

## Rare Earth Oxides/Sulfides as High Temperature Sulfur Adsorbents

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### Introduction

Removal of H<sub>2</sub>S from reformat gas streams is necessary to meet the stringent environmental regulations for sulfur emissions, prevent corrosion of the blades of the turbines in IGCC and fouling of the anode materials in fuel cell systems. Suitable sorbent materials should have favorable sulfidation equilibria, good kinetics, and high structural stability and regenerability at the operating temperature (650-800°C) to avoid heat exchanger penalties. Sorbent regeneration, necessary for applicability and economic viability of the process, has been considered via re-oxidation of the sorbent sulfides formed during the sulfidation step back to the oxides. However, due to phase changes between sulfide and oxide and potential sulfate formation during the regeneration step, gradual degradation of cyclic performance of sorbents is common with bulk single and mixed oxides.<sup>1</sup> Poor performance stability in cyclic operation of sulfidation and regeneration imposes major constraints on the choice of materials.

Rare earth oxides have received attention because of their excellent sulfidation equilibria, which allows sub-ppmv H<sub>2</sub>S levels to be achieved at temperatures as high as 800°C. In ongoing work, we have been investigating cerium and lanthanum oxides as high-temperature regenerable sorbents for the removal of H<sub>2</sub>S upstream of the SOFC anode<sup>2-5</sup>. The trivalent rare earth oxides, Re<sub>2</sub>O<sub>3</sub>, meet the criteria of high desulfurization efficiency<sup>6</sup> and fast sulfidation kinetics<sup>3,5</sup>. Single or mixed lanthanide (La, Pr) oxides are also a good choice for high-temperature desulfurization because of their excellent sulfidation thermodynamics in realistic reformat gas compositions.

In practical fuel cell applications, during the start-up mode the air-rich combustor exhaust gas can be used to heat up the sorber to the desired operation temperature. The effect of air-rich treatment on the sulfidation performance of pure and mixed lanthanide oxides, as well as the stability of the samples under intermittent operation have been investigated. Along the same line, the stability and regenerability of the sulfided lanthana-based samples has been examined when air-rich gas is employed to regenerate the desulfurization unit. Elution of SO<sub>2</sub> and formation of sulfate species during regeneration as well as identification of conditions for safe fuel cell operation are the primary objectives of the present investigation.

### Materials and Methods

Lanthanide oxide sorbents were prepared by a variation of the urea coprecipitation/gelation method (UGC), adapted for these materials in our laboratory. Sorbents were calcined either at 650°C or 800°C in air for 4 h. Sulfidation and regeneration were carried out in a packed-bed, quartz-tube micro-reactor (I.D.=1.0cm) to evaluate the sorbent sulfur capacity, sulfur removal efficiency and regenerability. Samples were first heated to the desired sulfidation temperature in 90%air-5%CO<sub>2</sub>-5%H<sub>2</sub>O gas mixture simulating the composition of the combustor exhaust

gas. The sulfidation gas mixture, simulating a realistic reformat gas composition (250ppmH<sub>2</sub>S-20%H<sub>2</sub>-25%CO-5%CO<sub>2</sub>-5%H<sub>2</sub>O-balance He), was then introduced. In cyclic tests, regeneration was performed in the same air-rich gas mixture used for reactor heat up.

### Results and Discussion

Lanthana-based sorbents with up to 30 at % Pr content prepared by the UGC method are suitable as high-temperature filters for once-through operation. The sulfur capacity for sub-ppmv breakthrough of H<sub>2</sub>S exceeds 50 mg S/g<sub>sorbent</sub> and in some cases we have found it to be ~70 mg S/g<sub>sorbent</sub>. In a two-step sulfidation experiment simulating intermittent operation, we found that desulfurization in the second step picks up from where it was left at the end of the first step. No SO<sub>2</sub> elution was noticed after cooling down and heating up in air/CO<sub>2</sub>/H<sub>2</sub>O in between the two steps. For the presulfided samples, if air-rich mixtures (boiler off gas) are to be used for intermittent operation, the choice of a very short contact time is crucial. Only then can sulfates be avoided, and subsequent operation in the fuel-rich gas is free of SO<sub>2</sub>/H<sub>2</sub>S which would be detrimental to the fuel cell materials. Figure 1 depicts this for a series of five cycles of surface adsorption/regeneration using air/CO<sub>2</sub>/H<sub>2</sub>O mixture in regeneration at 600 °C.

### Significance

Stability and regenerability of sulfided lanthana-based sorbents in air-rich gas mixtures is important for practical fuel cell applications. Intermittent (Stop-start) operation is also possible, but high space velocities are required to avoid sulfate formation.

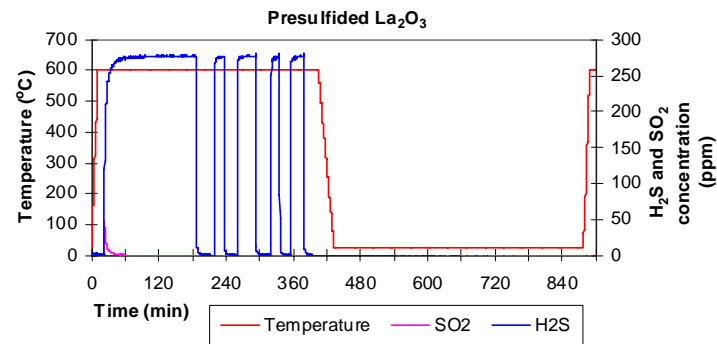


Figure 1. Five-cycle sulfidation/regeneration of presulfided La<sub>2</sub>O<sub>3</sub> at S.V.=360,000/h

### References

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