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# High-Temperature Desulfurization of Heavy Fuel-Derived Reformate Gas Streams for SOFC Applications

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# High-Temperature Desulfurization of Heavy Fuel-Derived Reformate Gas Streams for SOFC Applications

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## Abstract

Desulfurization of the hot reformate gas produced by catalytic partial oxidation or autothermal reforming of heavy fuels, such as JP-8 and jet fuels, is required prior to using the gas in a solid oxide fuel cell (SOFC). Development of suitable sorbent materials involves the identification of sorbents with favorable sulfidation equilibria, good kinetics, and high structural stability and regenerability at the SOFC operating temperatures (650 to 800 °C). Over the last two decades, a major barrier to the development of regenerable desulfurization sorbents has been the gradual loss of sorbent performance in cyclic sulfidation and regeneration at such high temperatures.

Mixed oxide compositions based on ceria were examined in this work as regenerable sorbents in simulated reformate gas mixtures and temperatures > 650 °C. Regeneration was carried out with dilute oxygen streams. We have shown that under oxidative regeneration conditions, high regeneration space velocities (>80,000 h<sup>-1</sup>) can be used to suppress sulfate formation and shorten the total time required for sorbent regeneration.

A major finding of this work is that the surface of ceria and lanthana sorbents can be sulfided and regenerated completely, independent of the underlying bulk sorbent. This is due to reversible adsorption of H<sub>2</sub>S on the surface of these sorbents even at temperatures as high as 800 °C. La-rich cerium oxide formulations are excellent for application to regenerative H<sub>2</sub>S removal from reformate gas streams at 650 to 800 °C.

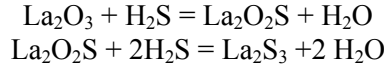
These results create new opportunities for compact sorber/regenerator reactor designs to meet the requirements of solid oxide fuel cell systems at any scale.

## Research Results and Discussion

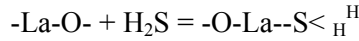
### Rationale for Sorbent Selection

Ce<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub> are excellent choices for hot gas desulfurization to <1 ppm H<sub>2</sub>S levels (ref. 1). Fully oxidized ceria, on the contrary, is a poor desulfurization material. The structural properties of this type sorbents in regenerative desulfurization need to be fully understood to enable proper design for the intended application. Cu-CeO<sub>x</sub> has good sulfidation kinetics (ref. 2) and was also found promising for low-temperature gas desulfurization (ref. 3). In recent work funded by the CTA program of the ARL, we examined both La- and Cu-doped cerium oxides as high-temperature regenerable sorbents for the removal of H<sub>2</sub>S upstream of the SOFC anode (ref. 4). Lanthana is a good additive, adding sulfur capacity and also thermally stabilizing ceria against sintering at high temperatures (ref. 5).

Bulk sulfidation of the rare earth oxides produces oxysulfides and higher sulfides. For example, sulfidation of lanthanum oxide gives:



In addition to the bulk sorbent sulfidation, the surface of the sorbent can further adsorb H<sub>2</sub>S:



As will become evident from this report, it is advantageous to design a swing adsorption/desorption process employing the surface of the sorbent only, altogether avoiding bulk sulfide regeneration.

### Sorbent Preparation, Characterization, and Testing

Table 1 lists key properties of the fresh (as prepared) sorbents. All lanthanum- or copper-containing ceria samples were made by the urea-gelation coprecipitation method, and had surface areas in the range of 71-100 m<sup>2</sup>/g after 650 °C-calcination in air for 4 h. The crystallite size of CeO<sub>2</sub> in each sample was calculated using the Scherrer equation based on the corresponding X-ray diffraction (XRD) pattern. The average CeO<sub>2</sub> particle sizes of as prepared ceria-based sorbents are from 7.5 to 9.2 nm.

