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Hydrogen Permeation Characteristics for Oxide/Metal Multilayered Films

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The effect of the hydrogen solubility in an oxide on hydrogen permeabilities of bronze-forming oxide/metal multilayered films was investigated with an electrochemical technique using a proton-conductive solid electrolyte. A V_2O_5/Cu, MoO_3/Cu, or (V−Mo mixed oxide)/Cu multilayered film was formed on the cathode side of a proton-conductive solid electrolyte disk. The hydrogen permeation rate was monitored using the electric current flowing through the specimen. The permeation rate was much larger for the solid electrolyte covered with V_2O_5/Cu or (V−Mo mixed oxide)/Cu multilayered film than for that covered with a single Cu layer. This appears to be due to the fact that a large amount of hydrogen absorbs in the oxide layer and the resulting hydrogen concentration gradient forms in the Cu layer. The amount of hydrogen absorbed in the oxide layer was estimated from the change in the electric current as a function of time. The hydrogen permeation rate was larger for the V_2O_5/Cu or mixed oxide/Cu multilayered film than for the MoO_3/Cu multilayered film because the V_2O_5 or mixed oxide layer absorbs more hydrogen than the MoO_3 layer.

Introduction

Some oxide/metal multilayered films have been found to exhibit significant hydrogen permeability.[1−4] As shown in Figure 1a, the color of an amorphous WO_3 (a-WO_3) film that was covered with a V_2O_5/Cu multilayered film turned blue because of the formation of tungsten bronze under an atmosphere of hydrogen. This indicates that hydrogen easily permeates the multilayered film and injects into the a-WO_3 layer. On the contrary, no coloration of the a-WO_3 layer occurred when it was covered with a single Cu layer.

This phenomenon is of particular interest not only for determining the mechanism of permeability but also for applications such as hydrogen separation and hydrogen permeable electrodes for fuel cells.

The hydrogen injection into the a-WO_3 layer through the multilayered film appeared to be a variation of hydrogen spillover,[5] wherein the oxide/metal multilayered film and the a-WO_3 layer correspond to the initiating phase and the acceptor phase, respectively. If the observed phenomenon is to be regarded as hydrogen spillover, then the hydrogen molecules would have to be dissociate and migrate on the surface of the initiating phase, i.e., the oxide/metal multilayered film, and diffuse into the a-WO_3 layer. However, the coloration of the a-WO_3 layer started from the region just under the V_2O_5 layer, as shown in Figure 1a, and the dissociated hydrogen permeated through the Cu layer. This phenomenon appears to be interesting because the hydrogen permeation through a part of the initiating phase has not been observed in conventional systems that exhibit hydrogen spillover.

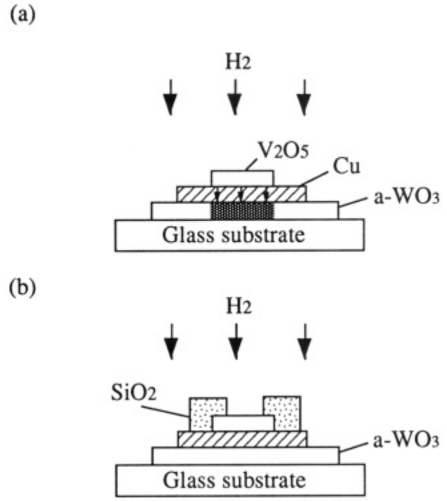

Figure 1. (a) Hydrogen permeation through a V_2O_5/Cu multilayered film. (b) The V_2O_5/Cu multilayered film wherein the perimeter of the V_2O_5/Cu interface is shielded with SiO_2. No hydrogen permeation occurs in this specimen.

It has been revealed that the hydrogen permeabilities of the oxide/metal multilayered films strongly depend upon the types of oxide layers.[2−4] The permeability increased when the oxide layer consists of bronze-forming oxides, such as V_2O_5, MoO_3, or V−Mo mixed oxide, which have large hydrogen storage capabilities. This suggests that the hydrogen storage capability of the oxide layer is one of the factors contributing to the hydrogen permeabilities of the oxide/metal multilayered films.

