TWO-STEP THERMOCHEMICAL CYCLES FOR HYDROGEN PRODUCTION WITH DISH TYPE SOLAR THERMAL SYSTEM

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Abstract

The two-step water splitting thermochemical cycle is composed of the T-R (Thermal Reduction) and W-D (Water Decomposition) steps. The mechanism of this cycle is oxidation-reduction, which produces hydrogen. The reaction temperature necessary for this thermochemical cycle can be achieved by a dish-type solar thermal collector (Inha University, Korea). The purpose of this study is to validate a water splitting device in the field. The device is studied and fabricated by Kodama et al (2010, 2011). The validation results show that the foam device, when loaded with $NiFe_2O_4$/m-ZrO_2 powder, was successfully achieved hydrogen production with 9 (10 with a Xe-light solar simulator, 2009, Kodama et al.) repeated cycles under field conditions. Two foam device used in this study were tested for validation before an experiment was performed. The lab scale ferrite-conversion rate was in the range of 24~76%. Two foam devices were designed to for structural stability in this study. In the results of the experiments, the hydrogen percentage of the weight of each foam device was 7.194 and 9.954μmol g^{-1} on average, and the conversion rates 4.49~29.97 and 2.55~58.83%, respectively.

1. Introduction

Energy is an essential element for the development of any country's industry and economy. Globally, the demand for energy has increased over the years. In particularly, it is predicted that energy consumption will increase with the continuing development of developing countries and that the amount of energy consumption in 30 years will be more than triple the amount of energy consumption at present (C.A. Dahl and L. McDonard, 1998). Furthermore, the unstable oil price situation in the world market and pollution problems related to fossil fuel energy have had the effect of increasing the demand the development of alternative energy types, such as hydrogen. The use of solar energy conversion systems for the production of hydrogen, which is a promising solar fuel, solves these problems (Stéphane Abanades, Gilles Flamant, 2006).

Hydrogen can be produced from a thermal process, an electrolytic process, and photolytic process (Korea Energy Economics Institute, 2007). Among these processes, the thermal process can use solar thermal energy as a heat source with the advantage of the abundance and sustainability of solar energy. In case of a direct thermal process from water, for a feasible process, heat source capable high-temperature 2500K is required and additional devices are necessary for the prevention of the creation of an explosive mixture (Kogan, A., 1998). For these reasons, the thermal process cannot easily be put into practical use. Therefore, a two-step thermochemical cycles is being studied, These methods involve hydrogen production by water splitting at a relatively low temperature (Aldo Steinfeld, 2005).

The equations below (eq. 1) and (eq. 2) denote the two-step thermochemical cycle using a ferrite redox pair (Nakamura, T, 1997).

$$Fe_3O_4 = 3FeO + \frac{1}{2}O_2 \qquad \text{(eq. 1)}$$

$$3FeO + H_2O = Fe_3O_4 + H_2 \qquad \text{(eq. 2)}$$

The first step is the thermal-reduction (T-R) step, which is highly and thermodynamically desirable at temperatures above 2500K under a pressure of 1 bar (eq. 1). The second water-decomposition (W-D) step is slightly exothermic and possible at temperatures of less than 1000K (eq. 2).

Kodama et al. (2003) performed a repeat cycle-experiment using a solar simulator for a two-step reaction with 10mm diameter $NiFe_2O_4$/m-ZrO_2 foam device. Patrice et al. (2007) drew a conclusion of the relation with the amount of hydrogen production according to the condition of temperature using a furnace.

In this study, two water-splitting devices are tested in the reactor installed onto a solar thermal collector. The first device was tested for feasibility of a continuous water-splitting reaction in actual climate conditions on site (Inha Univ. Incheon, Korea). The second device was reinforced against thermal stress, and more metal oxide was loaded onto it to increase hydrogen production. In this article, we refer to the experiment with the first device as "Case I" and to that of the second experiment, with the second water-splitting device as "Case II" for convenience. In Case I, a prototype of the reactor and the first water-splitting device are tested. With considerations of the previous results, a re-design and improved procedure are utilized for the second reactor and the second device in the subsequent experiment, of Case II.

