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Science **312**, 1508 (2006);

DOI: 10.1126/science.1125684

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signals received by several detectors. Our defect detection tool had a minimum size of detection of ~ 0.1 μm in the lateral direction. For the CMP experiments, pre-CMP defect wafer maps were subtracted from post-CMP wafer maps in order to determine the defect adders. Then the wafers were characterized for scratching by means of optical technique.

28. Z.L.W. thanks the NSF (DMR 9733160), the NASA Vehicle Systems Program and Department of Defense Research and Engineering, and the Defense Advanced Research Projects Agency for support. D.C.S. thanks the Cambridge-Cranfield High Performance Computing Facility, Engineering and Physical Science Research Council (GR/S48431/01, GR/S48448/01, and GR/S84415/01) for support.

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www.sciencemag.org/cgi/content/full/312/5779/1504/DC1
Figs. S1 to S9
Table S1

3 February 2006; accepted 10 April 2006
10.1126/science.1125767

Regenerative Adsorption and Removal of H_2S from Hot Fuel Gas Streams by Rare Earth Oxides

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Sorbent materials that allow for high-temperature, regenerative desulfurization of fuel gas streams for the anode of a solid oxide fuel cell have been developed. Reversible adsorption of H_2S on cerium and lanthanum oxide surfaces is demonstrated over many cycles at temperatures as high as 800°C , on both fresh or presulfided sorbents, and at very high space velocities. The adsorption and desorption processes are very fast, and removal of H_2S to sub-parts per million levels is achieved at very short (millisecond) contact times. Any type of sulfur-free gas, including water vapor, can be used to regenerate the sorbent surface. Preferably, the anode off-gas stream is used to sweep the desorbed H_2S to a burner.

Conversion of heavy fuels to a hydrogen-rich gas mixture to power solid oxide fuel cells (SOFC) is a cleaner and more efficient way to generate energy than the direct combustion of the fuel, but heavy liquid fuels and coal contain organosulfur compounds that are difficult and expensive to fully remove before fuel reformation. Critical developments will include sulfur-resistant catalysts for the reformers as well as sulfur sorbents that can be regenerated and that operate at temperatures in the range of 650° to 800°C without any performance degradation. Installed upstream of the SOFC anode, the sorbent will protect the nickel-based anode material from sulfuration, which causes irreversible fuel cell power losses.

Sorbents that can be used at SOFC temperatures regenerate poorly, which is a serious drawback that has plagued each of the single- or mixed-oxide combinations that has been considered for hot fuel gas desulfurization. Because of the deterioration of the sorbent structure over time, none of the proposed sorbent materials has become commercially viable (1).

The rare earth oxides, especially lanthanum and Ce(III) oxides, have excellent sulfidation thermodynamics in realistic reformat gas compositions, such as the ones produced by steam reforming, autothermal reforming, or partial oxidation of heavy oils, diesel, jet fuels, or by coal gasification (1–4). However, if bulk or deep sulfidation of the sorbent is allowed to proceed, the cyclic performance is quickly

degraded because of complexities in regeneration, most notably structural changes occurring during the transformation of the sulfided sorbent back to the oxide phase (5–13).

We report on a different approach to this problem: We used only the surface of the sorbent in sulfidation and regenerated only the surface of the sorbent upon saturation. By using very high space velocities or short contact times of the gas with the sorbent in regeneration (14), bulk regeneration of the sorbent with its attendant structural complexities is prevented. An added benefit of this approach is a very small footprint of the sorber and regenerator

units, which is highly desirable for small-scale applications of fuel cells, such as those used in confined locations and for auxiliary power units.

Figure 1A shows the changes in H_2S concentration for the cyclic sulfidation-regeneration of presulfided lanthanum oxide sorbent particles (<53 μm) loaded in a packed-bed reactor run isothermally at 800°C and at a gas hourly space velocity of $400,000$ hour^{-1} at standard temperature and pressure (STP). An expanded view of the H_2S concentration profile in one cycle of sulfidation/regeneration is shown in Fig. 1B. The sorbent had a surface area ($\pm\text{SD}$) of 3.5 ± 0.6 m^2/g at the test conditions (Table 1). The gas mixture composition was chosen to simulate the exit gas stream of a catalytic partial oxidation reformer of a heavy fuel oil, such as JP-8. An exaggerated amount of H_2S (0.1 volume %) was used to shorten the length of each cycle. The carrier gas was He rather than N_2 , but this did not affect the results. We also found that substituting H_2 and H_2O , respectively, for CO and CO_2 in the fuel gas had no effect on the adsorption efficiency and sulfur capacity of the sorbent.