On the other hand, the hydrogen permeabilities of the multilayered films appeared to depend upon the dissociation of the hydrogen molecules on the multilayered films.[4]

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The following model has been proposed for the mechanism of hydrogen permeation through the multilayered films.[6]

The hydrogen molecules are dissociated at the perimeter of the oxide/metal interface, and the resulting hydrogen atoms migrate into the interface. Subsequently, the dissociated hydrogen is absorbed simultaneously by the oxide and metal layers. The hydrogen solubility is much greater in the oxide layer than in the metal layer; therefore, the hydrogen migration proceeds more quickly for the bronze-forming oxide layer. Whereas, the hydrogen concentration increases in the oxide layer particularly near the metal/oxide interface, and a large hydrogen concentration gradient forms in the metal layer. Because of this concentration gradient, the hydrogen begins to penetrate the metal layer.

The driving force for the hydrogen permeation is the hydrogen concentration in the oxide layer; therefore, the evaluation of the effect of the hydrogen storage capability is very important to prove the validity of the model. The evaluation is difficult because the effects of hydrogen storage capability and hydrogen dissociation simultaneously change with varying oxide/metal combinations.

This difficulty appears to be solved with an electrochemical technique using a proton-conductive solid electrolyte. Hydrogen supplied from the solid electrolyte to the multilayered film is dissociated; therefore, we have no need to consider the capabilities of the dissociation of hydrogen molecules at the metal/oxide interface. To investigate the effect of the hydrogen storage ability of the oxide layer on the hydrogen permeabilities of the oxide/Cu multilayered films, the hydrogen permeation rates and hydrogen content in the oxides are determined by measuring the flow of electric current through the specimens, which consist of the solid electrolyte and multilayered films.

Experimental Section

The proton-conductive solid electrolyte (SE) was prepared using the starting materials of $Ba(CH_3COO)_2$, CeO_2, and Gd_2O_3, and sintering at 1923 K for 36 ks in air.[7,8] A rod of the proton conductor, produced by this method, had a composition of $BaCe_{0.8}Gd_{0.2}O_{3-x}$. Several disks (13 mm × 0.35 mm o.d.) were cut from the rod, and each face of the disk was mechanically polished.

The face of the disk was coated with Pt paste and was heated at 1173 K for 3.6 ks; thereby, the face was covered with porous Pt electrodes (area of coverage: 9.5×10^{-5} m^2). The oxide (V_2O_5, MoO_3, and V−Mo mixed oxide; thickness 0.30 μm, area of coverage 1.13×10^{-4} m^2) and Cu (thickness 0.50 μm, area of coverage 9.5×10^{-5} m^2) layers were formed on the opposite sides of the disks by means of vacuum evaporation and rf sputtering, respectively. The starting materials were reagent-grade V_2O_5 and MoO_3 (99.8%) powders and a 99.99% Cu target. The V−Mo mixed oxide was prepared according to the procedure of Anicon et al.[9] and Jerman et al.[10] The Mo/V ratio for the mixed oxide was determined to be 1.0 using the electron probe X-ray microanalysis (EPMA). Exposed perimeters of the SE/oxide and oxide/Cu interfaces were shielded with SiO_2 that was deposited by an rf sputtering method. The SiO_2 deposition was necessary to prevent the dissociation of hydrogen molecules at the perimeters. As shown in Figure 2, a dc voltage of 1 V was applied perpendicular to the disk under vacuum and 1.0×10^5 Pa of hydrogen gas at 673 K, and the change in the electric current as a function of time was recorded. The same measurement was performed on a disk in which only a Cu layer was formed on the opposite side of the platinum electrode. In this measurement, the entire surface of the sample was exposed to the hydrogen atmosphere.

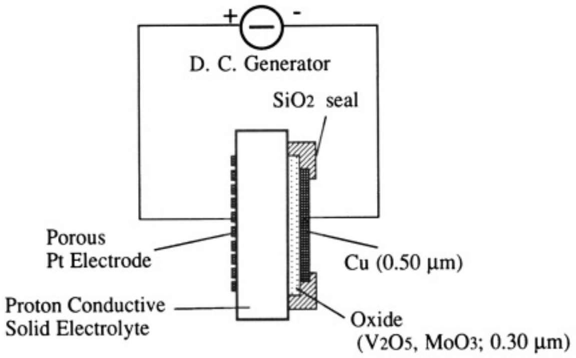

Figure 2. Specimen used for evaluating the hydrogen permeation rate for the multilayered film.

