Preparation and Characterization of Carbon Alloy Catalysts for Oxygen Reduction Reaction and Hydrogen Evolution Reaction

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For realization of sustainable society

- Hydrogen plays important roles
  To use hydrogen as a fuel for Proton Exchange Membrane Fuel Cell (PEMFC) effectively, a catalyst is required
  To produce hydrogen from water effectively, a catalyst is required
- At present, one of the most effective catalysts is Pt, however, it is expensive and has limited resource
- Pt alternative has been looked for
- As one of the candidates for Pt alternatives, carbon alloy catalysts have been studied

Background of the research

Phenol-Formaldehyde Resin (PFR)
＋ Transition metal complex

↓ Carbonization

Nano-Shell Containing Carbon

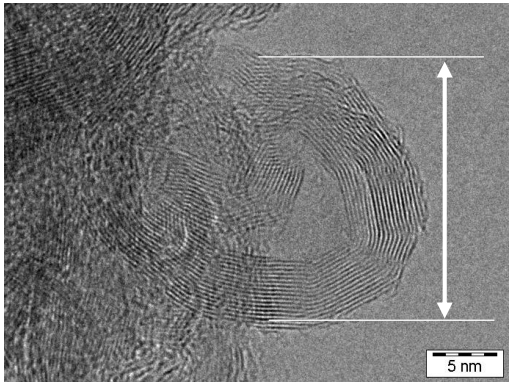
Having Activity for

Oxygen Reduction Reaction, ORR

Ozaki el al., *Electrochim. Acta* 50(2010)1864-1871.

Hydrogen Evolution Reaction, HER

J. Ozaki et. al., Carbon 2014, Jeju, Korea, 2014.6.29-7.4. ORT-6-49.



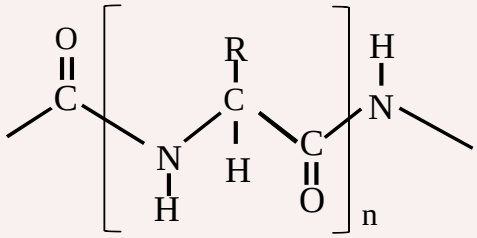
NS : Nano-shell
Spherical
Diameter:
20 – 50 nm

NSCC : Nano-shell-Containing Carbon
NSs are embedded in amorphous carbon

Protein＋ Metal salt

↓ Carbonization

Carbon alloy catalysts with ORR and HER activities



Repeating unit of protein

M. Takigami, J. Ozaki, Carbon 2014, Jeju, Korea, 2014.6.29-7.4. ORT-6-61.

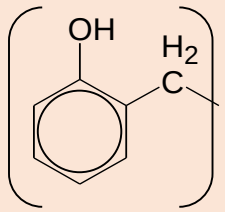
M. Takigami, J. Ozaki, Annual Meeting of the Carbon Society of Japan, 2014.12.8-10. B04.

Purposes of the present study

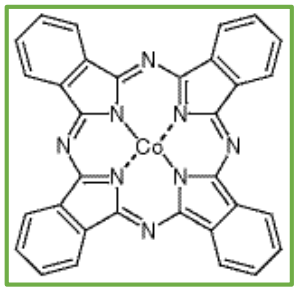
To clarify the following points

1. Roles of nitrogen and cobalt
2. Similarities and differences between phenol resin and protein based catalysts
3. Relation between ORR and HER activities

