2022.11.15

第11回SPring-8グリーンサスティナブルケミストリー研究会

水と電気を用いた電解触媒作用・反応の開拓

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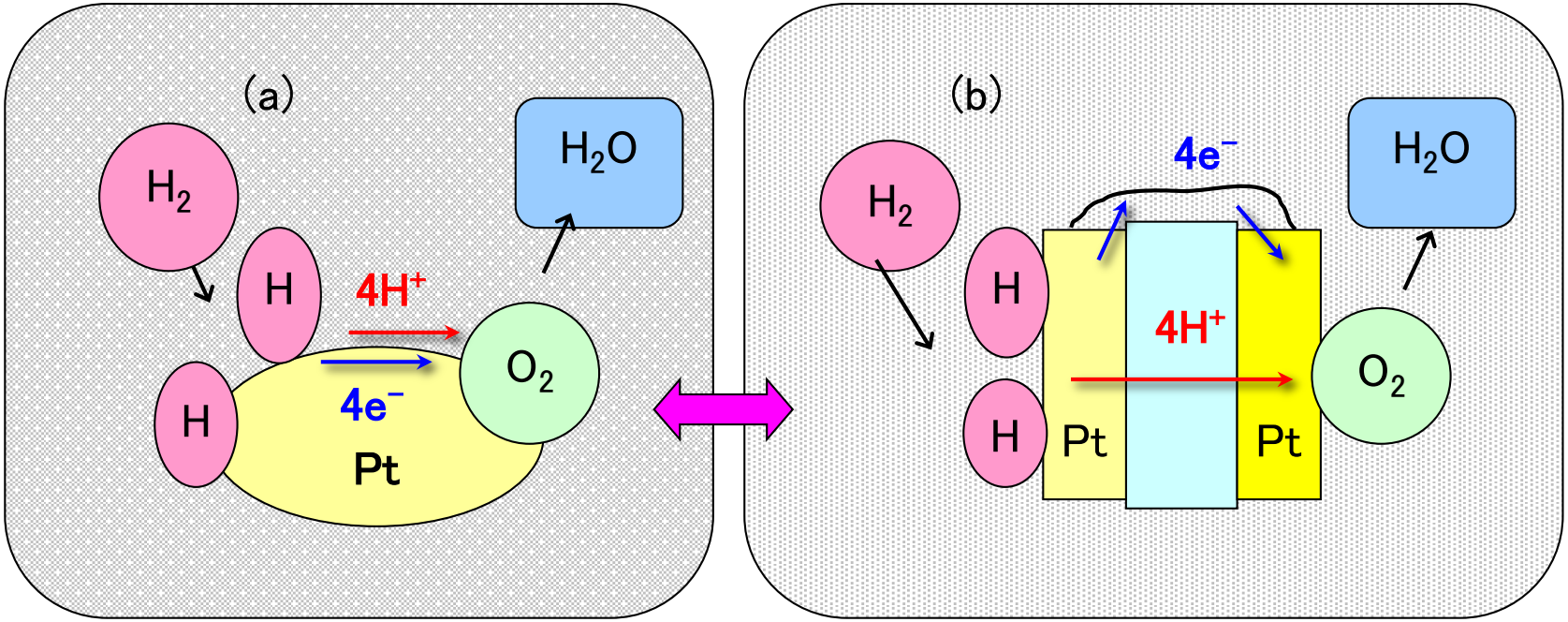
東京工業大学
物質理工学院　応用化学系

触媒反応と電気化学反応

水素と酸素の反応による水の生成



a. 酸化反応場と還元反応場の物理的分離

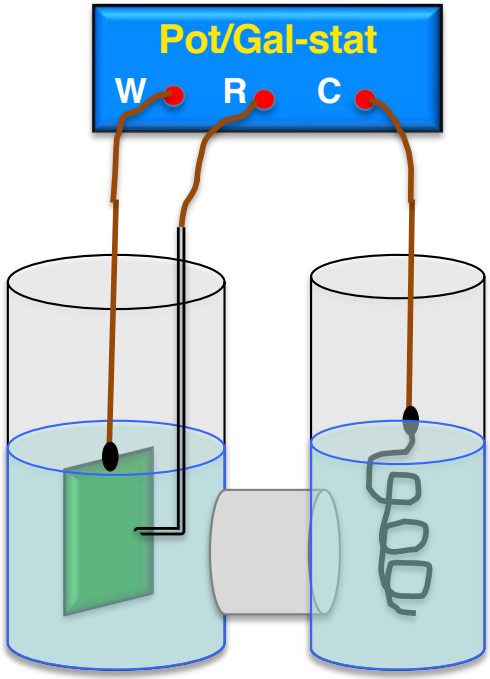
b. 酸化触媒と還元触媒を化学ポテンシャル場で接合

c.「イオン伝導体+リード線」、「混合導電体」で接合

隔膜(三相界面)電解法の特徴

$\Delta G = -nFE$　　$i = i_o \exp(\alpha n F \eta / RT)$

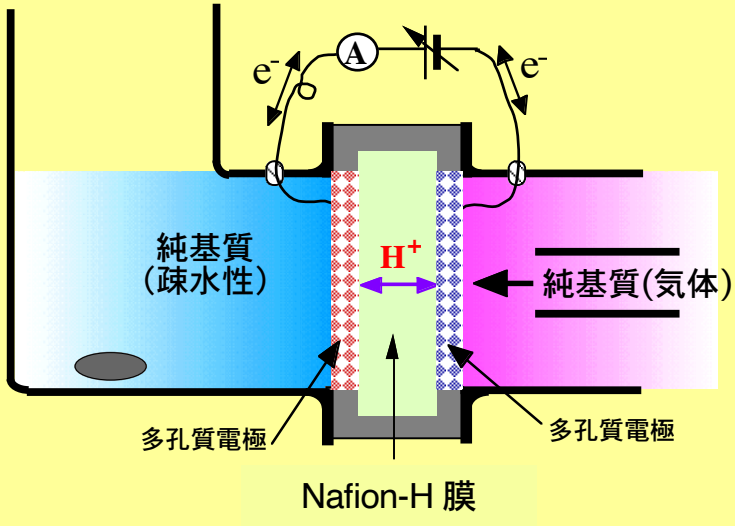
E:電位差,*F*:96485 C/mol, n:反応電子数,i_o : 交換電流密度,α: 透過係数0< α <1,η:過電圧



・作用極
・参照極
・支持電解質
・基質
・溶媒
・メディエータ

・対極
・支持電解質
・溶媒

多孔質電極(ガス拡散電極)を用いた三相界面電解法



a. 溶媒がいらない
b.生成物の分離が容易
c. 気体も気相電解できる
d.電池の組織により触媒反応が進行
e.触媒との組み合わせが容易

触媒反応における酸化と還元

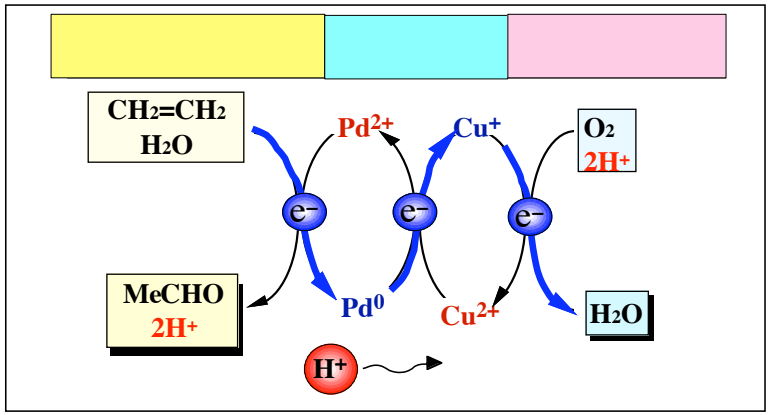
(1) ワッカー触媒によるエチレン酸化

$C_2H_4 + H_2O + PdCl_2 \rightarrow CH_3CHO + 2HCl + Pd^0$

$Pd^0 + 2CuCl_2 \rightarrow PdCl_2 + 2CuCl$

$2CuCl + 1/2O_2 + 2HCl \rightarrow 2CuCl_2 + H_2O$

$C_2H_4 + 1/2O_2 \rightarrow CH_3CHO$



Wacker 機構

(2) Mo–Bi–O触媒によるアリル酸化

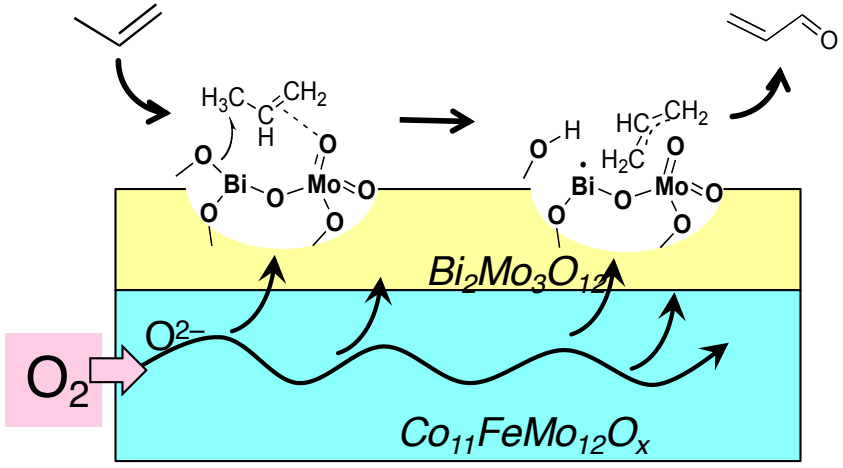
(Mo-Bi-M^{3+}-M^{2+}-M^{+}-X-Y-O多元系触媒)

$C_3H_6 + BiMoO_x \rightarrow CH_2CHCHO + BiMoO_{x-1}$

$BiMoO_{x-1} + CoFeMoO_y \rightarrow BiMoO_x + CoFeMoO_{y-1}$

$CoFeMoO_{y-1} + 1/2O_2 \rightarrow CoFeMoO_y$

$C_3H_6 + 1/2O_2 \rightarrow CH_2CHCHO$

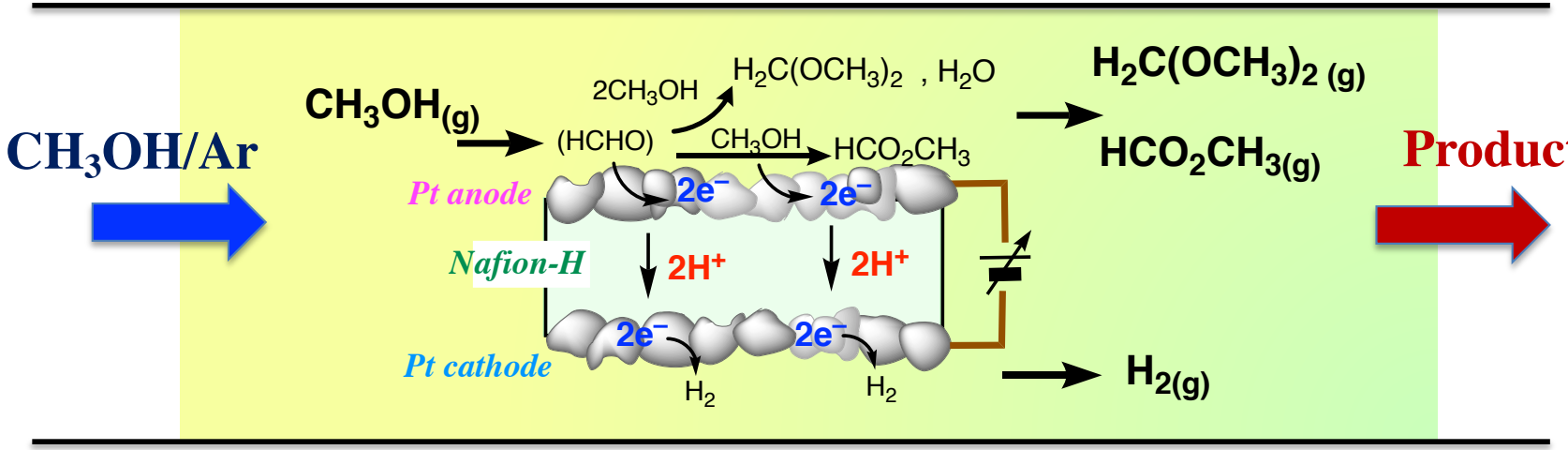


Mars-Van-Krevelen 機構

最初の思いつき

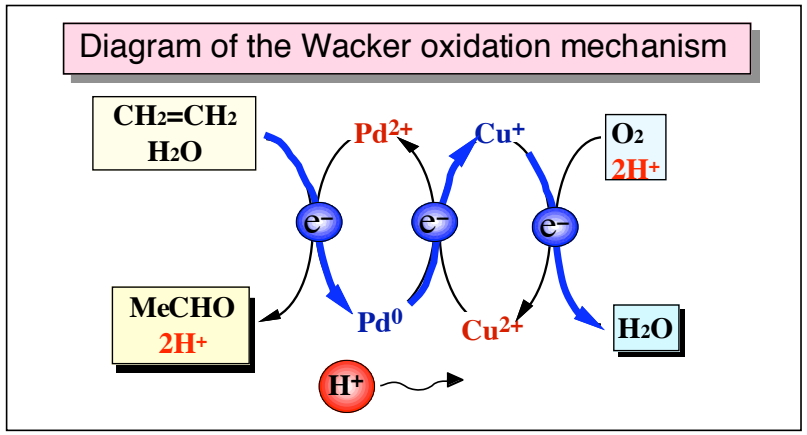
Appl. Catal. **1986**, *26*, 401.

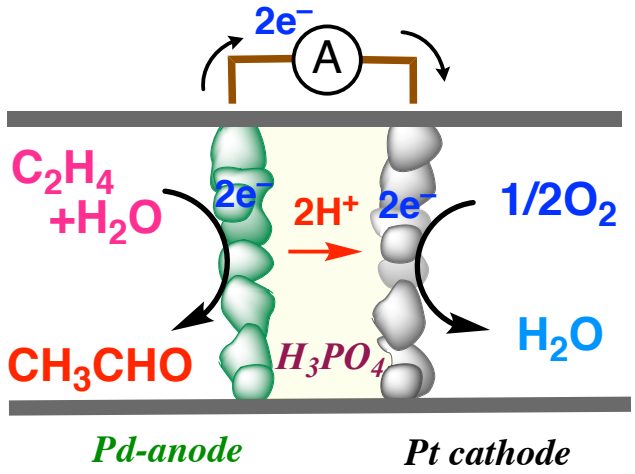
Pt-black | Nafion-H | Pt-black ユニットによるメタノールの気相電解



J.C.S. Chem. Commun. **1988**, 1272.

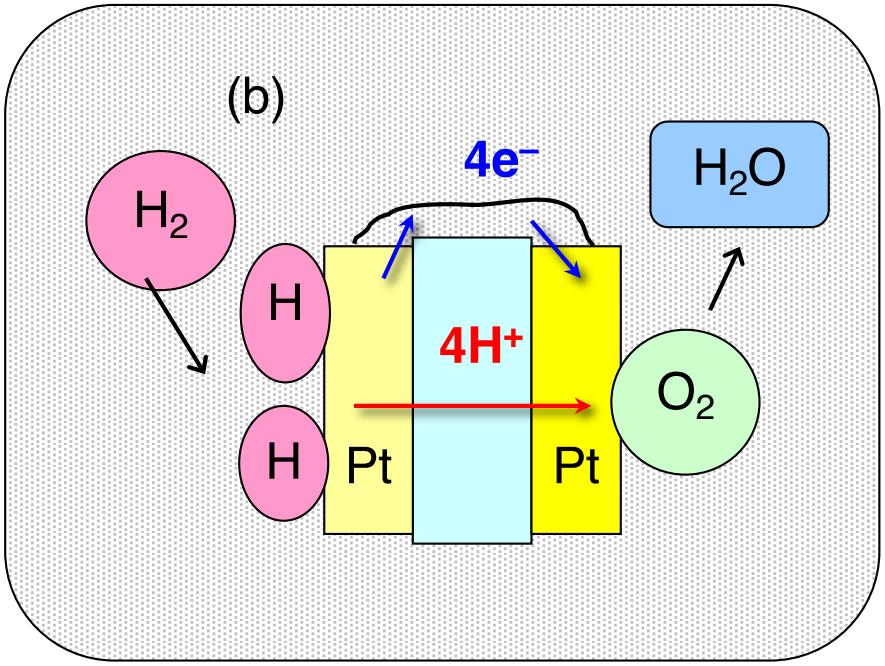
C_2H_4, Pd/Gr | H_3PO_4/SiO_2-wool | Pt/Gr, O_2 燃料電池によるMeCHO合成



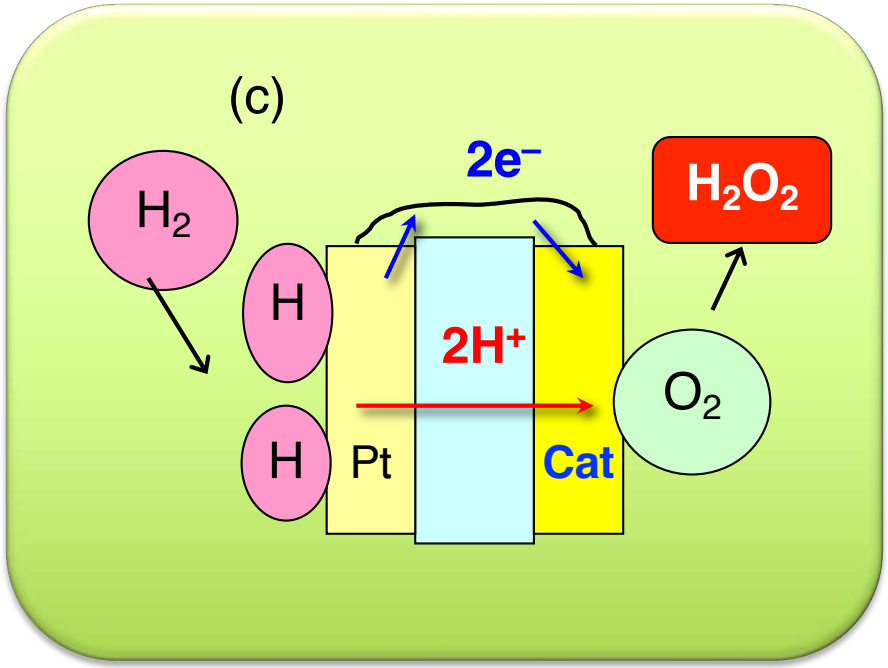


化学合成用燃料電池

水素と酸素の反応による
水の生成

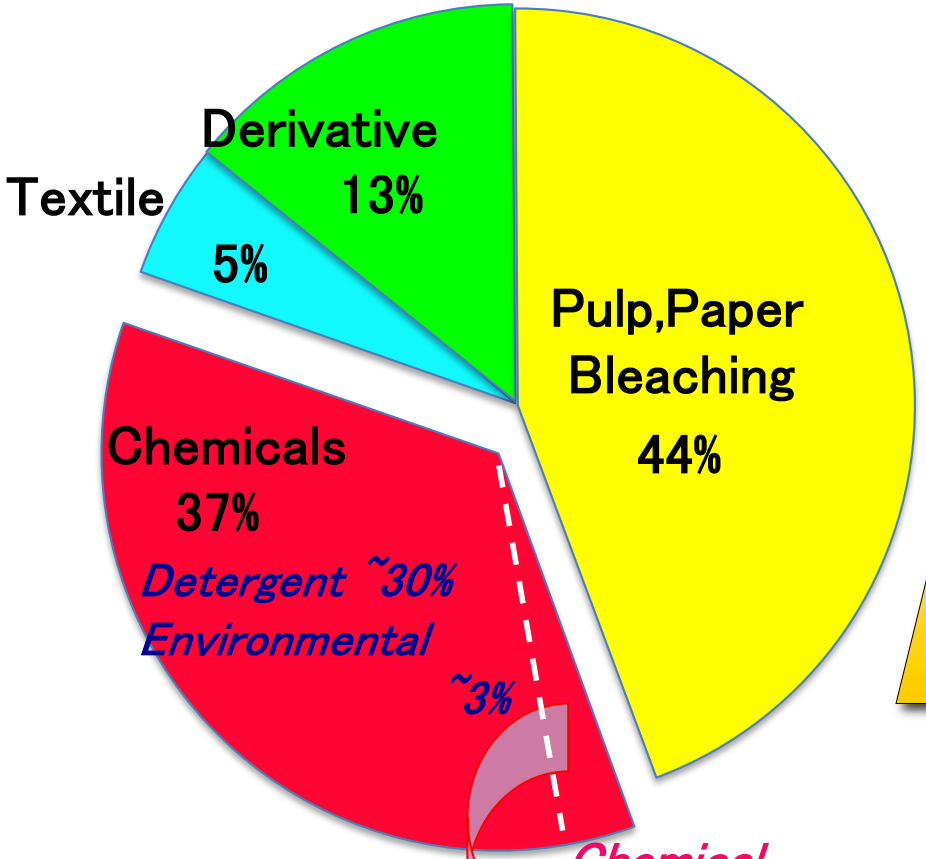


水素と酸素の反応による
過酸化水素の生成



- 酸化反応場と還元反応場の物理的分離
- 酸化触媒(ｱﾉｰﾄﾞ)と還元触媒(ｶｿｰﾄﾞ)を選択可能
- 燃料電池反応($\Delta G < 0$)と電解合成($\Delta G > 0$)

H_2O_2 の需要



Demand in Japan

1993　109,000 t/y

2003　184,000 t/y

2013　210,000 t/y

World ＞ 3,500,000 t/y

Chemical synthesis

To be large growth

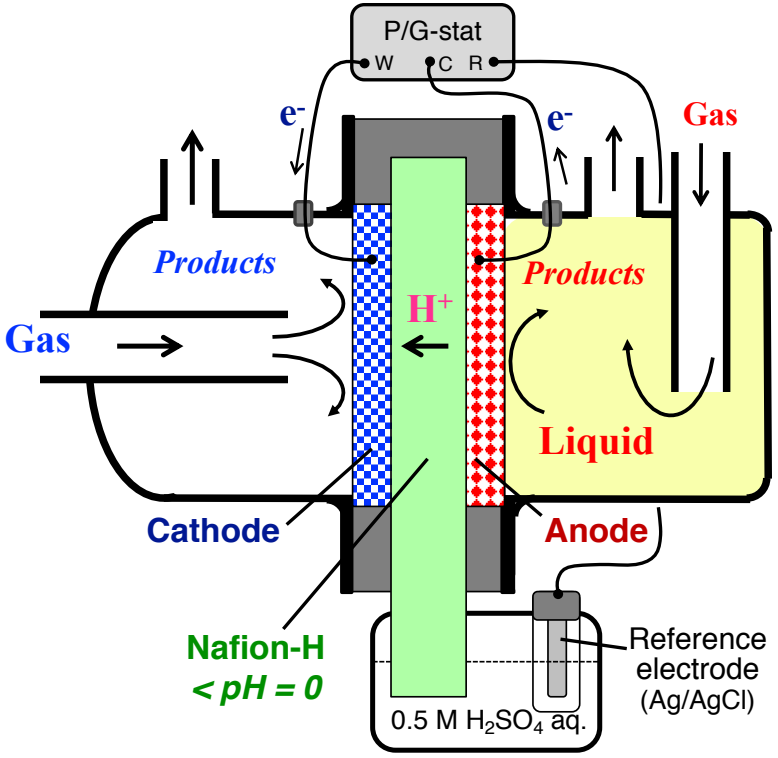
$$-C{=}C- + H_2O_2 \rightarrow -\overset{O}{\overset{\diagup\diagdown}{C}}-C- + H_2O$$