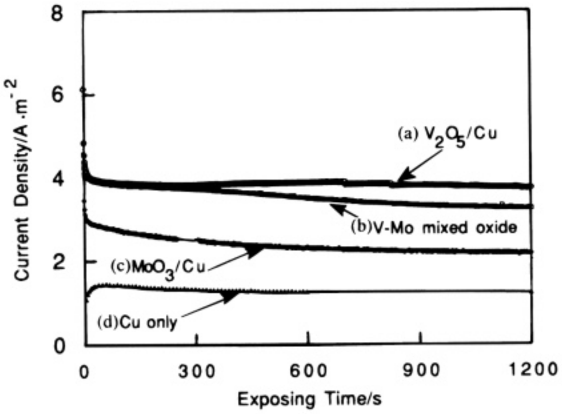

Figure 3. Electric current densities as a function of time: (a) Pt/SE/V_2O_5/Cu specimen; (b) Pt/SE/(V−Mo mixed oxide)/Cu specimen; (c) Pt/SE/MoO_3/Cu specimen; (d) Pt/SE/Cu specimen.

Results and Discussion

Figure 3 shows the change in the electric current as a function of time for each Pt/SE/oxide/Cu specimen under a hydrogen atmosphere. Although the electric current density was observed immediately after exposing to hydrogen and was relatively large, it decreased rapidly and became constant for all specimens containing the oxide layers. The measurements were carried out for 3.6 ks, and the electric current remained at the constant value. On the other hand, the electric current for the Pt/SE/Cu specimen under hydrogen was only 37% of the Pt/SE/V_2O_5/Cu specimen. Furthermore, no significant decrease in current was observed throughout the exposure.

Table 1 presents values of the electric current density obtained for the specimen illustrated in Figure 4 under various atmospheres when the dc voltage was applied with a positive polarity for the gas A side. The resulting current density at 673 K was much larger for the atmospheres of H_2 for gas A and of Ar for gas B (1.77 A/m^2) than for that of H_2 for B and of Ar for A (0.14

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Table 1. Electric Current Density Flowing through the Solid Electrolyte under Various Atmospheres

atmosphere		
gas A (+)	gas B (−)	electric current density (A/m²)
H_2	Ar	1.77 ± 0.04
Ar	H_2	0.14 ± 0.00
H_2	H_2	1.77 ± 0.10

A/m²). This indicates that the solid electrolyte exhibits considerable proton conductivity under a hydrogen atmosphere. On the other hand, the current density for gas A and gas B under an atmosphere of H_2 was equal to the current density for gas A under an atmosphere of H_2. Accordingly, the protons appear to migrate not on the surface but through the bulk of the solid electrolyte disk even if the entire surface of the specimen is exposed to a hydrogen atmosphere.

The solid electrolyte used is a perovskite-type oxide. The protonic conduction is considered to occur at the expense of the electron holes that initially existed in the crystal.[11] Under a hydrogen atmosphere, the electrons may migrate into the solid electrolyte and the protons may occupy the electron holes. The contribution of the electronic conduction was determined using a solid electrolyte disk, and the face of the anode side was shielded with an amorphous SiO_2 layer. In this specimen, the majority of the electron holes are filled by protons and the protons are impeded by the SiO_2 layer; therefore, the remaining electric current density observed, under a hydrogen gas atmosphere, is considered to be due to an electronic conduction. The resulting current density was less than 0.01 A/m². Therefore, the transport number of the proton for the solid electrolyte is approximately 1.0, and the electric current density for the specimens without the SiO_2 seal is attributed to the proton transfer, i.e., the hydrogen permeation through the specimen.

