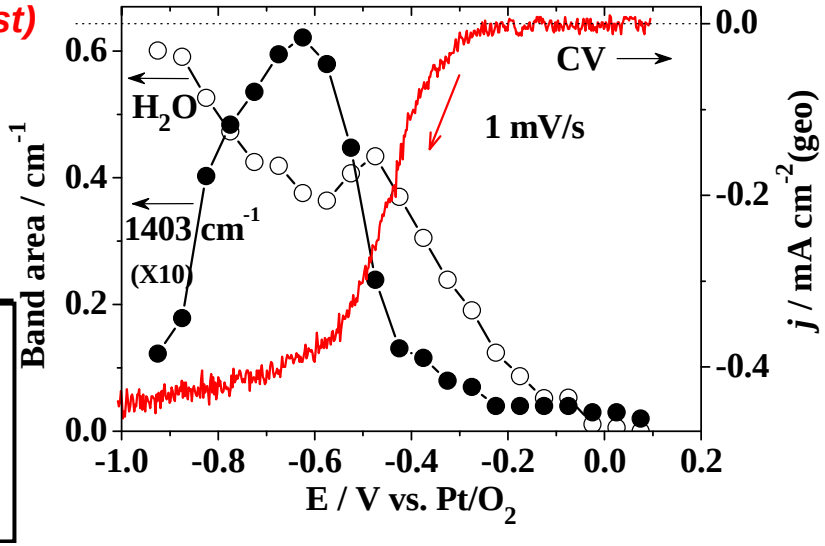


$O_2 \rightarrow O_{2ad}$ *(Sensitive to morphology)*

$O_{2ad} \rightleftarrows 2\ O_{ad}$ *(Pre-equiliblium)*

$O_{ad} + H^+ + e^- \rightarrow OH_{ad}$ *(slowest)*

$OH_{ad} + H^+ + e^- \rightarrow H_2O$

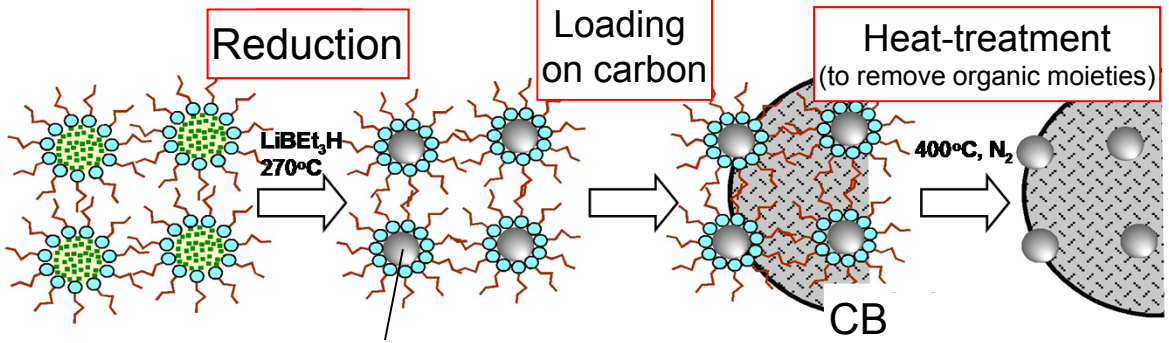


- **The low ORR activity at Pt(111) was ascribed to the low coverage of O_{ad}, at Pt(111) as compared to Pt polycrystalline.**
- **We have observed for the first time an oxygen species with a peak at 1403 cm^{-1} at a Pt/Nafion interface during ORR by using ATR-FTIR.**

Research and development on catalysts with high activity and durability

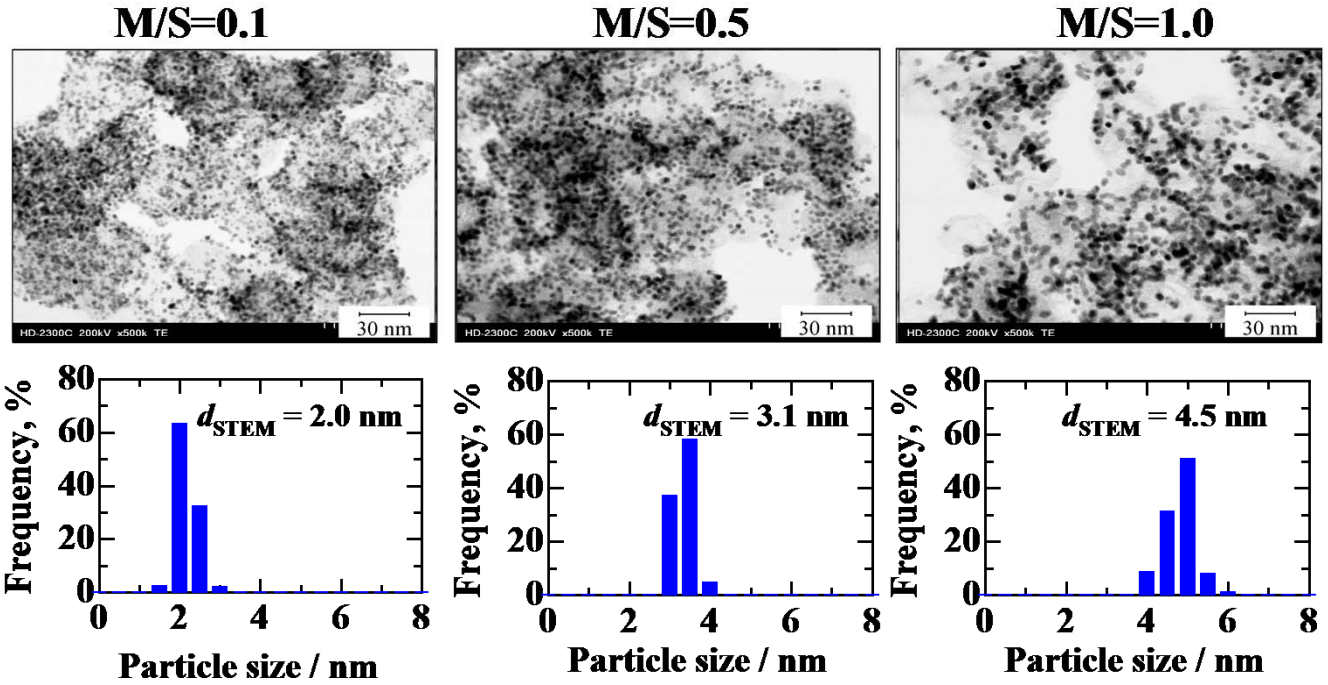
Size control of Pt-based catalysts by the nanocapsule method

Yamanashi Univ.



50 wt% Pt/C

M/S	Metal loaded (by TG)	Particle size	
	(wt%)	d_{XRD} (nm)	d_{STEM} (nm)
0.1	46.5	2.0	2.0 ± 0.2
0.5	48.8	2.9	3.1 ± 0.3
1.0	48.7	4.5	4.5 ± 0.4

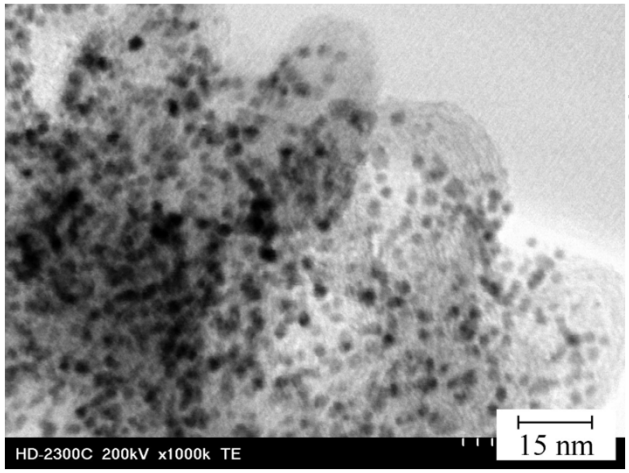


- We have succeeded to control the **Pt particle size** only by changing the **molar ratio of metal precursor(s) to surfactant (M/S)** in the preparation.
- We also succeeded to prepare **Pt-based alloy** catalysts with well-controlled particle size, composition and loading level.

