Hydrogen evolution by carbonaceous nanoparticle aggregates that were derived from cobalt phthalocyanine

Jun Maruyama,[1)] Tsutomu Ioroi,[2)] Takahiro Hasegawa,[1)] Zyun Siroma,[2)] Atsushi Mineshige,[3)] Takuya Mori,[4)] Yuki Orikasa,[4)] and Yoshiharu Uchimoto[4)]

1) Osaka Municipal Technical Research Institute; 2) National Institute of Advanced Industrial Science and Technology; 3) University of Hyogo; 4) Kyoto University, Japan

地方独立行政法人
大阪市立工業研究所
OMTRI

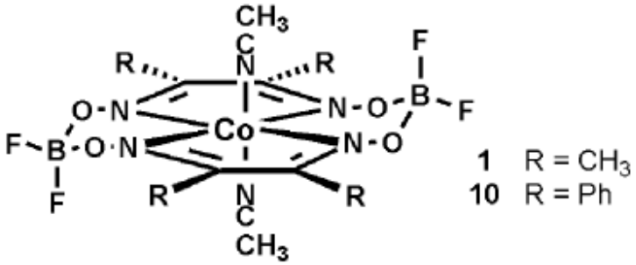
Polymer electrolyte membrane type water electrolyzer

Polymer electrolyte membrane (PEM) type water electrolyzer
・・・energy storage system suitable for wind turbines and photovoltaic cells

Pt black

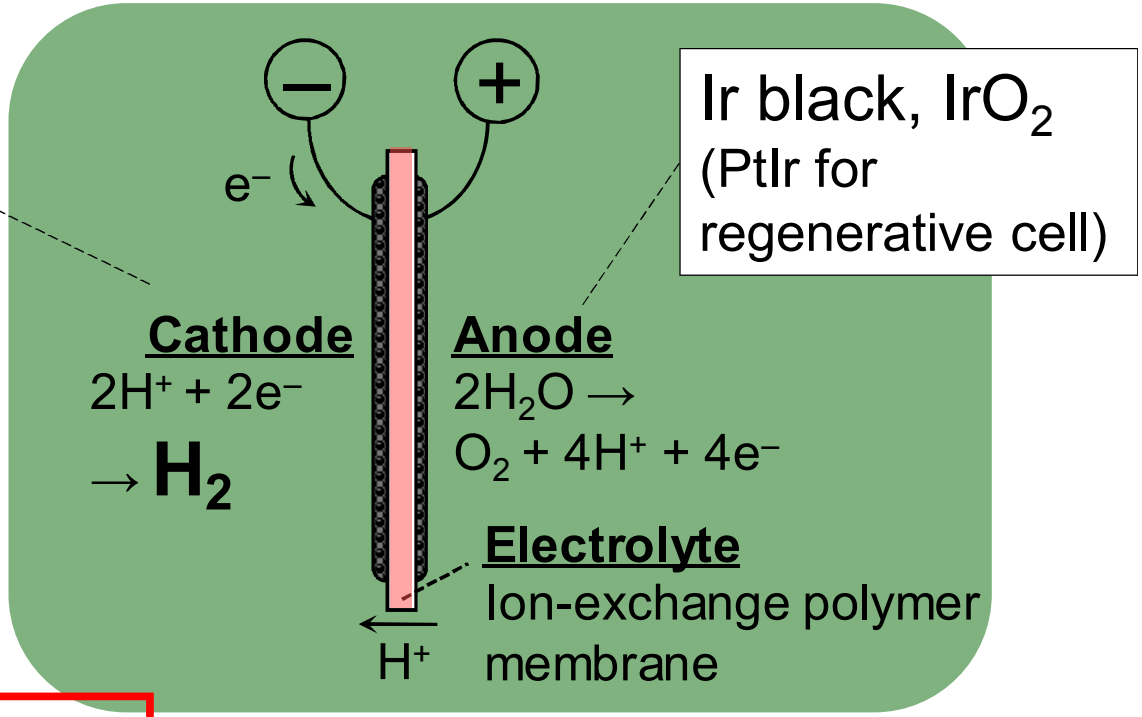
⇓

Noble-metal-free catalyst



and MoS_x, etc.

