

Experimental Screening of Singly- and Doubly-Substituted Strontium Ferrites for Solar Thermochemical Air Separation

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1. Introduction

An extensive screening was performed for singly- and doubly-substituted strontium ferrites. Different A- and B-site substituents were examined for improved reduction-oxidation (redox) capacities with the aim to maintain stability for solar thermochemical air separation applications. Singly- and doubly-substituted strontium ferrites $\text{Sr}_{1-x}[\text{A}']_x\text{Fe}_{1-y}[\text{B}']_y\text{O}_{3-\delta}$ where $\text{A}' = \text{La, Ba, Ca}$, $\text{B}' = \text{Co, Cr, Cu, Mn}$, and $x, y = 0, 0.1, 0.2$ were synthesized using the sol-gel method [1]. Ca^{+2} and Ba^{+2} A-site substituents were selected based on similar ionic radii to Sr^{+2} , and La^{3+} was selected to study the impact of increasing the average A-site charge. First-row transition metals with multiple oxidation states were selected for B-site substituents.

2. Experimental Methodology

Thermogravimetric analysis (TGA, Netzsch STA 449 F3 Jupiter $\pm 1 \mu\text{g}$) was performed to examine redox capacities as a function of temperature and O_2 partial pressure. $\text{Sr}_{1-x}[\text{A}']_x\text{Fe}_{1-y}[\text{B}']_y\text{O}_{3-\delta}$ powder samples were placed on an Al_2O_3 crucible shielded with a platinum foil to prevent unwanted reactions with the sample holder, and sample temperatures were measured by an S-type thermocouple. The relative mass losses were measured to determine redox capacities, and three separate screenings were performed to identify promising materials. Initially, a break-in step was performed for each sample to off-gas adsorbed species. The break-in cycle for *screen 1* consisted of a ramp to 1100 °C at 20 K/min, a 20 min isothermal dwell, a cool down to 300 °C at 20 K/min, and a 20 min isothermal dwell under 20% O_2/Ar . The target temperature was changed from 1100 °C to 1200 °C for *screen 2* and *screen 3*. A total gas flow rate of 200 $\text{mL}_{\text{N}}\cdot\text{min}^{-1}$ (where L_{N} denotes liters at nominal conditions, *i.e.*, 273 K and 1 bar) was used for all TGA.

Screen 1: After the initial break-in, samples were heated to 1100 °C at 20 K/min, held under isothermal conditions for 20 min to approach chemical equilibrium, cooled down at 20 K/min to 300 °C, and held under isothermal conditions for an additional 20 min to approach chemical equilibrium under 20% O_2/Ar .

Screen 2: A second screening was performed based on the initial findings for all materials except $\text{B}' = \text{Cr, Cu}$ and Mn , which were eliminated due to low redox capacities. The samples were heated to 1200 °C at 20 K/min, maintained at 1200 °C for 20 min, cooled down to 300 °C at 20 K/min, and held under isothermal conditions for 30 min, all under 20% O_2/Ar . A subsequent cycle was performed with the samples heated to 1200 at 20 K/min and held isothermal for 10 min under 100% Ar to promote greater reduction extents. The atmosphere was changed to 20% O_2/Ar to promote reoxidation, held for additional 10 min, then cooled to 300 °C at 20 K/min.

Screening 3: Temperature- and O_2 -pressure swing TGA were performed for $\text{A}' = \text{Ba}$ and La and $\text{B}' = \text{Co}$. After the initial break-in, samples were cycled between 250 and 1200 °C in a 20% O_2/Ar environment five times at heating and cooling rates of 20 K/min and held under isothermal conditions for 20 min. This was followed by five cycles between 0 to 20% O_2/Ar with the gas flow changed every 15 min at 750 °C.

3. Results

The results from *screen 1* are given in Table 1 with the reduction extent measured as the mass loss relative to the initial sample mass $\Delta m/m_0$. Samples are identified using the standard first-letter convention for perovskites, followed by numbers indicating the A and B substituent percentages (e.g. $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{FeO}_{3-\delta}$ \equiv BSF280 and $\text{SrCo}_{0.1}\text{Fe}_{0.9}\text{O}_{3-\delta}$ \equiv SCF019). For clarity, the convention was modified to include the full cation symbol for the substituents Ca, Cr, and Cu, while C represented cobalt. A-site substitutions increased redox capacities for all substituents. B' = Co was the only B-site substituent that resulted in an improved redox capacity with B' = Cr, Cu and Mn resulting in lower redox capacities.

Means and standard deviations for changes in oxygen vacancy concentration ($\Delta\delta$) calculated from measured mass loss for screen 3 are given in Table 2. $\overline{\Delta\delta}$ was consistent with the results from screen 2 with a $\sigma_{\Delta\delta}$ that was two orders of magnitude lower than $\overline{\Delta\delta}$ which demonstrates the sample redox repeatability. A-site substitutions of both Ba and La increased the redox capacity for the temperature swings but showed a lowered redox capacity for the O_2 pressure swings. B-site substitution of Co improved the redox capacity compared to strontium ferrite with mixed results relative to other singly-substituted samples.

X-ray diffractometry (XRD, Malvern PANalytical Alpha-1 MDP) was performed on all samples after synthesis and TGA screening to verify phase stability. Most materials had a tetragonal or cubic crystal structure. Scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDS) were performed on $\text{La}_{0.1}\text{Sr}_{0.9}\text{FeO}_{3-\delta}$ and $\text{Ba}_{0.1}\text{Sr}_{0.9}\text{FeO}_{3-\delta}$ to examine morphology and elemental distribution before and after thermal reduction and oxidation cycling experiments. Results from SEM showed smoothing and rounding of particle surfaces and particle sizes and no evidence of particle sintering or phase segregation.

References

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Table 1. Mass loss percentage from thermogravimetry in 20% O_2/Ar for temperatures between 300 and 1100 °C for singly-substituted strontium ferrites

Sample	$\Delta m/m_0$, %	Sample	$\Delta m/m_0$, %
$\text{SrFeO}_{3-\delta}$	2.23	-	-
BSF190	2.35	BSF280	2.22
CaSF190	2.32	CaSF280	2.35
LSF190	2.60	LSF280	2.39
SCF019	2.30	SCF028	2.27
SCrF019	1.78	SCrF028	1.37
SCuF019	1.79	SCuF028	1.86
SMnF019	1.87	SMnF028	1.99

Table 2. Average and standard deviation oxygen vacancy concentration for five temperature-swings between 250 and 1200 °C at 20% O_2/Ar and five pressure-swings between 0 and 20% O_2/Ar at 750 °C.

Sample	Temperature Swing		O_2 Pressure Swing	
	$\overline{\Delta\delta}$	$\sigma_{\Delta\delta}$	$\overline{\Delta\delta}$	$\sigma_{\Delta\delta}$
$\text{SrFeO}_{3-\delta}$	0.31	0.0033	0.14	0.0010
BSCF1919	0.32	0.0046	0.11	0.0032
BSF190	0.33	0.0025	0.12	0.0038
LSCF1919	0.35	0.0024	0.13	0.0044
LSF190	0.33	0.0040	0.13	0.0042