Ionomer-Free Electrode Catalyst Using Acid-Grafted Carbon Black As a Proton-Conductive Support

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Polymer Electrolyte Fuel Cell: PEFC

Polymer Electrolyte Membrane (PEM)

<table>
<thead>
<tr>
<th></th>
<th>anode</th>
<th>cathode</th>
<th>total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$H_2 \rightarrow 2H^+ + 2e^-$</td>
<td>$1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$</td>
<td>$H_2 + 1/2O_2 \rightarrow H_2O$</td>
</tr>
<tr>
<td>$E^0$</td>
<td>0 V</td>
<td>1.23 V</td>
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</tbody>
</table>

✓ High energy density  ✓ Clean

Commercialization for hydrogen society

https://panasonic.biz/appliance/FC
https://toyota.jp/mirai/grade/
https://ENE-FARM
Cost of PEFC

500,000 Systems/Year

- Bipolar Plates: 41%
- Membranes: 28%
- Catalyst + Application: 10%
- GDLs: 9%
-MEA Frame/Gaskets: 6%
- Balance of Stack: 6%

DOE Hydrogen and fuel cell Program Record, 2017

Catalyst layer

Catalyst: Pt

ca. 80 USD/g

Reduction of Pt amount is key

⇒ Pt cluster, Pt alloy

✓ Poor durability

⇒ Increase of Pt utilization efficiency
Increase of Pt utilization efficiency

Cathode:

\[ \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O} \]

Smooth mass diffusion is key

Ionomer distribution affects mass diffusion

Nafion

High proton conductivity due to phase separation

Ionomer

Hydrophobic

Hydrophilic
Problem of ionomer 1: Trade off, $O_2$ vs $H^+$

Nafion amount vs FC activity

- Decrease of cell voltage with increasing Nafion amount
- Increase of $O_2$ resistivity
- Increase of $O_2$ diffusion decreases $H^+$ conduction

Problem of ionomer 2: Pt poisoning

Oxygen reduction reaction (ORR) activity

- Decrease of Pt activity by ionomer addition

DFT: ionomer/Pt interface

Decrease of active site

Poisoning of Pt surface by ionomer

Strategy

Novel strategy to avoid critical issue

Fabrication of proton conductive carbon surface

Current study

- ionomer

- \( \Delta \) Pt poisoning
- \( \Delta \) \( \text{O}_2 \) diffusion resistance
- \( \Delta \) low \( \text{H}^+ \) conductivity by lowering of RH

This study

High grafting of acid groups

- ✓ Poison free?
- ✓ Effective \( \text{O}_2 \) diffusion?
- ✓ High \( \text{H}^+ \) conductivity at low RH?

Hopping \( \text{H}^+ \) condution
This study

Fabrication of proton conductive path on carbon surface by acid grafting

Grafting of sulfonic acid on CB surface

Radical addition

Mild reaction condition

Previous study

✓ Increase of activity at lower %RH

✓ Increase of durability


Grafting of CB

Grafting by diazonium salt

SO$_3$Na

\[
\text{CB} \quad \xrightarrow{\text{water}} \quad \text{SCB}
\]

\[70 \, ^\circ\text{C}, \, 3 \, \text{h}\]

Intensity (a.u.)

Grafting of SO$_3^-$

EtOH

CB

SCB

-8.5 mV

-46.1 mV

XPS

Binding Energy / eV

600 500 400 300 200 100 0

C 1s

O 1s

S 2$s$ S 2$p$

Fujigaya Laboratory

Kyushu University
Analysis of Graft Density

10 wt% grafting

Introduction of defect
Pt loading


SCB $\rightarrow$ Pt(acac)$_2$ (Acetone sonication (30 min)) $\rightarrow$ SCB

Pt(acac)$_2$ $\rightarrow$ SCB $\rightarrow$ Pt

(210 °C: 3 h, 240 °C: 3h)

SCB/Pt (Pt: 20 wt%)

**TEM**

✓ Uniform loading
✓ Diameter: 2.6 nm

**XPS**

Atomic Concentration %

<table>
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<tr>
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<th>Pt (0)</th>
<th>Pt (II)</th>
<th>Pt (IV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCB/Pt</td>
<td>56.8</td>
<td>18.7</td>
<td>24.7</td>
</tr>
<tr>
<td>CB/Pt</td>
<td>50.4</td>
<td>23.4</td>
<td>26.2</td>
</tr>
</tbody>
</table>

✓ Reduction of Pt

Good Pt dispersion
**LCV measurement**

- Voltage vs NHE / V
  - Current density / mA cm$^{-2}$
  - O$_2$
  - CB + Nafion
  - SCB

- 1600 rpm, 10 mV s$^{-1}$
- Diameter : 4 mm
- Pt : 14 µg cm$^{-2}$
- 0.1 M HClO$_4$

- Electrode potential / V
  - Kinetic current / mA cm$^{-2}$
  - Higher activity
  - Lower poisoning

- CB/Pt + Nafion
- SCB/Pt
**Fuel Cell Analysis**

### MEA preparation

- **Nafion** (I/C=0.8)
  - Nafion thickness: 0.05 mm
  - Pt loading: 0.1 mg cm$^{-2}$
  - MEA area: 1.0 cm$^2$

- CB-MEA
- SCB-MEA

**MEA preparation**

- Nafion 212
- CCM
- MEA
- 65 ºC
- (GDL 25BC)

### Single cell analysis

- **H$_2$**
- **N$_2$**
- **H$_2$O**
- 0.1 L min$^{-1}$
- 0.2 L min$^{-1}$
- **Cell temp.:** 80 ºC
- **Humidity %RH:** 100%
- **Scan rate:** 50 mA cm$^{-2}$
Single Cell (in-situ ECSA)

CV

ECSA (m² g⁻¹Pt)

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- Comparable ECSA

Proton access

H desorption

Current / mA cm⁻²

Voltage / V

Current: -6 to 6 mA cm⁻²

Voltage: 0.2 to 0.8 V

80 °C, 100%RH
Electrode: 1.0 cm²
Pt: 0.1 mg cm⁻²

Fujigaya Laboratory
Kyushu Univ. Department of applied chemistry
EIS (0.45 mV)

Proton resistance $R_p$ (Ω cm$^{-2}$)

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<th>Material</th>
<th>$R_p$ (Ω cm$^{-2}$)</th>
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<tr>
<td>CB/Pt + Nafion</td>
<td>0.14</td>
</tr>
<tr>
<td>SCB/Pt</td>
<td>2.9</td>
</tr>
</tbody>
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- Lower acidity than Nafion


$\text{H}_2$ → $\text{N}_2$  
0.1 L min$^{-1}$  
0.2 L min$^{-1}$

\[ |Z| = \sqrt{\frac{R_p}{C_{dl}}} \times \omega^{-1/2} \]

- Lower amount of $\text{SO}_3^-$
- Higher gap between $\text{SO}_3^-$

Larger H$^+$ resistance
Further improve by increase of the H+ conductivity
Larger porosity for ionomer–free catalyst layer
Preparation of acid-grafted CB

- Higher activity
- Higher activity at high current density region
  although lower H+ conductivity than Nafion FC