Problem: Low activity, unknown durability



地方独立行政法人
大阪市立工業研究所
OMTRI

Slide only for German-Japanese Carbon Seminar

H_2 evolution catalyst using carbon materials

Carbonaceous materials with Metal–N_x moiety on surface
--- promising noble-metal-free O_2 reduction catalyst
Use in the H_2 evolution: not studied
← presumably owing to the increased focus on fuel cells

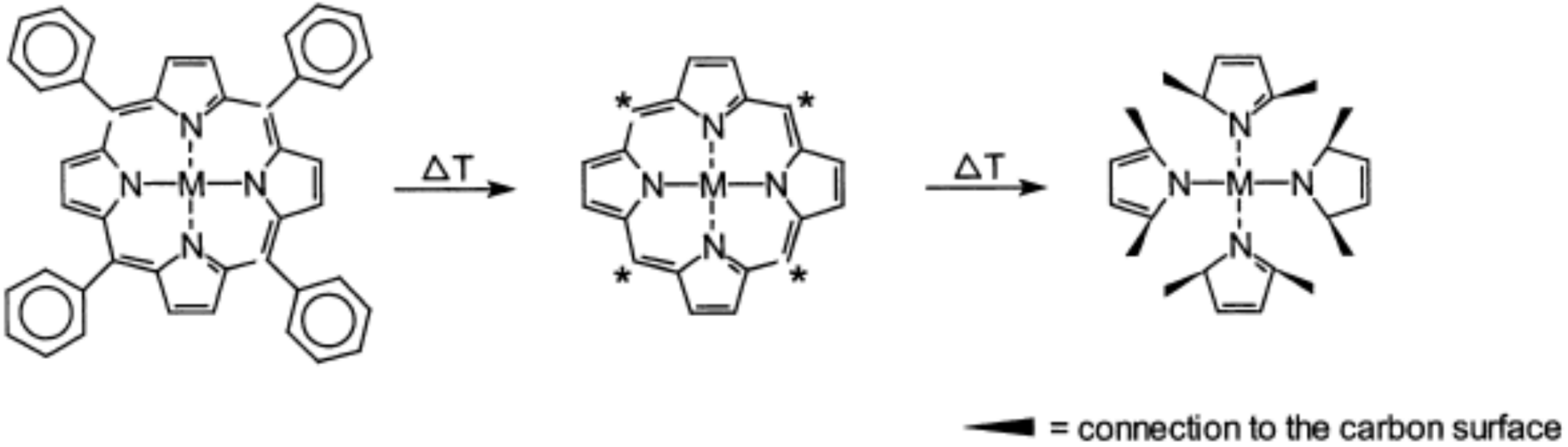


Fig. Schematic diagram of reaction of metal (M) porphyrin loaded on carbon surface during heat treatment (ΔT). [A. L. Boukamp-Wijnoltz, W. Visscher, J. A. R. van Veen, E. Boellaard, A. M. van der Kraan, S. C. Tang, J. Phys. Chem. B, 106 (2002) 12993.]

Methods for catalyst formation and evaluation

【Starting Materials】 Mixture of Cobalt phthalocyanine (CoPc) or phthalocyanine (Pc) and EC600JD (KB), (CoPc or Pc : KB = 2:1)

【Heat treatment】 The mixture was placed in a crucible with a cap.

Atmosphere: Ar
Increasing temperature at 1 ºC min^{-1}
Temperature: 800 ºC
Treatment time: 1 h