2. Experiment setup

2.1. $NiFe_2O_4$/m-ZrO_2/MPSZ Foam Device

$NiFe_2O_4$ is excellent for its reduction characteristics. It can stably create hydrogen without a change in the crystal structure. Furthermore, to enhance the cycle repetition characteristics and the thermal stability, MPSZ (MgO-Partially Stabilized Zirconia) was used as a supporter. Based on experimental results in 2010 (Case I), at foam device which was used in a 2011 experiment was created (Case II). Generally, a thick foam device has a larger surface area than a thin foam device. Consequently, more $NiFe_2O_4$ can be coated onto a thick foam device. However, a thick foam device is easier to break than a thin foam device. As zirconia has a high thermal expansion coefficient. The $NiFe_2O_4$ loading amount is high and the m-ZrO_2 loading amount is low on the foam device. High reactivity is expected, but prevention of the sintering of $NiFe_2O_4$ is not guaranteed (Nobuyuki Gokon et al. 2009). The features of the $NiFe_2O_4$/m-ZrO_2/MPSZ foam device, shaped as a disk, as shown in Fig.1. The specifications are listed in Tab. 1.

Fig. 1 $NiFe_2O_4$/m-ZrO_2/MPSZ foam device

Tab. 1: Properties of the foam device used in the experiment

Specification	Case I	Case II
Diameter (mm)	80	80
Thickness (mm)	15	20
Weight of ferrite foam device (g)	124.0	165.7
$NiFe_2O_4$ loading of $NiFe_2O_4$/m-ZrO_2 particles (wt%)	20	16
$NiFe_2O_4$ loading on MPSZ foam(wt%)	7.1	5.8
$NiFe_2O_4$ loading amount(g)	8.8	9.5
m-ZrO_2 loading amount(g)	32.8	50.1

2.2. Chemical Reactor

In the Case I experiment, Alumina (Al_2O_3) was used for the inside of the reactor. Alumina is strong against thermal shocks (ΔT>1,000°C). Another advantage is that the upper range of its temperature is high, at 2,000°C. However, it is a brittle material.

