Development of a New Thermo-chemical and Electrolytic Hybrid Hydrogen Production Process for Sodium Cooled FBR

Status and Future Plan

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Outline

- Background
- Principle of the new hybrid hydrogen production process
- Current status of R&D
- Future plan
In “Feasibility study on Commercialized Fast Breeder Reactor (FBR) Cycle Systems” of JAEA, a concept of a multi-purpose (Electricity supply, Hydrogen Production, etc.) small sized reactor has been studied.

Requirements for hydrogen production system of FBR
- Maximum temperature : 500-550 deg-C
- Thermal efficiency : higher than water electrolysis
- Hydrogen production from water : No use of fossil fuel, no CO₂ emission.
<table>
<thead>
<tr>
<th>Resource</th>
<th>Method</th>
<th>Proposed Tech.</th>
<th>Present Status</th>
<th>Features &amp; Issues</th>
</tr>
</thead>
</table>
| Water         | Electrolysis            | • Alkaline Water Electrolysis  
• SPEWE’  
• HTE’                                         | Commercialized R&D Stage   | • Mature Tech.  
• Low thermal efficiency (~36% for FBR)                                         |
|               | Thermochemical Cycle    | • I-S method  
• UT-3 method  
• W.H. method, etc                                                             | R&D Stage                | • Higher thermal efficiency (~50%)  
• High temperature heat source  
• Material corrosion                                                        |
| Fossil Fuels  | Steam Reforming         | • Steam Reforming of Natural Gas  
• SER’ Process  
• Membrane Reformer                                                           | Commercialized Demonstration Stage | • Excellent thermal efficiency (70%~)  
• High plant construction const; SER & MR  
• CO₂ emission                                                                 |

SPEWE: Solid Polymer Electrolyte Water Electrolysis, HTE: High Temperature Electrolysis, SER: Sorption Enhanced Reaction

**Development of a Lower Temperature Thermochemical Cycle**
**Principle of HHLT**

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

- \(2\text{H}_2\text{O} + \text{SO}_2 \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2\) \(<100\) deg-C (electrolysis: 0.17v) [1]
- \(\text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O} + \text{SO}_3\) 400 deg-C (thermal decomposition) [2]
- \(\text{SO}_3 \rightarrow \text{SO}_2 + \frac{1}{2}\text{O}_2\) 500-550 deg-C (electrolysis: 0.13v) [3]

**Westinghouse process**

- \(\text{SO}_3 \rightarrow \text{SO}_2 + \frac{1}{2}\text{O}_2\) \(>800\) deg-C (thermal decomposition) [3]

- The hybrid process consists of \(\text{H}_2\text{SO}_4\) synthesis and decomposition reactions. (Based on “Westinghouse process”)
- Maximum operation temperature is about 500-550 deg-C.
- Hydrogen and oxygen are produced from water.
- **Splitting voltage of SO$_3$** is 0.13V at 500°C.

![Graphs showing splitting voltage and thermal decomposition fraction of SO$_3$.](image)

- Thermal decomposition fraction of SO$_3$
- Splitting voltages of H$_2$O and SO$_3$
Steps of H₂ Energy Introduction & of Hybrid Tech. Development

<table>
<thead>
<tr>
<th>Year</th>
<th>Japan</th>
<th>US</th>
<th>EU</th>
</tr>
</thead>
<tbody>
<tr>
<td>2005</td>
<td>Verification Stage</td>
<td>Introduction Stage</td>
<td>Tech. Development &amp; Verification Stage</td>
</tr>
<tr>
<td>2010</td>
<td>Introduction Stage</td>
<td>Wide-Use Stage</td>
<td>Tech. Development &amp; Verification Stage</td>
</tr>
<tr>
<td>2020</td>
<td>Wide-Use Stage</td>
<td>Hydrogen Energy Society</td>
<td>Wide-Use Stage</td>
</tr>
<tr>
<td>2030</td>
<td></td>
<td></td>
<td>Hydrogen Energy Society</td>
</tr>
</tbody>
</table>

**Japan**
- FCV: 50k cars (Bus)
- H₂ Demand: 430M Nm³/y

**US**
- Tech. Development & Verification Stage

**EU**
- Tech. Development & Verification Stage

**TCE-Hybrid Tech.**
- JNC R&D: 60ml/h, 1 L/h, 100 L/h, 100~1,000 m³/h
- JAEA R&D: FBR Demonstration Plant (Japan), Commercialized FBR

**H₂ Demand**
- JNC R&D: 430M Nm³/y
- JAEA R&D: 6.5B Nm³/y
- JAEA R&D: 17B Nm³/y

※ Ref. FUKUDA, HTTR Seminar (2004)
Conceptual FBR-Hydrogen Plant Design

Hydrogen generation rate of 47000Nm³/h
The experimental apparatus for 1NL/h hydrogen production has been developed and an experiment was performed.
- To evaluate hydrogen production efficiency
- To extract technical problems to develop 100NL/h-h₂ production apparatus.

