Fuel Cell Electrode Materials
with Durability and Flexibility

Kazunari SASAKI
(sasaki@mech.kyushu-u.ac.jp)
(http://www.mech.kyushu-u.ac.jp/lab/ki06/index.html)

Kyushu University
Faculty of Engineering & Hydrogen Technology Research Center

Presented at ETH-Zürich
September 5, 2008
Kazu. Sasaki c/o Prof. Gauckler (1989-95)

(Cited from the HP of ETHZ-NMW)
Kyushu University “Hydrogen Campus”:
A Center-of-Excellence on Fuel Cells and Related Hydrogen Technologies

Kyushu University, Hydrogen Technology Research Center
Research topics:
Fuel cells, Electrolysis, Sensors, Combustion, Safety etc

AIST-Hydrogenius
(Research Center for Hydrogen Industrial Use and Storage)
Research topics:
Structural materials for high-pressure hydrogen energy systems, Tribology, Simulation techniques

Fukuoka Hydrogen Strategy Conference
(collaborating with ca. 330 private companies)

Kyushu Univ. ITO-campus

Kyushu University, INAMORI Frontier Research Center
Research topics:
Energy, Environment, Electronics, Nanotechnologies
Fukuoka “Hydrogen-Town” and “Hydrogen-Highway”

“Hydrogen-Town”

- Fukuoka-prefecture (“Kanton”)
- Maebaru-city
- Hydrogen-town near the Hydrogen Campus of Kyushu University

“Hydrogen-Highway”

- Fukuoka-prefecture (“Kanton”)
- To be extended to Tokyo!

150 stationary PEFCs will be installed!

Suitable for driving fuel cell vehicles
Hydrogen Society Proposed by Japanese Government for Fuel Cell Commercialization

- **Fuel cell vehicle (FCV)**
  - **Type of vehicles**
    - Public vehicles, Bus
    - Small cargos, Business use vehicles
    - General vehicles
  - **Expected numbers of FCV**
    - 50,000 in 2005
    - 5,000,000 in 2020
    - 15,000,000 in 2030
  - **Expected consumption of hydrogen**
    - 40,000 t in 2005
    - 580,000 t in 2020
    - 1,510,000 t in 2030
  - **Expected numbers of hydrogen stations**
    - 500 in 2005
    - 3,500 in 2020
    - 8,500 in 2030
  - **Expected hydrogen supply**
    - By-product hydrogen, Reformed fossil fuel, Electrolysis of water
    - Biomass fermentation, Heat disassembly of water

- **Stationary fuel cell**
  - **Spread scale**
    - 2 million kW in 2005
    - 10 million kW in 2020
    - 12.5 million kW in 2030
  - **Type of stationary fuel cell**
    - Polymer Electrolyte Fuel Cell (PEFC)
    - High temperature cogeneration system (SOFC)
    - High temperature combined cycle system
Hydrogen Energy based on Fuel Cell Technologies

- **Durability**
- High performance
- Low cost

⇒ Alternative electrode materials are desired!
Durable high-performance fuel cell electrodes

Alternative Electrode Materials for PEFC/DMFC

- Pt/Semiconducting oxide support
  - Pt/Carbon nanofiber support
  - Pt alloy/Carbon black support

Alternative Electrode Materials for SOFC

- Degradation mechanisms
  - Ni nanocomposite/Zirconia

Thermochemical stability is a key to ensure long-term durability of fuel cells!
Nanostructure: Pt/C(Carbon black, Vulcan)

FESEM-STEM observation

Colloidal impregnation

FESEM secondary-electron image

STEM image
PEFC electrocatalysts without catalyst support corrosion are desired!

Driving

\[ \text{Low cell voltage} \]

\[ \text{Idling} \]

\[ \text{High cell voltage} \]

Electrocatalysts tolerant against voltage cycling are desired!
Pourbaix diagram of C-H₂O systems at 80°C

strongly-acidic condition (PEFC electrolyte: Nafion)

Carbon (graphite) is thermochemically not stable especially under cathodic conditions!
Pourbaix diagram of Sn-H$_2$O systems at 80$^\circ$C

Fig. Pourbaix diagram of the Sn-H$_2$O system

SnO$_2$-supported *carbon-free* electrocatalysts !?
Preparation procedures of PEFC electrocatalysts

Preparation of catalyst supports

- SnCl₂ → SnCl₂.H₂O → Filtration -Washing -Drying → Calcination → SnO₂ (ammonia)
- SnO₂ sol → Evaporation-to dryness → Calcination → SnO₂ (sol)

Colloidal impregnation of electrocatalysts

- H₂PtCl₆・6H₂O → Pt-colloid preparation
- NaHSO₃ → pH5
- H₂O₂ → Filtration -Washing -Drying → Reduction → 20wt% Pt/SnO₂
Carbon-free Pt electrocatalysts successfully prepared!