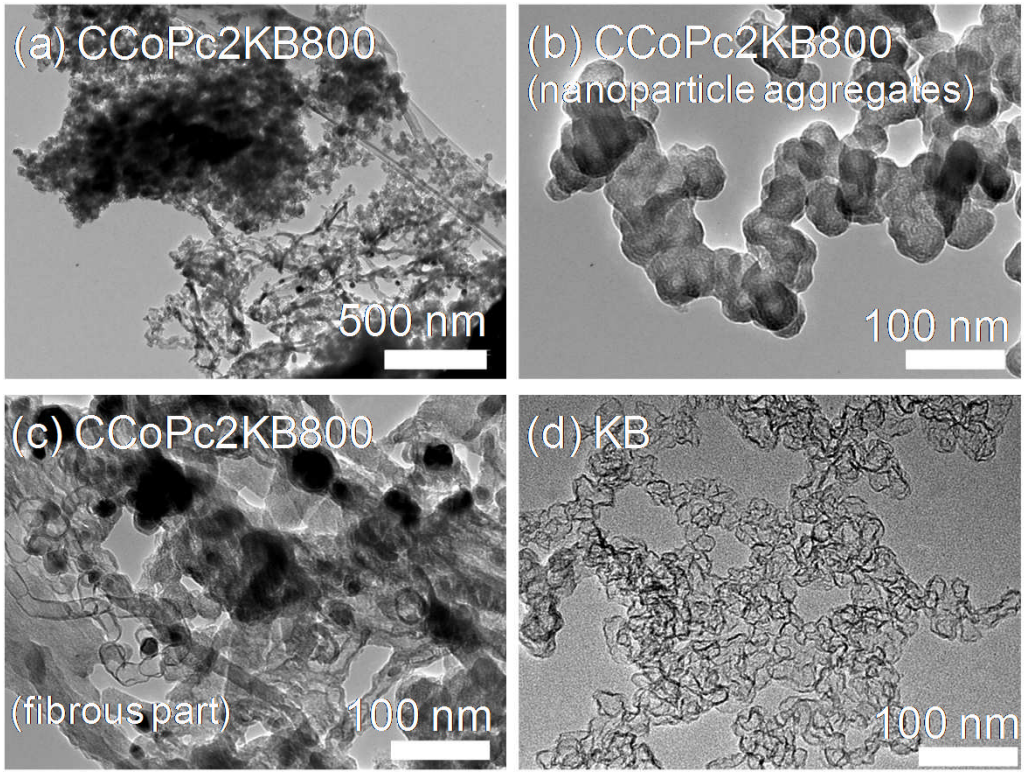
【Acid treatment】

immersed in 1 mol dm^{-3} H_2SO_4 for 1 h → removal of soluble cobalt species
starting material: CoPc, Pc → catalyst: CCoPc2KB800, CPc2KB800

【characterization】

- ✓TEM observation
- ✓Nitrogen adorption
- ✓XPS analysis
- ✓Evaluation of catalytic activity using rotating disk electrode

TEM images



- Primary particles connected each other to form aggregated structure
- Presence of fibrous structure

Fig. TEM images of (a) CCoPc2KB800, (b) aggregate part of CCoPc2KB800, (c) fibrous part of CCoPc2KB800, (d) KB.

