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Hydrogen production by water splitting on manganese ferrite-sodium carbonate mixture: Feasibility tests in a packed bed solar reactor-receiver

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ABSTRACT

The sodium manganese mixed ferrite thermochemical cycle $\text{Na}(\text{Mn}_{1/3}\text{Fe}_{2/3})\text{O}_2/(\text{MnFe}_2\text{O}_4 + \text{Na}_2\text{CO}_3)$ for sustainable hydrogen production has been implemented in a solar reactor-receiver, packed with indirectly heated $\text{MnFe}_2\text{O}_4/\text{Na}_2\text{CO}_3$ mixture pellets, with the aim of verifying its feasibility and of determining the critical aspects of the process. The reactor operates at nearly constant temperature in the range 750–800 °C; the shift between the hydrogen-producing and regeneration steps is obtained by switching the reactive gas from water to carbon dioxide. Hydrogen produced during 1-h operation of the reactor is in the range of 130–460 $\mu\text{mol/g}$ of mixture, depending on experimental conditions. Compared to other existing prototypes, the implemented process obtains comparable production efficiencies while operating at lower temperature both in the hydrogen production and regeneration phases.

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Introduction

Thermochemical cycles are recognized as suitable processes to generate hydrogen in a sustainable way, utilizing water as feed and concentrated sunlight as heat source. In traditional

two-step metal oxide based cycles, a metal oxide (MO) is reduced at high temperature liberating oxygen ($\text{MO}_{\text{ox}} = \text{MO}_{\text{red}} + \frac{1}{2}\text{O}_2$) and successively re-oxidized by water at lower temperature ($\text{MO}_{\text{red}} + \text{H}_2\text{O} = \text{MO}_{\text{ox}} + \text{H}_2$). The complete process splits water, producing hydrogen and oxygen in

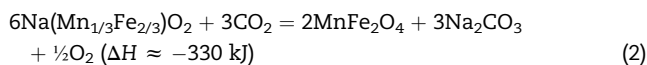
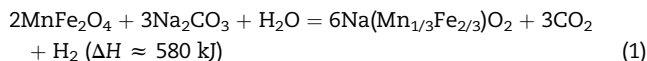
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separate steps. Numerous active chemical substrates have been proposed, together with different reactor concepts [1–7], for cycles operating in the 1000–2000 °C temperature range. Such temperature levels are challenging and pose severe demands on materials and reactor design [8,9].

The two-step sequence reported in Reactions (1) and (2):



describes the mixed sodium manganese ferrite cycle [10,11] where the standard metal oxide cycle ($\text{MO}_{\text{ox}}/\text{MO}_{\text{red}}$) is modified by the addition of sodium carbonate. In this case, contrarily to other metal oxide thermochemical cycles, the hydrogen generation Reaction (1) is the endothermic step of the process, while the oxygen release (Reaction (2)) represents the exothermic one. Sodium insertion into the manganese ferrite network (endothermic stage) promotes hydrogen formation from water, while the following oxygen release is driven by the formation of sodium carbonate from the mixed sodium manganese ferrite (exothermic step). Given the thermal characteristics of the process, the study of the response of the hydrogen production step under irradiation will have a major influence on cycle efficiency.

The optimal operative temperature for reactions involved in the cycle has been found to be 750 °C [11]. Hydrogen production at temperatures lower than 750 °C shows unfavorable kinetics [12], and complete regeneration of manganese ferrite/sodium carbonate composite cannot be accomplished for temperatures lower than 700 °C [13]. The upper limit is defined by the sodium carbonate melting point that occurs at 851 °C. These moderate temperature levels candidate the process for indirectly heated reactors: contrarily to other cycles, conventional metal alloys may be used.

Furthermore, compared to other metal oxide redox couples where reduction and oxidation are achieved by changing the operating temperature, the present cycle has the advantage of operating at a constant temperature. Oxidation and reduction of manganese compounds are driven by an adequate modification of the chemical environment: movement of sodium into and out of the manganese ferrite, coupled to carbon dioxide release and uptake, provides the thermodynamic driving force for manganese ions oxidation/reduction [11].

