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Oxygen-releasing step of $ZnFe_2O_4$/$(ZnO + Fe_3O_4)$-system in air using concentrated solar energy for solar hydrogen production

Yutaka Tamaura *, Hiroshi Kaneko

Research Center for Carbon Recycling and Energy, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152 8552, Japan

Abstract

The oxygen-releasing step of the $ZnFe_2O_4$/$(ZnO + Fe_3O_4)$-system for solar hydrogen production with two-step water splitting using concentrated solar energy was studied under the air-flow condition by irradiation with concentrated Xe lamp beams from a solar simulator. The spinel-type compound of $ZnFe_2O_4$ (Zn-ferrite) releases O_2 gas under the air-flow condition at 1800 K and then decomposes into Fe_3O_4 ($= Fe^{II}Fe_2^{III}O_4$) and ZnO with a nearly 100% yield ($ZnFe_2O_4 = ZnO + 2/3Fe_3O_4 + 1/6O_2$). The ZnO was deposited as the thin layer on the surface of the reaction cell wall. A thermodynamic study showed that the ZnO was produced by the reaction between the O_2 gas in the air and the metal Zn vapor generated from $ZnFe_2O_4$. With the combined process of the present study on the O_2-releasing step and the previous one on the H_2 generation step ($ZnO + 2/3Fe_3O_4 + 1/3H_2O = ZnFe_2O_4 + 1/3H_2$) for the $ZnFe_2O_4$/$(ZnO + Fe_3O_4)$-system, solar H_2 production was demonstrated by one cycle of the $ZnFe_2O_4$/$(ZnO + Fe_3O_4)$-system, where the O_2-releasing step had been carried out in air at 1800 K and the H_2 generation step at 1100 K.
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1. Introduction

Solar fuels, which are produced by solar/chemical energy conversion systems, can be stored until required and transported to any consuming site (Steinfeld, 1995; Steinfeld and Fletcher, 1991). Water can be directly split using solar process heat via direct thermal dissociation above 2500 K (Fletcher and Moen, 1977; Kogan, 1998). However, the gaseous products need to be separated at high temperature to avoid recombination or otherwise obtaining an explosive mixture (Kogan et al., 2000). To solve these problems, two-step water-splitting reactions (O_2-releasing step and H_2 generation step) using metal oxides have been suggested (Nakamura, 1977). The reactions can be represented as follows:

$$MO_{ox} + \text{thermal energy} = MO_{red} + 1/2O_2(g) \qquad (1)$$

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* Corresponding author. Tel.: +81 3 5734 3292; fax: +81 3 5734 3436.

E-mail address: ytamaura@chem.titech.ac.jp (Y. Tamaura).

and

$$MO_{red} = H_2O(g) = MO_{ox} = H_2(g) \qquad (2)$$
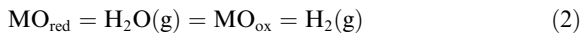
where MO_{ox} and MO_{red} denote the oxidized and reduced states of the metal oxide, respectively.

Current research has reported the two-step thermochemical water-splitting cycle using the Fe_3O_4/FeO (Nakamura, 1977) or ZnO/Zn (Fletcher, 1999; Palumbo et al., 1998; Weidenkaff et al., 1999) redox system. When their O_2-releasing step (reduction step) is operated in air or at $p_{O_2} = 0.1$ MPa, it requires operating temperatures above 2300 K (Sibieude et al., 1982; Tofighi and Sibiaude, 1984). Also, the reduction efficiency is limited because the O_2-releasing reaction should be quenched by rapid cooling of the products (reduced metal and O_2) which results in heat loss (Bamberger, 1978; Tofighi and Sibieude, 1980; Kuhn et al., 1992; Kaneko et al., 2002). To be energy efficient during the O_2-releasing step, one should try to operate the one (which, at best, is equivalent to a Carnot cycle) at the highest possible temperature. However, the higher the temperature, the greater the radiation losses (Fletcher, 1983; Steinfeld and Schubnell, 1993). It was demonstrated that the optimum operating temperatures vary from 800 to 1500 K for a blackbody cavity-receiver under a gaussian incident solar-flux distribution with peak concentrations between 1000 and 12,000 suns (Tofighi and Sibiaude, 1984). Thus, lowering the temperature during the O_2-releasing step to below 1500 K is important for the practical production of solar H_2. From thermodynamic data, the O_2-releasing reaction with the Fe_3O_4/FeO or ZnO/Zn redox system proceeds at 1673 K under a p_{O_2} of 10^{-7} MPa (Weidenkaff et al., 2000). This low O_2 partial pressure indicates that the production yield of O_2 (reaction yield) is very low and that this reaction should be carried out in the reactor closed to air with inert gas flow.

