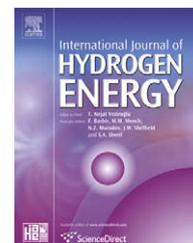


Available at [www.sciencedirect.com](http://www.sciencedirect.com)journal homepage: [www.elsevier.com/locate/he](http://www.elsevier.com/locate/he)

# The oxygen-releasing step in the water splitting cycle by $\text{MnFe}_2\text{O}_4\text{--Na}_2\text{CO}_3$ system

L. Seralessandri\*, M. Bellusci, F. Padella, A. Santini, F. Varsano

ENEA CR Casaccia, Via Anguillarese 301, 00123 Santa Maria di Galeria, Rome, Italy

## ARTICLE INFO

### Article history:

Received 13 March 2008

Received in revised form

1 August 2008

Accepted 1 August 2008

Available online 20 September 2008

### Keywords:

Thermochemical water splitting

Manganese ferrite

XRD

Rietveld analysis

Sustainable hydrogen production

## ABSTRACT

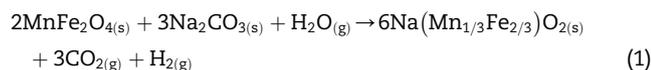
Investigation of the feasibility of the thermochemical two-step water splitting cycle based on  $\text{MnFe}_2\text{O}_4/\text{Na}_2\text{CO}_3$  system is reported. Influence of temperature and carbon dioxide pressure on the oxygen-releasing step was investigated. XRD analysis was applied to obtain phase identification of reacted powders at investigated experimental conditions. Different sodium sub-stoichiometric  $\text{Na}_{1-\delta}(\text{Mn}_{1/3}\text{Fe}_{2/3})\text{O}_{2-\delta/2}$  compounds were observed and their structure determined by using Rietveld analysis. Selected experimental conditions permitted to define a  $T/p_{\text{CO}_2}$  phase diagram, showing different solid phases coexistence regions. Experimental conditions that permit complete regeneration of the initial  $\text{MnFe}_2\text{O}_4/\text{Na}_2\text{CO}_3$  mixture were identified (field I in the reported diagram), demonstrating the possibility of full chemical cyclical operation of the system.

© 2008 International Association for Hydrogen Energy. Published by Elsevier Ltd. All rights reserved.

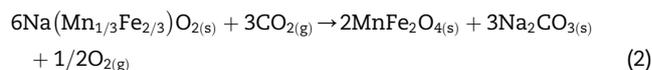
## 1. Introduction

In recent years several efforts have been done in order to develop chemical systems and solar reactor technology suitable for hydrogen production by  $\text{CO}_2$  free processes [1–5]. In particular a special interest was aroused by thermochemical cycles able to perform water splitting at temperatures lower than that required by direct water thermolysis [6–10].

The manganese ferrite thermochemical cycle [11,12] is a two-step water splitting process based on a  $\text{MnFe}_2\text{O}_4/\text{Na}_2\text{CO}_3$  reactive mixture. Water thermolysis occurs according to the following reaction sequence: in the first step (1) the reacting mixture  $\text{MnFe}_2\text{O}_4/\text{Na}_2\text{CO}_3$  is oxidized by water producing hydrogen, sodium ferrimanganite  $\text{Na}(\text{Mn}_{1/3}\text{Fe}_{2/3})\text{O}_2$  and releasing  $\text{CO}_2$ .



In the second step,  $\text{Mn}^{\text{III}}\text{--Mn}^{\text{II}}$  reduction in sodium ferrimanganite  $\text{Na}(\text{Mn}_{1/3}\text{Fe}_{2/3})\text{O}_2$  and  $\text{O}_2$  release occur in  $\text{CO}_2$  atmosphere and initial materials are restored according to the following reaction (2):



While hydrogen evolution has been studied in details and proved to be stoichiometric [13–15], some doubtful aspects concerning the oxygen evolution yield in reaction (2) were reported [16,17].