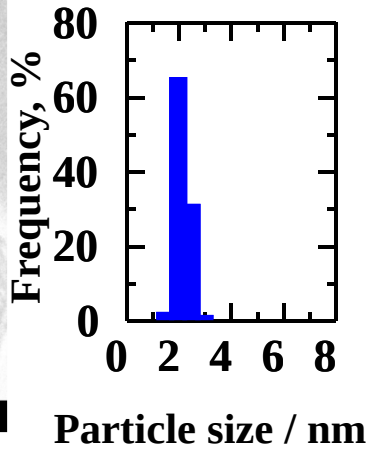
Control of alloy particle size and composition

Pt_3Co/C

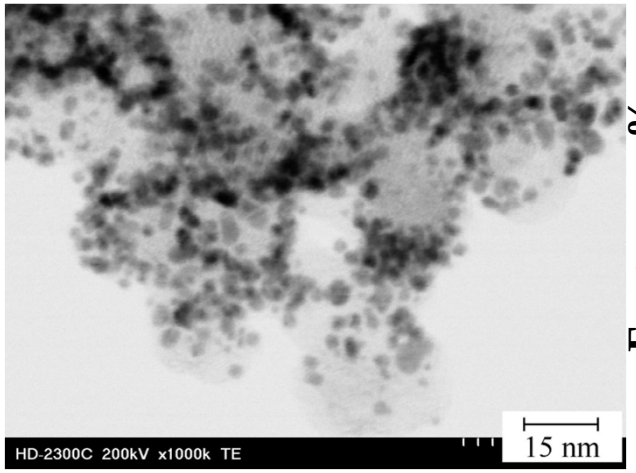
M/S=0.3



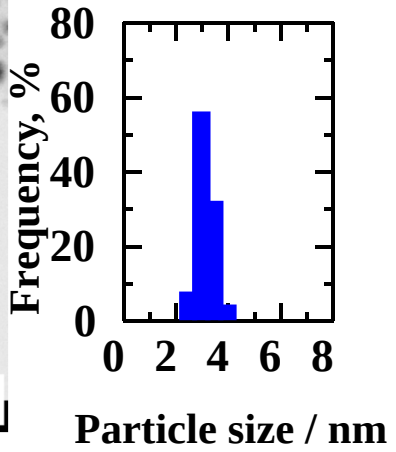
d = 2.0 nm



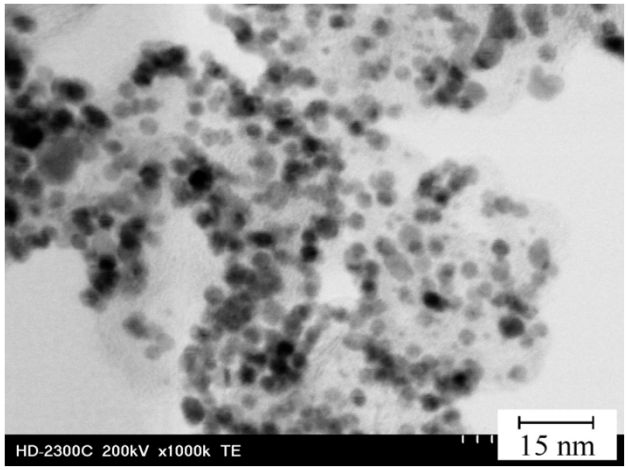
M/S=0.7



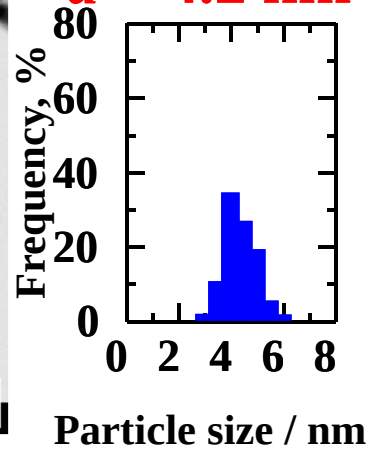
d = 2.9 nm



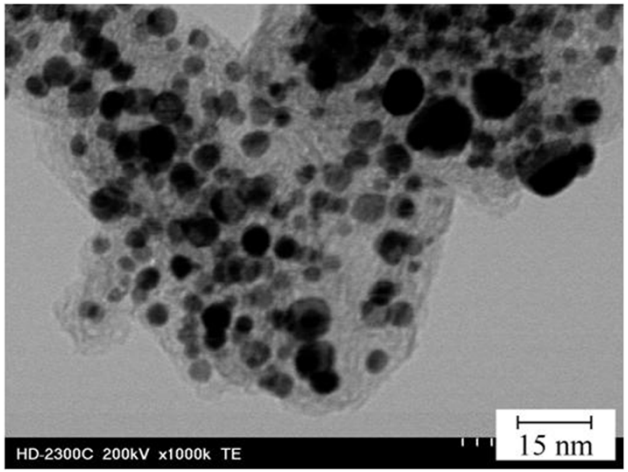
M/S=1.3



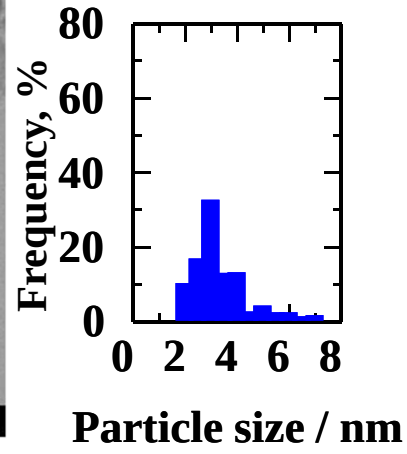
d = 4.2 nm



Commercial



d = 3.3 nm



Pt_3Co/CB prepared by nanocupsule method

M/S[a]	Loading (TG analysis)[b]	Composition[c]		Particle size
	(wt%)	Pt (atom.%)	Co (atom.%)	d_{STEM} (nm)
0.3	46.0	74.2 ± 1.4	25.8 ± 1.4	2.0 ± 0.2
0.7	48.1	76.0 ± 1.3	24.0 ± 1.3	2.9 ± 0.3
1.3	50.8	76.6 ± 1.2	23.4 ± 1.2	4.2 ± 0.6
Commercial	47.7	75.7 ± 8.2	24.3 ± 8.2	3.3 ± 1.3