Lundberg evaluated the redox pairs Mn_3O_4/MnO and Co_3O_4/CoO (Lundberg, 1993), which can be thermally reduced in air at 1810 K and 1175 K, respectively. However, they have a very low potential for the H_2 generation reaction with water. Their H_2 yield was too low to be of any economic interest. The present authors have studied the (Ni, Mn) ferrite system, whose O_2-releasing step works at around 1000 K in the inert gas flow of Ar, and experimentally demonstrated the two-step water splitting with the (Ni, Mn) ferrite using a solar furnace at around 1000 K (Tamaura et al., 1995; Kojima et al., 1996). The cation-excess (Ni, Mn) ferrite, which is formed from the (Ni, Mn) ferrite in the O_2-releasing step at >1173 K (in Ar flow condition), splits water to generate H_2 gas at <1073 K. However, the H_2 gas volume evolved in this system is quite low, since the water splitting is caused by the small magnitude of the non-stoichiometry in the ferrite. This system still has the disadvantage of using an inert gas with a $p_{O_2} < 10^{-7}$ MPa.

This paper describes the O_2-releasing step of the $ZnFe_2O_4/(ZnO + Fe_3O_4)$-system under air-flow conditions at 1800 K for solar hydrogen production with two-step water splitting (Eq. (3)).
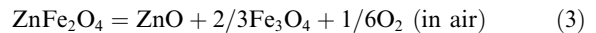
$$ZnFe_2O_4 = ZnO + 2/3Fe_3O_4 + 1/6O_2 \text{ (in air)} \qquad (3)$$

The H_2 generation step of the $ZnFe_2O_4/(ZnO + Fe_3O_4)$-system have already been studied and reported elsewhere (Tamaura et al., 2002; Uehara et al., 2001), in which the H_2 generation reaction readily proceeds at around 1000 K with nearly a 100% yield according to the reaction

$$H_2O + 3ZnO + 2Fe_3O_4 = H_2 + 3ZnFe_2O_4 \qquad (4)$$
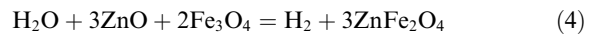
From Eqs. (3) and (4), the solar H_2 can be generated by the two-step water-splitting process with the $ZnFe_2O_4/(ZnO + Fe_3O_4)$-system if the O_2-releasing step is operated in air at 1800 K. This will also be demonstrated in the present study.

2. Experimental

2.1. Materials

The Zn-ferrite powder $(ZnFe_2O_4)$ was kindly donated by Toda Kogyo Co. The XRD measurement showed that the Zn-ferrite powder was the spinel-type ferrite of $ZnFe_2O_4$ with the lattice constant $a_0 = 0.8440$, which is nearly equal to that already reported $(a_0 = 0.84411$ nm; JCPDS card #22-1012).