By-product
: water
High atom. eff.
: 47%

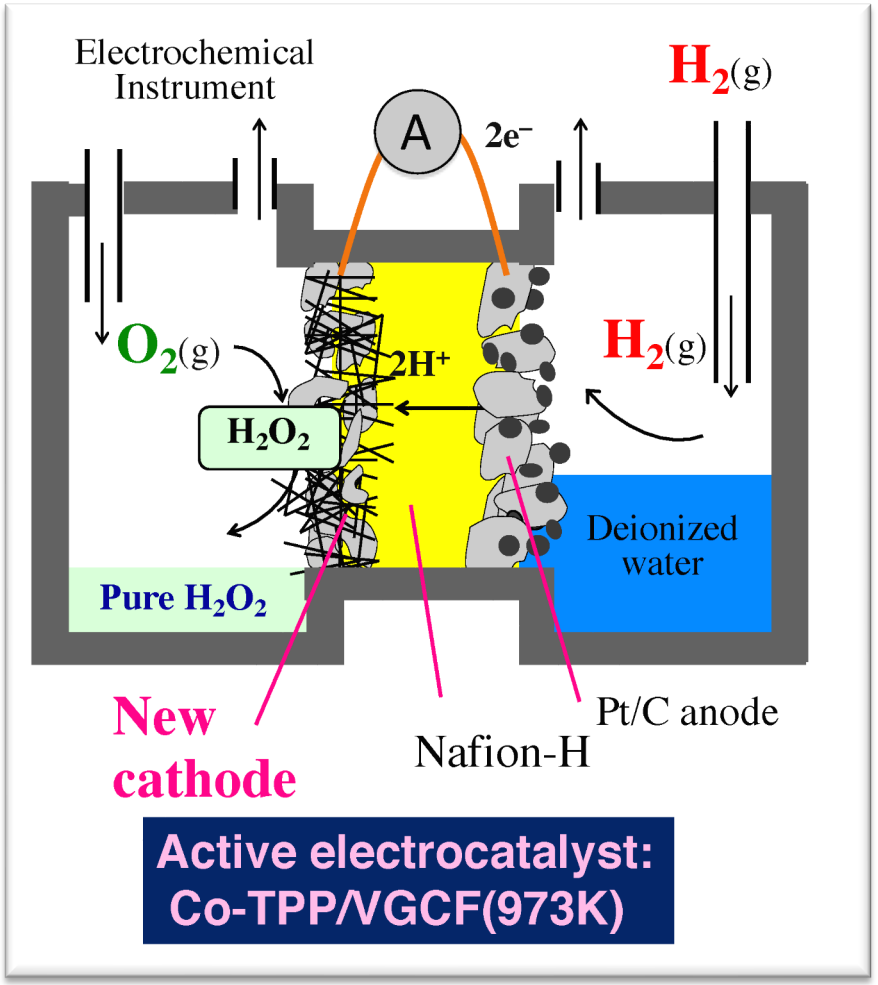
多孔質電極を用いたSPE電解の特徴

$$\Delta G = -nFE$$

$$i = i_o \exp(\alpha n F \eta / RT)$$

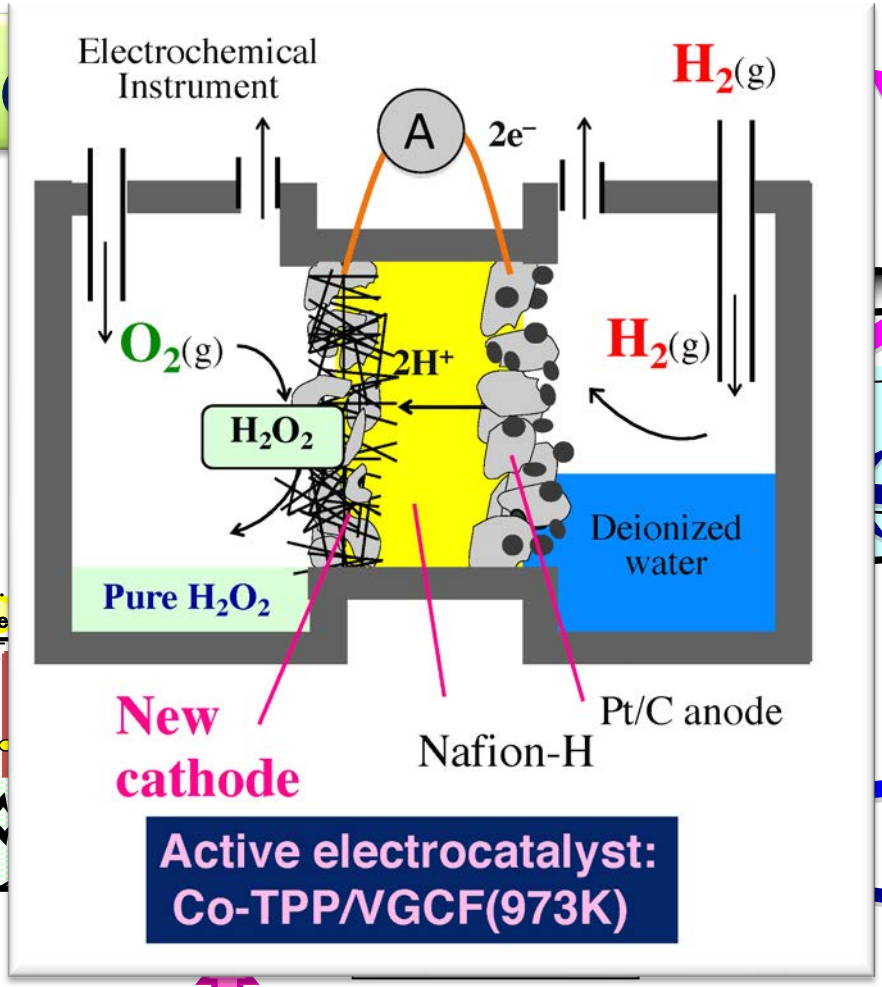


- 純液体も気体も電解可能
- 触媒化学との融合が可能
- 生成物分離が容易
- ΔG>0の時は燃料電池(触媒)反応が可能



Active electrocatalyst: Co-TPP/VGCF(973K)

その後

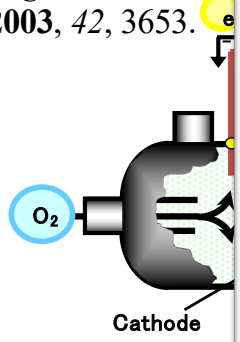


T. Iwasaki, *Electrocatalysis*, **2018**, *9*, 236
R. Ichihashi, *Electrochim. Acta*, **2013**,*108*, 321
S. Tazzawa, *ChemSusChem*, **2008**, *1*, 988;

T. Murayama
Angew. Chem. Int. Ed
2008, *10*, 1900

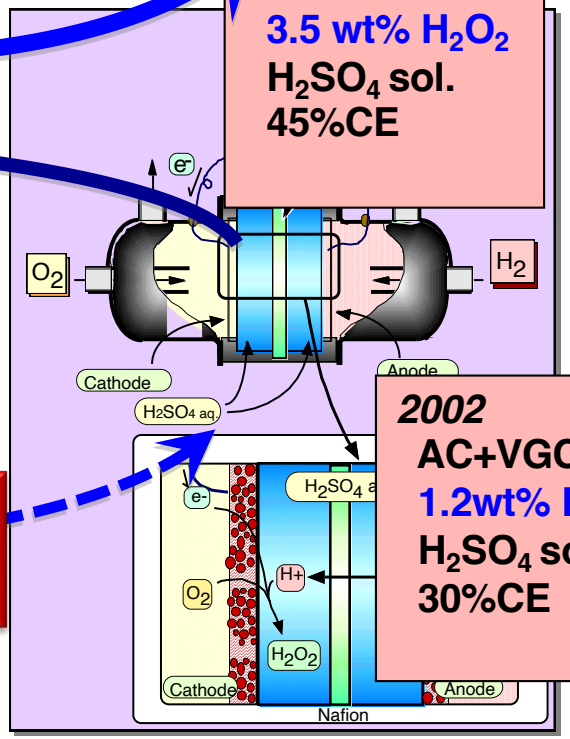
2008
Exp-SPE electrolysis
AC(ox)+VGCF
Pure 8wt% H_2O_2,
27%CE

T. Onizawa
Angew. Chem. Int.
2003, *42*, 3653.



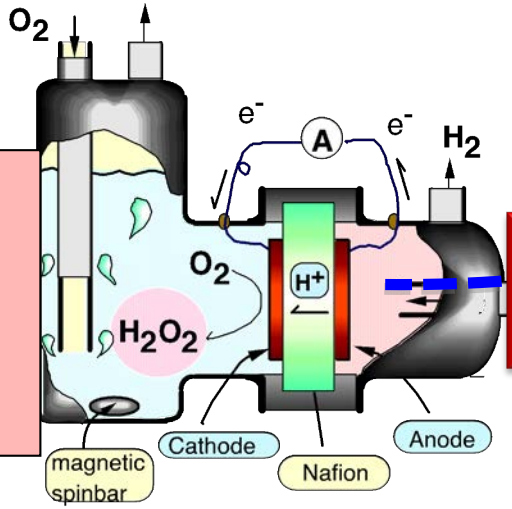
2006
Heat-treated
Mn-OEP/AC
3.5 wt% H_2O_2
H_2SO_4 sol.
45%CE

N. Hanaizumi
Chem. Lett.
2006, 1330



T. Hashimoto
Chem. Lett.
2002, 852

2002
AC+VGCF
1.2wt% H_2O_2
H_2SO_4 sol.
30%CE



1990
Au-mesh
0.2wt% H_2O_2
HCl sol.
10%CE

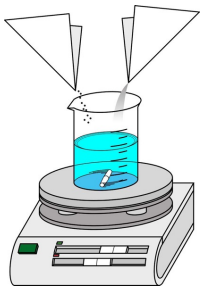
10年休止

Electrochim. Acta,
1990, *35*, 319.

実験

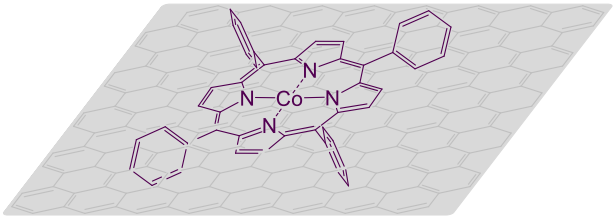
Electrocatalyst preparation

Co-TPP　　VGCF

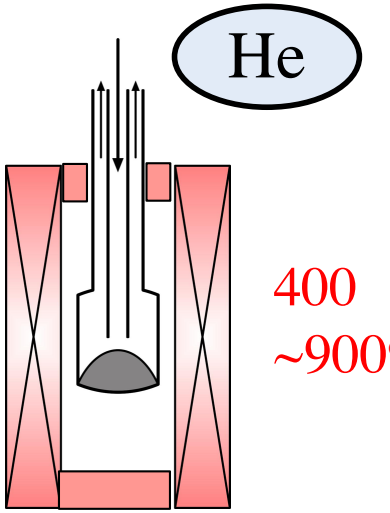


CH_2Cl_2

Impregnation method



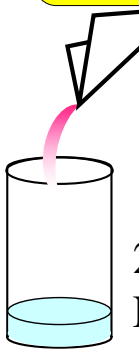
Dry
catalyst
precursor



400
~900°C

Activation by heat-treatment

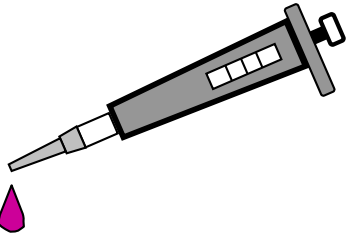
Cathode preparation :Coated method

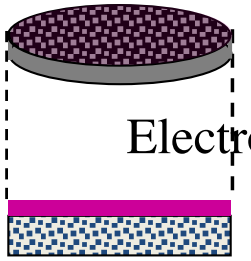


CoTPP /VGCF(1073K) 2 mg

2-PrOH 100μL
Nafion sol. 10μL

Ultra sonic

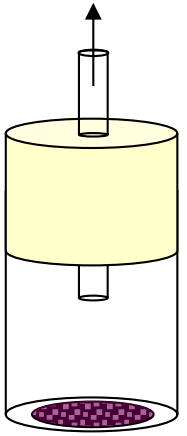




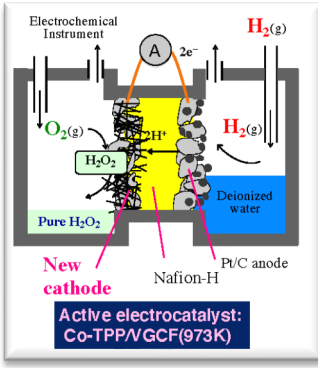
Electrocatalyst

Co: 8.5 nmol cm^{-2}

Base electrode
VGCF 48mg PTFE 3mg



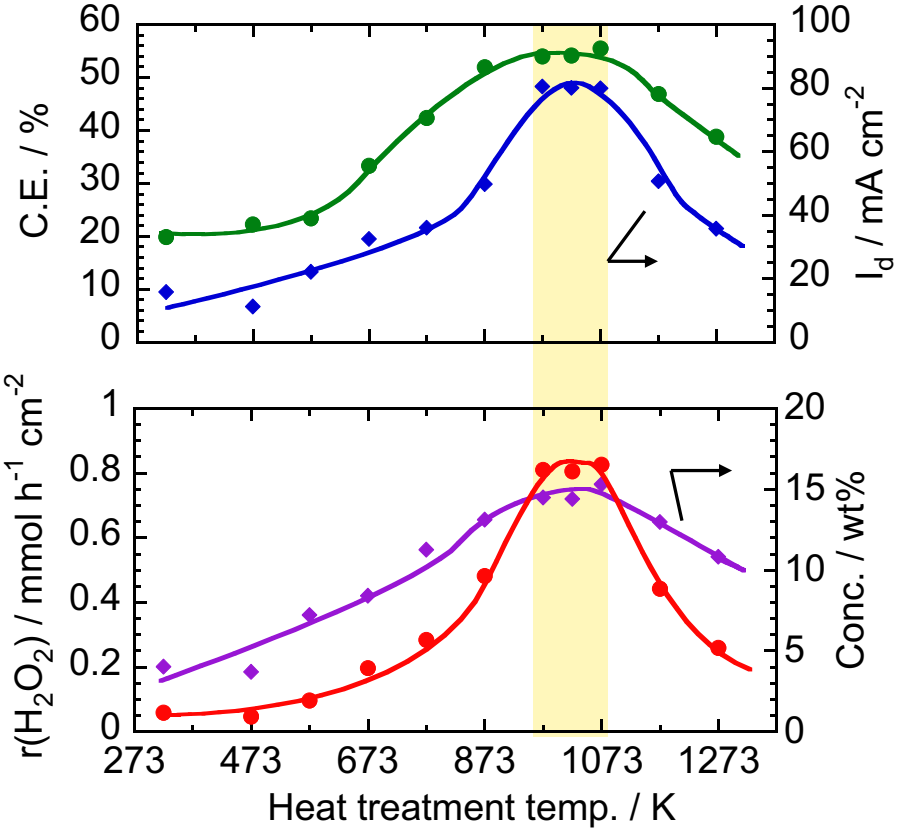
Dry in
a vacuum



Preparation
of MEA

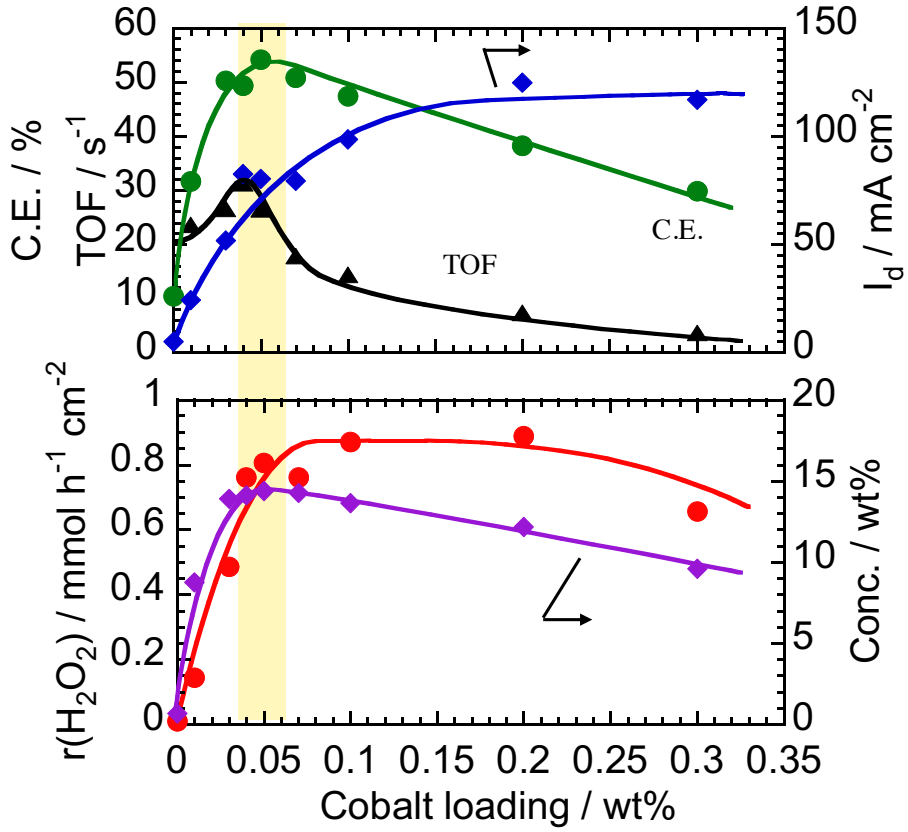
Co–TPP/KB調製条件の影響

活性化温度の影響



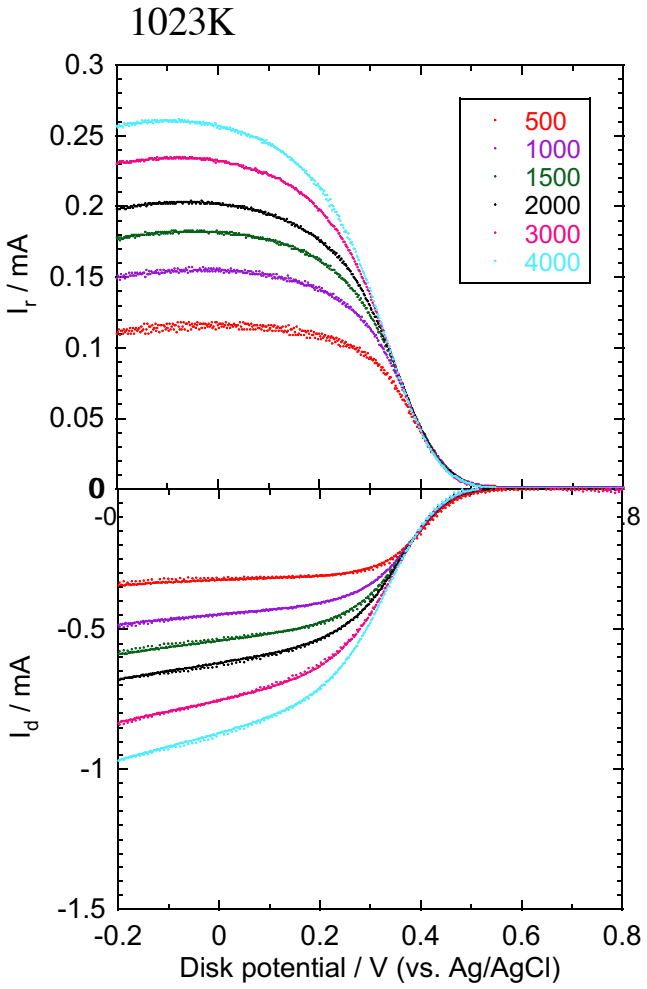
Suitable preparation Temp: 973~1073K

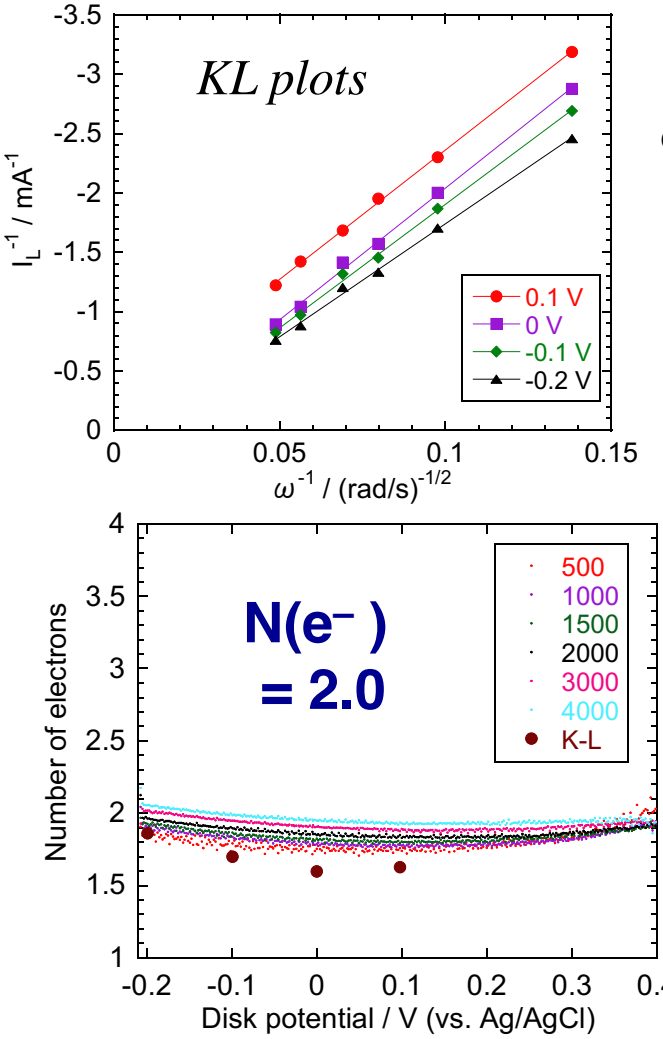
Co担持量の影響

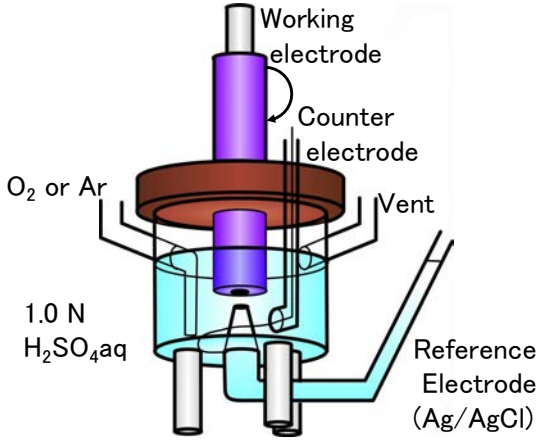


Suitable Co loading: 0.05 wt%, max CE = 56% with 31 s^{-1} TOF

RRDE voltammetry for O_2 reduction







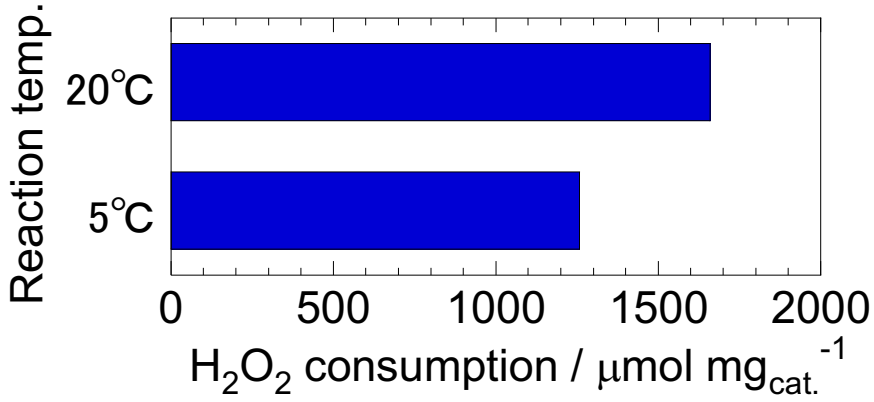
H_2O_2 selectivity: 100% (RRDE)

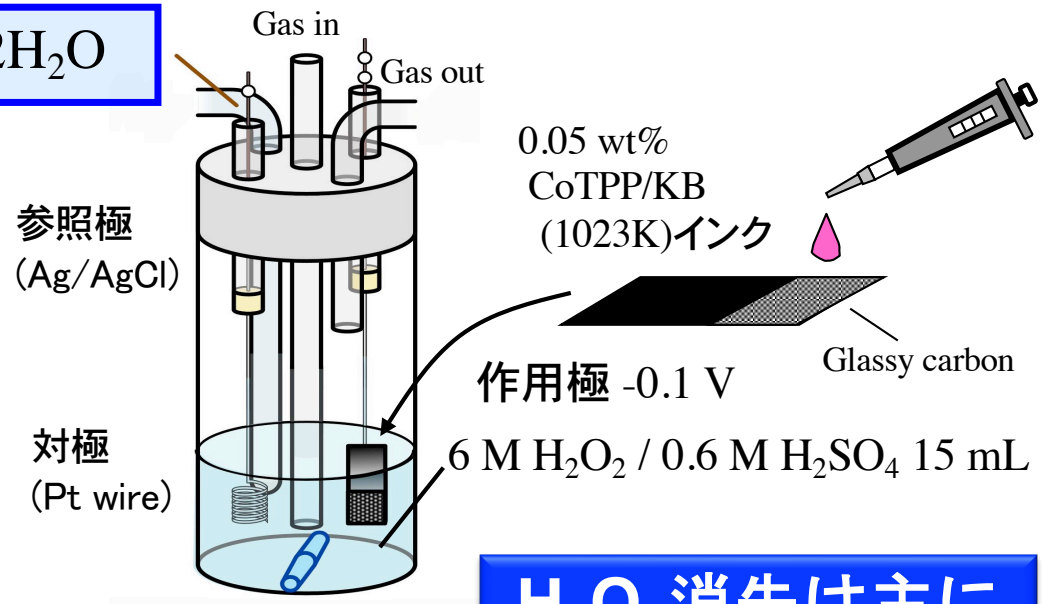
vs.