Pore structure, surface composition

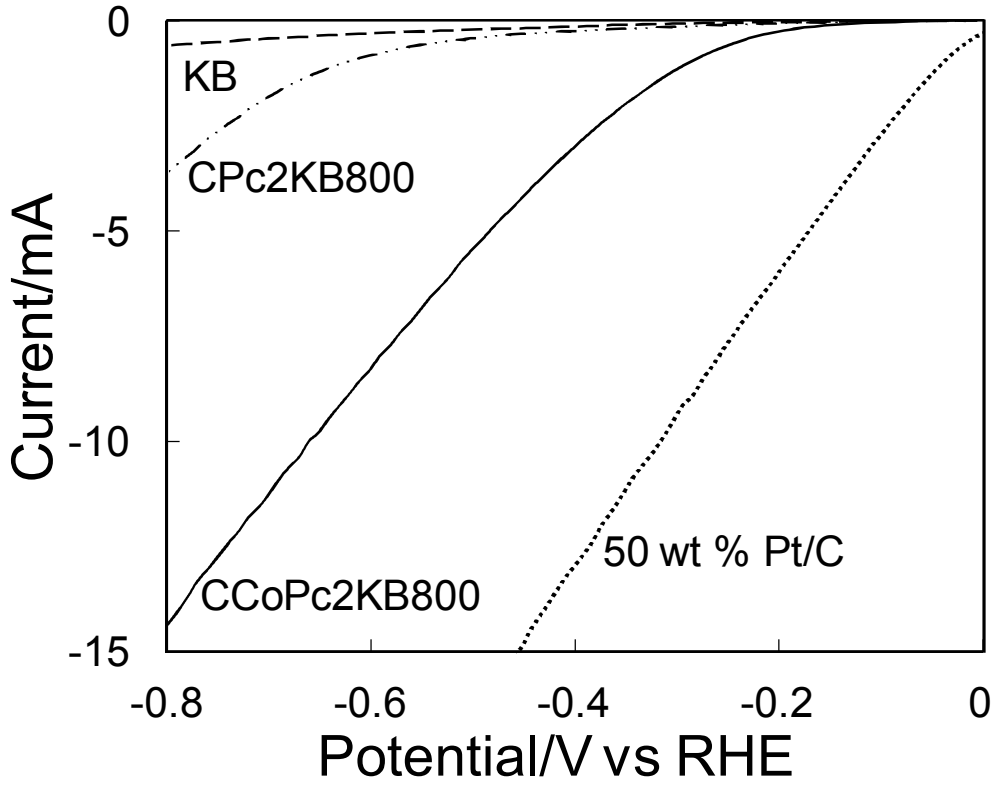
Table. Specific surface area (*S*), pore volume (*V*), and surface concentrations of C, N, Co, and O of the carbonaceous nanoparticle aggregates, KB, and KBox.

	S [$m^2\ g^{-1}$]	*V* [$cm^3\ g^{-1}$]	Surface concentration [atom %]			
			C	N	Co	O
KB	1277	1.983	98.87	–	–	1.13
CCoPc2KB800	63	0.261	90.64	4.71	0.50	4.15
CPc2KB800	543	0.851	95.92	2.46	–	1.62

- Decrease in *S* and *V*
  ←loading of carbonaceous thin film on KB surface
- Presence of Co and N on the surface

地方独立行政法人
大阪市立工業研究所
OMTRI

H_2 evolution reaction (HER) current



- KB: low current
  ←no activity on carbon surface
- CPc2KB800: higher current than KB
  ←low activity on N-doped carbon
- CCoPc2KB800: showing clear HER current
  active site: Co–N_4 moiety
- Lower activity than Pt/C
  →Further studies needed
  Tuning local structure of the active site

Fig. Relationships between electrode potential and H_2 evolution current measured in Ar-saturated 0.1 mol dm^{-3} $HClO_4$ aqueous solution at 25 ºC for CCoPc2KB800, KB, KBox, 50 wt % Pt/C, and CPc2KB800. The sign of the reduction (cathodic) current was taken as negative. The amount of the sample fixed on the electrode was 60 mg. The geometric electrode surface area was 0.196 cm^2. A reversible hydrogen electrode (RHE) was used as a reference electrode. The counter electrode was carbon cloth. The potential scan rate was 10 mV s^{-1}. The rotation rate of the electrode was 3600 rpm.

Methods for tuning active site and evaluation

【Starting Materials】 Mixture of Cobalt phthalocyanine (CoPc) and EC600JD (KB),
CoPc : KB = *m*:1 (*m* = 0.25, 0.5, 1, 2)

【Heat treatment】 The mixture was placed in a crucible with a cap.
→Double heat treatment

【1st step】	【2nd step】
Atmosphere: Ar	Ar
Increasing temperature: 1 ºC min^{-1}	5 ºC min^{-1}
Temperature: 700 ºC	*t* ºC (*t* = 800, 900, 1000, 1100)
Treatment time: 1 h	5 min

【Acid treatment】 Stirred in 6 mol dm^{-3} HCl → removal of soluble cobalt species
→ catalyst: CCoPc1KB700 (only by 1st step), CCoPc*m*KB700*t*

【characterization】
- ✓TEM observation
- ✓Nitrogen adorption
- ✓XPS analysis
- ✓Co-K edge X-ray absorption near-edge structure
- ✓Evaluation of catalytic activity using rotating disk electrode
- ✓Current-voltage curve at water elctrolyzer and its intermittent operation