2.2. Oxygen-releasing reaction

The O_2-releasing reaction was carried out under flowing air conditions. The experimental set-up of the O_2 release is schematically shown in Fig. 1. The $ZnFe_2O_4$ powder (18 mg) mounted on the Pt–Rh boat was placed in the reaction cell of a quartz tube ($\varnothing 28$ mm × L300 mm), and air was passed through the reaction cell at the flow rate of 200 ml/min. The temperature of the sample was raised to a specified value in the range of 1600–1900 K by irradiation of double Xe beams (Ushiopex 5 kW×2) as a simulated solar beam. The
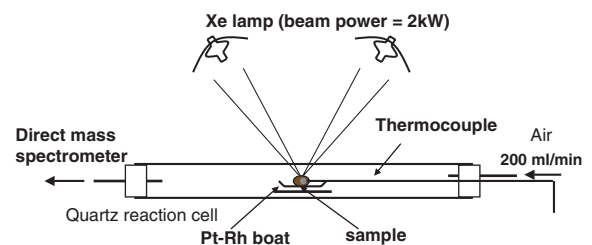
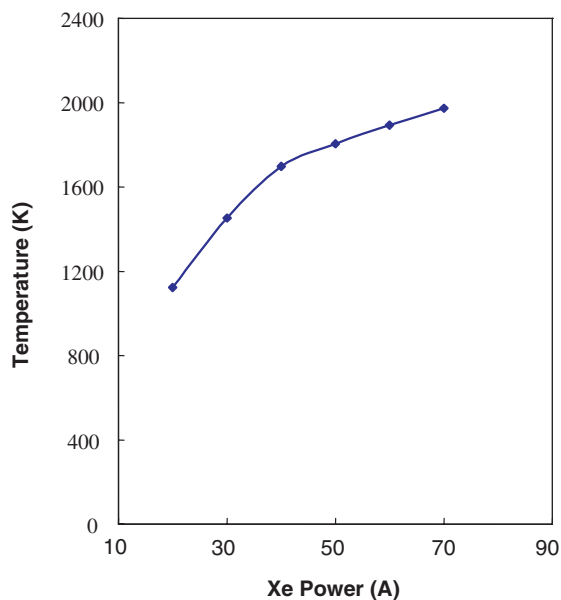

Fig. 1. Experimental set-up for O_2-releasing reaction.

Fig. 2. Calibration curve between the reaction temperature of samples and the power of Xe lamps.

Fig. 3. Experimental set-up for H_2-releasing reaction.

power flux at the superimposed-focal point ($\varnothing 8$ mm) was about $2150 \, kW/m^2$ measured by heat flux transducer (Medtherm Co.). The temperature was estimated from the calibration curve between the electric current of the Xe lamps and the temperature measured using a thermocouple (Pt–Pt/Rh) (Fig. 2). The O_2 gas evolution profile was recorded by direct-mass spectrometry (DMS) (THERMOLAB, VG Gas Analysis Co.), and the amount of the released O_2 gas was calculated from the peak area. The reaction was stopped by quenching (rapidly cooling the reaction cell with ice water) and the solid products were characterized by XRD and chemical analyses. The solid phase was identified by X-ray diffractometry (XRD) with FeKα radiation (Rigaku Co. Rint-UT21) and the lattice constant of the product was calculated by extrapolating the values of a_0 vs. the Nelson–Riley function, $\cos^2\theta/\sin\theta + \cos^2\theta/\theta$, to zero using the least squares method. The Fe^{2+}/Fe_{total} mole ratio of the sample was determined by colorimetry using 2,2′-bipyridil (Iwasaki et al., 1960). The Zn/Fe mole ratio of the solid was determined by atomic absorption spectroscopy (Shimadzu, AA-6650).

2.3. H_2 generation reaction

The experimental set-up for the H_2 generation reaction is shown in Fig. 3. The mixed powder of the ZnO and Fe_3O_4 (mole ratio = 1.5) was placed in a quartz cell reactor set-up in an infrared image furnace. The sample was heated to 1073 K and steam (20 mmol/min) was
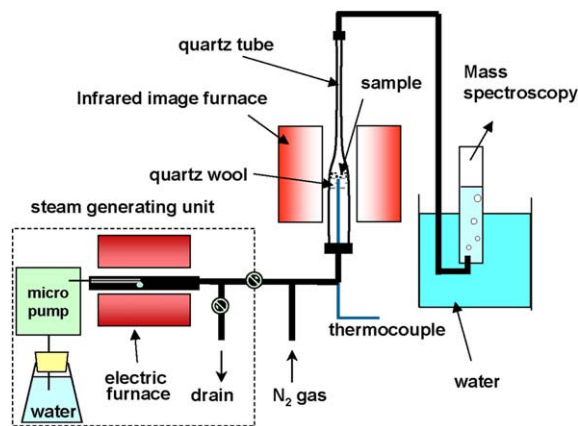
passed through with the N_2 carrier gas (100 ml/min), which was purified prior to use by passing over Cu at 873 K. The profile of the H_2 generation was recorded by DMS.