56% CE (synthesis)

逐次還元・分解活性

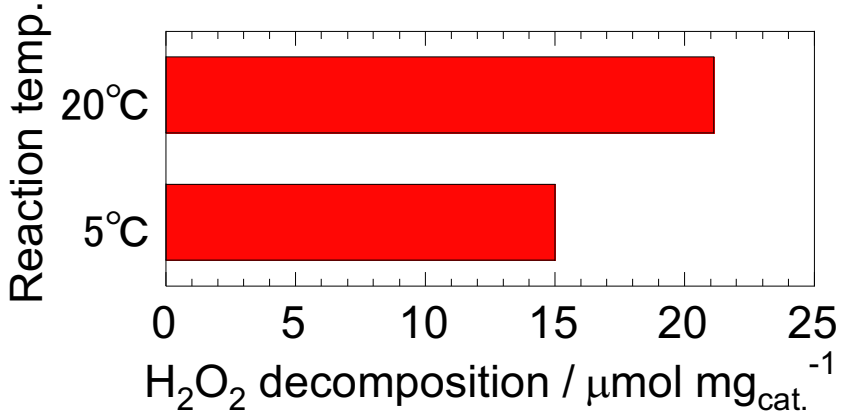
逐次還元反応：$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$

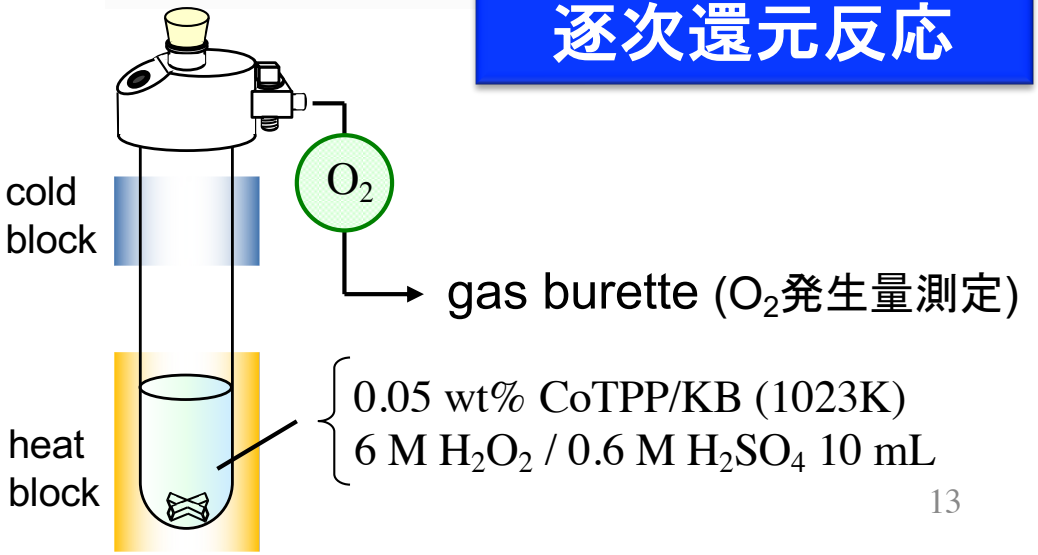




H_2O_2消失は主に逐次還元反応

分解反応：$H_2O_2 \rightarrow H_2O + 1/2O_2$



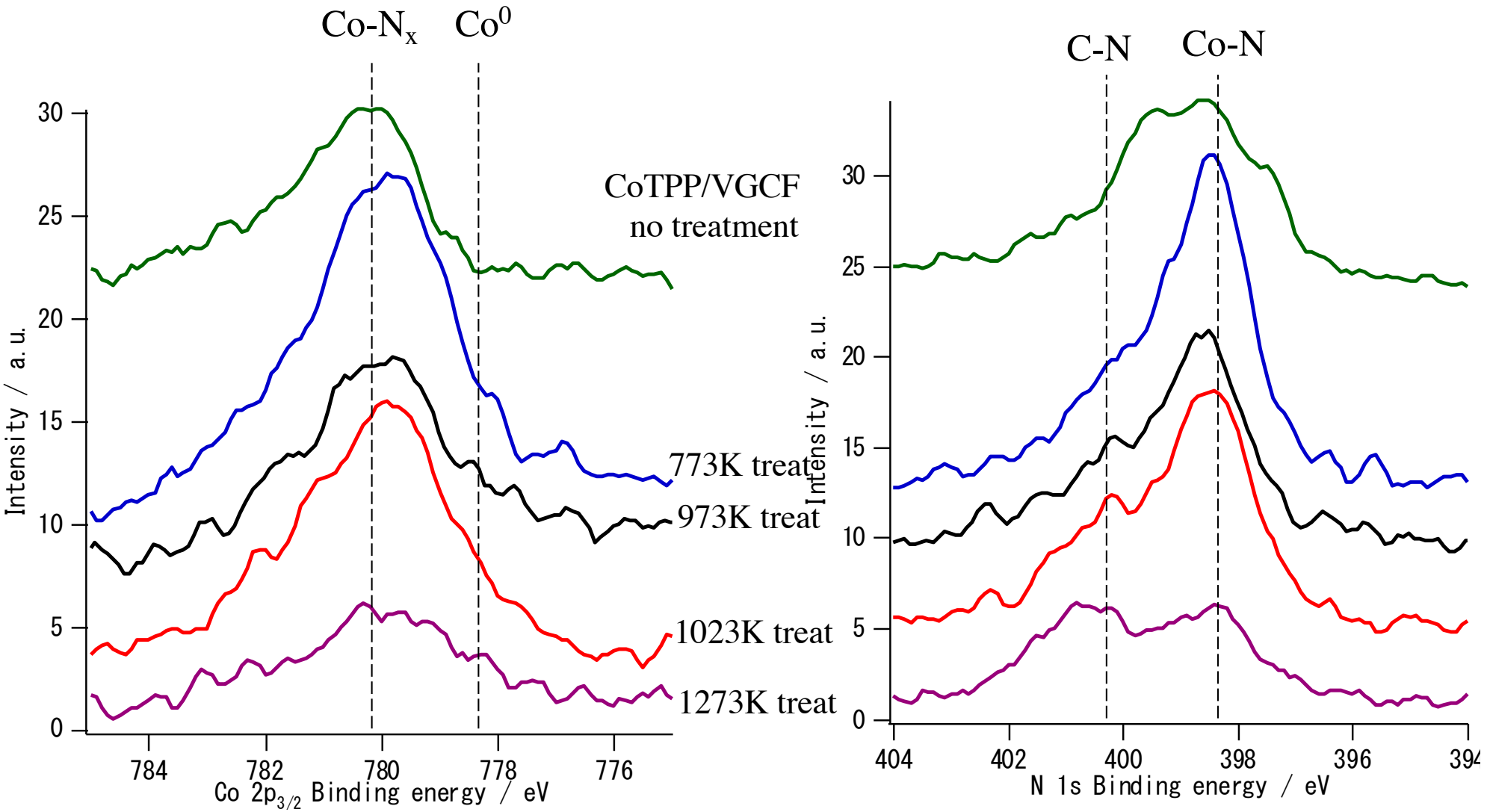


Co $2p_{3/2}$, N 1s XPS analysis

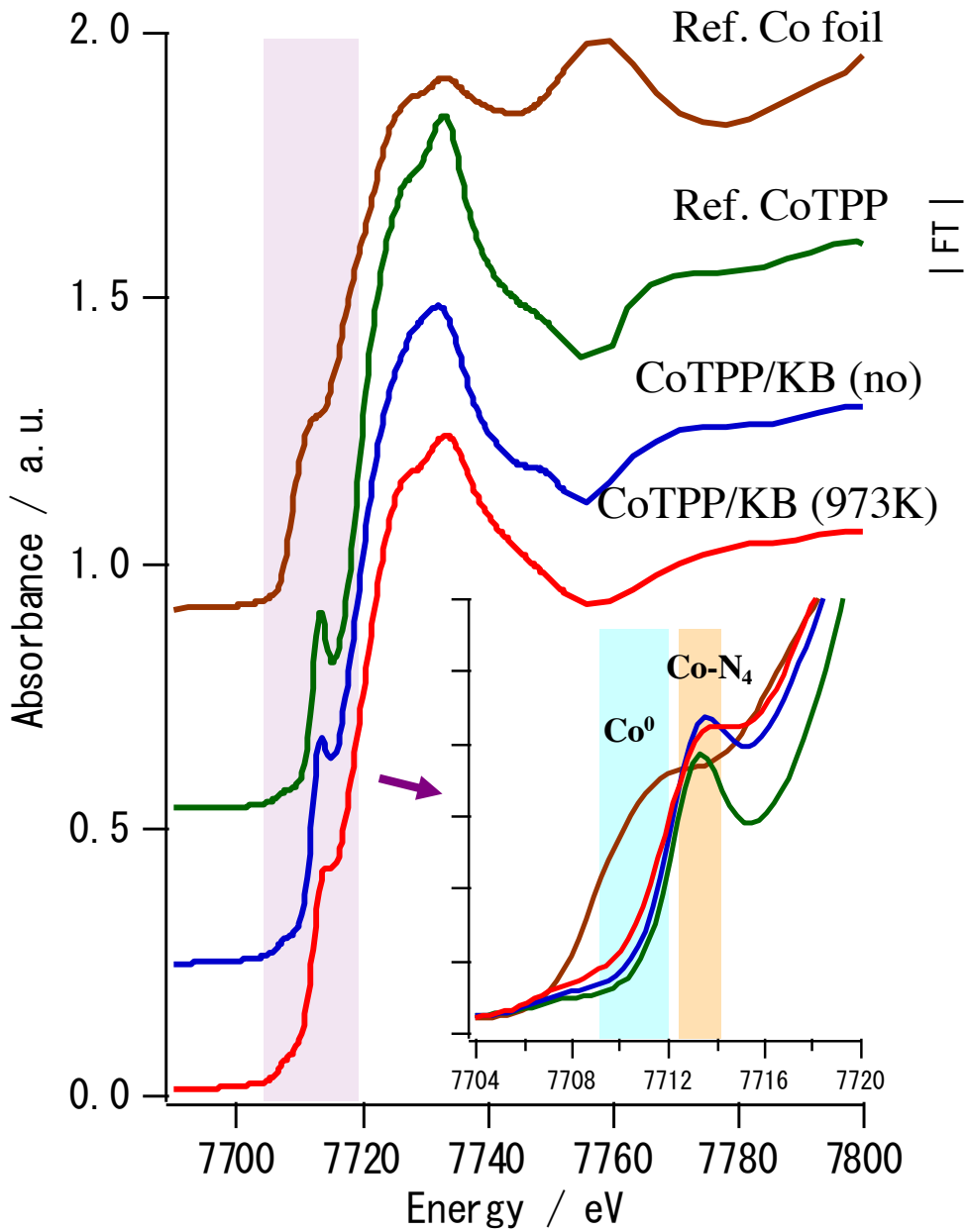
0.3wt% CoTPP/VGCF

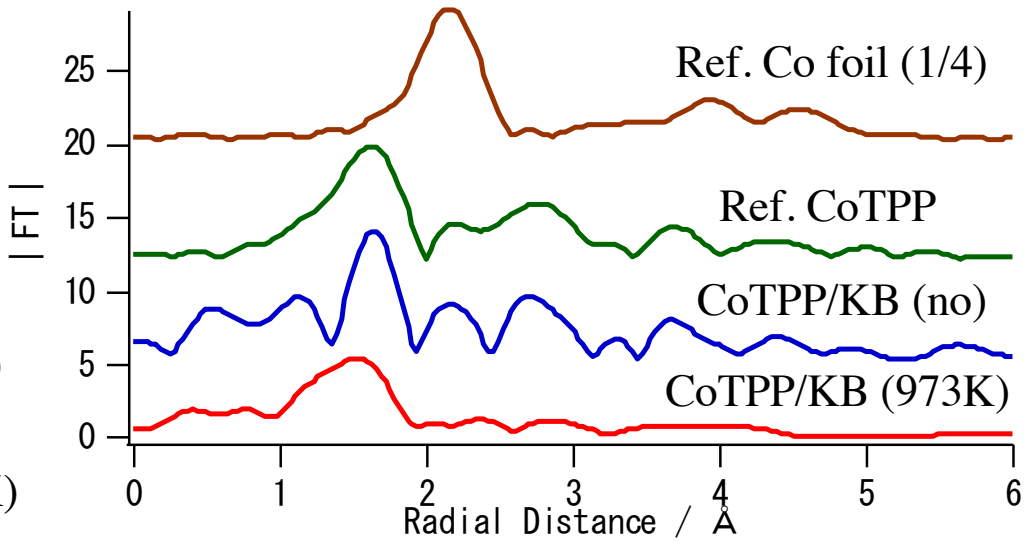
Co-N_x (Co^{II}) : 780.3 eV
Co^0 : 778.4 eV

Co-N: 398.3 eV around
C-N species: 400.5 eV



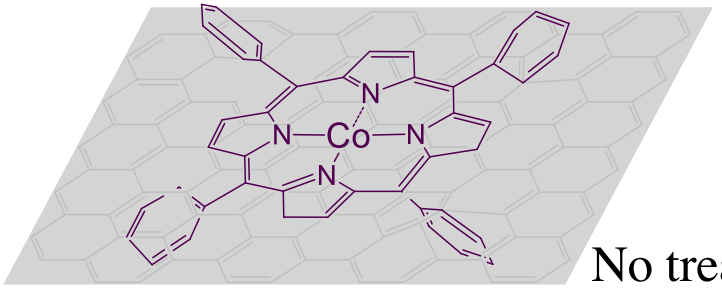
XAFS analysis 0.3wt% CoTPP/KB



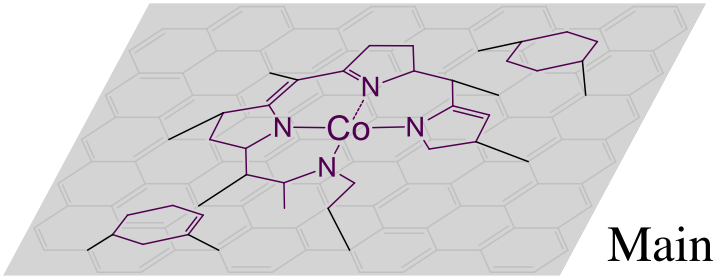


	N		Co	
	Num.	Dis.	Num.	Dis.
Co foil	-	-	12	2.5
CoTPP	**4.2**	2.0	2.4	3.0
CoTPP/KB (no)	**3.6**	2.0	0.9	2.5
CoTPP/KB (973K)	**2.5**	1.9	-	-

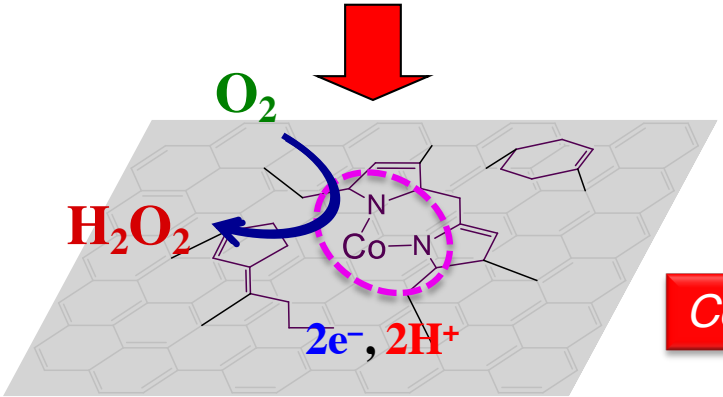
活性点



No treatment



Main species at 773K

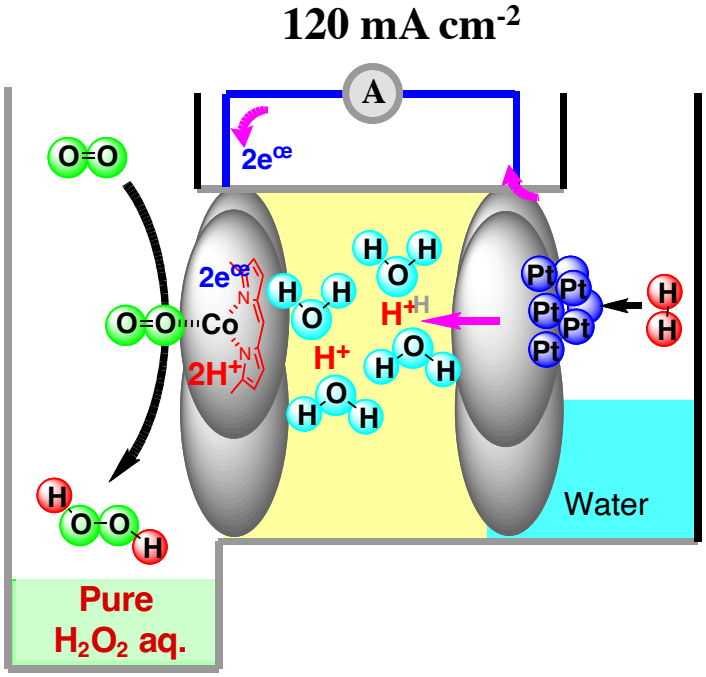


Main species at 1023K

Co-N_2C_x active site

0.05 wt% CoTPP/KB(1073K) electrocatalyst

Pure H_2O_2
Max 21 wt%(6.2 M)
68% CE (H_2 sel)
TOF 34 s^{-1}



CO_2の電解還元

電気エネルギー

CO_2

$CO_2 + nH^+ + ne^- \rightarrow C_xH_yO_z$

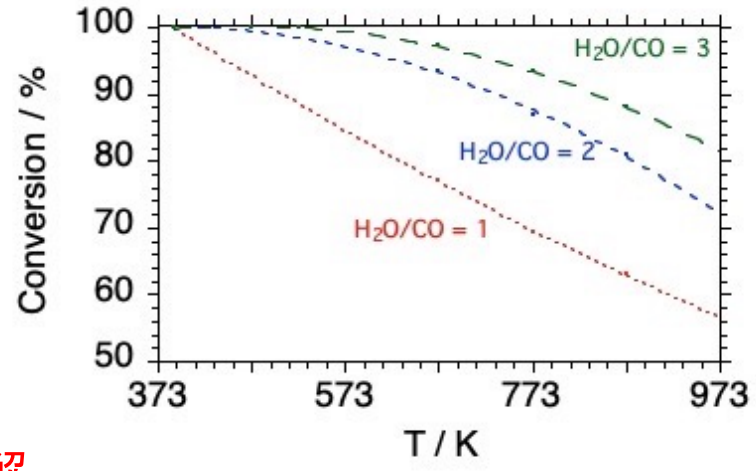
固定化，有用な物質に変換

$2CO_2 + 2H^+ + 2e^- \rightarrow H_2C_2O_4$	-0.475 V (SHE)
$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$	-0.199 V
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	-0.109 V
$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O$	-0.071 V
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	+0.030 V
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	+0.169 V

研究背景: CO_2電解還元の優位性

シフト反応→ $CO(g) + H_2O(g) \rightleftarrows CO_2(g) + H_2(g)$ $\Delta H_{298} = -40.3$ kJ mol^{-1}

(逆シフト反応←)



T > 873 K
担持金属触媒
Conv. ~50%

電気化学的CO_2分解

$2\ H^+ + 2\ e^- + ½\ O_2 \rightleftarrows H_2O(l)$ $E^0 = 1.23$ V ($\Delta G_{298} = -237.2$ kJ mol^{-1})
1.48 V ($\Delta H_{298} = -285.8$ kJ mol^{-1})

$CO_2(g) + 2\ H^+ + 2\ e^- \rightleftarrows CO(g) + H_2O\ (l)$ $E^0 =$ **- 0.11** V ($\Delta G_{298} = +21.2$ kJ mol^{-1})

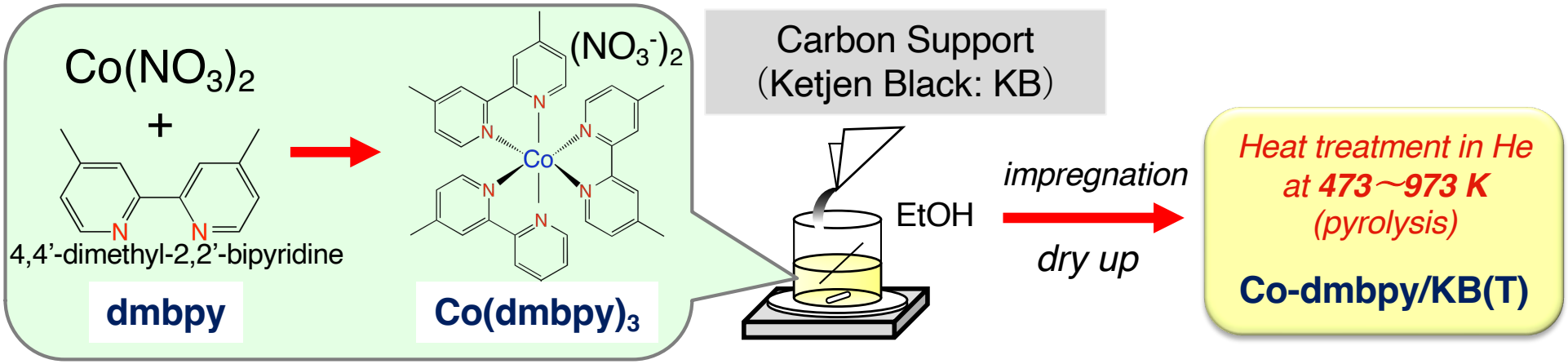
$CO_2(g) \rightleftarrows CO(g) + 1/2O_2\ (g)$ $E^0 =$ 1.34 V ($\Delta G_{298} = +258.4$ kJ mol^{-1})
1.47 V ($\Delta H_{298} = +283.03$ kJ mol^{-1})

$-\Delta\Delta G = RT \ln K = nF\eta$

η = 0.00 V, K = 1 (C.Pot: -0.11 V, conv = 50%**)**
η = **-0.10 V**, K = 2416 (C.Pot: -0.21 V, conv = **99.96%**)

CO_2電解還元

Preparation of Co-N-C electrocatalyst by impregnation method



Co loading = 1 ~ 3 wt%; dmbpy/Co = 5

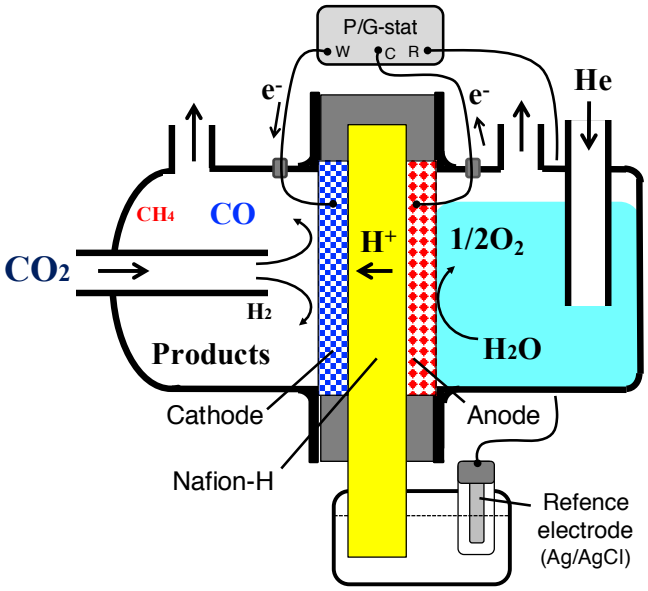
Cathode : Co-dmbpy/KB

$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$

E° = –0.11 V (SHE)

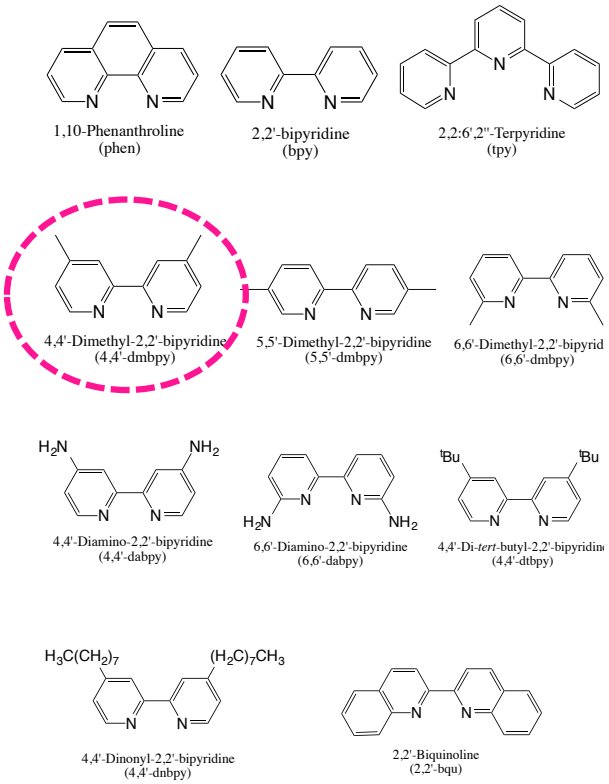
$2H^+ + 2e^- \rightarrow H_2$

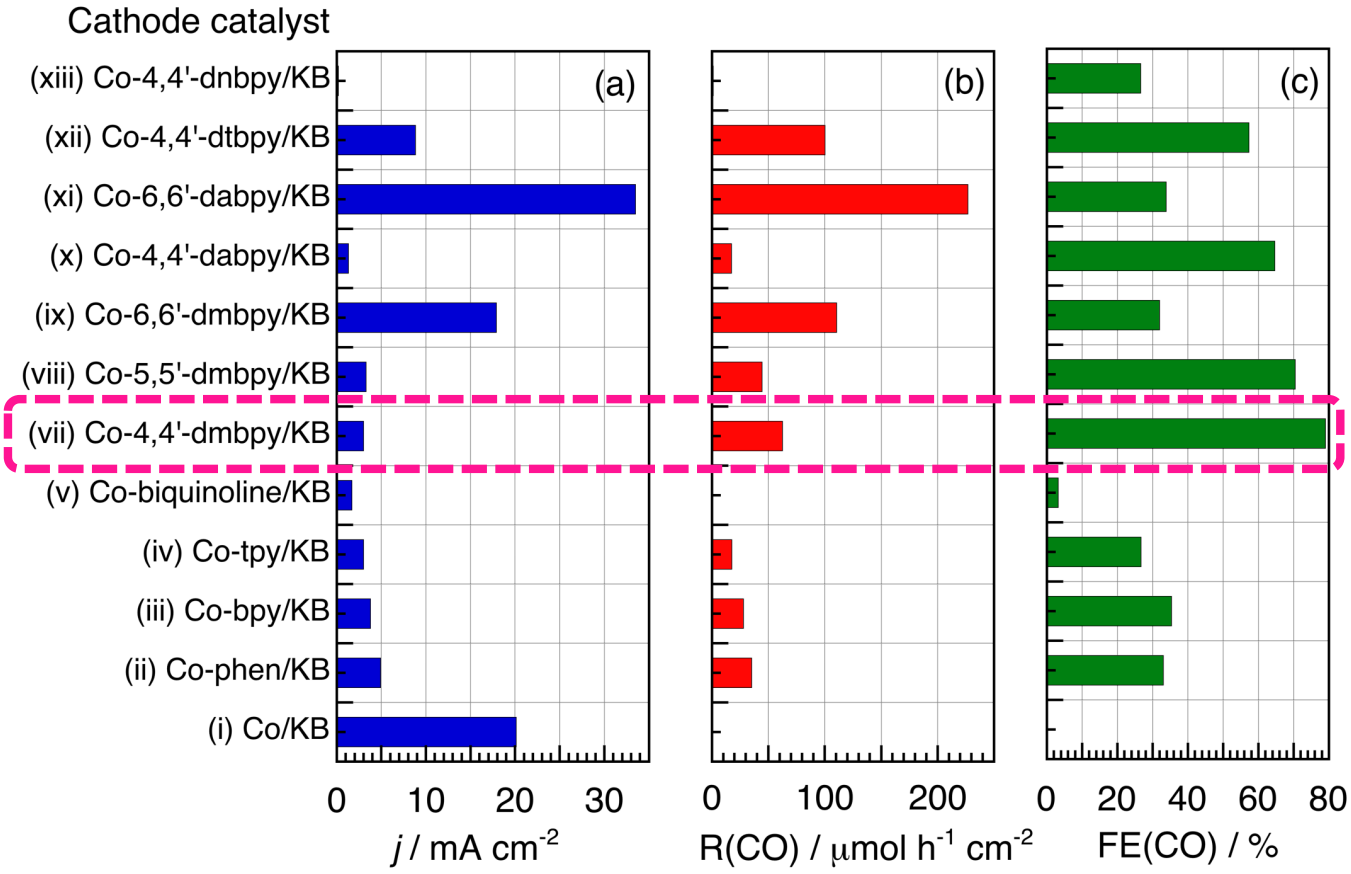
E° = –0.0 V (SHE)



