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Desorption behavior of hydrogen and water from Yb-doped $SrCeO_3$

S. Yamanaka*, M. Katsura

Department of Nuclear Engineering, Graduate School of Engineering, Osaka University, Yamadaoka 2-1, Osaka 565, Japan

Abstract

The Yb-doped $SrCeO_3$ was selected as a complex oxide. Thermal desorption of H_2 and H_2O was examined for Yb-doped $SrCeO_3$ exposed to O_2/H_2O atmosphere in the temperature range of 500–1100°C. The desorption of H_2 and H_2O from the oxide-containing hydrogen was observed and the total amount of released H_2O was twice as much as that of released H_2, independent of the hydrogen content in the specimen. From the analysis of the thermal desorption spectra, both H_2 and H_2O desorption was inferred to be controlled by a chemical reaction with first-order kinetics.

Keywords: Yb-doped $SrCeO_3$; Thermal desorption; H_2; H_2O

1. Introduction

Some perovskite-type complex oxides such as $SrCeO_3$ and $CaZrO_3$ exhibit an appreciable proton conduction in a hydrogen-containing atmosphere [1,2]. This type of proton conductor is applicable to fuel cells, hydrogen production and separation, and hydrogen sensors.

For the practical applications of the perovskite-type oxides, it is useful to understand hydrogen transport and dissolution behavior in the oxides. Although the electrochemical behavior of hydrogen in the oxides has been extensively studied [1,2], little information of hydrogen diffusion, solubility, permeability, and surface reaction have been available in the literature.

In our previous study [3], the hydrogen dissolution behavior of $SrCe_{0.95}Yb_{0.05}O_3$ complex oxide was examined, and the hydrogen solubility in $SrCe_{0.95}Yb_{0.05}O_3$ was found to decrease with the temperature and to increase with the water vapor pressure. In the present study, the desorption of hydrogen and water vapor from the complex oxide has been measured to obtain kinetic information on the hydrogen behavior in the oxide.

2. Experimental

The sintered pellet of $SrCe_{0.95}Yb_{0.05}O_3$ in the form of 12 mm $\phi\times3$ mm was selected as a specimen. The experimental apparatus consisted of a hydrogen-analyzing system and a hydrogenating system, the details of which were described in our previous paper [3]. The $SrCe_{0.95}Yb_{0.05}O_3$ specimen was annealed in wet oxygen at temperatures between 500 and 1100°C in the hydrogenating system. The water vapor pressures in oxygen were 872 and 3619 Pa, and the total pressure of the gas mixture of oxygen and water vapor was 10^5 Pa. After equilibration, the specimen was quenched and then transferred from the hydrogenating system to the hydrogen-analyzing system without air exposure. The specimen was heated at 5°C min^{-1} using an IR furnace, and the thermal desorption of hydrogen and water vapor from the specimen was monitored with a quadrupole mass spectrometer.

3. Results and discussion

The desorption spectra of H_2O and H_2 gases from a $SrCe_{0.95}Yb_{0.05}O_3$ specimen hydrogenated at a temperature of 700°C at a water vapor pressure of 872 Pa are shown in Fig. 1. It is found from this figure that one desorption peak exists in the desorption spectrum of H_2O. Though the shape of desorption spectrum of H_2 gas was similar to that of H_2O gas, the release rate of H_2 gas is much smaller than that of H_2O gas.

In Figs. 2 and 3, the normalized release rates of H_2O and H_2 are indicated for the specimens hydrogenated under various conditions. It is obvious from these figures that, for both H_2O and H_2 desorption, the shape of the spectra is quite similar, the peak temperature of which is about

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*Corresponding author. Tel.: +81 6 8797887; fax: +81 6 8755696; e-mail: yamanaka@nucl.eng.osaka-u.ac.jp

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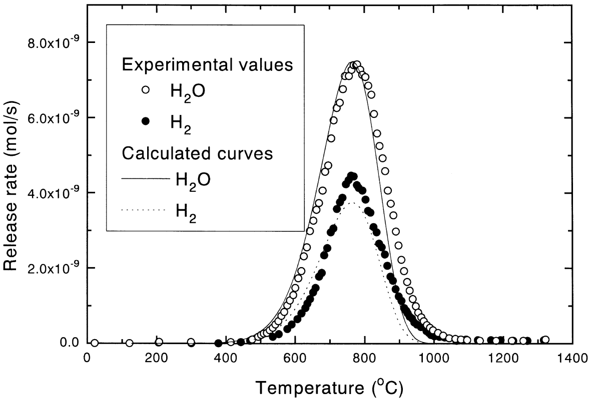

Fig. 1. Thermal desorption spectra for SrCe$_{0.95}$Yb$_{0.05}$O$_3$ hydrogenated at a temperature of 700°C at a water vapor pressure of 872 Pa.