Preparation of Carbon Alloy Catalysts



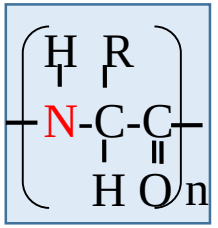
Phenol-Formaldehyde Resin : PFR



Cobalt Phthalocyanine : CoPc

PFR

Protein



Protein :
- Egg
- Wool

CoPc

$CoCl_2$

Carbonization; in N_2, 1000 ℃, 1 h

$CoCl_2$

Ball milling

Acid washing

PFR-C

Protein-C

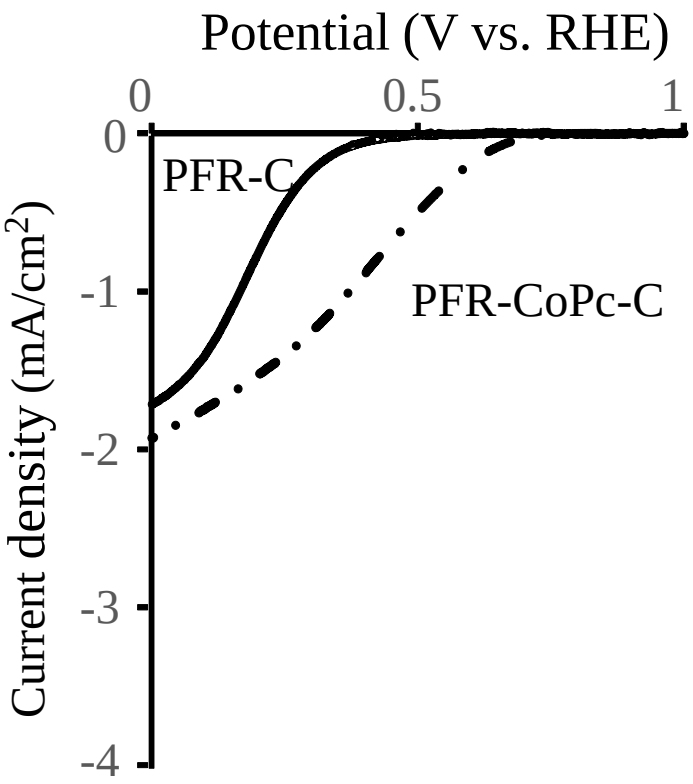
PFR-CoPc-C

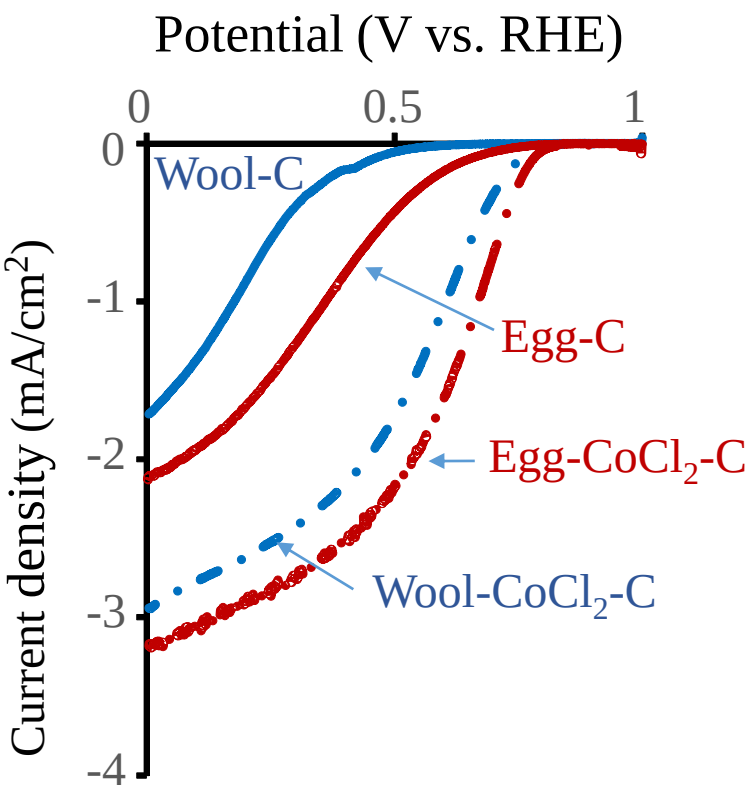
Protein-$CoCl_2$-C

Carbon Alloy Catalysts

ORR by Caron Alloy Catalysts

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





Rotating Disk Electrode

・Reference electrode: Reversible Hydrogen Electrode (RHE) ・Counter electrode: Glassy carbon ・Working electrode : Carbon alloy catalyst ・Electrolyte : 0.5 mol/L H_2SO_4

