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Perovskite Oxides for Solar Air Separation

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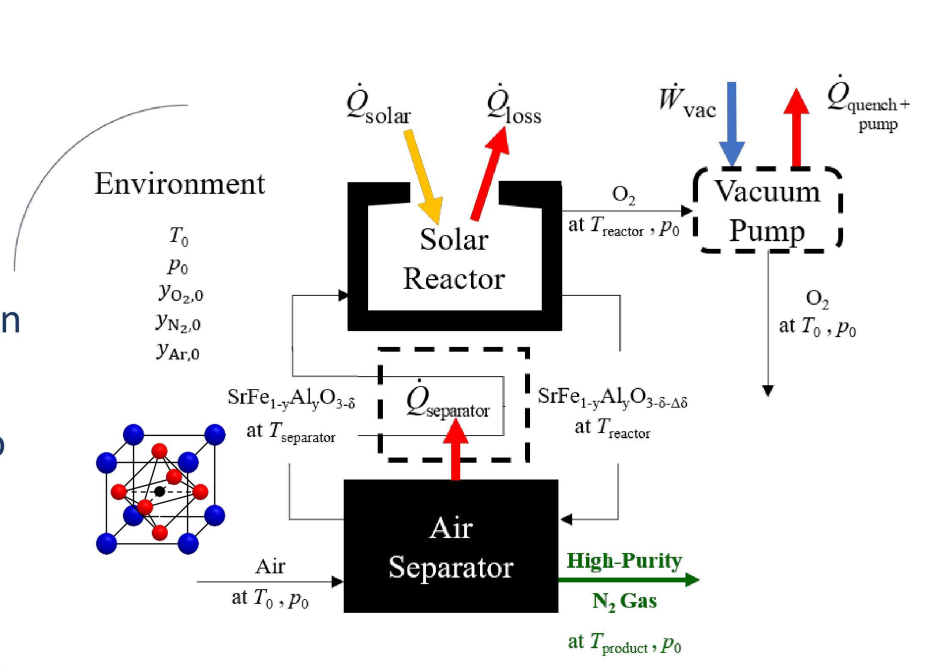
INTRODUCTION

Conventional NH_3 Production

- Haber Bosch process is currently used to produce NH_3 fertilizer for agriculture
- Energy intensive: chemical reactions require high temperatures and pressures
- Associated CO_2: 1% of global GHG emission

Proposed Alternative Cycle

- Solar reduction-oxidation (redox) cycles to separate pure N_2 from air
- N_2 reacted with H_2 to produce NH_3
- Low/no CO_2 emissions
- $SrFeO_{3-\delta}$: appealing perovskite oxide for air separation; Al-doped form (SAF) studied