With the aim to obtain a better understanding on factors limiting a full  $\text{Na}(\text{Mn}_{1/3}\text{Fe}_{2/3})\text{O}_2$  conversion, influence of temperature and carbon dioxide pressure on sodium manganese ferrite disproportionation (2) was investigated. XRD analysis performed on reacted powders showed that the reaction (2) can evolve toward unexpected mixture compositions as a function of different reaction conditions [18]. In this paper

\* Corresponding author. Tel.: +39 06 3048 3472; fax: +39 06 3048 6258.

E-mail address: [luca.seralessandri@casaccia.enea.it](mailto:luca.seralessandri@casaccia.enea.it) (L. Seralessandri).

identification of reaction products observed in different  $T/p_{\text{CO}_2}$  experimental conditions is pursued and additional information on the structure of the observed phases are obtained by applying Rietveld analysis on collected XRD patterns.

## 2. Materials and methods

All solid reactants used were of analytical grade and were supplied by Carlo Erba. Gaseous reactants were supplied by Alpha Gaz, Ar (Alpha Gaz2), O<sub>2</sub> (Alpha Gaz2), CO<sub>2</sub> (N 20). The sodium ferrimanganite reduction was performed at different carbon dioxide pressures ( $p_{\text{CO}_2} = 0.1, 0.2, 0.5, 0.8$  and  $1.0$  atm) and temperatures ( $T = 600, 700, 750$  and  $800$  °C), performing a whole cycle. Stoichiometric mixtures of MnFe<sub>2</sub>O<sub>4</sub> and Na<sub>2</sub>CO<sub>3</sub> were oxidized at  $750$  °C for  $2$  h in Ar/O<sub>2</sub> (40/10) flow (50 cc/min). Oxygen was then removed from the reactor by flowing Argon (50 cc/min) for  $30$  min. The resulting oxidation product Na(Mn<sub>1/3</sub>Fe<sub>2/3</sub>)O<sub>2</sub> was successively exposed to a flow (50 cc/min) of CO<sub>2</sub> diluted in Ar, to obtain different partial pressures, at different temperatures. With the aim to complete reaction (2), CO<sub>2</sub> treatments were carried on for  $12$  h. All cycles were performed inside a Netzsch STA 409 thermobalance. A schematic demonstrating the experimental set-up is reported in Fig. 1.

Reacted powders were analyzed by using X-ray diffraction (XRD) analysis. Samples were sealed in glass capillary (0.1 mm) to limit air exposure. Samples were analyzed by a Siemens D500 diffractometer (Mo K<sub>α1</sub> radiation) in the angular range  $4 < 2\theta < 40^\circ$ . Phase identification was obtained by comparison with JCPDF-ICDD database [19]. Structural characterization and chemical composition of detected phases were obtained by applying Rietveld analysis on collected XRD patterns [20,21]. This procedure consists in minimising the difference function between the observed data and a profile calculated on the basis of structural models. Several quality of fit indexes can be adopted to evaluate the obtained results [22]. In this work conventional guidelines were adopted [22] and the refinement procedure results were considered

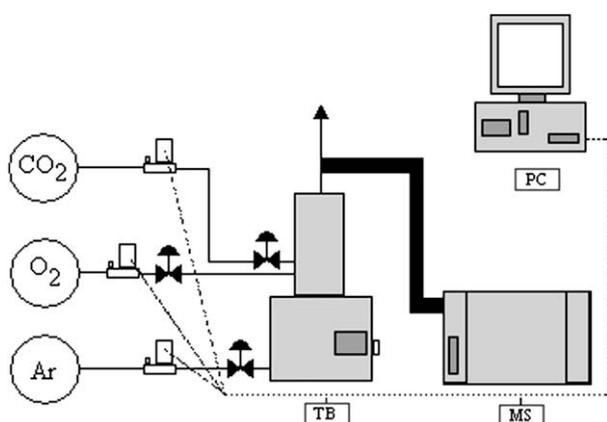


Fig. 1 – Scheme of the experimental set-up utilized for thermal analysis measurements. Netzsch STA 409 Thermobalance (TB) is coupled to a Balzer quadrupole Mass Spectrometer (MS). Computer controlled flow-meters regulate Argon, oxygen and carbon dioxide flows.