Regeneration was conducted in the same fuel gas mixture by switching off the H_2S feed gas. Other gas mixtures can be used to regenerate the sorbent surface equally efficiently (14, 15). The breakthrough time at 1 part per million (ppm) H_2S was the same for all 15 cycles shown in Fig. 1C. The surface sulfur capacity at breakthrough of 1 ppm of H_2S was 0.9 mg sulfur per gram sorbent ($\text{S}/\text{g}_{\text{sorbent}}$). Thus, lanthanum oxide can be used to

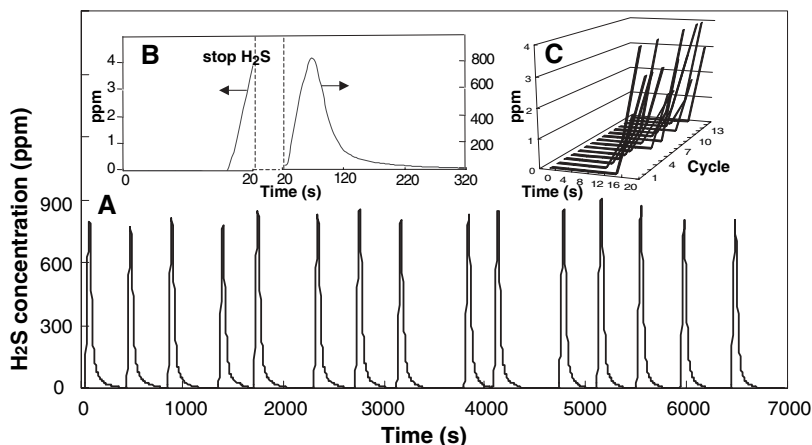


Fig. 1. (A) Consecutive sulfidation and regeneration of presulfided La_2O_3 in a packed-bed reactor with the use of simulated reformat gas at 800°C . Switch to desorption at 4 parts per million by volume (ppmv) H_2S . Sulfidation: 0.1% H_2S –20% H_2 –20% CO –1% CO_2 –10% H_2O –He, space velocity = $400,000$ hour^{-1} . Regeneration: 20% H_2 –20% CO –1% CO_2 –10% H_2O –He, space velocity = $400,000$ hour^{-1} . (B) Expanded view of the H_2S concentration profile in one cycle of sulfidation and regeneration of presulfided La_2O_3 . (C) H_2S breakthrough curves in successive sulfidation cycles of presulfided La_2O_3 .

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reversibly and very efficiently adsorb H_2S from reformat gas mixtures at 800°C to protect the anode of an SOFC. Similar results were obtained with ceria, doped ceria, mixtures of lanthana and ceria, and copper-containing ceria (1, 15).

Temperature-programmed desorption (TPD) of H_2S from the surface of the same presulfided lanthana sample (Fig. 2) shows that the H_2S adsorption takes place over a wide temperature range. Of importance to the SOFC application, we found reversibly bound H_2S on this material in the temperature range of 650° to 800°C , which matches the operating temperature of the SOFC. The total amount of H_2S (~ 1.5 mg $\text{S}/\text{g}_{\text{sorbent}}$) desorbed in TPD is higher than the amount adsorbed in each sulfidation half-cycle at the conditions of Fig. 1, because the latter took place in the presence of 10% water vapor. These results demonstrate that presulfided lanthana sorbents actually retain reversible surface sulfur adsorption capacity over a wide temperature window. Similar data were obtained with ceria-rich sorbents (15). As indicated by the TPD analysis, lanthana can also be used at lower temperatures as a regenerable sulfur sorbent. Cyclic performance data at 400°C are shown in figs. S5 and S6 (15). Rare earth oxides should prove a good sorbent choice for regenerative fuel gas desulfurization over the extended temperature range of 350° to 800°C , and for all types of fuel cells.