TEM images

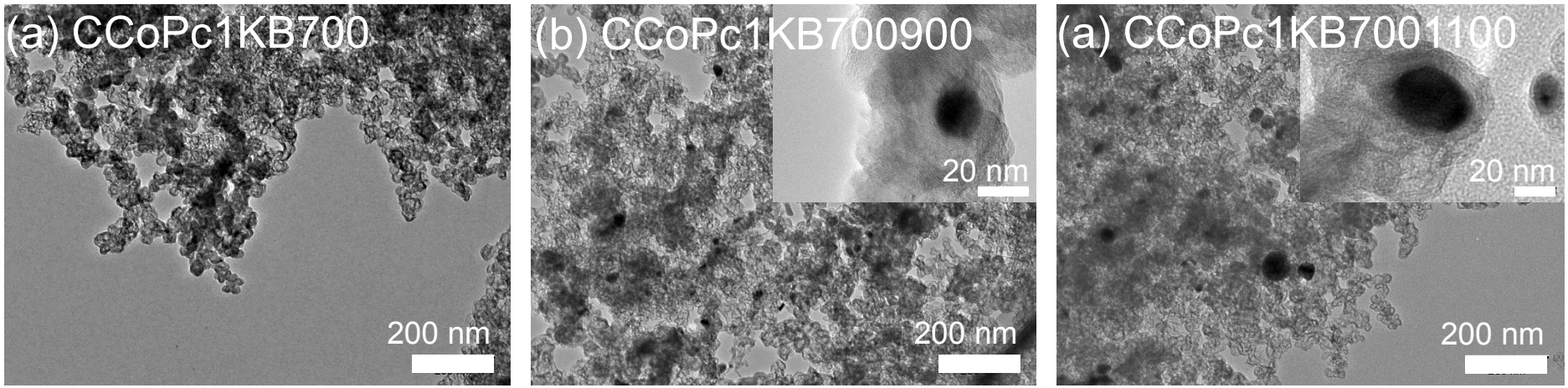
