EFFECT OF WATER VAPOR ON CATHODE REACTION IN SOFC

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ABSTRACT

The effect of water vapor on electrochemical reaction on SOFC was investigated. It is found that the surface reaction rate constant of oxygen isotope exchange on yttria stabilized zirconia (YSZ) was ca. 500 times larger in 28 hPa O\textsubscript{2} + 22 hPa H\textsubscript{2}O (wet atmosphere) than that in dry 28 hPa O\textsubscript{2} at 873 K. This is due to the fast exchange reaction between H\textsubscript{2}O molecule and oxygen vacancy in YSZ, which is dominant in a humid atmosphere at lower temperatures. The interfacial conductivity at cathode / electrolyte rapidly increased on change of the cathode atmosphere from dry air to humid air (+ 12 hPa H\textsubscript{2}O), and it gradually decreased in long-term exposure to the humid atmosphere. The former increase of the interfacial conductivity represents the expansion of active area for electrochemical reaction around triple phase boundary (TPB) and the latter decrease indicates that the adsorbed H\textsubscript{2}O molecule may prohibit the migration of adsorbed oxygen atom from electrode surface to TPB region.

INTRODUCTION

For recent several years, attempts of lowering the operation temperature of SOFC have been very popular using new electrolyte materials and cell designs. The operation of SOFCs below 1000 K has an advantage that it allows to use steel interconnect which may reduce the material and fabrication costs. However, the problems concerning the thermal stress due to expansion mismatch and the side sealing of planar-type cells still remain for the fabrication and operation of SOFCs at such intermediate temperatures. Furthermore, in the operation of electrode-supported type SOFCs with thin electrolytes at lower temperatures, the overpotential of electrode reactions will be much larger than IR loss of electrolytes. The charge transfer process in electrochemical reaction tends to be rate limiting which determines the total performance.

In the present paper, we focused on possible factors which may affect the electrochemical reaction at intermediate temperatures. It should be noted that such factors are not all the same as those at high temperatures. The effect of water in gaseous phase is one of the factors and it has been hardly addressed in any literature. However, it would be more significant at lower temperatures. Even a trace amount of water in a few per cent may make a drastic change in electrochemical performance. We have recently...
found that the reaction constant of oxygen isotope exchange on YSZ surface is actually sensitive to a slight amount of water vapor (1). The reaction constant \( k \) was 75 times larger in 25 hPa O\(_2\) + 21 hPa H\(_2\)O at 773 K. This phenomenon can be explained as follows: The oxygen exchange reaction at YSZ surface is governed by the interaction between water molecules and oxygen vacancies of YSZ.

\[
H_2O(g) + V_{o}^\circ \rightleftharpoons O_{o}^\circ + 2H^\circ
\]

Here, \( V_{o}^\circ \), \( O_{o}^\circ \), and \( H^\circ \) represent an oxygen vacancy, an oxide ion, and an interstitial proton in YSZ lattice. The reaction rate of eq. [1] is considered to be much faster than the reaction which may be dominant in dry O\(_2\):

\[
\frac{1}{2}O_2 + V_{o}^\circ \rightleftharpoons O_{o}^\circ + 2h^\circ
\]

The \( h^\circ \) represents an electronic hole in YSZ.

Since the existence of water vapor enhances the oxygen exchange reaction on the electrolyte surface, a similar mechanism may enlarge the active zone of electrochemical reactions on YSZ and may reduce the overpotential. The present paper reports the detail of the effect of water on the oxygen isotope exchange reaction for YSZ and on the cathodic reactions for platinum / YSZ, gold / YSZ, and lanthanum manganite / YSZ systems.

EXPERIMENTAL

Oxygen Isotope Exchange Experiment

YSZ single crystal (8 mol % \( Y_2O_3 \) - \( ZrO_2 \), Earth Jewelry Co. Ltd., (100) plane oriented) was cut into small pieces with 3 mm \( \times \) 3 mm \( \times \) 1 mm. A dense polycrystalline YSZ was prepared by sintering YSZ powder (TOSOH TZ-8Y) at 1773 K in air. Pre-annealing was carried out in 2 % H\(_2\)O + 2% O\(_2\) + 96 % N\(_2\) in order to minimize the chemical diffusion thermodynamic effect on the subsequent oxygen tracer exchange procedure. The sample was then placed in a closed system, and the system was evacuated and then the stable isotopes of oxygen (\( ^{16}O_2 \), ISOTEC Co. Ltd., 95% enriched) and/or water vapor (H\(_2^{18}\)O, 97 % enriched) were introduced. The partial pressures of water and oxygen were adjusted to those adopted in the pre-annealing treatment. The sample was rapidly heated with an infrared furnace, and kept at certain temperature for 300 or 420 s, and then quenched to room temperature. Heating and cooling rate was above 40 K/s. The intensities of the mass spectra around \( M/e = 16 \) and \( M/e = 18 \) were collected by secondary ion mass spectrometry (SIMS, CAMECA ims5f, primary ion: Cs\(^+\), 10 kV, secondary ions: negative, -4.5 kV). Three types of analyses were adopted: Depth profiles were taken by etching the sample surface with a strong primary ion beam (\( I(Cs^+) = 15 \sim 18\) nA), and secondary ion images and line profiles were taken on the cross section of the sample with a focused, low energy beam (\( I(Cs^+) = 10\) pA). After collecting the depth profiles, the depth of etched area was measured by a surface profiler (Dektak\(^3\),

