Carbon Alloy Catalysts
-A New Non-Precious Catalysts for Fuel Cells-

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Concentration of Carbon Dioxide
Increase in second half of 20th century
<table>
<thead>
<tr>
<th>Vehicle</th>
<th>Length/Width /Height (mm)</th>
<th>Type</th>
<th>Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4,735/1,815/,1,685</td>
<td>Storage</td>
<td>High Pressure Tank</td>
</tr>
<tr>
<td>Highest Speed</td>
<td>155 Km/h</td>
<td>Fuel</td>
<td>Storage Pressure</td>
</tr>
<tr>
<td>Cruising distance</td>
<td>830 Km</td>
<td></td>
<td>70 MPa</td>
</tr>
<tr>
<td>Mileage</td>
<td>139 Km/Kg (Gas engine conv. 38 Km/L)</td>
<td>Loading Hydrogen</td>
<td>6 Kg</td>
</tr>
<tr>
<td>Capacity</td>
<td>5 person</td>
<td>Price</td>
<td>Lease Price</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$9,000/month</td>
</tr>
</tbody>
</table>
Batteries

Electric Energy

Redox Reaction

Chemical Materials
Polymer Electrolyte Fuel Cell (PEFC)

Pt catalyst
We need **Non Precious Metal Catalysts**

**Pt cat in Fuel Cell Cars**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Small size cars</td>
<td>32 g Pt</td>
</tr>
<tr>
<td>Middle size cars</td>
<td>60 g Pt</td>
</tr>
<tr>
<td>Car Production per Year</td>
<td>35 million</td>
</tr>
<tr>
<td>Pt Requisite Amount</td>
<td>1750 t</td>
</tr>
<tr>
<td>Amount of Deposit</td>
<td>$5 \times 10^5$ t</td>
</tr>
<tr>
<td>Pt price</td>
<td>4600 JPY/g</td>
</tr>
</tbody>
</table>

No Hope for Fuel Cell Cars without Non Pt Cat. Invention!!!

**Carbon Alloy Catalysts**

- **Price**: 1/20 of Pt
- **Amount of Deposit**: Unlimited
How to prepare Carbons?

Starting Materials (Polymers)

Woods

PAN (Polyacrylonitrile)

Heat without O₂ → Charcoal

Heat without O₂ → Carbon fiber
Carbon Alloy Catalysts (CAC)

Phenolic resin

Fe phthalocyanine

Carbonization

Acid washing

ORR catalysts

FePc/PhRs

Higher density of active sites!?
Higher durability!?
Change to Carbon from Polymers

- Carbon Fiber
- Charcoal
- Carbon Alloy
- Catalyst
Preparation of Carbon Alloy Catalysts (CAC)

**Single Step Pyrolysis (Ozaki Method)**

Phenol Resin (3.275g) + MPc (1.00g) in Acetone (300mL)

- Evaporation
- 200 ~ 800 °C for 1h under N2

**Carbon Alloy Catalysts (CAC)**

- Wash with 37% HCl

**CAC-w**

MPc  M: Non, Fe, Co
Screening of Catalytic activity

**Electrochemical cell in this study**
Rotating ring-disc electrode (RRDE)

- **Working Electrode**: CAC
- **Electrolyte**: 0.5M H₂SO₄
- **Counter Electrode**: Pt
- **Reference Electrode**: Ag/AgCl

**Voltammogram of CAC**

Reaction: \(4H^+ + O_2 + 4e^- \rightarrow 2H_2O\)

- Active site ↑ ⇒ Current density ↑ ⇒ Onset potential ↑

**Onset potential**
Target 1.0V

- 1.23V
- 0 mA/cm²
- -2 µA/cm²

Higher current density
Higher onset potential

Potential / V (vs NHE)
Current density / mA cm⁻²
Single step pyrolysis

H$_2$Pc/PhRs

FePc/PhRs aw

Low Catalytic Activity
Effect of N, even no metals!?

Highest Catalytic Activity was at 600°C

0.5 M H$_2$SO$_4$, 1500rpm, 1 mV sec$^{-1}$
**N content**

- **H$_2$Pc**: N decrease until 550 °C
- **FePc**: N not decrease until 600 °C
- N decrease dramatically at 700-800 °C

**BET area**

<table>
<thead>
<tr>
<th>温度 / °C</th>
<th>FePc / PhRs</th>
<th>H$_2$Pc / PhRs</th>
</tr>
</thead>
<tbody>
<tr>
<td>550</td>
<td>506</td>
<td>595</td>
</tr>
<tr>
<td>600</td>
<td>515</td>
<td>545</td>
</tr>
<tr>
<td>650</td>
<td>437</td>
<td>530</td>
</tr>
<tr>
<td>700</td>
<td>444</td>
<td>547</td>
</tr>
<tr>
<td>800</td>
<td>407</td>
<td>501</td>
</tr>
</tbody>
</table>

400 ~ 600 m$^2$ g$^{-1}$
Phtharonitrile was detected

Phtharonitrile was not observed

Ion (Fe) prevented coming out of phtharonitrile
TEM of CAC

600°C

600°C aw

800°C

Fe particles bring up “Nano-shell” structure
Role of Ion (Fe) on Carbonization

Nabae et al., *Carbon* (2010).