3. Results and discussion

3.1. Oxygen-releasing reaction of $ZnFe_2O_4$ in air

Fig. 4 shows the time-variation profile of the O_2 releasing (recorded by DMS) for the $ZnFe_2O_4$ powder (18 mg) in flowing air at 1800 K. The O_2-releasing reaction took place immediately after the Xe-beam irradiation, and was completed within 2 min. During the O_2-releasing reaction, it was observed that white smoke was evolved from the solid sample and that a white layer was deposited on the reaction cell wall (Fig. 5). The
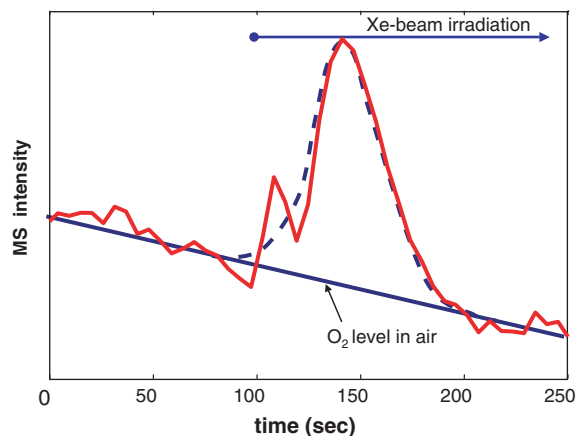

Fig. 4. Time-variation profile of the O_2 generation from $ZnFe_2O_4$ by Xe-beam irradiation in flowing air at 1800 K.
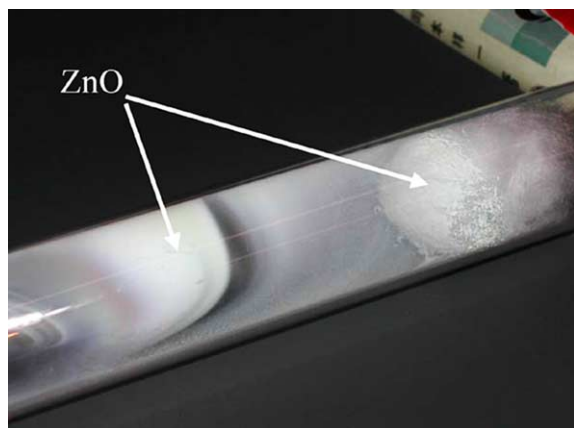
Fig. 5. Photo of the ZnO fine powder deposited on the reaction cell wall after the O_2-releasing reaction.

chemical analysis showed that the white layer was ZnO powder. In the XRD of the black-colored solid sample left at the sample-mounted position, only strong peaks of the cubic spinel-type structure were observed (Fig. 6(a)). The lattice constant of the spinel-type structure was $a_0 = 0.8397$ nm which corresponds to that of the stoichiometric Fe_3O_4 (JCPDS card #19-629); an XRD peak shift of the $ZnFe_2O_4$ spinel compound to that of the stoichiometric Fe_3O_4 (black color) was observed (Fig. 6(b)). The chemical analyses showed that 99.3% of the Zn ions were lost from the starting material