a: Mole ratio of metal salt/surfactant, **Pt : Co** = 3 : 1 = **75% : 25%**

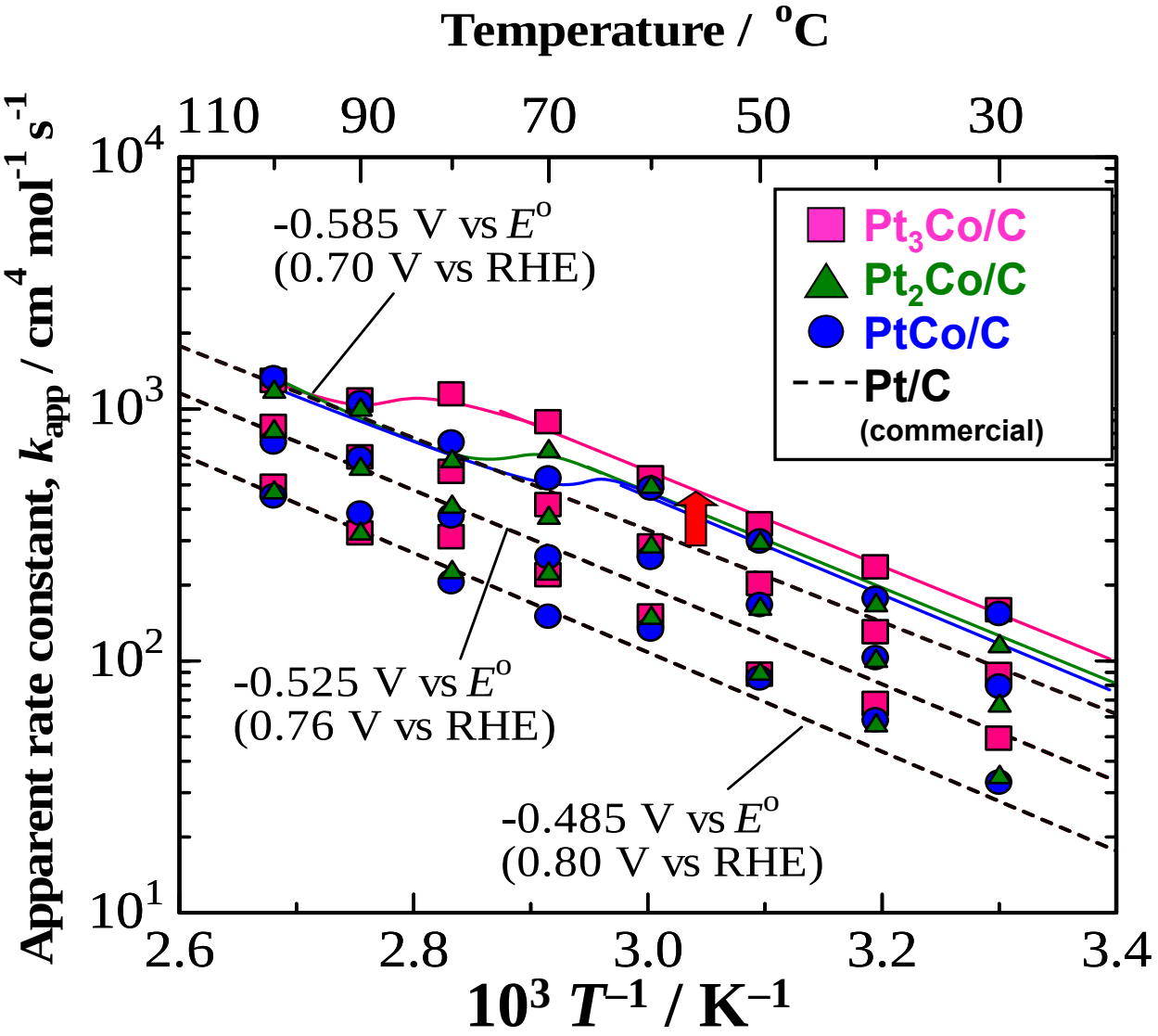
b: TG analysis after 600°C calcination in air; intended metallic composition was **50 wt%**

c: Average composition determined by EDX for 20 particles

Simultaneous control of particle size, composition and loading amount.

Arrhenius plot of ORR rate constants

$$k_{app} = -I_K / 4FS_{Pt}[O_2][H^+]$$



- In the low temp. region, k_{app} values at alloys were higher than that of Pt/C.
  - × 2.2 at Pt_3Co/C
  - × 1.5 at Pt_2Co& PtCo/C

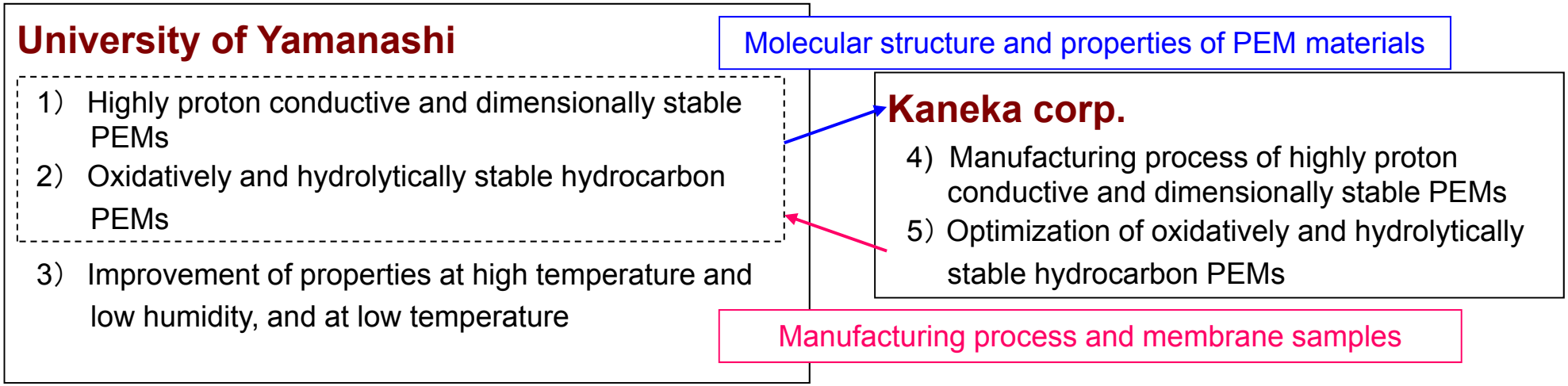
Hence, we can expect

×3 (A/g_{metal}) at *Pt_3Co/C*

or ×3.3 (A/g_{Pt})*

*Pt content in Pt_3Co was 90.4 wt%

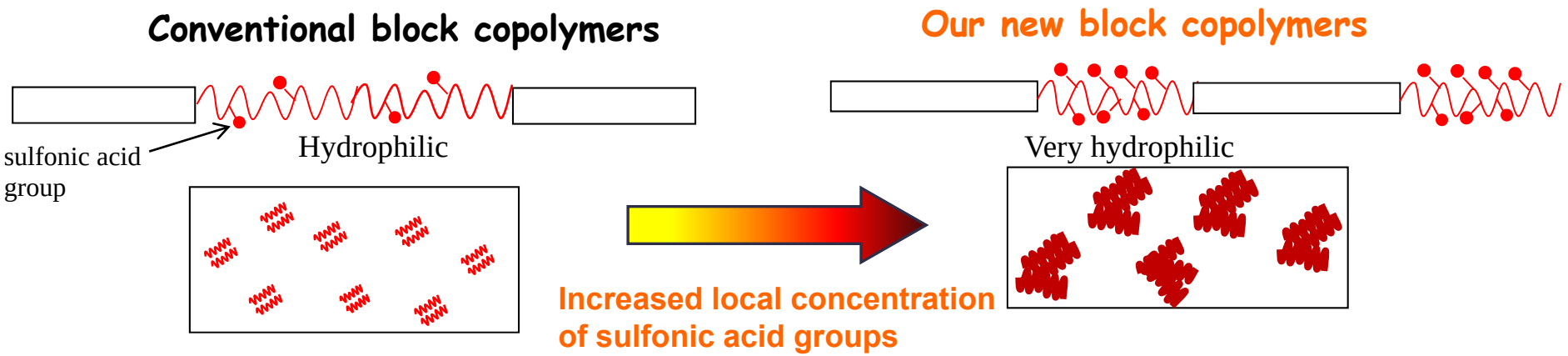
3. PEMs for wide range of temperatures and low humidity

