Solar Hydrogen from Water Splitting using Liquid Metal Oxidation/Reduction Cycles Promoted by Electrochemistry

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1. Introduction

Technological barriers have stymied commercialization efforts of CSP-based thermochemical water splitting systems[1]. Approximately 300 thermochemical water splitting cycles accessible to CSP integration have been proposed[2]. After decades of research only seven cycles have been developed beyond proof of concept[3], with even fewer demonstrated at kW solar reactor scales. Purely thermochemical fully stoichiometric simple metal oxide cycles require ultra-high process temperatures (T >2000 K) to reduce the metal oxide. In addition, the elemental metal or lower-valence metal oxide formed by thermal reduction melts or vaporizes. These issues severely challenge materials of construction for the receiver/reactor and cycle operations because costly separation processes are needed to purify and recycle the redox active moiety. Non-stoichiometric metal oxide cycles using non-volatile complex oxides are now universally researched in solar fuel production schemes to alleviate melting and vaporization. However, these cycles still require high processing temperatures (T >1700K) that present materials challenges for both chemically-active oxide and receiver/reactor structural components. These cycles also require costly separation processes to remove oxygen[4] and suffer from low H₂ production yields per mole of oxide because of material stability and thermodynamic constraints[5]. This community is still searching for a commercially viable functional oxide.

Here we introduce a fully stoichiometric, two-step metal oxide water-splitting concept that encapsulates the redox chemistry in a liquid metal solution (LMS) and invokes electrochemistry to accomplish reduction in order to solve the technological challenges associated with current CSP-based thermochemical water splitting systems. The concept preserves the benefit of utilizing a known, simple and highly efficient metal/metal oxide gas-splitting chemistry like Zn/ZnO[6] by replacing the high temperature thermolysis step (T >2000K) with an electrochemical reaction (process temperature tunable between 673K < T <1073K). Oxygen separation is easily managed by molten salt electrolyte and the thermodynamic constraints limiting H₂ yield are ameliorated. Furthermore, the LMS acts as heat transfer fluid, reaction medium, and electrical conduit to facilitate integration of solar industrial process heat using commercially established Gen2 solar collector technologies.

2. Results and Discussion

A schematic that captures the essence of the solar fuel production process is shown in Figure 1. A particular binary alloy composition (MₓM'₁₋ₓ) makes up the LMS and contains a mixture of redox active metal M in x at% and a redox inert metal M' in 1-x at%. The LMS is liquidous at temperatures above 673 K for a range of x compositions and is circulated between the H₂ production and oxide (MₓO) reduction reactors. H₂ is produced by reacting water vapor with M dissolved in the LMS. The M' component in the alloy remains inert to steam oxidation under process conditions even as the M component is converted to oxide. LMS carries MₓO from one reactor to the other. Upon oxidation (i.e., H₂ production) the MₓO remains highly
dispersed in the LMS and is transferred into the reduction reactor containing a molten salt electrolyte, electrodes, and electrolysis hardware where $M_xO$ is reduced electrochemically to close the cycle by evolving gaseous $O_2$. This talk will discuss methods used to select and screen suitable binary alloy compositions, as well as experimental validation of both the thermochemical water splitting activity in the chosen LMS and electrochemical reduction of $M_xO$ in a suitable electrolysis medium. Key to this innovation is encapsulating the redox chemistry within the LMS. We will discuss the unique chemical and physical properties of the LMS that make it a highly effective heat transfer fluid, reaction medium, and electrical conduit that facilitates integration of solar industrial process heat as well as electrolysis hardware.

Figure 1. Schematic of a solar powered water-splitting concept that uses a liquid metal solution to encapsulate a fully stoichiometric metal oxide cycle for producing hydrogen via direct water splitting. This concept offers an engineering solution to realize the potential of simple and highly efficient thermochemical cycles like Zn/ZnO.

References