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Reduction reactivity of CeO_2–ZrO_2 oxide under high O_2 partial pressure in two-step water splitting process

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Abstract

The O_2-releasing reaction under the air with the reactive ceramics of CeO_2–ZrO_2 oxides which can be applied to solar hydrogen production via a two-step water splitting cycle using concentrated solar thermal energy was investigated. CeO_2–ZrO_2 oxides were synthesized by polymerized complex method at different Ce:Zr molar ratio. The solid solubility of ZrO_2 in fluorite structure of CeO_2 was in good agreement with the initial content of Zr ions at the preparation in CeO_2–ZrO_2 oxide. The O_2-releasing reaction in air with CeO_2–ZrO_2 oxides was studied. Different solid solubility (0%, 10%, 20%, 30%) of ZrO_2 in CeO_2 were examined. The amount of O_2 gas evolved in the reaction with $Ce_{1-x}Zr_xO_2$ ($0 \leqslant x \leqslant 0.3$) solid solutions was more than that with CeO_2, and the largest yield of 2.9 cm^3/g was exhibited at $x = 0.2$ ($Ce_{0.8}Zr_{0.2}O_2$) for an O_2 release at 1500 °C in air. The reduced cerium ion in $Ce_{0.8}Zr_{0.2}O_2$ was about 11%, which is seven times higher than that with CeO_2. The optical absorption and luminescence spectra of the CeO_2–ZrO_2 oxide obtained before and after the O_2-releasing reaction suggest that the reduction of Ce^{4+} with formation of oxygen defect in the air. The enhancement of the O_2-releasing reaction with CeO_2–ZrO_2 oxide is found to be caused by an introduction of Zr^{4+}, which has smaller ionic radius than Ce^{3+} or Ce^{4+}, in the fluorite structure.

Keywords: Concentrated solar heat; Hydrogen production; Two-step water splitting reaction; Cerium oxides; O_2 release in air

1. Introduction

Hydrogen is one of the promising clean alternative fuels which is expected to be widely utilized for a fuel cell system. Hydrogen production by concentrated solar thermal energy via a two-step water splitting reaction with a metal oxide or double metals oxide has been proposed in the field of solar thermochemistry. Hydrogen production using an iron oxide redox system (Fe_3O_4/FeO) with a two-step water-splitting reaction by concentrated solar thermal energy has been proposed by Nakamura (1977). The Fe_3O_4/FeO redox system has been experimentally investigated in a solar furnace by Sibieude et al. and the thermal reduction of Fe_3O_4 to FeO above 1700 °C has been confirmed (Sibieude et al., 1982). Screening and thermodynamic analysis on other metal oxide process such as Mn_3O_4/MnO, Co_3O_4/CoO, In_2O_3/In and SnO_2/Sn has been conducted for a redox pair of a two-step water-splitting cycle (Sibieude et al., 1982; Lundberg, 1993; Steinfeld et al., 1998; Abanades et al., 2006; Meredig and Wolverton, 2009). The production of Zn and O_2 from ZnO in a high temperature solar decomposition and solar electrothermal process have been studied theoretically and experimentally (Fletcher and Norin, 1983; Fletcher et al., 1985; Parks et al., 1988; Palumbo and Fletcher, 1988; Palumbo et al., 1998; Steinfeld et al., 1998). Another ZnO/Zn redox system has been considered as one of the

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most favorable candidates for the two-step water-splitting cycle (Steinfeld, 2002). A maximum energy conversion efficiency of 29% is indicated on the closed cyclic process when using a solar cavity-receiver operated at around 2000 °C. The economic feasibility of the proposed solar process is strongly dependent on the development of an effective Zn/O_2 separation technique. A solar chemical reactor for the thermal dissociation of ZnO was fabricated and tested in a high-flux solar irradiation based on the chemical thermodynamic and kinetic constrains of the ZnO dissociation reaction (Haueter et al., 1999; Müller et al., 2006; Müller and Steinfeld, 2007). However, in this system, the condensation of zinc vapor is the difficult to achieve in the presence of the O_2 gas generated by the decomposition reaction of ZnO.

Subsequently, iron-based oxides of ferrites which are substituted a part of iron ion in Fe_3O_4 from another metal ion (AFe_2O_4 (A: metal ion) with a spinel-type structure) have been investigated in a two-step water splitting reaction to progress at lower O_2-releasing reaction temperature than that of Fe_3O_4. Tamaura et al. were the first to report production of oxygen and hydrogen from (Ni, Mn)-ferrite ($Ni_{0.5}Mn_{0.5}Fe_2O_4$) in a two-step water-splitting reaction by concentrated solar thermal energy (Tamaura et al., 1995); however, the amount of O_2 generated in the O_2-releasing reaction was small because of the low generation rate of the oxygen defects. Furthermore, two-step water-splitting reactions involving various types of ferrite compounds have been widely studied with the aim of efficient hydrogen production (Kaneko et al., 2002, 2005, 2006; Allendorf et al., 2006, 2008). However, it was found that the iron oxide, which melted at those high temperatures, constituted a significant impediment to an efficient H_2-generation reaction. Since the reduced ferrite powder is sintered and partially melted in this reduction step, the reactivity of the product with the steam generated during the water-splitting reaction is reduced by smaller than 90%.

