Technical Bottle-Necks for SOFC Operation in Conjunction with Biomass Gasification
バイオマスのガス化と連動したSOFC（固体酸化物形燃料電池）運用の技術課題

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Centralized system (large scale)
- Nuclear
  - CO₂ reduction • Energy Security
- Coal
  - Abundant resources
  - World-wide distribution
  - Well-established tech.
  - Low cost and easy to obtain
- Oil
  - Preferably, lesser dependence as an energy source for more concrete energy security
- Gas (LNG)
  - Applicable for any scale of energy conversion utility
  - (LNG power plant, Gas engines, Fuel cell system)
  - Deliverable and storable
  - Remarkable growth of importance as energy source
- Renewables
  - Little potential as energy source,
  - Attractive for environmental protection

Distributed system (small scale)

Time

11.3.2011
## Type of fuel cells

<table>
<thead>
<tr>
<th>Type</th>
<th>PEM</th>
<th>AFC</th>
<th>PAFC</th>
<th>DMFC</th>
<th>MCFC</th>
<th>SOFC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Name</strong></td>
<td>Proton Exchange Membrane</td>
<td>Alkaline</td>
<td>Phosphoric Acid</td>
<td>Direct Methanol</td>
<td>Molten Carbonate</td>
<td>Solid Oxide</td>
</tr>
<tr>
<td><strong>Applications</strong></td>
<td>Vehicles, Mobiles, CHP</td>
<td>Space application</td>
<td>Large scale CHP</td>
<td>Mobiles from micro to small scale</td>
<td>Medium and Large scale CHP up to MW</td>
<td>All sizes of CHP up to multi MW</td>
</tr>
<tr>
<td><strong>Operating Temp.[°C]</strong></td>
<td>50-100</td>
<td>50-200</td>
<td>ca. 220</td>
<td>ca. 70</td>
<td>ca. 650</td>
<td>500-1000</td>
</tr>
<tr>
<td><strong>Reaction Ion</strong></td>
<td>H⁺</td>
<td>OH⁻</td>
<td>H⁺</td>
<td>H⁺</td>
<td>CO₃²⁻</td>
<td>O²⁻</td>
</tr>
<tr>
<td><strong>Fuel</strong></td>
<td>Hydrogen</td>
<td>Hydrogen</td>
<td>Hydrogen</td>
<td>Methanol</td>
<td>H₂, CO₂, CH₄</td>
<td>H₂, CO, CH₄</td>
</tr>
<tr>
<td><strong>Cell Components</strong></td>
<td>Carbon-based</td>
<td>Carbon-based</td>
<td>Graphite-based</td>
<td>Carbon-based</td>
<td>Stainless-based</td>
<td>Ceramic</td>
</tr>
<tr>
<td><strong>Catalyst</strong></td>
<td>Platinum</td>
<td>Platinum</td>
<td>Platinum</td>
<td>Platinum/ruthanium</td>
<td>Nickel</td>
<td>Nickel, Perovskites</td>
</tr>
<tr>
<td><strong>Efficiency</strong></td>
<td>40-50%</td>
<td>60%</td>
<td>37-42%</td>
<td>30-40%</td>
<td>&gt; 50%</td>
<td>&gt; 50%</td>
</tr>
<tr>
<td><strong>Anode Reaction</strong></td>
<td>H₂ = 2H⁺ + 2e⁻</td>
<td>H₂ + 2(OH)⁻ = 2H₂O + 2e⁻</td>
<td>H₂ = 2H⁺ + 2e⁻</td>
<td>CH₃OH + H₂O = CO₂ + 6H⁺ + 6e⁻</td>
<td>H₂ + CO₃²⁻ = H₂O + CO₂ + 2e⁻</td>
<td>H₂ + O₂⁻ = H₂O + 2e⁻</td>
</tr>
<tr>
<td><strong>Cathode Reaction</strong></td>
<td>1/2O₂ + 2H⁺ + 2e⁻ = H₂O</td>
<td>1/2O₂ + H₂O + 2e⁻ = 2(OH)⁻</td>
<td>1/2O₂ + 2H⁺ + 2e⁻ = H₂O</td>
<td>3/2O₂ + 6H⁺ + 6e⁻ = 3H₂O</td>
<td>1/2O₂ + CO₂ + 2e⁻ = CO₃²⁻</td>
<td>1/2O₂ + 2e⁻ = O²⁻</td>
</tr>
</tbody>
</table>
Conversion with FC 91.8%