($ZnFe_2O_4$ powder), and that the Fe^{2+} content in the product solid phase was nearly equal to that ($0.33 = Fe^{2+}/Fe_{total}$) of the stoichiometric Fe_3O_4 (yield = nearly 100%). This Fe^{2+} content generated by the reduction of the Fe^{3+} ions in the $ZnFe_2O_4$ powder was nearly equal to the evolved O_2 gas volume estimated from the O_2 generation profile recorded by DMS. Thus, the stoichiometric Fe_3O_4 with a spinel-type structure was formed by the O_2-releasing reaction of the Zn-ferrite ($ZnFe_2O_4$) in flowing air at $T = 1800$ K with a nearly 100% yield. Also, the ZnO phase was separated from the Zn-ferrite ($ZnFe_2O_4$), and was deposited in the form of a ZnO layer on the reaction cell wall. This is denoted by

$$6ZnFe_2O_4 = 6ZnO \text{ (separated)} + 4Fe_3O_4 + O_2 \qquad (5)$$
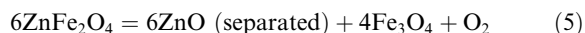
where the term "separated" in parenthesis means that the ZnO phase was separately deposited on the reaction cell wall.

In the present study, as described in the experimental section, the reaction temperature was estimated from the calibration curve between the electric current of the Xe lamps and the temperature measured by the thermocouple for the same sample (Fig. 2). The O_2-releasing reaction took place at the 1800 K, but did not proceed at the 1700 K estimated from the calibration curve. It was also observed that the O_2-releasing reaction proceeded when $ZnFe_2O_4$ melted (the melting point is 1590 °C [1863 K]). These results suggest that the reaction temperature required for the O_2-releasing step is around 1800 K.
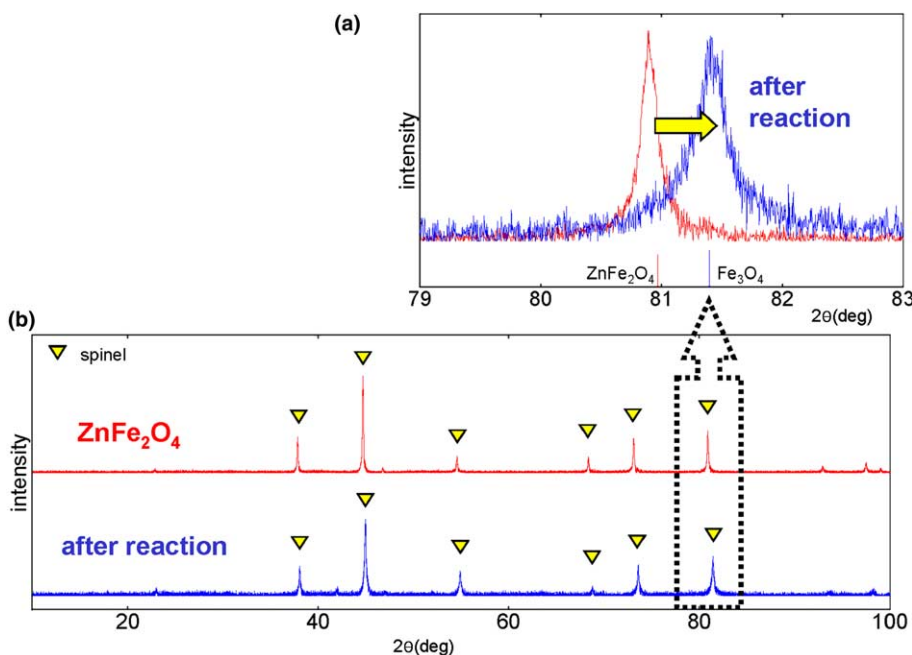

Fig. 6. XRD patterns (a) and the projected peaks (4 0 0) (b) for the solid products before and after the O_2-releasing reaction.

3.2. Thermodynamic study of the O_2-releasing step

The thermodynamics of the O_2-releasing reaction was studied using MALT2 software with the thermodynamic parameters.

