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Thermochemical two-step water-splitting for hydrogen production using Fe-YSZ particles and a ceramic foam device

Nobuyuki Gokon [a,*], Tomoki Hasegawa [a], Shingo Takahashi [a], Tatsuya Kodama [a,b]

[a] *Graduate School of Science and Technology, Niigata University, 8050 Ikarashi 2-nocho, Nishi-ku, Niigata 950-2181, Japan*
[b] *Department of Chemistry and Chemical Engineering, Faculty of Engineering, Niigata University, 8050 Ikarashi 2-nocho, Nishi-ku, Niigata 950-2181, Japan*

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ABSTRACT

Fe_3O_4 supported on cubic yttria-stabilized zirconia (Fe_3O_4/*c*-YSZ) is proposed as a promising redox material for the production of hydrogen from water via a thermochemical two-step water-splitting cycle. In this study, the evolution of oxygen and hydrogen during the cyclic reaction was examined using Fe_3O_4/*c*-YSZ particles in order to demonstrate reproducible and stoichiometric oxygen/hydrogen production through a repeatable two-step reaction. Subsequently, a ceramic foam device coated with Fe_3O_4 and *c*-YSZ particles was prepared and examined as a thermochemical water-splitting device in a directly irradiated receiver/reactor hydrogen production system. The Fe_3O_4/*c*-YSZ system formed a Fe-containing YSZ (Fe-YSZ) by high-temperature reaction between Fe_3O_4 and the *c*-YSZ support at 1400 °C in an inert atmosphere. The reaction mechanism of the two-step water-splitting cycle is associated with the redox transition of Fe^{2+}–Fe^{3+} ions in the *c*-YSZ lattice. The Fe-YSZ particles exhibit good reproducibility for reaction with a hydrogen/oxygen ratio of approximately 2.0 throughout repeated cycles. The foam device coated with Fe-YSZ particles was also successful for continual hydrogen production through 32 repeated cycles. A 20–27% ferrite conversion was obtained using 10.5 wt% Fe_3O_4 loading over an irradiation period of 60 min.

1. Introduction

Solar thermochemical water-splitting, in which water is used as the chemical source for hydrogen production and high-temperature solar heat is used as the energy source, provides one of the most promising ways to realize hydrogen production from water [1]. Hydrogen production using solar energy has significant possibilities to eventually eliminate green house gas emissions, in addition to offering advantages such as transportability and long-term storage capability of solar energy [2]. Direct solar insolation is reflected and concentrated using sun-tracking mirrors called heliostats or collectors set on the ground, and the concentrated solar radiation is focused on a solar receiver or reactor [3–5]. The solar receivers/reactors achieve high temperatures above 1500 °C, making it thermochemically possible to produce hydrogen from water by a two-step water-splitting process.

The thermochemical two-step water-splitting cycle using an iron-oxide redox pair is originally proposed as follows [6]:

$$Fe_3O_4 = 3FeO + \tfrac{1}{2}O_2 \tag{1}$$

$$3FeO + H_2O = Fe_3O_4 + H_2 \tag{2}$$

The first thermal-reduction (T-R) step of Fe_3O_4 to FeO (Eq. (1)) is highly endothermic and thermodynamically favorable at high temperature above 2200 °C under a pressure of 1 bar, whereas the second water-decomposition (W-D) step (Eq. (2)) is slightly exothermic and is possible at temperatures below 700 °C. In order to lower the temperature of the T-R step for two-step water-splitting, solid solution redox systems of $M_xFe_{3-x}O_4$ (M denotes Mn, Co or Ni; $x = 0$–1), have been examined by many researchers [7–13].

However, the Fe_3O_4/FeO (or mixed iron oxides) undergo rapid deactivation of the iron oxide particles during the T-R process. In order to resolve this problem, the present authors have demonstrated repeatable two-step water-splitting using highly active ferrite particles supported on monoclinic ZrO_2 particles (ferrite/*m*-ZrO_2) [11–14]. The ZrO_2 support has good resistance to agglomeration or sintering at temperatures of 1000–1400 °C, because it has a higher melting point than ferrite. In addition, partially stabilized tetragonal zirconia (*t*-PSZ) and yttria-stabilized cubic zirconia (*c*-YSZ) can be used as a support. When YSZ was used as a support, $NiFe_2O_4$/YSZ showed activity and repeatability for the cyclic reaction [15]. It has been suggested that $NiFe_2O_4$ reacts with the support, and that a solid solution is formed. It is known that Fe ions are incorporated into the tetragonal- or

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[*] Corresponding author. Tel./fax: +81 25 262 7542.
E-mail address: ngokon@eng.niigata-u.ac.jp (N. Gokon).