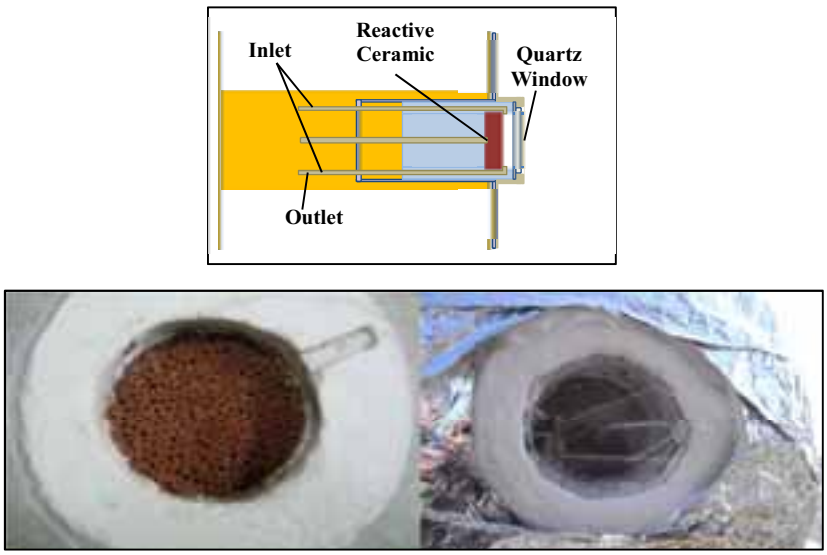

Fig. 2 Chemical reactor made of alumina: Case I

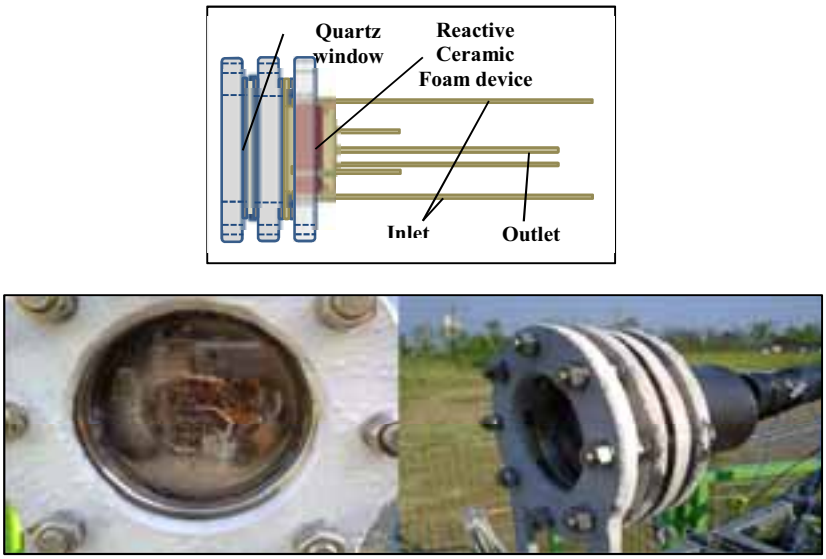

Fig. 3 Chemical reactor made of SUS304: Case II

For this reason, in the Case II experiment, the SUS304 reactor was used. Fig. 2 and Fig. 3 show external images of reactor used in the experiments.

The concentrated solar radiation of reactor was attached to quartz glass which transmittance is high and $NiFe_2O_4$/m-ZrO_2/MPSZ was located into the center of the inside of reactor. Inside the tube of the reactor, two gas inlets and one gas outlet in the center of the lower part were installed.

R-type thermocouples were also set in the center part and in the edge part of the foam device and the temperature was measured at these points.

2.3. Dish Type solar Thermal System

A Dish-type solar concentrator (Inha Dish-1) was used for the experiment in the field, Which took place under the sun. Using this system, the temperature required in the T-R and W-D steps was controlled by adjusting the exposure of the reflectors. Fig. 4 and Tab. 2 show an image and the specifications.

Fig. 4 Dish-type solar thermal system (Inha Dish-1)

Tab. 2: Specification of the Dish System

Specification	Size
From ground to center	1.83 m
Maximum height	4.11 m
Reflectivity of reflector	Above 95%
Diameter of reflector	3.2 m
Focal length	2 m
Total area of reflectors	5.90 m2
Rim angle	43.85˚

3. Experimental process

The devices used in the experiment are shown in Fig 5. The experiment was conducted by first purging using nitrogen gas, the cycling between the T-R step and the W-D step, and finally by conducting an analysis of the produced gas with a gas chromatography. Purging, conducted before the experiment, was done using an inflow of 99.999% pure nitrogen gas. This gas is not reactive in the tube and mitigates fouling in the tube.

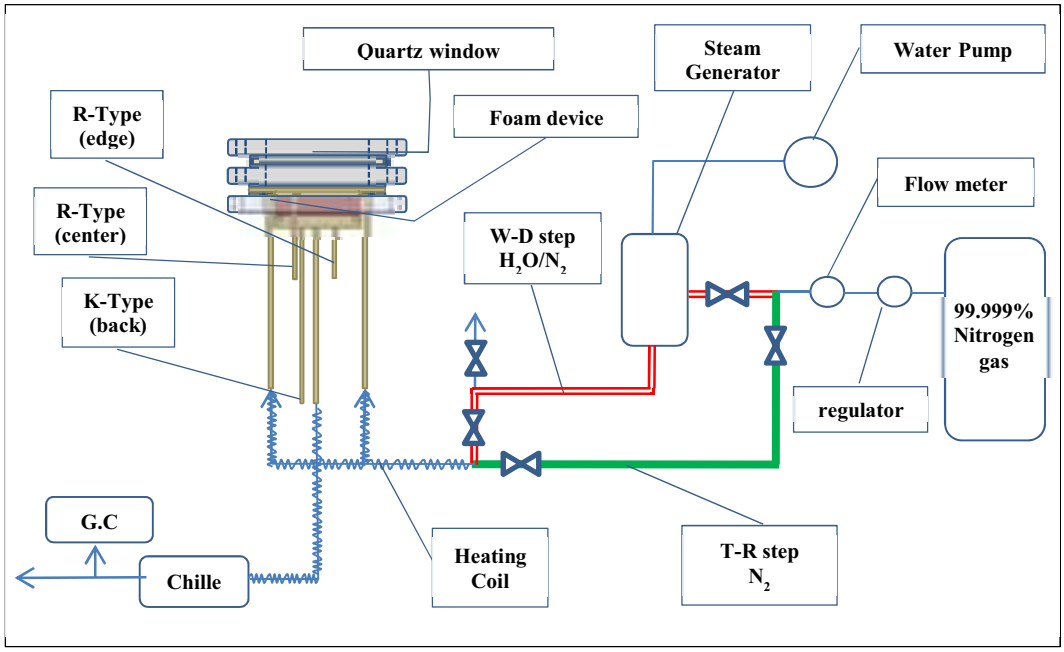

Fig. 5 Experimental set-up

In T-R step, nitrogen gas reaches the reactor through a flow meter and generates a reduction reaction in the device. In this step, the oxygen that is produced by reduction using the 99.999%pure nitrogen gas is released out through the gas outlet. The time for the performance for T-R step is essentially 20min at 1,500°C and about 20~30min at 1400~1500°C.

