EFFECTS OF WATER ON CATHODIC PERFORMANCE OF Ba$_{0.6}$La$_{0.4}$CoO$_3$ ON THE CELL USING LaGaO$_3$-BASED OXIDE FOR ELECTROLYTE

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ABSTRACT

Effects of water addition to oxidant on the cathodic overpotential of La-doped BaCoO$_3$ electrode were investigated. It was found that the overpotential of La-doped BaCoO$_3$ decreased by addition of H$_2$O to oxygen. In particular, the decrease in overpotential by addition of H$_2$O was significant with decreasing operating temperature of the cell. Therefore, it became clear that the maximum power density increased by addition of H$_2$O to oxidant. The improved cathodic activity by addition of H$_2$O was further studied by using $^{18}$O tracer exchange measurement. Although the diffusion coefficient was independent of the coexisting water, the surface exchange coefficient increased greatly by addition of water. $^{18}$O-$^{16}$O isotopic exchange reaction under coexisting H$_2^{16}$O demonstrated that the surface oxygen exchange reaction through H$_2$O is very fast and the coexisting water catalytically accelerates the dissociation reaction of gaseous oxygen molecule into oxide ion. The positive effects of humidified oxidant were stable over 50 hours of testing.

INTRODUCTION

Development of the intermediate-temperature solid oxide fuel cell (SOFC) is an important subject at present. In order to achieve a high power density at intermediate temperature, development of an electrolyte with low electrical resistance and an active electrode is essential (1). In our previous study, we found that LaGaO$_3$-based oxide exhibited high oxide ion conductivity (2) and that high power density could be achieved using LaGaO$_3$-based oxide for the electrolyte at intermediate temperature(3). Development of active cathode is another important subject because the apparent activation energy of the cathodic reaction on conventional LaMnO$_3$-based oxide is much larger than that of Ni-ZrO$_2$-doped Y$_2$O$_3$ cermet anode. Thus with decreasing operating temperature, cathodic overpotential becomes significant. From this point of view, development of active cathode catalyst is important for developing intermediate-temperature (IT) SOFCs. In our previous study, Co-based oxide was mainly investigated for the active cathode for IT-SOFC, and we found that La-doped BaCoO$_3$ was highly active for the cathodic reaction. In particular, Ba$_{0.6}$La$_{0.4}$CoO$_3$ exhibited a small overpotential, less than 50 mV at 1 A/cm$^2$ at 873K. Therefore, this BaCoO$_3$ oxide doped with La is expected to be the new cathode for IT-SOFC using LaGaO$_3$-based oxide electrolyte (4).
Recently, Sakai et al. (5) reported that the surface reaction of cathode oxide for the dissociation of oxygen molecule could be greatly accelerated by coexisting water. This phenomenon is very interesting because the cathodic overpotential could decrease by humidifying the oxidant. However, the humidification effect of oxidant on the cathodic overpotential has not been thoroughly investigated. In particular, the effects of water at intermediate temperature are still not clear. In this study, effects of water on the cathodic performance of BLC under operating condition of SOFC were investigated. In addition, because the mechanism causing the positive effects of coexisting H$_2$O on cathodic reaction is still not clear, influence of coexisting H$_2$O on the cathodic reaction was studied with tracer exchange and diffusion measurements.

**EXPERIMENTAL**

Preparation of Ba$_{0.6}$La$_{0.4}$CoO$_3$ (BLC) cathode and LaGaO$_3$-based oxide was performed by using the conventional solid state mixing method (2,4). For preparing LaGaO$_3$-based oxide, the commercial oxides of La$_2$O$_3$, Ga$_2$O$_3$, MgO, and CoO and the commercial SrCO$_3$ were mixed in a ball mill mixer. The composition of La$_{0.8}$Sr$_{0.2}$Ga$_{0.5}$Mg$_{0.15}$Co$_{0.05}$O$_3$ (LSGMC) was always used in this study. The obtained powder mixture was precalcined at 1473 K for 3 hours and mixed with a small amount of organic binder, then made into sheet with the tape-casting method. Details of the preparation were discussed in our previous paper (6). After cutting into the desirable shape, the final sintering was performed at 1723 K for 6 hours in air. XRD measurement demonstrated no significant peaks from the secondary phase. Therefore, it is considered that the single phase of LSGMC was successfully obtained by the tape casting method. The thickness of the electrolyte was always set to 0.26 mm by grinding with the diamond wheel. The BaCoO$_3$ oxide doped with La was also prepared by calcining the precursor obtained from La(CH$_3$COO)$_3$, Ba(NO$_3$)$_2$, and Co(NO$_3$)$_2$ at 1473 K for 6 hours. The prepared cathode and commercial NiO were screen printed onto each surface of the LSGMC disk.

The power-generating property of the cell was measured with four proven methods. About 3 vol% humidified H$_2$ was used for fuel (100 mL/min), and O$_2$ mixed with 3 vol% H$_2$O was fed to the cathode side. The overpotentials of anode and cathode were estimated by using the complex impedance method (Solartron 1260) and the current interruption method. The constant current was generated by using a current pulse generator (Hokuto HC1111), and the potential response was measured with the Memory Hicorder (Hioki 8835).