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Veeco/Sloan Co. Ltd., USA). The depth profiles of normalized fraction of $^{18}\text{O}$ ($X$) in YSZ were then calculated from the intensities of $^{16}\text{O}$ and $^{18}\text{O}$ ions.

$$X(\text{^{18}O \, normalize \, fraction}) = I(\text{^{18}O}) / (I(\text{^{16}O}) + I(\text{^{18}O}))$$  \[3\]

Oxygen isotope diffusion coefficient ($D^{*}_{\text{O}}$) and surface reaction rate constant ($k$) were determined by fitting depth profiles to the diffusion equation which was solved for semi-infinite media assuming surface reaction (2).

$$\frac{X - X_{bg}}{X_{g} - X_{bg}} = \text{erfc} \left( \frac{z}{2\sqrt{(D^{*}_{\text{O}}t)}} \right) - \exp(bz + b^{2}D^{*}_{\text{O}}t)\text{erfc} \left( \frac{z}{2\sqrt{(D^{*}_{\text{O}}t)}} + b\sqrt{(D^{*}_{\text{O}}t)} \right)$$  \[4\]

$$\text{Where } b = k/D^{*}_{\text{O}},$$  \[5\]

$X_{g}$ and $X_{bg}$ are the isotope fractions in gaseous phase ($= 0.96$) and background ($= 0.002$), respectively, $t$ is the annealing time, and $z$ is the depth.

**Electrochemical Measurement**

The surface of the dense YSZ polycrystalline disk (17 mm in diameter and 2 mm thick) was polished by using diamond paste. Platinum (Pt paste, TR-7905, Tanaka Kikinzoku Co. Ltd., Japan), gold (Au paste, TR-1301 Tanaka Kikinzoku Co. Ltd., Japan) and (La$_{0.85}$Sr$_{0.15}$)$_{0.95}$MnO$_{3}$ (Powrex Co. Ltd., Japan) were used as working electrodes, which were painted and dried on one surface of YSZ disk. Platinum paste was used as counter electrode on the opposite surface of the disk. A platinum wire was used as reference electrode, attached to the side of the YSZ disk. The working electrode was exposed to dry or humid air ($p(\text{O}_2) = 2.13 \times 10^{2}$ hPa). The partial pressure of water was determined as 0.6 hPa (dew point $= -25 \, ^\circ\text{C}$) in dry air by hygrometer (Moisture Monitor Series 35, Panametrics Japan Co. Ltd.). The water partial pressure of humid air was controlled by flowing air through H$_2$O trap, and it was kept at 12 hPa. The reference and counter electrodes were always exposed to dry air. The flow rate was kept at 100 cm$^3$ min$^{-1}$. AC impedance was measured at temperatures from 773 to 1173 K under an approximately open circuit condition by an impedance analyzer (SI1260 / SI 1287, Solatron), in a frequency range from 10 mHz to 1 MHz with 50 mV amplitude.

**RESULTS AND DISCUSSION**

**Effect of Water on Isotope Exchange Reaction Rate**

Fig. 1 shows the temperature dependence of diffusion coefficient ($D^{*}_{\text{O}}$) and surface reaction rate constant ($k$) of YSZ in the humid atmosphere (21 hPa H$_2$O + 25 - 30 hPa O$_2$). The literature data reported by Manning et al. for YSZ and CGO single crystals in dry O$_2$ ($p(\text{O}_2) = 1 \, \text{atm} = 1013 \, \text{hPa}$) is shown as lines in the figure (3, 4). The present data of reaction rate constant in the humid atmosphere exhibit 75 - 500 times larger values than those in dry O$_2$ from 773 to 1073 K, which indicates that the reaction is governed by the fast reaction including water molecule as shown in eq. [1].
The oxygen isotope exchange reaction in dry atmosphere can be described with the following steps:

\[ \frac{1}{2}^{18}\text{O}_2 (g) \rightleftharpoons ^{16}\text{O}_{\text{ad}} \]  
\[ ^{18}\text{O}_{\text{ad}} + V_0^{**} \rightleftharpoons 2h^* + ^{18}\text{O}_0^{x} \]  
\[ 2h^* + ^{16}\text{O}_0^{x} \rightleftharpoons ^{16}\text{O}_{\text{ad}} + V_0^{**} \]  
\[ ^{16}\text{O}_{\text{ad}} \rightleftharpoons \frac{1}{2} ^{16}\text{O} (g) \]

