A new thermochemical and electrolytic hybrid hydrogen production process for FBR

Toshio Nakagiri1*, Taiji Hoshiya1 and Kazumi Aoto1

1Japan Nuclear Cycle Development Institute, O-Arai, Higashi-Ibaraki, Ibaraki, 311-1393, Japan

A new thermochemical hybrid hydrogen production process is under investigation to realize the hydrogen production from water by using the heat generation of coolant of sodium in Fast Breeding Reactor (FBR). Newly proposed cycle is based on sulfuric acid (H2SO4) synthesis and the decomposition processes developed earlier, and SO3 decomposition process at about 500 °C is facilitated by electrolysis with ionic oxygen conductive solid electrolyte which is extensively utilized for high-temperature electrolysis of water.

Measured decomposition voltage of sulfur trioxide (SO3) with 8mol yttria stabilized zirconia (8molYSZ) solid electrolyte and platinum electrode were lower than 0.5V at 500 °C-600 °C, and oxygen permeation rate through YSZ into N2 purge gas agreed well with the calculated permeation rate from measured cell current. Preliminary measured oxygen permeation rate through La0.9Sr0.1Ga0.8Mg0.2O3 (LSGM) in air supplied experiments were higher than the rate through 8molYSZ. These results show the possibility of development of higher performance electrolytic cell using other solid electrolytes than YSZ. Thermal efficiency of the proposed cycle based on chemical reactions was 47.3% with no heat recovery.

KEYWORDS: hydrogen, hydrogen production, thermochemical hybrid process, middle temperature range, solid electrolyte, electrolysis, sulfuric acid

I. Introduction

More than 2,000-3,000 thermochemical hydrogen production processes have been proposed to produce hydrogen from water with no exhaust of CO2 and with thermal efficiency higher than 40%, and application study for High Temperature Gas cooled Reactor (HTGR) have been investigated for some decade 1). Nevertheless, application study for Fast Breeder Reactor (FBR) have not been performed because high temperature over 800 °C was required for thermochemical processes.

A thermochemical and electrolytic hybrid hydrogen production process (thermochemical and electrolytic Hybrid Hydrogen process in Lower Temperature range : HHLT) for sodium cooled FBR is proposed by Japan Nuclear Cycle Development Institute (JNC) 2). HHLT is based on sulfuric acid (H2SO4) synthesis and the decomposition processes (named “Westinghouse process”) developed earlier 1,3), and SO3 decomposition process is facilitated by electrolysis with ionic oxygen conductive solid electrolyte which is extensively utilized for high-temperature electrolysis of water.

In the present study, electrolytic SO3 decomposition experiments using yttria stabilized zirconia (YSZ), preliminary experiments on ionic oxygen conductivity measurement of higher performance solid electrolytes and evaluation of thermal efficiency of HHLT based on chemical reactions were performed. Furthermore, advantages and technical problems of HHLT were discussed.

II. Principle and characteristics of HHLT

1. Principle of HHLT

Westinghouse process requires high temperature over 800 °C only for SO3 decomposition reaction, and other reactions can be performed below 500 °C. If SO3 decomposition can be performed in lower temperature than 800 °C, hydrogen production using lower temperature heat source such as FBR can be realized, and corrosion problems depending on high temperature and corrosive atmosphere can be reduced.

SO3 decomposed thermally only 7.8% at 500 °C as shown in Fig.1, and also only about 20% in the case membrane reactor technique is used at 500 °C. Therefore, some other energy are required to obtain higher decomposition fraction of SO3.

Fig.1 Thermal decomposition fraction of SO3
Electrolysis by ionic oxygen conductive solid electrolyte is applied to increase decomposition fraction of SO₃ in HHLT. HHLT is composed from the reactions shown below.

\[
\begin{align*}
2 \text{H}_2\text{O} + \text{SO}_2 & \xrightarrow{\text{electricity}} \text{H}_2\text{SO}_4 + \text{H}_2 \quad (1) \\
\text{H}_2\text{SO}_4 & \xrightarrow{\text{\text{80 }^\circ\text{C}}} \text{H}_2\text{O} + \text{SO}_3 \quad (2) \\
\text{SO}_3 & \xrightarrow{\text{electricity}} \frac{1}{2} \text{O}_2 + \frac{1}{2} \text{SO}_2 \quad (3)
\end{align*}
\]

Characteristics of HHLT are shown below.

1. Low electricity required
   Required voltage for reaction (3) are calculated by equation (3) \[ E_G = -\frac{\Delta G}{nF} \] \[(4)\]

Calculated splitting voltages of H₂O and SO₃ are shown in Fig.2, and splitting voltage at 500 °C is lower than 0.2V.