Co-(N-Ligand)のスクリーニング

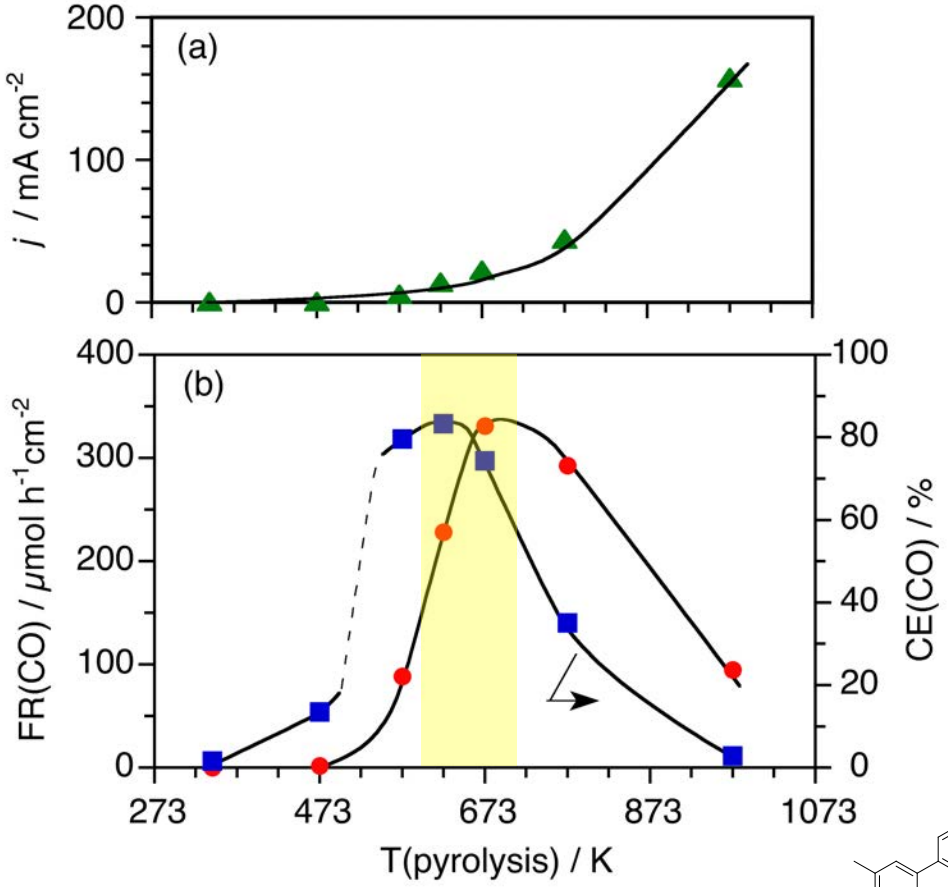
T. Maezuru, *ChemistySelect*, **2016**, *1* (17), 5533



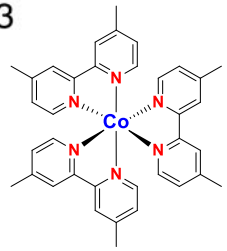


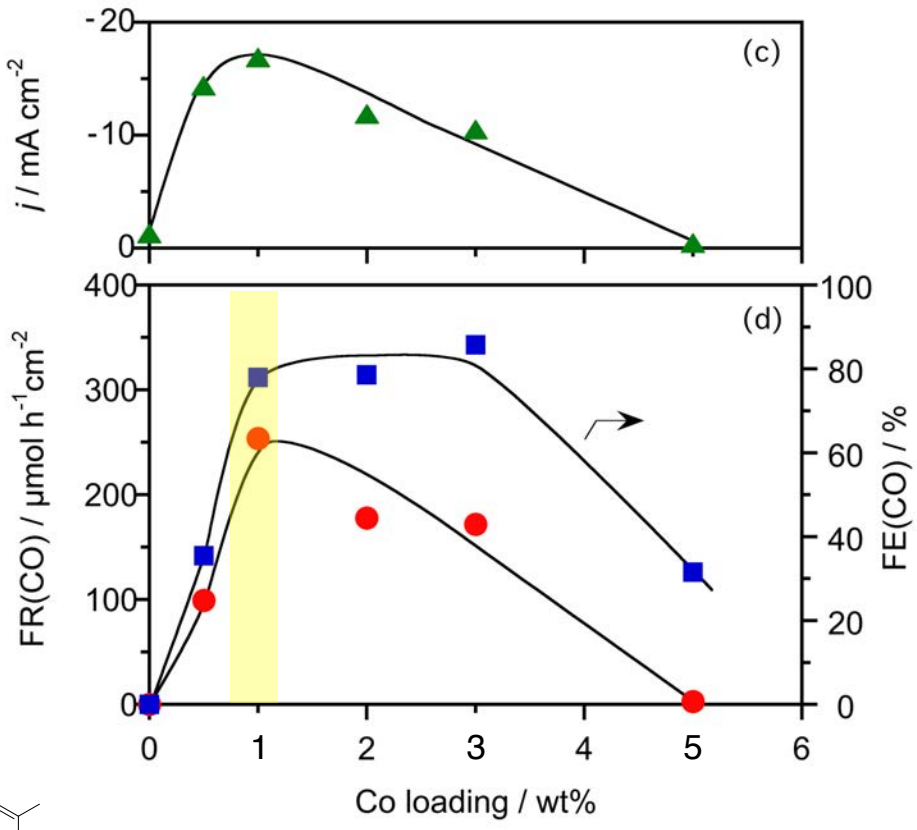
Co-ligands/KB activated at 673 K in He,
cathode potential -0.7 V and T = 273 K.

Co-dmbpy/KB 熱処理温度とCo担持量の効果



Catalyst : 1 wt%Co-(4,4'-dmbpy)/KB(T K)
Cathode Pot. : -0.75 V



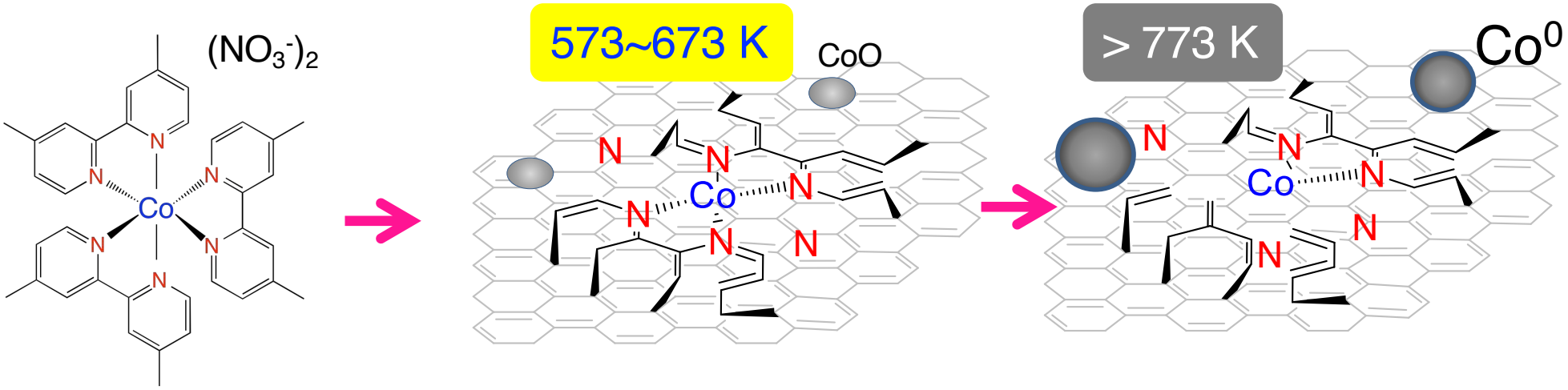


Catalyst : X wt%Co-(4,4'-dmbpy)/KB(673 K)
Cathode Pot. : -0.75 V

- CO_2 reduction activity was abruptly increased at 573 K.
- $FR(CO)_{max}$ = 0.33 mol h^{-1} cm^{-2} and TOF = 217 h^{-1} were at 673K.
- Heat treatment at > 773 K promoted H_2 evolution rather than CO_2 reduction.
- 1.0 wt% Co-loading is best.

Co-dmbpy/KB活性点構造

Y. Ogishima, *ACS Omega* **2020**, *5*, 19453



no reaction → **Selective reduction of CO_2** → **H_2 evolution**

$Co(dmbpy)_3$ has no CO_2 electroreduction activity.

No access of CO_2 to Co center.

• Decomposition of dmbpy results in forming atomically-dispersed Co-N_4 like structure.

• The Co-N_4 species should be the active site for electro reduction of CO_2.

• The Co-N_4 species converted to Co-N_2 species by a higher heat-treatment, which has no reduction activity of CO_2

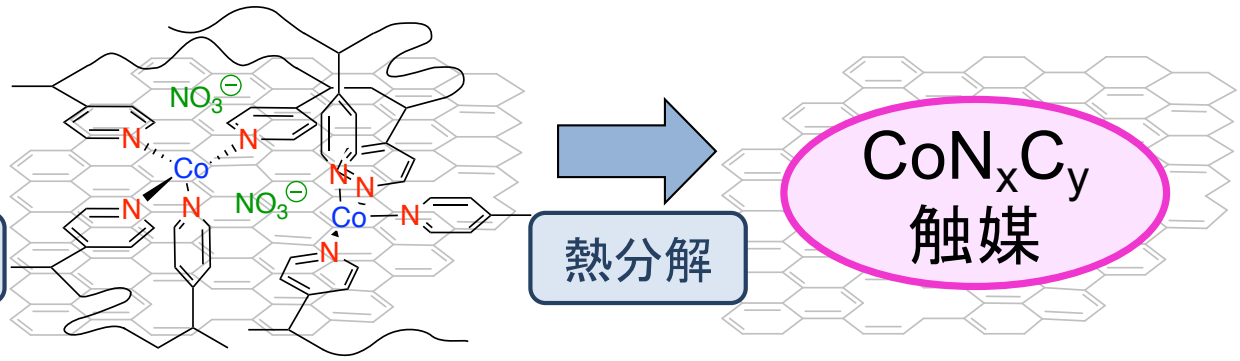
• Co^0 particle: H_2 evolution only takes place.

Co-N-C電極触媒高活性化

$Co(NO_3)_2$

KB

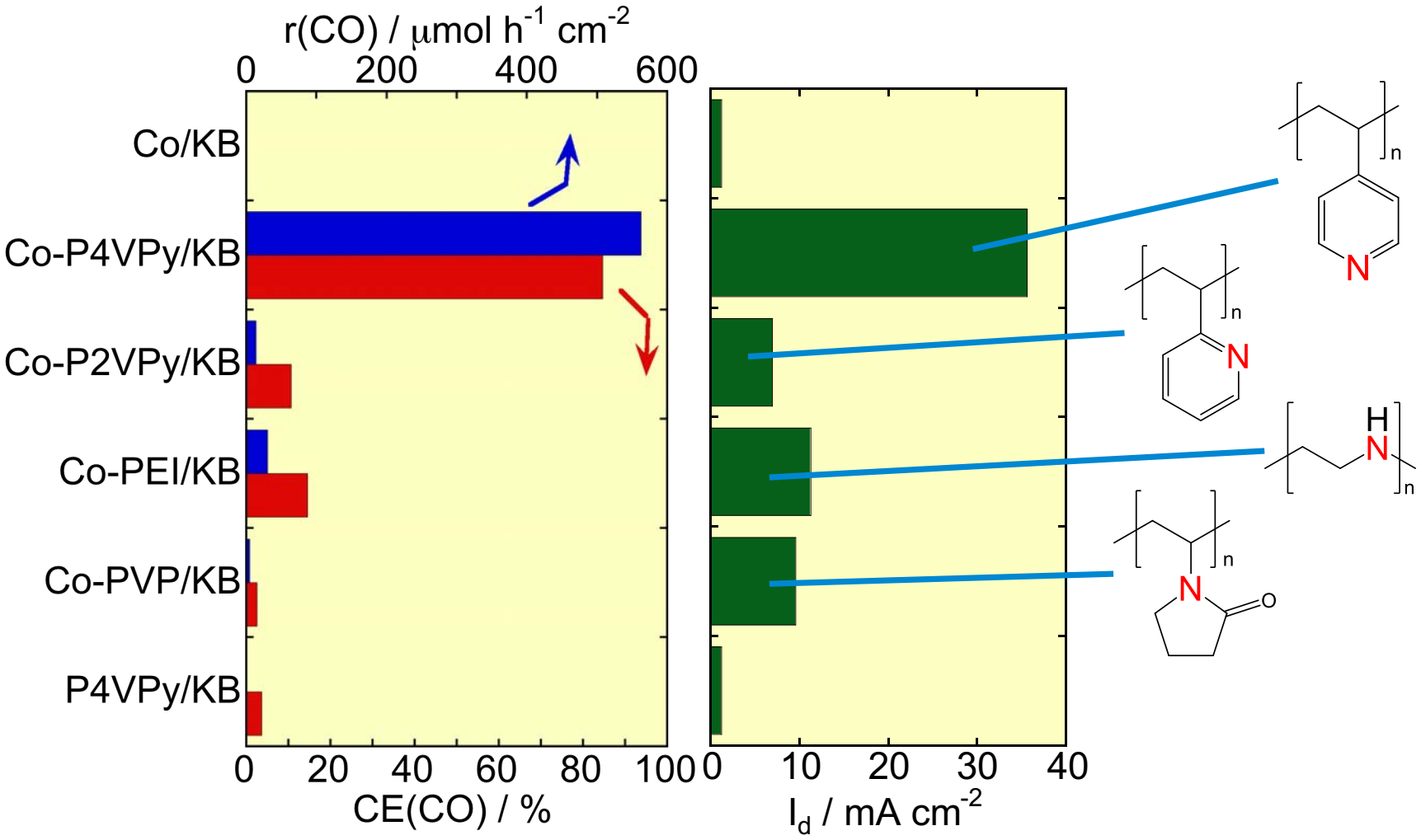
N-Polymer



Poly(4-vinylpyridine) (P4VPy),
Poly(2-vinylpyridine) (P2VPy),
Polyethylenimine (PEI),
Polyvinylpyrrolidone (PVP)

- N源として含Nポリマーを用いより高いCO_2還元活性を示すCo-N-C触媒の開発
- 活性点構造・反応機構の解明

Co-(polymer)/KB(773 K)によるCO_2電解還元

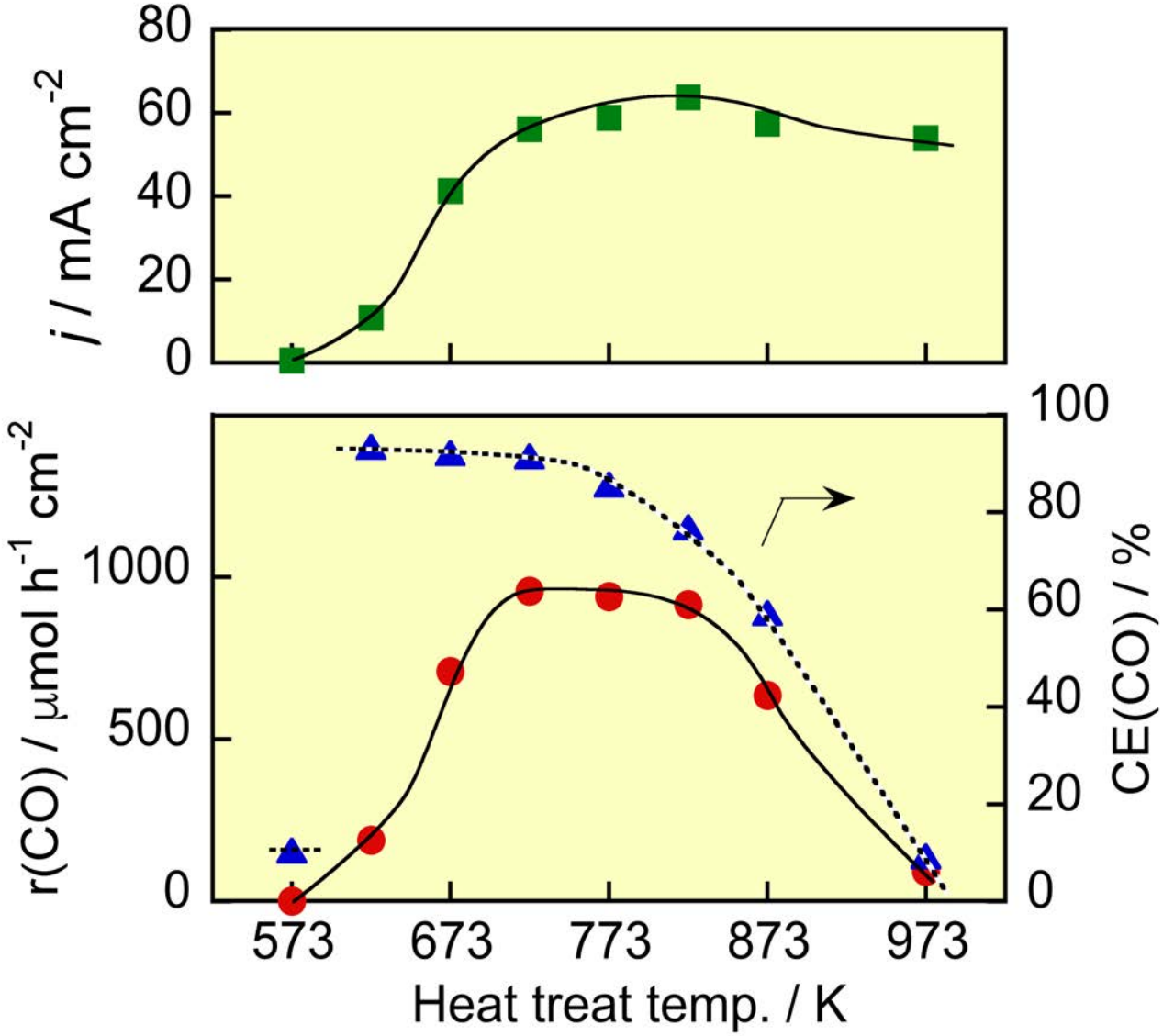


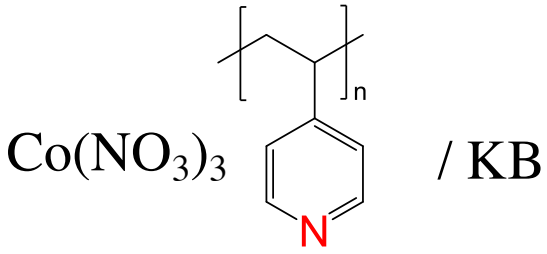
Reaction conditions

Cat.: Co-Polymer/KB(773 K), Co loading: 2 wt%,Polymer loading: 40 wt%,
Cathode Pot.: **-0.50 V** (SHE), Reaction temp.: **273 K**

Co-P4VPy/KBの熱処理温度依存性

-0.60 V (SHE) 定電位電解

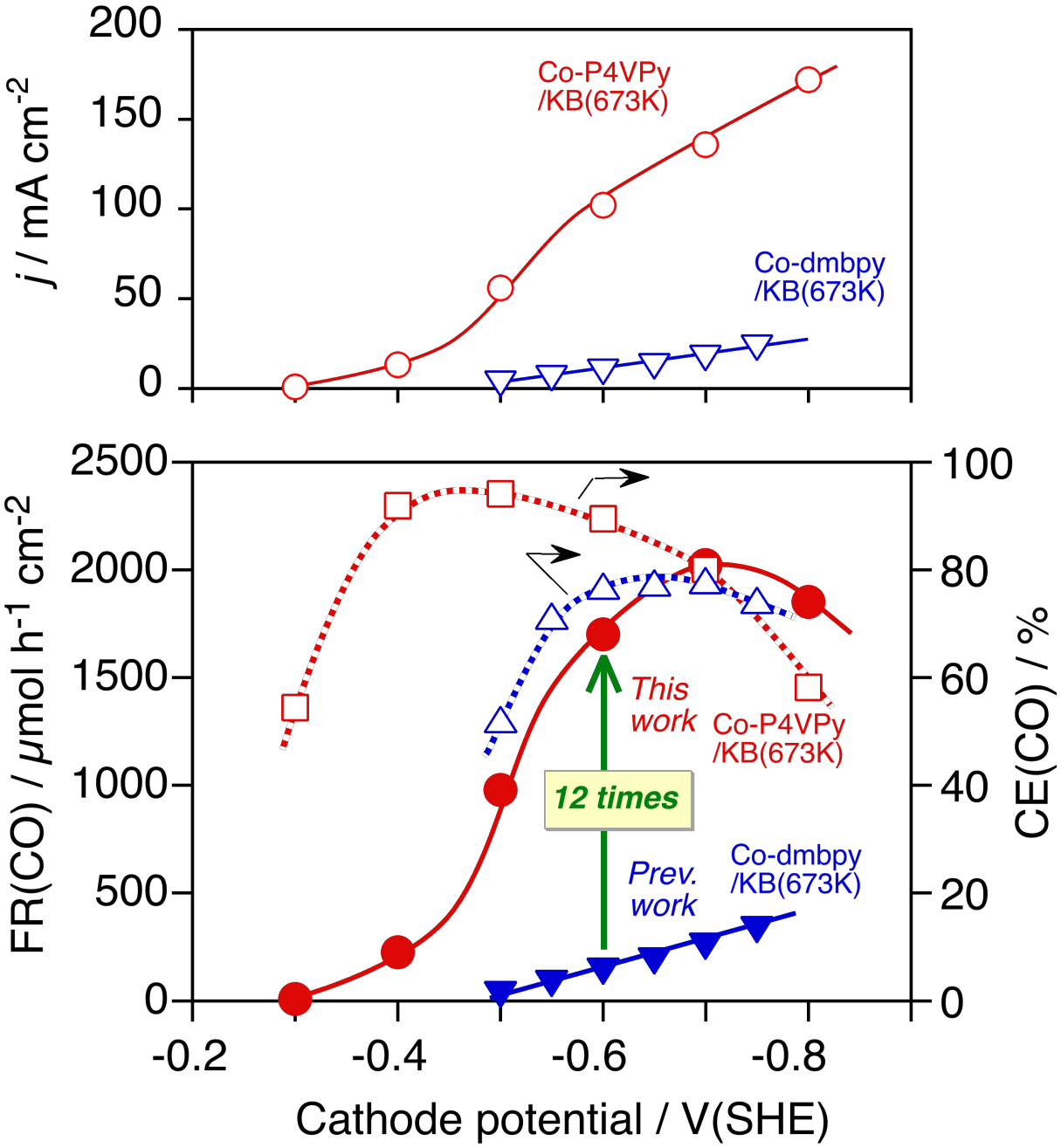


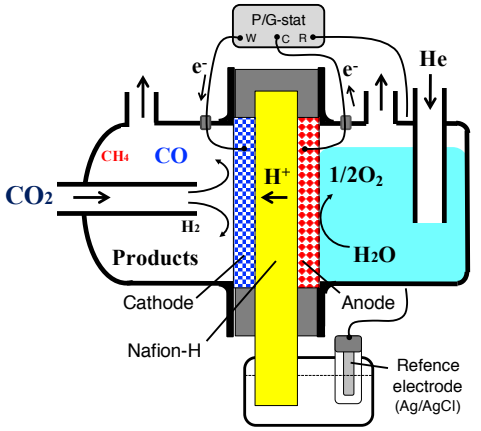


P4VPy

Reaction condition
Cat.: Co-P4VPy/KB(T K),
Co loading: 2 wt%,
P4VPy loading: 40 wt%,
Reductant: H_2O,
Heat treat.: 573 ~973 K,
Cathode Pot.: -0.60 V (SHE),

Co-P4VPy/KB(673K) vs Co-dmbpy/KB(673K)



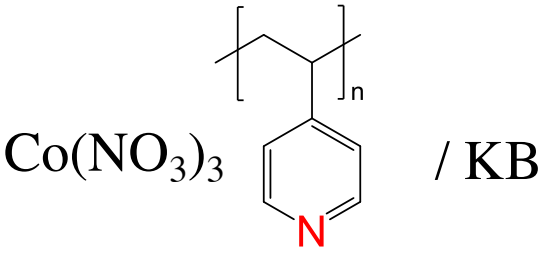


T: 298 K,

Cathode: Co-P4VPy/KB(673 K),

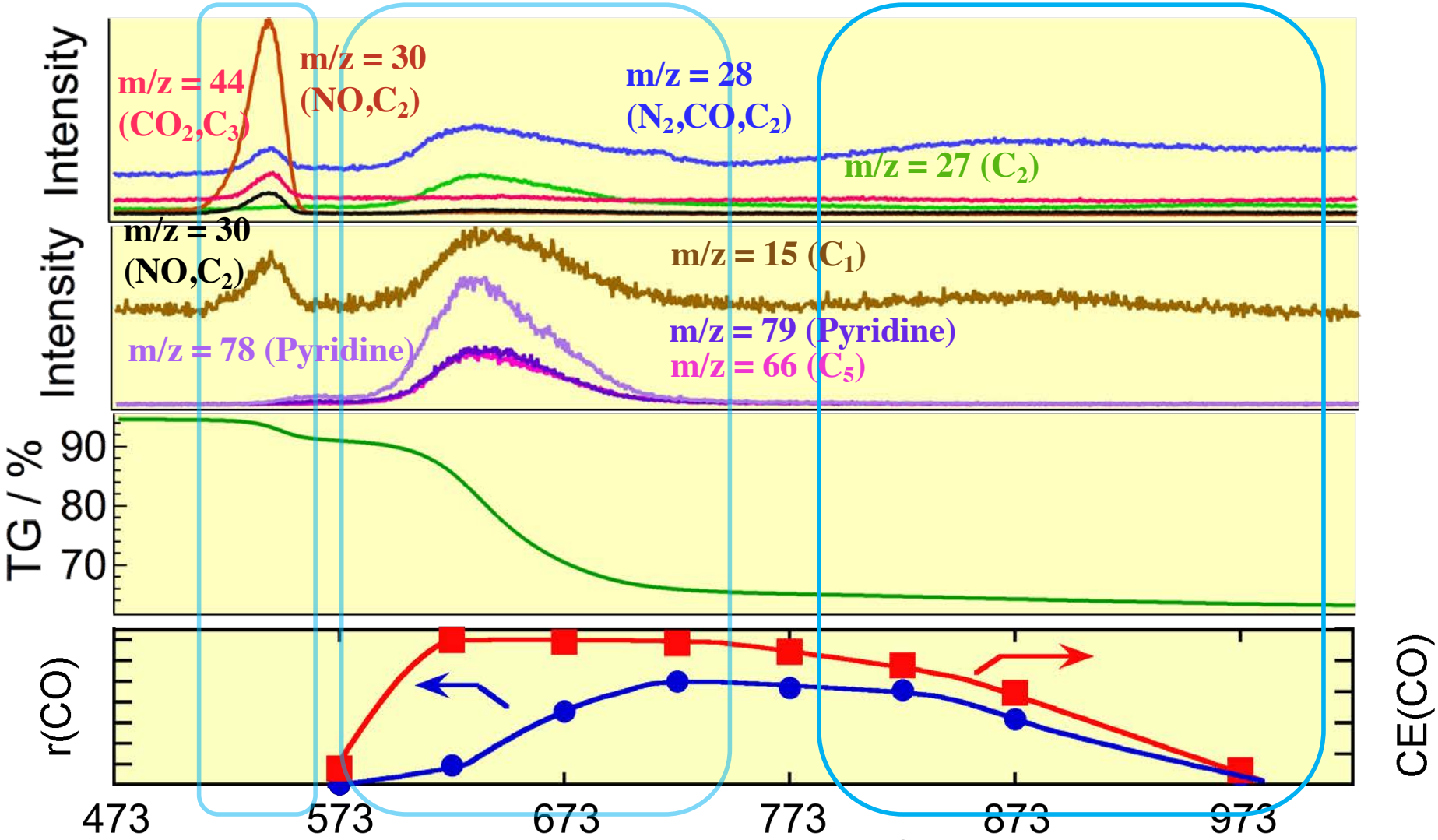
P(CO_2): 1.0 atm,

Anode: Ir/KB, H_2O.