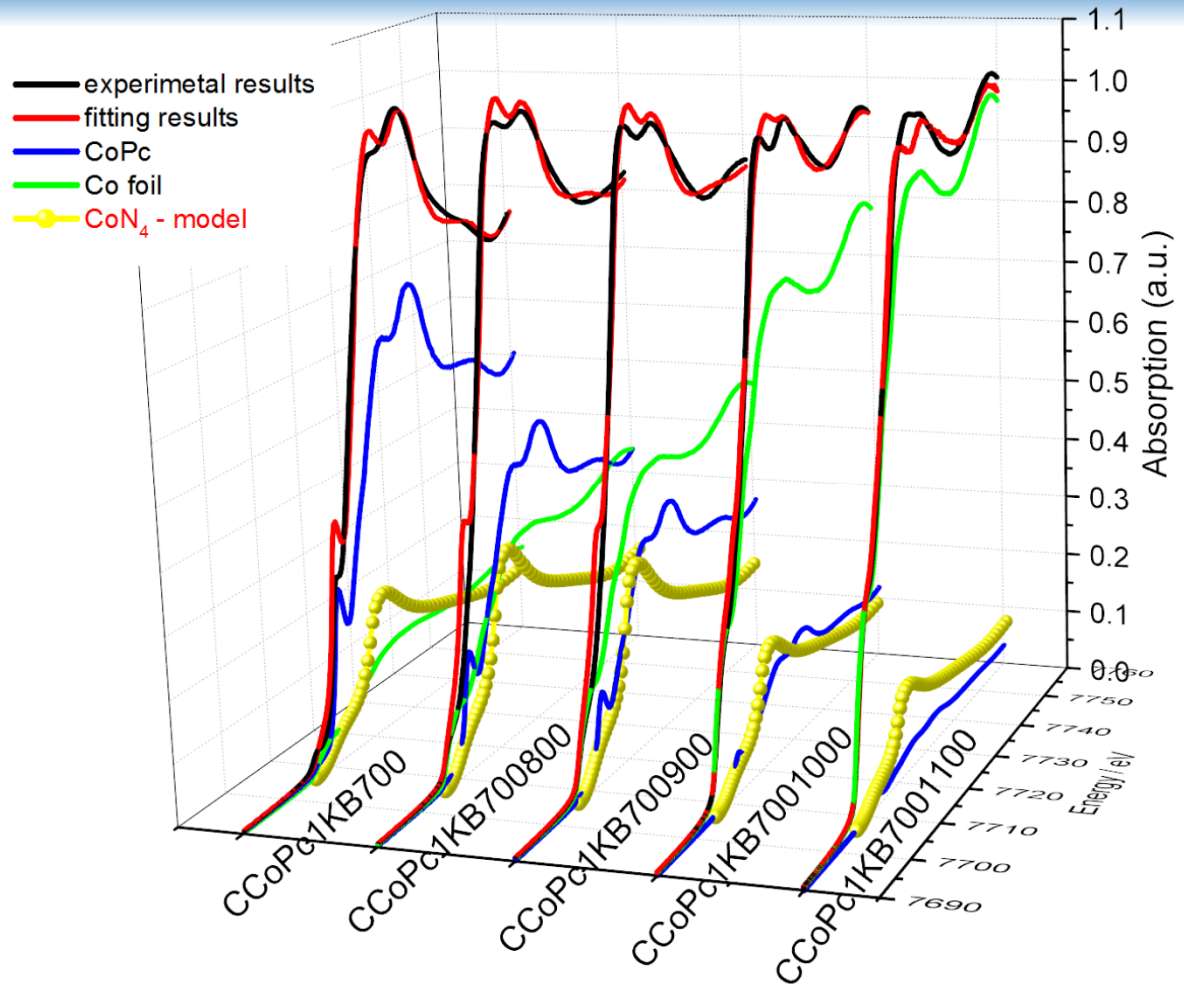


