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# Novel oxygen storage mechanism based on redox of sulfur in lanthanum oxysulfate/oxysulfide

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**A sulfur redox cycle between $La_2O_2SO_4(S^{6+})$ and $La_2O_2S(S^{2-})$ phases was found for the first time to achieve the oxygen storage of 2 mol $O_2$ mol$^{-1}$, which is eight times larger than that of the conventional $CeO_2$–$ZrO_2$ system.**

So-called oxygen storage materials have become important after being applied to three-way automotive exhaust catalysts to compensate for the fluctuation between lean (oxidizing) and rich (reducing) conditions.[1–3] The $CeO_2$–$ZrO_2$ binary system is a key component for this purpose due to its reversible and rapid release and sorption of oxygen at relatively low temperatures (≤400 °C) as described below.

$$Ce^{4+} + 1/2O^{2-} \underset{O_2}{\overset{H_2}{=}} Ce^{3+}$$

The quantity of oxygen storage should therefore not exceed 0.25 mol $O_2$ mol$^{-1}$ (21 cm$^3$ $O_2$ g$^{-1}$ at 25 °C). Oxygen storage materials seem to be useful not only for automotive catalysts, but also for other high-temperature processes, where instant oxygen scavengers are required. For instance, it was reported that the performance of $H_2$–$O_2$ fuel cells can be improved by incorporating the oxygen storage material into a cathode.[4] To open up such new applications of the oxygen storage materials, a larger storage capacity per unit solid volume is highly desirable. Actually, however, no such materials have been developed so far. In this communication, we report a novel oxygen storage mechanism based on the redox of sulfur in a lanthanum oxysulfate/oxysulfide ($La_2O_2SO_4$/$La_2O_2S$) system. The large storage capacity of 2 mol mol$^{-1}$ can be attained without losing the sulfur content. This is the first example of oxygen storage that uses non-metallic elements as a redox site.

A single phase of lanthanum oxysulfate, $La_2O_2SO_4$, could be synthesized by heating commercial $La(SO_4)_3\cdot 9H_2O$ powders (Rare Metallic Co., Ltd.) at 900 °C for 5 h in air as shown in the XRD patterns (Fig. 1a, b). The oxysulfate thus obtained was stable in air even at 1200 °C, but it was completely converted into $La_2O_2S$ after heating at 900 °C in a flowing $H_2$. The dynamic reduction behavior of $La_2O_2SO_4$ was evaluated by the temperature programmed reduction (TPR), which was carried out in a conventional flow system by heating at 10 °C min$^{-1}$ in a stream of 10% $H_2$–He. The concentration of $H_2$ in the gas leaving the solid was monitored by a quadrupole mass spectrometer. As shown in Fig. 2a, the consumption of $H_2$ started at *ca.* 680 °C and required at least 1 h to be completed at 900 °C. After completion of $H_2$ consumption, the oxysulfate turned into oxysulfide ($La_2O_2S$) as was shown in Fig. 1c. The oxysulfide thus formed was next subjected to temperature programmed reoxidation (TPRO) in a stream of 5% $O_2$–He as shown in Fig. 2b. Oxygen consumption started at *ca.* 500 °C, giving rise to a peak at 740 °C. After completion of the reoxidation, a single phase of the oxysulfate was restored as evident from the XRD pattern (Fig. 1d). The cumulative consumptions of $H_2$ and $O_2$ in TPR/TPRO measurement were estimated to be 3.8 and 1.9 mol mol$^{-1}$, respectively, supporting the occurrence of the following stoichiometric reaction.

$$La_2O_2SO_4 \underset{O_2}{\overset{H_2}{=}} La_2O_2S$$

According to our preliminary experiments, the oxysulfate/oxysulfide phases could also be formed in a similar way from several other lanthanide sulfates containing $Pr^{3+}$, $Nd^{3+}$, $Sm^{3+}$, etc. By contrast, this is not the case for the sulfate of $Ce^{4+}$, which eliminates all of sulfate species as $SO_2$/$O_2$ at < 700 °C to produce $CeO_2$. Similarly, many sulfates containing s-, p-, and d-block metals were decomposed to evolve $SO_2$/$O_2$ at elevated temperatures. Recently, various composite metal oxysulfides have been synthesized by heating mixtures of oxide–sulfide under evacuation, or by heating metal oxides in a flowing $H_2S$.[5–7] These oxysulfides are generally decomposed into a mixture of oxides and sulfates when heated in the presence of $O_2$. The reversible phase transformation between oxysulfate and oxysulfide is the characteristic of several lanthanides including the present system. We also point out that these lanthanoid oxysulfates would be useful as starting materials for a wide variety of composite oxysulfides.