Theoretical voltage of sulfuric synthesis reaction (equation (1)) is 0.17V-0.28V, therefore, total theoretical voltage in HHLT is expected to be lower than 0.5V which is about half of the theoretical voltage of direct water splitting, about 1V.

2. Technical problems to realize HHLT

   (1) Proof of SO₃ electrolysis using solid electrolyte
   Electrical SO₃ decomposition reaction (reaction(3)) is the most important part of HHLT, but no experimental data about the reaction has been reported. JNC has performed experiments to confirm SO₃ decomposition using YSZ in the temperature range of 450 to 600 °C, and to measure ionic oxygen conductivity in SO₃ atmosphere.

   (2) High performance solid electrolyte
   Two kinds of YSZs (3molYSZ, 8molYSZ) have been utilized in high temperature electrolysis, but ionic oxygen conductivity at about 500 °C is not large enough to obtain realistic hydrogen production efficiency in HHLT. To obtain higher hydrogen production efficiency, higher ionic oxygen conductive solid electrolytes are necessary. Some solid electrolyte shown in Fig.3 such as Ce-Sm-O, La-Ga-O, Bi-Y-O have almost equivalent ionic oxygen conductivities in the temperature range between 500 °C and 600 °C to those in YSZ in 800 °C-1,000 °C. Preliminary experiments to measure ionic oxygen conductivities in SO₃ atmosphere were performed using LSGM (La₀.₈Sr₀.₂Ga₀.₈Mg₀.₂O₃) and ScSZ (10molSc/CeSZ).

3. Investigation of structural material
   Corrosion problem of structural materials in H₂SO₄ boiling environment is considered to be one of the severe
issues in IS process①. In HHLT process, this reaction (reaction(2)) can be performed in electrolysis cell which is composed of corrosion-resistant solid electrolyte ceramics, therefore, corrosion problem can be effectively reduced.

But, H₂SO₄ will be high corrosive aqueous solution to obtain higher efficiency in H₂SO₄ synthesis reaction (reaction(1)), so ferrous materials for piping or reactor for the concentration of H₂SO₄ (reaction (2)) must be investigated.

(4) Development of electrolytic cell for H₂SO₄ synthesis
Three-component electrolytic cell for H₂SO₄ synthesis have already developed by Struck et al. of KFA. Solid polymer electrolyte such as Nafion125 (DuPont), NEOSEPTA (Tokuyama Soda) were used in this cell. In recent years, higher performance solid polymer electrolytes have been developed, so higher performance electrolytic cell can be developed using these solid polymer electrolytes.

For H₂SO₄ synthesis cell, continuous SO₂ and H₂O supply, and continuous H₂SO₄ extraction with high efficiency, are required for continuous hydrogen production.

(5) Substantiation of HHLT process
In addition to the investigations shown above, test apparatus to substantiate whole process of HHLT must be developed. Actual efficiency of HHLT process, durability of structural materials under sulfuric acid, and performance of electrolysis cells, can be evaluated by using this substantiation apparatus.

III. Experiments and thermal efficiency calculation

1. Electrolytic SO₃ decomposition experiment
(1) Test apparatus and experimental conditions
Electrolytic SO₃ decomposition experiments in the temperature range between 450 and 600 °C were performed by test apparatus shown in Fig.4. Tubular 8molYSZ with a dimension of 2mm in thickness was used as electrolyte, and Pt electrode was made on both (inner and outer) surfaces of the tube. N₂ purge gas was supplied to SO₃ evaporator at flow rate of 200ml/min, and SO₃ vapor was generated from the mixture of dry sulfuric acid and solid SO₃. Concentration of SO₃ in N₂ gas was about 3%. SO₃ was supplied for about 10 minutes in each experiment. Electrolysis voltage was controlled from 0.0V to 1.0V by potentiostat, and cell current was measured simultaneously. O₂ decomposed from SO₃ was permeated through YSZ from inside to outside, and was carried to oxygen meter by N₂ purge gas (flow rate was 200ml/min).

(2) Measured cell current and oxygen concentration in N₂ purge gas
Obtained relationship between cell voltage and cell current is shown in Fig.5-a, and relationship between cell voltage and oxygen concentration in N₂ purge gas is shown in Fig.5-b. As shown in these figures, cell current and oxygen concentration in N₂ purge gas increased as cell voltage and cell temperature increased.