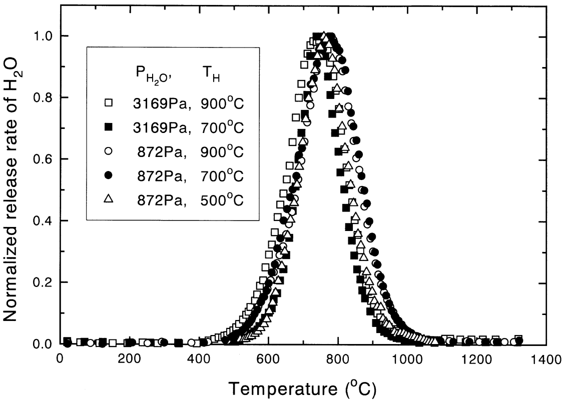

Fig. 2. Comparison of thermal desorption spectra of H_2O for SrCe$_{0.95}$Yb$_{0.05}$O$_3$ hydrogenated under various conditions.

750°C. This is independent of hydrogenating conditions, such as temperature and water vapor pressure.

The total amounts of released H_2O and H_2 are shown in Fig. 4 as a function of hydrogenating temperature. As shown in this figure, the amount of hydrogen released in the form of H_2O gas is estimated to be twice as much as that in the form of H_2 gas, and this was independent of the hydrogenating conditions. The total amount of dissolved hydrogen in the specimens ranges from 1×10^{-2} to 3×10^{-2} mol H/mol oxide, which agrees with the literature data [4,5]. The hydrogen content in the specimen slightly decreases with the hydrogenating temperature and increases with the water vapor pressure. Although a decrease in the initial hydrogen content in the specimen reduces the desorption rate of H_2O and H_2, it does not affect the desorption peak temperature.

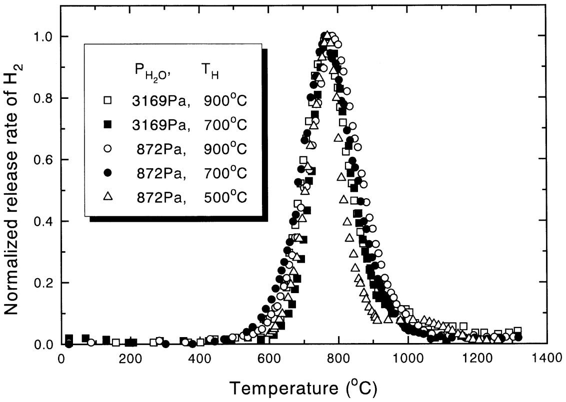

Fig. 3. Comparison of thermal desorption spectra of H_2 for SrCe$_{0.95}$Yb$_{0.0}$5O$_3$ hydrogenated under various conditions.

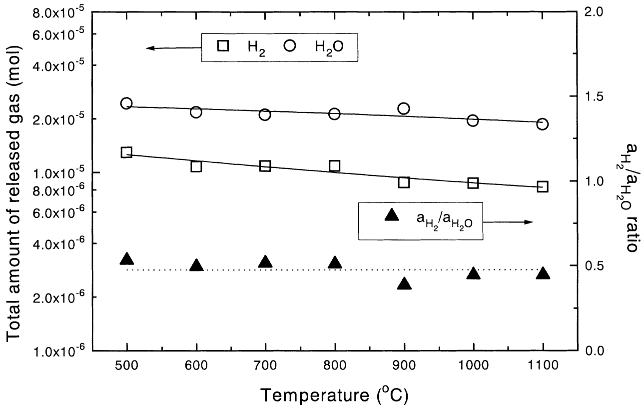

Fig. 4. Change in the total amounts of released gases and the ratio of amounts of H_2O with that of H_2, a_{H_2O}/a_{H_2}, with hydrogenating temperature.

Since the shape of desorption spectra was not changed by the initial hydrogen content of the specimen, diffusion of hydrogen-containing species in the specimen is not a rate-limiting process for the thermal desorption of H_2O and H_2 from SrCe$_{0.95}$Yb$_{0.05}$O$_3$. The desorption appears to be controlled by a chemical process. Since the peak temperature was not influenced by the initial hydrogen content of the specimen, the chemical process appears to have first-order reaction kinetics and may involve the surface dissociation of hydrogen-containing cluster such as H_3O: $H_3O(ad)=1/2H_2(g)+H_2O(g)$.