・Rotation: 1500 rpm ・ Temperature: RT ・Scanning : 1 ~ 0 V, 1 mV/s

E_{O2}s and Tafel slopes of carbon alloy catalysts for ORR

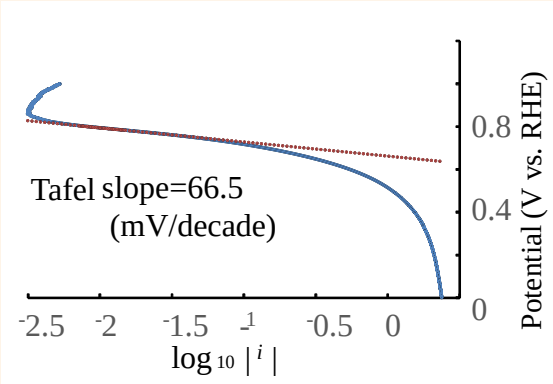
Sample	E_{O2} (V vs. RHE at -10 μA/cm^2)	Tafel slope (mV/decade)
PFR-C	0.491	-159
Egg-C	0.787	-166
Wool-C	0.617	-159
PFR-CoPc-C	0.743	-79
Egg-$CoCl_2$-C	0.854	-60
Wool-$CoCl_2$-C	0.815	-58

E_{O2} of carbon alloy catalysts

- Egg-$CoCl_2$-C > Wool-$CoCl_2$-C > Egg-C > PFR-CoPc –C > Wool-C > PFR-C
- N and Co contribute to improve E_{O2}