In the case supplied electricity is used only for ionic oxygen conduction, the relationship between cell current and oxygen permeation rate through YSZ into N₂ purge gas is calculated as follows ⑩.

\[
v_{\text{cal}} = 0.115 (i/n)
\]

The \(v_{\text{measured}}/v_{\text{cal}}\) Value calculated from measured oxygen

![Fig.4 Test apparatus of SO₃ splitting experiment](image)

**Fig.5-a** Relationship between cell voltage and cell current

![Fig.5-b Relationship between cell voltage and O₂ concentration in N₂ purge gas](image)
concentration in purge gas and measured cell current are shown in Fig.6 (surface area of solid electrolyte is 158.8 cm$^2$). The ratio is about 1.0 at temperatures higher than 550 °C, and at the temperature of even 500 °C when the cell voltage was higher than 0.5V, 100% of supplied electricity is considered to be used for ionic oxygen conduction in these cases. The ratio is lower at 500 °C when the cell voltage was lower than 0.25V and at 450 °C, and it is considered that other mechanisms which is not oxygen conduction consumed electricity.

(3) Oxygen ion conductivity of YSZ

Oxygen ion conductivity was calculated from oxygen concentration in N$_2$ purge gas for the experiments at temperatures higher than 500 °C by equation (6).

$$\sigma_i = \frac{i}{E \cdot \left( \frac{v_{measured}}{v_{cal}} \right)}$$

Calculated $\sigma_i$ are shown in Fig.7 with the $\sigma_i$ value for 8mol YSZ in Ref.9. Oxygen ion conductivity of YSZ in 3 mol% SO$_3$ atmosphere almost agree with other experimental results.

![Figure 6](image1)

**Fig.6** $\frac{v_{measured}}{v_{cal}}$ vs. Cell voltage (V)

![Figure 7](image2)

**Fig.7** Ionic oxygen conductivity calculated from oxygen permeation rate into N$_2$ purge gas

Furthermore, YSZ was used in SO$_3$ atmosphere for about 3 h (about 20 experiments) in the temperature range of 450 °C to 600 °C in this study, but ionic oxygen conductivity did not decreased as shown in Fig.7.

(4) Discussions

From experimental results shown above, it was confirmed that electrolytic SO$_3$ decomposition using YSZ solid electrolyte is possible in the temperature range of 550 °C to 600 °C and at cell voltage lower than 0.5V, and in the case of 500 °C the cell voltage higher than 0.5V is needed. Furthermore, ionic oxygen conductivity of YSZ in 3% SO$_3$ atmosphere almost agree with other experimental results.

Nevertheless, SO$_3$ concentration in this experiment was only 3% which is much lower than the SO$_3$ concentration expected in HHLT, and YSZ was in SO$_3$ atmosphere only for 3h at 450 °C to 600 °C.

Therefore, experiments in higher SO$_3$ concentration over 50%, and experiments for more long time should be performed to investigate the degradation of solid electrolyte and electrode.

Furthermore, because of other solid electrolytes which have higher ionic oxygen conductivity must be investigated to obtain higher hydrogen production efficiency.

2. Preliminary experiment on ionic oxygen conductivity of solid electrolytes in SO$_3$ atmosphere

Preliminary experiments are now performed to obtain ionic oxygen conductivity of four solid electrolytes, 8 mol YSZ, ScSZ (10 mol Sc/SZ) and LSGM (La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_3$) in SO$_3$ atmosphere at 500 °C. Test apparatus and instruments for measurement were almost same as electrolytic SO$_3$ decomposition experiment. Dimensions of the solid electrolyte samples were 17mm square, and the thickness were 0.5mm for 8molYSZ, 0.35mm for ScSZ and 0.16mm for LSGM, respectively. Pt electrodes with area of 0.5cm$^2$ were made on both surfaces. Supplied gas was air, and several 100 ppm of SO$_3$ will be supplied as mixture of SO$_3$ and N$_2$ at flow rate of
100ml/min. Flow rate of N₂ purge gas was 200ml/min, and cell voltage was of 0.0V to 1.0V.

Measured oxygen concentration in N₂ purge gas in air supplied experiments are shown in Fig.8. However the thickness of LSGM sample was thinner about one third of 8molYSZ sample, oxygen concentrations in purge gas with LSGM were higher than the oxygen concentration with 8molYSZ, therefore, oxygen permeation rate with LSGM were considered to be higher than the rate with 8molYSZ in these experiments. These results show the possibility of development of higher performance electrolytic cell using other solid electrolytes than YSZ. Ionic oxygen conductivity and durability in SO₃ atmosphere must be clarified experimentally. Further experiments using new solid electrolytes such as, Ce-Sm-O and Bi-Y-O will be needed.