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monoclinic-ZrO_2 crystal lattice by heat treatment at approximately 1600 °C in air, and the cubic ZrO_2 crystal structure is stabilized at room temperature [16]. We have proposed new reaction mechanisms for the two-step reaction of Fe_3O_4/t-PSZ and Fe_3O_4/c-YSZ particles [17–19]. For Fe_3O_4/c-YSZ, the following mechanism is proposed:

$$\tfrac{x}{3}\mathrm{Fe_3O_4} + \mathrm{Y}_y\mathrm{Zr}_{1-y}\mathrm{O}_{2-y/2} = \mathrm{Fe}_x^{2+}\mathrm{Y}_y\mathrm{Zr}_{1-y}\mathrm{O}_{2-y/2+x} + \tfrac{x}{6}\mathrm{O_2}$$
(first thermal reduction) (3)

$$\mathrm{Fe}_x^{2+}\mathrm{Y}_y\mathrm{Zr}_{1-y}\mathrm{O}_{2-y/2+x} + \tfrac{x}{2}\mathrm{H_2O} = \mathrm{Fe}_x^{3+}\mathrm{Y}_y\mathrm{Zr}_{1-y}\mathrm{O}_{2-y/2+3x/2} + \tfrac{x}{2}\mathrm{H_2}$$
(W-D step) (4)

$$\mathrm{Fe}_x^{3+}\mathrm{Y}_y\mathrm{Zr}_{1-y}\mathrm{O}_{2-y/2+3x/2} = \mathrm{Fe}_x^{2+}\mathrm{Y}_y\mathrm{Zr}_{1-y}\mathrm{O}_{2-y/2+x} + \tfrac{x}{4}\mathrm{O_2}$$
(T-R step) (5)

Fe^{2+}-YSZ is first formed by high-temperature reaction between the YSZ and Fe_3O_4 supported on the YSZ, at 1400 °C and in an inert atmosphere: when the y value is 0.15, the x value is determined to be 0.08 [18,19]. The advantages of the Fe-YSZ redox system are as follows. Melting of the FeO phase on the YSZ support during the high-temperature T-R step can be avoided; exfoliation of the reactant FeO crystals from the YSZ support does not occur in the present case, because the reactant Fe^{2+} ions remain in the YSZ lattice throughout the repeated two-step cycle. However, the stoichometry and repeatability of hydrogen/oxygen production for the Fe-containing YSZ (Fe-YSZ) system has scarcely been examined or demonstrated. In particular, the present paper is the first report of the release behavior of oxygen in the Fe-YSZ system.

In parallel to the basic research on redox working materials, many solar chemical receiver/absorber/reactors have been proposed, developed and demonstrated to realize solar two-step water-splitting with redox working materials [11,20–25]. The proposed solar chemical reactors are assumed to be combined with newly developed solar reflective towers or beam-down optics [26,27]. Thus, solar chemical reactors are equipped with transparent quartz window to allow the passage of concentrated solar radiation, and the direct heating of redox working materials such as ZrO_2- or YSZ-supported ferrites. In addition, a solar chemical reactor equipped with multi-channeled ceramic (siliconized and recrystallized SiC) honeycomb coated with active ferrite powder has been demonstrated for solar hydrogen production [23]. The ferrite-coated ceramic honeycomb, which is used as the solar receiver/absorber, is installed in the solar reactor, and concentrated solar irradiation is used for direct heating up to 1200 °C, with subsequent thermal reduction of the ferrites coated on the ceramic honeycomb while passing N_2 gas through it. In principle, this reactor is feasible for multi-cycling of the two-step water-splitting process using concentrated solar irradiation. When steam is flowed on and off through the honeycomb, hydrogen and oxygen can be repeatedly produced. However, if Fe_3O_4/YSZ particles are loaded and used as the redox material on a ceramic receiver/absorber, deactivation of the ferrite due to sintering at high temperature can be alleviated, because the reactant Fe^{2+} ions remain in the YSZ lattice [25]. This could realize the stable hydrogen production, or at least minimize fluctuant hydrogen production.