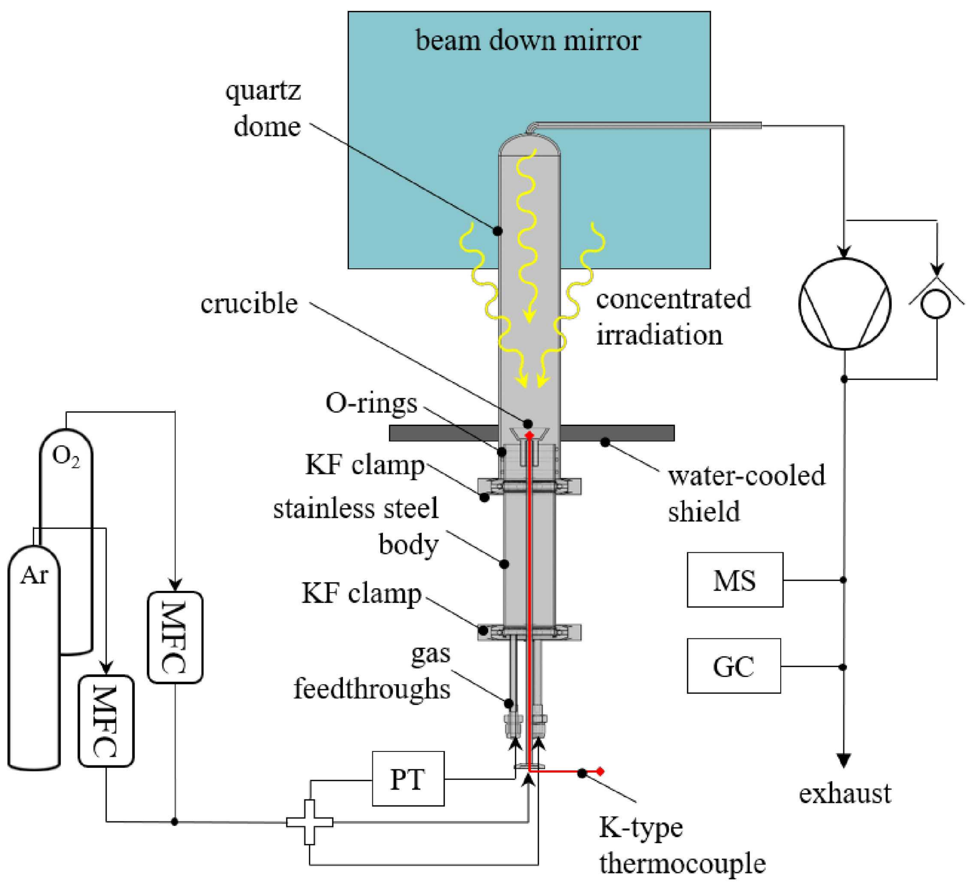
KINETIC STUDIES

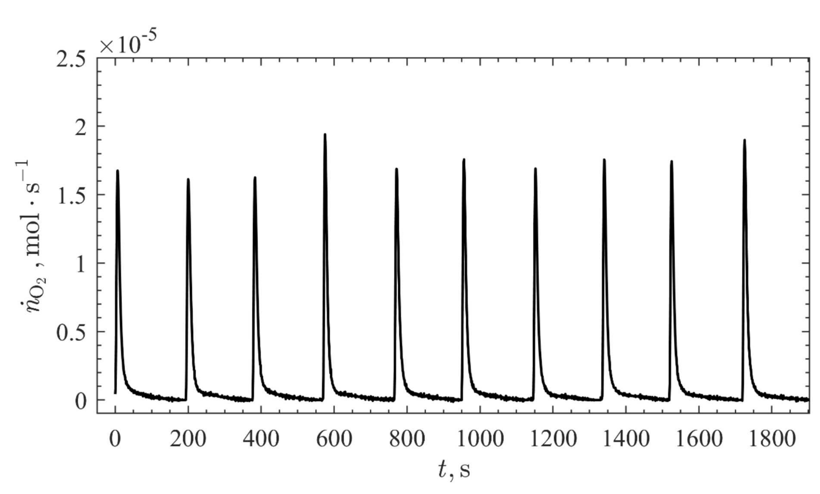
Experimental Method

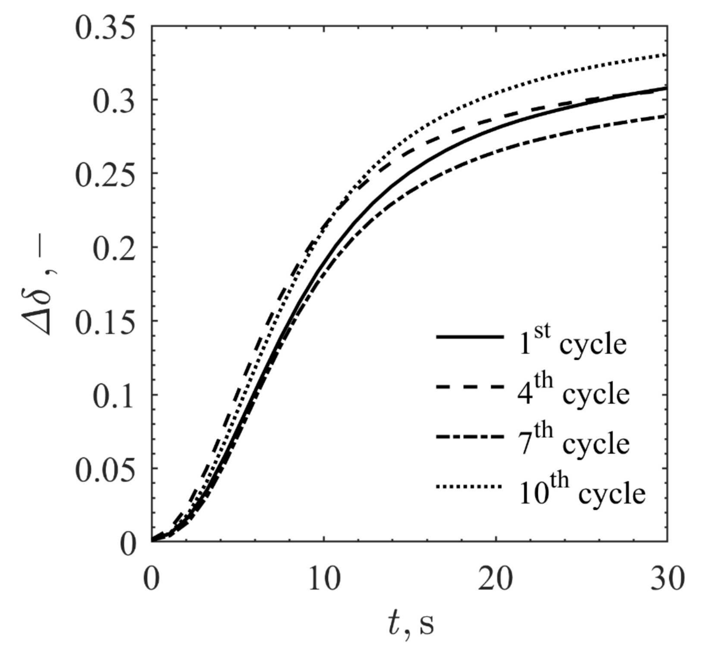
- On-sun reduction at low vacuum (Ar), off-sun oxidation (O_2) cycles
- Radiative input from high flux solar simulator (HFSS)
- Rapid initial heating > 50 K/s for kinetic studies
- Upward flow reactor (UFR) with optimized gas transport
- Reduction monitored via MS and GC measurements of O_2 flow