3. Evaluation of thermal efficiency

Thermal efficiency of HHLT considering chemical reactions (reaction (1)-(3)), latent heat and sensible heat, was evaluated. Electrical and thermal energies (ΔG and ΔH - ΔG) required for the reaction are shown in Table 1 and latent heat and sensible heat are shown in Table2. Pressure used in the calculation was 1 bar (=0.987atm). Energy flow from heat source and process flow of HHLT were shown in Fig.s9 and 10, respectively. Reaction temperatures of reaction (1) and reaction (3) are 500°C and 50°C, respectively, and reaction temperature of reaction (2) is 372°C at which ΔG is 0. Electrical energy ΔG is converted from thermal energy with the efficiency of 40% which is almost the generation efficiency of FBR. Electrical energy and thermal energy required in HHLT are 113.3 kJ/mol and 321.0 kJ/mol, respectively with no heat recovery in cooling processes C1-C4. Total thermal energy required for heat source is 321.0kJ/mol + 113.3kJ/mol/0.4 = 604.4kJ/mol.

Generally, thermal efficiency of hydrogen production process (η) is defined in equation (7)²

\[ \eta = \frac{H_{\text{HHV}}}{H_{\text{in}}} \]

Thermal efficiency of HHLT is evaluated to be 0.473 (≈47.3%) using equation (7) with no heat recovery.

---

**Fig.9** Energy flow from heat source

**Fig.10** Process flow of HHLT
In this evaluation, voltage loss in electrolytic cells, heat loss in heat transmission, energy loss in mass transfer, effect of gas concentration in cells and heat recovery are not included. These effects must be considered in the evaluation of practical efficiency.

**IV. Conclusions**

A thermochemical hybrid hydrogen production process (HHLT) for sodium cooled FBR is proposed, electrolytic SO$_3$ decomposition experiments using YSZ and evaluation of thermal efficiency of HHLT were performed taking into consideration of chemical reactions. Furthermore, advantages and technical problems of HHLT were considered and experiments to obtain the ionic oxygen conductivity in SO$_3$ atmosphere for some solid electrolytes are now performed. Conclusions are summarized as follows.

(1) Electrolytic SO$_3$ decomposition using 8molYSZ was capable at the voltage lower than 0.5V in the temperatures of 550°C to 600°C and at the voltage higher than 0.5V at 500°C. Therefore, electricity required for HHLT process is expected to be much lower than the electricity for direct water electrolysis. Measured ionic oxygen conductivities in 3% SO$_3$ almost agree with the values measure in other experiments. Ionic oxygen conductivity of 8molYSZ did not decrease after 20 (3h) experiments, and performance of YSZ and Pt electrode were not considered to be degraded.

(2) However the thickness of LSGM sample was thinner about one third of 8molYSZ sample, oxygen permeation rate through LSGM in air supplied experiments were higher than the rate through 8molYSZ. These results show the possibility of development of higher performance electrolytic cell using other solid electrolytes than YSZ. Ionic oxygen conductivity and durability of solid electrolytes in SO$_3$ atmosphere must be clarified experimentally.

(3) Evaluated thermal efficiency of HHLT process considering chemical reactions, latent heat and sensible heat was about 47.3% with no heat recovery. Voltage loss in electrolysis, heat transmission loss, concentration of gas in electrolysis cells, heat recovery should be considered in realistic evaluation.

Further investigation on durability of solid electrolytes, electrodes and structural materials in SO$_3$ atmosphere at about 500°C, development of electrolysis cell for H$_2$SO$_4$ synthesis and experimental apparatus to substantiate whole process of HHLT, and application study of HHLT process for FBR plant are planned.

**Nomenclature**

EG : splitting voltage (V)  
$\Delta G$ : Gibbs energy change (kJ/mol)  
$n$ : number of electron (=2 for 1 oxygen atom)  
$F$ : Faraday constant.  
$v_{cal}$ : calculated oxygen volume flow rate permeating into N$_2$ purge gas (cm$^3$(STP)/sec/cm$^2$)  
i : cell current (A/cm$^2$)  
$\sigma$ : ion conductivity (S/cm)
E : cell voltage (V)
\( \eta \) : thermal efficiency (-)
H_{H_{2}V} : higher heat of hydrogen (= 285.8 kJ/mol)
H_{in} : heat from heat source (604.4 kJ/mol in this paper)

Acknowledgement

The authors wish to thank Dr. S. Shimizu, Dr. K. Onuki, Dr. M. Nomura of JAERI for their advice and encouragement. Special thanks are due to Messrs. K. Takagi of KAKEN Co. and T. Sasaki of KRI Inc. who performed experimental work.

References
1) IAEA, “Hydrogen as an energy carrier and its production by nuclear power”, IAEA-TECDOC-1085.