Carbon Alloy Catalysts for Oxygen Reduction Reaction Derived from a Humic Acid

M. Takigami, S. Baba and J. Ozaki
Graduate School of Science and Technology
Gunma University
Japan

Background of this research

Thermosetting polymer
+ transition metal compound

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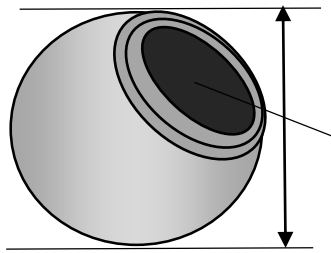
Carbon having catalytic activity for oxygen reduction reaction (ORR)



Nanoshell carbon
spherical
20 – 50 nm

NSCCs NS carbons embedded in amorphous carbons

- The catalytic activities of the carbons are enhanced by doping nitrogen to the carbons.
- Carbons having catalytic activity and heterogeneity in elemental components and/or structure were defined "Carbon Alloy Catalysts".

NSCCs : CA catalysts

Natural products ⟹ Carbons with high ORR activities

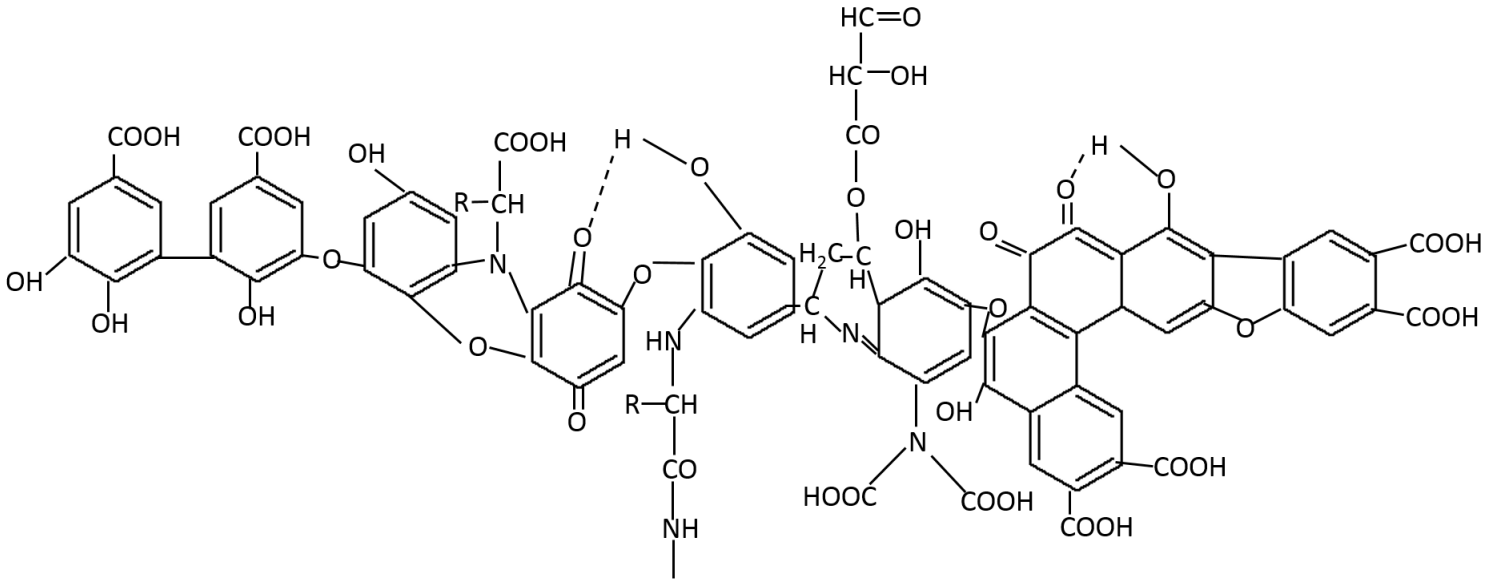
Why “Humic Acid”?