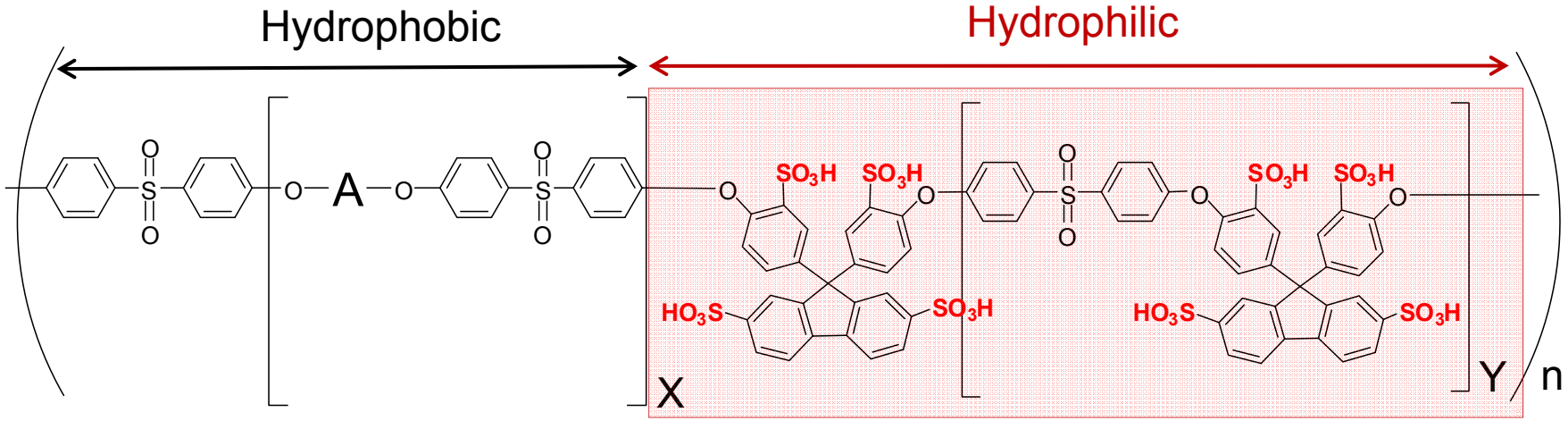


- Highly proton conductive and dimensionally stable PEMs
  - A) Molecular structure to promote proton conduction
  - B) Hydrocarbon PEMs to achieve high catalyst utilization and gas diffusivity
- Oxidatively and hydrolytically stable hydrocarbon PEMs
  - Electronically and sterically designed PEMs for better stability
- Improvement of properties at high temperature and low humidity
  - Molecular design of PEMs for high temperature and low humidity conditions
- Manufacturing process of highly proton conductive and dimensionally stable PEMs
  - Membrane fabrication in > 10 g scale and 100 cm^2
- Optimization of oxidatively and hydrolytically stable hydrocarbon PEMs
  - Provision of membrane samples to UY

New SPE block copolymers

Univ. of Yamanashi



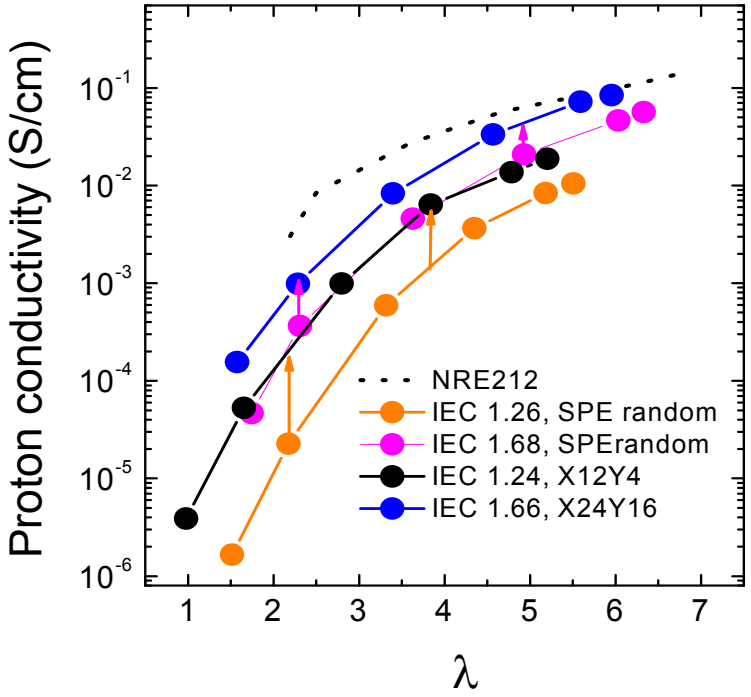


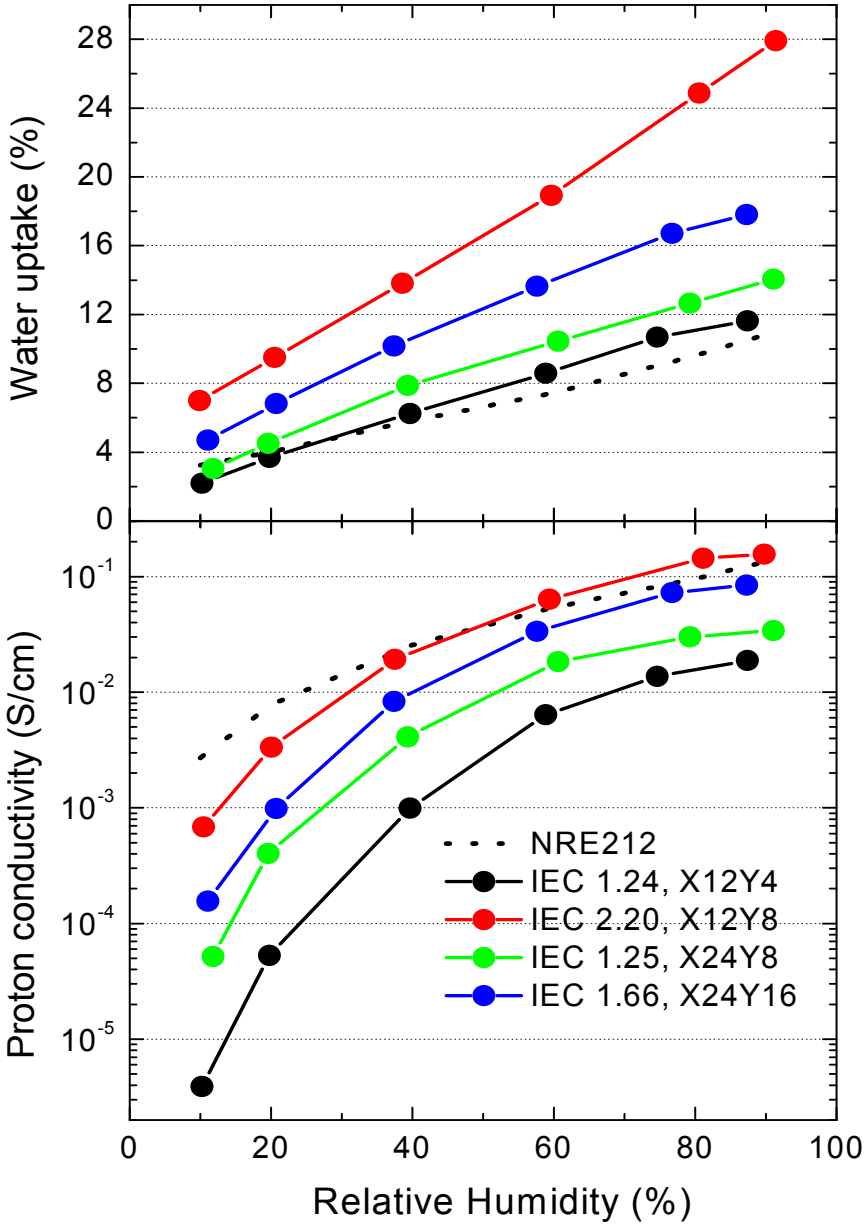
Water uptake and proton conductivity

Univ. of Yamanashi

◆ Block SPEs showed much higher conductivity than the random SPEs.