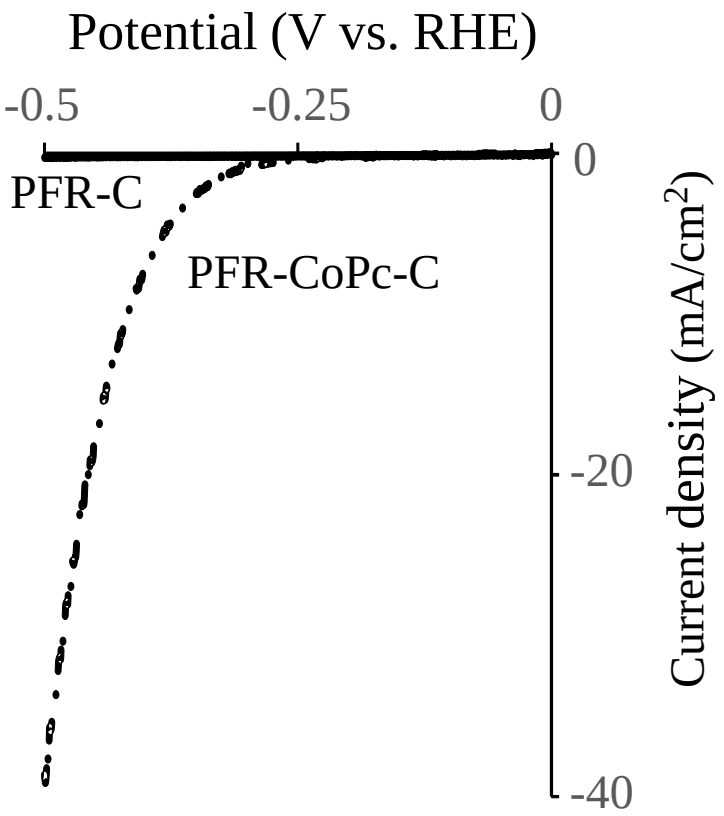
|Tafel slope|

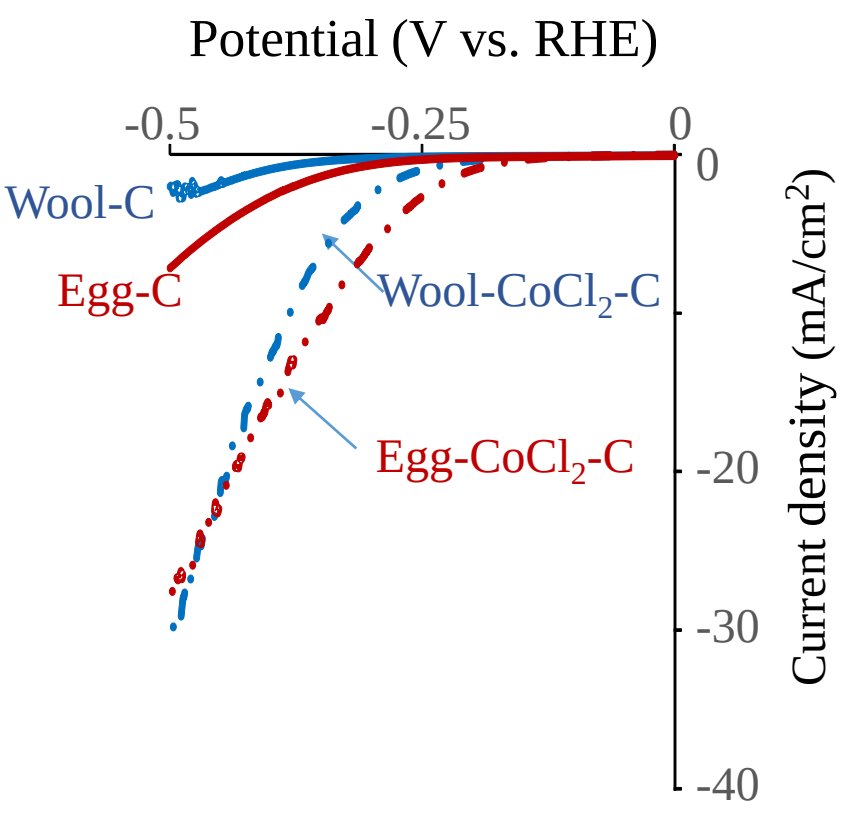
- Egg-$CoCl_2$-C, Wool-$CoCl_2$-C < PFR-CoPc-C < PFR-C, Egg-C, Wool-C
- Onset mechanism of ORR is the same for
  PFR-C, Egg-C and Wool-C
  Egg-$CoCl_2$-C and Wool-$CoCl_2$-C



HER by Carbon Alloy Catalysts

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





Rotating Disk Electrode

・Reference electrode: Reversible Hydrogen Electrode (RHE) ・Counter electrode: Glassy carbon ・Working electrode : Carbon alloy catalyst ・Electrolyte : 0.5 mol/L H_2SO_4

・Rotation: 1500 rpm ・ Temperature: RT ・Scanning : 0 ~ -1 V, 1 mV/s

E_{H2}s and Tafel slopes of carbon alloy catalysts for HER

Sample	E_{H2} (V vs. RHE at -1 mA/cm^2)	Tafel slope (mV/decade)
PFR-C	-0.666	-193
Egg-C	-0.330	-152
Wool-C	-0.408	-152
PFR-CoPc-C	-0.330	-115
Egg-$CoCl_2$-C	-0.203	-107
Wool-$CoCl_2$-C	-0.254	-117

$|E_{H2}|$ of carbon alloy catalysts

Egg-$CoCl_2$-C < Wool-$CoCl_2$-C < Egg-C, PFR-CoPc –C < Wool-C < PFR-C

N and Co contribute to improve E_{H2}

|Tafel slope|

Egg-C = Wool-C < PFR-C

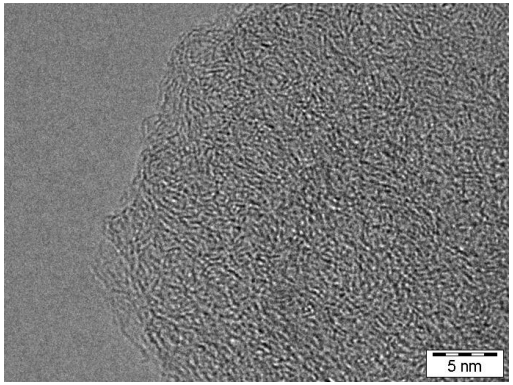
PFR-CoPc-C = Egg-$CoCl_2$-C = Wool-$CoCl_2$-C

