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

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.

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

<table>
<thead>
<tr>
<th>Additive</th>
<th>Chemical formula</th>
<th>Abbreviation</th>
<th>Solubility in water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt phthalocyanine</td>
<td>$C_{32}H_{16}CoN_8$</td>
<td>CoPc</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Cobalt chloride</td>
<td>CoCl$_2$</td>
<td>CoCl$_2$</td>
<td>53g/100mL</td>
</tr>
<tr>
<td>Phthalocyanine</td>
<td>$C_{32}H_{18}N_8$</td>
<td>H$_2$Pc</td>
<td>Insoluble</td>
</tr>
</tbody>
</table>

**Comparison**

<table>
<thead>
<tr>
<th>HA-CoPc and HA-H$_2$Pc</th>
<th>Effect of Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA-CoPc and HA-CoCl$_2$</td>
<td>Effect of Co distribution Effect of N</td>
</tr>
<tr>
<td>HA-CoPc and HA-CoCl$_2$-H$_2$Pc</td>
<td>Effect of Co distribution Effect of N</td>
</tr>
</tbody>
</table>

Cited from Chemical Book
Preparation of carbon precursors

1. HA solution + Additive
2. Mixing by ultrasonication
3. Drying
4. Ball milling
   Sieved to be <106 μm
5. Carbon precursor
Structure of carbon-precursors – FT-IR

Absorbance (a.u.)

- COOH
- COO⁻

HA-CoCl₂-H₂Pc
HA-H₂Pc
HA-CoPc
HA-CoCl₂
HA

1800 1700 1600 1500 1400 1300
Wavenumber (cm⁻¹)
Summary of precursors

* Cobalt distributes uniformly in HA-CoCl$_2$, however, the distribution is partially disturbed in HA-CoCl$_2$-H$_2$Pc, because of H$_2$Pc.
* 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.
Summary of precursors

* Cobalt distributes uniformly in HA-CoCl$_2$, however, the distribution is partially disturbed in HA-CoCl$_2$-H$_2$Pc, because of H$_2$Pc.
* 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.
Preparation of carbon alloy catalysts

Carbon precursor

Carbonization
N\textsubscript{2} stream, 10\(^{\circ}\)C/ min, 800 – 1000 \(^{\circ}\)C, 1 h

Ball milling
<106 \(\mu\)m

Acid treatment
1 M HCl, 70\(^{\circ}\)C, 2 h, 3 times
To remove metal

Carbon alloy catalyst
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

$E_{O2}$: Onset potential (10 mA/cm$^2$)
$i_{0.7V}$: Current density at 0.7 V
What required to have highly active ORR CA catalysts

Comparison

<table>
<thead>
<tr>
<th>Information</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>HA-CoPc and</td>
<td>Co is essential</td>
</tr>
<tr>
<td>HA-H₂Pc</td>
<td></td>
</tr>
<tr>
<td>HA-CoPc and</td>
<td>Without N, uniform distribution of Co does not result in high ORR</td>
</tr>
<tr>
<td>HA-CoCl₂</td>
<td></td>
</tr>
<tr>
<td>HA-CoPc and</td>
<td>Uniform distribution of Co causes high ORR in the presence of N</td>
</tr>
<tr>
<td>HA-CoCl₂-H₂Pc</td>
<td></td>
</tr>
</tbody>
</table>
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.