◆ The conductivity of block SPEs was comparable to that of Nafion at >40%RH.

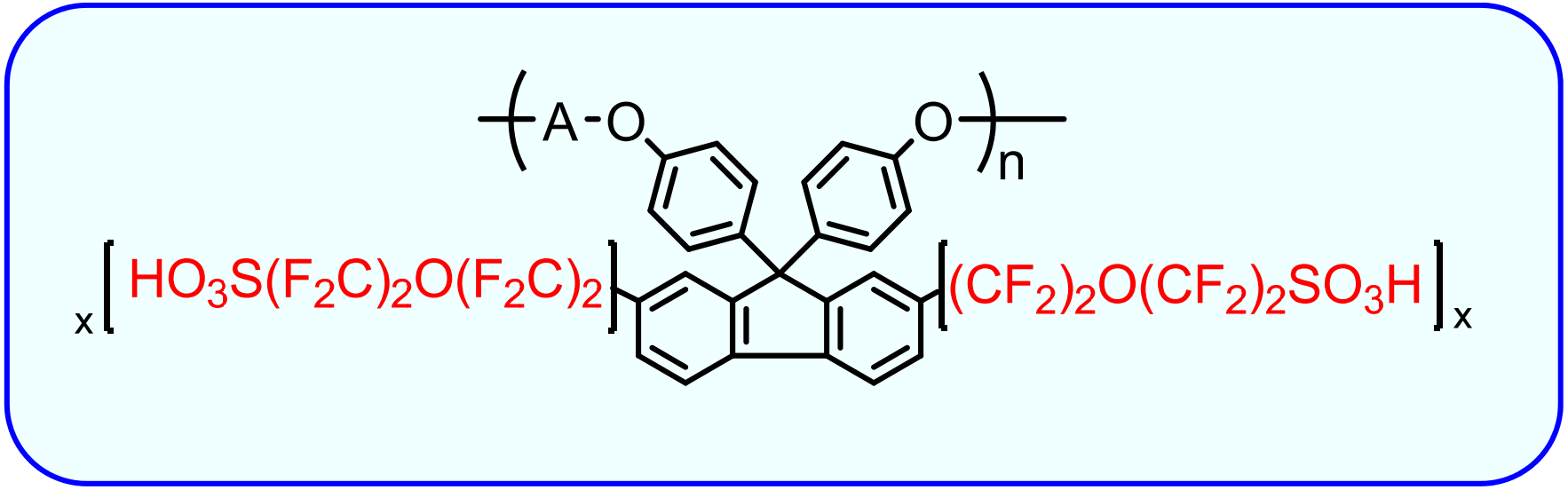


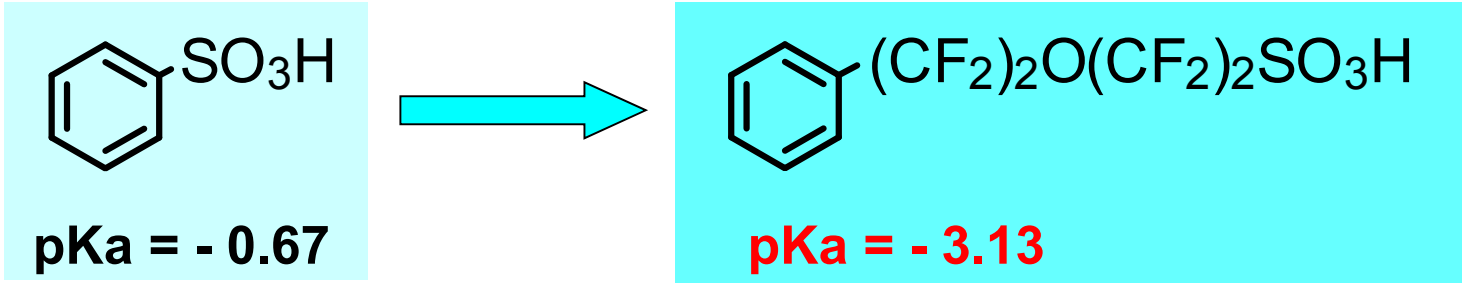


SPEs with superacid groups (FSPE)

Univ. of Yamanashi

Superacid groups were introduced onto SPEs to improve proton conductivity at low humidity.

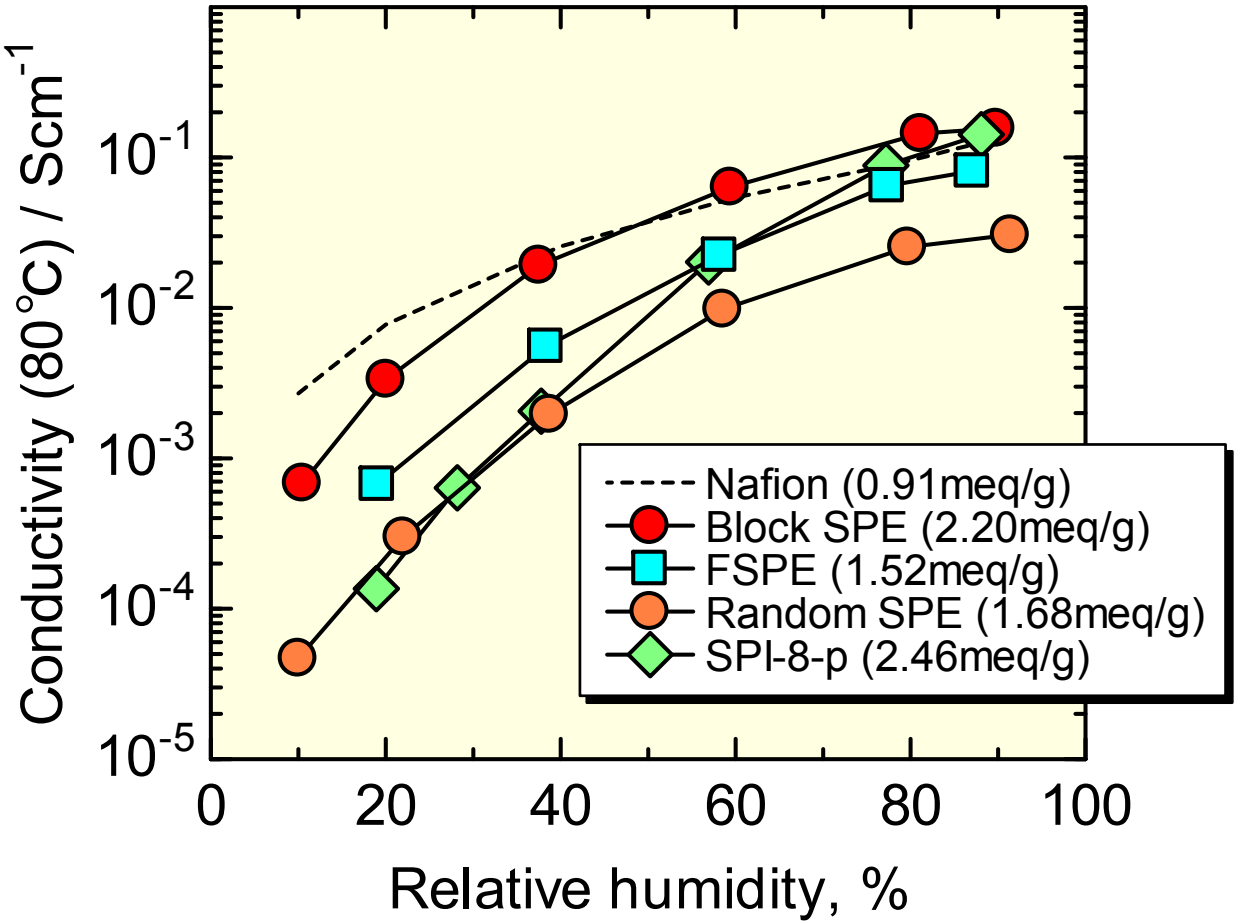




Calculated by pKa data base

Conductivity data of our new PEMs

Univ. of Yamanashi, Kaneka



◆ Significant improvement was achieved in the proton conductivity at low humidity.