Onset mechanism of ORR is the same for

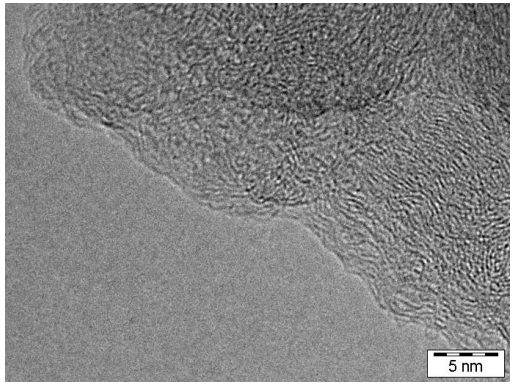
Egg-C and Wool-C

PFR-CoPc-C, Egg-$CoCl_2$-C and Wool-$CoCl_2$-C

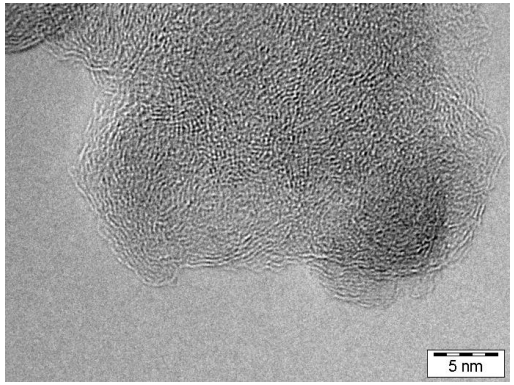
TEM of Carbon Alloy Catalysts



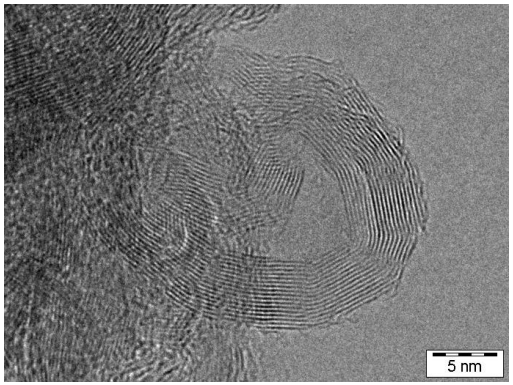
PFR-C



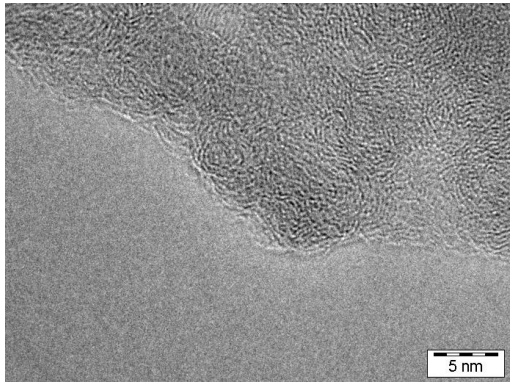
Egg-C



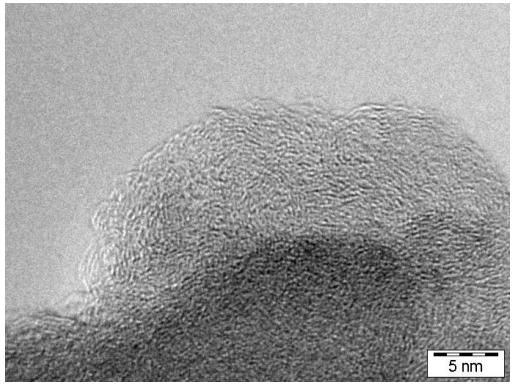
Wool-C



PFR-CoPc-C



Egg-$CoCl_2$-C

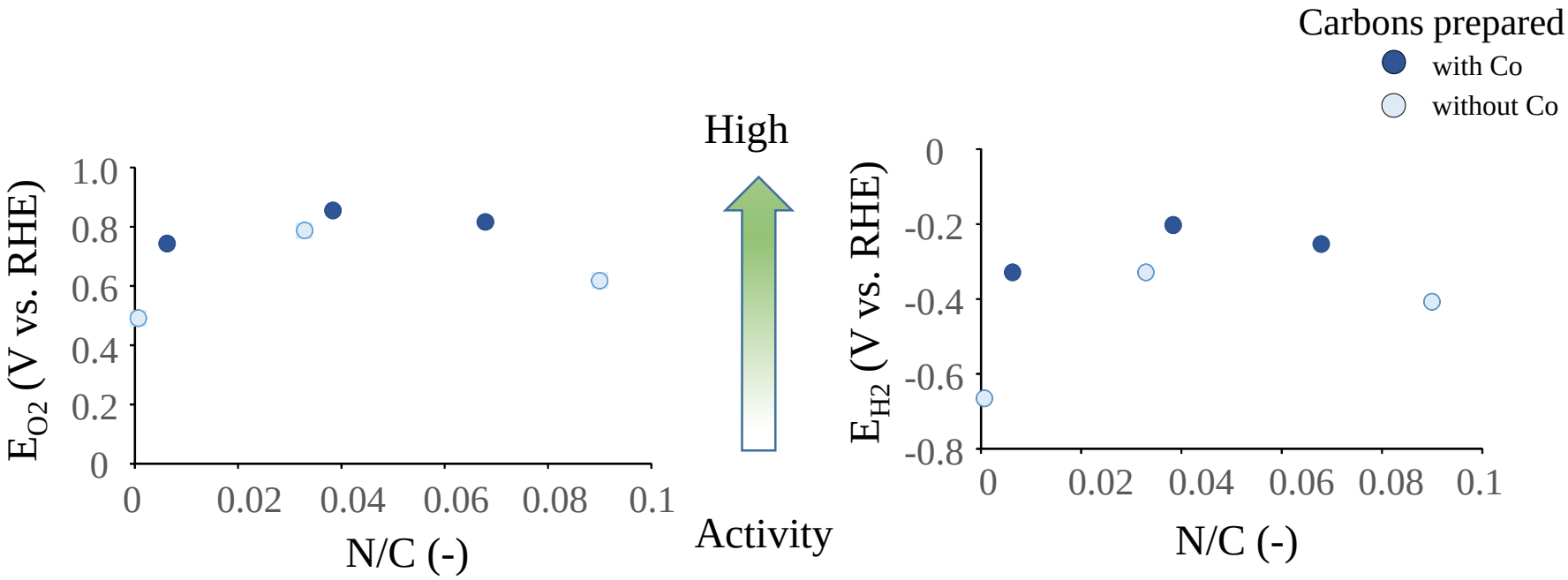


Wool-$CoCl_2$-C

PFR-C: Amorphous —Co→ PFR-CoPc-C: NS

Protein-C: Amorphous —Co→ Protein-$CoCl_2$-C: Amorphous

N in Carbon Alloy Catalysts



