TWO-STEP THERMOCHEMICAL SOLAR-TO-FUEL EFFICIENCY COMPUTATION OF STRONTIUM AND CHROMIUM DOPED LANTHANUM MANGANITE PEROVSKITE OXIDES USING CALPHAD

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Reducing greenhouse gas emissions and profiting on novel synthetic fuels to store and buffer energy from renewable sources (such as solar or wind) is a prime strategy to encounter the global energy challenge. Here, two-step thermochemical fuel production is an energy technology utilizing intermittent solar power to convert water and carbon dioxide into syngas, a renewable fuel that can be stored easily and mitigate CO_2 emissions. Success of the technology relies on the discovery of materials with a high thermochemical solar-to-fuel efficiency. Perovskites have attracted much attention recently due to impressive fuel productivity[1, 2]. Although a high fuel productivity shows the feasibility of a material, it does not imply that it is the optimum and most efficient material as it depends largely on the operation of the solar-to-fuel reactor [3, 4]. Literature on thermochemical solar-to-fuel efficiency of perovskites is limited and none of the existing studies measures the thermodynamic properties in the entire temperature range relevant for solar-to-fuel production, namely 1000-1800K.

In this work, we use oxygen nonstoichiometry from CALPHAD data libraries on A-site doped $La_{1-x}Sr_xMnO_{3-\delta}$ and B-site doped perovskite $La_{0.6}Sr_{0.4}Mn_{1-y}Cr_yO_{3-\delta}$ in a relevant temperature range of 1073-1873K to determine the solar thermochemical efficiency. The oxygen nonstoichiometry and thermodynamic properties extracted from CALPHAD libraries are compared to earlier studies of $La_{1-x}Sr_xMnO_{3-\delta}$ for thermochemical fuel production. We discuss diffferences between the earlier extrapolated models and the CALPHAD descriptions on the presented material examples. Specifically, we show thermochemical equilibrium models of fuel productivity supplemented by validations with experimental results on $La_{1-x}Sr_xMnO_{3-\delta}$ in literature. We make predictions on the most efficient material in the composition space $La_{1-x}Sr_xMn_{1-y}Cr_yO_{3-\delta}$ for different conditions.

It is shown that the amount of experimental work can be reduced substantially by using the CALPHAD approach and further making predictions for multi-component systems that would be practically unattainable without this method. The solar-to-fuel field will benefit directly from additional thermodynamic data on perovskites in the relevant temperature range. Further, we provide guidelines in terms of key CALPHAD experiments that enables a mapping of the thermodynamic properties of a wide compositional space of perovskites to find materials with a high thermochemical efficiency.

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