The ferrite compounds combined with yttria stabilized zirconia (YSZ) or ZrO_2 for a two-step water-splitting reaction have been considered to inhibit the sintering of ferrite compound (Ishihara et al., 2005, 2006, 2008a,b; Kodama et al., 2005, 2008; Gokon et al., 2006). The YSZ and ZrO_2 are well known as a material having high thermal stability, and their melting points are respectively 2500 and 2680 °C. However, the hydrogen production yield per weight of sample was relatively low, since the loading amount of ferrite into YSZ or ZrO_2 was limited. Abanades have developed the CeO_2/Ce_2O_3 redox system for a two-step water-splitting reaction without melting and sintering (Abanades and Flamant, 2006). The melting point of CeO_2 with high thermal stability is 1950 °C. The O_2-releasing and H_2-generation reactions proceeded stably at 2000 and 400–600 °C with the CeO_2/Ce_2O_3 system, respectively. The two-step water-splitting reaction of the thermochemical system consisting of the CeO_2/Ce_2O_3 pair can be represented as follows:

$$\begin{aligned} O_2\text{-releasing step}: & 2CeO_2 + \text{thermal energy} = Ce_2O_3 \\ & + 1/2O_2(g), \qquad (1) \\ & (\Delta H: 387\,\text{kJ at } 1500\,^\circ C) \\ H_2\text{-generating step}: & Ce_2O_3 + H_2O(g) = 2CeO_2 + H_2(g), \qquad (2) \\ & (\Delta H: -128\,\text{kJ at } 1000\,^\circ C) \end{aligned}$$

where thermal energy is supplied by a concentrated solar beam for solar H_2 production. Hydrogen and oxygen are obtained by alternately repeating these two steps in a two-step water-splitting cycle.

In the O_2-releasing reaction, metal oxide can absorb concentrated solar thermal energy and store it in the form of internal energy of oxide. The high-flux energy (1000–3000 kW/m^2) should be sufficiently absorbed in the O_2-releasing reaction at the high temperatures (above 700 °C) for effective utilization of solar thermal energy (Fletcher and Moen, 1977). It is necessary to lower the temperature for the O_2-releasing reaction with CeO_2/Ce_2O_3 system for large solar energy conversion efficiency. The solid solution of CeO_2-transition metal (Mn, Fe or Ni) oxide (Kaneko et al., 2007a, 2008; Kaneko and Tamaura, 2009), and CeO_2–ZrO_2 solid solution (Taku et al., 2007, submitted for publication) have been investigated at the O_2-releasing reaction temperature around 1500 °C.

On the other hand, the beam-down solar concentrating system (Hasuike et al., 2006) and a rotary-type solar reactor (Kaneko et al., 2007b) was developed to produce solar H_2 feasibly with a utilization of the two-step water-splitting reaction. In a practical application of the two-step water-splitting reaction with absorbing concentrated solar thermal energy, it is necessary to be accomplished the progress of the O_2-releasing reaction in a high O_2 partial pressure such as the air in addition to the progress at lower temperatures than operating temperature limit of the reactor. Since the O_2 partial pressure of surroundings near the material vigorously evolving the O_2 gas becomes higher and higher at a reaction temperature with an irradiation of concentrated solar beam, the O_2-releasing reaction needs to proceed immediately at a high O_2 partial pressure in order to continue the O_2 gas evolution by absorption of concentrated solar heat. The three aspects mentioned later are pointed out as advantages of the O_2-releasing reaction in air. (1) The energy loss carried away by an inert carrier gas and the cost for flow of an inert gas are reduced. (2) It is unnecessary to separate and recover an inert gas from mixture of inert carrier gas and evolved O_2 gas. (3) The quartz glass window for irradiation of concentrated solar beam is unnecessary.

However, many of ferrite compounds melt and sinter in the O_2-releasing reaction at the temperature around 1600 °C, where the reaction proceeds under the air. So far, it was reported that the O_2-releasing reaction can proceed in the air with only $NiFeO_4$ (Kaneko et al., 2003, 2004) and $ZnFe_2O_4$ system (Tamaura and Kaneko, 2005). The O_2-releasing reaction with $NiFeO_4$ or $ZnFe_2O_4$ cannot proceed after the subsequent H_2-generation reaction, since