Development of the thermo-chemical and electrolytic hybrid hydrogen production process for sodium cooled FBR

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Toshio NAKAGIRI, Takeshi KASE, Shoichi KATO and Kazumi AOTO

Japan Atomic Energy Agency
Objective
- Long time hydrogen production experiment
- Technical problems to develop higher performance (1NL/h-H₂) hydrogen production system

Conclusions
To confirm the durability of the hydrogen production experimental apparatus with the hybrid process

To extract technical problems to develop higher performance (1NL/h-H₂) hydrogen production system
**Principle of HHLT**

**HHLT** (thermo-chemical and electrolytic Hybrid Hydrogen process in Lower Temperature range)

\[ 2\text{H}_2\text{O} + \text{SO}_2 \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2 \quad <100^\circ \text{C} \text{ (electrolysis:0.17v)} \quad [1] \]

\[ \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O} + \text{SO}_3 \quad 400^\circ \text{C} \text{ (thermal decomposition)} \quad [2] \]

\[ \text{SO}_3 \rightarrow \text{SO}_2 + \frac{1}{2}\text{O}_2 \quad 500-550^\circ \text{C} \text{ (electrolysis:0.13v)} \quad [3] \]

**Westinghouse process**

\[ \text{SO}_3 \rightarrow \text{SO}_2 + \frac{1}{2}\text{O}_2 \quad >800^\circ \text{C} \text{ (thermal decomposition)} \quad [3'] \]

- The hybrid process consists of H$_2$SO$_4$ synthesis and decomposition reactions. (Based on “Westinghouse process”)
- Maximum operation temperature is about 500-550°C.
- Hydrogen and oxygen are produced from water.
Electrolytic SO$_3$ splitting with oxygen conductive solid electrolyte

- **Splitting voltage of SO$_3$ is 0.13V at 500$^\circ$C.**

Thermal decomposition fraction of SO$_3$

Splitting voltages of H$_2$O and SO$_3$
Electrolytic SO₃ splitting was confirmed experimentally.

Test apparatus of SO₃ splitting experiment

Relationship between cell voltage and cell current
Stable hydrogen and oxygen generation (max. 5 hours) by HHLT was already confirmed by JNC.

Measured cell current in previous experiments (for principle confirmation)
Experimental apparatus for hydrogen production
Improvement of SO$_3$ electrolysis cell

- Pt electrode was manufactured by plating on both side of YSZ
- Diameter of the outlet piping of SO$_3$ electrolysis cell was increased. (1/2 inch -> 3/4 inch)

-> Cell current at same cell voltage increased to 10 times.
## Experimental conditions

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Temperature (deg-C)</th>
<th>Cell voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{SO}_4$ vaporizer</td>
<td>400</td>
<td>-</td>
</tr>
<tr>
<td>$\text{SO}_3$ electrolysis cell</td>
<td>550</td>
<td>0.13</td>
</tr>
<tr>
<td>$\text{SO}_2$ absorber</td>
<td>Approx. 10</td>
<td>-</td>
</tr>
<tr>
<td>$\text{H}_2\text{SO}_3$ solution electrolysis cell</td>
<td>Room Temp.</td>
<td>0.85～0.9</td>
</tr>
</tbody>
</table>
Experimental result

- Total duration of present experiment was about 56 hours.
  (terminated by blockage of inlet pipe of SO₂ absorber)
- H₂SO₃ solution was added in the anolyte at about 20 and 40 hours after the experiment started.
- The anode surface was polished by emery paper at about 20 hours after, and stirring by N₂ gas bubbling around the anode was started at about 40 hours after.

![Generation rate of H₂ and O₂](image-url)
Post experiment observation

Cut image of outlet piping of SO₃ electrolysis cell

inside surface of YSZ tube

from H₂SO₄ vaporizer
to SO₂ absorber
	no plated gold remained

inner surface of outlet piping of SO₃ electrolysis cell

thickness of plated gold decreased.

no plated gold remained
Post experiment analysis

Blockage of the inlet pipe of SO$_2$ absorber

Composition of white powder in the SO$_2$ absorber by SEM-EDS analysis

<table>
<thead>
<tr>
<th>element</th>
<th>weight fraction (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>56.07</td>
</tr>
<tr>
<td>Cr</td>
<td>6.35</td>
</tr>
<tr>
<td>Fe</td>
<td>33.97</td>
</tr>
<tr>
<td>Cu</td>
<td>3.61</td>
</tr>
</tbody>
</table>
The performance of Pt plated YSZ electrolyte for \( \text{SO}_3 \) electrolysis did not degrade during about 60 hour operation in 550\text{deg}-\text{C} \) gaseous sulfuric acid.Outlet piping of the \( \text{SO}_3 \) electrolysis cell was corroded by condensed sulfuric acid. Sulfuric acid resistant material (high Silicon cast iron,...) should be used in the new experimental apparatus.
The hydrogen production rate in \( \text{H}_2\text{SO}_3 \) solution electrolysis cell for decreased in several hours, and the amount of \( \text{H}_2\text{SO}_3 \) solution supplied to the anode surface is considered to be not enough.
The performance of Pt plated YSZ electrolyte was about one order higher than YSZ with Pt paste electrode. The thickness of the Pt plated electrode is much thinner than Pt paste electrode, and SO₃ or O₂ molecule diffusion on the Pt plated electrode surface to the reaction area called three phase (gas/electrode/electrolyte) boundary is assumed to be much faster than on Pt paste electrode.

Total area of three phase boundary must be increased for higher performance.
- thinner Pt plating electrode
- smaller size Pt particle (catalyst)
- mixed conductive electrolyte (ceria etc.)

SEM images of Pt paste and Pt plated electrodes (× 1000)
Technical problems (2)

- development of higher performance of H₂SO₃ solution electrolysis cell -

- Improvement to increase the amount of H₂SO₃ solution or SO₂ gas supplied to the anode surface.

- Use of flow type electrolysis cell with gas diffusion type electrode is promising.

Image of flow type electrolysis cell

Relationship between mixture gas (5%SO₂+N₂) flow rate and cell current (preliminary experiment)
Conclusions

The experiment for about 60 hours was performed to investigate the durability of the experimental apparatus by the hybrid process.

Technical problems to develop higher performance hydrogen production system were extracted.

1NL/h-H$_2$ production experiment are going to be performed in fiscal year 2005.