- Humic acid (HA) is a natural product based on biomaterials and a sustainable material.
- HA has some similarity with phenol resin, which is a popular raw material for NSCCs.

Structure of humic acid

Humic acid (HA) is produced by biodegradation of dead organic matters and it does not have a single molecular structure. It contains a small amount of nitrogen. It is a complex mixture of acids including a lot of carboxyl and phenolate groups. HA distributes on the surface of the earth; in soil, in lakes and rivers as sediments. In the present study, we examine the carbons from a type of HA.

Humic acid



F. J. Stevenson, Humic Chemistry : Genesis, Composition, reactions, 2nd Ed., (1994), John Wiley &Sons, Canada, p.289.

Aims of the research

Do HA give catalysts with high ORR activity?

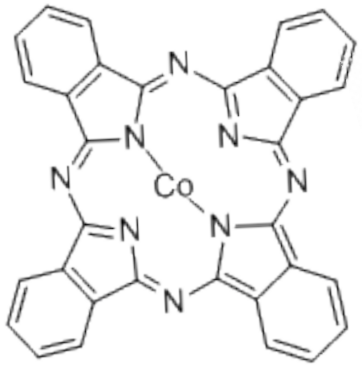
What kinds of role do cobalt and nitrogen

have for ORR reaction?

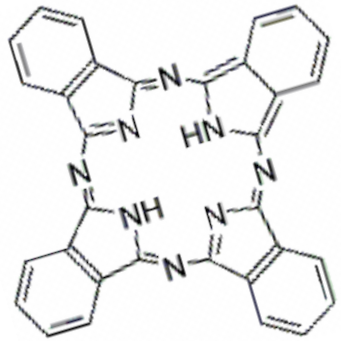
What are required to have CA catalysts with higher ORR activities?

Properties of additives

Additive	Chemical formular	Abbreviation	Solubility in water
Cobalt phthalocyanine	$C_{32}H_{16}CoN_8$	CoPc	Insoluble
Cobalt chloride	$CoCl_2$	$CoCl_2$	53g/100mL
Phthalocyanine	$C_{32}H_{18}N_8$	H_2Pc	Insoluble



