

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 NO_x 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 The rapid data collection at 17-BM at the Advanced Photon Source (APS) enabled us to monitor structural changes as a function of time and temperature. Cycling experiments were done at 600 °C under alternating atmospheres of air and H_2 . Refined unit cell volume evolution with time confirmed the cycling stability for the A= Lu, Y and Yb analogues. We also observed that there is a clear correlation between kinetics of oxidation and the A-site cationic radii. Bond valence sum calculations for the Fe-site done using high resolution synchrotron X-rays, collected on the 11-BM beamline at APS, showed that the more under-bonded the Fe-site is, the more reactive the metal oxide becomes. The analysis of this study showed that A= Yb, Y and Lu perform well as OSMs.

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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