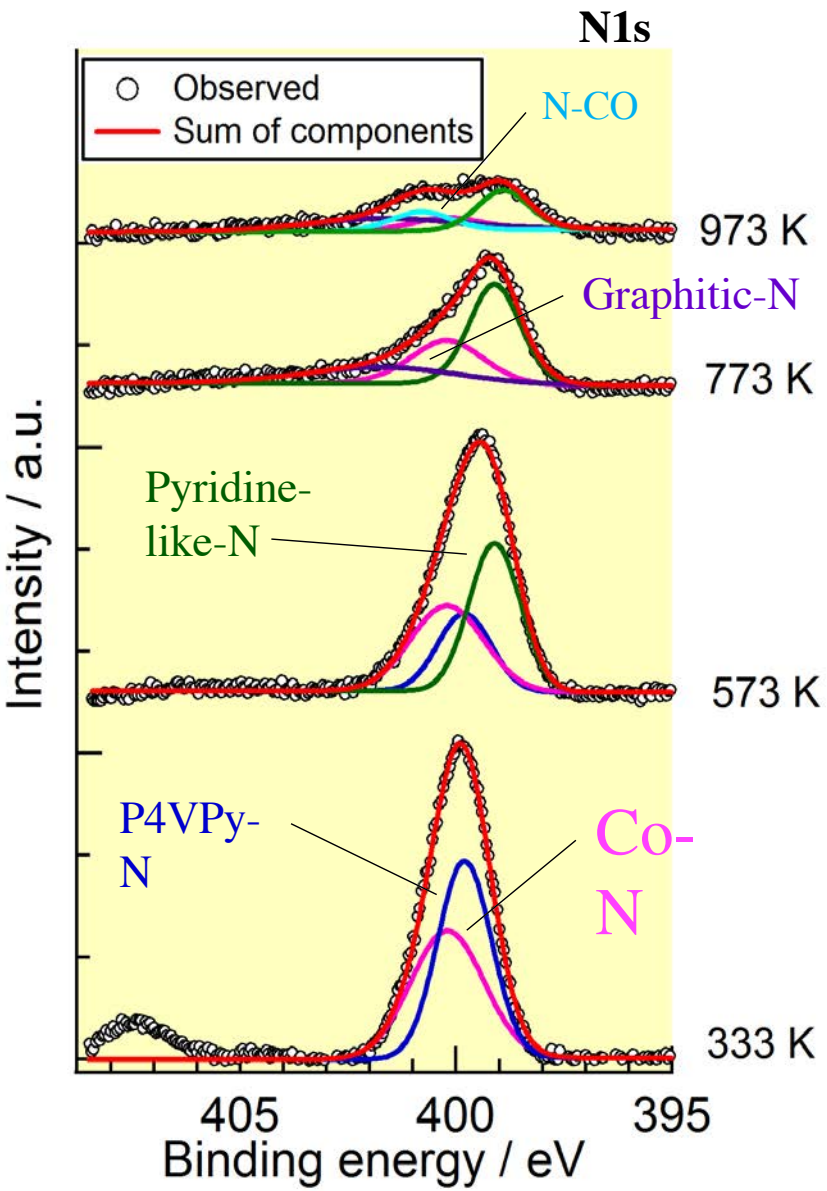
P4VPy

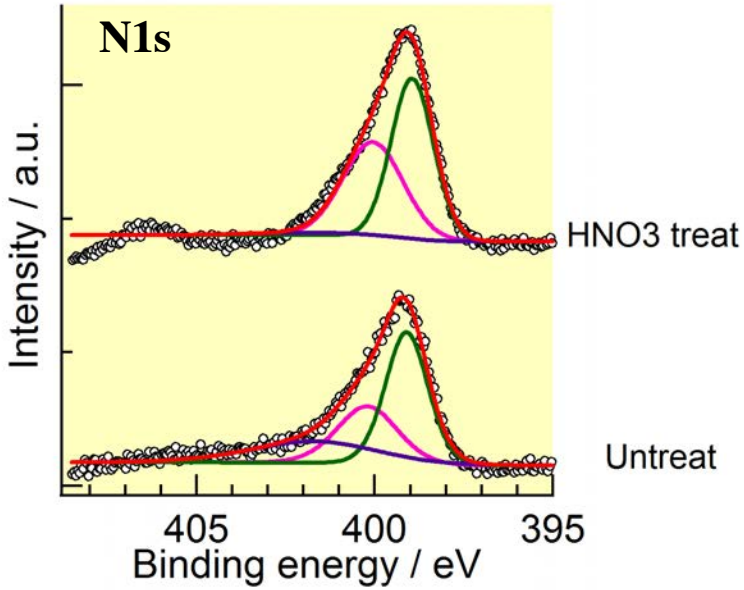
TG-MS:活性点形成過程の観察

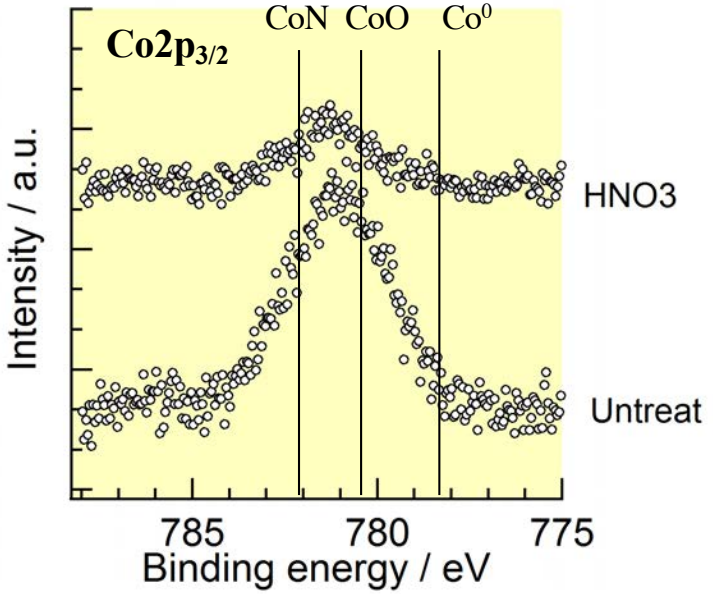


XPS:N1s & $Co2p_{3/2}$

2 wt%Co-P4VPy/KB(T K)

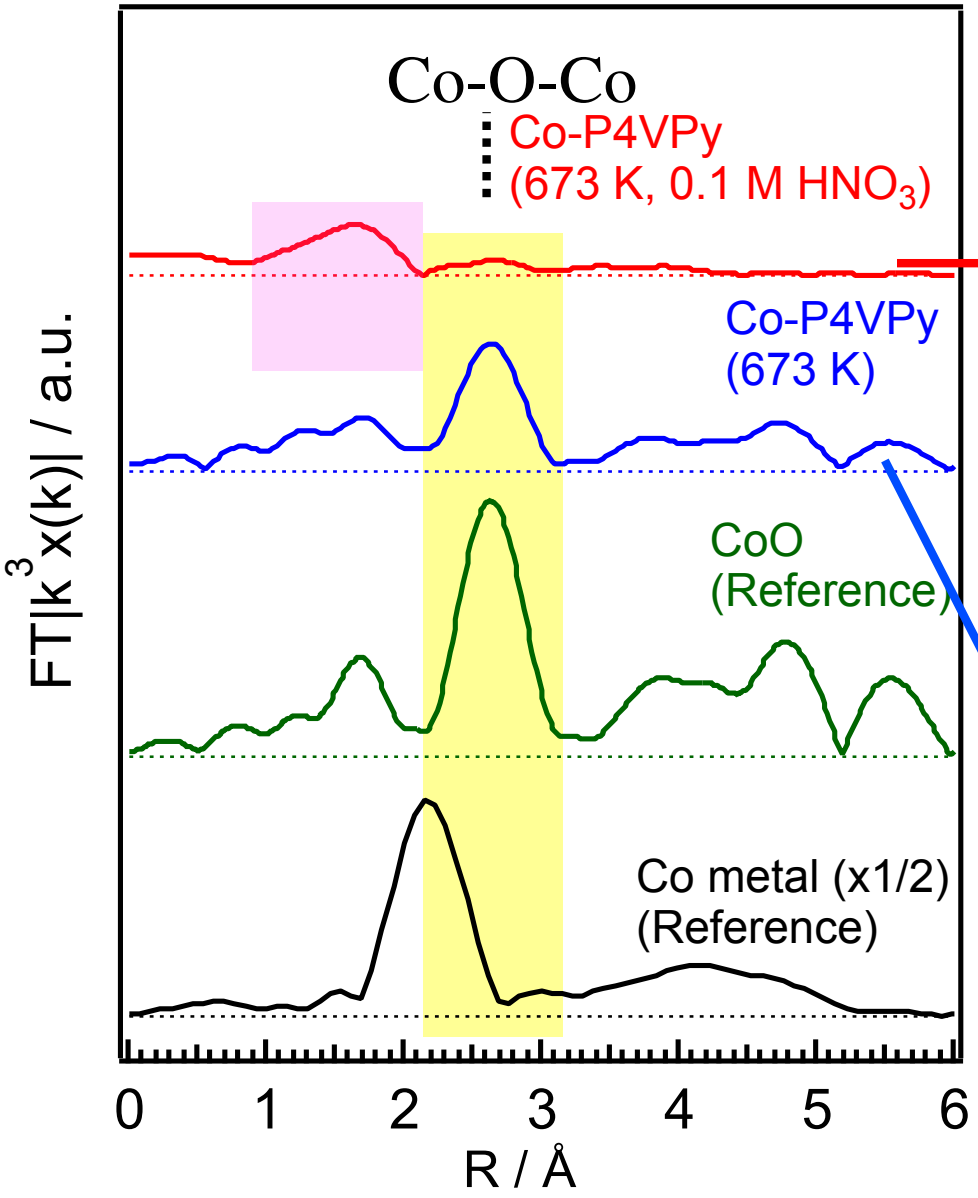


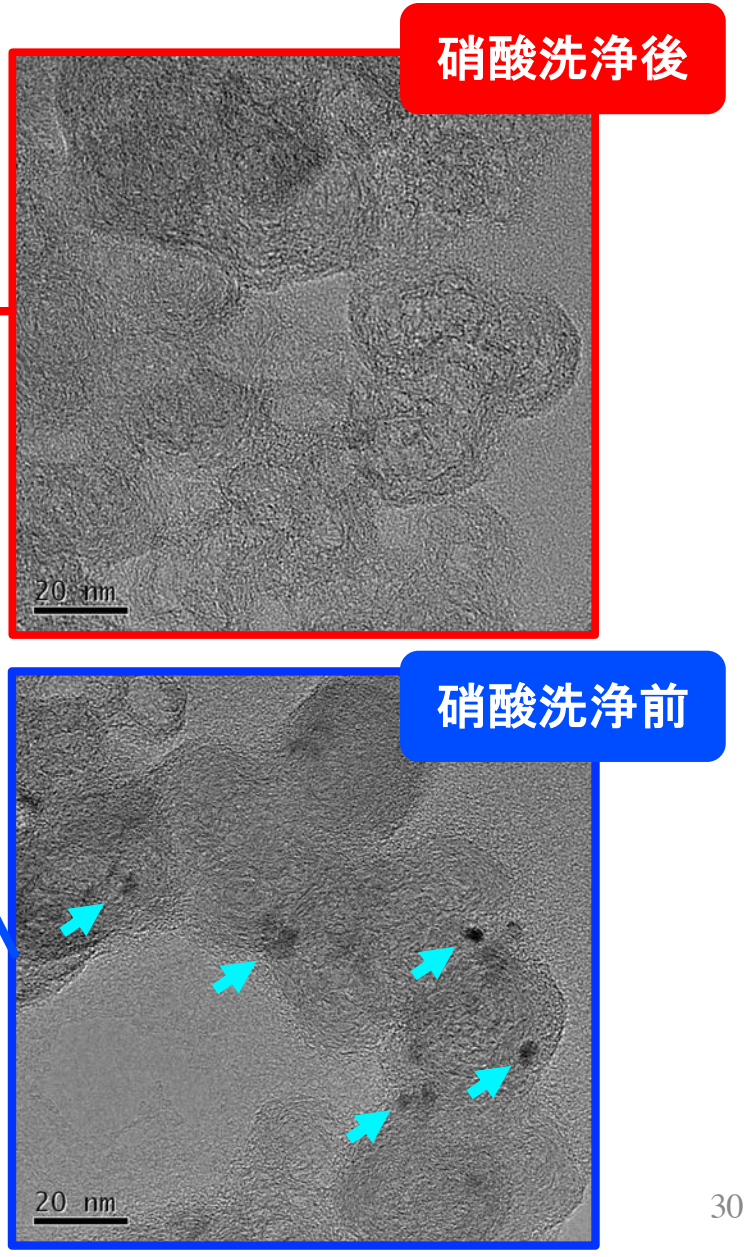




—P4VPy-N, —Co-N, —Pyridine-N, —Graphitic-N, —N-CO

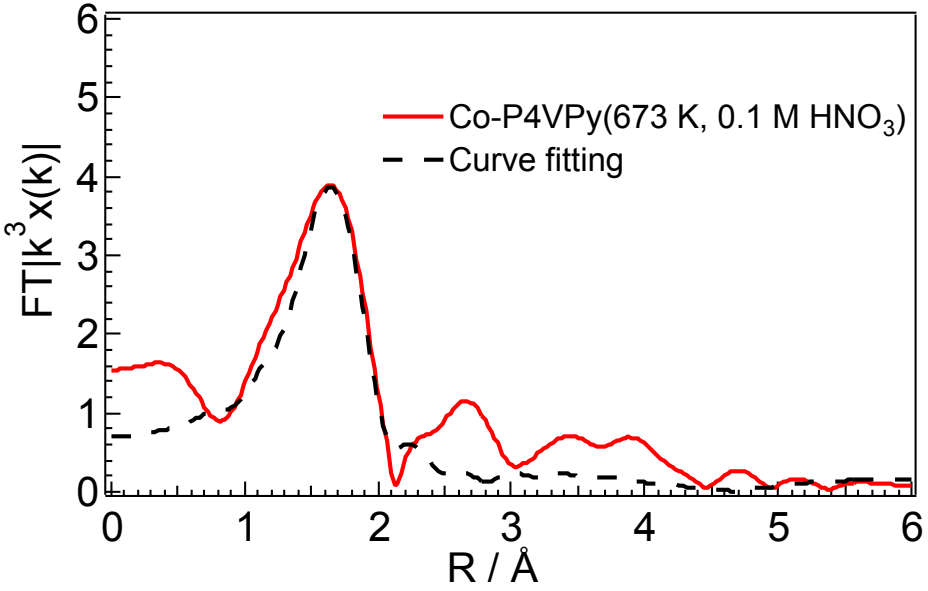
Co K吸収端のFT-EXAFS



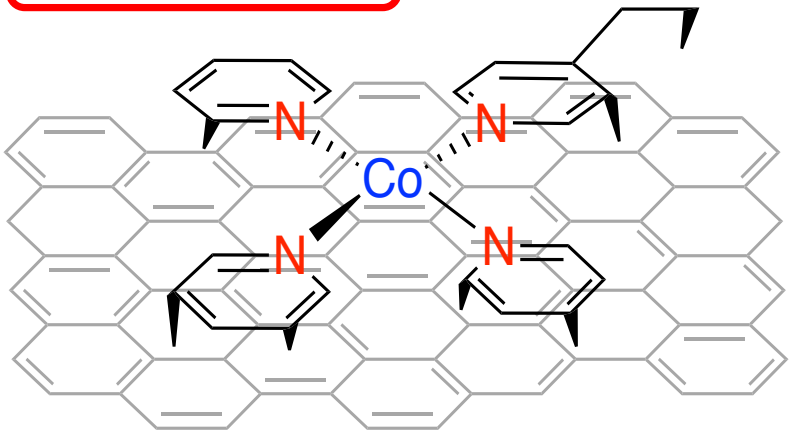


カーブフィッティング

Co-P4VPy(673 K, 0.1 M HNO_3)



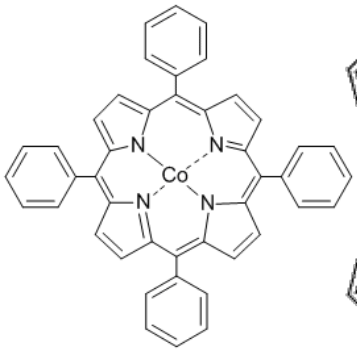
構造モデル



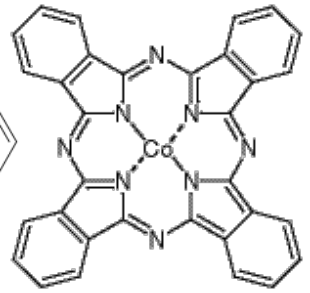
Co-N_4-C

Co-N フィッティング結果(0.57 ~ 2.24 Å)

	N(配位数)	R(結合距離)/Å
Co-P4VPy (673 K, 0.1 M HNO_3)	**4.38**	**2.09**
CoPc[1]	4.0	1.91
CoTPP[2]	4.2	1.96