Fig. TEM images of (a) CCoPc1KB700, (b) CCoPc1KB700900, and (c) CCoPc1KB7001100. The insets show expanded images of Co particles.

- Co aggregate: distinct spherical black particles
- almost absent in (a).
- generation by double heat treatment
- grown by high heat treatment temperature

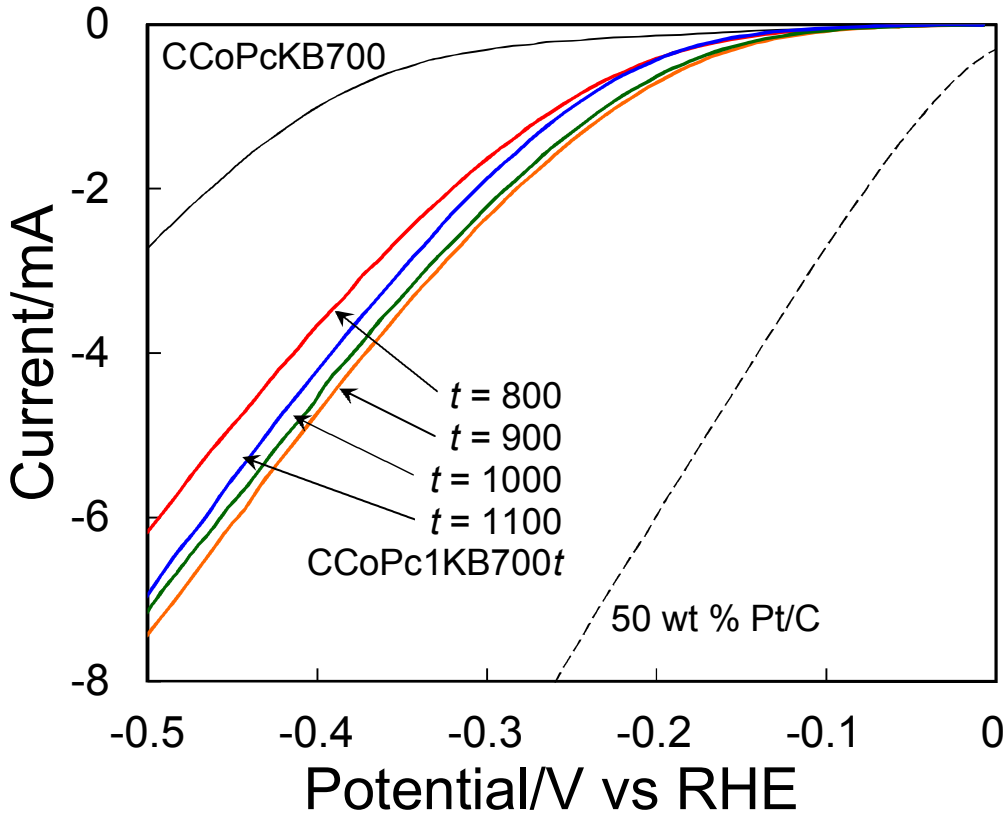
XANES



- Co aggregate growth
- Retention of Co–N_4 moiety of CoPc center
- Surrounding of Co–N_4: transformation to disordered carbon matrix by double heat treatment

Fig. XANES spectra at the Co-K edge for CCoPc1KB700 and CCoPc1KB700*t*. The measurements were performed in the transmission mode in air at room temperature using synchrotron radiation. The simulated XANES curve obtained by the weighted addition of those for CoPc, Co foil, and that calculated using FEFF8.2 for the 5-atom model consisting of Co surrounded by 4 nitrogen atoms in a square-planar coordination (Co–N_4 model).

HER current



- Current increase by double heat treatment
- Dependent on the 2nd heat treatment temperature; maximum at 900 ºC
- Lower activity than Pt/C
  Further studies needed.

Fig. Relationships between electrode potential and H_2 evolution current measured in Ar-saturated 0.1 mol dm^{-3} $HClO_4$ aqueous solution at 25 ºC for CCoPc1KB700*t*, CCoPc1KB700, and 50 wt % Pt/C. The sign of the reduction (cathodic) current was taken as negative. The amount of the sample fixed on the electrode was 60 μg. The geometric electrode surface area was 0.196 cm^2. A reversible hydrogen electrode (RHE) was used as a reference electrode. The counter electrode was carbon cloth. The potential scan rate was 10 mV s^{-1}. The rotation rate of the electrode was 3600 rpm.

Factors for determining HER activity

Table. H_2 evolution current at –0.5 V vs RHE (I), specific surface area (S), surface concentration of Co (c_s(Co)) and N (c_s(N)) in CCoPc1KB700 and CCoPcmKBt. In each cell, the values are arranged as follows.

	S [m^2 g^{-1}]
$-I$ [mA]	c_s(Co) [atom %]
	c_s(N) [atom %]

		m			
		0.25	0.5	1	2
CCoPc1KB700				267 2.78 0.70 5.31	
CCoPcmKB700T					
	800			287 6.23 0.52 3.41	
	900	851 5.91 0.08 1.09	622 7.00 0.20 2.23	274 7.49 0.45 3.22	90 6.83 0.77 3.23
t	1000			326 7.21 0.23 1.90	
	1100			316 7.01 0.18 1.73	

- Heat treatment at 900 ºC:
  Increases in surface area and Co surface concentration → Activity increase
  ▸▸▸ maximum at m = 1

- m = 1 ▸▸▸ maximum at t = 900
  - S: nearly the same
  - Co concentration: decreased by double heat treatment and temperature increase
  factor other than surface area and Co surface concentration
  ▸▸▸Co–N_4 moiety surrounded by disordered carbon atoms