TABLE 1.—EFFECT OF GAS AND HEAT TREATMENT ON SORBENT SURFACE AREA

Sorbent	Specific Surface area after treatment (m <sup>2</sup> /g)		
	650 °C 4 h Air	650 °C 1 h 50%H <sub>2</sub> -10%H <sub>2</sub> O-He <sup>a</sup>	800 °C 1 h 50%H <sub>2</sub> -10%H <sub>2</sub> O-He <sup>a</sup>
CeO <sub>2</sub>	71	73.1	25.1
Ce10at%LaO <sub>x</sub>	100	73.2	32.3
Ce30at%LaO <sub>x</sub>	85	61	28.3
Ce50at%LaO <sub>x</sub>	87.2	59.7	25.9
Ce70at%LaO <sub>x</sub>	85.3	38.2	13.8
La <sub>2</sub> O <sub>3</sub>	5	3.4	1.4
10at%Cu-CeO <sub>2</sub>	100	56.5	<1

<sup>a</sup>Sorbents were first calcined in air at 650 °C for 4 h; the surface area of each material after calcinations is shown in column 1.

In a typical fixed-bed sulfidation process, initially sulfidation of the top layer of the sorbent takes place while the rest of the sorbent is being exposed to H<sub>2</sub>S-free reformat gas. Therefore, it is necessary to examine potential structural effects of this reduction process on the sorbent properties. For practical application, the pre-reduced sorbent structure, rather than the fresh one, is of importance in rank ordering the activity/regenerability of various sorbent compositions. The surface areas of selected sorbents after exposure to the H<sub>2</sub>S-free 50%H<sub>2</sub>-10%H<sub>2</sub>O-He gas mixture at different temperatures are listed in table 1. Prior to the reduction test, each sorbent had been calcined at 650 °C, 4 h in air. The corresponding initial surface areas are also shown in table 1 (1st column). Compared with the as prepared sorbents, after pre-reduction at 650 °C, the surface areas of all sorbents dropped appreciably. When reduction temperature rose to 800 °C, the loss of surface area was higher for all sorbent compositions. Clearly, the most dramatic surface area loss was suffered by the Cu-containing ceria samples at 800 °C. However, these materials retained adequate surface area after reduction at 650 °C.

Sulfidation tests were run at atmospheric pressure in a packed-bed quartz-tube microreactor (1.0 cm i.d.) to evaluate the sorbent H<sub>2</sub>S removal efficiency and sulfur capacity. Particles of diameter less than 53 μm were used in the reactivity tests. Typically, 0.34 g sorbent was loaded on a quartz frit, located at the center of the reactor. To mimic the conditions in a fixed-bed sorber where most of the bed is initially exposed to sulfur-free gas, pre-reduction of the sorbents in H<sub>2</sub>S-free fuel gas at the corresponding sulfidation temperature was carried out prior to each sulfidation test. All gas mixtures were of analytical grade (H<sub>2</sub>S (Airgas, He/H<sub>2</sub>S of 99.5/0.5), H<sub>2</sub> (Airgas, 99.999%), He (Airgas, 99.999%), O<sub>2</sub> (Airgas, He/O<sub>2</sub>

of 90/10)). Samples were first heated in helium to the desired sulfidation temperature. A 50% H<sub>2</sub>-10% H<sub>2</sub>O-bal.He mixture gas was switched in to pre-reduce the sorbents for 1 h. The sulfidation gas mixture, 0.1% H<sub>2</sub>S-50% H<sub>2</sub>-10% H<sub>2</sub>O-bal. He, was then introduced. This mixture contained no CO (all is made up by hydrogen); and an exaggerated amount of H<sub>2</sub>S (0.1 percent) is used to reduce testing time. A flow rate of 40 mL/min (STP) was used in most tests conducted at 16,000 h<sup>-1</sup> gas hourly space velocity. H<sub>2</sub>S and SO<sub>2</sub> concentrations in the exit gas were measured on-line by a Western Research Series 900 UV-VIS analyzer (Ametek). Data from runs at 650 and 800 °C are presented here.

Cyclic sulfidation and regeneration tests were conducted in the quartz-tube microreactor under flow conditions. Prior to each sulfidation test, pre-reduction was conducted with the H<sub>2</sub>S-free gas mixture at the sulfidation temperature for 1 h, then sulfidation was carried out at the same temperature with 16,000/h (STP) space velocity, using a gas mixture of 0.1%H<sub>2</sub>S, 50%H<sub>2</sub>, and 10%H<sub>2</sub>O bal. He. Regeneration was conducted with two different gases at the same sulfidation temperature under 80,000/h space velocity. 3%O<sub>2</sub>/He was first used followed by H<sub>2</sub>S free reformat gas (50%H<sub>2</sub>-10%H<sub>2</sub>O-He). Each step was performed until the H<sub>2</sub>S and SO<sub>2</sub> exit concentrations lower than 10 ppm. H<sub>2</sub>S and SO<sub>2</sub> concentrations in the exit gas stream were measured continuously by a UV-visible analyzer. Any sulfur species eluted during this step was counted in the sulfur balance.