CoTPP

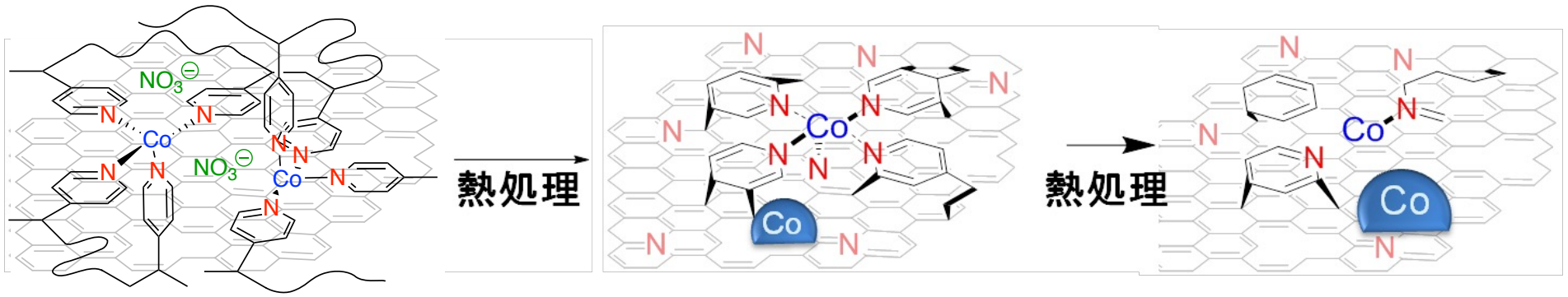


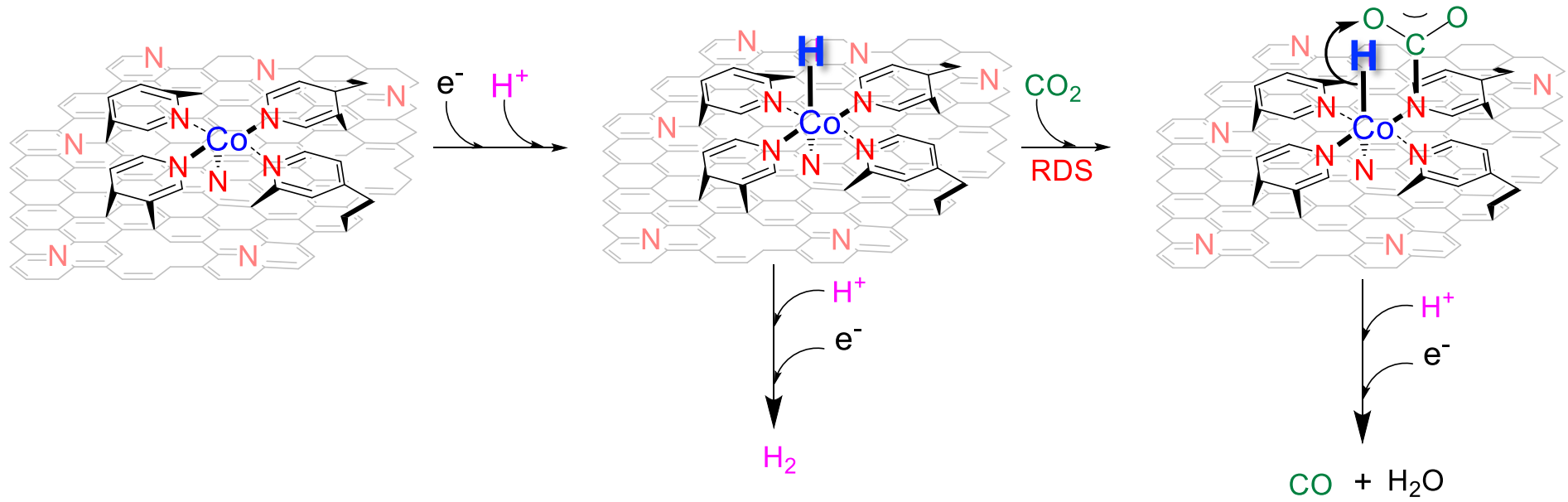
CoPc

(1) X. Wang et al. / ChemElectroChem 5 (2018) 3478 – 3485

(2) I. Yamanaka et al. / Electrochimica Acta 108 (2013) 321–329

活性点形成モデル


$NO_3^{\ominus}$
$NO_3^{\ominus}$
Co
Co
Co
Co
熱処理
熱処理


e⁻
H⁺
H
CO₂
RDS
H⁺
e⁻
H₂
O
C
O
H
H⁺
e⁻
CO + H₂O

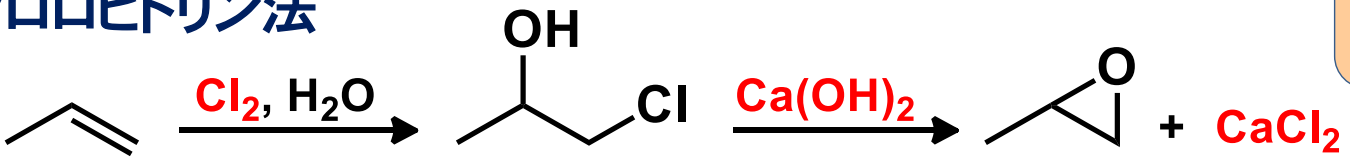
プロピレンオキシド(PO)合成

POの生産・用途

・石油化学工業の基幹中間体　年産約7.5 Mt
・ポリウレタン、ポリエステル、ポリプロピレングリコールの原料

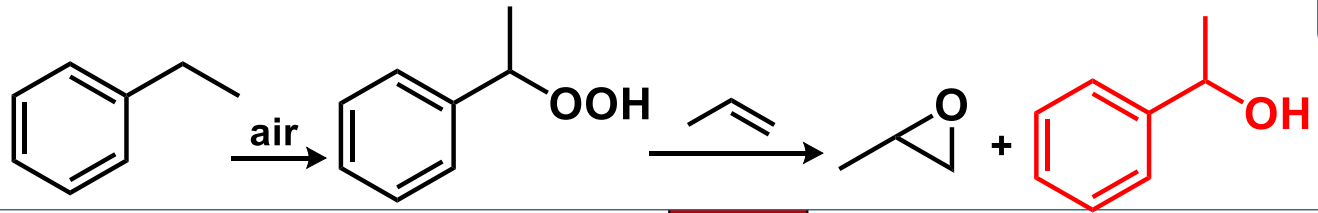
POの工業的製法

クロロヒドリン法



・多段階プロセス
・環境負荷が大きい

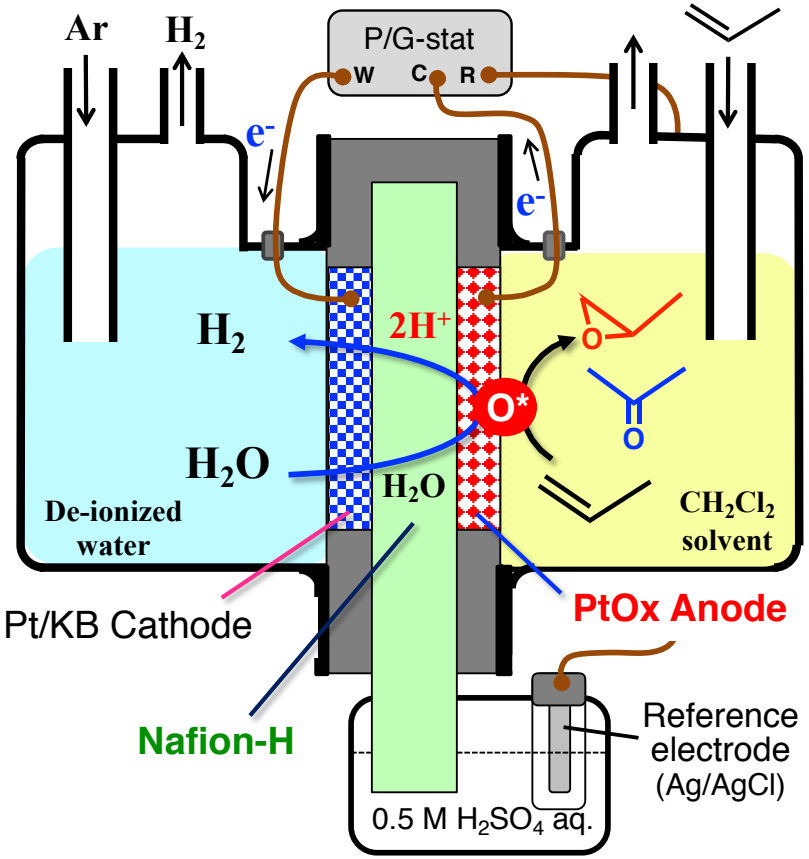
ハイドロパーオキサイド法



・多段階プロセス
・副産物

効率的な新規酸化法の開発が必要

研究背景



Anode

$H_2O \rightarrow O^* + 2H^+ + 2e^-$

$2O^* \rightarrow O_2$

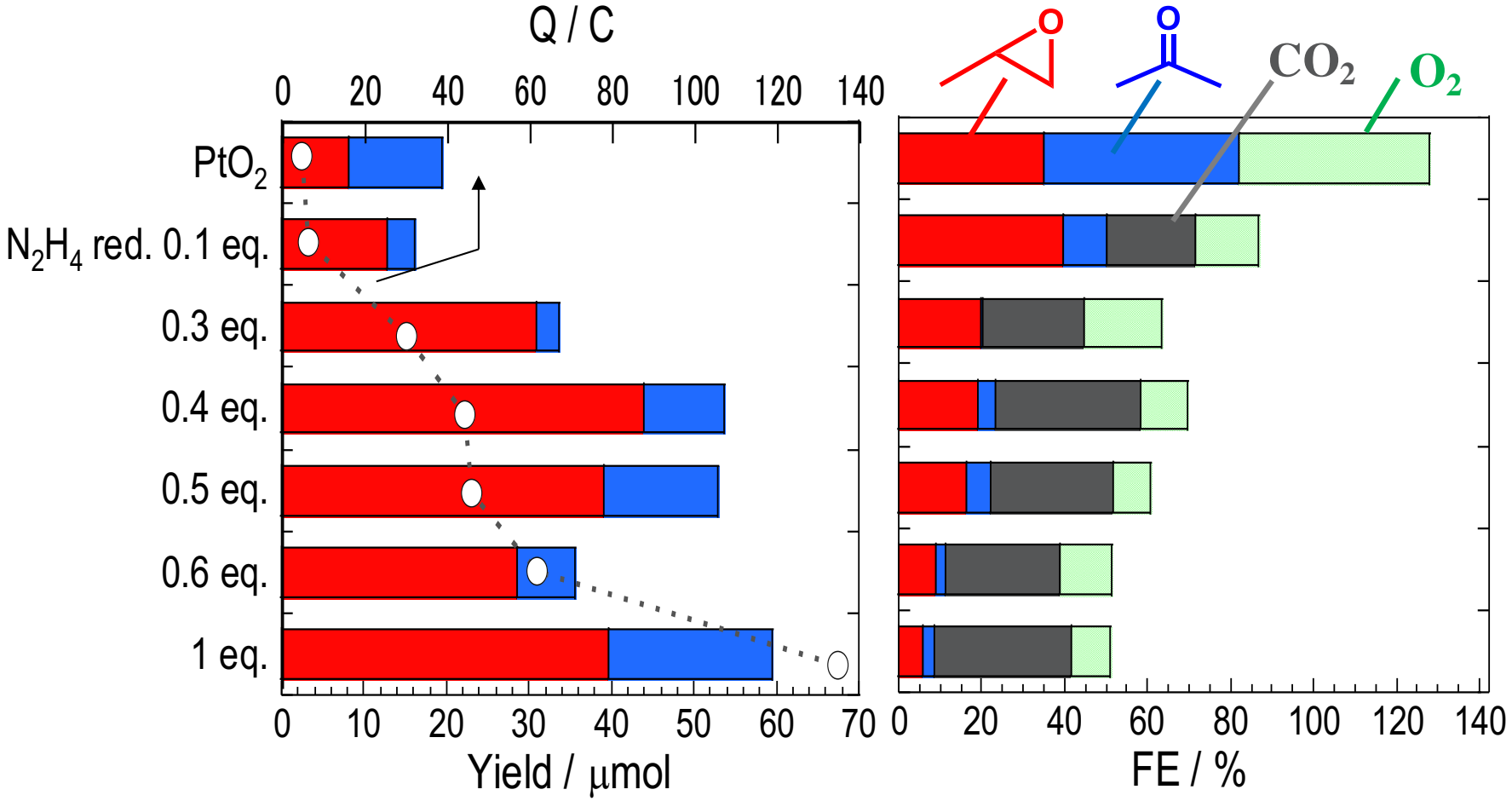
$C_3H_6 + O^* \rightarrow C_3H_6O$

***PO*生成活性発現**

Pt_3O_4 —0.5当量N_2H_4 還元処理→ PtOx

Pt^0 —酸化処理→ PtOx

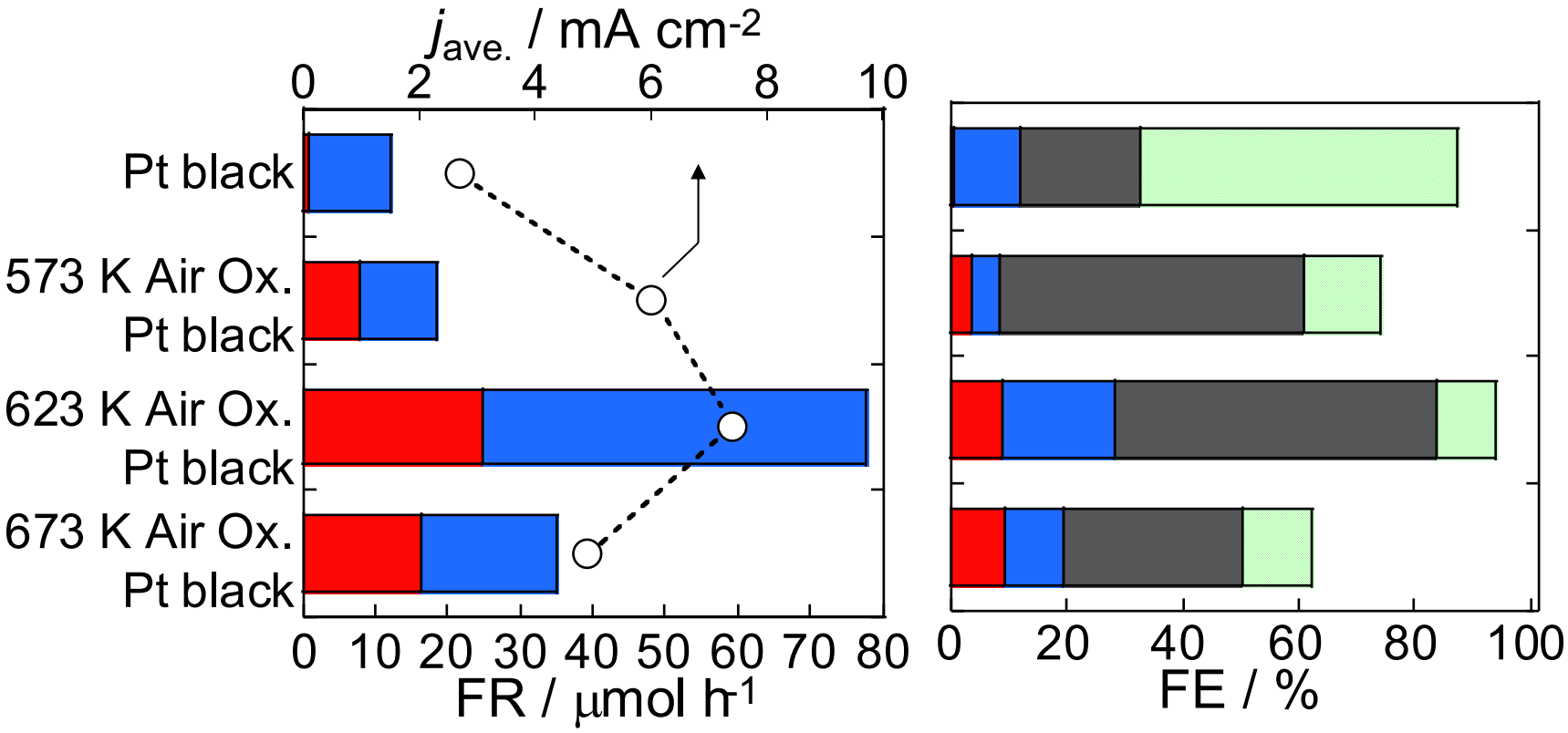
N_2H_4還元PtO_2によるプロピレン電解酸化



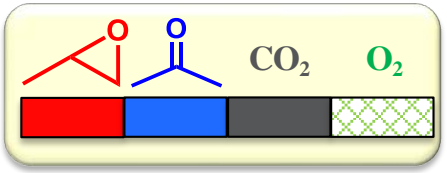
- N_2H_4 0.4等量でPO収量最大
- 0.4等量でFE19%, PO選択率82%

アノード触媒: N_2H_4還元PtO_2 70 mg
アノード溶液: CH_2Cl_2 30 mL
アノード電位: 1.6 V (SHE)

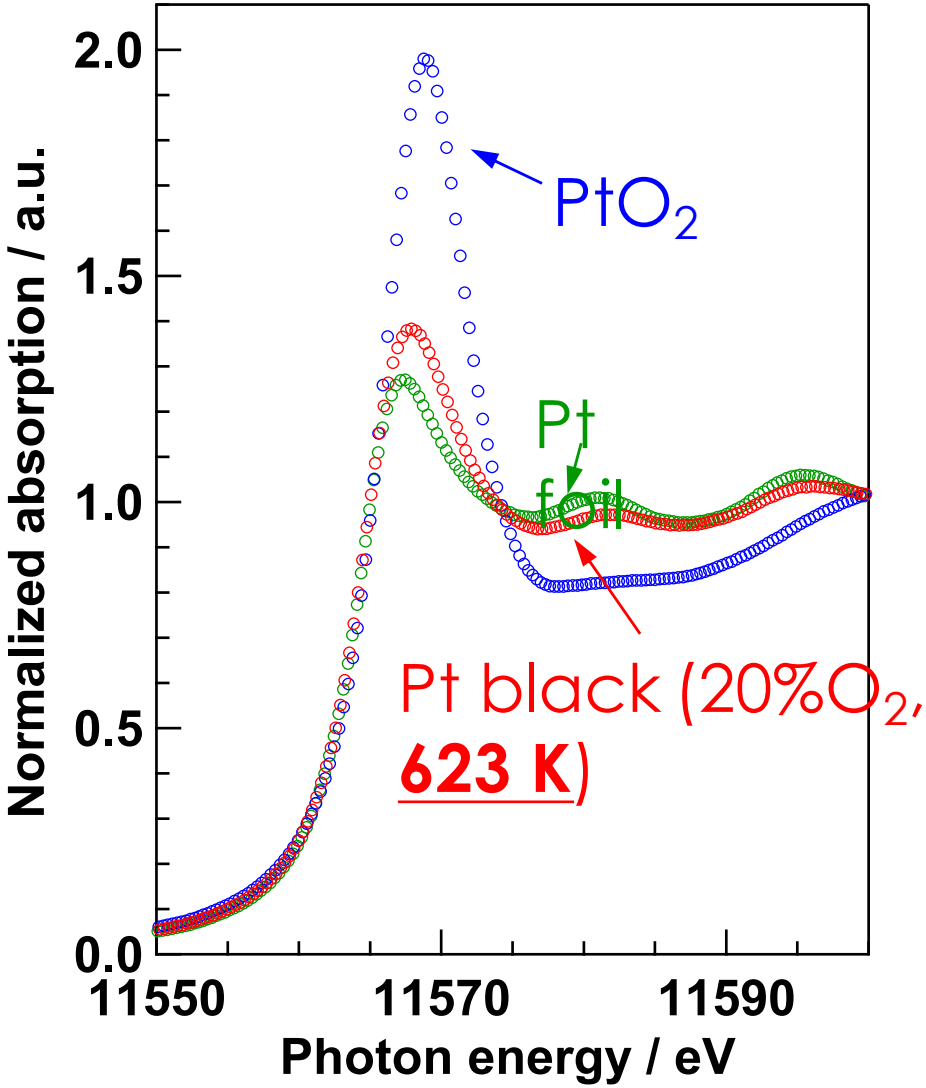
空気酸化したPt blackによるプロピレン電解酸化

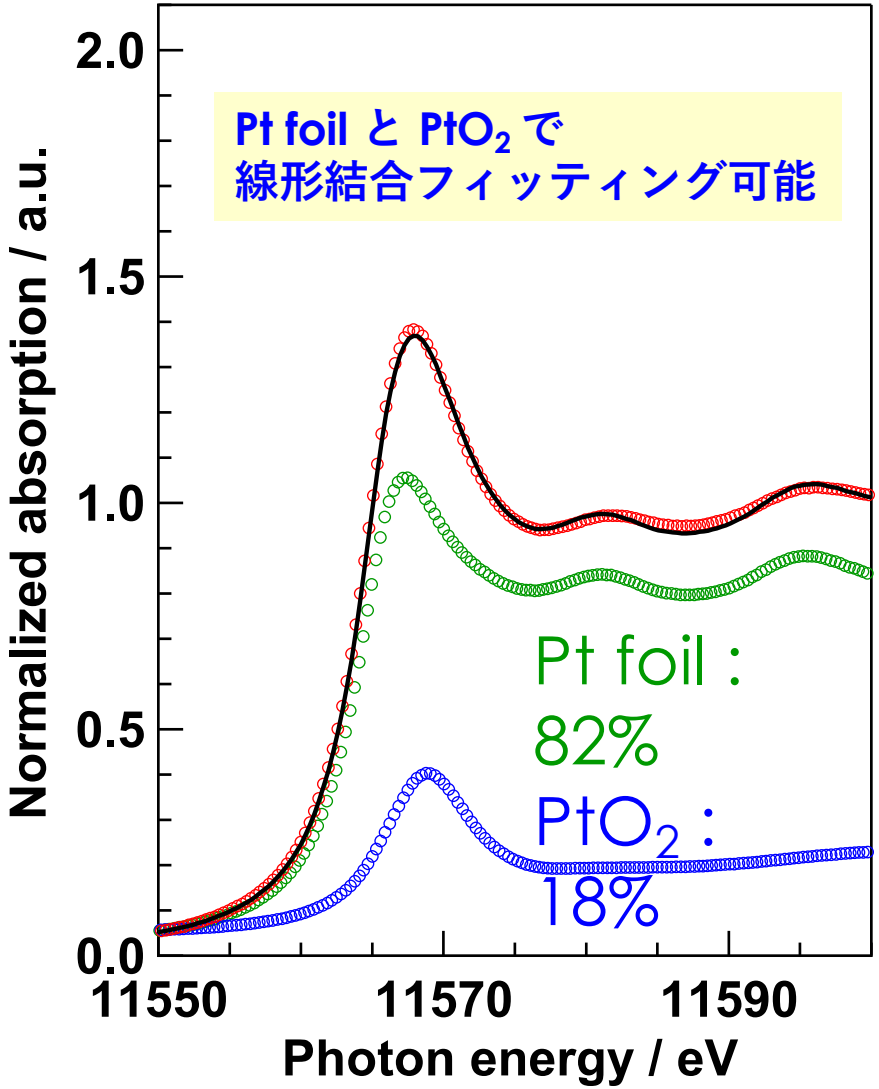


定電位電解(1.6 V vs. SHE)