Stable sulfur loadings at 1 ppm H_2S breakthrough (Table 1) were measured at different sulfidation space velocities, but the same regeneration space velocity [$80,000$ hour $^{-1}$ (STP)], over three different presulfided sorbents. The surface area (10.2 ± 0.4 m $^2/\text{g}$) of the presulfided CeO_2 was about three times as high as that of the presulfided lanthana, but its sulfur capacity did not scale with the surface area, indicating an effect of sorbent surface composition on the H_2S adsorption equilibrium. Of greater practical importance is the observation that a variation of the gas hourly space velocity in the range of $80,000$ to $400,000$ hour $^{-1}$ had no effect on the sulfur capacity of any of the sorbents listed in Table 1. Only the breakthrough time changed, inversely proportional to the space velocity. Thus, adsorption of H_2S is indeed a very fast process limited only by the supply of the adsorbate.

Table 1. Stabilized surface sulfur capacities at 1 ppm H_2S breakthrough for different sulfidation space velocities (S.V.). Presulfidation: 0.25% H_2S –50% H_2 –He, S.V. = 12,000 hour $^{-1}$, $T = 800^\circ\text{C}$. Sulfidation: temperature $T = 800^\circ\text{C}$, 0.1% H_2S –50% H_2 –10% H_2O –He. Regeneration: $T = 800^\circ\text{C}$, 50% H_2 –10% H_2O –He, S.V. = 80,000 hour $^{-1}$. Surface areas are shown \pm SD.

Sorbents	Sulfur loading at 1 ppmv H_2S breakthrough (mg $\text{S}/\text{g}_{\text{sorbent}}$) at sulfidation S.V. =		Surface area (m $^2/\text{g}$)	
	80,000 hour $^{-1}$	160,000 hour $^{-1}$ or 400,000 hour $^{-1}$	After presulfidation	After cyclic tests
CeO_2	1.00	1.20*	10.2 ± 0.4	9.8 ± 0.2
$\text{Ce}70\%\text{LaO}_x$	1.20	1.30†	9.2 ± 0.3	8.5 ± 0.2
La_2O_3	0.80	0.90†	3.5 ± 0.6	3.4 ± 0.5

*S.V. = 160,000 hour $^{-1}$ (STP). †S.V. = 400,000 hour $^{-1}$ (STP).

The regeneration times in each of the 15 cycles shown in Fig. 1A are 8 to 10 times as long as the sulfidation times. At first glance, this is a drawback, because it would require multiple beds for a continuous cyclic process. However, delayed regeneration was due to re-adsorption of the eluted H_2S on the subsequent layers of sorbent in the packed bed.

The desorption rate of H_2S from the sorbent surface is actually very fast. To compare the time constants of adsorption and desorption, we used another reactor setup that avoids re-adsorption of eluted H_2S on subsequent sorbent layers as occurs in a packed bed reactor. Here, a thermogravimetric analyzer (TGA) was used with a few milligrams of the sorbent powder loaded as a thin layer on quartz wool in the quartz pan of the TGA. The weight change of the sorbent was recorded as a function of the gas composition. After sulfidation was carried out for 100 s, H_2S was switched off and the 50% H_2 –3% H_2O –He gas mixture continued to be supplied at the same flow rate, effectively removing the adsorbed H_2S (Fig. 3A). Alternatively, both the H_2S and H_2 were switched off and water vapor in He was used for sorbent regeneration in Fig. 3B. The total gas flow rate was 500 ml/min (STP) for both sulfidation and regeneration. The gas mixtures used in the TGA tests contained no CO or CO_2 , and only $\sim 3\%$ water vapor was carried in by saturation of the feed gas at ambient conditions, simplifying the operation of the TGA. These choices do not affect the sorbent's ability to regenerate. If water competes with H_2S for adsorption sites, the use of a lower concentration of water will slightly improve the rate of adsorption and the sulfur loading. Indeed, the stable sulfur capacity of the sorbent in the TGA tests is twice as high (1.8 mg $\text{S}/\text{g}_{\text{sorbent}}$) as the one measured at the conditions of Fig. 1 or Table 1. The important key finding from the TGA tests, however, is the demonstration that the time constants of sulfidation and regeneration are similar and very short (<1 ms) (Fig. 3). Hence, with proper choice of sorber design—for example, by using thin wall coatings of sorbent on a honeycomb monolith—re-adsorption of H_2S will be greatly suppressed, and just two units of sorbent alternating between the H_2S adsorption and desorption modes would suffice.

