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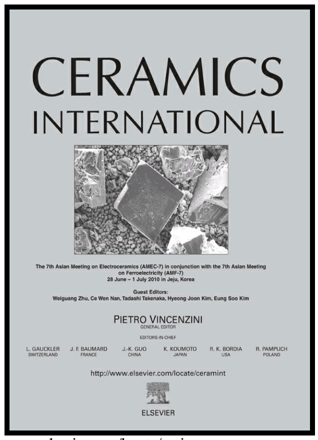

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Thermal Oxygen Exchange Cycles in Mixed Manganese Perovskites

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Abstract

Oxygen exchange properties of a series of mixed manganese perovskites were studied using a thermocycling reactor system designed and built in-house. Experiments were carried out under 1200°C, much lower than the 1500°C often required for oxygen exchange in other systems such as ceria. Strontium manganese oxide was identified as a particularly promising candidate for further development, whose further microstructural control may lead to its emergence as a valuable oxygen exchange material.

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1. Background

The unchecked burning of fossil fuels is not sustainable, and it is important to investigate strategies to increase the value of waste CO_2. One such strategy is to use thermal cycles of solid oxides to reduce CO_2 to CO (and H_2O to H_2), as demonstrated in a seminal report by Chueh et al in 2010.[1] CO and H_2 are together known as syngas, and they can be very easily converted in synthetic fuels and other products via the Fischer-Tropsch process.[2] Cheuh's thermal cycle of ceria for carbon dioxide reduction featured two steps as follows:

1500°C: $$CeO_2 \rightarrow CeO_{2-\partial} + \frac{\partial}{2} O_2 \quad (1)$$

900°C: $$CeO_{2-\partial} + CO_2 \rightarrow CeO_2 + \partial CO \quad (2)$$

The high temperature step is carried out under inert gas flow, which sweeps away the evolved oxygen, and the low temperature step features the re-oxidation of ceria using CO_2 (or H_2O) as an oxidant, which yields CO (or H_2). Such processes will be referred to generally here as thermal oxygen exchange cycles, since they feature the ejection and subsequent injection of oxygen atoms for a solid oxide system at different temperatures, for a given solid oxide and gaseous oxidant system.

The temperature used for Chueh's process (especially the 1500°C high temperature step) is extraordinarily high. For reference, steel often melts at a temperature of about 1370°C. Although it is possible to use solar concentrators to reach these temperatures, such a feat requires very high quality solar concentrators and exceptional reactor engineering. And such a CO_2 cycling system only makes sense if it is driven by renewable (solar) energy. Thus it is of interest to engineer oxide systems that may exhibit such thermal oxygen exchange cycles at lower temperatures, so that simpler solar concentrator systems may be employed.

Ceria certainly has a host of physical and chemical properties that make it interesting, especially for oxygen exchange, and there have been efforts in doping ceria to achieve lower temperature results.[3] An increasing amount of attention is being paid, however, to manganese perovskite systems,[4] some of which are reported to operate at temperatures as low as 1200°C.[5] It is thought that the perovskite crystal structure is more amenable to chemical doping and substitution, and thus represents a wider chemical space to explore, compared to the fluorite structure of ceria.[4]