



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

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## ABSTRACT

Fe<sub>3</sub>O<sub>4</sub> supported on cubic yttria-stabilized zirconia (Fe<sub>3</sub>O<sub>4</sub>/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<sub>3</sub>O<sub>4</sub>/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<sub>3</sub>O<sub>4</sub> 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<sub>3</sub>O<sub>4</sub>/c-YSZ system formed a Fe-containing YSZ (Fe-YSZ) by high-temperature reaction between Fe<sub>3</sub>O<sub>4</sub> 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<sup>2+</sup>–Fe<sup>3+</sup> 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<sub>3</sub>O<sub>4</sub> loading over an irradiation period of 60 min.

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## 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]:



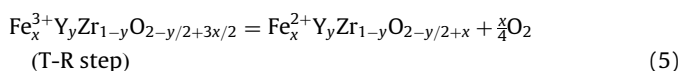
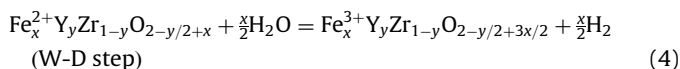
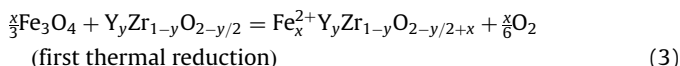
The first thermal-reduction (T-R) step of Fe<sub>3</sub>O<sub>4</sub> to FeO (Eq. (1)) is highly endothermic and thermodynamically favorable at high temperature above 2200 °C under a pressure of 1 bar, whereas the second water-decomposition (W-D) step (Eq. (2)) is slightly exothermic and is possible 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<sub>x</sub>Fe<sub>3–x</sub>O<sub>4</sub> (M denotes Mn, Co or Ni; x = 0–1), have been examined by many researchers [7–13].

However, the Fe<sub>3</sub>O<sub>4</sub>/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<sub>2</sub> particles (ferrite/*m*-ZrO<sub>2</sub>) [11–14]. The ZrO<sub>2</sub> 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<sub>2</sub>O<sub>4</sub>/YSZ showed activity and repeatability for the cyclic reaction [15]. It has been suggested that NiFe<sub>2</sub>O<sub>4</sub> 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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monoclinic-ZrO<sub>2</sub> crystal lattice by heat treatment at approximately 1600 °C in air, and the cubic ZrO<sub>2</sub> crystal structure is stabilized at room temperature [16]. We have proposed new reaction mechanisms for the two-step reaction of Fe<sub>3</sub>O<sub>4</sub>/t-PSZ and Fe<sub>3</sub>O<sub>4</sub>/c-YSZ particles [17–19]. For Fe<sub>3</sub>O<sub>4</sub>/c-YSZ, the following mechanism is proposed:



Fe<sup>2+</sup>-YSZ is first formed by high-temperature reaction between the YSZ and Fe<sub>3</sub>O<sub>4</sub> 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<sup>2+</sup> ions remain in the YSZ lattice throughout the repeated two-step cycle. However, the stoichiometry 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<sub>2</sub>- 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<sub>2</sub> 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<sub>3</sub>O<sub>4</sub>/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<sup>2+</sup> 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 stoichiometric oxygen/hydrogen production is demonstrated through a repeatable two-step reaction using YSZ-supported Fe<sub>3</sub>O<sub>4</sub> particles. A water-splitting device was developed using a new reactive working material, where Fe<sub>3</sub>O<sub>4</sub> and c-YSZ particles are loaded on a ceramic foam receiver/absorber. The hydrogen productivity of

water-splitting devices with different amounts of Fe<sub>3</sub>O<sub>4</sub>/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<sub>3</sub>O<sub>4</sub> powder

Particles of zirconia doped with 8 mol%Y<sub>2</sub>O<sub>3</sub> (c-YSZ or YSZ; Tosoh TZ-8YS) with cubic crystal structure were used to support Fe<sub>3</sub>O<sub>4</sub>. The c-YSZ support was characterized as having purity of 99%, particle size smaller than 1 μm and a relative surface area of 7 ± 2 m<sup>2</sup> g<sup>−1</sup>.

YSZ-supported Fe<sub>3</sub>O<sub>4</sub> (Fe<sub>3</sub>O<sub>4</sub>/YSZ) was prepared by coating the YSZ particles with Fe<sub>3</sub>O<sub>4</sub> 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<sub>2</sub>-free distilled water, while passing N<sub>2</sub> over the suspension for a few hours. FeSO<sub>4</sub> was then dissolved in the YSZ suspension. The pH of the solution was adjusted to 8.5 by adding 0.15 mol dm<sup>−3</sup> NaOH solution, thus resulting in the formation of Fe(OH)<sub>2</sub>. 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 mol dm<sup>−3</sup> NaOH solution. During aerial oxidation of the Fe(II) hydroxide suspension, the hydrolyzed metal FeOH<sup>+</sup> ions in the solution are adsorbed onto the substrate surface; these ions undergo oxidation in air, resulting in the deposition of Fe<sub>3</sub>O<sub>4</sub>. The Fe<sub>3</sub>O<sub>4</sub> 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<sub>3</sub>O<sub>4</sub>/YSZ was then calcined at 900 °C in an N<sub>2</sub> 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<sub>3</sub>O<sub>4</sub> 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<sub>2</sub> and O<sub>2</sub> production using Fe<sub>3</sub>O<sub>4</sub>/c-YSZ powder

Approximately 1.0 g of Fe<sub>3</sub>O<sub>4</sub>/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 °C s<sup>−1</sup> using an infrared furnace (RHL-VHT-E44, Ulvac-Rico), while passing N<sub>2</sub> gas (purity 99.999%) through the reactor at a flow rate of 1.0 N dm<sup>3</sup> min<sup>−1</sup>, in order to perform the T-R step. The temperature of the Fe<sub>3</sub>O<sub>4</sub>/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

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