First, it was assumed that the $ZnFe_2O_4$ was decomposed into the Fe_3O_4 solid phase and the $ZnO(g)$ (gaseous phase), as given by

$$6ZnFe_2O_4 = 6ZnO(g) + 4Fe_3O_4 \text{ (solid)} + O_2 \qquad (6)$$
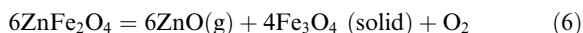
The ΔG of Eq. (6) is negative over 2500 K, and the equilibrium constant (K_1) for Eq. (6) is given by

$$K_1 = p_{ZnO}^6 \times p_{O_2} \qquad (7)$$

where p_{ZnO} and p_{O_2} denote the partial pressures of $ZnO(g)$ and O_2, respectively. In the present experiment, the p_{O_2} was kept constant by flowing air having a p_{O_2} of $10^{-0.167}$ MPa. The p_{ZnO} (gaseous zinc oxide content) calculated for $p_{O_2} = 10^{-1.67}$ MPa is shown by curve A in Fig. 7. As can be seen from curve A, the reaction of Eq. (6) seems to take place above $T = 2300$ K. This temperature is much higher than the practical experimental temperature of the O_2-releasing reaction, as described above (1800 K). Based on the higher vapor pressure of the metal Zn at 1800 K, the $ZnFe_2O_4$ seems to be dissociated into the metal Zn vapor and O_2 as described by

$$3/2ZnFe_2O_4 = 3/2Zn(g) + Fe_3O_4 + O_2 \qquad (8)$$
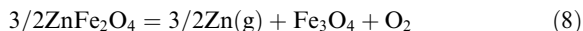
In the present experimental set-up, there is a thermal gradient in the reaction cell between the sample position and the reaction cell wall whose outer side is in contact with the air (heat sink at room temperature). Therefore, the vaporized metal Zn gas formed by Eq. (8) will be readily oxidized to $ZnO(solid)$ near the surface of the cell wall by the O_2 gas in the air passing through the reaction cell.

The ΔG of Eq. (8) is negative over 2015 K, and the equilibrium constant (K_2) of Eq. (8) is given by
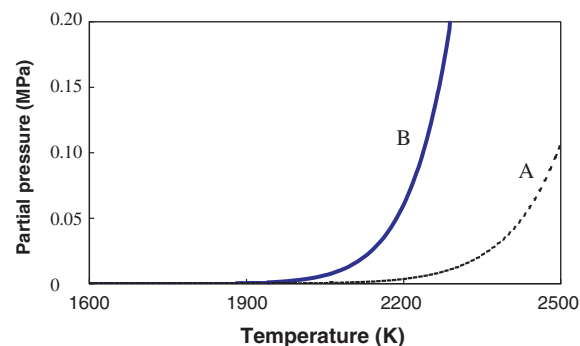
$$K_2 = p_{Zn}^{3/2} \times p_{O_2} \qquad (9)$$

The temperature dependence of $p_{Zn}^{3/2}$ with Eq. (8) at $p_{O_2} = 10^{-1.67}$ MPa is given by curve B in Fig. 7. As can be seen here, a predominant increase in the p_{Zn} occurs above 2200 K, which is lower by 300 K compared with curve A for the case of $ZnO(g)$.

In order to examine the Zn metal vapor generation from the $ZnFe_2O_4$ powder according Eq. (8), the O_2-releasing reaction was evaluated using the reaction cell equipped with a water-cooled condenser for trapping the Zn vapor as metallic Zn by quenching. In this experiment, the $ZnFe_2O_4$ sample was irradiated with the Xe beams at 1800 K in flowing Ar. The O_2 evolution was observed in the DMS. After the reaction, the metal Zn powder (black) was deposited on the condenser. The deposited metal Zn was identified by XRD. These results suggest that, at the lower O_2 partial pressure (in flowing Ar), the O_2-releasing reaction of $ZnFe_2O_4$ will readily occur according to Eq. (8) at 1800 K.

