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# Thermodynamic Analysis of Two-Step Solar Water Splitting With Mixed Iron Oxides

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***Abstract – A two-step thermochemical cycle for solar production of hydrogen from water has been developed and investigated. It is based on metal oxide redox pair systems, which can split water molecules by abstracting oxygen atoms and reversibly incorporating them into their lattice. After successful experimental demonstration of several cycles of alternating hydrogen and oxygen production, the present work describes a thermodynamic study aiming at the improvement of process conditions and at the evaluation of the theoretical potential of the process. In order to evaluate the maximum hydrogen production potential of a coating material, theoretical considerations based on thermodynamic laws and properties are useful and faster than actual tests.***

***Keywords: Mixed Iron Oxides; Ferrite; Thermochemical Cycle; Water Splitting; Hydrogen; Thermodynamics.***

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## INTRODUCTION

Hydrogen is one of the most promising options for storing and transportation of solar energy [1]. It can be produced from water by electrolysis with electricity coming from solar power, but this technology is currently expensive and has a low total efficiency. Thermochemical cycles appear to be a promising alternative, which potentially offer both, higher efficiencies and lower costs [2]. A promising family of thermochemical cycles is the two-step water-splitting cycle using redox systems. During the first step of this cycle (watersplitting step) the reduced and therefore activated material is oxidized by abstracting oxygen from water and producing hydrogen. In the next step (the reduction step) the material is reduced again, setting some of its lattice oxygen free. Several redox materials consisting of oxide pairs of multivalent metals (e.g. $Fe3O4/FeO$ [3,4], $Mn3O4/MnO$ [5]) or systems of metal oxide/metal (e.g. $ZnO/Zn$ [6]) have been evaluated for such applications. Recently a lot of attention has been laid on ferrites and mixed iron oxides [7–9] and different approaches on solar receiver concepts for using mixed ferrites [10–12] have been developed. In the scope of the project HYDROSOL and the consecutive project HYDROSOL-2, both funded by the EC, mixed iron oxides have been used as redox materials [13]. The basic idea was to combine a support structure capable of achieving high temperatures when heated by concentrated solar radiation, with a redox pair system suitable for the performance of water dissociation and for reduction at these temperatures. In particular, the iron oxides have been fixed on ceramic honeycomb monolithic structures, which are placed inside a solar receiver reactor. With this approach, complete operation of the whole process (water splitting and reduction of the metal oxide) can be achieved with a single solar energy converter. The process has been tested in the solar furnace of DLR in Cologne resulting in the proof of principle, in proving the ‘cyclability’ of the involved materials, and in performing parametric studies. The redox systems favoured in HYDROSOL-2 are zinc and nickel/zinc based ferrites. Through thermodynamic calculations it is possible to predict the theoretical maximum output of $H2$ a redox-material can produce under certain conditions. Within the present theoretical work, a simulation based on thermodynamic considerations was performed for the two mixed iron oxides nickel–iron-oxide (Ni–Fe-oxide) and zinc–iron-oxide (Zn–Fe-oxide).

## REVIEW OF LITERATURE:

Thermodynamic calculations is possible to predict the theoretical maximum output of $H2$ from a specific redox-material under certain conditions. Calculations were focussed on the two mixed iron oxides nickel–iron-oxide and zinc–iron-oxide. In the simulation the amount of oxygen in the redox-material is calculated before and after the water-splitting step on the basis of laws of thermodynamics and available material properties for the chosen mixed iron oxides. For the simulation the commercial Software Fact Sage and available databases for the required material properties were used. The analysis showed that a maximum hydrogen yield is achieved if the reduction temperature is raised to the limits of the operation range, if the temperature for the water splitting is lowered below 8001C and if the partial pressure of oxygen during reduction is decreased to the lower limits of the operational range. The predicted effects of reduction temperature and partial pressure of oxygen could be confirmed in experimental studies. The increased hydrogen yield at lower splitting temperatures of about 8001C could not be confirmed in experimental results, where a higher splitting temperature led to a higher hydrogen yield. As a consequence it can be stated that kinetics must play an important role especially in the splitting step.

