

# Influences of morphology and structure on Mn-based multi-step thermochemical H<sub>2</sub>O splitting cycle

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## Abstract

The multi-step thermochemical water splitting cycle based on MnFe<sub>2</sub>O<sub>4</sub>–Na<sub>2</sub>CO<sub>3</sub> has emerged as an attractive process due to its relatively low reaction temperature. The main challenges are how to enhance its H<sub>2</sub>/O<sub>2</sub> release rates and capacities. Herein, a series of MnFe<sub>2</sub>O<sub>4</sub> with different microstructures synthesized by hydrothermal method were tested in H<sub>2</sub>O splitting reaction. It was found that MnFe<sub>2</sub>O<sub>4</sub> samples with smaller particle size and fine crystallinity exhibited higher H<sub>2</sub> production which was benefit from enhanced intimate contact between homogeneous particles and better ionic transport within fine crystals. In order to enhance the reaction kinetics of the O<sub>2</sub> release reaction, a hydrolysis treatment was introduced to the multi-step cycle. As a result, the lamellar structure of Na<sup>+</sup> extracted Na<sub>1–x</sub>(Mn<sub>1/3</sub>Fe<sub>2/3</sub>)O<sub>2</sub> oxide became unstable and collapsed into cubic MnFe<sub>2</sub>O<sub>4</sub> spinel structure more easily under heating, a structure characteristic suitable for O<sub>2</sub> release reaction. Compared to direct O<sub>2</sub> release reaction between layered Na(Mn<sub>1/3</sub>Fe<sub>2/3</sub>)O<sub>2</sub> oxide and CO<sub>2</sub>, the hydrolysis treatment lead to much faster reaction rate.

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## 1. Introduction

Solar energy is an infinite and clean renewable resource compared to fossil fuels (Lewis and Nocera, 2006). It is no doubt that solar energy resource will play an important role in the future energy system. Solar thermochemical H<sub>2</sub>O/CO<sub>2</sub> splitting cycles based on metal oxide redox materials (Müller and Steinfeld, 2008; Steinfeld et al., 1999; Abanades and Flamant, 2006; Abanades et al., 2008; Chueh et al., 2010; Jiang et al., 2014) offer promising paths

for solar energy conversion. Most of these thermochemical cycles are based on two-step redox reactions owing to their advantages of simplicity and easy manipulation, while the reduction temperature for oxygen evolution is too high, usually over 1300 °C, for most two-step thermochemical cycles. In order to reduce the reduction temperature of two-step thermochemical cycles, thermochemical process based on multicomponent compounds, such as CoFe<sub>2</sub>O<sub>4</sub> (Arifin et al., 2012; Scheffe et al., 2013; Tong et al., 2015), NiFe<sub>2</sub>O<sub>4</sub> (Gokon et al., 2013; Fernández-Saavedra et al., 2014), ABO<sub>3</sub> perovskites (Jiang et al., 2014) with better redox performance than simple oxides have received increasing attentions. Compared with two-step thermochemical cycles, multistep thermochemical cycles charac-

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terized by lower operation temperature (<1000 °C) appear to be another promising process. However, most multistep cycles, such as S–I (Machida et al., 2011), Cu–Cl (Ozbilen et al., 2014) and MnO–NaOH (Sturzenegger and Nüesch, 1999) cycles, are dependent on the aid of strong acid/base compounds (H<sub>2</sub>SO<sub>4</sub>, HCl, NaOH). These reactants bring strict requirements on reactor design and operation security considering their significant corrosion issues. Fortunately, metal oxide and mild base constituted thermochemical cycle, for example MnFe<sub>2</sub>O<sub>4</sub>–Na<sub>2</sub>CO<sub>3</sub> cycle, is a promising multi-step process thanks to the mild chemical properties of its reactants.

The manganese ferrite thermochemical water splitting cycle is a multi-step cycle based on MnFe<sub>2</sub>O<sub>4</sub>–Na<sub>2</sub>CO<sub>3</sub> interaction (Alvani et al., 2006, 2005; Tamaura et al., 1999). Water splitting occurs according to the following steps (Scheme 1):