**Electricity**
Exergy: 3779.7 [kJ]
Energy: 3779.7 [kJ]

**Chem.**
Exergy: 3779.7 [kJ]
Energy: 4116.2 [kJ]

**Ther.**
Exergy: 0.0 [kJ]
Energy: 336.5 [kJ]

Conversion with ICE 31.8%

**Electricity**
Exergy: 1309.3 [kJ]
Energy: 1309.3 [kJ]

**Chem.**
Exergy: 1309.3 [kJ]
Energy: 4116.2 [kJ]

**Ther.**
Exergy: 0.0 [kJ]
Energy: 2806.6 [kJ]

Steam (1073K)
Exergy: 1309.3 [kJ]
Energy: 4116.2 [kJ]

Electricity
Exergy: 3779.7 [kJ]
Energy: 3779.7 [kJ]

Exhausted Heat
Exergy: 0.0 [kJ]
Energy: 2806.6 [kJ]

\[ E = (H_2 - H_1) - T_o (S_2 - S_1) \]
**Working principle in PEMFC and SOFC**

**Proton Exchange Membrane FC**
- Temp.: 50-100°C
- Fuel.: H₂ only (City Gas with reformer)
- Electrolyte: Solid polymer membrane
- Reaction ion: Proton (H⁺)
- Catalyst: Pt-based
- Application: Vehicles, Mobiles, CHP
- Operation: Quick start/stop

**Solid Oxide FC**
- Temp.: 500-1000°C
- Fuel.: H₂, Hydrocarbons (without reformer)
- Electrolyte: Ceramic oxide
- Reaction ion: Ionized oxygen (O²⁻)
- Catalyst: Ni, Perovskite
- Application: large scale CHP
- Operation: Steady operation
Fuel flexibility in SOFC: Internal and spontaneous reforming in high-T SOFC.

When $\Delta G$ is negative, a process will proceed spontaneously.

- CO$_2$ reforming of CH$_4$
  $\text{CH}_4 + \text{CO}_2 = 2\text{H}_2 + 2\text{CO}$
  
- Steam reforming of CH$_4$
  $\text{CH}_4 + 2\text{H}_2\text{O} = 4\text{H}_2 + \text{CO}_2$

**Solid Oxide FC**

- **Temp.:** 500-1000°C
- **Fuel:** H$_2$, Hydrocarbons (without reformer)
- **Electrolyte:** Ceramic oxide
- **Catalyst:** Ni, Perovskite
- **Application:** large scale CHP
- **Operation:** Steady operation
SOFC Operation in conjunction with biomass gasification.

Lessons learned from our previous works about degradation behaviors of SOFC due to the chemical interaction between trace gaseous impurities in coal syngas and Ni-YSZ anode.

Relevant papers on this topics:
Kuramoto et al., ECS Transactions, 25(2) 2149-2154 (2009)
Kuramoto et al., ECS Transactions, 41(12) 81-90 (2012)
Kuramoto et al., ECS Transactions, 57(1) 3077-3086 (2013)
Advancement in coal conversion tech.

**Pulverized Coal Fired Power Generation**

Coal

Boiler

Steam

Turbine

**Integrated Gasification Combined Power Generation (IGCC)**

Coal

Gasification

Gas turbine

Heat Recovery

Boiler

Steam Turbine

**Integrated Gasification Fuel Cell Combined Power Generation (IGFC)**

Coal

Gasification

Gas turbine

Heat Recovery

Boiler

Steam Turbine

Fuel Cell

CO/H₂ mixtures

gas cleaning

**Integrated Gasification Fuel Cell Combined Power Generation with CCS (A-IGFC)**

Coal

Gasification

CCS

Gas turbine

Heat Recovery

Boiler

Steam Turbine

Fuel Cell

H₂ enriched gas

SHIF: CO + H₂O → H₂ + CO₂

CO₂ to be fixed
IGCC in Japan: Past, present and future

  - Multi-purpose Coal Gasification Tech. Dev.
  - 8MW (150t/d) \( \cdot \) \( \mathrm{O}_2 \)-blown gasifier

- Jyoban-Power co. at Nakoso (TEPCO, Tohoku-EPCO)
  - #6 175MW (Oil-fired)
  - #7-9 1450MW (PCC)
  - #10 250MW (IGCC-1700t/d)

- Osaki CoolGen PJ (2012-)
  - 170MW (1180t/d)

- x8 Scale-up

- IGCC \( \downarrow \) IGCC+CCS

- IGCC \( \downarrow \) IGCC+CCS

- IGFC with CCS

- IGCC \( \downarrow \) IGCC+CCS
OCG PJ.: Large-scale IGCC, CCS, IGFC demonstration plant in Hiroshima

Demonstration PJ on IGCC+CCS/A-IGFC in Japan
Integrated Gasification Fuel Cell (IGFC) power plants (Anticipated)

Coal syngas with H₂, CO etc.

