Thermochemical CO_2 and H_2O Splitting via Chemical-Looping with Cerium and Cobalt Mixed Oxides for Oxygen Generation.

Ari Fischer, Chunxiang Zhu, George M. Bollas
[*] *Department of Chemical & Biomolecular Engineering, University of Connecticut, Storrs, 191 Auditorium Road, Unit 3222, Storrs, CT, 06269-3222, USA. Email:ari.fischer@uconn.edu*

Reliable oxygen supply for NASA exploratory manned space missions is of strategic importance. The best method to provide the O_2 required for manned missions is to recycle the oxygen contained in CO_2 and H_2O produced by the astronauts in the space vessel. To accomplish this goal, this projects bridges elements of materials science and reactor and process design in an effort to break the thermodynamic equilibria of the unfavorable splitting of CO_2 and H_2O, at a minimum energy penalty and system size. This presentation will discuss progress made in enhancing the oxygen production from CO_2 and H_2O by utilizing, in a sequential manner, the oxidation and reduction properties of CeO_2 and Co_3O_4, respectively. Co_3O_4 has been shown to release oxygen via a process known as Oxygen Uncoupling at temperatures 800-900°C.[2] This work will explore the feasibility of pairing the thermal oxygen uncoupling (reduction) of Co_3O_4, with a regeneration step of oxygen transport from CeO_2, which in turn is oxidized by CO_2 in a separate process step. Oxygen uncoupling operates on the principle that for certain metal oxides (e.g., Co_3O_4) it is thermodynamically feasible to uncouple gaseous oxygen, while being exothermally reduced in an inert atmosphere. At the same time, certain metals (e.g., CeO) show favorable kinetics for oxidation by CO_2 at elevated temperatures. It is also well known that metals alloys allow for the transport of oxygen between the metals comprising them. Thus, one can envision a process, in which a Ce-based oxygen carrier performs CO_2 splitting in an endothermic process, transports the captured oxygen to a Co-based oxygen carrier, which then uncouples it to gaseous oxygen in an exothermic process. The objective of this work is to explore experimentally such mixed metal oxygen carriers and show the thermodynamic and kinetic feasibility envelopes for an oxygen production process.

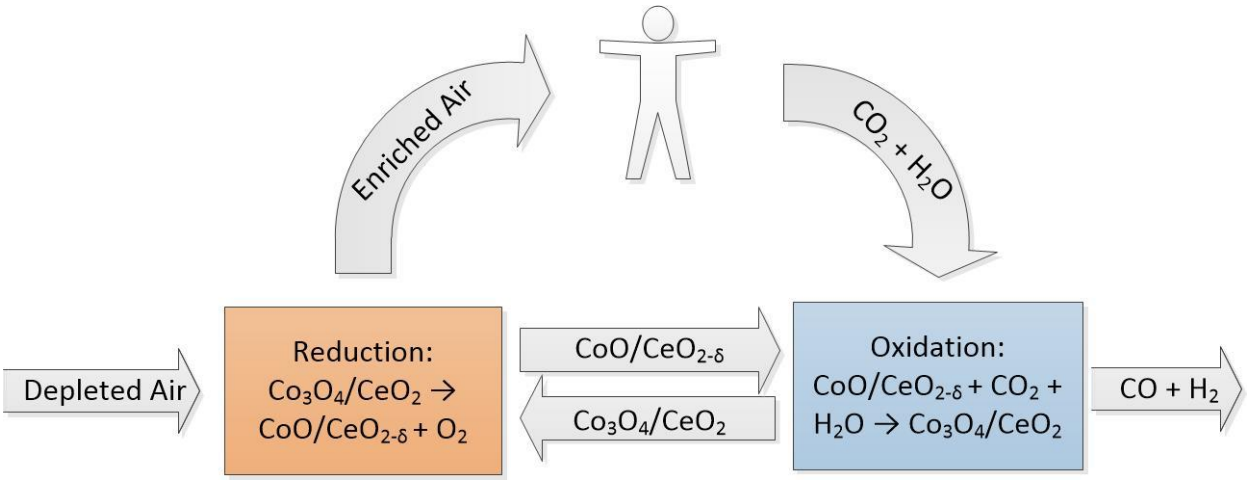


Figure 1: Basic concept of CO_2 and H_2O splitting via chemical-looping with cerium and cobalt oxides.

High temperature cycling of CeO_2 and Co_3O_4 mixed metal oxides can achieve thermochemical splitting of H_2O and CO_2. CO_2 and H_2O are stable molecules; for example H_2O requires prohibitive temperatures of about 4100 K before direct thermolysis is thermodynamically feasible.[1] However, metal redox cycles using cerium oxide (CeO_2) have been proven capable of CO_2 and H_2O reduction at temperatures as low as 900°C, as described by Scheffe et al.[1] This cycle was tested by Chueh et al.[3] under realistic solar concentrating conditions over 500 cycles to yield syngas that reflected in composition the CO_2 and H_2O feed ratio[1]. Figure 1 shows a basic diagram for the oxidation and reduction reactions. The reduction phase occurs at high temperature via nonstoichiometric oxygen release (the cerium oxide lattice structure is retained despite oxygen vacancies) in the cerium and by the cobalt oxide uncoupling reaction. In the oxidation phase, $CeO_{2-\delta}$ is oxidized by CO_2 and H_2O to produce CeO_2 and syngas. Oxygen transport from the ceria oxidizes CoO to form Co_3O_4. For pure ceria cycles, δ is limited to 0.25 and therefore the extent of oxygen generation is small. By pairing CeO_2 and Co_3O_4 oxides, the CO_2 and H_2O splitting properties of ceria and the oxygen uncoupling properties of cobalt oxide can increase the amount of oxygen released. In this study, CeO_2 and Co_3O_4 mixed oxides were prepared using a co-precipitation method. These oxygen storage materials were characterized using XRD, SEM, and TGA. A fixed-bed reactor was used to study high temperature oxygen release in an inert gas and CO_2 reduction over the oxygen depleted material.

Acknowledgments
This work is supported by the Fall 2013 Connecticut Space Grant Consortium Undergraduate Research Fellowship.

References:

1. Scheffe JR, Steinfeld A. Oxygen exchange materials for solar thermochemical splitting of H2O and CO2: a review. *Mater. Today* 2014;00(00):1-8.

2. Adanez J, Abad A, Garcia-Labiano F, Gayan P, de Diego LF. Progress in Chemical-Looping Combustion and Reforming technologies. *Prog. Energy Combust. Sci.* 2012;38(2):215-282. doi:10.1016/j.pecs.2011.09.001.

3. Chueh W, Haile S. A thermochemical study of ceria: exploiting an old material for new modes of energy conversion and CO2 mitigation. *Philos. Trans. A. Math. Phys. Engr. Sci.*, vol. 368, no. 1923, pp. 3269-94, Jul. 2010.