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# Ferrite/zirconia-coated foam device prepared by spin coating for solar demonstration of thermochemical water-splitting

Nobuyuki Gokon<sup>a,b,c,\*</sup>, Tatsuya Kodama<sup>b,c</sup>, Nobuki Imaizumi<sup>c</sup>, Jun Umeda<sup>c</sup>, Taebeom Seo<sup>d</sup>

<sup>a</sup>Center for Transdisciplinary Research, Niigata University, 8050 Ikarashi 2-nocho, Nishi-ku, Niigata 950-2181, Japan

<sup>b</sup>Department of Chemistry and Chemical Engineering, Faculty of Engineering, Niigata University, 8050 Ikarashi 2-nocho, Nishi-ku, Niigata 950-2181, Japan

<sup>c</sup>Graduate School of Science and Technology, Niigata University, 8050 Ikarashi 2-nocho, Nishi-ku, Niigata 950-2181, Japan

<sup>d</sup>Department of Mechanical Engineering, Inha University, #253 Yanghyundong, Namgu, Incheon 402-751, Republic of Korea

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## ABSTRACT

A Ferrite/zirconia foam device in which reticulated ceramic foam was coated with zirconia-supported  $\text{Fe}_3\text{O}_4$  or  $\text{NiFe}_2\text{O}_4$  as a reactive material was prepared by a spin-coating method. The spin-coating method can shorten the preparation period and reduce the coating process as compared to the previous wash-coating method. The foam devices were examined for hydrogen productivity and cyclic reactivity in thermochemical two-step water-splitting. The reactivity of these foam devices were studied for the thermal reduction of ferrite on a laboratory scale using a sun simulator to simulate concentrated solar radiation, while the thermally reduced foam devices were reacted with steam in another quartz reactor under homogeneous heating in an infrared furnace. The most reactive foam device,  $\text{NiFe}_2\text{O}_4/\text{m-ZrO}_2/\text{MPSZ}$ , was tested for successive two-step water-splitting in a windowed single reactor using solar-simulated Xe-beam irradiation with a power input of 0.4–0.7  $\text{kW}_{\text{th}}$ . The production of hydrogen continued successfully in the 20 cycles that were demonstrated using the  $\text{NiFe}_2\text{O}_4/\text{m-ZrO}_2/\text{MPSZ}$  foam device. The  $\text{NiFe}_2\text{O}_4/\text{m-ZrO}_2/\text{MPSZ}$  foam device produced hydrogen at a rate of 1.1–4.6  $\text{cm}^3$  per gram of device through 20 cycles and reached a maximum ferrite conversion of 60%.

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## 1. Introduction

Thermochemical water-splitting using concentrated solar energy has attracted interest as a renewable method for producing hydrogen from water [1–5]. The direct thermal dissociation of water requires temperatures above 2500 °C to achieve a reasonable degree of dissociation; further, it requires an effective technique for the separation of  $\text{H}_2$  and  $\text{O}_2$  to avoid their explosive recombination. In addition, the requisite high temperatures restrict the materials that can be used in the

construction of a reactor, which makes it difficult to design a reactor that can perform the thermal dissociation of water. Thermochemical water-splitting is divided into several steps that allow the operation to proceed at relatively moderate upper temperatures and without the problem of  $\text{H}_2/\text{O}_2$  separation. The most interesting approach involves a two-step cycle based on metal-oxide redox reactions.

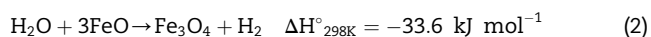
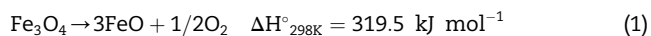
This two-step water-splitting thermochemical cycle using a redox pair of  $\text{Fe}_3\text{O}_4/\text{FeO}$  was first proposed by Nakamura [6] and proceeds as follows:

\* Corresponding author. Center for Transdisciplinary Research, Niigata University, 8050 Ikarashi 2-nocho, Nishi-ku, Niigata 950-2181, Japan. Tel./fax: +81 25 262 6820.

E-mail address: [ngokon@eng.niigata-u.ac.jp](mailto:ngokon@eng.niigata-u.ac.jp) (N. Gokon).