In the thermodynamic calculations the thermodynamic equilibrium composition of the system consisting of the solid metal oxide and a gas phase was calculated. In the splitting step and in the reduction step, oxygen atoms are exchanged between the gas phase and the metal oxide. In the thermodynamic equilibrium the rate at which atoms are exchanged in both directions is the same and the equilibrium composition is reached. Is a parameter changed within the system, it will adapt until a new thermodynamic state of equilibrium is reached. During the water-splitting step and the reduction of a two-step thermochemical cycle the metal oxide is oxidized and reduced again resulting in a permanent change of the oxygen content in the metal oxide. The oxygen content in the metal oxide YO2 can be defined as the amount of oxygen molecule-equivalents divided by the amount of metal molecules in a metal-oxide. Before the water-splitting step the system is in thermodynamic equilibrium and the metal oxide has a defined oxygen content YO2 . Now water vapour is constantly put into the system. The water dissociates partially into hydrogen and oxygen because of the elevated temperature. We assume that the input gas is in its thermodynamic equilibrium and consists of water, hydrogen and oxygen. The partial pressure of oxygen in the gas phase is equal to the equilibrium partial pressure of oxygen for the thermal dissociation of water at that certain temperature. The metal oxide is now going to take up oxygen atoms out of the gas phase as long as YO2 reaches the value where pMe O2 is equal to the partial pressure of oxygen in the input gas. The determination of YO2 after a water-splitting step at 10001C for a certain Ni–Fe-oxide when the thermodynamic equilibrium is reached. the correlation between pMe O2 and YO2 . A very small change in oxygen partial pressure is reflected in a rather wide range of compositional change (between YO2 ¼ 0:520:62) because in that state different components are in equilibrium with the given oxygen partial pressure, which remains the same until one component has transformed completely into the other. As well the partial pressure of oxygen for the thermal dissociation of water at 10001C is drawn into the plot as a horizontal line. It is about 105 bar. When pMe O2 is equal to the partial pressure of oxygen for the dissociation of water, the thermodynamic equilibrium between the gas phase and the metal oxide is reached and a stable value of YO2 has adjusted. That means the oxygen content in the metal oxide YO2 that is reached in the thermodynamic equilibrium in the splitting step can be determined when the partial pressure of oxygen in the dissociated water vapour and the correlation between YO2 and pMe O2 is known. For the reduction step the approach is similar. Now we assume argon with a partial pressure of oxygen of 106 bar is continuously added to the system. That means that pMe O2 in the thermodynamic equilibrium is equal to 106 bar. how YO2 can be determined after a reduction step at 12001C for a certain Ni–Fe-oxide. The correlation for YO2 and pMe O2 at 12001C is the horizontal line depicts the partial pressure of oxygen in the input gas, in this case 106 bar. At the intercept point the oxygen content YO2 after the reduction step can be read off (vertical line). With this approach the oxygen content YO2 after the water-splitting step and after the reduction step in thermodynamic equilibrium can be determined. The hydrogen which is produced during a water-splitting step can be calculated as follows when the oxygen content YO2 before YO2;1 and after the splitting step YO2;2 is known.

## INFLUENCE OF WATER-SPLITTING TEMPERATURE:

the hydrogen yield dependent on the water-splitting temperature TSplit for a Zn–Feoxide and for a Ni–Fe-oxide system. As can be seen the hydrogen yield decreases with increasing temperature. A closer look at the slope of the curves points out that in the temperature range below about 10001C the influence of water-splitting temperature on yield is rather low. Therefore it is possible to conduct the watersplitting step at rather high temperatures up to 10001C without significant losses of yield. This ensures positive effects on reaction kinetics and an enhancement of thermal efficiency, since thermal losses due to temperature cycling decrease. Although the thermodynamic simulations predict that a lower water-splitting temperature of about 8001C is more favourable for the hydrogen output, the results in the solar furnace lead to opposite conclusions [12]. The discrepancy between the experimental results obtained in the solar furnace test and the thermodynamic calculations lead to the conclusion that kinetics play an important role especially in the watersplitting step. Because of this disagreement kinetic investigations are highly recommended.

## INFLUENCE OF REDUCTION TEMPERATURE:

The series of curves depicted exemplarily for the nickel-based redox system for different reduction temperatures indicates that YO2 decreases if the reduction temperature increases for a constant pMe O2 . After completion of the reduction step pMe O2 is equal to the partial pressure of the adjacent gas phase. Therefore, with higher reduction temperatures a lower YO2 can be reached. The influence of the reduction temperature TRed on the hydrogen yield for a Zn–Feoxide system and for a Ni–Fe-oxide system. From the plot it is clear that the hydrogen yield increases with increasing reduction temperature.

## INFLUENCE OF PARTIAL PRESSURE OF OXYGEN IN THE REDUCTION STEP:

YO2 decreases over proportionally during the metal oxide reduction if the oxygen partial pressure is decreased within a range between 108 and 109 bar. This is due to the flat slope of the curve describing the dependency of pMe O2 on YO2 in that specific range. The slope of that curve is much steeper for higher partial pressures. Since the difference of YO2 before and after the metal oxide reduction determines the oxygen uptake capacity, also the hydrogen yield increases if the oxygen partial pressure is lowered for the reduction step. The influence of the partial pressure of oxygen in the flushing gas during the reduction step for a Zn–Fe-oxide system and for a Ni–Fe-oxide system. It can be seen that as the partial pressure decreases up to 10-9 bar the hydrogen yield increases drastically. The impact of the oxygen partial pressure is stronger than that of the other parameters. A lowering of this partial pressure within the discussed range may result in an increase of hydrogen yield of more than one order of magnitude.

## INFLUENCE OF THE COMPOSITION OF THE METAL OXIDE:

The influence of the amount of non-ferrous metal—nickel or zinc—in the mixed iron oxide system on the hydrogen yield. The hydrogen yield decreases with increasing zinc content YZn. The behaviour of the nickel system is different. There is a minimum hydrogen output at a ratio of about 35% Ni to total metal content. For higher amounts of nickel the hydrogen output increases.

## CONCLUSION:

The thermodynamic simulations predict that for a high hydrogen yield the reduction temperature should be as high as possible. In the actual experiments the reduction temperature is restricted through materials' stability to below 13001C. The partial pressure of oxygen in the flushing gas during the metal oxide reduction should be as low as possible. The partial pressure is though limited by the technical possibilities concerning gas purities as well as by the price, since a higher gas quality also leads to higher prices for the flushing gas. The thermodynamic simulations indicate a negative effect of increasing the water-splitting temperature on hydrogen yield. This is contradictory to the experiments, which is most probably due to domination of reaction kinetics.

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