CoPc

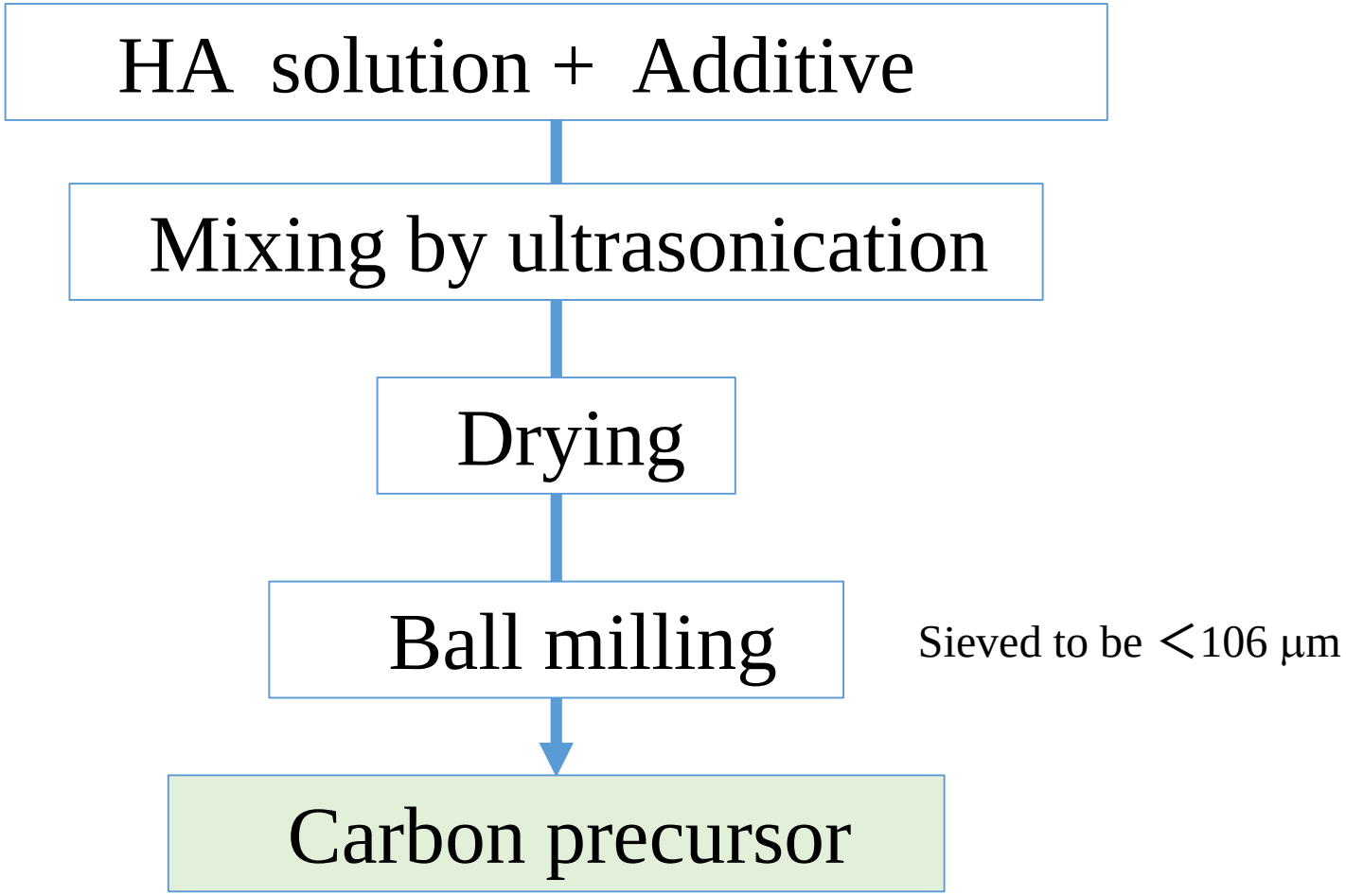


H_2Pc

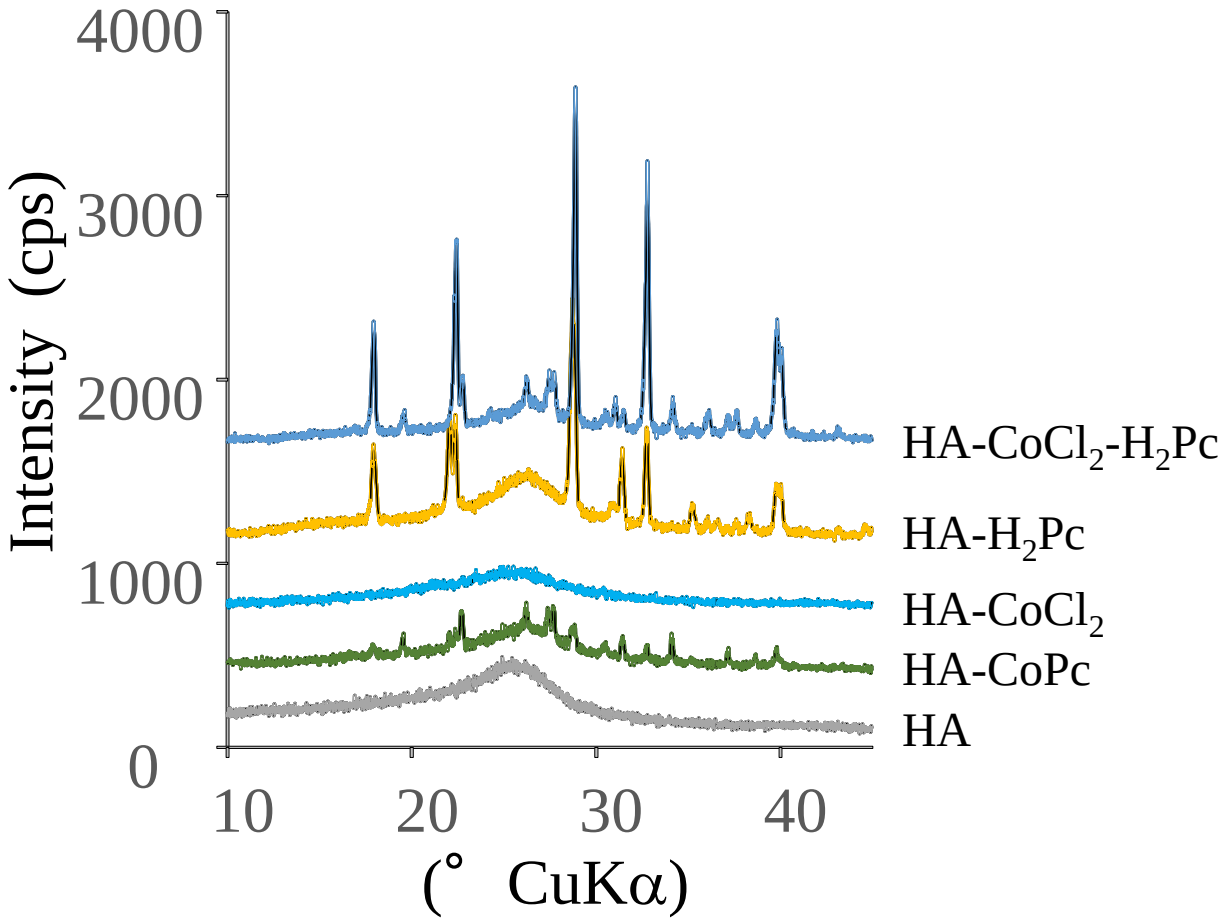
Cited from Chemical Book

Comparison	Expected information
HA-CoPc and HA-H_2Pc	Effect of Co
HA-CoPc and HA-$CoCl_2$	Effect of Co distribution Effect of N
HA-CoPc and HA-$CoCl_2$-H_2Pc	Effect of Co distribution Effect of N