The cyclic sulfidation/regeneration performance of 10at%Cu-CeO<sub>2</sub> and Ce70at%LaO<sub>x</sub> sorbents was examined at 650 and 800 °C. Pre-reduction in a 50%H<sub>2</sub>-10%H<sub>2</sub>O-He gas mixture was conducted at the corresponding sulfidation test temperature for 1 h. A gas mixture with 3%O<sub>2</sub>/He was used for regeneration followed by reduction in the 50%H<sub>2</sub>-10%H<sub>2</sub>O-He gas mixture. The sulfur loadings at 30 ppm H<sub>2</sub>S breakthrough are shown in figure 1 for Ce70at%LaO<sub>x</sub>. The sulfur capacities for the first cycle under both sulfidation temperatures (650 and 800 °C) are close to each other and are the highest (~30 mg S/g sorbent) among all cycles. A drop in sulfur loading took place with cycling, reaching a stable level of 3-4 mg S/g sorbent after the third cycle. There is no significant temperature effect on the stabilized sulfur loading of Ce70at%LaO<sub>x</sub> at the two different temperatures. This can be explained by the presence of a large amount of lanthanum oxide in this sorbent. Pre-reduction does not change the oxidation state of lanthanum oxide, thus the temperature effect on the extent of cerium oxide reduction here is not as important as in the cerium oxide-rich sorbents. Surface sulfidation only is displayed after the first two cycles. This is due to the high space velocity used in the tests. However, the much higher

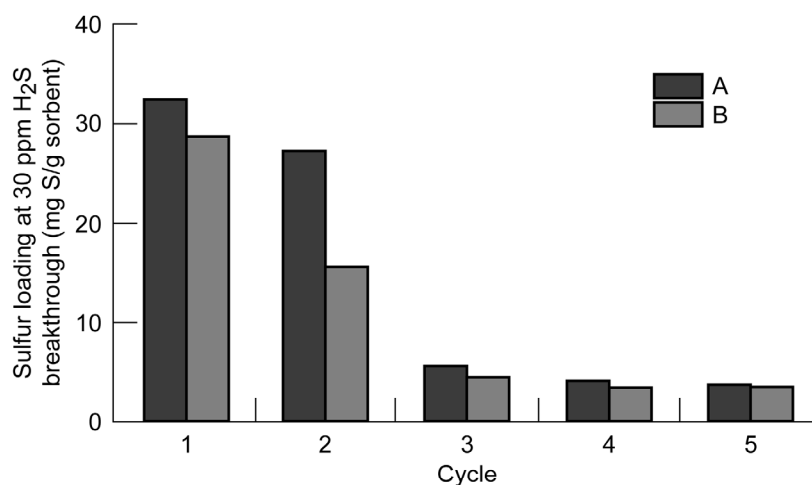
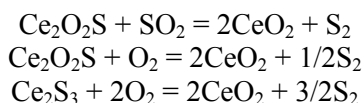


Figure 1.—Sulfur capacity of Ce 70% LaO<sub>x</sub> at 30 ppm H<sub>2</sub>S breakthrough in cyclic sulfidation/regeneration: A: pre-reduction: 650 °C, S. V. = 80,000 h<sup>-1</sup>; sulfidation: 650 °C, S. V. = 16,000 h<sup>-1</sup>; regeneration: 650 °C, S. V. = 80,000 h<sup>-1</sup>. B: pre-reduction: 800 °C, S. V. = 80,000 h<sup>-1</sup>; sulfidation: 800 °C, S. V. = 16,000 h<sup>-1</sup>; regeneration: 800 °C, S. V. = 80,000 h<sup>-1</sup>. Pre-reduction gas: 50% H<sub>2</sub>-10% H<sub>2</sub>O-He; sulfidation gas: 0.1% H<sub>2</sub>S-50% H<sub>2</sub>-10% H<sub>2</sub>O-He; regeneration gas: 3% O<sub>2</sub>/He.