Relation of E_{o2} (left) and E_{H2} (right) vs N/C measured by XPS

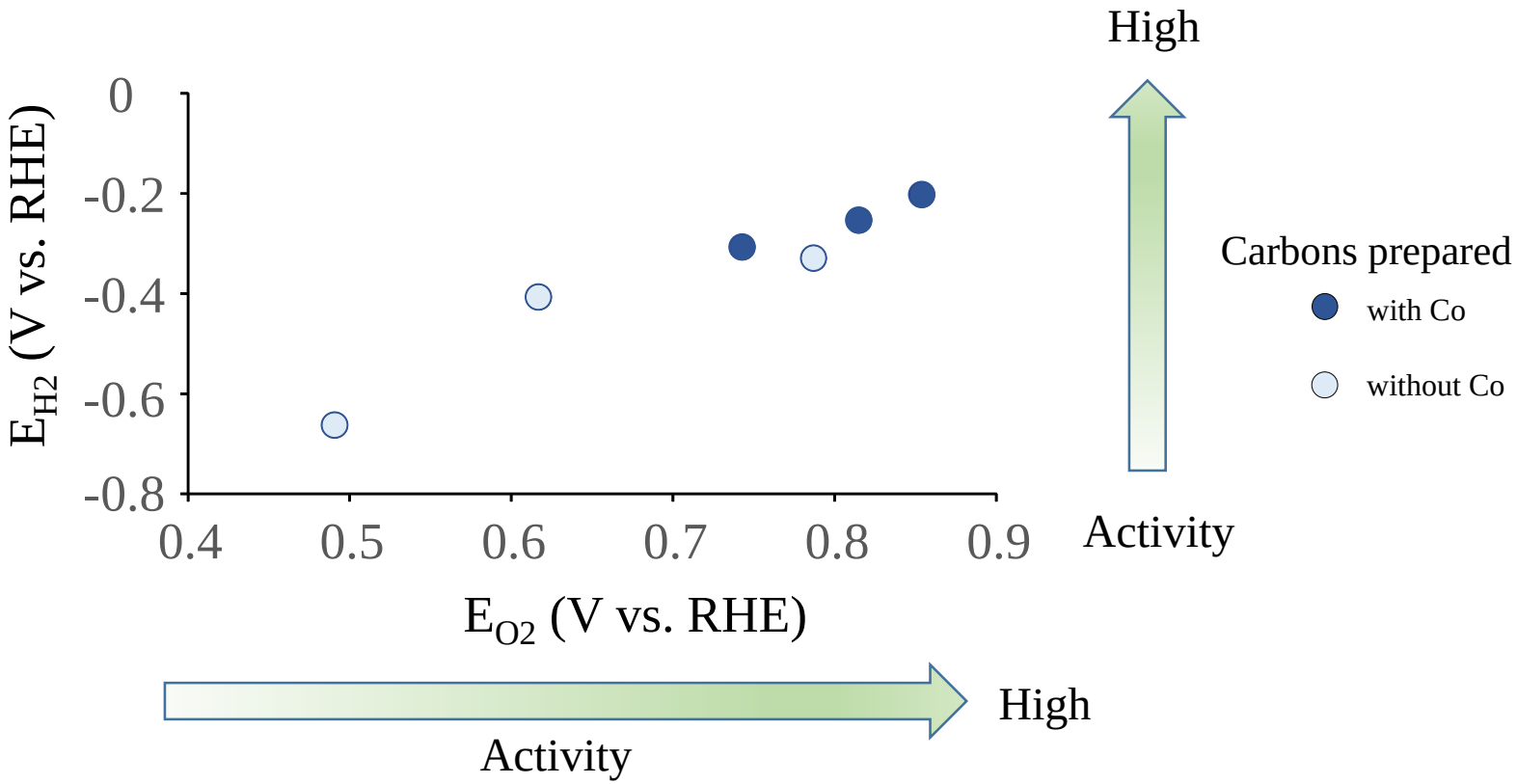
N contents

Depend on carbon precursors

N/C does not correlate directly to E_{O2} / E_{H2}

Graphs of E_{O2} / E_{H2} vs. N/C are similar in shape

Relation between E_{O2} and E_{H2}



Relation between E_{O2} and E_{H2}

Carbons with higher ORR activities have higher HER activities

Conclusions

1. Roles of nitrogen and cobalt

   Nitrogen is valid to improve onset potentials for ORR and HER. Beside, cobalt contribute to promote ORR and HER.

2-1. Similarities in PFR and protein derived carbon alloy catalysts

   Nitrogen and cobalt contribute to improve activities of carbon alloy catalysts for ORR and HER

2-2. Differences in PFR and protein derived carbon alloy catalysts

   Addition of CoPc to PFR formed nanoshell structure in PFR-CoPc-C

   Addition of $CoCl_2$ to protein did not cause distinct differences in carbon structure

3. Relation between ORR and HER activities

   One carbon alloy catalyst works for both ORR and HER

   The higher the ORR activity of the carbon alloy catalyst, the higher the HER activity of the carbon

Danke Shön

Photograph taken at Gunma University