Oxygen Storage Properties and Structural Evolution of AFe_2O_4 (A= Lu, Y, Yb, In) Under Chemical Looping Conditions.

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Chemical looping reactions (CLRs) involve an oxy-fuel combustion process with the participation of a metal oxide system that act as the oxygen storage material (OSM) delivering oxygen from air to the fuel reactor. OSMs eliminate the need to purify and isolate oxygen by the costly process of cryogenic distillation. Furthermore, it enables easy sequestration of CO_2 by distilling out water and prevents contamination from NOx gas formation. Binary metal oxides as OSMs lack long term stability due to agglomeration and sintering at high temperature. Ternary metal oxides on the other hand are extensively researched as OSMs owing to their high structural stability and flexibility.[1]

In a study done in 2013, $LuFe_2O_4$ was proposed as an OSM for the first time due to its reversible cycling capability between its reduced (Fe +2.5) and oxidized (Fe +3) states at 500 °C under H_2 and a dynamic vacuum.[2] In our most recent study, we explored four A-site analogues of AFe_2O_4 (A= Y, Yb, Lu and In) with high temperature gas flow experiments combined with in situ synchrotron X-ray powder diffraction.[3] Cycling experiments done at 600 °C under alternating atmospheres of air and H_2 showed the reversible structural transition between the reduced and the oxidized phases. In our current study we are working on solving the structure of the maximally oxidized phase with powder diffraction data. We have been able to obtain a reasonable model for the structure of this oxidized phase using simulated annealing and Fourier difference map.

To be used as an OSM for CLRs, the reactivity with a fuel such as CH_4 should also be explored. In our most recent in situ neutron powder diffraction experiments on the POWGEN beamline at SNS, the reactivity under CH_4 for AFe_2O_4 (A = Lu, Yb) was confirmed. Experiments were conducted emulating the conditions in a chemical looping reactor. The samples were reacted at 600°C under alternating atmospheres of air and CH_4 while collecting in situ neutron diffraction patterns. CH_4 was able to regenerate the pristine structure of these materials, and this reactivity under CH_4 has never been reported before for these oxides.

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(3) Jayathilake, R.; Levitas, B.; Rodriguez, E. E, "*In situ* diffraction studies on reversible oxygen uptake and release in $A Fe_2O_{4+\delta}$ (*A*=Lu, Yb, Y, In)", *J. Mater. Chem. A.*, **2018**, *6*, 4801-4810. (DOI 10.1039/C7TA09823E)