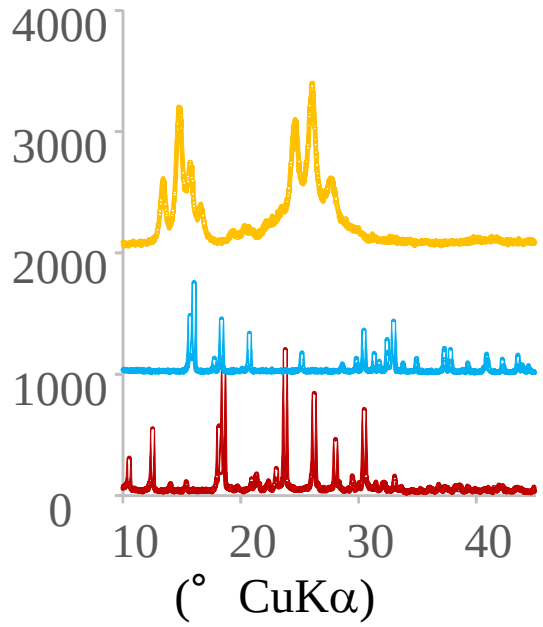
Preparation of carbon precursors



Structure of carbon-precursors - XRD

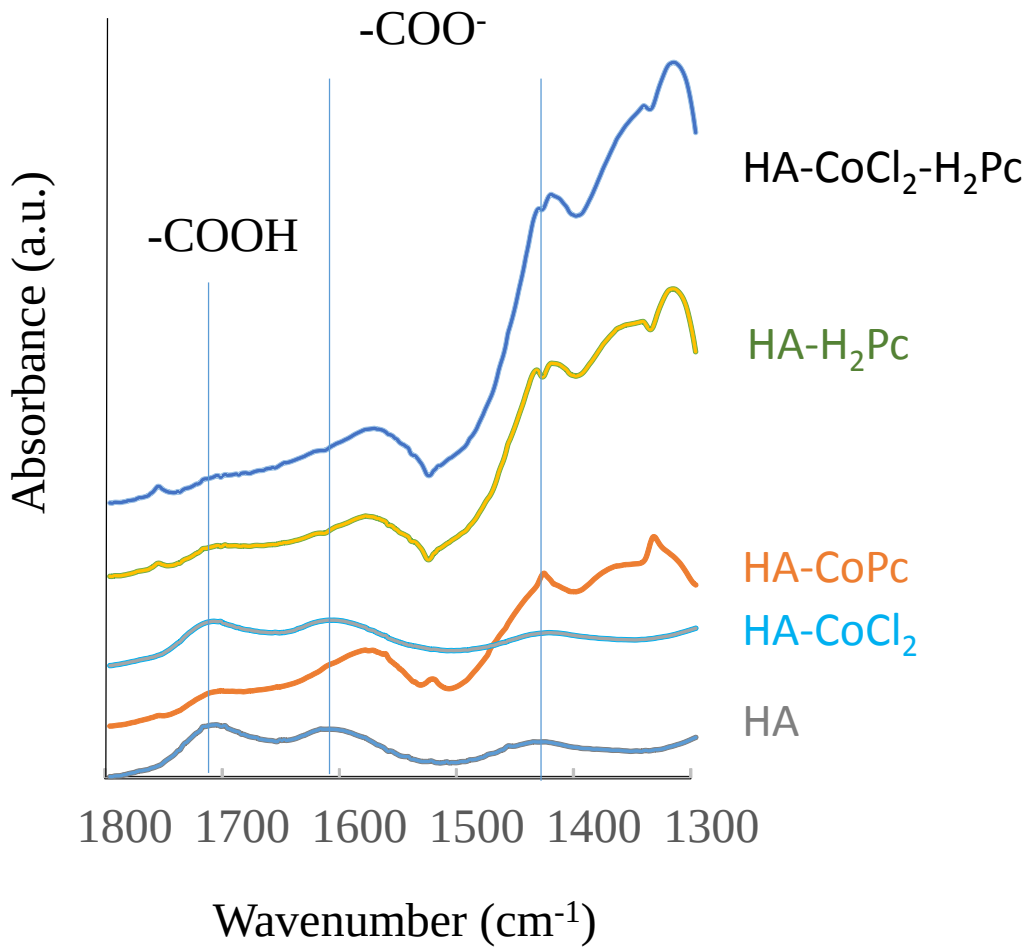


Precursors



Additives

Structure of carbon-precursors – FT-IR



Summary of precursors

* Cobalt distributes uniformly in HA-$CoCl_2$, however, the distribution is partially disturbed in HA-$CoCl_2$-H_2Pc, because of H_2Pc.
*Cobalt exists as counter ion of carboxyl groups which is contained in HA abundantly.
*In HA-CoPc, Co does not distribute uniformly because of the solubility of CoPc in water.

