



ELSEVIER

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

ScienceDirect

journal homepage: [www.elsevier.com/locate/ijhydene](http://www.elsevier.com/locate/ijhydene)

# Iron precipitated onto ceria-zirconia nanoparticle mixtures for the production of hydrogen via two-step thermochemical water splitting

Samantha J. Roberts <sup>a</sup>, Nathan G. Carr <sup>a</sup>, Jonathan McLaughlin <sup>a,b</sup>,  
Helena E. Hagelin-Weaver <sup>a,\*</sup>

<sup>a</sup> Department of Chemical Engineering, University of Florida, P.O. Box 116005, Gainesville, FL 32611, United States

<sup>b</sup> Department of Chemical Engineering, Loughborough University, Loughborough, Leicestershire, United Kingdom

## ARTICLE INFO

### Article history:

Received 25 July 2017

Received in revised form

1 May 2018

Accepted 7 May 2018

Available online xxx

### Keywords:

Thermochemical water-splitting

Hydrogen production

Iron oxide

Zirconia and ceria nanoparticles

Temperature programmed

reduction (TPR)

X-ray diffraction (XRD)

## ABSTRACT

Several novel materials were synthesized by precipitating iron oxide (using the previously optimized 10% Fe loading by weight) onto mixtures of nanoparticle zirconia and ceria to investigate the effects of adding CeO<sub>2</sub> to FeO<sub>x</sub>/ZrO<sub>2</sub> materials in the thermochemical water splitting reaction. At water splitting temperatures of 1000 °C (after thermal reduction at 1450 °C), the stability of the CeO<sub>2</sub>-containing materials was lower than for the FeO<sub>x</sub>/ZrO<sub>2</sub> material, and there was no advantage to adding CeO<sub>2</sub> to the FeO<sub>x</sub>/ZrO<sub>2</sub> material. However, when operating at a water splitting (WS) temperature of 1200 °C, the stability increased and the hydrogen production was significantly higher over most materials compared with a water splitting temperature of 1000 °C. At a WS temperature of 1200 °C the FeO<sub>x</sub>/Zr<sub>75</sub>Ce<sub>25</sub>O<sub>2</sub> (75% Zr<sub>75</sub>O<sub>2</sub> and 25% CeO<sub>2</sub> by weight) and FeO<sub>x</sub>/Zr<sub>50</sub>Ce<sub>50</sub>O<sub>2</sub> materials performed slightly better than the FeO<sub>x</sub>/ZrO<sub>2</sub> material, and X-ray photoelectron spectroscopy data revealed that the surface concentration of iron is less important compared with water splitting at 1000 °C. The temperature programmed reduction data indicated that the FeO<sub>x</sub>-CeO<sub>2</sub> interactions were weaker compared with FeO<sub>x</sub>-ZrO<sub>2</sub> interactions, since the FeO<sub>x</sub> reduction occurred at lower temperatures for the CeO<sub>2</sub>-containing materials. The weaker interactions can explain why the stability was lower for the materials containing CeO<sub>2</sub> (sintering of FeO<sub>x</sub> was likely more pronounced). The X-ray diffraction data revealed that ZrO<sub>2</sub>-CeO<sub>2</sub> solid solutions formed after activation at 1450 °C and lattice volume calculations indicated that iron did incorporate into the ZrO<sub>2</sub>-CeO<sub>2</sub> matrices. More incorporation was observed after water-splitting at 1200 °C compared with a lower temperature (1000 °C), and likely explains why the materials were more stable during water-splitting at 1200 °C.

© 2018 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

## Introduction

The production of hydrogen for use as a renewable energy carrier is an attractive pathway to help mitigate the negative

environmental impacts of fossil fuels [1]. Renewable hydrogen can be produced through the use of concentrated solar energy by a two-step solar thermochemical water splitting cycle. Solar energy is a largely available and abundant renewable resource and can provide the energy required to dissociate

\* Corresponding author.

E-mail address: [hweaver@che.ufl.edu](mailto:hweaver@che.ufl.edu) (H.E. Hagelin-Weaver).

<https://doi.org/10.1016/j.ijhydene.2018.05.043>

0360-3199/© 2018 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

water into its constituent parts, hydrogen (H<sub>2</sub>) and oxygen (O<sub>2</sub>). Using solar thermochemical cycles to produce hydrogen also has potential benefits of presenting higher energy conversion efficiencies than water electrolysis [2].

Several solar thermochemical water splitting cycles are based on a two-step process that utilizes a metal oxide to aid in water decomposition [1,3]. Direct water splitting, without the use of a metal oxide, is thermodynamically unfavorable and requires operating temperatures in excess of 2000 °C and is therefore incredibly energy intensive [3,4], in addition to resulting in highly explosive mixtures. In contrast, a two-step metal oxide process can significantly reduce the maximum operating temperature, and also allows for separation of H<sub>2</sub> and O<sub>2</sub> in the two steps. For a thermochemical cycle using iron oxide as the primary reactive material [5–7], the cycle can be represented by the following chemical reactions:

$3\text{FeO} + \text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2$	(water splitting, WS)	Step 1
$\text{Fe}_3\text{O}_4 \rightarrow 3\text{FeO} + \frac{1}{2}\text{O}_2$	(metal oxide regeneration/ thermal reduction, TR)	Step 2

In the first exothermic step (water splitting), a reduced metal oxide (oxygen-deficient material) reacts with steam to produce hydrogen. In the second, endothermic step, the oxidized material is heated until oxygen desorbs from the material and the reduced metal oxide is regenerated. The material is then cycled back to a WS step and the TR is repeated for multiple cycles. Inert gas flows over the material during the thermal reduction to reduce the partial pressure of O<sub>2</sub> near the material while also preventing immediate reoxidation of the oxygen-deficient material [8]. Since the reduced metal oxide is regenerated, the net reaction is the dissociation of water to produce hydrogen and oxygen in two separate steps.