Redox Performance

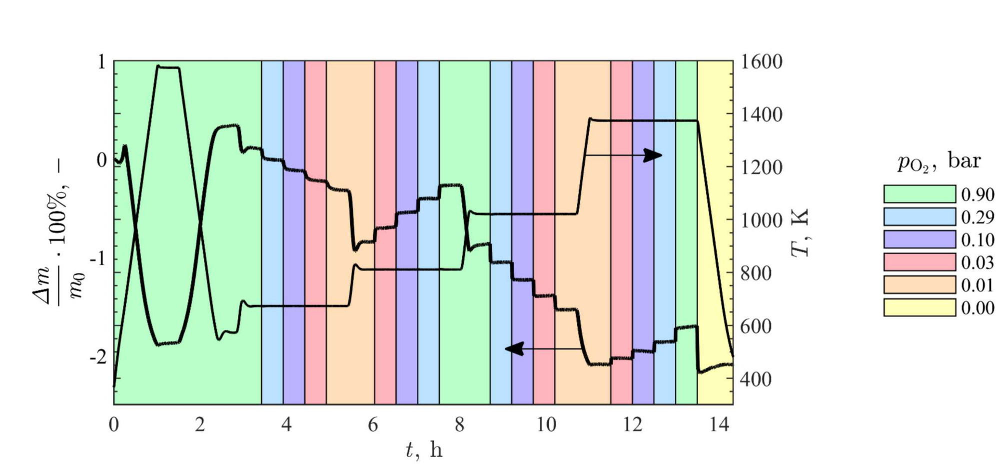
- Very high redox extents reached, $\Delta\delta > 0.30$ for multiple cycles
- Rapid kinetics, equilibrium attained within approximately 30s
- No degradation or significant $\Delta\delta$ variation over ten redox cycles