acceptable for weighted residual pattern index  $R_{wp}$  value less than 10%. In detail,  $R_{wp} = (\sum w_i(y_{oi} - y_{ci})^2 / \sum w_i y_{oi}^2)^{1/2}$  where  $y_{oi}$ ,  $y_{ci}$  and  $w_i = 1/y_{oi}$  are respectively the observed intensity, the calculated intensity and the weight of the intensity observed at the  $i$ th step. As a supplementary verification of the goodness of results obtained by the refinement, the metal ratio (Na:Mn:Fe = 3:1:2) in the calculated final phases composition was checked (chemical validation). Rietveld analysis was performed by using GSAS (General Structure Analysis System) [23] software. Structural models were obtained from ICSD database [24] or developed on the basis of chemical considerations.

## 3. Results and discussion

In Fig. 2 conversion degree values of reaction (2) are reported as a function of  $T$  and  $p_{\text{CO}_2}$  conditions. As shown in the figure, Na(Mn<sub>1/3</sub>Fe<sub>2/3</sub>)O<sub>2</sub> readily reacts with carbon dioxide. In the

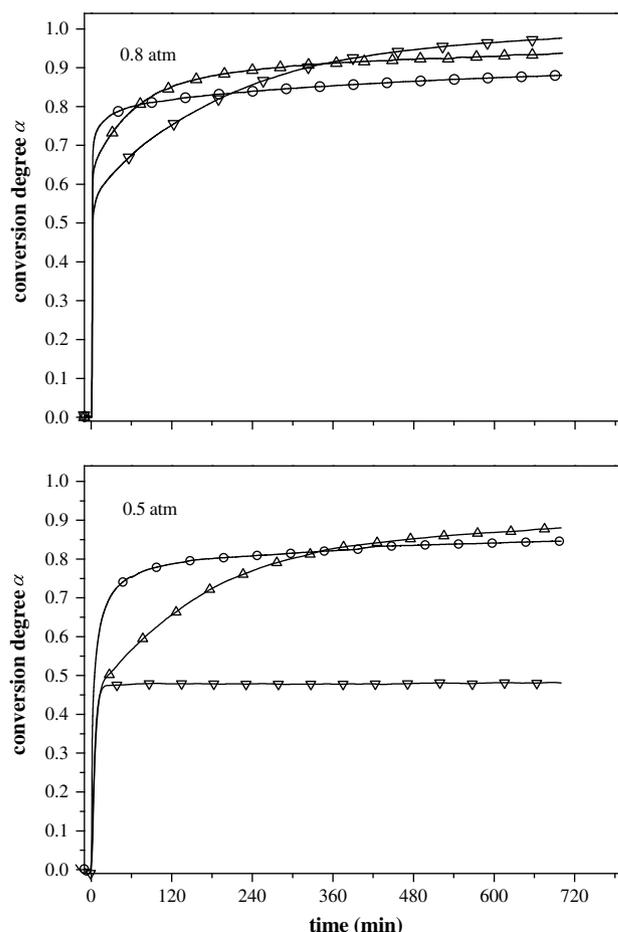


Fig. 2 – Conversion degree values from thermogravimetric curves observed for reduction step (2) performed at  $p_{\text{CO}_2} = 0.8$  and  $0.5$  atm and  $T = 600$  °C (○),  $750$  °C (△) and  $800$  °C (▽). Mass gains are reported as conversion degree  $\alpha = wt_{\text{obs}}/wt_{\text{exp}}$ , where  $wt_{\text{obs}}$  is the observed weight gain and  $wt_{\text{exp}}$  the expected one for a complete regeneration of the MnFe<sub>2</sub>O<sub>4</sub>/Na<sub>2</sub>CO<sub>3</sub> initial mixture (17.49%).

Download English Version:

<https://daneshyari.com/en/article/1273868>

Download Persian Version:

<https://daneshyari.com/article/1273868>

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