

THESIS DEFENSE

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Design of Perovskites for Solar Thermochemical Hydrogen Production

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Hydrogen is one of the most widely produced and used commodity “chemicals” in the world. Besides its current widespread use in the petrochemicals and ammonia production industries, it also has the potential to be used as an energy carrier for future power, transportation and storage applications. However, the environmental sustainability of hydrogen for such applications can only be assured if it can be obtained from renewable sources.

Solar thermochemical hydrogen production (STCH) is a carbon-free technique that uses solar thermal heat to split water and produce hydrogen. The predicted high process efficiencies and scalability make this technique preferred for large scale hydrogen production over electrolysis or thermolysis.

The current state-of-the-art material for STCH is ceria (CeO_2), which produces hydrogen via a relatively straightforward two-step water splitting (WS) cycle. In the first step, carried out at a high temperature, the oxide reduces by creating oxygen vacancies and releases oxygen. In the second step, carried out at a lower temperature, the oxygen deficient oxide splits

the water molecule and reoxidizes, thereby releasing hydrogen. The great challenge of using ceria is the high temperature required for the first reduction step, which is over 1600 °C. In this work I propose four new materials for WS $\text{BaCe}_{0.25}\text{Mn}_{0.75}\text{O}_3$ and $\text{Ce}_a\text{Sr}_{2-a}\text{MnO}_4$ ($a = 0.1, 0.2$ and 0.3) that meet or exceed ceria’s water splitting performance, but at much lower temperatures (~1350-1400 °C).

$\text{BaCe}_{0.25}\text{Mn}_{0.75}\text{O}_3$ (BCM) is shown to produce about 3X more H_2 than ceria at a lower reduction temperature (1350 °C) and is demonstrated to have a higher steam-to-hydrogen conversion than other promising perovskite candidates. This steam-to-hydrogen conversion concept was shown to be of extreme importance for the application of the STCH process in a realistic reactor. The thermodynamic properties of BCM were investigated to further understand the underlying reasons for its outstanding performance. This study led to the discovery of a beneficial polytype phase change that may take place during STCH cycling in this materials system and that likely contributes to its performance.

Motivated by my discovery of the BCM system, I subsequently identified a Ruddlesden-Popper phase, $\text{Ce}_a\text{Sr}_{2-a}\text{MnO}_4$ (CSM) which also showed excellent potential for STCH WS. Importantly, this phase had never before been reported in the literature. After a structure characterization study, this new materials system was demonstrated to produce 2-3X more hydrogen than ceria at the reduction temperature of 1400 °C. Both the BCM and CSM systems open up new directions for the design and optimization of redox-active STCH materials that can provide higher performance at lower temperatures than CeO_2 , thereby underscoring remaining opportunities to further discover new materials for this important renewable energy application.

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