

SOLAR THERMOCHEMICAL WATER SPLITTING: ADVANCES IN MATERIALS AND METHODS

Anthony McDaniel, Sandia National Laboratories, Livermore, CA
amcdani@sandia.gov

Debora Barcellos, Michael Sanders, Jianhua Tong, and Ryan O'Hayre, Colorado School of Mines, Golden, CO
Nadia Ahlborg, Chirranjeevi Balaji Gopal, and William Chueh, Stanford University, Stanford, CA
Antoine Emery and Christopher Wolverton, Northwestern University, Evanston, IL
James Miller, Sandia National Laboratories, Albuquerque, NM

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Photoelectrochemical (PEC) water splitting, termed artificial photosynthesis, converts solar energy into hydrogen by harvesting a narrow spectrum of visible light using photovoltaics integrated with water-splitting electrocatalysts. While conceptually attractive, critical materials issues currently challenge technology development(1) and economic viability(2). Despite decades of active research, this approach has not been demonstrated at power levels above a few watts, or for more than a few days of operation.

High-temperature solar thermochemical (STCH) water splitting is an alternative approach that converts solar energy into hydrogen by using the deceptively simple metal oxide-based thermochemical cycle presented in figure 1. The STCH process requires very high temperatures, achieved by collecting and concentrating solar energy. Unlike PEC, two-step metal oxide water-splitting cycles have been demonstrated at the 100kW scale(3), and continuous operation at even higher power levels is nearing pre-commercial demonstration (HYDROSOL-3D). Nonetheless STCH, like PEC, faces critical materials issues that must be addressed for this technology to achieve commercial success.

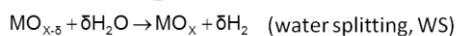
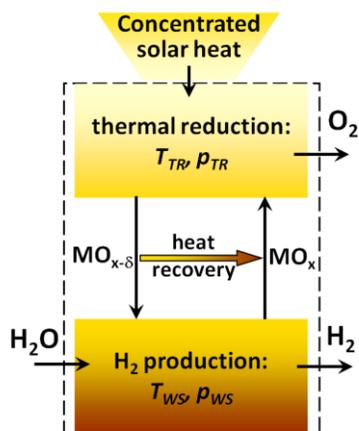


Figure 1 – Schematic of a two-step thermochemical cycle for H₂ production powered by concentrated solar energy.

Reduction of the oxide occurs at

$T_{TR} \sim 1773\text{K}$ and O_2 pressure $p_{TR} \sim 10\text{Pa}$.

Water splitting occurs at a lower temperature ($T_{WS} \sim 1273\text{K}$) and comparatively higher pressure in steam.

The net endothermic WS reaction is divided into two separate reactions, each occurring in thermodynamically favorable, non-overlapping temperature and pressure ranges.

This presentation will focus on the challenges associated with discovering optimal STCH materials within the family of nonstoichiometric oxides (perovskite and fluorite crystal structures). Through the course of a multi-year R&D effort funded by the US Department of Energy, we have developed a basic understanding of composition-property relationships important to identifying viable STCH materials. Our methods of redox-active compound formulation and screening are based on both first principles theory (DFT) and chemical intuition.

Key factors affecting material selection will be reviewed within the context of reactor design, a perspective that is critically important but often overlooked in this research field. Our goal is to understand how to manipulate oxide stoichiometry in order to engineer materials with optimal redox thermodynamics, and also explore the underpinnings of important relationships between oxide composition, functionality (i.e., reaction kinetics and solid-state transport), and solar-to-hydrogen (STH) conversion efficiency. We will show by example the effectiveness of our approach, and summarize the outcome of this research effort that has screened hundreds of prospective oxides. We will also offer our outlook on the future of this technology, and the need to find a clear answer to which of the materials proposed for this chemistry will ultimately lead to the highest overall STH efficiency and be viable enough for commercialization.

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