Pt nanoparticles of ca. 2-3 nm in diameter are supported on SnO₂. Metal(Pt) / semiconductor(SnO₂) junctions!
II-V of MEA using SnO$_2$-supported Pt electrocatalysts

Fig. I-V characterization of single cells with 20% Pt/SnO$_2$ (0.6 mg-Pt cm$^{-2}$), and 20% Pt/C (0.6 mg-Pt cm$^{-2}$), cathodes. Anode catalyst: 46% Pt/C (0.4 mg-Pt cm$^{-2}$). The cell was operated with H$_2$/Air at a rate of 150 ml min$^{-1}$, Cell temperature at 80°C, atmospheric pressure, and humidification temperature at 80°C. Temperature in the figure indicates the calcination temperature of SnO$_2$.

Comparable performance of Pt/SnO$_2$ with conventional Pt/C has been obtained.
Durability of Pt/C and Pt/SnO$_2$

Electrochemical surface area (ECSA) of Pt remained almost constant, while Pt/C lost ECSA with cycles.
Durable high-performance fuel cell electrodes

< Alternative Electrode Materials for PEFC/DMFC >

- Pt/Semiconducting oxide support
- **Pt/Carbon nanofiber support**
- Pt alloy/Carbon black support

< Alternative Electrode Materials for SOFC >

- Degradation mechanisms
- Ni nanocomposite/Zirconia

*Thermochemical stability is a key to ensure long-term durability of fuel cells!*
Structure of carbon nanofibers as catalyst supports

- Tubular
- Herringbone
- Platelet
PEFCs with Pt/CNF electrode catalysts

Pt/CNF(VGCF) electrocatalyst layers

Fig.: FESEM micrograph of catalyst layer using CNF electrode supports
Pt/CNF surface modified by activation procedures

Pt/Platelet electrocatalyst after steam-activation

Pt particles are well impregnated “into” the surface.
Durable high-performance fuel cell electrodes

< Alternative Electrode Materials for PEFC/DMFC >

- Pt/Semiconducting oxide support
- Pt/Carbon nanofiber support
- Pt alloy/Carbon black support

< Alternative Electrode Materials for SOFC >

- Degradation mechanisms
- Ni nanocomposite/Zirconia

Thermochemical stability is a key to ensure long-term durability of fuel cells!
Pourbaix diagram of Ti-H$_2$O systems at 80$^\circ$C

Fig. pH-potential equilibrium diagram for system Ti-H$_2$O

Ti is a stable element under PEFC conditions.

Pt/Ti alloy electrocatalysts
**Pt-Ti electrocatalysts are successfully prepared!**

Fig. STEM micrograph of PtTi/C electrocatalysts, showing nanocrystalline Pt-Ti alloy particles, where surface Ti may be oxidized.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Particle size / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(200)</td>
<td>3.5</td>
</tr>
<tr>
<td>Pt(450)</td>
<td>3.9</td>
</tr>
<tr>
<td>Pt(700)</td>
<td>4.7</td>
</tr>
<tr>
<td>Pt3Ti1(900)</td>
<td>4.2</td>
</tr>
<tr>
<td>Pt1Ti1(900)</td>
<td>4.6</td>
</tr>
<tr>
<td>Pt1Ti3(900)</td>
<td>4.3</td>
</tr>
</tbody>
</table>

(Kawasoe et al., *J. Electrochem. Soc.*, 154, B969 (2007))

**Pt-Ti alloy or Pt-TiO$_2$ nanocomposite?**
Catalytic activity of Pt-Ti electrocatalysts

Figure. Kinetic current densities (\(j_k\)) at 0.85, 0.80 and 0.75 V vs. RHE in 0.1 M HClO\(_4\) solution saturated with O\(_2\). Sweep rate: 10 mV/s, temperature: 25 °C. The current density was normalized to ECSA measured by CV.

Comparable or even higher catalytic activity was obtained for Pt-Ti catalysts. But, Pt-Ti alloy or Pt-TiO\(_2\) nanocomposite?

(Kawasoe et al., J. Electrochem. Soc., 154, B969 (2007))
Durable high-performance fuel cell electrodes

< Alternative Electrode Materials for PEFC/DMFC >

- Pt/Semiconducting oxide support
- Pt/Carbon nanofiber support
- Pt alloy/Carbon black support

< Alternative Electrode Materials for SOFC >

- Degradation mechanisms
- Ni nanocomposite/Zirconia

Thermochemical stability is a key to ensure long-term durability of fuel cells!
Importance of “chemical degradation” of SOFCs

Chemical degradation
Major origins:
- Practical fuels
- Ambient air
- System components

Practical fuels
- H2
- CO
- Natural gas
- Alcohol
- Biogas
- LP gas
- Kerosene
- Gasoline
- Coal gas
- Various energy resources

Minor constituents in practical SOFC fuels
- Sulfur-related impurities (City gas, LP gas, Coal gas, Coke oven gas, Biogas, Petroleum-related fuels)
- Halogen-gas (Cl₂ gas in water, HCl in coal gas etc.)
- Ammonia (Biogas)
- Aromatic compounds (Petroleum-related fuels)

System components
- Heat insulation materials
- Structural components
- Electric insulator
- Materials for heat exchanger
- Fuel supply tubes
- Air supply tubes
- Bonding materials

Internal or external reforming

Ambient air
- SOx in contaminated air
- Salt-containing mist near seashore
- Humidity in ambient air

Anode poisoning

Cathode poisoning
C-H-O ternary diagram: Carbon deposition region

Equilibrium compositions can be specified by the C:H:O ratio.