Multiple metal oxide pairs can be used for this type of thermochemical process and a lot of effort has been devoted to cycles based on iron oxide (Fe<sub>3</sub>O<sub>4</sub>/FeO) and cerium dioxide (ceria, CeO<sub>2</sub>/CeO<sub>2-δ</sub>), although more complex mixed oxides, such as perovskites have also been used as the active metal oxide materials [1,9–34]. Oxide pairs, such as Fe<sub>3</sub>O<sub>4</sub>/FeO and CeO<sub>2</sub>/CeO<sub>2-δ</sub>, are particularly interesting as they are non-volatile and avoid recombination of gas phase products or immediate reoxidation of the reactive material in gas phase. The iron oxide cycle has favorable thermodynamics and multiple redox states available, but suffers from a low melting point of the reduced oxide (in a pure FeO<sub>x</sub> cycle, FeO melts before all the Fe<sub>3</sub>O<sub>4</sub> is reduced). Therefore, iron oxide must be deposited onto a high temperature, thermal shock resistant support, such as zirconia or stabilized-zirconia [35–39], to avoid detrimental melting, agglomeration and sintering. However, this introduces a large amount of inert material and, thus, reduces the thermal efficiency of the material. The iron oxide can also be doped with a component that reduces the temperature required in the thermal reduction step which can lead to further improvements [40–48]. The ceria-based cycles benefit from the ability to cycle between Ce<sup>4+</sup> and Ce<sup>3+</sup> oxidation states without structural collapse [33]. Unfortunately, the extent of reduction for ceria (i.e. the fraction of

CeO<sub>2</sub> which is reduced to Ce<sub>2</sub>O<sub>3</sub>) is small at typical operating temperatures (approximately 1450 °C maximum), as temperatures closer to 2000 °C are required for a significant extent of reduction [33]. Since reducing bulk ceria is difficult at the temperatures of interest, the ceria surface is the primary region where reduction occurs [49]. To improve the reduction yield and properties of ceria, a number of dopants have been investigated [50–62]. Of particular interest is zirconium, as both experimental [62–65] and theoretical studies [66–68] reveal that this dopant can improve the oxygen storage capacity and reduction properties of ceria. By introducing Zr<sup>4+</sup> into the CeO<sub>2</sub> structure, the bulk reduction of ceria is favored [62,66] allowing for a higher extent of reduction at an operating temperature of 1450 °C, and therefore a higher hydrogen production compared with pure ceria [69–76]. The smaller size of the zirconium cations can also help to alleviate strain during the cycling between Ce<sup>4+</sup> and Ce<sup>3+</sup> oxidation states, and detrimental sintering can also potentially be inhibited due to zirconia's high thermal resistance. However, since zirconia is an inert material, there is a limit to the benefits of zirconia addition and there exists an optimal balance between the increased reduction yields from Zr<sup>4+</sup> addition and amount of reducible Ce<sup>4+</sup> in the solid solution [71,73,75].

A potential development to the iron oxide water splitting cycle would be to decrease the amount of inert material present, perhaps by replacing at least part of the inert support material with an active material, such as ceria. While iron oxide and ceria combinations have been investigated in the water splitting reaction [54,60,77,78] (or CO<sub>2</sub> splitting [79]), the effects of adding iron to ceria-zirconia mixtures have only been tested in the thermochemical splitting of CO<sub>2</sub> [80]. Therefore, in this investigation novel iron-ceria-zirconia materials were examined for the production of hydrogen via thermochemical water splitting. More specifically, the objectives of this study were to examine the effects of ceria concentration in iron-ceria-zirconia mixed oxide materials in the water-splitting reaction and determine if the hydrogen production of these systems is enhanced compared to the iron-zirconia and iron-ceria materials.

## Experimental

### Material synthesis

The reactive materials were synthesized by mixing commercially available nanoparticle powders of zirconia (ZrO<sub>2</sub>) and ceria (CeO<sub>2</sub>) (Nanostructured & Amorphous Materials Inc.) and depositing iron onto the solid mixture using a precipitation method reported previously [39]. In the precipitation method, an aqueous solution of metal nitrate precursor (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) (Alfa Aesar, 98.0–101.0%) was added to an aqueous dispersion of the support mixture. The support mixtures are labeled according to the weight percent (wt%) of ZrO<sub>2</sub> and CeO<sub>2</sub>, i.e. y wt% ZrO<sub>2</sub> and (100–y) wt% CeO<sub>2</sub> or Zr<sub>y</sub>Ce<sub>(100–y)</sub>O<sub>2</sub>. Therefore, Zr<sub>25</sub>Ce<sub>75</sub>O<sub>2</sub> corresponds to a material prepared using a 25:75 mixture by weight of ZrO<sub>2</sub> and CeO<sub>2</sub>. Each ceria-zirconia mixture was prepared to have a 10 wt percent iron loading based on the optimal iron loading determined previously [39]. The resulting dispersion was

Download English Version:

<https://daneshyari.com/en/article/7705404>

Download Persian Version:

<https://daneshyari.com/article/7705404>

[Daneshyari.com](https://daneshyari.com)