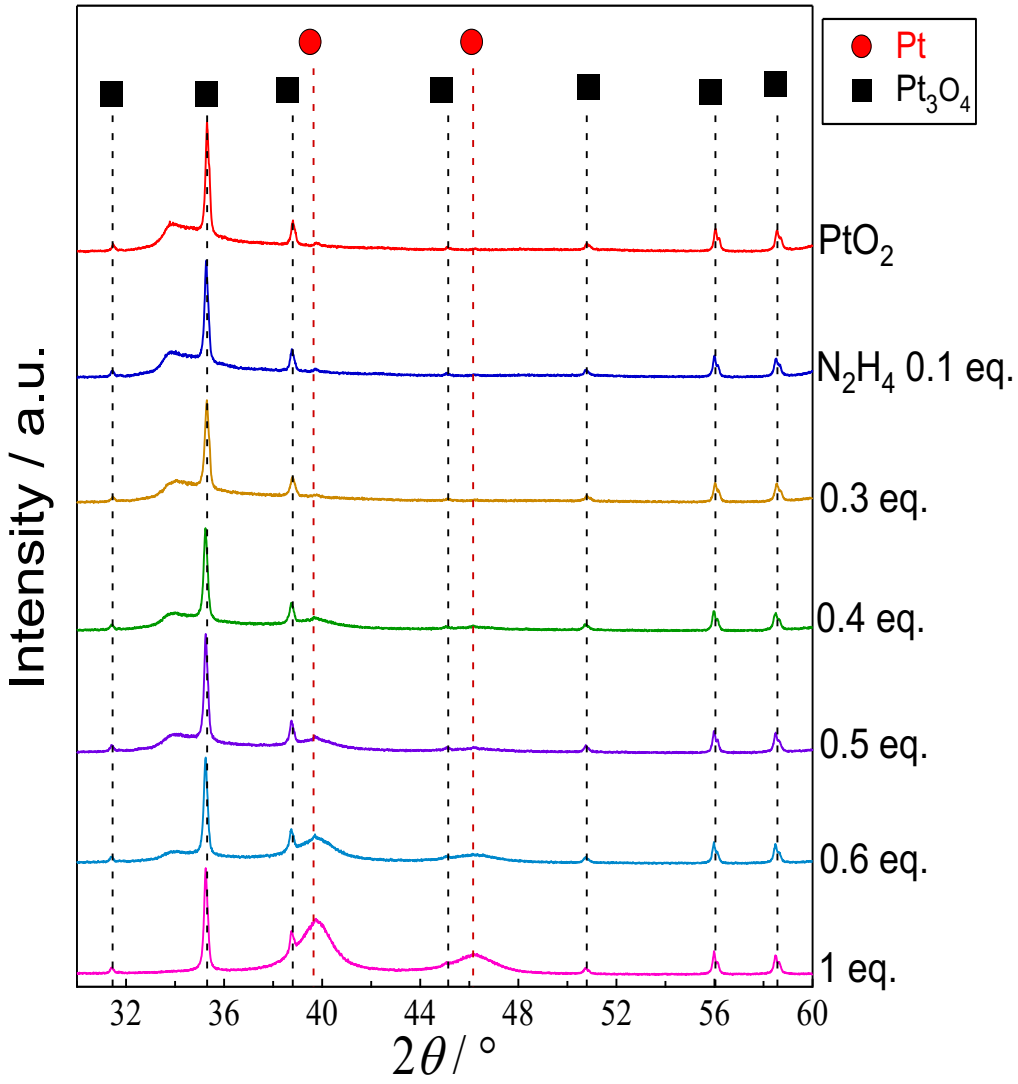
Pt L_3-edge XANESスペクトルのLCF解析



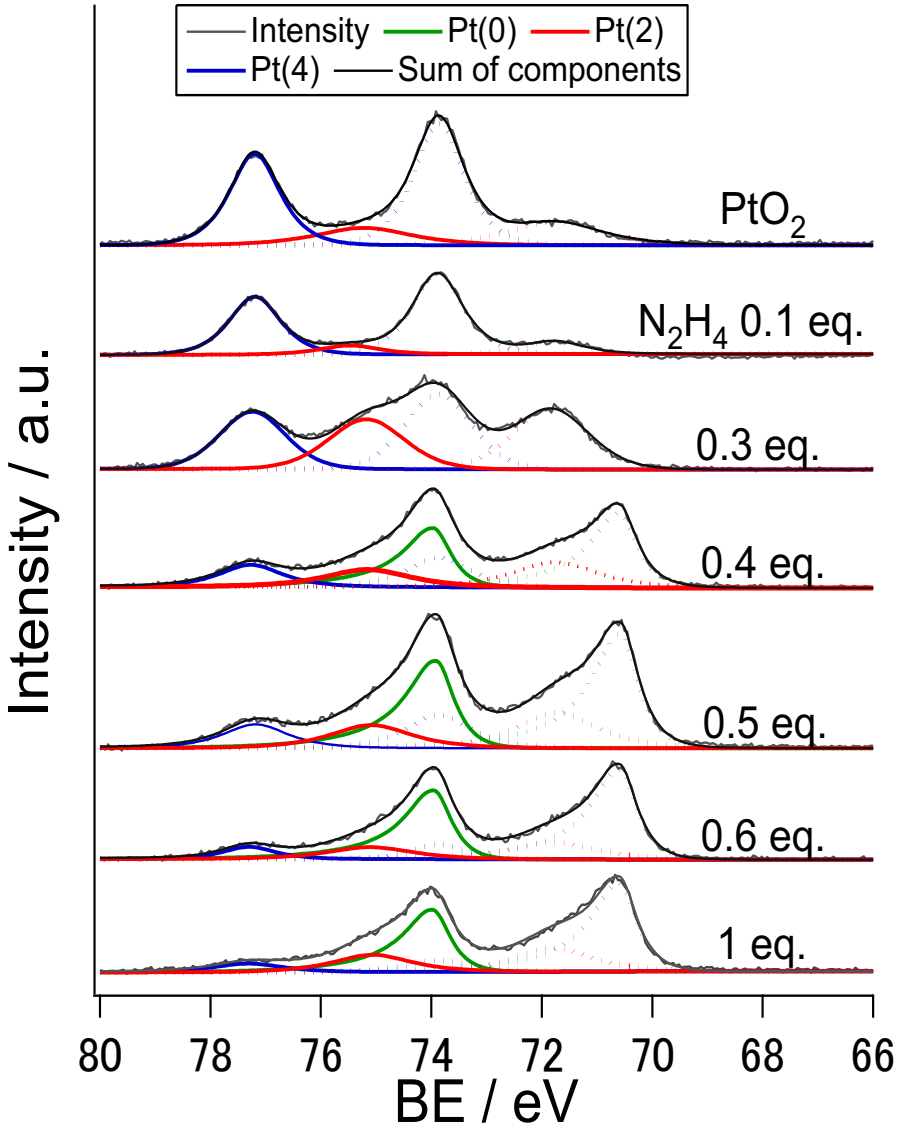


N_2H_4還元PtO_2のキャラクタリゼーション

XRD

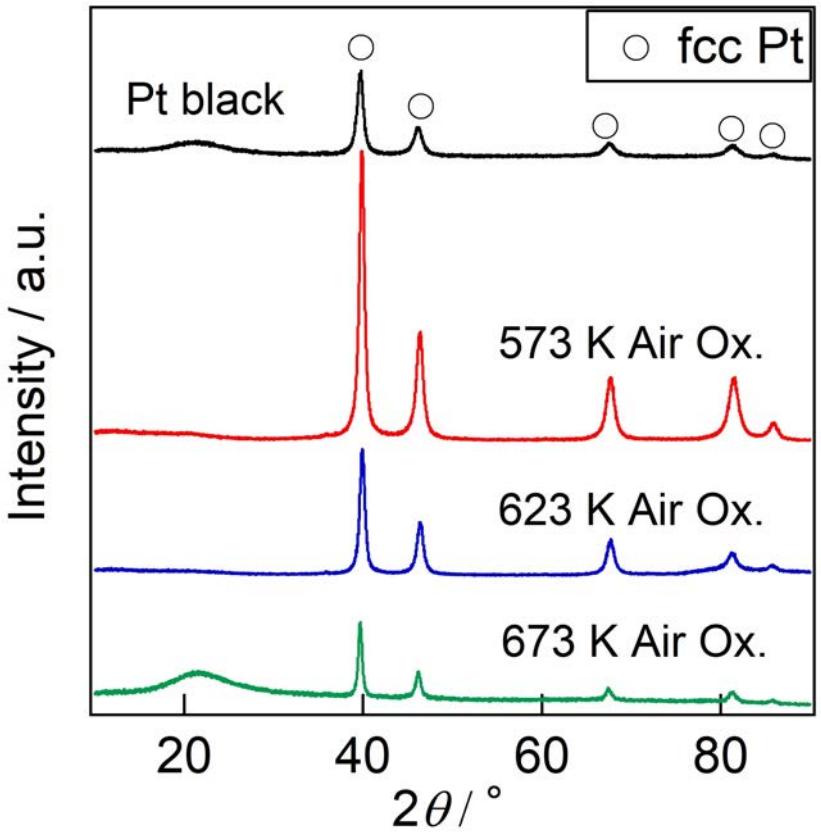


XPS

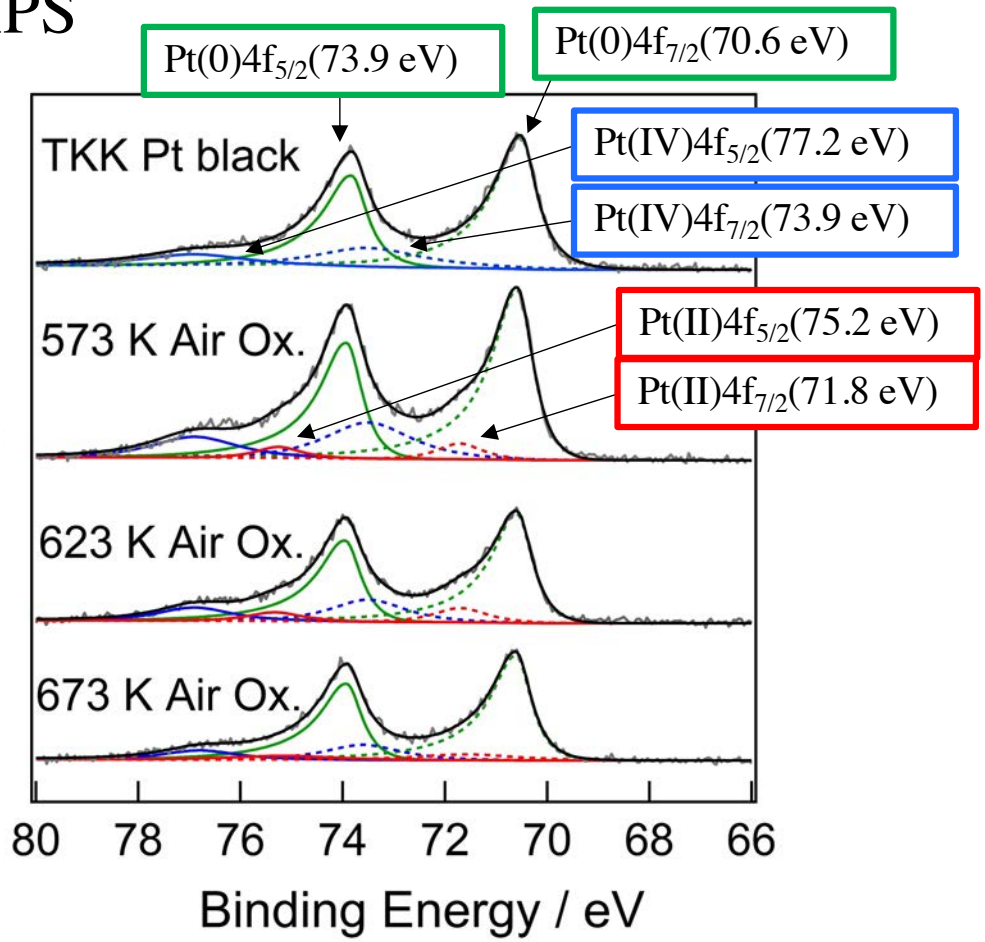


空気酸化したPt blackのキャラクタリゼーション

XRD

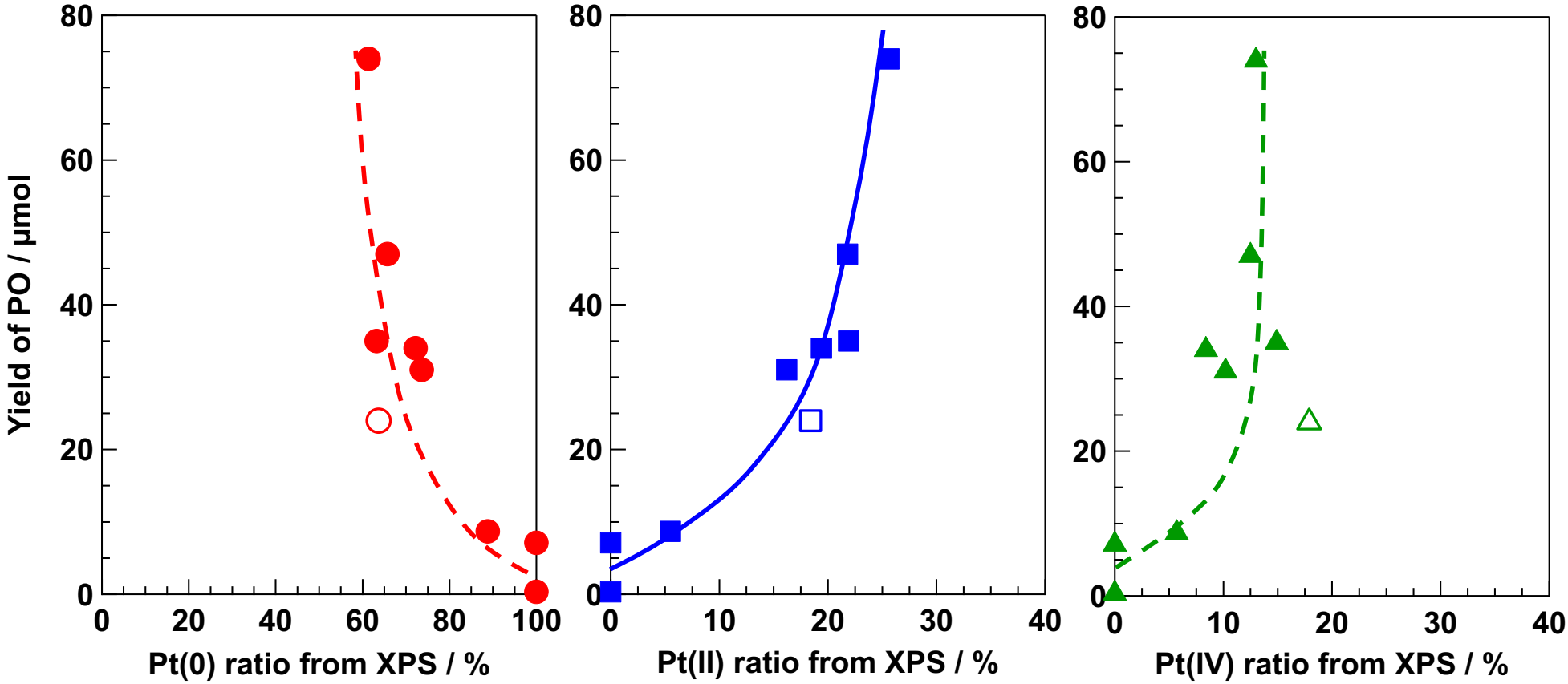


XPS



XRD　fcc Ptのみが観測
XPS　空気酸化によりPt(II)由来のピークが観測

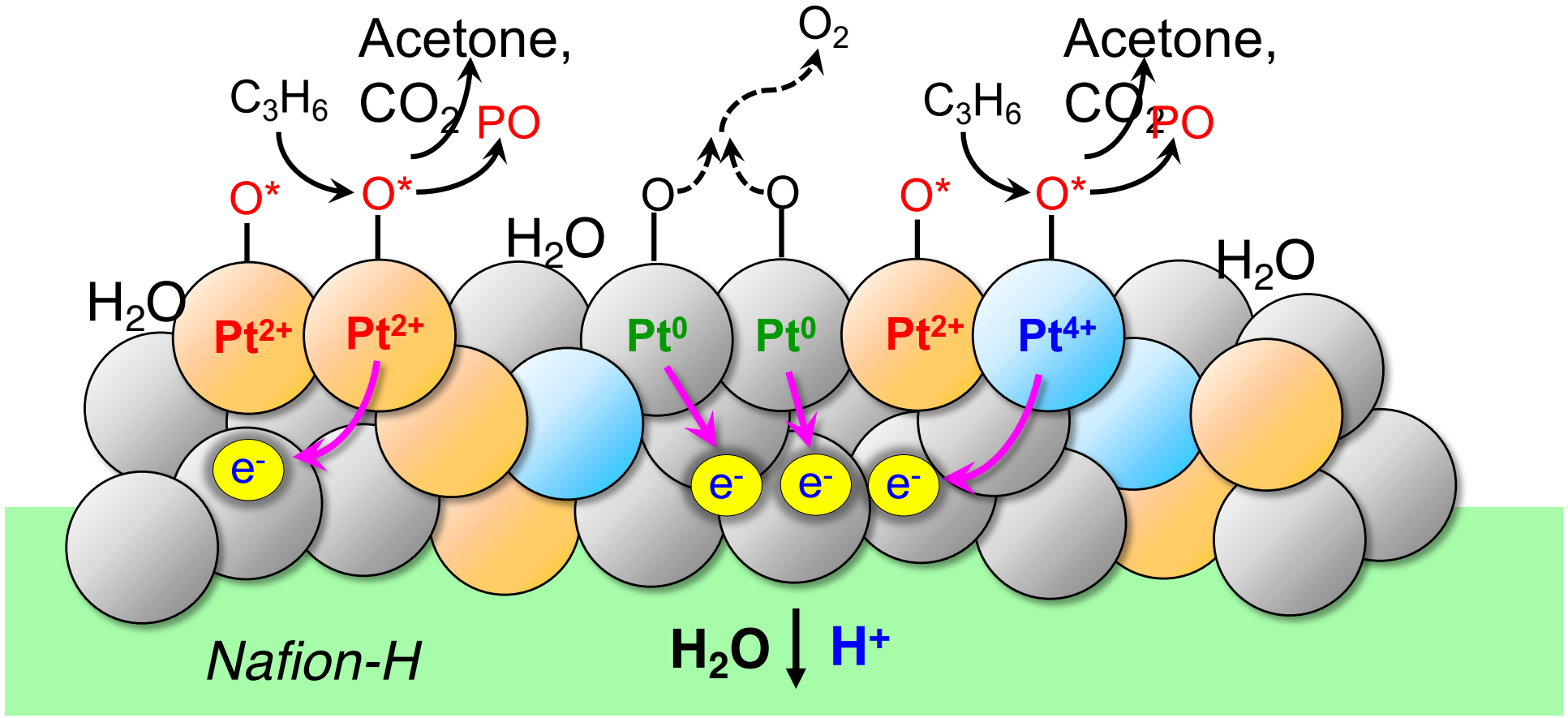
PtOx 触媒の表面酸化状態と活性の関係

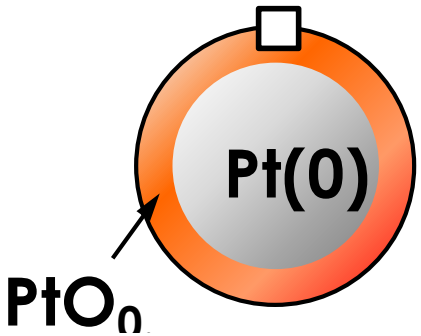


（●■▲：Pt black 酸化処理触媒　○□△：PtO_2 還元処理触媒）

Pt(II), Pt(IV) の割合が大: PO 生成量増加

Pt black 酸化処理触媒のイメージ

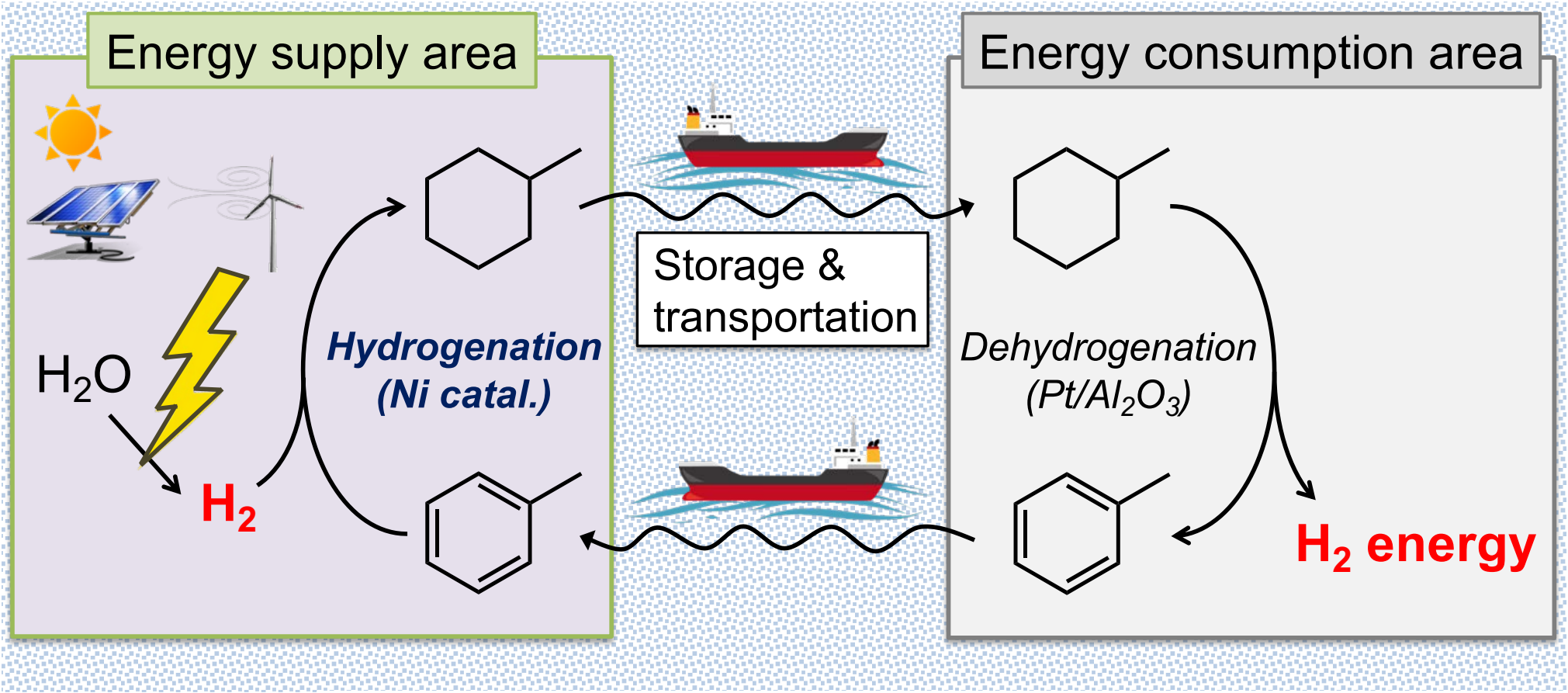




Pt^{2+}, Pt^{4+} → 活性酸素種（H_2O酸化の中間種）が発生
PO，アセトン，CO_2が生成

Pt^0 → 電気伝導性の付与

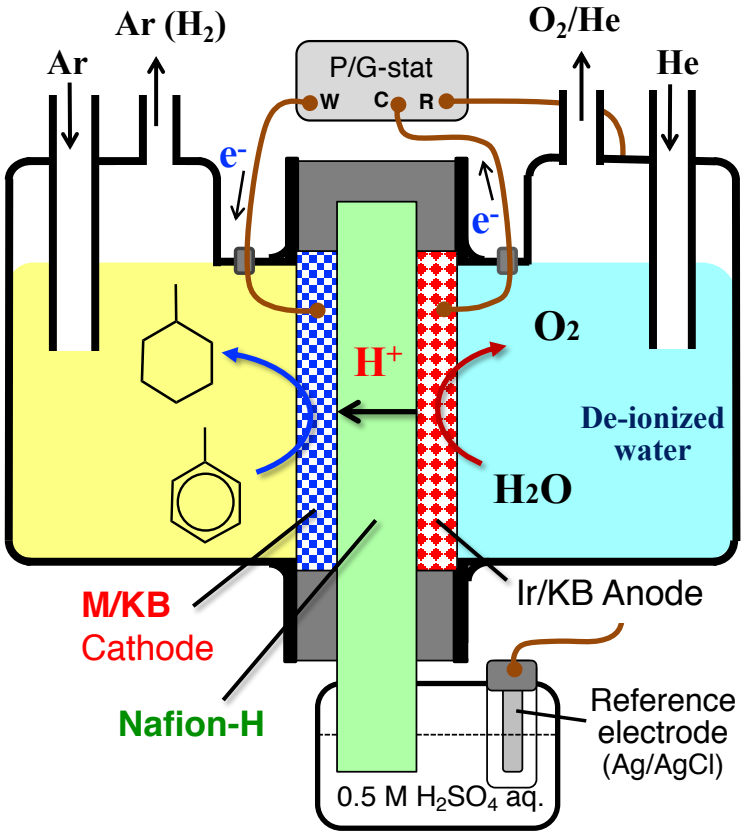
有機ハイドライド電解合成



Y. Okada (Chiyoda Chem. Eng. Co.), *J. Jpn. Inst. Energy.*, **91**, 473-478 (2012)

× Storage & transportation of H_2 gas are not easy.

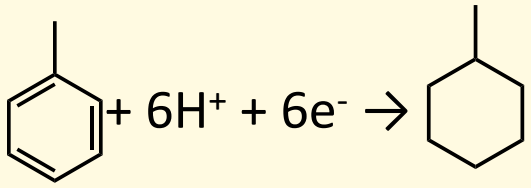
トルエン電解水素化



Galvanostatic Electrolysis(50 mA cm^{-2})
Reaction Temp.：298 K
Reaction Time：2 h
Reference Electrode : Ag/AgCl

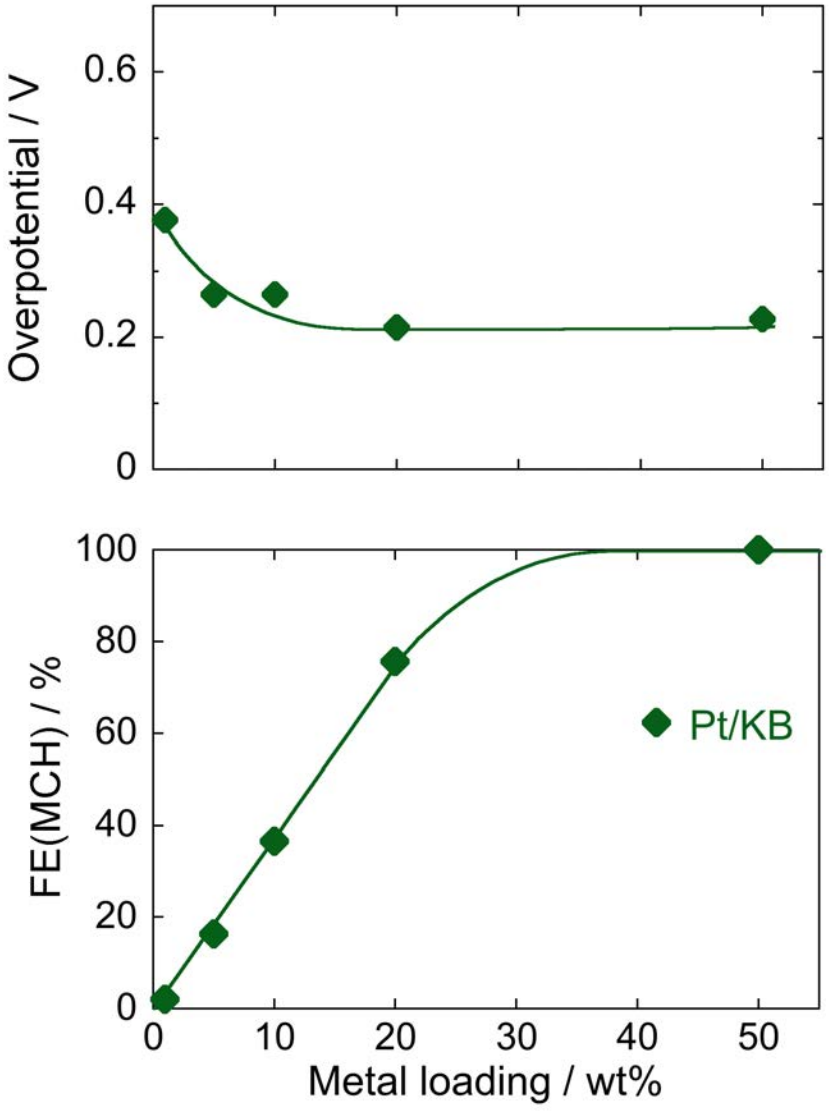
C.E. = 流した電流のうち
反応に使われた電流の割合

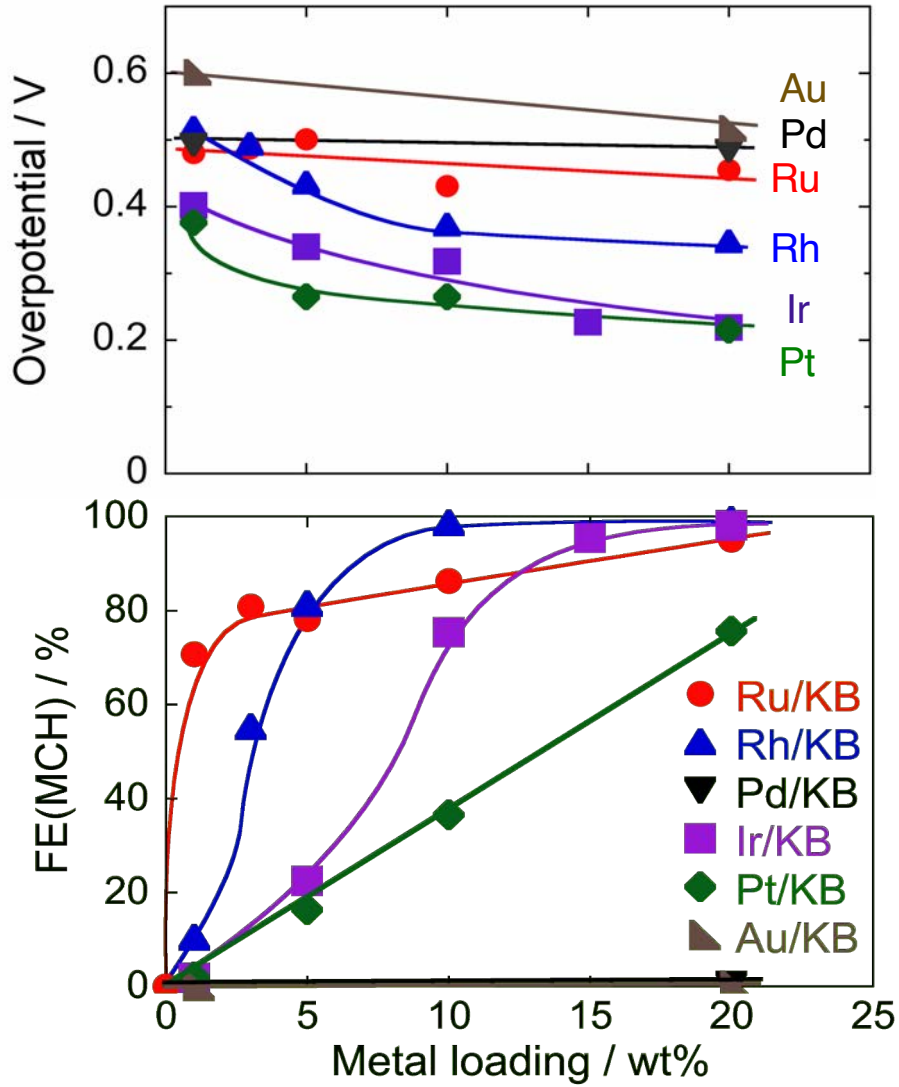
Anode : $2H_2O \rightarrow 4H^+ + 4e^- + O_2$ $E^\circ = +1.23$ V vs. SHE