sulfur loading in the first cycle indicates irreversible bulk absorption by the lanthana portion of the sorbent. Because of the high space velocity used in regeneration (80,000 h<sup>-1</sup>), the absorbed amount of sulfur in the first 1 to 2 cycles is retained in the bulk of the sorbent, while the stabilized amount of sulfur loaded in subsequent cycles is attributed to surface sulfidation only.

The type and amount of sulfur species eluted during the regeneration and reduction steps are shown in table 2. Only stabilized results, which were obtained after two cycles, are shown. Similar regeneration off-gas distributions were obtained at both temperatures examined when the sulfidation space velocity was 16,000 h<sup>-1</sup> (STP). At 650 °C, for example, about 52 percent of the total adsorbed sulfur was eluted in regeneration, in the form of H<sub>2</sub>S and SO<sub>2</sub> at a ratio of 10:1. Another ~26 percent was eluted in the following reduction step, mostly as H<sub>2</sub>S with only ~2 percent in the form of SO<sub>2</sub>. The sulfur species eluted during the reduction step indicate sulfate formation during the regeneration step. This is thought to be a result of reaction of the SO<sub>2</sub> eluted during regeneration with part of the oxide sorbent. Also, the total sulfur balance is less than 100 percent, with about 22 percent of sulfur being unaccounted for. Equilibrium calculations show that elemental sulfur can be formed during oxidative regeneration of cerium sulfides,



Elemental sulfur is gaseous and undetectable in the experimental setup used here.

TABLE 2.—REGENERATION OFFGAS COMPOSITION

Sorbent	Temp (°C)	Sulfidation space velocity <sup>a</sup> (h <sup>-1</sup> )	Regeneration <sup>b</sup>		Reduction <sup>c</sup>	
			3%O <sub>2</sub> /He		50%H <sub>2</sub> -10%H <sub>2</sub> O/He	
			$\frac{\text{SO}_{2,\text{out}}}{(\text{H}_2\text{S})_{\text{ads}} (\%)}$	$\frac{\text{H}_2\text{S}_{,\text{out}}}{(\text{H}_2\text{S})_{\text{ads}} (\%)}$	$\frac{\text{SO}_{2,\text{out}}}{(\text{H}_2\text{S})_{\text{ads}} (\%)}$	$\frac{\text{H}_2\text{S}_{,\text{out}}}{(\text{H}_2\text{S})_{\text{ads}} (\%)}$
CeO <sub>2</sub>	800	16,000	23.0	40.5	12.9	15.6
	800	80,000	14.3	52.3	5.7	22.8
Ce70%LaOx	650	16,000	4.7	47.6	2.3	23.4
	800	16,000	7.3	47.8	2.4	23.5
	800	80,000	7.0	56.0	2.0	25.0
10%CuCeO <sub>2</sub>	650	16,000	25.8	24.9	15.1	23.1
	650	80,000	15.3	37.6	8.5	26.7
	800	16,000	14.4	56.6	2.9	21.1
	800	80,000	8.0	59.9	1.8	28.3

<sup>a</sup>Sulfidation: 650/800 °C, 0.1%H<sub>2</sub>S-50%H<sub>2</sub>-10%H<sub>2</sub>O-He, S.V. = 16,000 or 80,000/h (STP)

<sup>b</sup>Regeneration: 650/800 °C, 3%O<sub>2</sub>/He, S.V. = 80,000/h (STP)

<sup>c</sup>Reduction: 650/800 °C, 50%H<sub>2</sub>-10%H<sub>2</sub>O-He, S.V. = 80,000/h (STP)

Figure 2 shows the cyclic sulfidation capacity of 10at%Cu-CeO<sub>2</sub> at 30 ppmv H<sub>2</sub>S breakthrough. This sorbent has good regenerability already from the first cycle both at 650 and 800 °C. At the space velocity of 16,000 h<sup>-1</sup>, the sulfur capacity at 650 °C (~5mg S/g sorbent) is higher than that at 800 °C (1–1.3 mg S/g sorbent). This can be attributed to two reasons: first, reversible sulfidation of the copper part of this sorbent takes place at 650 °C. However, the contribution of copper is lost at 800 °C due to the severe