Development of higher performance electrolysis cells and structural materials for H₂SO₄ corrosion have been performed.
Development of the experimental apparatus for 1NL/h hydrogen production

Internal structure of SO₂ electrolysis cell

SO₂ electrolysis cell (for oxygen generation)

Sulfuric acid heater

SO₂ solution electrolysis cell (for hydrogen generation)

SO₂ absorber

Photo of the experimental apparatus

Experimental apparatus for 1NL/h H₂ production
# Experimental conditions of the hydrogen production experiment

## Experimental conditions

<table>
<thead>
<tr>
<th>Item</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$SO$_4$ vaporizer Temperature</td>
<td>600-700 deg-C</td>
</tr>
<tr>
<td>SO$_3$ electrolysis cell Temperature</td>
<td>600 deg-C -&gt;550 deg-C</td>
</tr>
<tr>
<td></td>
<td>0.85V</td>
</tr>
<tr>
<td>SO$_2$ solution electrolysis cell</td>
<td>8 deg-C</td>
</tr>
<tr>
<td></td>
<td>1.2V-1.1V</td>
</tr>
<tr>
<td>H$_2$SO$_4$ concentration</td>
<td>50wt%</td>
</tr>
<tr>
<td>H$_2$SO$_4$ flow rate</td>
<td>2ml/min</td>
</tr>
</tbody>
</table>

## Target value

<table>
<thead>
<tr>
<th>Item</th>
<th>condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$ production rate</td>
<td>0.5NL/h</td>
</tr>
<tr>
<td>(current value: 1.2A)</td>
<td></td>
</tr>
<tr>
<td>O$_2$ production rate</td>
<td>0.25NL/h</td>
</tr>
<tr>
<td>(current value: 1.2A)</td>
<td></td>
</tr>
<tr>
<td>Experimental duration</td>
<td>1-several hours</td>
</tr>
</tbody>
</table>
Experimental result

- \( \text{H}_2 \) production rate: 0.42NL/h, \( \text{O}_2 \) production rate: 0.21NL/h

Measured cell current in the hydrogen production experiment
Evaluated efficiency

\[ \eta = \frac{H_{\text{HHV}} \cdot M_x}{P + Q} \quad (1) \]

- \( M_x \): amount of generated \( X \) gas (mol, \( X = \)hydrogen, oxygen)
  - \( M_x = \frac{\sum I_x \cdot f}{96485 \cdot \text{ex}} \)
  - \( I_x \): cell current of \( X \) gas (A)
  - \( f \): data sampling period (20 sec)
  - \( \text{ex} \): number of electron (2 for hydrogen molecule, 4 for oxygen molecule)
- \( H_{\text{HHV}} \): higher heat value of hydrogen (285.8 kJ/mol)
- \( P \): electricity supplied to both electrolysis cell (kJ)
  - measured by potentiostats (\( \text{SO}_3 \) electrolysis & \( \text{SO}_2 \) solution electrolysis)
- \( Q \): heat from heat source (kJ)
  - No heat loss was considered
  - equilibrium composition of gas phase was calculated by MALT-II & GEM

Evaluated thermal efficiency was 2.1%.
Influence of efficiency of SO$_3$ electrolysis

Relationship between H$_2$ production efficiency and SO$_3$ electrolysis efficiency
A hydrogen production experiment was performed using the 1NL/h-$h_2$ level apparatus.
- hydrogen production efficiency will be evaluated as about 2%. Efficiency of the electrolysis cells must be increased to obtain higher hydrogen production efficiency.
- durability of the apparatus must be improved.
SO₃ electrolysis cell using small YSZ tube (6mm in diameter, 100mm in length and 0.5mm in thickness) was manufactured.
PEFC (Polymer Electrolyte Fuel Cell) was modified for hydrogen production supplying SO₂ gas and H₂O. Investigation on SO₂ cross-over behavior through some cation exchange membranes has been performed.
Future Plan

(1) SO₃ electrolysis cell (O₂ production)

(2) SO₂ solution electrolysis cell (H₂ production)

(3) H₂ production experiment

(4) H₂ storage & transportation

Prospect of practical use

Prototype Plant
(100-1000Nm³/h)
The experimental apparatus for 1NL/h-h$_2$ production by the hybrid sulfur process was developed and technical problems were extracted from the hydrogen production experiment performed in 2006.

Development of electrolysis cells will be continued for a few years, then development of 100NL/h-h$_2$ apparatus will be started.