4. Automotive MEAs with high performance and reliability

R&D scheme

University of Yamanashi (UY)

1) Elucidation of the limiting performance in conventional MEAs

2) Development and evaluation of hydrocarbon based MEAs with high catalyst utilization

3) Development and evaluation of hydrocarbon based MEAs with high heat cycleability and high stability with respect to load fluctuations

Evaluation of MEA and disclosure of technical information

Kaneka Corporation

4) Development of hydrocarbon electrolyte for ionomer coating electrocatalyst

Sample of the electrolyte membrane and ionomer

◆ A new evaluation method of the catalyst effectiveness was developed. The method enables us to distinguish the performance under various operating conditions. (UY)

◆ The preparation of MEAs based on hydrocarbon membrane and binder, and the process for scale-up production have been investigated. Durability tests of the membrane demonstrated problems to be solved: decrease in molecular weight, gas leakage, and swelling of the binder resin. (UY and Kaneka)

◆ Investigation of anti-flooding GDLs showed that the GDLs with small pore diameters are tolerant of flooding. (UY)

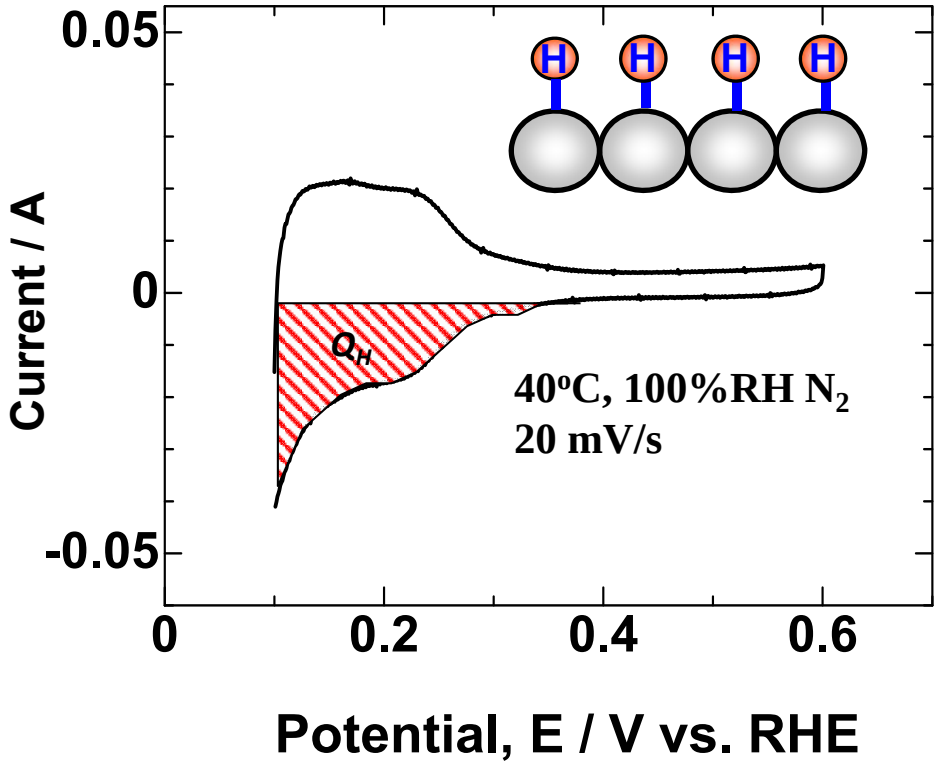
*We are ready to cooperate with Tanaka Kikinzoku Kogyo K.K. (TKK), Fuji Electric Advanced Technology Co., Ltd., and Panasonic Corporation in specifying materials for MEAs and establishing the standard conditions of the operation and evaluation of the fuel cell performance.

New evaluation method on "Real Pt Utilization"

Motivation

- To develop high performance PEFCs, it is essential to increase both the mass activity (*MA*) for the oxygen reduction reaction (ORR) and the Pt utilization (U_{Pt}) in the catalyst layer.
- It has been reported that the utilization of Pt reaches 60-80% according to a conventional evaluation method. On the other hand, it has been shown that it is necessary to reduce the Pt loading of the MEA, according to industry requirements, to 1/10, for cost reduction.
- If this information is correct, it is clear that there is little room for improvement in reducing the Pt loading.
- We believe that there are no clear indices to evaluate U_{Pt} under various operating conditions for PEFCs.
- In the present research, we propose a new evaluation method for the effectiveness of Pt (Ef_{Pt}) under actual operating conditions.

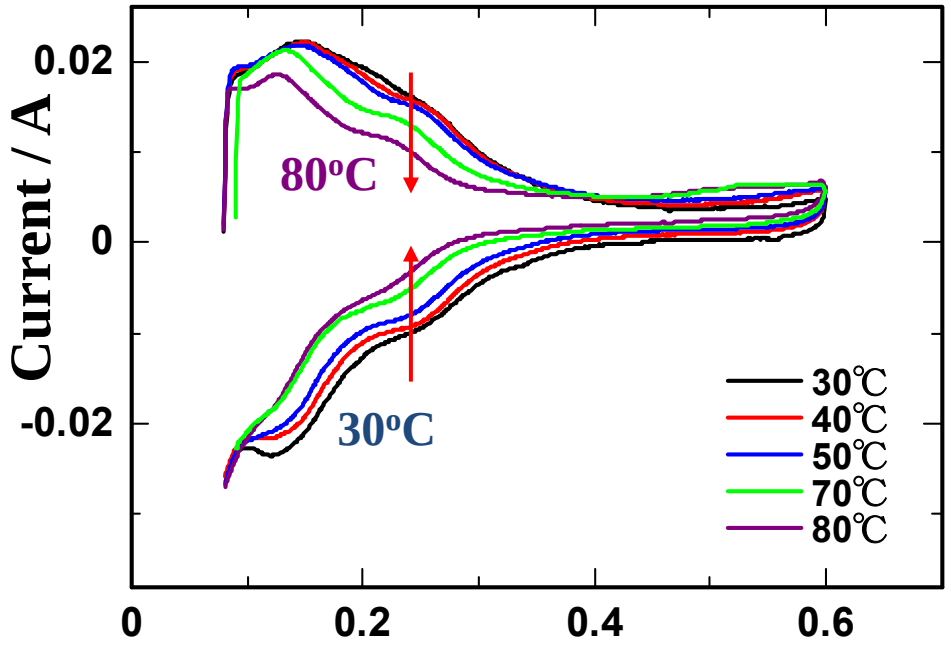
Conventional method to evaluate Pt utilization (U_{Pt})