In the equations, \( O_{\text{ad}} \) represents an oxygen atom adsorbed on the YSZ surface. In a dry atmosphere, the charge transfer reactions are maintained by the electronic holes \( (h^*) \) as shown in eqs. [6b] and [6c]. Since hole conductivity is considered to be very low in YSZ, the charge transfer reactions are generally slow so that they become the rate determining steps. The surface reaction constants of CGO in dry O\(_2\) are ca. 10 times larger than those of YSZ, which clearly represents the difference in magnitude of hole or electronic conductivity.

On the contrary, the oxygen isotope exchange reaction in a humid atmosphere can be divided into the following steps.

\[ \text{H}_2^{18}\text{O} (g) \rightleftharpoons \text{H}_2^{18}\text{O}_{\text{ad}} \]  
\[ \text{H}_2^{18}\text{O}_{\text{ad}} + V_0^{**} \rightleftharpoons 2\text{H}_i^* + ^{18}\text{O}_0^{x} \]  
\[ 2\text{H}_i^* + ^{16}\text{O}_0^{x} \rightleftharpoons \text{H}_2^{16}\text{O}_{\text{ad}} + V_0^{**} \]  
\[ \text{H}_2^{16}\text{O}_{\text{ad}} \rightleftharpoons \text{H}_2^{16}\text{O} (g) \]

\( \text{H}_2\text{O}_{\text{ad}} \) represents a water molecule adsorbed on the electrolyte surface. As shown in eqs. [7b] and [7c], the charge transfer for oxygen reduction is maintained by the protons \( (\text{H}_i^*) \) which are dissolved in YSZ lattice. The present experimental results indicate that these reaction are much faster than reactions [6b] and [6c].

The effect of water seems to be more significant at lower temperatures, which agrees well with the fact that the adsorbed molecules are more stable at lower temperatures. The literature values of reaction rate constant in dry O\(_2\) exhibit different slopes in temperature dependence above / below 900 K. The activation energy of surface reaction rate constant was 212 kJ mol\(^{-1}\) (2.2 eV) above 900 K and 67 kJ mol\(^{-1}\) (0.7 eV) below 900 K for YSZ in dry atmosphere (3). On the contrary, the results in the humid atmosphere did not show any anomaly in temperature dependence, and an activation energy of 116 kJ mol\(^{-1}\) (1.2 eV) was obtained in a whole temperature range from 773 to 1073 K. It can be considered that the values in dry O\(_2\) below 900 K may include the plausible effect of those water, which may be contaminated in a trace amount in the system.

It should be also noted that the present results of diffusion coefficient \( (D_{O_2}^*) \) in the humid atmosphere were lower than the literature data in dry O\(_2\). This fact does not agree
with the result that no change was observed in bulk conductivity of YSZ between dry and humid atmosphere which will be shown in the next section. Hence, the difference in diffusion coefficients in isotope exchange will be correlated with the effect of chemical potential gradient of water in the electrolytes, which will be clarified in future work.

**Effect of Water on Electrochemical Property**

Fig. 2 shows the Cole-Cole plots for the polycrystalline YSZ with platinum electrode at 761 K. The large arc represents the interfacial resistance and capacitance between electrode and electrolyte, and it decreased in the humid atmosphere. The bulk ($\sigma_{\text{bulk}}$) and interfacial conductivity ($\sigma_{\text{i}}$) were determined by fitting the plots to the equivalent circuits. The results are shown in Table 1, in which the interfacial conductivity drastically increased on change to the humid atmosphere whereas the bulk conductivity was unchanged. This unchanged bulk conductivity is consistent with the literature results (3).

Fig. 3 shows the interfacial conductivity of Pt / YSZ on change of atmosphere as a function of time at 757 K. The interfacial conductivity rapidly increases on change to the humid atmosphere, but it gradually decreased in long-term exposure to the humid atmosphere. This indicates that the effects of water on electrochemical performance of Pt / YSZ consist of two opposite factors, that is, rapid improvement and gradual degradation. Fig. 4 shows the result at higher temperature ($T = 969$ K), and indicates that the degradation effect is more significant at a higher temperature. At 1175 K, only degradation was observed without enhancement, shortly after switching the atmosphere.