Cathode :  $E^\circ = +0.162$ V vs. SHE

$2H^+ + 2e^- \rightarrow H_2$ (side reaction) $E^\circ = +0.00$ V vs. SHE

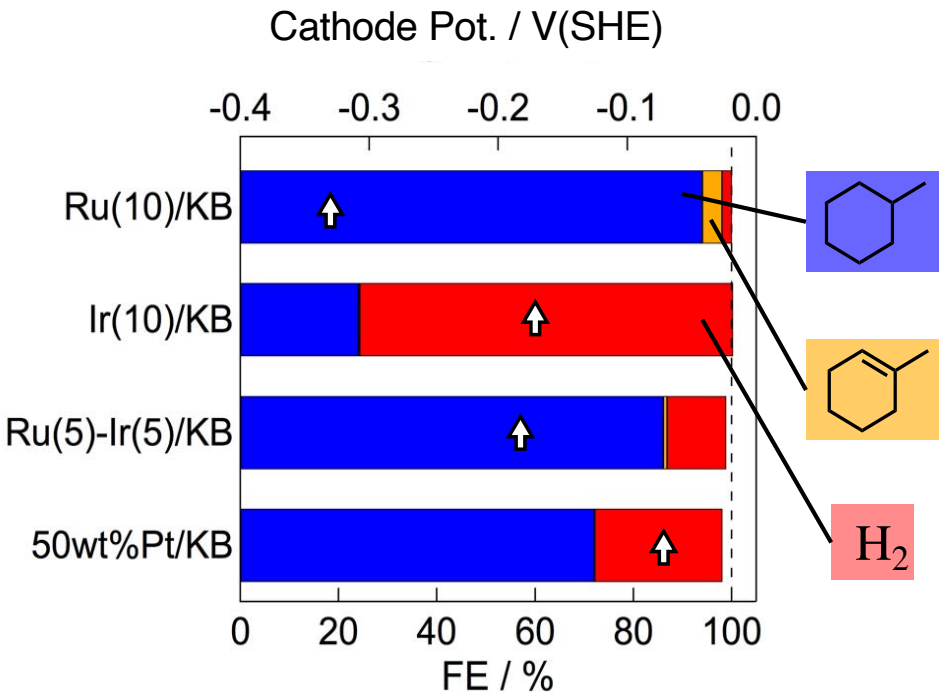
Pt/KBカソード：担持量影響



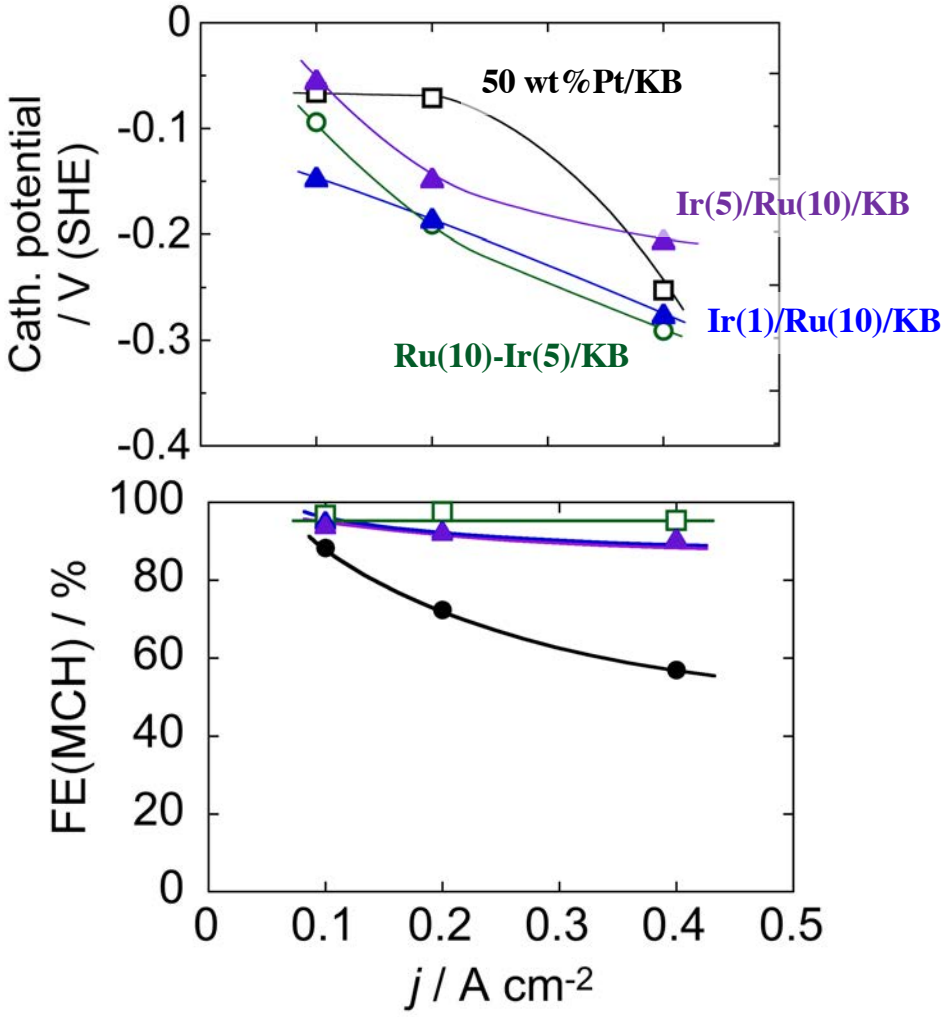


R. Temp. 298 K, Galv. Electrolysis (50 mA cm^{-2}), Electrolysis time 2 h,
Reference : Ag/AgCl

RuとIr間の協奏効果発見

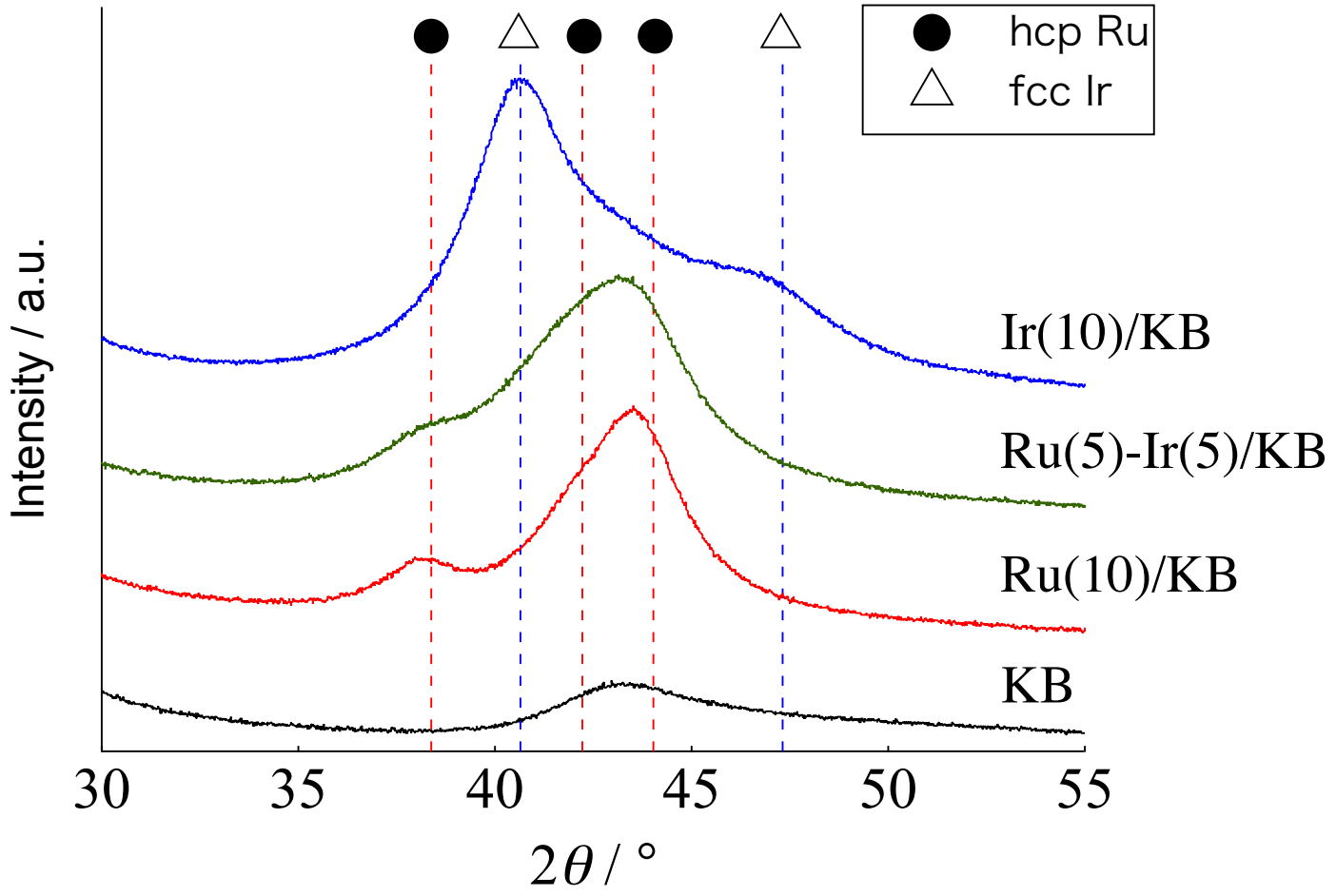


Cathode Cat. 10 wt% metal/KB (2 mg cm^{-2})
T 298 K, Galv. Electrolysis 0.2 A cm^{-2}
Electrolysis time 2 h



Ir(5)/Ru(10)/KBカソード
・小さい過電圧、高い電流効率
・50wt%Pt/KBを凌駕

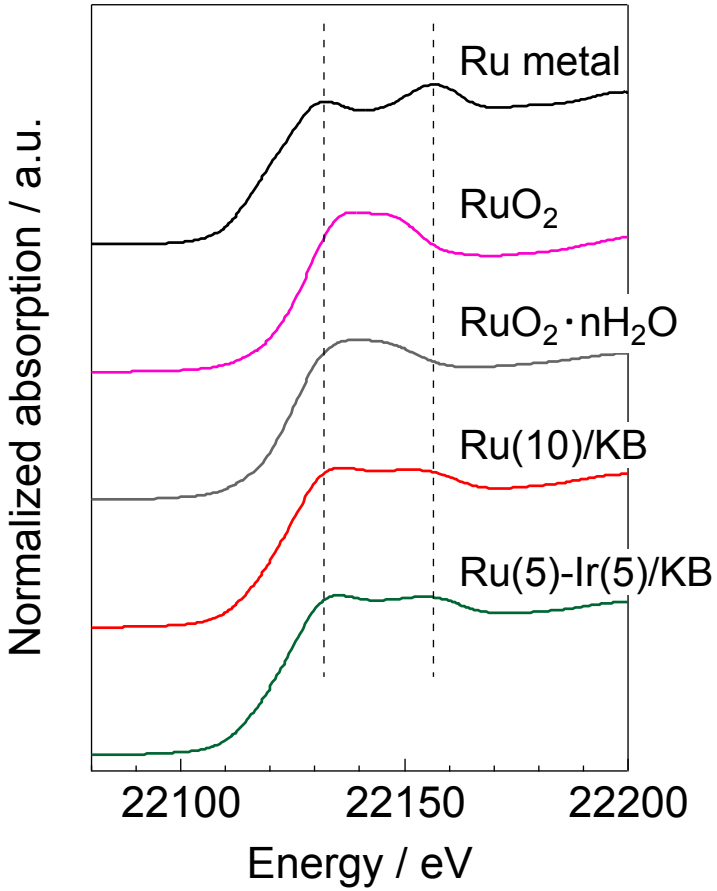
XRD分析



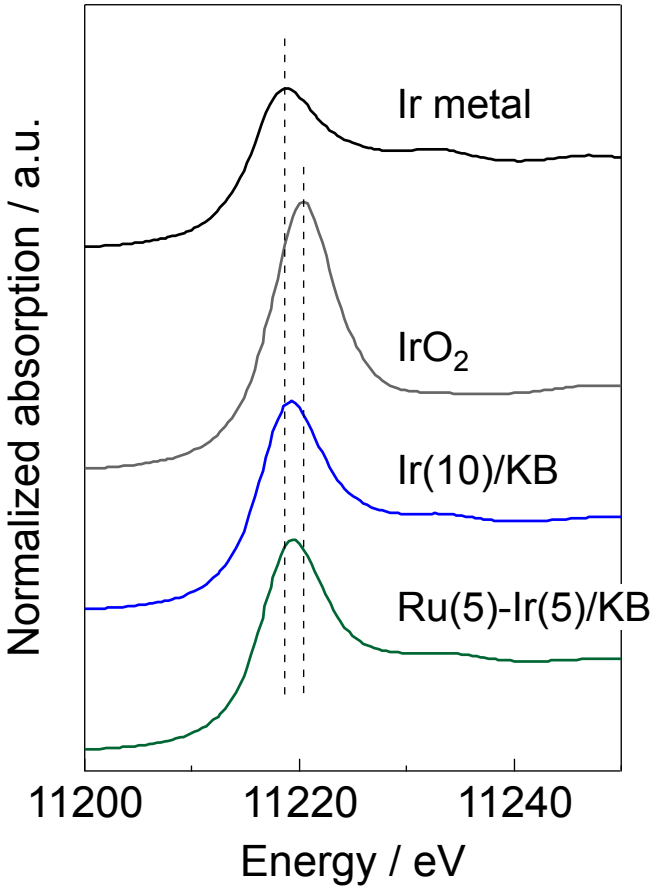
Diffraction line of Ru(002) shifted to lower angel, suggesting ***formation of hcp-structured Ru-Ir alloy***

XANES 解析

Ru K-edge



Ir L_{III}-edge

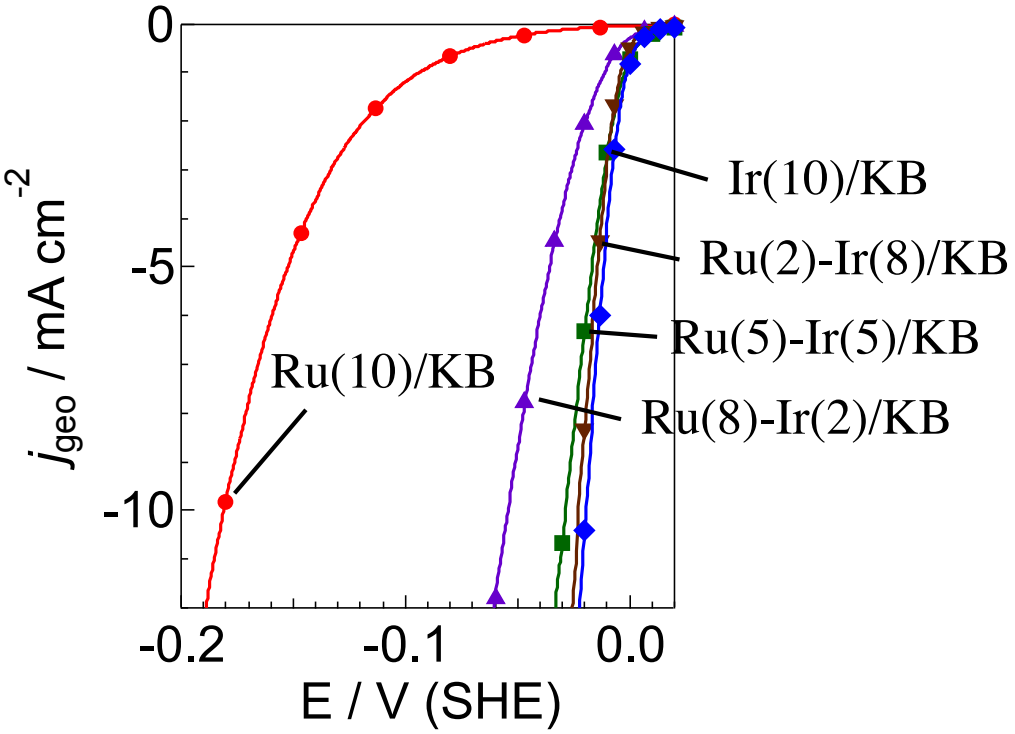


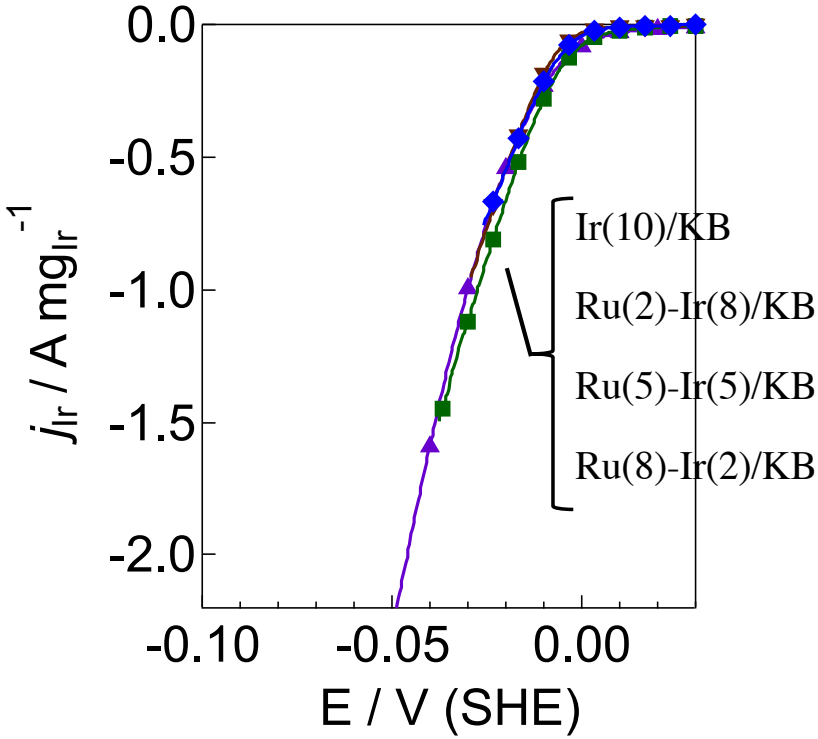
Spectrum of Ru-Ir/KB is similar to Ru/KB and Ir/KB.

Electronic interanion of Ru and Ir is weak.

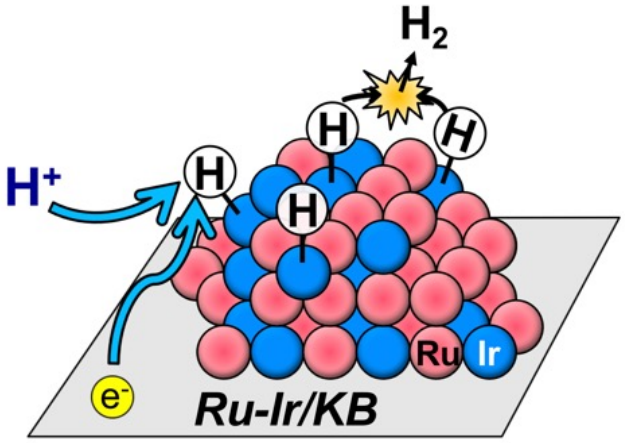
水素発生電流(LSV)の比較

LSV in 0.5 M H_2SO_4 aq. ($2H^+ + 2e^- \rightarrow H_2$)

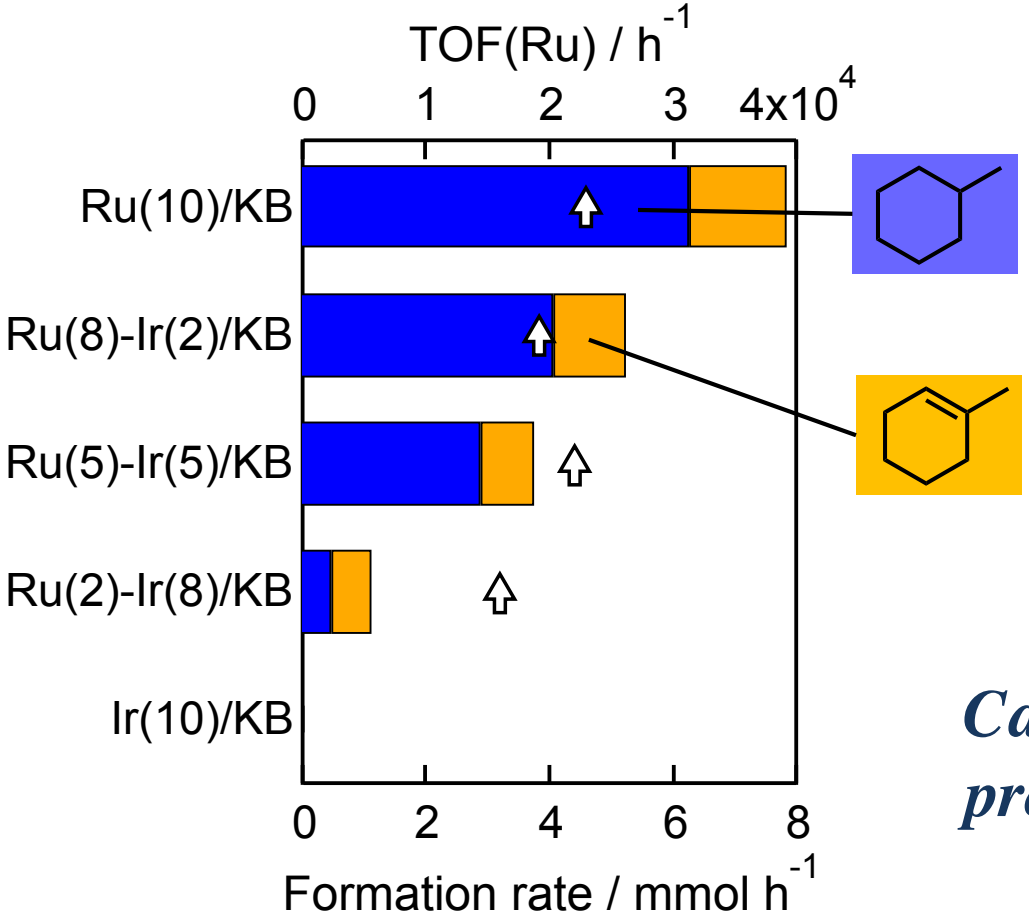




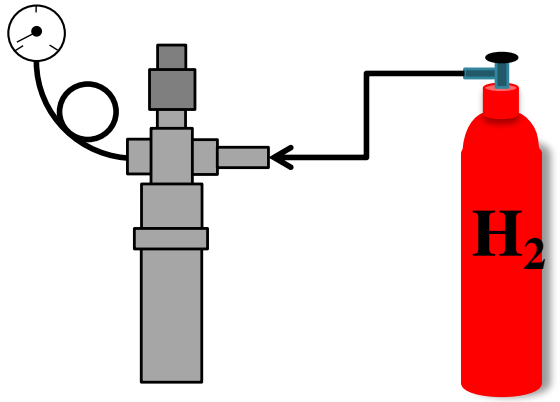
- ✔ By the addition of Ir, overpotential drastically decreased
- ✔ Normalized LSVs were very similar.
  → ***HER proceed on Ir dominantly.***



各種触媒トルエンの水素化反応



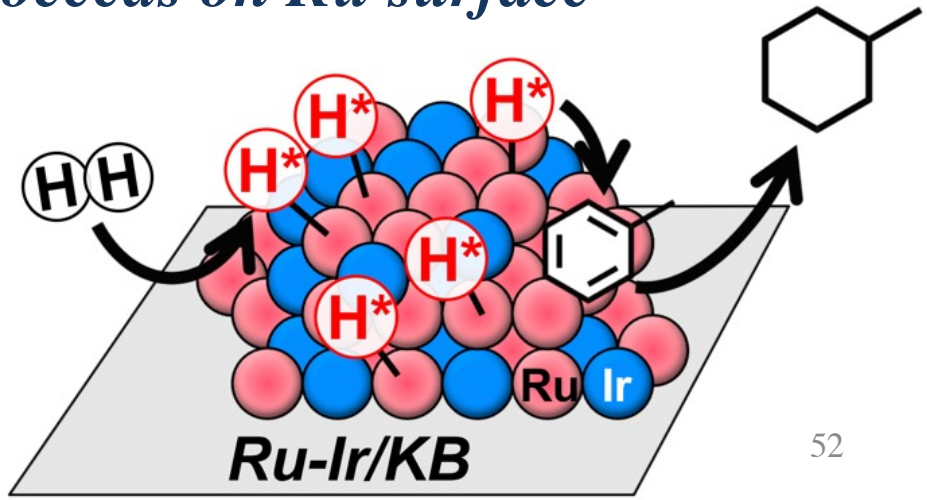
T: 298 K, 6.0 MPa H_2



Autoclave reactor

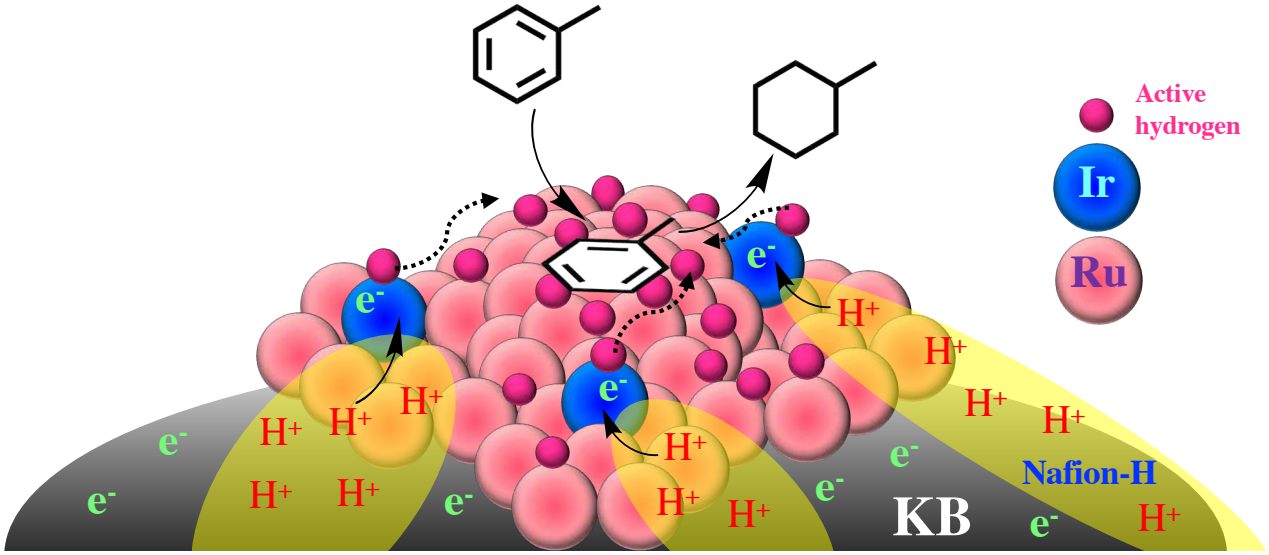
- ✔ Formation rates decreased as Ru loading decreases.
- ✔ TOF(Ru) were constant.

Catalytic hydrogenation proceeds on Ru surface



Ru とIrの協奏効果機構

Y. Inami, *ACS Catal*. **2019**, *9*, 2448.

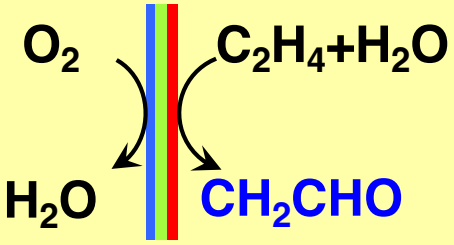


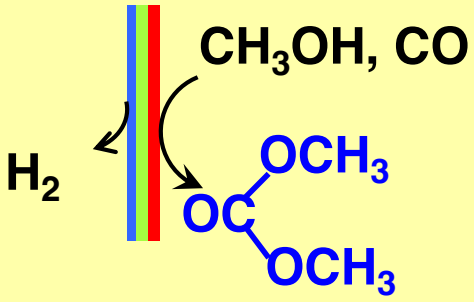
(i) $H^+ + e^- \longrightarrow H_{ad}\text{-Ir}$
(ii) $H_{ad}\text{-Ir} + Ru \longrightarrow H_{ad}\text{-Ru} + Ir$
(iii) $6H_{ad}\text{-Ru} + TL_{ad}\text{-Ru} \longrightarrow MCH$

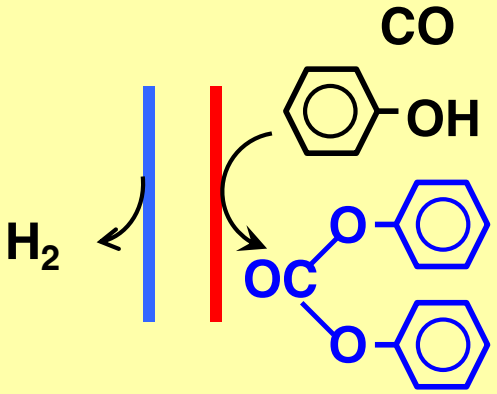
Ir: electrocatalyst for the formation of H_{ad}
Ru: catalyst for the hydrogenation of toluene

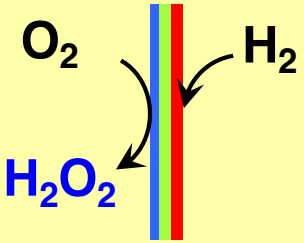
Formation of H_{ad} is accelerated by the addition of Ir
→ decrease of overpotential for the electrohydrogenation.

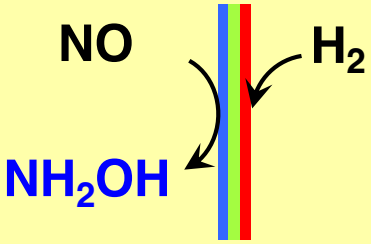
新電極触媒の開発により各種反応達成

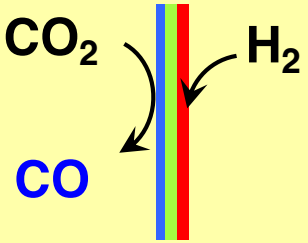


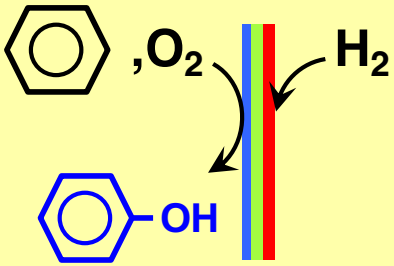


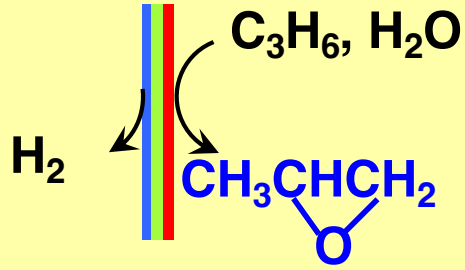


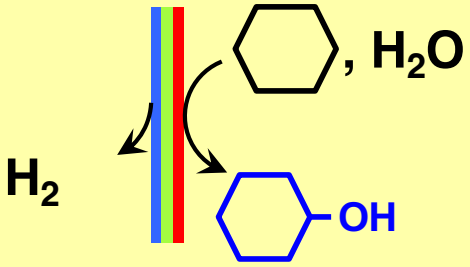












XAFSによる活性点構造の特定が新触媒開発に展開