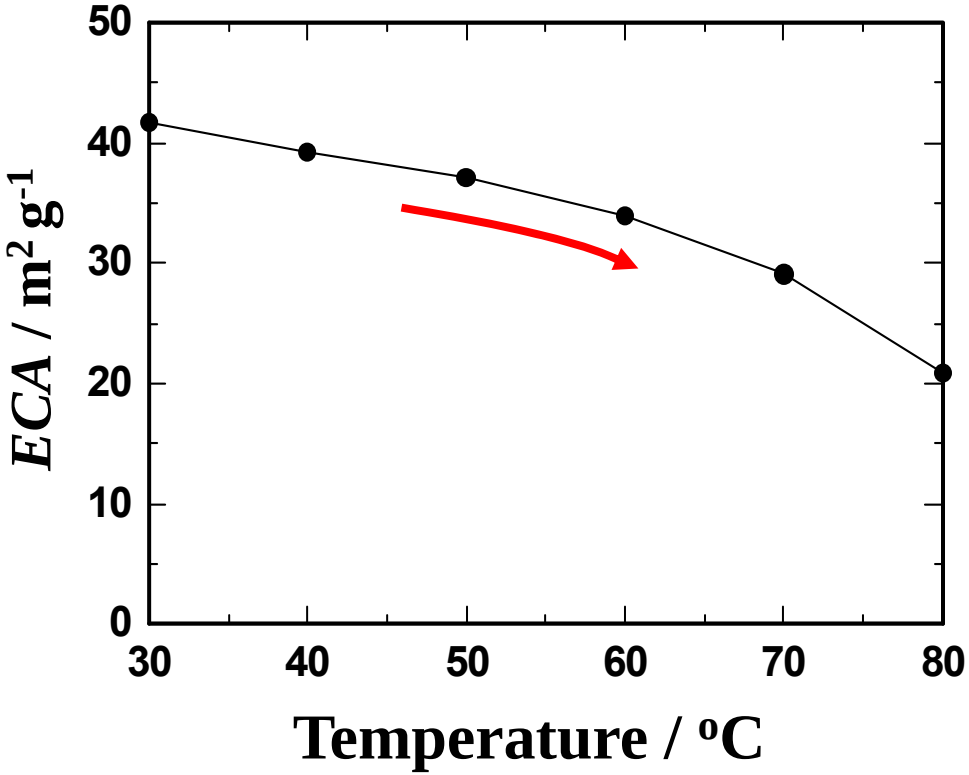


$$U_{Pt}(\%) = \frac{ECA \text{ (determined by CV)}}{S_{Pt} \text{ (determined by TEM)}} \times 100\% \quad [1]$$

- The U_{Pt} value is defined by eq. [1] by using the electrochemically active area (*ECA*) determined from the hydrogen adsorption/desorption charge Q_H in the cyclic voltammogram, where S_{Pt} is the total surface area calculated from the Pt particle size.

Problem of conventional method: Effect of temperature on ECA

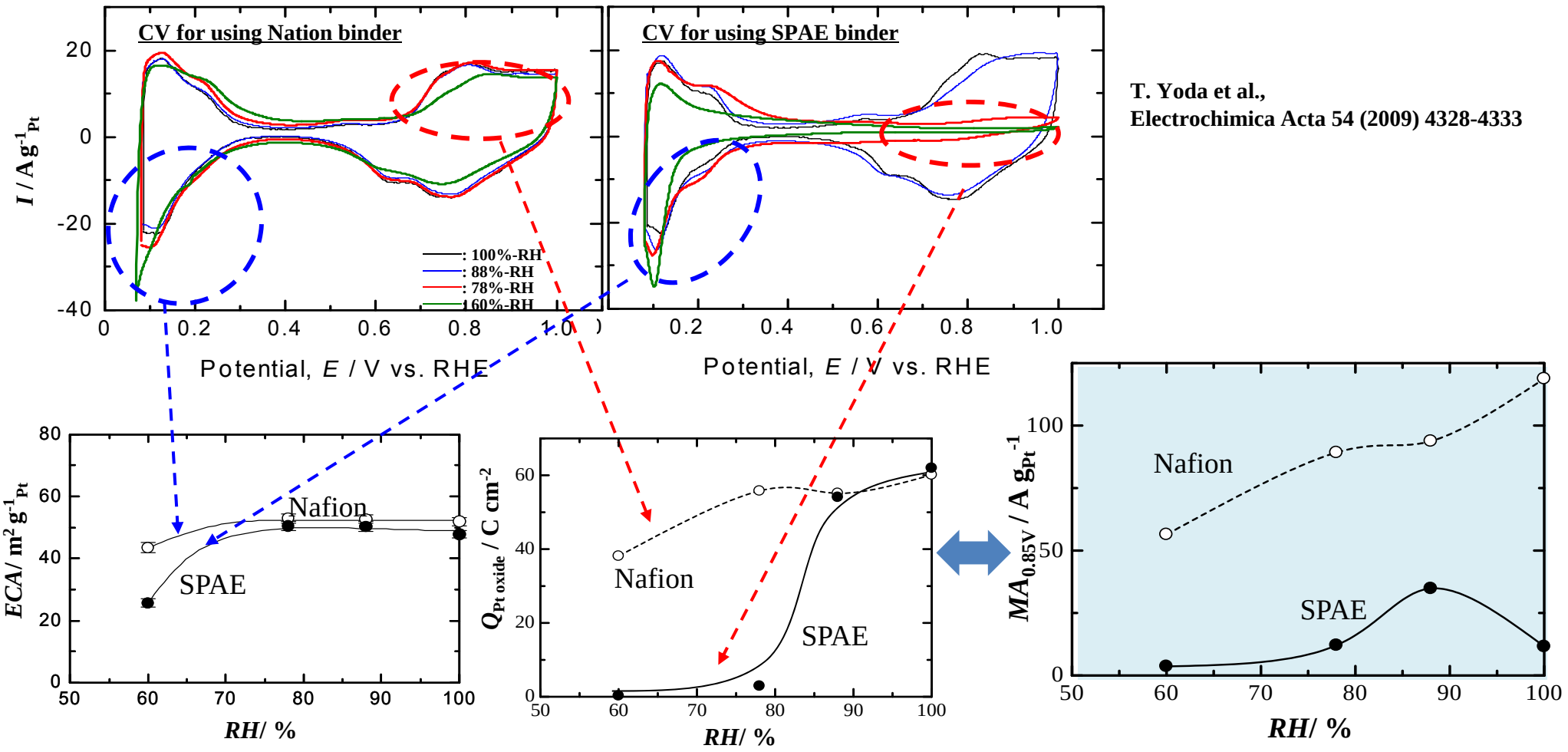




- *ECA* decreases with increasing T_{cell}, because the hydrogen coverage on the Pt surface decreases at high temperature.
- Hence, the real value of *ECA* cannot be obtained from Q_H measured at T_{cell} > 50 °C.

H. Uchida, M. Watanabe, *Electrochemistry*, **75**, 489 (2007).

Problem of conventional method: Specific adsorption effect



T. Yoda et al.,
Electrochimica Acta 54 (2009) 4328-4333

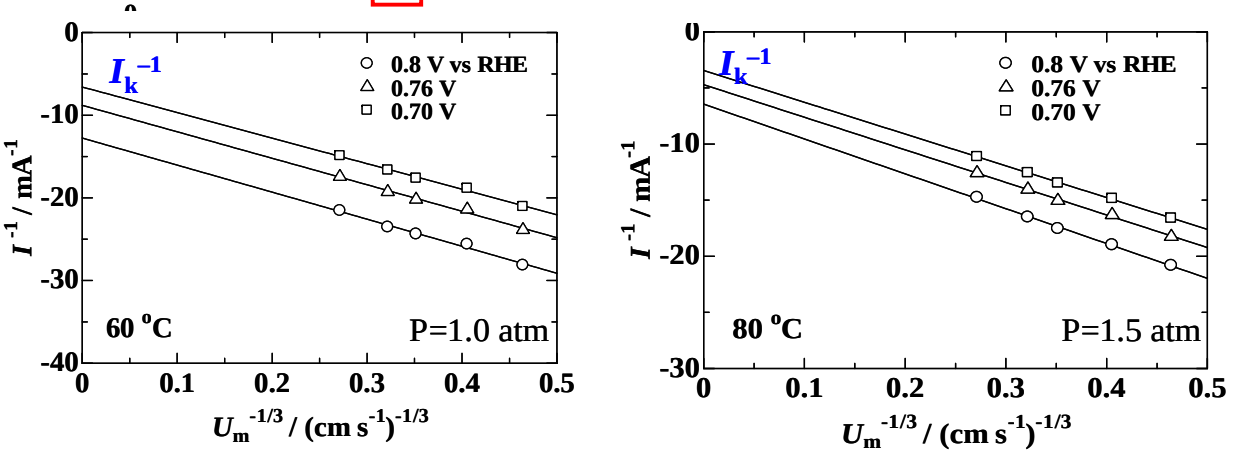
- The RH-dependence of *MA* (0.85V) at SPAE-GDE was not consistent with that of *ECA*, but was similar to that of Q_{Pt} oxide at $E > 0.6$ V.
- It was found that the SPAE binder specifically adsorbed on the Pt catalyst surface, blocking the active sites for the ORR.