At the end of the T-R step, the W-D step is conducted. During this step, an oxidation reaction is generated by injecting nitrogen gas and vapor. In the W-D step, the temperature of the foam device is maintained within the range of 1,100~1,200°C and the experiment until the amount of oxygen detection among the produced gases becomes zero.

Because these experiments used solar energy and not solar simulator, the performance time is adjusted after considering solar radiation and temperature.

To eliminate H_2O component completely, a cooling device is positioned at the end part of the gas outlet. After the final amount of gas produced via this process component was analyzed by gas chromatography (Agilent 7890A) using a 0.5ml syringe. This was done every three minutes.

4. Result

4.1 Insolation and the temperature of the $NiFe_2O4/m\text{-}ZrO_2/MPSZ$ foam device

The experiment was conducted during clear weather to minimize a weather effect. Generally, in the T-R step, the temperature was maintained in the range of 1,300~1,500°C while the temperature of the W-D step remained in the range of 1,000~1,200°C. The time necessary for each step is shown in Tab. 3. The T-R step is controlled on the basis of 20 minutes as regards the solar radiation and temperature at each step of the performance. The W-D step proceeded until the content of hydrogen became zero among the produced gases. Fig. 6(a)-(i) show each cycle experimental boundary condition. It shows center temperature of foam device in reactor and solar radiation during the experiment.

The R-type thermocouple located at the edge of foam device was damaged as a consequence of exposure. According to this, the data of thermocouple was excluded from the results of the experiment.

Although the experiment could not take a stable solar radiation due to the use of solar as a source of light, the foam device could attain enough solar radiation to maintain the reaction temperature. The cycle

performed near sunset, it was impossible to take a uniform temperature in chemical reactor because the sun tracking sensor system could not note the location of the sun given its scattered focus.

Tab. 3: Duration of each cycle

Cycle No.	Date	T-R step	W-D step
1st Cycle	May 13th 2011	14:50 ~ 15:10	15:15 ~ 16: 18
2nd Cycle	May 14th 2011	10:57 ~ 11:17	11:27 ~ 12:35
3rd Cycle	June 20th 2011	13:11 ~ 13:34	13:37 ~ 14:06
4th Cycle	June 21th 2011	14:13 ~ 14:35	14:41 ~ 15:34
5th Cycle	June 21th 2011	15:41 ~ 16:00	16:05 ~ 17:20
6th Cycle	June 21th 2011	13:43 ~ 14:04	14:11 ~ 14:36
7th Cycle	June 21th 2011	14:44 ~ 14:59	15:05 ~ 15:27
8th Cycle	June 21th 2011	16:22 ~ 16:38	16:44 ~ 17:16
9th Cycle	June 21th 2011	11:01 ~ 11:23	11:29 ~ 11:58