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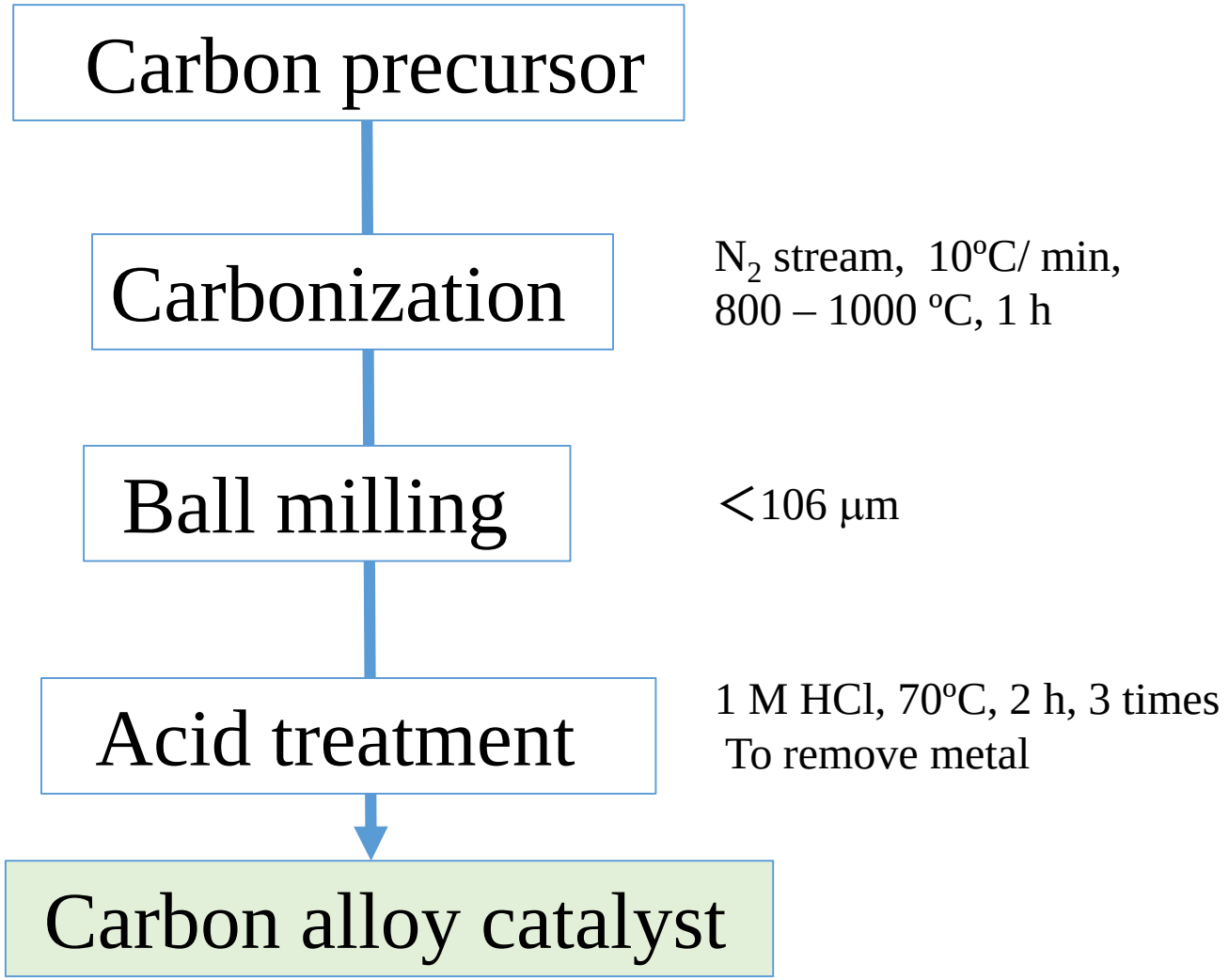
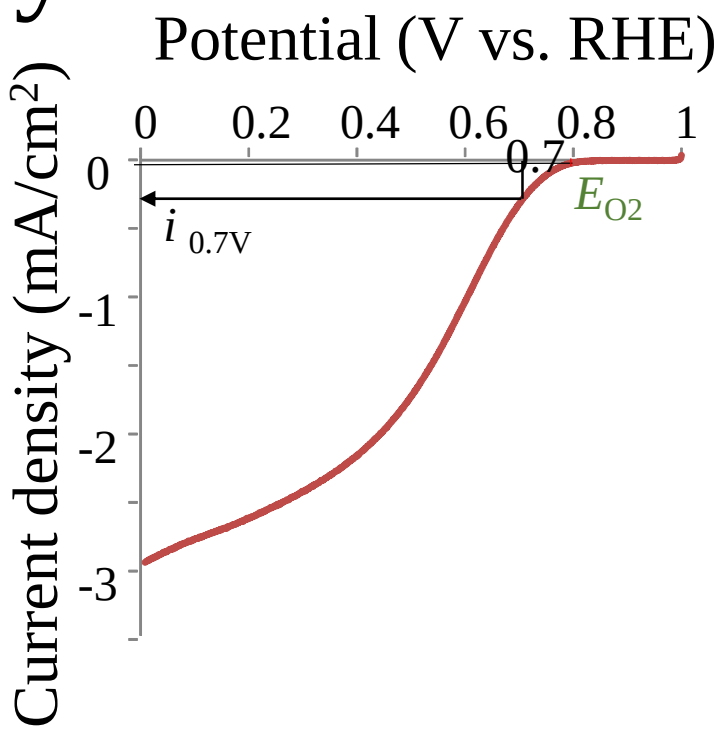
Preparation of carbon alloy catalysts