Reactivity of Ni with minor impurities can be described in the C-H-O diagrams!
Poisoning by H$_2$S up to 1000 hours

Stable cell voltage up to 1000 hours is confirmed. Cell voltage drop is reversible.

(K. Haga et al., Solid State Ionics, in press)
Degradation mechanisms for each impurities

Cl₂: sublimation&precipitation type
Siloxane: precipitation (deposition) type
P, B: eutectic-type, grain-growth-type

Poisoning / degradation mechanisms I

Adsorption-type
- X: Impurity
- X^ad
- H_2
- Electrolyte
- O_2^-

Sublimation-type
- X: Impurity
- Ni-X
- Electrolyte
- O_2^-

Deposition-type
- X: Impurity
- H_2
- Electrolyte
- O_2^-

Sulfur (low concentration)

Chlorine

Siloxane

(K. Sasaki et al., Proc. 8th Europ. SOFC Forum, Schoenbein Medal 2008 awarded!)
Poisoning / degradation mechanisms - II

**Reaction-type**
- X: Impurity
- **Anode (Ni)**
- **NiX`Y** (Solid)
- **Electrolyte**
- **O²⁻**
- **Sulfur** (high conc., low temp.)

**Grain-growth-type**
- X: Impurity
- **Anode (Ni)**
- **Ni (+X`)**
- **Electrolyte**
- **O²⁻**
- **Boron**

**Eutectic-type**
- X: Impurity
- **Anode (Ni)**
- **NiX`Y** (Liquid)
- **Electrolyte**
- **O²⁻**
- **Phosphorus Sulfur** (high conc., high temp.)

(K. Sasaki et al., Proc. 8th Europ. SOFC Forum, Schoenbein Medal 2008 awarded!)
Durable high-performance fuel cell electrodes

< Alternative Electrode Materials for PEFC/DMFC >

- Pt/Semiconducting oxide support
- Pt/Carbon nanofiber support
- Pt alloy/Carbon black support

< Alternative Electrode Materials for SOFC >

- Degradation mechanisms
- Ni nanocomposite/Zirconia

Thermochemical stability is a key to ensure long-term durability of fuel cells!
Stable compounds in the SOFC anode atmosphere

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>BeO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- **Lanthanides**: CeO₂, Pr₂O₃, Nd₂O₃, Sm₂O₃, Eu₂O₃, Gd₂O₃, Tb₂O₃, Dy₂O₃, Ho₂O₃, Er₂O₃, Tm₂O₃, Yb₂O₃, Lu₂O₃
- **Actinides**: ThO₂, UO₂, NpO₂, PuO₂

**Legend**:
- Light blue: Stable as an oxide in H₂-3%H₂O at 1000°C
- Yellow: Stable as a metal in H₂-3%H₂O at 1000°C
Preparation of anode materials via spray-mist dryer

Temperature: 200°C

Air: 50L/min

Pump

Heater

Air: 0.69MPa

Starting solutions

Temp.: 80°C

Powders prepared
Spray-mist-dryer for anode materials synthesis

In oxidizing atmosphere

NiMeOx

In reducing atmosphere

NiMeOx

Pinning effect to keep larger electrode reaction area against poisoning and to prevent Ni agglomeration!

⇒ Larger electrode reaction area

(J. Yamamoto et al.)
Impurity tolerant anode, Ni-MnO/Zirconia, has been developed. Cell voltage drop due to sulfur poisoning decreased considerably.

(J. Yamamoto et al.)
Summary

Various electrode materials have been developed for fuel cells with high durability and flexibility, based on thermochemical stability and nanostructuring:

<PEFC/DMFC>
Carbon-free electrocatalysts have been developed using semiconducting oxide support.

Various nanostructured electrocatalysts have been developed with thermochemical and geometrical stability.

<SOFC>
Degradation mechanisms by foreign species have been specified.

Sulfur-tolerant Ni-Mn based nanocomposite anode has been developed.
Sasaki-Lab. in Kyushu University

Contributing to various fuel cell applications via materials synthesis, cell preparation, electrochemical / materials characterizations!

Fuel Cell Laboratory

Fuel Cell Evaluation Systems
(30 systems available)

- Fuel cell materials preparation facilities (Apparatus for various wet-chemical procedures)
- Fuel cell fabrication facilities (Automated spray-coating systems, Hot-press etc.)
- Fuel cell evaluation facilities (30 evaluation systems available for SOFC/PEFC/DMFC, 20 are full-automated.)
- Electrochemical experimental apparatus (4 impedance analyzers, 5 CV, RDE etc.)
- Microscopes (FESEM-STEM-EDX, AFM-STM) (Own STEM-EDX-EELS & FIB-MS will be installed in this year.)
- Materials analytical instruments (XRD, XPS, DTA-TG-MS etc.)
- Gas analytical instruments (GC-MS, automated GC etc.)
- Materials database