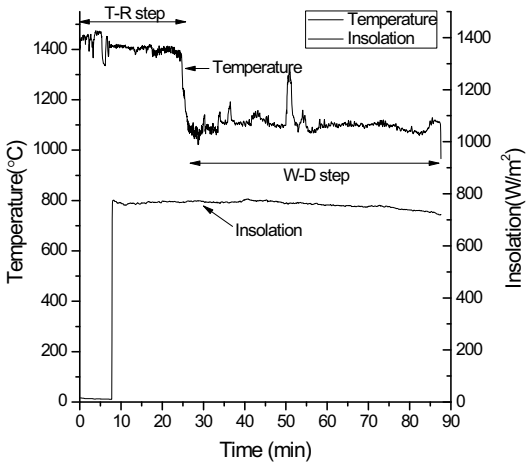

Fig. 6 (a) 1st Cycle

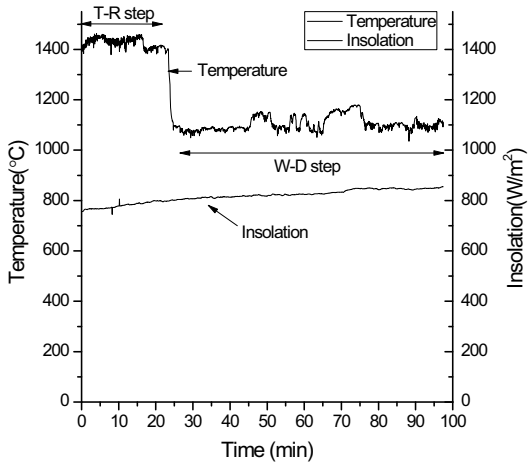

Fig. 6 (b) 2nd Cycle

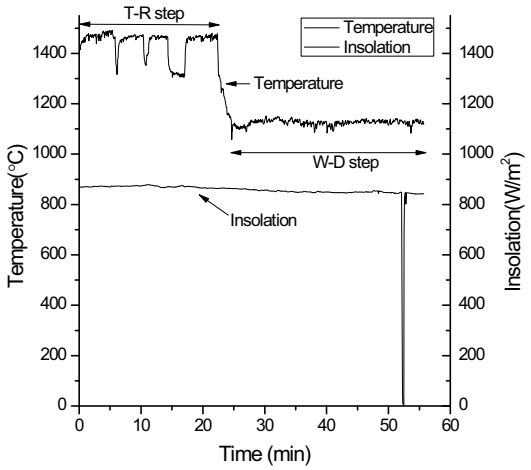

Fig. 6 (c) 3rd Cycle

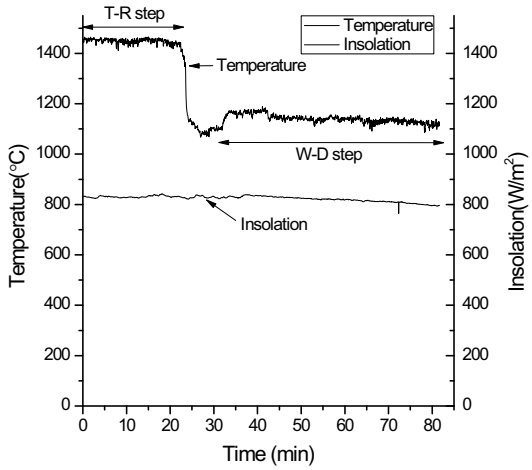

Fig. 6 (d) 4th Cycle

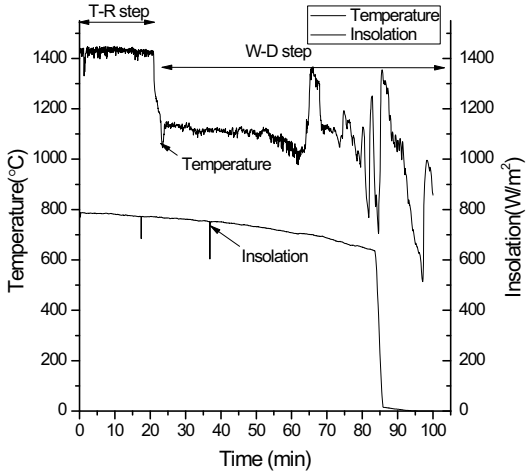

Fig. 6 (e) 5th Cycle

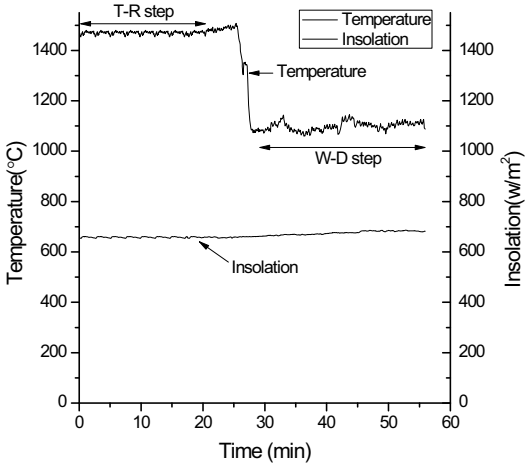

Fig. 6 (f) 6th Cycle

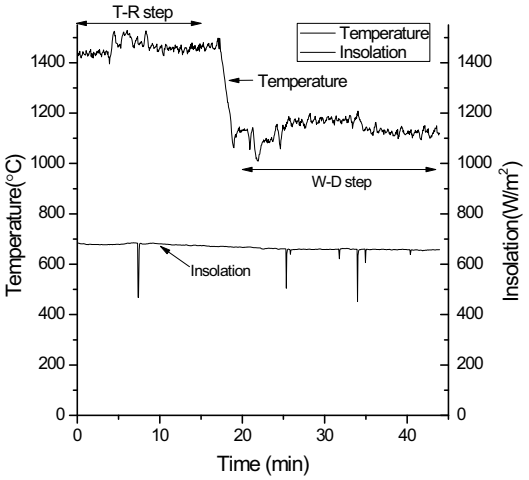

Fig. 6 (g) 7th Cycle

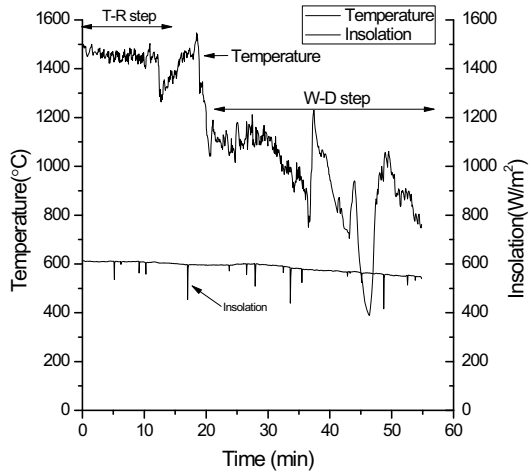

Fig. 6 (h) 8th Cycle

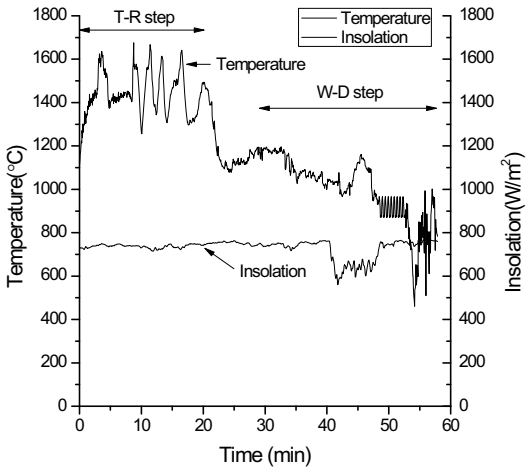

Fig. 6 (i) 9th Cycle

4.1 The amount of hydrogen production

Fig. 7 shows, the performance period and the amount of hydrogen production during the W-D step. In each cycle, the amount of hydrogen production early in the W-D step reached at its peak. Subsequently, it diminished gradually.

Tab. 4 and 5, it indicates the results of the Case I and Case II experiments, respectively. These results calculated the ferrite conversion rate and the amount of hydrogen production using equations (eq. 3) and (eq. 4) as shown below. With the T-R step and in the W-D step, the stability of hydrogen production was confirmed in an analysis of the results of the experiment.

$$\text{Ferrite conversion rate}(\%) = \frac{\text{Mole of hydrogen produced}}{\text{Mole of } NFe_2O_4} \qquad \text{(eq. 3)}$$

$$H_2\left[\frac{ml}{g}\right] = \frac{H_2 \text{ pressure } [\%] * \text{Flow rate } \left[\frac{ml}{min}\right] * \text{Interval of time } [min]}{100 * \text{Weight of foam device } [g]} \qquad \text{(eq. 4)}$$

Additionally, the repeat cycle count and the amount of hydrogen production increased beyond these results for the foam device used in the Case I experiment as the thermal stress endurance had improved.