In general cathode reactions in SOFC, the surface reaction on electrolyte is considered to be very slow, so that the active area of electrochemical reaction is restricted in the vicinity of the triple phase boundary (TPB) of gas / electrode / electrolyte interface. However, if we assume the existence of a slight amount of water vapor, the fast oxygen exchange reaction will be expected according to eq. [1] on the surface of YSZ. If the interstitial protons ($H_1^*$) is mobile inside YSZ to TPB, the following cathode reaction is possible:

$$2H_1^* (\text{from YSZ}) + O_{\text{ad}} (\text{on Pt surface near TPB}) + 2e (\text{from Pt}) \rightarrow H_2O (g)$$ \[8\]

Hence the electro-catalytic effect of water is expected with the combination of eq. [1] and [8]. This effect expands the active area for cathode reactions from TPB to the YSZ / gas interface region, and apparently results in the increase of interfacial conductivity.

The degradation effect of water can be explained by considering the effect of adsorbed water molecules on platinum electrode. Schwardt et al. reported that the diffusion of adsorbed oxygen atom from electrode surface to TPB is the rate determining step for Pt / YSZ in a dry atmosphere (5). In a humid atmosphere, water molecules are adsorbed on electrode surface as well as oxygen, and they may prevent the diffusion of adsorbed oxygen to TPB. Usually, the chemically adsorbed oxygen is discussed in relation with the electrochemical reactions,. Similarly, the chemical adsorption of OH will be of interest for a relatively long term degradation. As shown in eq. [8], depletion of adsorbed oxygen at TPB may also prevent the completion of the catalyzed
electrochemical reaction in a humid atmosphere. The effects of water are schematically summarized in Fig. 5.

For the case of Au / YSZ, the improvement effect was more significantly observed even at higher temperature than that of Pt / YSZ. Fig. 6 shows that the interfacial conductivity was improved about 30% in the humid atmosphere at 970 K. In Au / YSZ, the species which are adsorbed only near TPB can contribute to the electrochemical reaction(5), so that the diffusion of adsorbed species on electrode surface is not important, which may be the reason why Au / YSZ exhibited lesser degradation than the Pt / YSZ case.

Fig. 7 shows the result of LSM / YSZ at 968 K, which is very similar to that of Pt / YSZ at 757 K. The present results indicate that the effect of water vapor on cathode reaction can be explained in terms of the combination of two opposite effects, that is, the improvement due to the expansion of active reaction zone and the degradation due to the prevention of diffusion on electrode. The improvement effect is more significant at lower temperatures and degradation effect becomes dominant at higher temperatures. These effects are observed in all electrodes / YSZ electrolyte cases investigated in the present study, although the apparent profile of interfacial conductivity changes with the complex combination of two effects.

It should be concluded that the effect of water becomes very important to clarify those electrochemical reactions especially at low temperatures where the electrode reaction is rate-limited by charge transport processes.

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Fig. 1 Temperature dependence of oxygen tracer diffusion coefficient ($D_0^*$ closed symbols) and surface reaction rate constant ($k$, open symbols). Present data in $H_2^{18}O + ^{18}O_2$: ○, YSZ single crystal; □, YSZ polycrystalline
Literature data in dry $O_2$: YSZ Single crystal: $D^*$, $k$ (3) Gd$_{0.31}$Ce$_{0.69}$O$_{2-d}$: $D^*$, $k$ (4)

Fig. 2 Effect of atmospheres on complex impedance plots for YSZ polycrystalline with platinum electrodes at $T = 761$ K:
$\Delta$; dry air (100 ml min$^{-1}$) for both sides of YSZ,
$\blacktriangle$; cathode side: air + $H_2O$ (12 hPa), anode side: dry air.
Table 1 Bulk and interfacial conductivity derived from the Cole-Cole plot in Fig. 2

| $T = 761$ K | Dry air, $p(H_2O) = 0.7$ hPa | Humid air $H_2O$ $p(H_2O) = 12$ hPa |
|---|---|---|
| $\sigma_{bulk}/$ S m$^{-1}$ | $5.76 \times 10^2$ | $5.76 \times 10^2$ |
| $\sigma_{f}/$ S m$^{-2}$ | 2.439 | 3.546 |

Fig. 3 Interfacial conductivity of platinum / YSZ at $T = 757$ K. $I = 1$ mA.
●; Dry air, ●; Humid air.

Fig. 4 Interfacial conductivity of platinum / YSZ at $T = 969$ K. $I = 30$ mA.
●; Dry air, ●; Humid air.

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Fig. 5 Effect of water vapor on cathode reaction in SOFC.

Fig. 6 Interfacial conductivity of gold/YSZ at $T = 969$ K. $I = 1$ mA.

- ; Dry air, ●; Humid air
Fig. 7 Interfacial conductivity of LSM / YSZ at $T = 968$ K. $I = 5$ mA.

○; Dry air, ●; Humid air