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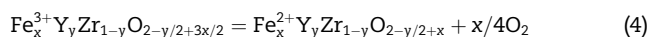
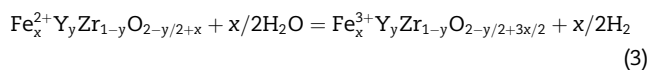


The first step, the high temperature thermal reduction (T-R) of  $\text{Fe}_3\text{O}_4$ , is highly endothermic, whereas the second step, the low-temperature water-decomposition (W-D) by FeO, is slightly exothermic. Several oxide pairs of multi-valent metals [7–11] have also been developed and evaluated as redox materials. Mixed solid solutions of  $(\text{Fe}_{1-x}\text{M}_x)_3\text{O}_4/(\text{Fe}_{1-x}\text{M}_x)\text{O}$  between the redox system of  $\text{Fe}_3\text{O}_4/\text{FeO}$  and  $\text{M}_3\text{O}_4/\text{MO}$  are expected to decrease the reaction temperatures relative to those used in the  $\text{Fe}_3\text{O}_4/\text{FeO}$  system. The possibility exists of thermodynamically combining good  $\text{H}_2$  yields in the  $\text{Fe}_3\text{O}_4/\text{FeO}$  system with the low reduction temperature of an  $\text{M}_3\text{O}_4/\text{MO}$  ( $\text{M} = \text{Mn}, \text{Co}, \text{Mg}$ ) system [1,7].

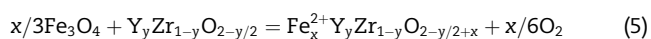
One of the problems presented by the  $(\text{Fe}_{1-x}\text{M}_x)_3\text{O}_4/(\text{Fe}_{1-x}\text{M}_x)\text{O}$  redox pair as the reactive working material, however, is the rapid deactivation of the iron oxide particles during the cyclic reaction. This takes place because of the high-temperature melting and sintering of the iron oxide particles, which results in a rapid decrease in the iron oxide surface area.

The present authors successfully demonstrated a repeatable two-step water-splitting cycle using  $\text{Fe}_3\text{O}_4$  or other metal-doped iron oxides (ferrites) supported on monoclinic  $\text{ZrO}_2$  ( $m\text{-ZrO}_2$ ) [12–16]. The  $\text{ZrO}_2$  support alleviated the coagulating or sintering of the solid reactant of the iron oxides, so the two-step reaction could be repeated with a relatively strong degree of activity in a temperature range of 1000–1400 °C. The  $m\text{-ZrO}_2$  support is thus a chemically inert material for a repeatable two-step water-splitting cycle using  $\text{Fe}_3\text{O}_4$  or ferrites at high temperatures.

The present authors also demonstrated that a new redox reaction occurs on  $\text{Fe}_3\text{O}_4$  supported on yttrium-stabilized cubic zirconia ( $\text{Fe}_3\text{O}_4/c\text{-YSZ}$ ) [17–19]. When  $c\text{-YSZ}$  particles were used as a support for  $\text{Fe}_3\text{O}_4$ , the XRD studies indicated that the new cyclic reaction proceeds as follows:



where  $y \geq 0.15$ .  $\text{Fe}^{2+}\text{-YSZ}$  is first formed by the high-temperature reaction between the YSZ and the  $\text{Fe}_3\text{O}_4$  supported on the YSZ, at a temperature above 1400 °C and in an inert atmosphere:



When  $\text{Fe}_3\text{O}_4/c\text{-YSZ}$  ( $y = 0.15$ ) is thermally reduced at 1400 °C, the  $x$  value as estimated by chemical wet analysis is 0.08 [18,19]. In the subsequent hydrolysis reaction, the formed  $\text{Fe}^{2+}\text{-YSZ}$  is reacted with steam at 1000 °C to generate hydrogen and is oxidized to  $\text{Fe}^{3+}\text{-YSZ}$ . The repeatability and stoichiometry of hydrogen/oxygen production has been examined using T-R step temperatures of 1450–1600 °C [20].