**H$_2$Pc/PhRs**

- ~200°C
- 400~550°C
- FePc/PhRs

- ~200°C
- 400~550°C
- 600~800°C

**Fe** must be atomic

**600°C** Highly Active

**700~800°C**

**Fe** must be metal particles

**Nano Shell**

High content of N

Fe catalyst

**N$_2$**

**N$_2$**
Effect of Ion (Fe) on Carbonization of FePc/PhRs

- Below 600 °C, Fe increased N content by coordination of Fe to nitrile nitrogen
- Above 600 °C, Fe promoted elimination of N
- Fe metal particles made Nano-shell structure (high crystallinity)
- The highest activity was obtained by treatment at 600 °C
Preparation of MEA

Cathode electrode layer
(CAC, 4mg cm$^{-2}$ + Nafion)

Anode electrode layer
(46 wt% Pt/C 0.5 mg cm$^{-2}$ + Nafion)

MEA

Screen print

Screen print

Teflon sheet

Teflon sheet

Bake

Bake

hot press, $T$, $t$ with Nafion-115

Geometric area: 1 cm$^2$
Single step pyrolysis: MEA initial performance

FePc/PhRs(600) aw

OCV: 1.01 V
Max. output: 0.33 W cm\(^{-2}\)

H\(_2\)-O\(_2\), cell \(T\) 80°C
Pressure: 0.2MPka
Single step pyrolysis: Durability test

By monitoring the change of cell voltages with time at fixed current density.

$\text{H}_2 \ 0.1\text{MPka, air} \ 0.1\text{MPka} \ \text{Cell:} \ 80^\circ\text{C} \ i = 0.1 \ \text{A/cm}^2$
**Hypothesis**

- The active points are already built up at 600°C
- Higher temperature treatment may increase durability!? 
- Ion metal particles destroy the active points at high temperature

Ion metal particles of FePc/PhRs (600) must be removed, and then, high temperature treatment?
Multi step pyrolysis: Methodology

Precursor: FePc/PhRs (Fe: 3 wt%)

600-I: 600°C (inert gas) Acid Wash (AW) Single step

800-II-N₂: 600°C (inert gas) AW 800°C (inert gas) AW Multi step

800-II-NH₃: 600°C (inert gas) AW 800°C (NH₃) AW

1000-III-NH₃: 600°C (inert gas) AW 800°C (NH₃) AW 1000°C (NH₃) AW
## Property of the catalysts

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Elemental analysis (wt. %)</th>
<th>EPMA results: Fe (wt%)</th>
<th>BET surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600-I-N₂</td>
<td>84.0 2.0 3.0</td>
<td>2.2</td>
<td>384</td>
</tr>
<tr>
<td>800-II-N₂</td>
<td>92.3 1.1 1.6</td>
<td>0.8</td>
<td>432</td>
</tr>
<tr>
<td>800-II-NH₃</td>
<td>87.9 1.3 2.9</td>
<td>0.7</td>
<td>533</td>
</tr>
<tr>
<td>1000-III-NH₃</td>
<td>95.8 0.9 0.9</td>
<td>0.6</td>
<td>849</td>
</tr>
</tbody>
</table>

1000-III-NH₃:
Multi step pyrolysis: MEA initial performance

T: 80ºC; Anode: Pt/C 45.7 wt% 0.5 mg cm⁻², H₂ 0.2 MPa; Cathode: Carbon alloy 4 mg cm⁻², O₂ 0.2 MPa.
Anode: 0.5mg/cm² Pt/C 0.2MPka H₂; Cathode: 0.2MPka O₂; Membrane: Nafion® 115; Cell: 80°C

Multi step pyrolysis: MEA initial performance

Cell potential / V vs. i / Acm⁻²
Multi step pyrolysis: Durability test

Cell voltage: 0.1 A cm$^{-2}$; T: 80ºC; Anode: H$_2$ 0.1 MPa; Cathode: Air 0.1 MPa.
How can Carbon reduce $O_2$?

In case of Pt

Interaction between d electron of Pt and free electron of $O_2$

In case of Carbon?
Model of Active Points

**Metal-N coordination**

M-N coordination can not be observed in catalysts that were treated at high temperature!?

![Metal-N coordination](image)

**Figure 1.** Proposed moiety of the high-temperature catalytic site.


**Nitrogen doped carbon**

Zigzag edge has high state density


Nitrogen doped carbon

Conclusion

• Carbon alloy catalysts (CAC) was successfully prepared nitrogen containing polymers.
• Ion (Fe) plays important role for nitrogen control and nano-shell formation.
• Single cell using CAC achieved 0.56 Wcm$^{-2}$ that was 65% output of Pt cell.
• Output power was the highest in fuel cells that were made using non precious metal catalyst.

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