THERMODYNAMIC MODELING

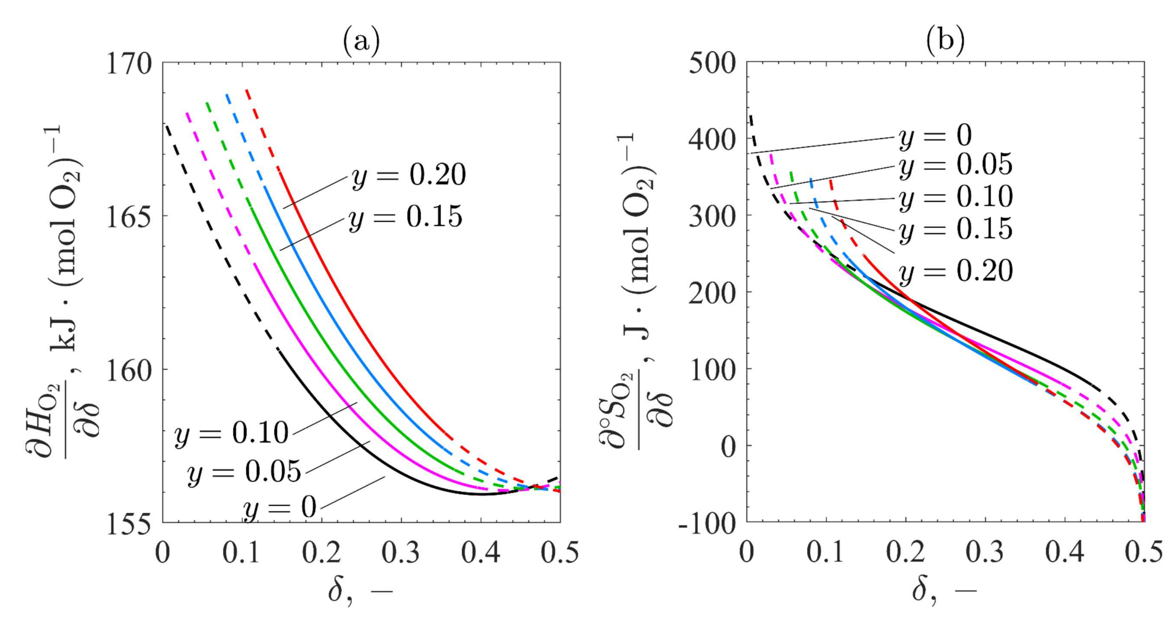


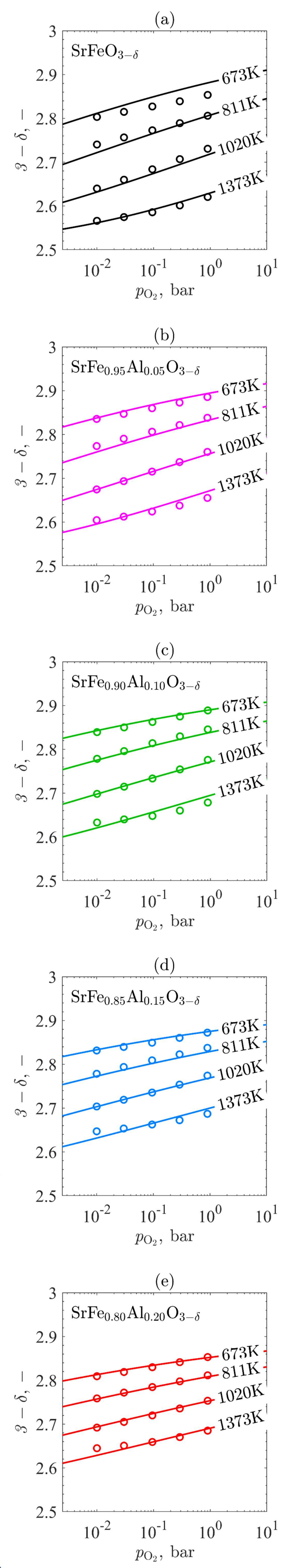
Experimental Method

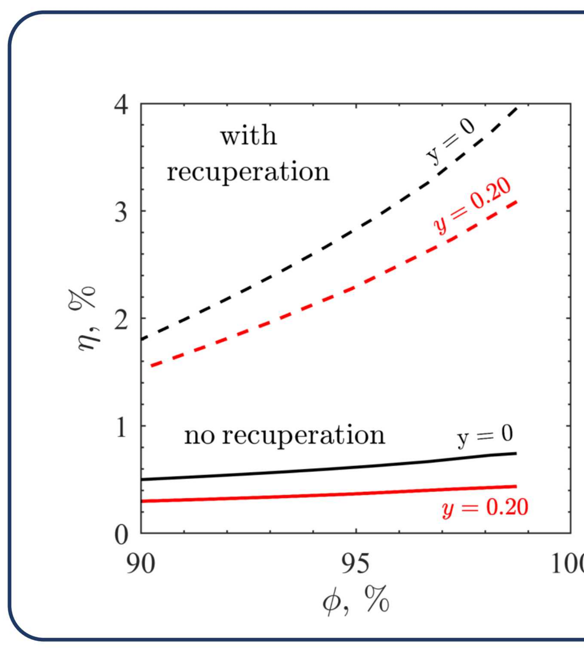
- Reduction-oxidation equilibria experiments performed in a thermogravimetric analyzer (TGA) in O_2/Ar
- Temperatures from 673 to 1373 K, O_2 pressures from 0.01 to 0.90 bar, Al-dopant concentrations from 0 to 20%

Compound Energy Model

- SAF modeled as weighted sum of end members, with added terms for mixing entropy and sublattice interactions
- Nonlinear ΔG_{redox} minimization used to fit TGA experiments to predict redox extent $\delta = f(T, p_{O2}, y)$
- Predictions of δ and redox enthalpy were consistent with experiments and density functional theory predictions
- Interaction terms were highly significant, consistent with vacancy ordering previously observed for $SrFeO_{3-\delta}$





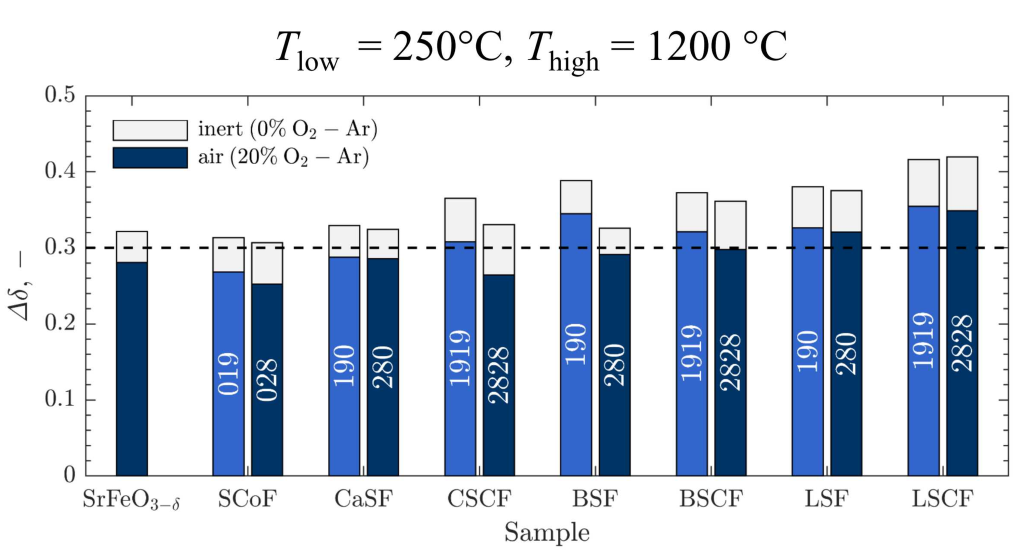


Air Separation Cycle Model

- Solar $SrFeO_{3-\delta}$/SAF reduction reactor
- Off-sun N_2/O_2 air separator
- High-purity N_2 production
- Model optimized T, p_{O2} of reactors, SAF Al-concentration
- Efficiency η improves as N_2-purity ϕ increases.

NEXT STEPS

- Broad material screening study performed of substituted $SrFeO_{3-\delta}$
- Goal: identifying optimal materials for air separation
- Several compositions identified that exceed $SrFeO_{3-\delta}$ performance
- Detailed thermodynamic and kinetic characterization underway
- Novel N_2-carrier materials for NH_3 formation currently in development



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