Different concepts regarding solar reactor-receivers that use ferrites or mixed iron oxides have been proposed and demonstrated by several research groups [5,21–40]. These

proposed solar chemical reactors are assumed to be combined with developed solar reflective towers, parabolic dishes, or beam-down optics. Thus, solar reactors-receivers are equipped with a transparent quartz window to allow the direct heating of redox working materials by the passage of concentrated solar radiation, which yields high temperatures at a reaction site.

The present authors have developed ceramic foam devices whose foam matrix is made of MgO-partially stabilized zirconia (MPSZ); the foam matrix is coated with zirconia and ferrite particles (ferrite/zirconia/MPSZ foam device). The advantage of using a ceramic foam device is that it makes possible the effective absorption of light irradiation due to the large specific surface area. Multicycling of the two-step water-splitting process have been demonstrated using these foam devices [37–40]. When these foam devices were prepared previously using a wash-coating method, however, a great deal of time was required for the coating processes with the zirconia and ferrite particles, including a number of calcinations at a high temperature of 1000 °C (for example, 40–50 coating steps with  $\text{NiFe}_2\text{O}_4/m\text{-ZrO}_2$  particles and same number of calcinations [39]).

In the present study, the authors address a method of preparation of  $\text{NiFe}_2\text{O}_4/m\text{-ZrO}_2/\text{MPSZ}$  and  $\text{Fe}_3\text{O}_4/c\text{-YSZ}/\text{MPSZ}$  foam devices that can shorten the preparation period and reduce the coating process as compared to the previous preparation method. The water-splitting foam devices are prepared using a new method of spin coating. The activity and reactivity of the water-splitting foam devices are first examined using solar-simulated Xe-light irradiation for the T-R step and then using another quartz reactor and an electric furnace for the subsequent W-D step. Most reactive foam device of  $\text{NiFe}_2\text{O}_4/m\text{-ZrO}_2/\text{MPSZ}$  was tested in a windowed single reactor for successive two-step water-splitting under Xe-beam irradiation to simulate solar radiation. The hydrogen productivity and reactivity of the  $\text{NiFe}_2\text{O}_4/m\text{-ZrO}_2/\text{MPSZ}$  foam devices were evaluated.

## 2. Experimental procedure

### 2.1. Synthesis of ferrite/zirconia particles

Zirconia-supported ferrites were prepared as follows. Monoclinic zirconia ( $m\text{-ZrO}_2$ ), or cubic yttrium-stabilized zirconia ( $c\text{-YSZ}$ ) doped with 8 mol%  $\text{-Y}_2\text{O}_3$  ( $(\text{ZrO}_2)_{1-z}(\text{Y}_2\text{O}_3)_z$  at  $z = 0.08$ ), were used as supports for  $\text{Fe}_3\text{O}_4$  or  $\text{NiFe}_2\text{O}_4$ . The  $m\text{-ZrO}_2$  support had a purity of 98%, a particle size smaller than 1  $\mu\text{m}$ , and a Brunauer–Emmett–Teller (BET) relative surface area of 13  $\text{m}^2 \text{g}^{-1}$ . The  $c\text{-YSZ}$  support had a purity of 99%, a particle size smaller than 1  $\mu\text{m}$ , and a BET relative surface area of  $7 \pm 2 \text{ m}^2 \text{g}^{-1}$ . The zirconia-supported ferrites were prepared by coating the  $m\text{-ZrO}_2$  or  $c\text{-YSZ}$  particles with the ferrite ( $\text{Fe}_3\text{O}_4$  or  $\text{NiFe}_2\text{O}_4$ ), using the aerial oxidation method of aqueous suspension of the Fe(II) hydroxide with/without Ni(II) hydroxide [12–20]. The loadings of  $\text{Fe}_3\text{O}_4$  or  $\text{NiFe}_2\text{O}_4$  in the zirconia-supported ferrites were about 20% on a weight basis. The zirconia-supported ferrites ( $\text{Fe}_3\text{O}_4/m\text{-ZrO}_2$ ,  $\text{Fe}_3\text{O}_4/c\text{-YSZ}$ ,  $\text{NiFe}_2\text{O}_4/m\text{-ZrO}_2$  and  $\text{NiFe}_2\text{O}_4/c\text{-YSZ}$ ) were calcined at 900 °C in

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