Highly durable and active cathode catalysts for polymer electrolyte fuel cells using Nb-containing oxide supports

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Toward the future FCV

**China**: 1271 sales @2017 (commercial vehicles)

One Billion target sales until 2030

*Bus/Truck/Train ⇒ Vehicles*

**USA**: 2313 sales @2017

Vehicles ⇒ *Bus/Truck/Train*

**Germany**: Train @2017

FCV @2018

Vehicles/Train

**Japan**: 849 sales @2017

0.8 Billion target sales (until 2030)

Vehicles ⇒ *Bus/Truck/Train*

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FCV has some priority in the vehicle size and mileage compared to the EV, HV and PHV.

In future, FCV system will be developed toward the high durability, high efficiency and high power.
**Advantage and issues of current electrocatalysts**

### Typical electrocatalyst: Pt catalyst supported on carbon

#### Advantage
- High electrical conductivity
- High porosity
- High BET surface area
- Convenient surface morphology

#### Issue
- Intrinsic thermodynamic instability

\[
C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^- \quad E = 0.207 \text{ V SHE}
\]

- **Advantage**
  - High electrical conductivity
  - High porosity
  - High BET surface area
  - Convenient surface morphology

- **Issue**
  - Intrinsic thermodynamic instability

**FCV operation**

**Highly durable cathode catalysts are required!**

At start up / shut down operation, cathode catalysts are exposed to higher potential condition over 1.5V

- Carbon degradation
- Ostwald ripening

**Power (kW)**

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<th>Cell voltage (V)</th>
<th>Start up</th>
<th>Shut down</th>
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**Start up**

**Shut down**

**Introduction**

**Cell performance**

**Design concept**

**Future plan**
Alternative electrocatalyst: Pt/Nb-SnO$_2$ catalyst

NB-SnO$_2$ support

Pt/Nb-SnO$_2$ catalyst

Fused aggregate network microstructure


- ✔ High surface area
- ✔ Fused aggregate network structure
- ✔ Chemical stability of the support
- ✔ Pt orientation on highly crystallized supports

→ High Pt dispersion
→ High electronic conductivity and gas transport
→ High durability
→ Suppression of Pt migration
Single cell performance using Pt/Nb-SnO₂ cathode catalyst without carbon additives was equal to that using Pt/GCB. The Nb-SnO₂ support has a unique microstructure, the **fused aggregate network microstructure**, which reduces the contact resistance between each nanoparticle and increases the electrical conductivity.

Startup / shutdown durability of Pt/Nb-SnO$_2$ catalyst layers is superior to that of Pt/GCB catalyst layers and relies on the strong bonding between Pt and Nb-SnO$_2$. 

Start up / shut down durability of Pt/Nb-SnO$_2$

- Electrochemically active surface area, ECA / m$^2$ g$^{-1}$
  - Pt/Nb-SnO$_2$
  - Commercial Pt/GCB

- Number of potential step cycles, N / cycle
  - $1/2$ of initial ECA of Pt/Nb-SnO$_2$
  - $1/2$ of initial ECA of Pt/GCB

- ECSA after 60000 cycles: 70% of initial value
  - (Pt/GCB: less than 40% of initial value)

- Catalyst Particle Detachment
  - Aggregation

Load cycle durability of Pt/Nb-SnO$_2$ catalyst layers is also superior to that of Pt/GCB catalyst layers.
Cross-section image of Pt/Nb-SnO_2 and Pt/GCB catalyst layers after load cycle test (50,000 cycles)

Pt/Nb-SnO_2 (I/S = 0.12) 50,000 cycles

Pt/Nb-SnO_2 cathode

Pt/Nb-SnO_2 catalyst layer

Pt/Nb-SnO_2 catalyst layer

Pt/CB anode

Pt band was not detected in the Nafion membrane of the MEA using Pt/Nb-SnO_2 catalyst after load cycle testing.

Pt band

Pt/GCB (I/S = 0.70) 50,000 cycles

Pt/GCB cathode

Pt/GCB catalyst layer

Pt band

Pt/CB anode

Evaluation of solubility of Pt/SnO$_2$


Solubility in 1 N sulfuric acid (H$_2$SO$_4$), 80$^\circ$C, 8 days

Introduction  Cell performance  Design concept  Future plan
Evaluation of electrochemical activity of Pt/SnO₂

K.Kakinuma, M.Uchida, T.Kamino, H.Uchida, M.Watanabe
K.Kakinuma, Y.Chino, Y.Senoo, M.Uchida, T.Kamino,

Temperature: 25°C
Substrate: 5 mmφ (0.196 cm²)
Pt loading: 11.0 μg cm⁻²
Nafion coverage: 0.05 μm

CE: counter electrode
WE: working electrode
RHE: reversible hydrogen electrode
The relation ship between the kinetically controlled current density ($j_k$) and mass activity ($MA_k$) of Pt$_{100-x}$Co$_x$/Ta-SnO$_2$ shows a volcano curve. The maximum ORR activity reached ca. 3 times higher than that of commercial Pt/carbon.
Conclusion 1

The strategy to enhance the catalytic activity of Pt/SnO$_2$ catalyst

Design concept of Pt/SnO$_2$ catalyst layers - ionomer -


Mass activity of single cells using Pt/Nb-SnO$_2$ cathodes

- **Pt/Nb-SnO$_2$**
  - I/S = 0.24
  - Scale bar: 20 nm

- **Pt/GCB**
  - I/S = 0.45
  - Scale bar: 20 nm

- **Pt/Nb-SnO$_2$ with Pt/GCB**
  - Mass activity: $0.8 \text{ V} / \text{A g}_\text{Pt}^{-1}$
  - $\times 2$ times vs. Pt/GCB


- **Mitigation of specific sulfonic acid adsorption**
- **Decrease of gas diffusion resistance at Pt/ionomer interface**

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Porosity of Pt/SnO₂ catalyst layer

Primary pore volume (320 m² cm⁻³)

Primary pore volume (360 m² cm⁻³)

Pore (≥10 nm) distribution

Simulated by Rigaku

120°C operation by Pt/Nb-SnO$_2$ catalysts

Operation at 120°C High humidity & back pressure are required.

Single cell performances (power/durability) using Pt/Nb-SnO$_2$ catalyst layers is superior to those using current Pt supported on carbon (Pt/CB).
Conclusion 2
Toward the high power and durable PEFC

Present materials

80°C operation

New materials

100°C + α operation

Max. 120°C operation

Present concept

Pt alloy
Skin
Core-shell
Carbon
Nafion

New concept

Pt nanowire
Fused-aggregated network
Conducting ceramic nanoparticles
Aromatic membrane with reinforce

New materials

Pt/ceramic/ionomer interface control
high dimension fractal
Platinum anti-dissolution mechanism (PADM)
Atmospheric resistive switching mechanism (ARSM)

Present concept

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Acknowledgement

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Thank you very much for your kind attention!