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# Thermodynamic assessment of an electrically-enhanced thermochemical hydrogen production (EETHP) concept for renewable hydrogen generation

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## ABSTRACT

A novel concept for coupling a thermochemical cycle with an electrochemical separation device for the generation of hydrogen from steam is reported and a thermodynamic analysis of the system is presented. In a conventional thermochemical cycle, an oxygen carrier material is thermally reduced, cooled, and then reoxidized in steam thereby generating hydrogen. However, this process often requires high temperatures (>1700 K) and/or low oxygen partial pressures (<0.001 atm) in order to meet thermodynamic requirements. Such extreme conditions can adversely affect the stability of the reactive oxides, reactor materials, and system efficiency. In our proposed technology, we seek to decrease the required reduction temperature by several hundred degrees Kelvin by relaxing the requirement for spontaneous oxidation reaction at atmospheric pressure. This is accomplished by incorporating a proton-conducting membrane (PCM) to separate hydrogen produced at equilibrium concentrations from reactant steam. We also suggest the use of mixed ionic-electronic conducting (MIEC) oxygen carrier materials that reduce through a continuum of oxidation states at lower temperatures (~1200 °C). This concept allows the generation of a high-quality hydrogen stream while avoiding the challenging high temperatures/low partial pressures required in conventional water-splitting reaction schemes.

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## Introduction

Thermochemical water-splitting cycles, wherein heat rather than electrical work is used to derive H<sub>2</sub> from water, have long been of interest, with the concept originating at least as early as 1966 in a nuclear power context [1,2]. More recently, the concept has attracted renewed interest, particularly from the

concentrating solar (CS) community. The higher temperatures available through CS relative to nuclear power conceptually enables the water splitting process to proceed in only two reaction steps, overcoming thermodynamic realities which require three or more process steps at lower temperatures if the process is driven by heat alone. The CS community, beginning with Nakamura who reported the now archetypical ferrite cycle in 1977 [3], has focused largely on two-step, metal

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oxide based thermochemical cycles for water splitting. Some of the many reasons for this focus include their perceived simplicity, good cyclability, and potential for high thermodynamic efficiency [4,5]. Alternatively, coupled photovoltaic-electrolytic systems have been thoroughly investigated for renewable hydrogen production, such as the HyCon solar hydrogen generator (predicted efficiency of 19.5%) [6] and the system developed by General Motors (operating at 12.4% efficiency) [7]. However, in this paper we focus on a concept for improving thermochemical cycles for hydrogen production.

The standard two-step metal oxide process is devised as follows: In a first step, a “working” metal oxide is heated above a reduction temperature at which point oxygen evolves from the material, leaving it in a reduced state. In a second lower-temperature step, the now oxygen-deficient material is exposed to steam whereupon the material re-oxidizes back to its original state by reducing the water, yielding H<sub>2</sub>. To conserve thermal energy and improve the efficiency in a continuous process, sensible heat can be transferred from the cooling step of the reduced oxide to the reheating step of the oxidized material.

Many different metal oxide systems have been evaluated as working materials for the two-step process, with the evaluations generally following a somewhat logical progression of increasing scope and complexity over time from basic binary oxides, both volatile and non-volatile (e.g., ferrites, and ZnO/Zn), to blended or substituted oxides (e.g., cobalt ferrites), to synergistic composite materials (e.g., zirconia-supported ferrites), to simple reducible mixed-ionic electronic conducting (MIEC) oxides (e.g., ceria), to more complex MIECs (e.g. perovskite formulations). Several reviews of materials for this application are available [8–11]. A simplified summary comparison of the materials candidates is that the relatively simple binary and mixed oxides are preferable from a thermodynamic point of view, but suffer greatly from other issues such as very poor reaction kinetics. Conversely, ceria has outstanding reaction kinetics, but is less favorable thermodynamically [12]. As a result, the conversions (i.e. the amount of oxygen and hydrogen produced per unit of oxide) of both materials systems are practically limited to small values per cycle, presenting a major challenge to efficiency [4,13,14]. Nonetheless, ferrite [15] and ceria [16] currently remain the subject of ongoing evaluation and of on-sun demonstrations which show continuing progress in the field. Going forward, the development of tailored, complex MIECs offers the opportunity to benefit from rapid reaction kinetics while improving upon the thermodynamics of ceria [10,17–19].

Improving the thermodynamics of a material for this application is often equated with decreasing the reduction temperature. This is driven by the desire to sidestep the complications resulting from the very high temperature requirements of materials such as ceria, for which a temperature of 1725 °C is required to achieve a modest reduction of CeO<sub>2</sub> to CeO<sub>1.95</sub> in air [20,21]. These complications include limited choices for materials of construction, oxide volatility, high thermal losses, sintering and loss of surface area, solid/solid reactions (high temperature materials incompatibility), and a limited choice of solar platforms, among others. To partially ameliorate the high temperature requirement, the current practice is to facilitate lower temperature reduction by

performing the reaction under reduced oxygen partial pressure either through pumping or an inert sweep gas. Faced with these challenges, manipulating the materials composition to lower the reduction temperature seems an appealing alternative. However, it is imperative to fully understand and appreciate the implications of manipulating the thermodynamics of the reducible material, as will be studied in the analysis presented subsequently.

The thermodynamics of reduction and oxidation are not independent; shifting the temperature of one shifts the other in the same direction. Manipulating materials chemistry to favor reduction at lower temperatures also pushes the temperatures where oxidation is thermodynamically favorable to lower temperatures. This introduces other complications, such as the thermodynamically spontaneous oxidation temperature possibly becoming so low that the kinetics of steam oxidation are extremely slow or non-existent. If the reduction temperature is pushed low enough (<1000 °C or so), the materials simply will not possess the reducing power to be spontaneously reoxidized by water or steam at any temperature [1,12]. Simply put, one must take care that the modifications meant to improve the reduction process do not compromise the oxidation half of cycle.

In response to these challenges, Palumbo et al. proposed a metal oxide-electrochemical hybrid approach to enable the utilization of materials that reduce at more moderate temperatures while preserving many of the appealing features of high-temperature thermochemical metal oxide cycles [22]. The basic concept of this approach is the integration of thermally-reduced metal-oxides into an aqueous-based electrolytic water-splitting cell. With this configuration, a portion of the energy required to split the water is provided thermally (through the metal oxides), while the remainder is supplied by electrical power. It was envisioned that the products from thermal reduction would be utilized as a chemically-active anode material in a water-splitting electrolyzer, and as such that the electrical input required to split water would be substantially decreased. Conceptually, the electrolysis reaction would no longer be:



but is rather modified to:



where red and ox subscripts represent the oxygen stoichiometry relative to the metal (or metals) in the reduced and oxidized state. As written, the presence of the reduced material decreases the ideal water decomposition voltage from the 1.23 V needed in a conventional cell to values as low as 0.23 V. Furthermore, the H<sub>2</sub> recovery is simplified relative to the conventional thermochemical scheme as it is more concentrated.

This hybrid metal oxide concept, referred to as decoupled water electrolysis (DWE), was demonstrated in initial proof of concept experiments [22]. This work and additional consideration has exposed a number of complexities impacting the

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