These results evidence that oxygen storage in the present system is accompanied by the redox of sulfur between oxidation numbers in 6+ ($SO_4^{2-}$) and 2− ($S^{2-}$). This corresponds to the maximal storage capacity of 2 mol $O_2$ mol$^{-1}$, which is eight times larger than that of conventional $CeO_2$-based materials. Due to the large mass of La, the advantage of the present system decreases when the capacity is measured per unit weight (122 cm$^3$ $O_2$ g$^{-1}$). However, it is still six times larger than $CeO_2$–$ZrO_2$. It is very interesting that the present system utilizes the redox of sulfur in contrast to that the

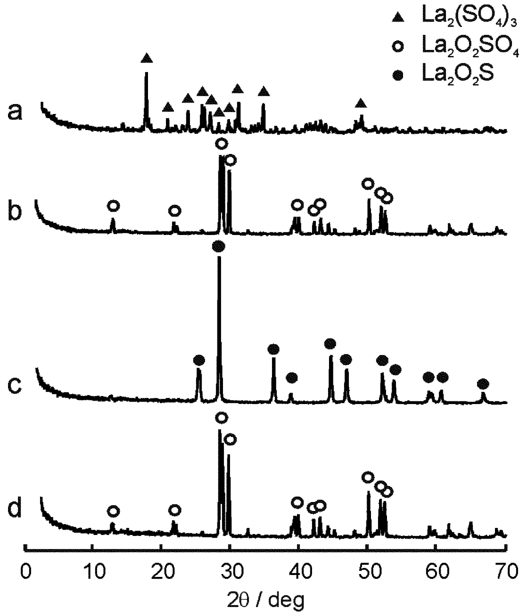

**Fig. 1** Powder XRD patterns of $La_2(SO_4)_3$ after heating in air at (a) 500 °C, (b) 900 °C, and subsequent (c) TPR, (d) TPRO measurements shown in Fig. 2.

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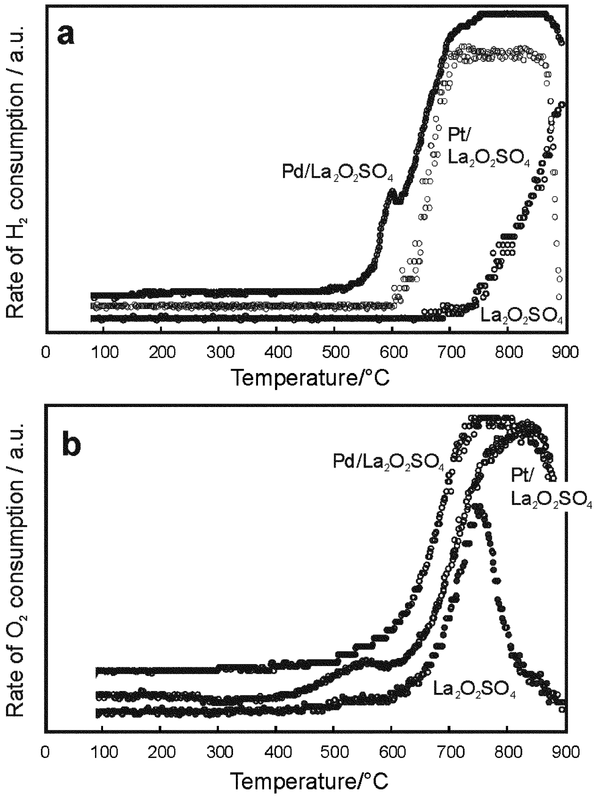
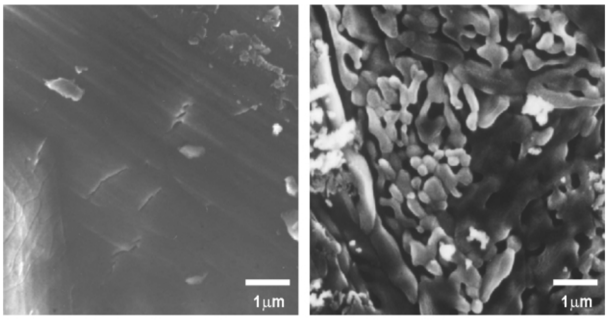


