

Substituted Strontium Ferrite Thermodynamics for Solar Air Separation

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1. Introduction

Solar thermochemical air separation cycles (Fig. 1) are a renewable alternative to conventional cryogenic air and pressure swing absorption processes, which can mitigate the significant greenhouse gas emissions of industrial gas and ammonia [1] production. Strontium ferrite ($\text{SrFeO}_{3-\delta}$) is an appealing candidate for solar-thermal air separation due to significant reduction-oxidation (redox) activity across attainable changes in temperature and oxygen partial pressure [2]. A- and B-site substitution can enhance the thermodynamic, kinetic, and stability properties of the oxide and tune these properties to optimal process conditions [3]. Thermodynamic characterization of the redox properties, including reduction extent and enthalpy/entropy, is essential for air separation process design, and is the first step in analyses of cycle efficiency, subcomponent heat/mass transfer, and technoeconomics. The compound energy formalism (CEF) [4] is a powerful scheme for this characterization which allows the explicit comparison of substituents through simultaneously determined, empirical parameters for each species.

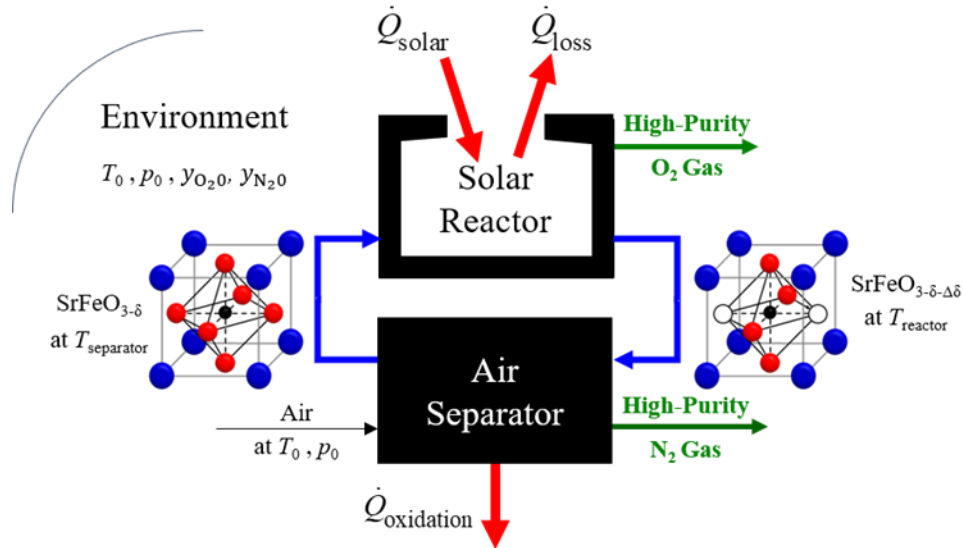


Fig. 1. Schematic of a simplified solar thermochemical air separation cycle.

2. Methods

Substituted $\text{SrFeO}_{3-\delta}$ was synthesized using a solution method and characterized via x-ray diffraction and scanning electron microscopy. Equilibrium nonstoichiometry was calculated from the measured relative mass loss/gain in thermogravimetric (TGA) experiments (Fig. 2). Multiple sample and blank run replicates enabled estimation of experimental variability due to buoyancy and gas flow dynamics. The CEF was simultaneously applied to all TGA measurements to thermodynamically model substituted $\text{SrFeO}_{3-\delta}$ redox behavior as a function of temperature, O_2 pressure, substituent composition, and substituent ratio.

3. Results and Discussion

CEF fits to the experimental nonstoichiometry for the compositions $\text{Ba}_{0.1}\text{Sr}_{0.9}\text{FeO}_{3-\delta}$ (BSF1090) and $\text{La}_{0.05}\text{Sr}_{0.95}\text{FeO}_{3-\delta}$ (LSF595) are shown in Fig. 3. The CEF predicted nonstoichiometry for these substituents at A-site

concentrations of 0 – 20 mol %, temperatures from 400 – 1100 °C, and O₂ concentrations from 1 – 90%. Van't Hoff estimates of the partial enthalpy of reaction derived from the CEF were consistent with prior computationally [5] and experimentally [3] determined average values. Ba- and La-substitution decreased the enthalpy of reduction and therefore the necessary energy input per mol N₂ at a given temperature. Ba-substitution increased the nonstoichiometry under the most oxidizing conditions, while La-substitution decreased it, making the species more appealing for lower and higher temperature cycle operation, respectively.

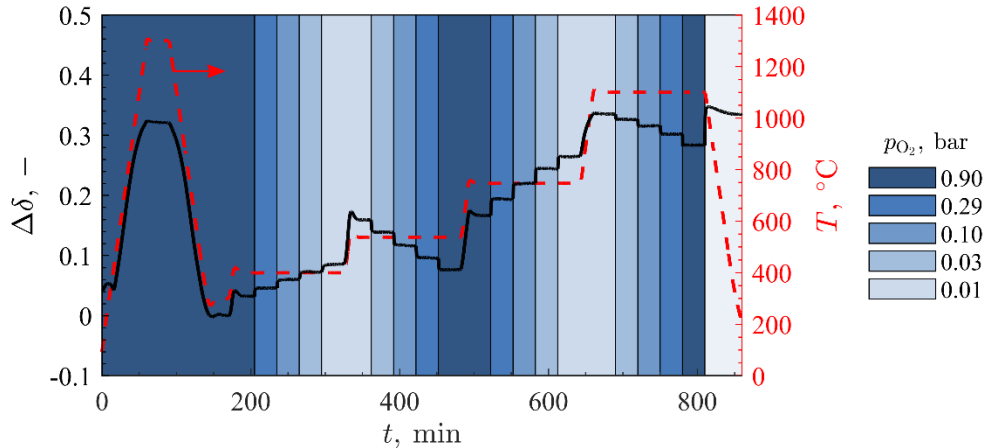


Fig. 2. TGA-measured nonstoichiometry vs. temperature and O₂ pressure for a substituted strontium ferrite.

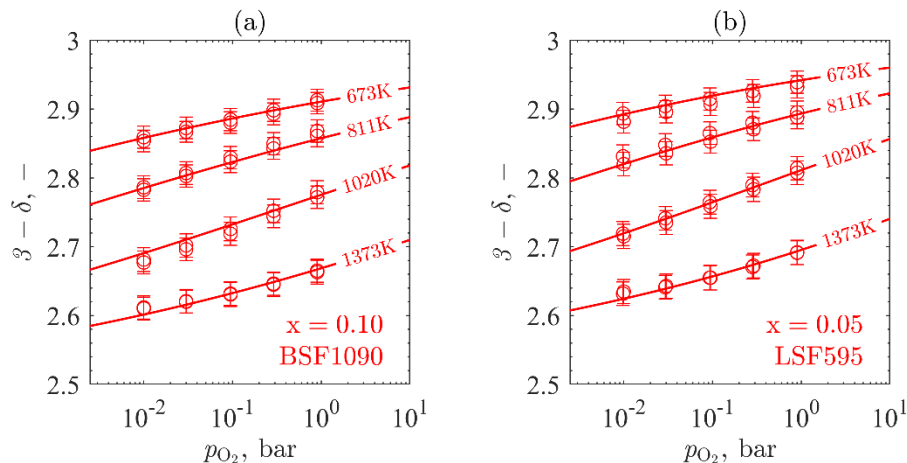


Fig. 3. Measured (markers) vs. CEF-modeled (lines) nonstoichiometry for (a) BSF and (b) LSF compositions.

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