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

IAEA International Conference on Non-Electric Applications of Nuclear Power, April 2007 O-Arai, Japan

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Background

- Principle of the new hybrid hydrogen production process
- Current status of R&D
- Future plan



Background

- 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.





Applicability of Hydrogen Production Technologies for FBR Plant

Resource	Method	Proposed Tech.	Present Status	Features & Issues
Water	Electrolysis	 Alkaline Water Electrolysis SPEWE* HTE* 	Commercialized R&D Stage	 Mature Tech. Low thermal efficiency (~36% for FBR)
	Thermo- chemical 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 <u>Hybrid Hydrogen process in Lower</u> <u>Temperature range</u>)

$2H_2O + SO_2$	->	$H_2SO_4 + H_2$
$H_2 \overline{SO}_4$	->	$H_2O + SO_3$
SO ₃	->	SO ₂ + 1/2O ₂

<100 deg-C (electrolysis:0.17v) [1] 400 deg-C (thermal decomposition) [2]

500-550 deg-C (electrolysis:0.13v) [3]

Westinghouse process

 SO_3 -> $SO_2 + 1/2O_2$ >800 deg-C (thermal decomposition) [3]'

- The hybrid process consists of H₂SO₄ synthesis and decomposition reactions. (Based on "Westinghouse process")
- -Maximum operation temperature is about 500-550 deg-C.
- Hydrogen and oxygen are produced from water.



Electrolytic SO₃ splitting with oxygen conductive solid electrolyte

• Splitting voltage of SO_3 is 0.13V at 500°C.



Steps of H₂ Energy Introduction & of Hybrid Tech. Development



Conceptual FBR-Hydrogen Plant Design





Current status of R&D

- 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 $100NL/h-h_2$ 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



Photo of the experimental apparatus

Experimental apparatus for 1NL/h H₂ production



Experimental conditions of the hydrogen production experiment

Experimental conditions

Target value

ltem	Condition	item	condition
H₂SO₄ vaporizer Temperature	600-700 deg-C	H ₂ production rate	0.5NL/h (current value:1.2A)
SO ₃ electrolysis cell Temperature cell voltage SO ₂ solution electrolysis cell Temperature Cell voltage	600 deg-C ->550 deg-C 0.85V 8 deg-C 1.2V-1.1V	O ₂ production rate Experimental duration	0.25NL/h (current value:1.2A) 1-several hours
H₂SO₄ concentration H₂SO₄ flow rate	50wt% 2ml/min		

Experimental result



-H₂ production rate: 0.42NL/h, O₂ production rate: 0.21NL/h

JAEA

Evaluated efficiency

$$\eta = \frac{H_{HHV} * Mx}{P + Q} \qquad (1)$$

- Mx : amount of generated X gas (mol, X=hydrogen, oxygen)
 - $=\frac{\Sigma Ix^*f}{96485^*ex}$

 - Ix : cell current of X gas (A)
 - f : data sampling period (20sec)
 - ex : number of electron (2 for hydrogen molecule, 4 for oxygen molecule)

H_{HHV}: higher heat value of hydrogen (285.8kJ/mol)

- : electricity supplied to both electrolysis cell (kJ) -measured by potentiostats (SO₃ electrolysis & SO₂ 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 SO₃ electrolysis



Relationship between H₂ production efficiency and SO₃ electrolysis efficiency

Summary of the hydrogen production experiment

- A hydrogen production experiment was performed using the 1NL/h-h₂ 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.

Development of SO₃ electrolysis cell

 SO₃ electrolysis cell using small YSZ tube (6mm in diameter, 100mm in length and 0.5mm in thickness) was manufactured.



SO₃ electrolysis cell using small YSZ tube

Development of Hydrogen production cell (SO₂ electrolysis)

- 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.



Liquid-gas separator

Hydrogen production cell (PEFC base: Electrode area 25cm²)



cation membranes





Conclusion

- The experimental apparatus for 1NL/h-h₂ 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-h₂ apparatus will be started.