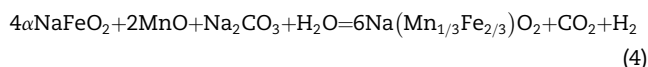
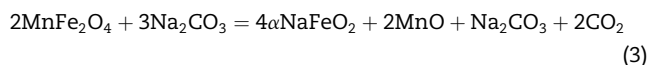
Isothermal thermochemical cycles are of greatest interest for practical exploitation [14,15]. In fact, thermal and time losses that occur during the repeated heating and cooling of the metal oxide substrates are avoided as well as material stresses associated to thermal shock.

Even though the $\text{Na}(\text{Mn}_{1/3}\text{Fe}_{2/3})\text{O}_2/(\text{MnFe}_2\text{O}_4 + \text{Na}_2\text{CO}_3)$ cycle has been studied at laboratory scale, very little work has been done to implement it on-sun at an appreciable scale. In the present work, as a first approach, a simple packed bed solar reactor-receiver was assembled, utilizing pellets of $\text{MnFe}_2\text{O}_4/\text{Na}_2\text{CO}_3$ mixture as water-splitting active material, with the aim of obtaining preliminary information circa the

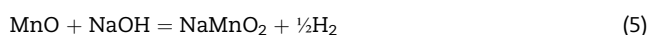
on-sun behavior of the mixed sodium manganese ferrite cycle at moderate temperature. The experimental temperature range reflects the solar irradiation in the real operative conditions and water concentrations in the feed has been selected on the basis of previous studies carried out on this cycle [12].

Chemical background

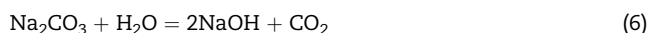
When firstly reported [10], the sodium manganese–ferrite cycle was considered the two-step cycle already described by Reactions (1) and (2). Actually, both the hydrogen evolution stage (1) and the regeneration of initial reactants (2) are not single-step chemical reactions and a more complex reactive frame was evidenced [11,13,16,17]. Concerning the hydrogen evolution Reaction (1) a partial, non oxidative de-carbonation takes place when the manganese ferrite-sodium carbonate mixture is heated in inert gas (Reaction (3)) [11,17]. The reaction leads to the formation of a solid mixture of $\alpha\text{-NaFeO}_2$, MnO , Na_2CO_3 able to capture oxygen from water and evolve hydrogen as described in (4):



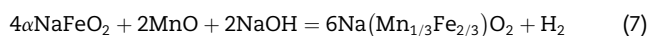
Reaction (4) evidences some similarities with the so-called sodium–manganese cycle [18–20] in which manganese oxide reacts with liquid sodium hydroxide to produce hydrogen and sodium manganite according to Reaction (5):



the major difference being that in the mixed ferrite cycle NaOH is continuously produced in-situ according to Reaction (6):



and the oxidation of manganese oxide by liquid sodium hydroxide results in the formation of a single stable phase, $\text{NaMn}_{1/3}\text{Fe}_{2/3}\text{O}_2$, as reported in Equation (7):



The role of $\alpha\text{-NaFeO}_2$ is that of providing the structural frame in which the sodium manganese ferrite dissolves to form the mixed ferrite. Such structure/composition is essential for closing the cycle. Exposure to CO_2 during regeneration of the material induces sodium depletion from the lamellar $\text{Na}(\text{Mn}_{1/3}\text{Fe}_{2/3})\text{O}_2$ structure and growth of the Na_2CO_3 compound. When the residual content of sodium ions in the depleted mixed sodium manganese ferrite network does not allow retaining the compound's structural stability, a collapse of the crystalline network occurs. Oxygen liberation (reported in Reaction (2)) takes place at this stage [13]. In absence of iron, NaMnO_2 involved in Reaction (5) cannot be completely deprived of sodium [20,21] not allowing reduction of

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