- Particulate
- H₂S, COS, NH₃, HCl, HF etc.
- Trace elements: Hg, As, P, Se, K, Na...

Cleaned syngas
H₂/CO/CO₂/N₂ =20/50/4/26

Post-CCS syngas
H₂/N₂ =75/25

Coal
Gasifier
Scrubber De-S process
Shift convertor Amine absorption
SOFK (to be installed)
Gas turbine
Steam turbine

Impurities removed

CO₂
Coal syngas with $\text{H}_2$, CO etc.

- $\text{H}_2\text{S}$, COS, $\text{NH}_3$
- HCl, HF etc.
- Particulate
- Trace elements
  - Hg, As, P, Se, K, Na...

Cleaned syngas

$\text{H}_2/\text{CO}/\text{CO}_2/\text{N}_2 = 20/50/4/26$

Integrated Gasification Fuel Cell (IGFC) power plants (Anticipated)

- Gasifier
- Scrubber De-S process
- Shift convertor Amine absorption
- SOFC (to be installed)
- Gas turbine
- Steam turbine

What are required for fuel for SOFC ???

Integrated Gasification Fuel Cell (IGFC) power plants (Anticipated)
Relevant reactions in SOFC power generation

Anodic reaction: \[ 2H_2 + 2O^{2-} \rightarrow 2H_2O + 4e^- \] & \[ CO + O^{2-} \rightarrow CO_2 + 2e^- \]

Cathodic reaction: \[ O_2 + 4e^- \rightarrow 2O^{2-} \]

Total reaction: \[ 2H_2 + O_2 \rightarrow 2H_2O \] & \[ 2CO+O_2 \rightarrow 2CO_2 \]
Experimental setup for SOFC power generation tests with direct feed of syngas from steam reforming of coal
Raw syngas-feed test: Remarkable performance loss of SOFC

Coal: Chinese Coal (Hwangling coal)
- Size: 250-750μm, coal feed rate: 0.1g min⁻¹
- Gasification temperature: 1173K
- $P_{H_2O}$ in fluidizing gas: 0.098MPa

Graph showing the concentration of gas products (vol-%) over time (min)

- $N_2$:
- $H_2$:
- $CO$:
- $CO_2$:
- $CH_4$:

Time [min]

Graph showing the current density [mA.cm⁻²] over time [min]

- Coal-derived syngas
- Ni-ScSZ/ScSZ/Pt
- Cell temperature: 1173K
- Imposed voltage: -0.8V(vs.Re(Air))
- Cleaning: filtration only

Comparison with filtration plus water washing and with filtration only.
SEM observation of spent SOFC anode: wet H$_2$ (left) and coal syngas (right)

spent cell in test fueled by wet H$_2$

spent cell in test fueled by coal syngas

5μm

10μm

5μm

anode (Ni-based)

electrolyte
Experimental apparatus for fuel cell test at AIST
～Simulated coal syngas injection test～

- Impurity Source (N₂ balanced)
- MFC
- H₂ MFC
- CO MFC
- CO₂ MFC
- N₂ MFC
- Temp.-controlled Humidifier
- Heater
- Test Cell
- Anode
- Exhaust
- Pt mesh
- Ni-YSZ (Anode)
- LSM (Cathode)
- Reference (Air)
- Dry air
- MFC

Simulated coal syngas (e.g. CO/H₂/CO₂/N₂ = 50/20/4/26)
Attempts to clarify the allowable range of H$_2$S under different fuel operations with post-CCS gas and coal syngas

- **Fuel gas**
  - Case 1: Simulated coal syngas
    \[
    \text{CO/H}_2\text{CO}_2/N_2/H_2O = 42/17/22/3/17 \text{ [mol%]} \]
  - Case 2: Hydrogen-enriched fuel gas (Post-CCS)
    \[
    \text{H}_2/N_2/H_2O = 80/3/17 \text{ [mol%]} \]

- **Trace H$_2$S as a possible impurity in practice**
  - 0.02, 0.5 or 2.0ppm-H$_2$S

- **Test cells used**
  - Nextcell (by FUEL CELL MATERIALS, USA)
Effects of H$_2$S concentration on performance loss of SOFC fueled by simulated coal syngas
Effect of fuel composition on the SOFC performance loss caused by 2ppm-$H_2S$

(a) wet-$H_2$ fueled

(b) SCS fueled
Observed change with time in the performance during the injection of trace $\text{H}_2\text{S}$ with different concentrations.