**Fig. 2** (a) TPR and (b) TPRO profiles $La_2O_2SO_4$ in a flow of 10% $H_2$–He and 5% $O_2$–He, respectively. Heating rate: 10 °C $min^{-1}$.

conventional oxygen storage is due to the redox of metallic ions. The storage capacity of metal oxide systems should generally be limited to less than 0.5 mol $O_2$ $mol^{-1}$, because in many cases the change of oxidation numbers does not exceed two. By contrast, the present result implies the possibility of a much larger capacity for solid materials containing non-metallic redox sites. The rhombohedral lattice of $La_2O_2SO_4$ is constructed by alternate stacking of $La_2O_2^{2+}$ and $SO_4^{2-}$ layers, which is similar to the orthorhombic $La_2O_2S$ consisting of stacking of $La_2O_2^{2+}$ and $S^{2-}$ layers. The structural similarity would be one of the reasons for the reversible and stable redox cycles.

One may consider the loss of sulfur due to vaporization in the redox cycles. Although we have not detected directly the release of sulfur as $H_2S/SO_2$ in the redox treatments, following facts would give preliminary estimations. In TPR and TPRO measurements, both $H_2S$ and $SO_2$ in the effluent were less than the limit of detection of the mass spectrometer ($< 50$ ppm). The XRF analysis of the solid sulfur content was conducted after repeating reduction in a stream of $H_2$ at 700 °C for 1 h and subsequent reoxidation in a stream of $O_2$ at 900 °C for 5 h. The ratio of La/S in the solid was kept constant at 2.0 ± 0.05 during 10 cycles of the redox treatment. Considering the $H_2/O_2$ flow rates in these treatments, the concentration of $H_2S/SO_2$ in the gas effluent should be $< 10$ ppm. No precipitation of $La_2O_3$ was detected by XRD after the redox cycles. With these results taken into consideration, the release of $H_2S/SO_2$ would be negligible. The stability in a long-term experiment is currently under investigation. The present system is expected to work stably even in the presence of $H_2S$ or $SO_2$.

One drawback of the present oxygen storage material is the high operation temperature. The $CeO_2$–$ZrO_2$ system can work at lower temperatures $< 400$ °C, compared to $> 700$ °C required for the present system. To reduce the temperatures for oxygen storage, the effect of impregnated noble metals was studied. Fig. 2 also exhibits TPR and TPRO profiles of 1 wt% Pt or Pd-impregnated $La_2O_2SO_4$. Clearly, the temperatures for the consumption of $H_2/O_2$ became lower in the presence of these precious metals. More prominent effects on the TPR profiles imply that hydrogen spillover onto the surface of $La_2O_2SO_4$ promotes the reduction to $La_2O_2S$. It has been suggested that the reduction of several metal oxides is facilitated by spillover hydrogen, because of the higher reactivity of atomic hydrogen compared to molecular hydrogen.[8] Thus, one possible way to reduce the temperature for the present oxygen storage reaction is to apply the spillover effect for the various lanthanide oxysulfates.



$La_2(SO_4)_3$ $La_2O_2S$

**Fig. 3** SEM photographs of sulfate and oxysulfide.

Other interesting feature of the present oxygen storage material can be seen in the microstructure as shown in the SEM photographs (Fig. 3). The starting material, $La_2(SO_4)_3$, consisted of nonporous columnar crystals with a smooth surface. The conversion to the oxysulfate/oxysulfide retained the similar external morphology, but their interior exhibited skeletonized porous texture due to the elimination of $SO_2/O_2$. As a result, the surface area increased from $< 1$ $m^2$ $g^{-1}$ ($La_2(SO_4)_3$) to 22 $m^2$ $g^{-1}$ ($La_2O_2SO_4$) and 19 $m^2g^{-1}$ ($La_2O_2S$). The $N_2$ adsorption–desorption isotherms measured at 77 K were very similar to type III (IUPAC), which was flat up to the relative pressure of *ca.* 0.8 and then sharply increased near saturation of the vapor pressure. This is consistent with the presence of macropores with pore sizes more than 50 nm as was observed by SEM (Fig. 3). Formation of the porous texture would be significantly effective in facilitating the gas diffusion and solid–gas reactions in the redox cycles. No textural change was observed after repeating reduction at 700 °C and subsequent reoxidation at 900 °C for 10 cycles. The thermal stability is therefore enough for the high operation temperature.

In conclusion, this study has successfully revealed a novel oxygen storage mechanism, which utilizes sulfur as a redox site instead of metal cations. This finding will contribute to further development of oxygen storage materials and their applications.

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