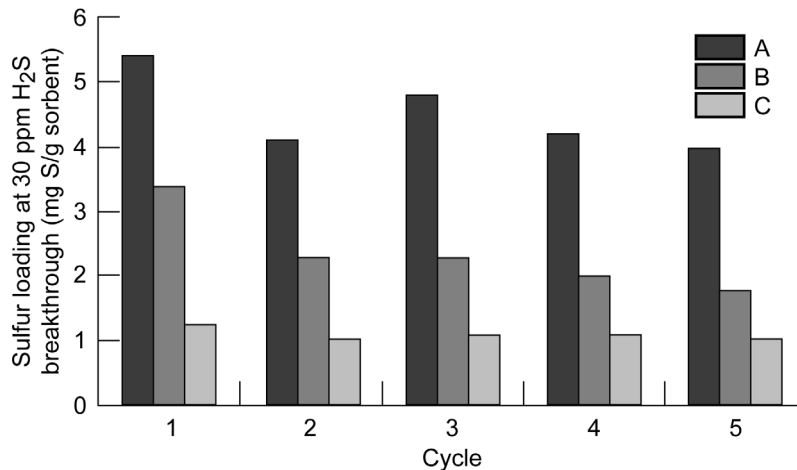


Figure 2.—Sulfur capacity of 10% CuCeO<sub>2</sub> at 30 ppm H<sub>2</sub>S breakthrough in cyclic sulfidation/regeneration: A: pre-reduction: 650 °C, S. V. = 80,000 h<sup>-1</sup>; sulfidation: 650 °C, S. V. = 16,000 h<sup>-1</sup>; regeneration: 650 °C, S. V. = 80,000 h<sup>-1</sup>. B: pre-reduction: 650 °C, S. V. = 80,000 h<sup>-1</sup>; sulfidation: 650 °C, S. V. = 80,000 h<sup>-1</sup>; regeneration: 650 °C, S. V. = 80,000 h<sup>-1</sup>. C: pre-reduction: 800 °C, S. V. = 16,000 h<sup>-1</sup>; regeneration: 800 °C, S. V. = 80,000 h<sup>-1</sup>; pre-reduction gas: 50% H<sub>2</sub>-10% H<sub>2</sub>O-He; sulfidation gas: 0.1% H<sub>2</sub>S-50% H<sub>2</sub>-10% H<sub>2</sub>O-He; regeneration gas: 3% O<sub>2</sub>/He.

sintering of the copper and ceria particles and to the lower affinity of copper for H<sub>2</sub>S at 800 °C. The latter is the main reason why more extensive bulk sulfidation takes place at 650 °C. The effect of sulfidation space velocity on sulfur loading was examined at 650 °C. As shown in figure 2(b), under higher sulfidation space velocity, 80,000 h<sup>-1</sup> (STP), lower sulfur capacity was measured due to less bulk sorbent sulfidation at 650 °C.

The effect of higher sulfidation space velocity (80,000 h<sup>-1</sup>) on the sorbent sulfur capacity was also investigated at 800 °C. Results are shown in figure 3 for three different sorbents, including undoped ceria. At this temperature, for all sorbents, increasing the sulfidation space velocity had no effect on the sorbent stabilized sulfidation capacity. Thus, surface adsorption of H<sub>2</sub>S is a fast process, faster than the contact time corresponding to either of the two space velocities used in figure 3.

The regeneration off-gas distributions at the conditions of figure 3 are shown in table 2. We define the sorbent regenerability here as the ratio of total sulfur desorbed to total adsorbed sulfur, and this can be obtained by simply adding all desorbed sulfur amounts from the results listed in table 2. It is clear that the regenerability was improved at the higher sulfidation space velocity (80,000 h<sup>-1</sup>), for example, 95 versus 92 percent for CeO<sub>2</sub>, 90 versus 81 percent for Ce70at%LaO<sub>x</sub> and 98 versus 95 percent for 10at%CuCeO<sub>2</sub>. This corroborates our argument that high space velocity suppresses bulk sorbent sulfidation. It also proves that surface adsorption of H<sub>2</sub>S is very fast and limited only by the supply of gas to the surface. These results are important for practical design of the desulfurization/regeneration process using cerium oxide-based sorbents. Thus, high sulfidation space velocity offers the potential for compact sorber reactor design, while using a high regeneration space velocity will bring closer the times required for sulfidation and regeneration, so that only two reactors will be required alternating as a sorber and a regenerator.