High $P_{\text{CO}}$ in fuel gas might cause chemical deactivation of Ni catalysis because;

$\rightarrow$ enhancement of S activity*

$\rightarrow$ partial solid solution of C to Ni**


Experimental setup for \(H_2S/HCl/TEOS\) exposure tests

For Power generation test of SOFC single cell

- **Cell temperature**: 1173K (900°C)
- **Configuration**: Fuel gas/Ni mesh/Ni-YSZ/YSZ/LSM-GDC/LSM/Pt mesh/dry air
- **Fuel gas**: \(H_2/N_2 = 75/25\) [vol-%] (simulated post CCS fuel gas)
- **Impurities doped**: \(H_2S\) 1, 3.3, 6.6ppm
  - \(HCl\) 1, 10ppm
  - \(Si(OC_2H_5)_4\) 0.14, 0.24ppm (TEOS)
**H₂S Exposure test: Effect of time of H₂S exposure on the cell performance**

- A step-wise voltage drop was observed soon after the 1ppm-H₂S introduction.
- No further performance loss can be seen after the initial voltage drop for 1000 hours.
- The voltage was recovered to initial level even after the 1000-hours H₂S exposure. (recoverable)
- SEM observation confirms that there is a little progression of sintering of component particles in anode.
HCl Exposure test: Effect of HCl conc. on the cell performance

- No performance loss can be seen during the injection of 1- and 10ppm-HCl.
TEOS exposure test: Effect of Si impurities on the cell performance

Change in $V_{RE-A}$ during TEOS exposure test

$\Delta Z'_{\text{Ohmic}} < \Delta Z'_{\text{Polarization}}$: TEOS injection causes the increase in resistance in electrochemical oxidation and/or transportation of reactant in the anode.
**BSE images of the surface of the anode exposed to TEOS vapor**

Possible Si polymerization took place over the anode surface through the following reactions*:

\[
\text{Si(OC}_2\text{H}_5\text{)}_2 + 4\text{H}_2\text{O} = \text{Si(OH)}_4 + 4\text{C}_2\text{H}_5\text{OH}
\]

\[
\text{Si(OH)}_4 = \text{SiO}_2 (s) + 2\text{H}_2\text{O}
\]

- Si deposits having a string-like appearance can be seen over the anode surface.

Accumulation of Si in the boundary between diffusion and reaction layers

- The preferential accumulation of Si took place between the coarse diffusion layer and fine reaction layer.
- This preferentially accumulated Si might act as an obstacle for the electrochemical oxidation process.
**C$_7$H$_8$ Exposure test: Effect of concentration of tar on the cell performance**
The boundary of carbon deposition region in the C–H–O phase diagram at 1 atm

Partial collapsing of Ni-YSZ anode caused by carbon deposition

wet H₂ injected
500 ppm-C₇H₈ at S/C = 3
50 ppm-C₇H₈ at S/C = 0
50 ppm-C₇H₈ at S/C = 30
What we found are:

1. Melting of Ni in SOFC anode occurred due to chemical interaction with trace impurities contained in coal-derived fuel gas.

2. The Ni-YSZ SOFC anode showed little performance loss during the 1000-hour 1ppm-H$_2$S exposure tests.

3. A step-wise voltage drop occurred soon after the H$_2$S injection and the extent of the voltage drop increased with H$_2$S concentration and current density.

4. Impact of 1-10ppm HCl contamination on performance of the Ni-YSZ anode was invisible during the present 1000-hour exposure tests.

5. Trace TEOS injection test resulted in the preferential accumulation of Si in the boundary region between the (coarse) diffusion layer and (dense) reaction layer, where the chemical oxidation of fuel proceeded.

6. The ppm levels of tar (toluene) caused partial C deposition, resulting in severe collapsing of Ni-YSZ cermet.

7. For the SOFC with biomass gasification, chemical impacts of AAEM (e.g. Na, K) on the SOFC performance are needed to be clarified.