These findings suggest that one can consider the following reaction mechanism as follows. The gaseous atmosphere surrounding the sample heated to 1800 K by the Xe-beam irradiation has a fairly lower oxygen partial pressure due to the successive generation of the metal zinc vapor. This successive vaporization would be facilitated by the rapid removal of the vaporized metal Zn by the oxidation with O_2 gas in the air that passes through the reaction cell (The metal zinc vaporization will more favorably take place, if the metal zinc vapor generated near the sample powders is successively and instantly removed from the sample powders). This process is given by

$$Zn(g) + 1/2O_2 \text{ (in air gas)} = ZnO \text{ (solid)} \qquad (10)$$
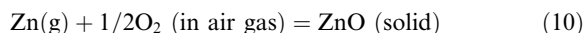
where "in air gas" denotes that the O_2 gas is mostly air passing through the reaction cell. Eq. (10) will be accelerated at the lower temperature near the surface of the reaction cell wall, and fine particles will mostly be deposited as a thin layer on the reaction cell wall. The total reaction of Eqs. (8) and (10) can be written as

$$ZnFe_2O_4 = ZnO \text{ (separated)} + 2/3Fe^{II}Fe_2^{III}O_4 + 1/6O_2 \qquad (11)$$
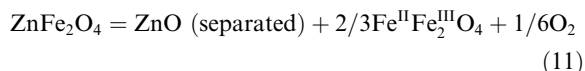
Eq. (8) is the apparent reaction equation representing that the O_2-releasing reaction proceeds at 1800 K in the air flowing condition.

Fig. 8 shows the phase diagram representing the stability field of the Fe_3O_4 phase in terms of temperature and O_2 partial pressure. The intersection of the dotted lines in Fig. 8 is the phase equilibrium point determined by the temperature and the p_{O_2} corresponding to those of the present experimental conditions ($p_{O_2} = 10^{-1.67}$ MPa, $T = 1800$ K). As can be seen here, the Fe_3O_4 phase is located in the fairly stable area, indicating that the Fe_3O_4 solid produced by the O_2-releasing reaction is stable even in air.
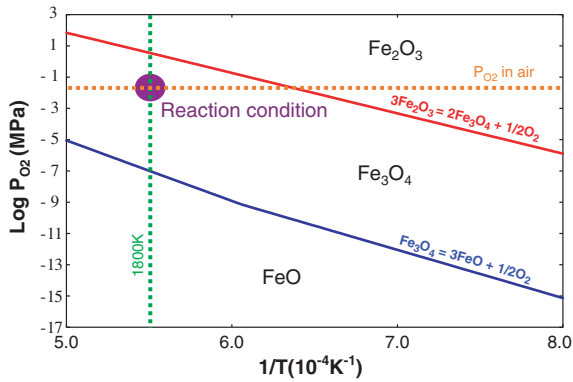

Fig. 7. (A) ZnO vapor pressure p_{ZnO} and (B) Zn vapor pressure p_{Zn} for decomposition of $ZnFe_2O_4$ at $p_{O_2} = 10^{-0.167}$ MPa.

Fig. 8. Phase diagram representing the stability field of the Fe_3O_4 phase in terms of temperature and O_2 partial pressure.

Fig. 9. Partial pressure of Zn vapor (p_{Zn}) with the temperature variation (at partial pressure of O_2 fixed in 2×10^{-5} MPa).

From the batch experiment where the $ZnFe_2O_4$ powder was contained in the sealed reaction cell filled with air, the gas chromatography for the product gas analysis showed that the O_2-releasing reaction of $ZnFe_2O_4$ took place even in the reaction cell sealed with air at the reaction rate of the O_2-releasing process. The reaction rate is sufficiently high to practically operate a solar reactor using a concentrated solar beam flux. The result on the batch experiment indicates that the 100% content of the O_2 gas bearing the fine ZnO particles will be obtained from the outlet line of the reactor without any quenching of the outlet gas, when the solar reactor is operated by dropping the Zn-ferrite powder into the solar reactor without blowing any gases.