In the present study, reproducible and stoichometric oxygen/hydrogen production is demonstrated through a repeatable two-step reaction using YSZ-supported Fe_3O_4 particles. A water-splitting device was developed using a new reactive working material, where Fe_3O_4 and c-YSZ particles are loaded on a ceramic foam receiver/absorber. The hydrogen productivity of water-splitting devices with different amounts of Fe_3O_4/c-YSZ loading was tested for optimization of the Fe loading and for the demonstration of a long-life repeatable two-step reaction on a laboratory scale, using Xe-beam irradiation to simulate solar radiation.

2. Experimental

2.1. Preparation of YSZ-supported Fe_3O_4 powder

Particles of zirconia doped with 8 mol%Y_2O_3 (c-YSZ or YSZ; Tosoh TZ-8YS) with cubic crystal structure were used to support Fe_3O_4. The c-YSZ support was characterized as having purity of 99%, particle size smaller than 1 μm and a relative surface area of $7 \pm 2\ \mathrm{m^2\,g^{-1}}$.

YSZ-supported Fe_3O_4 (Fe_3O_4/YSZ) was prepared by coating the YSZ particles with Fe_3O_4 using a method involving the aerial oxidation of aqueous suspensions of Fe(II) hydroxide [18,19,28,29]. The YSZ powder was suspended in oxygen- and CO_2-free distilled water, while passing N_2 over the suspension for a few hours. $FeSO_4$ was then dissolved in the YSZ suspension. The pH of the solution was adjusted to 8.5 by adding $0.15\ \mathrm{mol\,dm^{-3}}$ NaOH solution, thus resulting in the formation of $Fe(OH)_2$. After heating the solution to 65 °C, air was bubbled into the suspension while the pH was continually maintained at 8.5 by adding $0.15\ \mathrm{mol\,dm^{-3}}$ NaOH solution. During aerial oxidation of the Fe(II) hydroxide suspension, the hydrolyzed metal $FeOH^+$ ions in the solution are adsorbed onto the substrate surface; these ions undergo oxidation in air, resulting in the deposition of Fe_3O_4. The Fe_3O_4 loading on the YSZ support was set to approximately 20 wt%. The solid product was collected by centrifuging at 4000 rpm (KS-4000, Kubota), washed with distilled water, then with acetone, and dried in vacuo at 60 °C for 1 day. The prepared Fe_3O_4/YSZ was then calcined at 900 °C in an N_2 atmosphere before performing the high-temperature cyclic reactions.

The powder samples were characterized using X-ray powder diffraction (XRD) with Cu Kα radiation (MX-Labo, MAC Science) for identification of the phases formed. In order to determine the loading of Fe_3O_4 on the YSZ support, the powder sample was dissolved in an aqueous HCl solution, and the resulting solution was analyzed using inductively coupled plasma-atomic emission spectrometry (ICP-AES; SPS-1500PV, Seiko Instruments).

2.2. H_2 and O_2 production using Fe_3O_4/c-YSZ powder

Approximately 1.0 g of Fe_3O_4/c-YSZ powder was packed into a platinum crucible (10 mm in diameter and 7 mm deep), and mounted on the ceramic bar in a quartz reaction chamber (SSA-E45, Ulvac-Rico) with an inner diameter of 45 mm (Fig. 1(a)). The powder sample was first heated to 1400 °C with a heating rate of $23.3\ ^\circ\mathrm{C\,s^{-1}}$ using an infrared furnace (RHL-VHT-E44, Ulvac-Rico), while passing N_2 gas (purity 99.999%) through the reactor at a flow rate of $1.0\ \mathrm{N\,dm^3\,min^{-1}}$, in order to perform the T-R step. The temperature of the Fe_3O_4/YSZ powder was controlled using an R-type thermocouple in contact with the platinum crucible. After heating the powder sample at a constant temperature of 1400 °C for 30 min, it was cooled to room temperature. An aliquot of the effluent gas from the reaction chamber was taken through a capillary tube and introduced to a residual gas analyzer mass spectrometer (RG-102P, Ulvac) to determine the composition of product gases and measure the production rates of oxygen. During the T-R step, variations of oxygen partial pressure in the product gases were measured with respect to reaction time, and the