To avoid sulfate formation during oxidative regeneration, potentially other gas compositions may be used at similarly high space velocities. It is also possible that higher regeneration space velocities (>80,000 h<sup>-1</sup>) can achieve this goal. As shown in figure 4, for two different sorbent formulations, when the regeneration space velocity increased from 80,000 to 400,000 h<sup>-1</sup>, the total desorbed sulfur amounts during the reduction step decreased; from ~27 to ~22 percent and from ~30 to ~25 percent for Ce70%LaO<sub>x</sub> and 10%CuCeO<sub>2</sub>, respectively. These results indicate that sulfate formation during oxidative

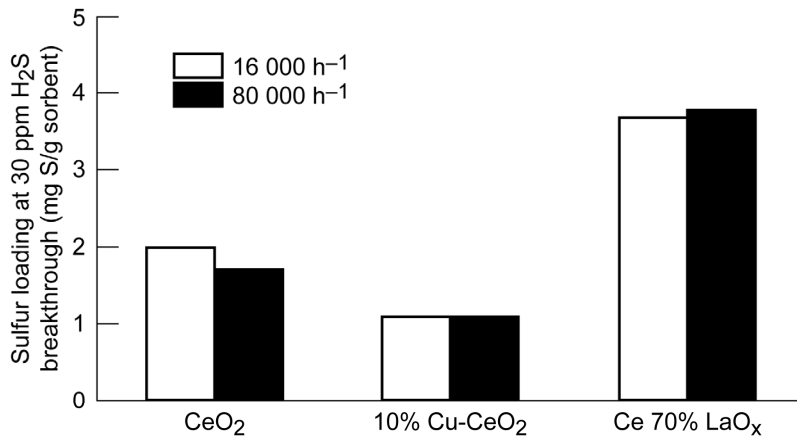


Figure 3.—Stabilized sorbent sulfidation capacity at 30 ppm H<sub>2</sub>S breakthrough at two different sulfidation space velocities. Pre-reduction: 800 °C, 50% H<sub>2</sub>-10% H<sub>2</sub>O/He, S. V. = 80,000 h<sup>-1</sup>; sulfidation: 800 °C, 0.1% H<sub>2</sub>S-50% H<sub>2</sub>-10% H<sub>2</sub>O/He; regeneration: 800 °C, 3% O<sub>2</sub>/He, S. V. = 80,000 h<sup>-1</sup>.