The mechanism of the hydrogen permeation for the oxide/Cu multilayered films formed on the solid electrolyte is presumed to be as follows: Hydrogen atoms are dissociated into protons and electrons at the surface of the Pt electrode. On the Pt/SE/V_2O_5/Cu specimen, the protons permeate the solid electrolyte and extend to the SE/V_2O_5 interface. On the other hand, electrons are supplied from the Cu layer into the V_2O_5 layer. V_2O_5 is one of the well-known electrochromic materials[12,13] and allows the injection of protons. Therefore, the protons and electrons migrate into the V_2O_5 layer from the solid electrolyte and the Cu layer, respectively. Hydrogen has been reported to be dissociated into protons and electrons in V_2O_5.[14,15] However, the electrons are impeded at the interface between the solid electrolyte and the V_2O_5 layer because the solid electrolyte exhibits no electronic conduction, and the protons and electrons concentrate in the V_2O_5 layer at an electrically neutral state. V_2O_5 is a hydrogen bronze forming oxide and absorbs a considerable amount of hydrogen that allows for an extensive proton injection from the solid electrolyte into the V_2O_5 layer. The proton injection continues until a sufficient amount of hydrogen is stored in the V_2O_5. The V_2O_5 film was prepared by vacuum evaporation and was confirmed to be amorphous. The open structure of such an amorphous film appears to weaken the O−H interaction and to enhance the mobility of protons in comparison to the crystalline film. When an adequate concentration gradient of hydrogen is formed at the interface of the V_2O_5 and Cu layers, hydrogen percolates into the Cu layer and recombines into hydrogen molecules at the surface of the Cu layer. The resulting hydrogen molecules are released into the atmosphere.

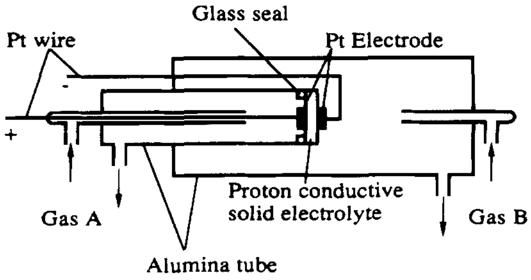

Figure 4. Cell used for characterizing the solid electrolyte.

Table 2. Hydrogen Permeation Rate for the Multilayered Films Formed on the Solid Electrolyte

film construction	electric current density (A/m²)	hydrogen permeation rate (×10⁻⁵ mol s⁻¹ m⁻²)	amount of hydrogen stored in the oxide layer (×10⁴ mol/m³)
Cu	1.03 ± 0.05	0.53 ± 0.03	
V−Mo oxide/Cu	3.69 ± 0.20	1.66 ± 0.10	1.90
V_2O_5/Cu	3.80 ± 0.23	1.97 ± 0.12	2.08
MoO_3/Cu	1.72 ± 0.22	0.89 ± 0.11	1.27

The hydrogen permeation rate was calculated from the current density for each specimen, and the resulting values are presented in Table 2. The hydrogen permeation rate for the Pt/SE/V_2O_5/Cu specimen was approximately the same as the Pt/SE/(V−Mo mixed oxide)/Cu specimen, and the value was almost 3 times as large as the Pt/SE/Cu specimen, which had no bronze-forming oxide layer.

According to the mechanism of hydrogen permeation, the relationship between the change in the electric current as a function of time and the hydrogen permeation is interpreted. During the initial period of exposure to hydrogen, the proton injection proceeds remarkably into the empty V_2O_5 layer such that the electric current becomes large. The concentration of hydrogen in the V_2O_5 layer quickly reaches a saturated value such that the rate of hydrogen permeation through the specimen, i.e., the electric current density, decreases rapidly. The electric current reaches a constant value when the hydrogen concentration in the V_2O_5 layer approaches a steady state. Under vacuum, virtually no electric current flows because protons are not supplied to the system. The slight electric current that is observed appears to be due to the electron hole conduction in the solid electrolyte.

For the Pt/SE/Cu specimen, no layer exists that can absorb hydrogen between the solid electrolyte and the Cu layer. In this case, a large concentration gradient of hydrogen that provides a driving force of hydrogen injection into the Cu layer is not formed at the SE/Cu boundary. Consequently, the amount of hydrogen sup-

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plied to the Cu layer is small, and the electric current appears to be smaller the Pt/SE/V_2O_5/Cu specimen.