Evaluation of ORR catalytic activity

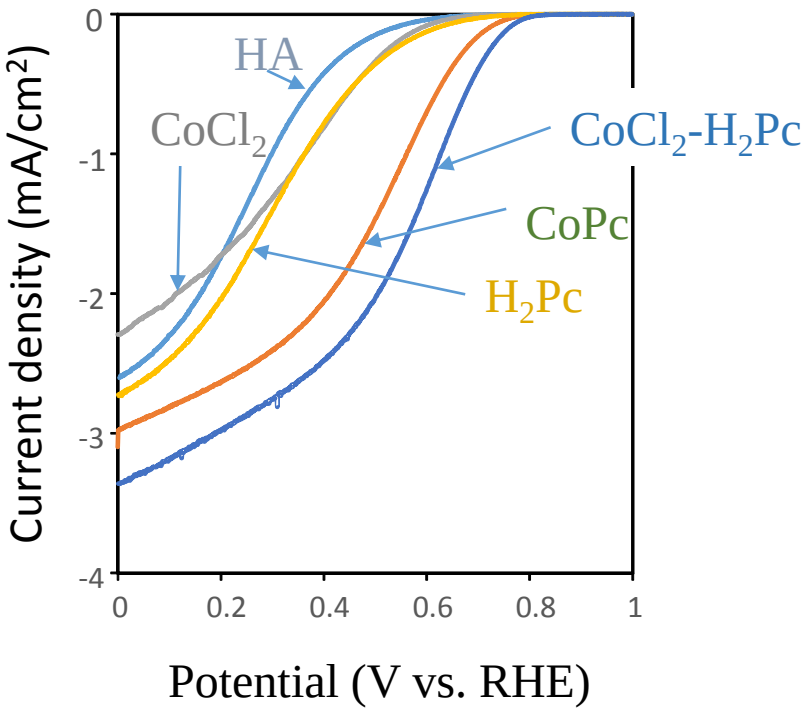
Rotating Ring Disk Electrode
Reference electrode: Reversible hydrogen electrode
Counter electrode: Glassy carbon
Working electrode : Carbon catalyst
Electrolyte : 0.5M H2SO4
Rotation: 1500 rpm
Temperature: RT
Scanning : 1～0 V, 1 mV/sec



ORR voltammogram of carbon derived from HA-CoPc

E_{O2}: Onset potential (10 mA/cm^2)
$i_{0.7V}$: Current density at 0.7 V

What required to have highly active ORR CA catalysts



HA-additive-800

Comparison	Information	Results
HA-CoPc and HA-H_2Pc	Co	Co is essential
HA-CoPc and HA-$CoCl_2$	Co distribution N	Without N, uniform distribution of Co does not result in high ORR
HA-CoPc and HA-$CoCl_2$-H_2Pc	Co distribution N	Uniform distribution of Co causes high ORR in the presence of N

Conclusions

HA gives catalysts with high ORR activity.

Co and N are essential to have highly active ORR CA catalysts. Both of them contribute to large E_{O2} and $|i_{0.7V}|$.

Coexistence of Co and N, and uniform distribution of Co are important to have high ORR CA catalysts.