Assuming that the thermal desorption of H_2O and H_2 from SrCe$_{0.95}$Yb$_{0.05}$O$_3$ is controlled by the same first-order chemical reaction, we developed the following desorption model: the release rates of H_2O and H_2 from the unit volume of the specimen at time t, $q_{H_2O}(t)$ and $q_{H_2}(t)$ (mol s^{-1} m^{-3}), can be expressed as,

$$q_{H_2O}(t)=1/2q_{H_2}(t)=-\mathrm{d}C_H(t)/\mathrm{d}t=kC_H(t)$$

where $C_H(t)$ (mol H m^{-3}) is the hydrogen content in the specimen at time t (s) and k is the reaction rate constant (s^{-1}). The reaction rate constant k is written as a function of temperature $T(t)$ in K as follows:

$$k=k_0\exp(-E/RT(t)).$$

In this equation, k_0 is the pre-exponential factor, E is the activation energy of the reaction, and R is the gas constant.

In the present study, temperature $T(t)$ can be related to time t as,

$$T(t) = T_0 + \beta t$$

where T_0 is room temperature and β is the heating rate, which is 0.0833 K s^{-1} in the present study. In the case of the first-order reaction, the desorption peak temperature changes with the values of the activation energy, the pre-exponential factor and the heating rate, but it is independent of the initial hydrogen content of the specimen.

On the basis of the desorption model, the desorption spectra for H_2O and H_2 were calculated, which are indicated in Fig. 1. The spectra in this figure were calculated using the following rate constant:

$$k = 1 \times 10^2 \exp(-10^5\ (\mathrm{J\ mol}^{-1})/RT).$$

As revealed in this figure, the calculated spectra well express the characteristics of the experimental desorption spectra.

The calculated release rates of H_2O and H_2 were susceptible to the initial hydrogen content of the specimen. In Fig. 5, the calculated maximum release rates are compared with the experimental values as a function of the initial hydrogen content. The calculated maximum release rate increases linearly with the initial hydrogen content, as evidenced by this figure. The calculated rates are in good agreement with the experimental ones for the initial hydrogen content up to 225 mol H m^{-3}. Although for the highest hydrogen content the desorption peak temperature and the ratio of the release rate of H_2O and H_2 were almost the same as those for the samples with smaller hydrogen contents, the experimental release rates show deviations from the calculated curves. At higher hydrogen contents, the desorption of H_2O and H_2 may be controlled not only by the first-order chemical reaction but also by other mechanisms such as diffusion and other chemical reactions. Further studies are required to clarify the hydrogen desorption behavior from the oxides with higher hydrogen contents.

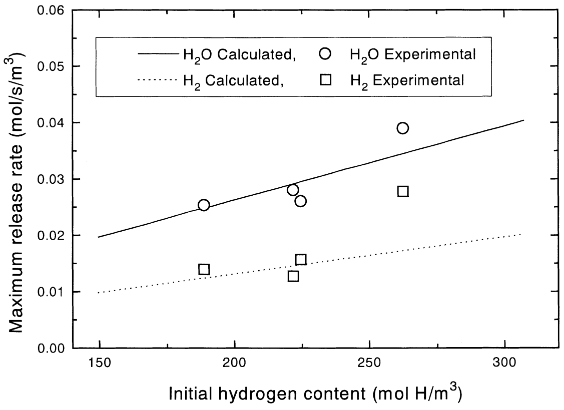

Fig. 5. Change in the maximum release rate of H_2O and H_2 with the initial hydrogen content in $SrCe_{0.95}Yb_{0.05}O_3$.

It should be noted that the release rate of H_2O from the Yb-doped $SrCeO_3$ is twice as much as that of H_2. The same first-order chemical reaction is inferred to control the desorption of H_2O and H_2 from the Yb-doped $SrCeO_3$. Water vapor H_2O was the hydrogen-containing species released from ZrO_2; however, H_2 was not observed as a released species [6]. Although both H_2O and H_2 were released from Li_2O, the desorption peak temperature for H_2O was significantly different from that for H_2 [6]. The Yb-doped $SrCeO_3$ markedly differs in the desorption behavior of hydrogen-containing species from other oxides such as ZrO_2 and Li_2O. This difference may be associated with a proton conduction mechanism in the Yb-doped $SrCeO_3$.

4. Conclusion

Thermal desorption behavior of hydrogen-containing species has been studied for Yb-doped $SrCeO_3$ exposed to an O_2/H_2O atmosphere in the temperature range of 500–1100°C. The desorption of H_2 and H_2O from the oxide-containing hydrogen was observed and the total amount of released H_2O was twice as much as that of released H_2, irrespective of the initial hydrogen content in the specimen. The thermal desorption spectra were analyzed, and both H_2 and H_2O desorption were found to be controlled by a first-order reaction. The temperature dependence of the reaction rate constant was obtained on the basis of the desorption model.

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