The sulfided lanthanide oxide sorbents can be regenerated with an oxidative gas mixture (1). Notably, however, any gas composition can be used to regenerate the saturated sorbent surface, including water vapor, a hydrogen-rich gas, inert gases, and water vapor and air mixtures (fig. S2) (15). When an oxidizing gas is used to regenerate the sorbent, some of the eluted sulfur from a packed-bed of sorbent is in the form of SO_2 (1, 15) (fig. S2).

Water vapor alone can be used to remove the H_2S from the lanthana sorbent (Fig. 3B). The use of water to sweep away the desorbed H_2S in the regeneration step is practical for many power-generation systems. In the case of an SOFC, a simple and very attractive regeneration scheme would be to pass the anode off-gas (largely composed of water vapor and some unconverted fuel gas) over the saturated sorbent to sweep away H_2S . This gas stream is typically taken to a combustor where any unconverted fuel is fully burned and the heat is supplied to the primary fuel reformer. In the burner, H_2S will be oxidized to SO_2 , which would be emitted with the exhaust gases if it met the required emission standards or

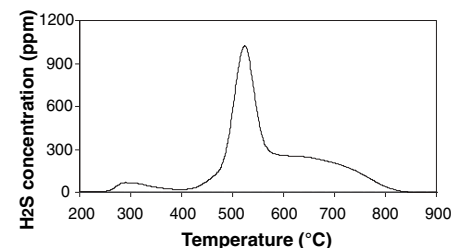


Fig. 2. TPD of H_2S from presulfided La_2O_3 . Adsorption gas: 0.25% H_2S –50% H_2 –He, flow rate = 50 ml/min. Desorption gas: 50% H_2 –He, flow rate = 50 ml/min, heating rate = $10^\circ\text{C}/\text{min}$.

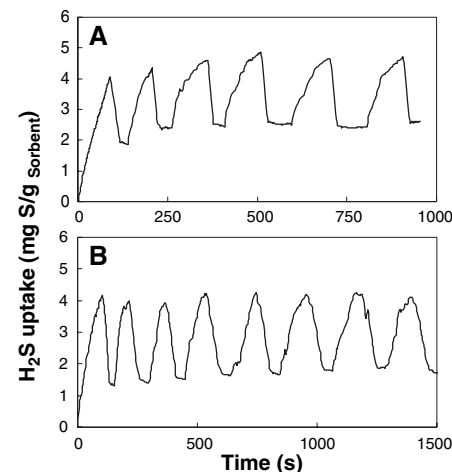


Fig. 3. Cyclic sulfidation and regeneration of presulfided La_2O_3 in a thermogravimetric analyzer at 800°C . Sulfidation gas composition: 0.1% H_2S –50% H_2 –3% H_2O –He. Regeneration gas in (A) is 50% H_2 –3% H_2O –He and in (B) is 3% H_2O –He.

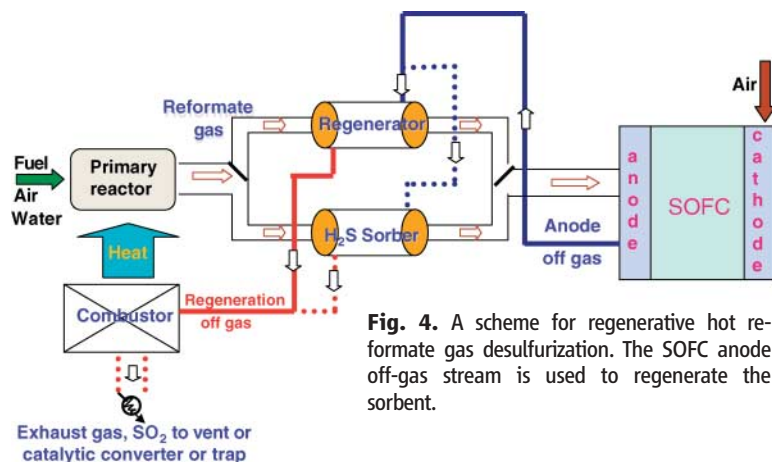


Fig. 4. A scheme for regenerative hot reformat gas desulfurization. The SOFC anode off-gas stream is used to regenerate the sorbent.

otherwise would be trapped or converted as appropriate.