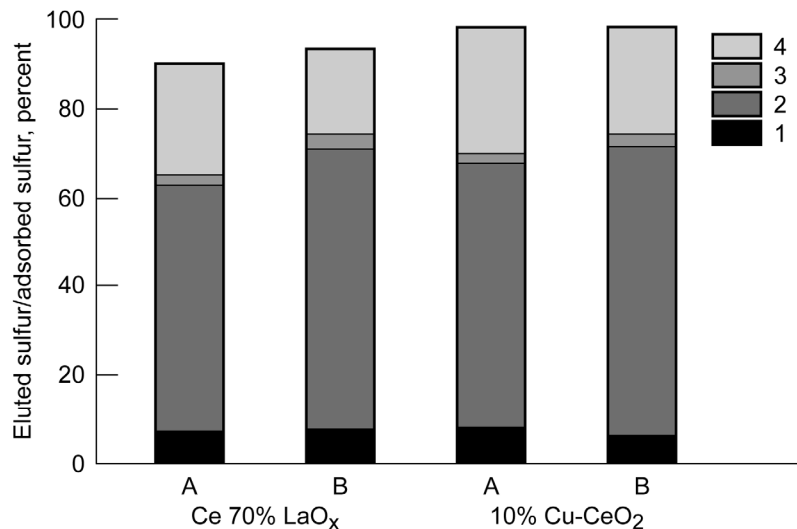


Figure 4.—Stabilized regeneration off gas composition at different regeneration space velocities. A: S. V. = 80,000 h<sup>-1</sup> (STP); B: S. V. = 400,000 h<sup>-1</sup> (STP). Pre-reduction: 800 °C, 50% H<sub>2</sub>-10% H<sub>2</sub>O/He, S. V. = 80,000 h<sup>-1</sup> (STP); sulfidation: 800 °C, 0.1% H<sub>2</sub>S-50% H<sub>2</sub>-10% H<sub>2</sub>O/He; S. V. = 80,000 h<sup>-1</sup> (STP); regeneration: 800 °C, 3% O<sub>2</sub>/He. Legend for figure: 1: % SO<sub>2</sub> eluted in 3% O<sub>2</sub>/He regeneration step. 2: % H<sub>2</sub>S eluted in 3% O<sub>2</sub>/He regeneration step. 3: % SO<sub>2</sub> eluted in 50% H<sub>2</sub>-10% H<sub>2</sub>O/He reduction step. 4: % H<sub>2</sub>S eluted in 50% H<sub>2</sub>-10% H<sub>2</sub>O/He reduction step.

regeneration can be suppressed by using higher regeneration space velocities. The other advantage of using a higher regeneration space velocity here was that without affecting the sulfur capacity and regenerability, the regeneration time was reduced three-fold, approaching the time it took for each surface sulfidation half cycle.

## Conclusions

A major finding of this work is that the surface capacity of ceria and lanthana sorbents can be used regeneratively to adsorb/desorb H<sub>2</sub>S from reformat gas mixtures at temperatures in the range 650 to 800 °C. In other words, we have found that adsorption of H<sub>2</sub>S on the surface of these sorbents is reversible. A swing adsorption/desorption process can thus be designed with La-rich cerium oxide sorbents. Matching the time of sulfidation and regeneration is important to enable the use of two reactors only, alternating between a sorber and a regenerator. In such a scheme, the slow and often difficult processes of bulk sorbent sulfidation and regeneration are not important. Indeed, as we have shown under the CTA Power and Energy program, pre-sulfided sorbents can be used equally efficiently (ref. 6). The high space velocity used in regeneration keeps the bulk sorbent in sulfided form. In future designs, honeycomb monoliths with the sorbent material coated on the ceramic walls should be employed to effectively suppress sulfur species re-adsorption and reduce the regeneration time.

These results create new opportunities for compact sorber/regenerator reactor designs to meet the requirements of reformat gas desulfurization at any scale.

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<b>13. SUPPLEMENTARY NOTES</b>					
<b>14. ABSTRACT</b> Desulfurization of the hot reformate gas produced by catalytic partial oxidation or autothermal reforming of heavy fuels, such as JP-8 and jet fuels, is required prior to using the gas in a solid oxide fuel cell (SOFC). Development of suitable sorbent materials involves the identification of sorbents with favorable sulfidation equilibria, good kinetics, and high structural stability and regenerability at the SOFC operating temperatures (650 to 800 °C). Over the last two decades, a major barrier to the development of regenerable desulfurization sorbents has been the gradual loss of sorbent performance in cyclic sulfidation and regeneration at such high temperatures. Mixed oxide compositions based on ceria were examined in this work as regenerable sorbents in simulated reformate gas mixtures and temperatures >650 °C. Regeneration was carried out with dilute oxygen streams. We have shown that under oxidative regeneration conditions, high regeneration space velocities (>80,000 h <sup>-1</sup> ) can be used to suppress sulfate formation and shorten the total time required for sorbent regeneration. A major finding of this work is that the surface of ceria and lanthanum sorbents can be sulfided and regenerated completely, independent of the underlying bulk sorbent. This is due to reversible adsorption of H <sub>2</sub> S on the surface of these sorbents even at temperatures as high as 800 °C. La-rich cerium oxide formulations are excellent for application to regenerative H <sub>2</sub> S removal from reformate gas streams at 650 to 800 °C. These results create new opportunities for compact sorber/regenerator reactor designs to meet the requirements of solid oxide fuel cell systems at any scale.					
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