The hydrogen permeation rate for the Pt/SE/(V–Mo mixed oxide)/Cu was approximately equal to the Pt/SE/V_2O_5/Cu specimen. On the other hand, the rate for the specimen having the MoO_3/Cu multilayered film was smaller than the V_2O_5/Cu and V–Mo mixed oxide/Cu multilayered films. The difference in the hydrogen permeation rates appears to be due to the difference in the hydrogen storage density between these oxide layers.

Electrochemical methods for studying the chemical diffusion of ions in solids, namely, the potentiostatic intermittent titration (PITT) and the galvanostatic intermittent titration (GITT), have been developed by Wepper, Huggins, and co-workers.[16–18] According to the PITT, the chemical diffusion flux of protons, $L(t)$, from the solid electrolyte to the oxide layer is estimated from the electric current density as a function of time, $I(t)$:

$$L(t) = I(t)/F \qquad (F\text{, Faraday constant}) \qquad (1)$$

A similar PITT method was applied in the present study. In this case, since the hydrogen in the oxide layer permeates into the Cu layer, the hydrogen flux, $G(t)$, is considered, and the amount of hydrogen taken up by the oxide layer, H, is represented by the following equation:

$$H = \int \{L(t) - G(t)\}\, dt \qquad (2)$$

Hydrogen is considered to migrate in the oxide/metal multilayer under an electrically neutral state, and no direct information of $G(t)$ is obtained from the $I(t)$ curve. The hydrogen flux, $G(t)$, is assumed to increase proportionally to the hydrogen concentration, $C(t)$, in the oxide layer, i.e.

$$G(t) = AC(t) \qquad (3)$$

where A is a constant. On the other hand, protons from the solid electrolyte must be injected into the oxide layer against the hydrogen concentration gradient; therefore, the hydrogen migration into the oxide layer appears to become more difficult with increasing hydrogen concentration in the oxide layer. Therefore, the hydrogen flux from the solid electrolyte, $L(t)$, is assumed to be proportional to the difference between the saturated concentration of hydrogen in the oxide, Cs, and the hydrogen concentration in the oxide at some time, $C(t)$, i.e.

$$L(t) = A'\{Cs - C(t)\} \qquad (4)$$

When a steady state of the hydrogen flux is reached at $t = T$, $L(t)$ is equal to $G(t)$. Furthermore, no hydrogen is stored in the oxide layer at $t = 0$, and $G(t)$ is expressed by the following equation:

$$G(t) = \frac{L(t)}{L(0) - L(T)}\{L(0) - L(t)\} \qquad (5)$$

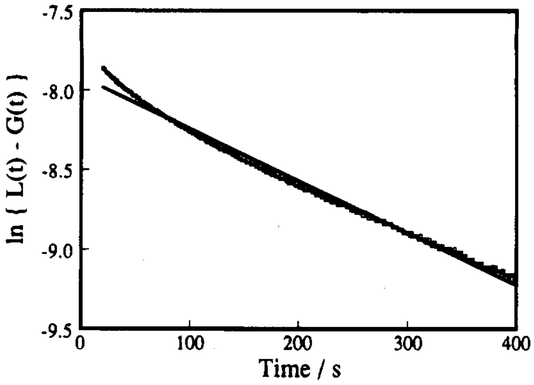

Figure 5. Plots of $\ln\{L(t) - G(t)\}$ versus time for the Pt/SE/(V–Mo mixed oxide)/Cu specimen. (–, theoretical).

Both $L(t)$ and $G(t)$ are obtained from the values of $I(t)$, and the resulting amount of hydrogen stored in the oxide layer, H, is calculated using eq 2. In this study, the integration of eq 2 was performed from $t = 0$ to 1200 s.

The assumptions presented by eqs 3 and 4 provided the basis for the estimation of the amount of hydrogen absorbed by the oxide layer. The validity of these assumptions should be carefully judged. The following relationship is derived from the eqs 2–4:

$$L(t) - G(t) = Ce^{-Kt} \qquad (6)$$

$$K = (A' + A)/V$$

where C is an integration constant and V is the volume of the oxide layer. Therefore, a linear relationship is expected when $\ln\{L(t) - G(t)\}$ is plotted versus time t. As shown in Figure 5, an essentially linear relationship was obtained, and the assumption of eqs 3 and 4 was concluded to provide a relatively good basis for estimating the amount of hydrogen stored in the oxide layer from the $I(t)$ curve.