Figure 4 shows a conceptual flowchart of fuel reforming for SOFC use, including regenerative desulfurization over a lanthanide oxide sorbent in the temperature range of 650° to 800°C. This shows that all of the SOFC anode off-gas stream can be used to regenerate the sorbent surface. That is, no split streams are required, because regeneration can take place at high space velocity that corresponds to using the whole anode off-gas stream over the saturated sorbent. This design also avoids the use of a new gas stream, such as air and its attending compressor equipment, for the regeneration step. The dual sorber and regenerator units can be made as small as desired for different applications. In certain designs, some of the anode off-gas may be directed straight to the reformer to add steam to the fuel-reforming process. In such cases, a split stream of the anode off-gas would be used to regenerate the sorbent units.

Various configurations of reactors can be envisioned for the desulfurization system. Because of its low pressure drop, a ceramic honeycomb monolith with the sorbent coated as a thin layer on the channel walls is considered a suitable choice. Sizing the reactor volume for a 5-kilowatt electric (kWe)-rated SOFC, at a 400,000 hour⁻¹ space velocity, a 0.2-liter monolith (0.02-liter sorbent) can be used in each of the two (sorber and regenerator) units (16). The corresponding switch time for a gas containing 500 to 50 ppm H₂S would be 0.5 to 5 min, respectively (16). For a first-order process, the lower the content of H₂S in the fuel gas, the lower the sulfur capacity will be. This was not considered in the above estimate because a compensating effect can come from the use of sorbents with much higher surface area than the one used here. The flexibility that this design entails should be of interest to any scale of power generation, but more importantly to limited-footprint applications, such as auxiliary power units, portable fuel cells, and confined-space installations.

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- Approximately 50 liters/min H₂ (STP) per 5 kWe is required for a Polymer Electrolyte Membrane (PEM) fuel cell (17). Taking this as the basis for an SOFC, a flow rate of 125 liters/min reformat gas with 40% H₂ will be required to power a 5-kWe SOFC. At space velocity = 400,000 hour⁻¹, about 20 cm³ of sorbent or 200 cm³ monolith volume (larger by a factor of 10) will be required. For two units, 400 cm³ would be required. The switching time, *t*, is estimated for a sorbent density of 2 g/cm³ and for a surface sulfur capacity of 1 mg S/g_{sorbent}. Based on the mass balance, the following equation can be established: (500 or 50 × 10⁻⁶) × 125 liters/min × *t* = [1 mg S/g_{sorbent} (2 g/cm³ × 20 cm³)]/32,000 mg/mol × 22.4 liters/mol. Thus, *t* = 0.5 min for 500 ppm H₂S or 5 min for 50 ppm H₂S-laden fuel gas.
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- This work was supported by the Army Research Laboratory, Power and Energy Collaborative Technology Alliances (CTA) program.

Supporting Online Material

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Materials and Methods

Figs. S1 to S6

Table S1

References

1 February 2006; accepted 13 April 2006

10.1126/science.1125684

Near-Synchronous Interhemispheric Termination of the Last Glacial Maximum in Mid-Latitudes

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Isotopic records from polar ice cores imply globally asynchronous warming at the end of the last glaciation. However, ¹⁰Be exposure dates show that large-scale retreat of mid-latitude Last Glacial Maximum glaciers commenced at about the same time in both hemispheres. The timing of retreat is consistent with the onset of temperature and atmospheric CO₂ increases in Antarctic ice cores. We suggest that a global trend of rising summer temperatures at the end of the Last Glacial Maximum was obscured in North Atlantic regions by hypercold winters associated with unusually extensive winter sea ice.

Terminations of asymmetric 100,000-year glacial cycles represent one of the most fundamental climate signals of late Quaternary time (1). Isotopic compositions in Antarctic ice cores and in benthic foraminifera from marine sediment cores show well-defined changes beginning between about 19 × 10³ to 17 × 10³ years ago (ka) (2), interpreted to

represent the onset of the termination of the Last Glacial Maximum (LGM) (3–7). In contrast, Greenland ice cores register continued stadial cold conditions between 17 ka and 14.7 ka (8, 9). At the same time, North Atlantic sediments reveal a major pulse of iceberg discharge (10) accompanied by a near-shutdown of the meridional overturning circu-