PEM water electrolyzer test

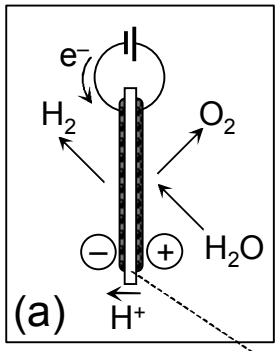
Cathode, 10 cm²

Reaction

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

Compostion

CCoPc1KB700900,
10 mg cm^{-2}
Nafion, 10 mg cm^{-2}



Anode, 10 cm²

Reaction

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

Compostion

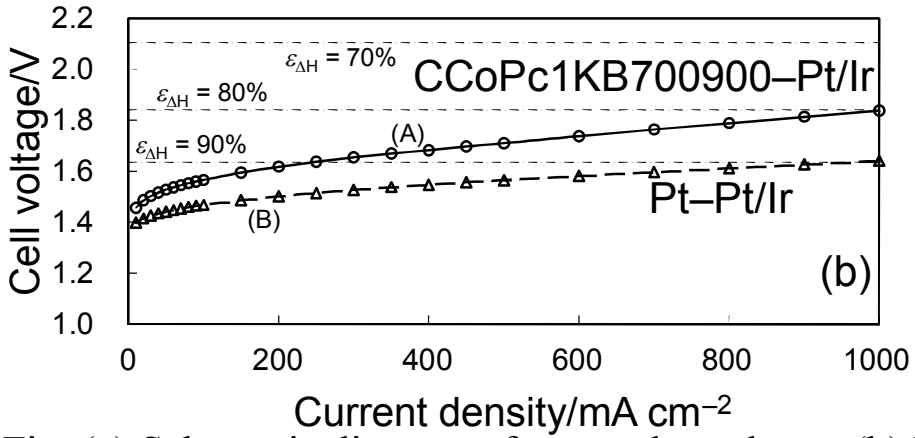
Pt black, 1.7 mg cm^{-2}
Ir black, 0.8 mg cm^{-2}
Nafion, 0.2 mg cm^{-2}
Polytetrafluoroethylene,
0.1 mg cm^{-2}

Cell temperature, 80 ºC

Electrolyte

Perfluorosulfonate ion-exchange polymer membrane (Nafion 117)

- Confirming electrolysis Enthalpy efficiency, $\varepsilon_{\Delta H}$ = 80% at 1 A cm^{-2}
- Almost no degradation during intermittent operation for 80 h



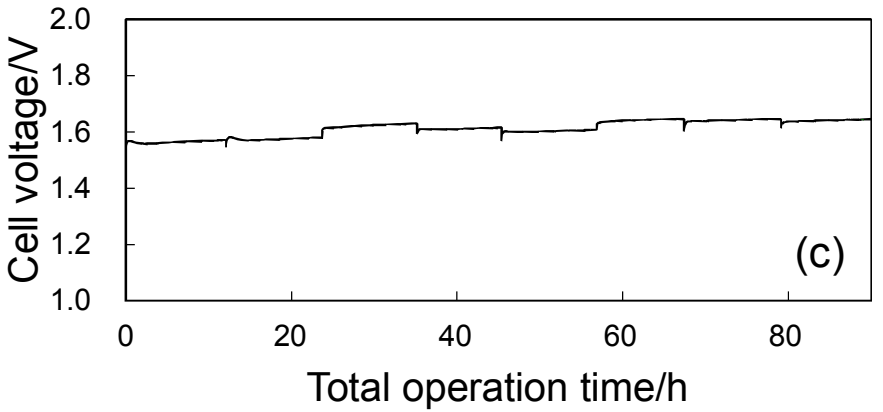


Fig. (a) Schematic diagram of water electrolyzer. (b) Relationships between cell voltage and current density at 80 ºC for water electrolyzers. (c) Change in cell voltage at 80 ºC of water electrolyzer formed using CCoPc1KB700900 during continuous operation at 100 mA cm^{-2} but suspended overnight every 7–10 h

地方独立行政法人
大阪市立工業研究所
OMTRI

Summary

◆CoPc sublimation, deposition on KB, pyrolysis
→ Carbonaceous nanoparticle aggregate with Co–N_4 moiety
→ H_2 evolution catalyst

◆Double heat treatment
→ Development of Co–N_4 moiety surrounded by disordered carbon atoms
→ Enhancement of H_2 evolution activity

◆Confirmation of water electrolysis
Enthalpy efficiency of 80% at 1 A cm^{-2}
Almost stable during 80 h operation

地方独立行政法人
大阪市立工業研究所
OMTRI