New evaluation method for Pt utilization: Effectiveness of Pt (Ef_{Pt})

$$Ef_{Pt}\ (\%) = MA / MA_{max} \times 100$$

Measured by Channel flow double electrode (CFDE) method

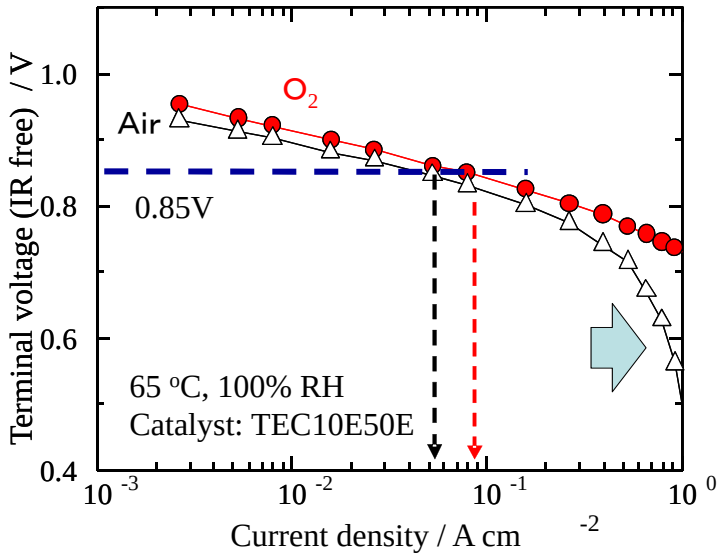
$$\frac{1}{I} = \frac{1}{I_k} + \frac{1}{1.165\,nF[O_2]w(D^2 x_1^{\,2}/b)^{1/3}} U_m^{-1/3}$$



O_2-saturated 0.1 M $HClO_4$, Scan rate: 0.5 mV s^{-1},
U_m =10-50 cm s^{-1}, Catalyst: TEC10E50E

H. Uchida, K. Izumi, K. Aoki, and M. Watanabe, Phys.Chem.Chem.Phys, 11, 1771-1779 (2009)

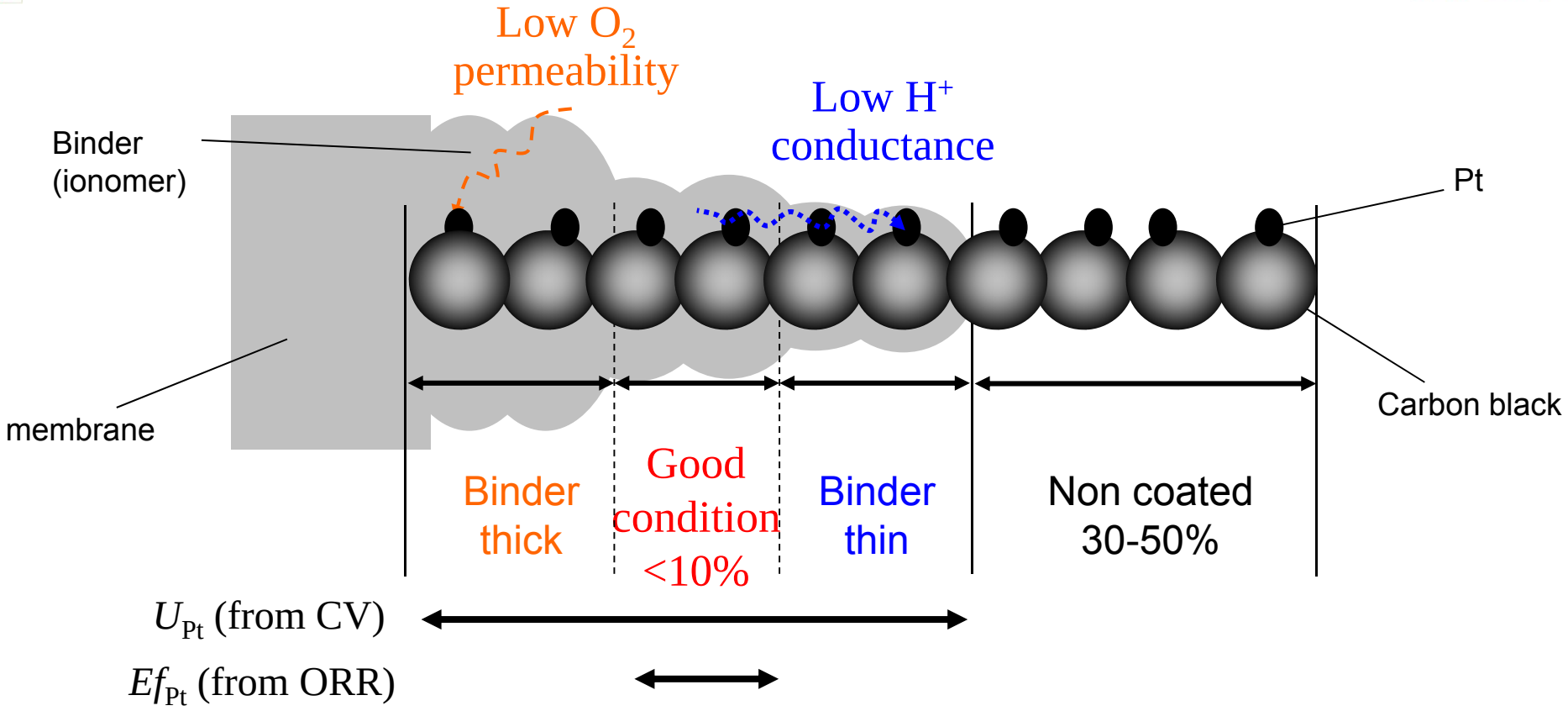
Measured by MEA



MA_{max} =I_k (A) / Pt loading (g): determined under ideal electrochemical conditions

MA = I_{cell} (A) / Pt loading (g): determined under practical fuel cell operating conditions

Image of the Ef_{Pt} value



- The Ef_{Pt} indicates the extent to which Pt particles exist in the catalyst layer in a good condition of binder coverage.
- The value of Ef_{Pt} was found to be 10% or less under actual operating conditions.
- This value shows the ratio of catalysts existing in an effective reaction environment during actual operation.
- We have much room for improvement for the design of catalyst layers.

A Strategy of the Cost Reduction of Catalysts for Large PEFC Markets

"Thorough Reduction of Pt Catalysts Used"
That is the Shortest, the Best and the Most Practical Approach !

How the 1/10～1/20 reduction could be realized ?

"Ippon" with "Awase-waza"

Pt-skin on the alloy of Pt & non-precious metal(s) ×a few times
Nano-sized catalyst × a few times
Effectiveness of MEA × a few times
High temperature operation × a few times
Synergy effect of catalysts with the supports × a few times
Optimization of operation mode × a few times

2^6～3^6 times

My Dream !

FC-driven “Wheel Chair”

Research Build. 3,000m² **Office area** ca.1,500m² **Land Space** ca.12,000m²

In corporation with Clean Energy Research Center(燃料電池部門 約2,300m²)、we will promote extensively the FC-R&D together with breeding of talented persons in this field.

Acknowledgements

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Co-workings:

My colleagues, companies and students


Thank you very much
for your attention!