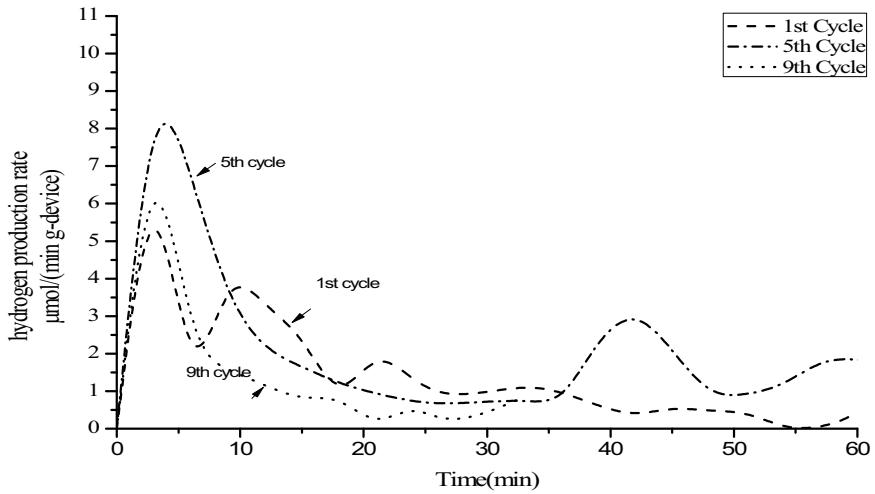

Fig. 7 Hydrogen production

Tab. 4: Case I experimental results of hydrogen production and ferrite conversion in the repeated two-step water splitting

Cycle Number	1st	2nd	3rd	4th	5th
Hydrogen production (μmol/g-device)	10.97	13.19	6.87	3.29	1.65
Ferrite conversion rate (%)	29.9	36.0	18.7	8.99	4.49

Tab. 5: Case II experimental results of hydrogen production and ferrite conversion in the repeated two-step water splitting

Cycle NO.	1st	2nd	3rd	4th	5th	6th	7th	8th	9th
Hydrogen production (μmol/g-device)	14.63	4.19	1.86	21.17	23.85	2.69	1.03	11.98	8.19
Ferrite conversion rate(%)	36.31	10.41	4.61	52.55	58.83	6.65	2.55	29.55	20.20

5. Conclusion

In this study, the experiment was conducted involving concentrated solar radiation in a system with a capacity of $5kW_{th}$, the experiment was the two-step water splitting thermochemical cycle experiment that was done to compare its results to those of an experiment conducted in Case I and Case II. In the Case I experiment, for five cycles, hydrogen production as a percentage of the weight of the material was 7.194μmol g^{-1} on average. However, five cycles of the Case II experiment obtained hydrogen per weight at 13.14μmol g^{-1} on average. After a total of nine cycles, hydrogen per weight of material was 9.954μmol g^{-1} on average. In addition the Case II experiment showed an increase in the number of repeated cycle compared to Case I.

A $NiFe_2O_4$/m-ZrO_2/MPSZ foam device was performed for two-step water splitting thermochemical cycle on a laboratory scale using a solar simulator. This experiment could be repeated for 10 cycles, the hydrogen production was shown the typical profiles (Nobuyuki Gokon et al. 2009). In this study, the experiment not using a solar simulator, but using the sun in the experimental environment indicated above, influenced directly the solar radiation of the foam device owing to the fluctuation in the solar radiation, and the thermal stress. Consequently, trend of hydrogen production was not shown or was minimal. In the future, study of the optimization of the $NiFe_2O_4$/m-ZrO_2/MPSZ foam device considering the thickness of the foam device and the $NiFe_2O_4$ loading amount should be done.

6. References

C.A. Dahl and L. McDonard, 1998. Forecasting Energy Demand in the Developing World, Energy Sources, Vol. 20, 875-889.

Korea energy economics institute, 2007. Hydrogen production cost estimation research report, South Korea

Kogan, A., 1998. Direct solar thermal splitting of water and onsite separation of the products. Ⅱ. Experimental feasibility study, Int. J. Hydrogen Energy 23, 89-98.

Aldo Steinfeld, 2005. Solar thermochemical production of hydrogen-a review, Solar Energy, Vol. 78, pp.603 ~ 615.hhh

Nakamura, T., 1997. Hydrogen production from water utilizing solar heat at high temperatures. Solar Energy 19, 467-475.

Kodama, T., 2003, High-temperature solar chemistry for converting solar heat to chemical fuels, Progress in Energy Combustion Science, Vol. 29, No. 6, pp. 567~597.

Patrice Charvin, Stephane Abanades, Gilles Flamant and Florent Lemort, 2007. Two-step water splitting thermochemical cycle based on iron oxide redox pair for solar hydrogen production, Energy, Vol. 32, pp. 1124~1133.

Nobuyuki Gokon, Hiroko Marayama, Ayumi Nagasaki and Tatsuya Kodama, 2009. Thermochemical two-step water splitting cycles by monoclinic ZrO_2-supported $NiFe_2O_4$ and Fe_3O_4 powders and ceramic foam devices, Solar Energy, Vol. 83, pp. 527~537.