Solar thermochemical hydrogen production using ceria zirconia solid solutions: Efficiency analysis

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ABSTRACT

In this work thermochemical hydrogen production using ceria zirconia redox materials of the form $Ce_{1-x}Zr_xO_2$, with x varied in the range 0-0.2, is investigated. A number of literature sources are used to fix the thermodynamic properties such as the partial molar entropies and enthalpies of reduction. From this, a full thermodynamic analysis of the fuel production is possible, where the heat required was assumed to be supplied by concentrated solar power. An efficiency model is presented and the materials are compared. The extent of reduction for a given temperature and oxygen partial pressure increases with increasing Zr concentration. However, the addition of Zr also has a negative effect on the oxidation reaction, requiring lower temperature oxidation and thus a larger temperature swing between the reaction steps. The thermodynamic analysis suggests that for cycles with a reduction temperature of 1773 K, the improvement in yield offered by $Ce_{1-x}Zr_xO_2$ does improve the efficiency, with $Ce_{0.8}Zr_{0.2}O_2$ having the highest solar to fuel production efficiency of the materials considered. To achieve this efficiency the oxidation would need to be performed at lower temperature ($\leq$800 °C for $Ce_{0.8}Zr_{0.2}O_2$) than is common in experimental demonstrations, and may be kinetically limited.

Introduction

Thermochemical cycles driven by concentrated solar power have been heavily investigated as a method of renewable hydrogen production [1-6]. An example of such a cycle is illustrated in Fig. 1, which shows a schematic of a two-step metal oxide redox cycle, where the oxide is reduced at high temperature releasing oxygen and then the reduced oxide is re-oxidised with steam producing hydrogen.

This work is focused on two-step thermochemical cycles utilizing ceria based materials as the redox pair. Ceria can be partially reduced at high temperatures [7,8], with very rapid kinetics [9,10], and while remaining in the fluorite phase [11-13]. The fact that there is no phase change means that ceria reduction and oxidation offers a very practical and achievable thermochemical cycle for fuel production [14]. The reduced ceria can then be used to split both H_2O and CO_2, producing hydrogen and carbon monoxide respectively [15]. This process has been extensively investigated in recent years both theoretically [16-21] and experimentally [22-24]. Recently, Marxer et al. used cerium dioxide to perform over 200 cycles in a lab scaled reactor, producing 700 standard litres of syn-gas, which was then processed via the Fischer-Tropsch process to produce Kerosene [25].

The redox properties of CeO_2 can be somewhat tuned by replacing some of the cerium cations in the fluorite crystal

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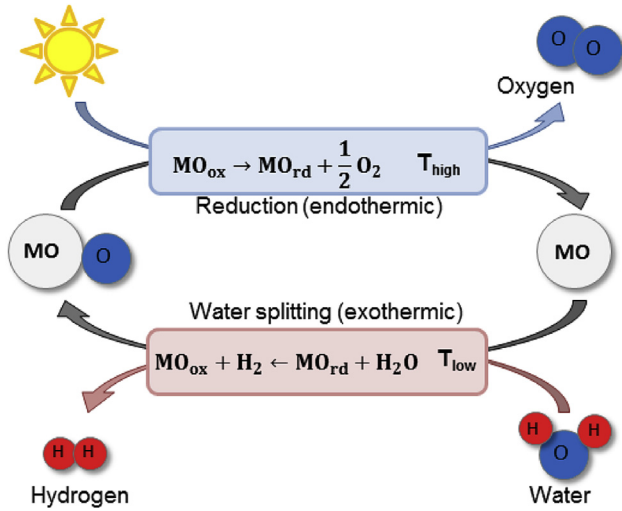E-mail address: bulfinb@tcd.ie (B. Bulfin).

Fig. 1 – A schematic showing a two-step thermochemical hydrogen production cycle using a metal oxide as the redox material and powered by solar energy.
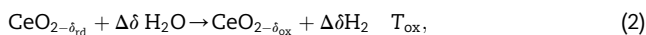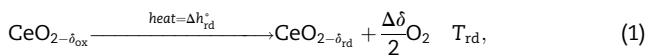
structure with other metals. The addition of ions which have the same valence, but lower ionic radius than ceria, such as Zr^{4+} and Hf^{4+}, can increase the reducibility [26–34]. This is very important as the reduction is the energy intensive step, suggesting there could be benefits for the overall efficiency of the cycles [35].

A recent study by Takacs et al. suggests that although Zr improves the reducibility of ceria, it also negatively impacts the water splitting step, and ultimately offers no improvement in hydrogen production efficiency [36]. However, in this study the yield was fixed and the reduction temperature was set accordingly. This could nullify the positive effect Zr has on the yield. Here we expand upon this work, investigating more Zr concentrations and use a more sophisticated efficiency model with a more in-depth look at the oxidation step.