The calculated hydrogen concentration stored in the oxide layer (Table 2) was larger for the V_2O_5 and V–Mo mixed oxide layers than for the MoO_3 layer. Therefore, the hydrogen concentrations in the oxide layers evidently influence the hydrogen permeation rates for the multilayered films.

The stabilities of hydrogen bronzes of the oxides appear to be important for discussing the hydrogen permeability of the specimen. The stabilities of the bronzes should be examined under an atmosphere of hydrogen with an applied electric field at 673 K because the amount of hydrogen in the oxide layer may change if an electric field is applied. The oxide layers on the solid electrolyte, however, could not be characterized directly because the oxide layers were covered with the Cu electrode. With respect to the crystalline oxides, Hirata and Yagisawa reported that the hydrogen bronze of V_2O_5 decomposes into H_2O and suboxides at temperatures above 673 K in vacuo.[19] Tinet et al. also suggested the instabilities of hydrogen bronzes in the same temperature region.[14] Such hydrogen bronze decompositions have been interpreted to be due to the formation of strong O–H interaction in the bronzes.

If such a hydrogen bronze decomposition occurs, a drastic change in the current density is expected for the

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specimen through the measurement. However, for all specimens containing the oxide/Cu multilayered film, the current density remained at a constant value after the initial drop in the current. The current density was repeatedly measured under hydrogen for one Pt/SE/V_2O_5/Cu specimen. It was confirmed that the electric current always reached to the same constant value. The specimen then was cooled in vacuo and was preserved in Ar at room temperature for 2 weeks. Consequently, the same phenomena for the change in the electric current were reproduced. These results appear to suggest that the change in the chemical properties of the oxide layer, due to the decomposition of the hydrogen bronze, did not occur with repeated measurements.

One example of hydrogen injection into materials under an electric field is water electrolysis using a hydrogen storage material, such as Pd and $LaNi_5$ cathodes. In this case, hydrogen absorbs in the materials depending upon the equilibrium potential.[20] The equilibrium potential of the electrolysis is logarithmically related with the equilibrium hydrogen pressure for hydrogen absorption into the materials from gaseous hydrogen. In some cases, a 0.1 V change in the equilibrium potential corresponds to a change in the equilibrium pressure in several orders of magnitude. In this study, protons were forcefully injected into the bronze-forming oxide layer from the solid electrolyte under an electric field. Although a hydrogen pressure equivalent to 1 V of dc voltage could not be estimated, there is a possibility that the condition of hydrogen injection under the electric field became close to values obtained using a very high hydrogen pressures. The amounts of hydrogen taken up by the V_2O_5 and MoO_3 layers in atoms per formula weight were 1.5 and 1.3, respectively. These values appear to be very large and could not be expected at 673 K under ordinary hydrogen pressures. Although, the values are smaller than the crystalline bulk of the oxides at 343 K ($H_{3.8}V_2O_5$ and $H_{1.65}MoO_3$).[21] This appears to occur because the hydrogen injection into the oxide layers proceeds under an electric field.

Conclusions

To clarify the effect of the hydrogen storage capabilities of oxides on hydrogen permeabilities for the oxide/metal multilayered films, the hydrogen permeation rate and the hydrogen concentration in the oxides were determined with an electrochemical method using the proton conductive solid electrolyte. The hydrogen permeation rate was much larger for the solid electrolyte covered with the bronze-forming oxide/Cu multilayered film than for that covered with a single Cu layer. This appears to be due to the large hydrogen concentration in the bronze-forming oxide layer which provides a hydrogen concentration gradient in the Cu layer. The Pt/SE/MoO_3/Cu specimen exhibited a lower hydrogen permeation rate in comparison with the Pt/SE/V_2O_5/Cu and Pt/SE/(V−Mo mixed oxide)/Cu specimens because the hydrogen solubility was lower for the MoO_3 layer than for the V_2O_5 and V−Mo mixed oxide layers.

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