3.3. Two-step water splitting with the $ZnFe_2O_4$/ ($ZnO + Fe_3O_4$)-system

The H_2 generation step of the $ZnFe_2O_4$/(ZnO + Fe_3O_4)-system have already been studied and reported elsewhere (Tamaura et al., 2002; Uehara et al., 2001); the H_2 generation reaction readily proceeds at around 1000 K with a nearly 100% yield according to the reaction of Eq. (4). Therefore, it seems to be possible that the solar H_2 can be generated by the two-step water-splitting process with the $ZnFe_2O_4$/(ZnO + Fe_3O_4)-system, in which the O_2-releasing step can be operated in air at 1800 K. The present authors have examined whether the Fe_3O_4 and the ZnO solids, which are separately produced by the O_2-releasing reaction of the $ZnFe_2O_4$ powder, can generate H_2 gas by Eq. (4). The Fe_3O_4 solid obtained after the O_2-releasing reaction was ground in a mortar and mixed with ZnO powder, which had been recovered from the reaction cell wall. The mole ratio of Fe_3O_4/ZnO was adjusted to 1.5. The H_2 generation experiment was carried out using the experimental set-up as shown in Fig. 3. The H_2 generation reaction took place with a nearly 100% yield (from XRD) at 1073 K,
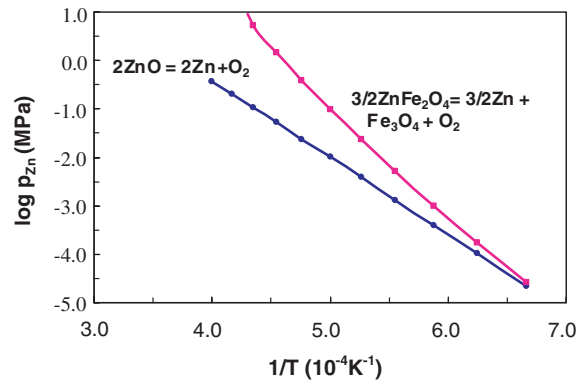
which was the same result previously reported (Tamaura et al., 2002; Uehara et al., 2001).

This system has several advantages compared to the Zn/ZnO system; the present system can more efficiently absorb the concentrated solar beam due to the black color of the Zn-ferrite (ZnO; white color) and the lower operation temperature (vaporizing temperature difference between Zn-ferrite and ZnO = 150 K) (Fig. 9).

4. Conclusion

Under flowing air-flow condition at 1800 K, the spinel-type compound of $ZnFe_2O_4$ (Zn-ferrite) released O_2 gas and decomposed into Fe_3O_4 ($= Fe^{II}Fe_2^{III}O_4$) and ZnO with a nearly 100% yield. Also, the ZnO phase was separately deposited as a thin layer on the surface of the reaction cell wall. The XRD measurement and chemical analysis showed that the O_2-releasing reaction can be described by $ZnFe_2O_4 = ZnO + 2/3Fe^{II}Fe_2^{III}O_4 + 1/6O_2$. The thin layer ZnO deposition seems to proceed via vaporization of the metal zinc according to $3/2ZnFe_2O_4 = 3/2Zn(g) + Fe_3O_4 + O_2$ and via rapid removal of the vaporized metal zinc by the oxidation with O_2 gas in air-flowing through the reaction cell. The O_2-releasing reaction of $ZnFe_2O_4$ takes place even in the reaction cell sealed with air (1800 K) at the reaction rate, which is sufficiently high to practically operate a solar reactor using a concentrated solar beam flux. This result gave the important conclusion that we will be able to operate the solar reactor having no window by suction and flowing air, and that we can successively feed the Zn-ferrite powders to the reactor by dropping them into the reactor without using any inert gases.

Also, the result of the batch experiment indicated that it seems to be possible to get 100% O_2 gas bearing the fine ZnO particles, which will be generated in the solar reactor, from the outlet line of the reactor without any quenching of the outlet gas.

The one cycle of the two-step water-splitting process with $ZnFe_2O_4/(ZnO + Fe_3O_4)$-system was demonstrated, indicating that the solar H_2 will be produced by repetition of these two steps for the $ZnFe_2O_4/(ZnO + Fe_3O_4)$-system using concentrated solar energy for the O_2-releasing step in air or maybe with a higher O_2 partial pressure. This is the first demonstration for the two-step water-splitting process whose O_2-releasing step can be operated in air at 1800 K with nearly 100% yield. The temperature of 1800 K is the lowest in air condition for the two-step of water-splitting process, which could be applied for the solar hydrogen production using concentrated solar energy.

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