Thermodynamic data from the literature for both CeO_2 [7,37–39] and $Ce_{1-x}Zr_xO_2$ [36,40,35] is used to perform a fully optimised thermodynamic analysis of solar hydrogen production. Higher concentrations of Zr ($x > 0.2$) could not be considered in this work due to a lack of thermodynamic data in the literature.

Thermodynamics

In order to perform an efficiency analysis, one must first know the thermodynamic properties of the reactions. The cerium dioxide thermochemical water splitting cycle is described by

$$CeO_{2-\delta_{ox}} \xrightarrow{heat = \Delta h_{rd}^\circ} CeO_{2-\delta_{rd}} + \frac{\Delta\delta}{2}O_2 \quad T_{rd}, \quad (1)$$

$$CeO_{2-\delta_{rd}} + \Delta\delta\, H_2O \rightarrow CeO_{2-\delta_{ox}} + \Delta\delta H_2 \quad T_{ox}, \quad (2)$$

$$\Delta T = T_{rd} - T_{ox} \quad \text{and} \quad \Delta\delta = \delta_{rd} - \delta_{ox}, \quad (3)$$

where the reactions in Eqs. (1) and (2) sum to water splitting. The ceria is reduced at a temperature T_{rd}, to a vacancy

concentration of δ_{rd}. It is oxidised at a temperature T_{ox} in a 1 bar H_2O atmosphere to a vacancy concentration δ_{ox}. The maximum yield per cycle and per mole of metal oxide is the difference in the equilibrium vacancy stoichiometry $\Delta\delta$. For convenience, the deviations from stoichiometry δ, is defined as a unit-less oxygen vacancy concentration

$$\delta = \frac{[O_{vac}]}{[Ce]}, \quad (4)$$

where $[O_{vac}]$ is the concentration of oxygen vacancies and $[Ce]$ is the concentration of cerium atoms.

Since (1) and (2) sum to water splitting, their change in Gibbs free energies must also sum to that of the water splitting reaction, namely

$$\Delta g_{O,ws}^\circ = \Delta g_{O,rd}^\circ + \Delta g_{O,ox}^\circ, \quad (5)$$

where the subscript O indicates per mole of atomic oxygen. Given that $\Delta g_{O,ws}^\circ$ is known, an expression for $\Delta g_{O,rd}^\circ$ will also give the thermodynamics of the oxidation reaction.

The standard partial molar change in Gibbs free energy for the reduction reaction is given by

$$\Delta g_{O,rd}^\circ(\delta, T) = \Delta h_{O,rd}^\circ(\delta) - T\Delta s_{O,rd}^\circ(\delta), \quad (6)$$

where $\Delta h_{O,rd}^\circ$ and $\Delta s_{O,rd}^\circ$ are the standard partial molar enthalpy and entropy of the reduction reaction given in Eq. (1). Partial molar enthalpy and entropy values from the literature were fit empirically, with the fits shown in Figs. 2 and 3. This shows the effect that adding Zr to ceria has on the redox thermodynamics. It reduces the change in enthalpy of the reduction reaction, which should allow the material to be more easily reduced. However, it also reduces the change in entropy, which according to Eq. (6) also reduces the driving force $T\Delta s_{O,rd}^\circ$, for the reduction reaction.

An equation of state for the reduction reaction can be obtained using the formulae

$$\Delta g_{O,rd}(\delta, T) = \Delta g_{O,rd}^\circ + \frac{1}{2}RT \ln\left(\frac{p_{O_2}}{p^\circ}\right), \quad (7)$$
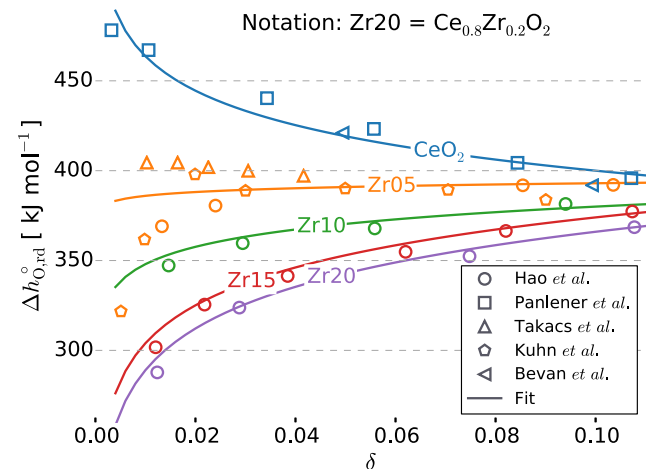

Fig. 2 – $\Delta h_{O,rd}^\circ(\delta)$ fits of CeO_2 [7,37–39], $Ce_{0.95}Zr_{0.05}O_2$ [35,36,40] and $Ce_{1-x}Zr_xO_2$ for $x = 0.05, 0.1, 0.15, 0.2$ [35], are plotted along with some of the literature data.