In the first step, manganese ferrite (MnFe<sub>2</sub>O<sub>4</sub>) is oxidized by water under the participation of Na<sub>2</sub>CO<sub>3</sub> to produce hydrogen. In the second step, Mn<sup>III</sup> is reduced to Mn<sup>II</sup> within sodium ferrimanganite (Na(Mn<sub>1/3</sub>Fe<sub>2/3</sub>)O<sub>2</sub>) compound under CO<sub>2</sub> atmosphere and the reactive material is regenerated simultaneously. As for the net reaction, the only input substance is H<sub>2</sub>O and the outputs are H<sub>2</sub> and O<sub>2</sub>. In the past decades, researches were focused on the oxygen release step (Scheme 1, step 2) of MnFe<sub>2</sub>O<sub>4</sub>–Na<sub>2</sub>CO<sub>3</sub> system (Varsano et al., 2011; Seralessandri et al., 2009, 2008, 2006; Kaneko et al., 2001a,b). The oxygen release mechanisms have been extensively investigated, while no efficient strategy was developed to enhance the oxygen release rate and efficiency. Recently, MnFe<sub>2</sub>O<sub>4</sub> synthesized by high-energy ball milling method and solid-state reaction method were tested in this cycle (Alvani et al., 2005). The results have shown that different synthesis methods influenced H<sub>2</sub> release rate and productivity. The literature results suggest that structure and morphology of MnFe<sub>2</sub>O<sub>4</sub> are important to its reactivity and the oxygen release reaction kinetics is influenced greatly by the phase and structure of the H<sub>2</sub>O oxidized sodium ferromanganese oxide (Na(Mn<sub>1/3</sub>Fe<sub>2/3</sub>)O<sub>2</sub>).

The reactivity of MnFe<sub>2</sub>O<sub>4</sub> seems to be dependent on its micro-structure and morphology. Here, we applied a hydrothermal synthesis method to prepare MnFe<sub>2</sub>O<sub>4</sub> and to investigate its influences on H<sub>2</sub>O splitting reactivity in details. Furthermore, we developed a new method to enhance O<sub>2</sub> release rate and efficiency. Our results show that particle size and crystallinity of MnFe<sub>2</sub>O<sub>4</sub> are important parameters to its performance in MnFe<sub>2</sub>O<sub>4</sub>–Na<sub>2</sub>CO<sub>3</sub> thermochemical H<sub>2</sub>O splitting cycle. Smaller particle size and

fine crystallinity of MnFe<sub>2</sub>O<sub>4</sub> lead to higher H<sub>2</sub> generation rate and production. The hydrolysis assisted O<sub>2</sub> release is proved to be more efficient than other routes, i.e. direct oxygen release reaction between layered Na(Mn<sub>1/3</sub>Fe<sub>2/3</sub>)O<sub>2</sub> and CO<sub>2</sub> (Scheme 1) is relatively slow and takes more than 3 h to be finished (Varsano et al., 2011). It is noteworthy that both H<sub>2</sub> and O<sub>2</sub> release capacities and efficiencies can be improved by using the new preparation methods. These results demonstrated the possibilities for developing low temperature thermochemical cycles for overall water splitting. While, it should be clarified that this is an explorative study made to improve the multi-step Mn-based cycle but that at the present moment the cycle has not been completely closed, i.e. the parameters of the hydrolysis reaction (Scheme 2, step 2) should be further investigated.

## 2. Experimental section

### 2.1. Materials synthesis

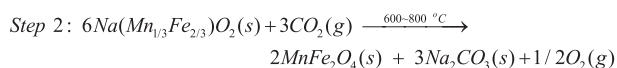
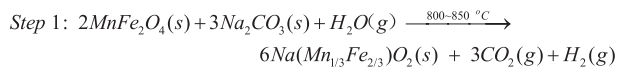
All reagents used in the experiments were of analytical grade and used without further purification. MnFe<sub>2</sub>O<sub>4</sub> samples were synthesized by a modified hydrothermal method (Wang et al., 2004). In a typical synthesis process, 10 mmol manganese chloride (MnCl<sub>2</sub>·4H<sub>2</sub>O) and 20 mmol ferric chloride (FeCl<sub>3</sub>·6H<sub>2</sub>O) were dissolved in 200 ml deionized water under magnetic stirring. Appropriate amount of NaOH was dissolved into 30 ml deionized water. Then, the NaOH solution was slowly added to the mixed chloride salt solution drop by drop under magnetic stirring and further stirred for 30 min to get a uniform pre-reaction mixture. At last, the brown reaction mixture was transferred to a 300 ml teflon-lined autoclave and hydrothermal reacted at designed conditions. Finally, the obtained products were separated by filtration and washed several times with distilled water, then dried at 60 °C in vacuum oven.

### 2.2. Materials characterization

The synthesized MnFe<sub>2</sub>O<sub>4</sub> and used samples were characterized by powder X-ray diffraction (XRD) on a Rigaku D/Max-2500/PC powder diffractometer using Cu K $\alpha$  radiation with operating voltage of 40 kV and operating current of 200 mA. The scan rate of 5° min<sup>−1</sup> was applied to record the XRD patterns in the range of 5–80° at a step size of 0.02°. Scanning Electron Microscopy (SEM) images technique (a Quanta 200FEG scanning electron microscope) was used to characterize the morphology and particle size of the samples. The metal (Na, Mn, Fe) contents are measured by inductively coupled plasma spectroscopy (Shimadzu ICPS-8100).

### 2.3. Reactivity test

The reactivity test was carried out in an temperature programmed erect quartz reactor ( $\Phi = 20$  mm) equipped



Scheme 1.

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