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High Temperature Measurements for Simulated Solar Thermal Reduction of Metal Oxides

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Thermal reduction of metal oxides with concentrated sunlight may provide viable paths to solar energy storage and/or renewable fuel production [1-3]. Various oxide materials and structures [4-7] have been proposed for use in redox cycles with a high-temperature endothermic reduction step (on-sun). The reduction step releases oxygen from the oxide under very rapid heating, typically to temperatures >1000 °C depending on the oxide. The reduced material can be stored in a low-oxygen atmosphere for later re-oxidation with an oxidant for fuel production and/or energy release. Identifying oxide materials with favorable redox thermodynamics and kinetics for cost-effective and durable systems requires carefully controlled lab-scale characterization, that can mimic the high heat fluxes and heating rates (> 100 °C/min) encountered under concentrated solar conditions. This study presents experimental measurements and associated challenges for characterizing oxide-based redox cycles with very rapid heating rates.

Bench-scale infrared furnaces are employed to simulate thermal reductions driven by concentrated sunlight. While the spectral distribution of radiation in infrared furnaces does not match the solar spectral distribution, infrared furnaces do provide rapid heating rates, which may induce non-equilibrium kinetics in the oxide reduction. Control of these furnaces and the associated radiation-based heating can be difficult because of the rapid heating rates and also because of the generally unknown spectrally-resolved optical properties of the relevant oxides. Robust thermocouples in the samples used as a control signal for the furnace have time constants on the order of 10 seconds, which complicates furnace temperature control. Furthermore, the radiative heat transfer characteristics of different samples can vary widely, further complicating the heat transfer within the sample bed. The intricacies of high temperature measurements and our solutions to control of such systems are discussed.

Our team has performed various measurements in a controlled infrared furnace of small packed beds of various reducible oxides with a particular emphasis on doped-ceria oxides for splitting CO_2 in solar-driven redox cycles. Cycle-to-cycle measurements of a promising oxide, nano-fibrous $Ce_{0.975}Zr_{0.025}O_2$ fabricated via electrospinning to produce high-surface area ceramic fibers [8, 9], are illustrated in Figure 1. Reliable temperature control to achieve reproducible cycle temperature profiles provides consistent high-temperature reduction as well as CO_2-based reoxidation at low-temperatures as measured by raman analysis of the effluent (O_2 and CO). Due to the very rapid CO_2 splitting reaction (Figure 1), integration of the peak areas for accurate measures of total degree of oxide reduction requires rapid gas composition analysis (1 second or less). Well-characterized measurements in rapid heating furnace measurements are critical for assessing promising oxide materials like $Ce_{0.975}Zr_{0.025}O_2$ for concentrated solar reactor performance.

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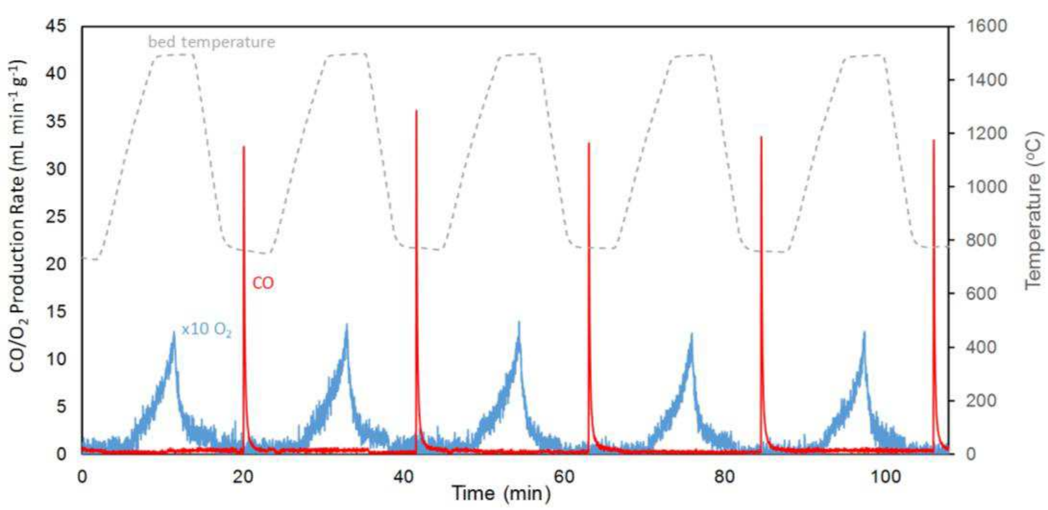

Figure 1. Metal oxide ($Ce_{0.975}Zr_{0.025}O_2$) fibers subjected to a thermal reduction in at 1500°C in an infrared furnace. The high temperature reduction step leads to O_2 release, and is followed by a re-oxidation at 800°C via exposure to CO_2. Heat rates are 100°C/min to minimize temperature overshoot and ensure sample temperature is accurately measured.