Isotopic exchange reaction was measured with the conventional closed circulating system, which was connected to the evacuation line. 7.4x10$^3$ Pa of commercial $^{18}$O$_2$ (95 at% pure) was mixed with 7.4x10$^3$ Pa $^{16}$O$_2$, and the gas composition was measured with a quadrupole mass filter. The diffusion coefficient and surface exchange reaction coefficient were measured after annealing a dense Ba$_{0.7}$La$_{0.3}$CoO$_3$ sample in 1.5x10$^4$ Pa $^{18}$O$_2$ at 1073 K for 30 minutes. After quenching the sample the fractured surface, which was polished with a diamond paste up to 0.25 µm, was analyzed with SIMS (Atomica 4100) with the Cs$^+$ primary ion source at the accelerated voltage of 10 kV.
RESULTS AND DISCUSSION

Effects of Humidification of Oxidant on the Power Generating Property of the SOFC Using LaGaO₃-Based Oxide Electrolyte

Figure 1 shows the power-generating property of the cell using dry and humidified oxygen at 1073 K. Almost the theoretical open circuit potential was exhibited on both cells. Therefore, it was obvious that the partial electronic hole conduction was not significant in La₀.₈Sr₀.₂Ga₀.₈Mg₀.₁₅Co₀.₀₅O₇ electrolyte under SOFC operating conditions. Because the thickness of the used electrolyte is half of that in the previous study, the maximum power density of the cell increased compared with the cell using 0.5-mm-thick electrolyte, and the achieved maximum power density of the cell was as high as 800 mW/cm² at 1073K when dry O₂ was used for an oxidant (3). On the other hand, it was seen that the power density of the cell increased by using humidified oxygen for the oxidant. The increase in power density at high current density is significant. Therefore, it can be said that the humidification of oxidant is effective for increasing the power density of the cell. Coexisting H₂O generally disturbs the diffusion of oxygen in a pore of cathode oxide. Thus, the phenomena causing positive effects of humidification, present significantly at higher current densities, are highly interesting because the diffusion limit becomes more dominant at higher current densities.

Detailed analysis of the internal resistance of the cell demonstrated that the improved power density by adding H₂O to the oxidant was mainly due to the decreased overpotential of cathode. The main internal resistance of the cell is electrical resistance, mainly due to the electrolyte, and the improvement in power density from decreasing the cathodic overpotential is not significant (Figure 1). However, the activity of BLC cathode for oxygen dissociation could increase by addition of H₂O to oxidant.

Figure 2 shows the overpotential of Ba₀.₆La₀.₄Co₀.₃ cathode as a function of current density. The overpotential of BLC cathode is initially small, even in the dry atmosphere; however, it is much smaller in wet oxygen at the examined current density. In addition, temperature dependence of the cathodic overpotential is almost negligible in a wet atmosphere. Therefore, the coexisting water is highly effective for decreasing the cathodic overpotential. These results are in good agreement with those reported by Sakai et al. on a YSZ cell (5). According to Sakai et al. (5), one reason for decreasing cathodic overpotential is the improved conductivity at the boundary between the electrolyte and electrode. However, another chemical modification effect on the surface reaction seems to exist because the temperature dependence of the cathodic overpotential became very small. More detailed analyses of the improved activity of BLC cathode by H₂O addition are needed.

Apparent activation energy for cathodic reaction was estimated by the Arrhenius plots of the current density at the cathodic overpotential of 5 mV in dry and wet O₂ atmospheres (Figure 3). In the dry atmosphere, apparent activation energy for the cathodic reaction on BLC is estimated to be ~0.45 eV. However, in the wet atmosphere, though the same BLC was used for the cathode, temperature dependence of the cathodic polarization became small, as discussed, and the apparent activation energy was as little as 0.03 eV, which is an order of magnitude less than that in the dry atmosphere. Therefore, it is obvious that the cathodic reaction can be improved by coexisting water.
Figure 4 is an impedance plane plot of the BLC cathode at open circuit condition in dry and wet oxygen. It can be seen that the electrical resistance at the x-axis intercept at the higher frequency decreased in wet oxygen. Sakai et al. reported that the electrical resistance at the interface between electrode and electrolyte decreased under coexisting humidity, as discussed (5). In this study, a decrease in the interface resistance was also observed. The semicircle that appeared in the complex impedance plots consisted of several semicircles. Therefore, there are several reaction steps, at least two containing the cathodic reaction. It is clear that the semicircle appeared in the high-frequency region, which could be due to the surface reaction decreasing by the coexistence of water. Therefore, we considered that the coexisting water on the cathodic side plays a catalytic role to accelerate the dissociation of oxygen molecule into oxide ion. In any case, it is obvious that the humidification of oxidant is effective for improving cathodic electrode activity. However, it is also anticipated that the long-term stability of the cell decreased by using the humidified oxygen for oxidant.

Terminal potential of the cell at 0.4 A/cm² constant current using 2.8 vol% H₂O containing oxygen for oxidant is shown in Figure 5 as a function of time. It can be seen that the terminal potential decreased slightly with time. The decrease in terminal voltage within the first 20 hours is rather fast; however, after 20 hours the power density of the cell becomes stable up to 42 hours of testing.

Figure 6 shows the time dependence of the internal resistance of the cell shown in Figure 5. The potential drop by the electrical resistance, IR, gradually increased, in particular, IR loss at anodic side. However, it is seen that the overpotential of anode and cathode is stable over the examined 40 hours. Therefore, the decrease in power density of the cell shown in Figure 5 could be assigned to the increased IR loss, and it seems that the chemical stability of the BLC cathode is high enough in the humidified oxygen. This is also confirmed by XRD measurement after the stability test because no diffraction peaks from secondary phase were observed. Because the IR loss at the anodic side increased, the chemical stability of Ni-SDC cermet is not high enough; and it is thought that the aggregation of Ni occurs during the long-term stability measurement. We believe that the sintering and aggregation of Ni particle mainly occur in the initial period. The larger decrease in the potential in the first 20 hours is also in good agreement with the expected Ni aggregation performance. Because it is well known that the thermal stability of Ni is not high, improvement of the stability of Ni-SDC anode by optimizing the amount of SDC and the precalcination temperature will improve the long-term stability of the cell using LaGaO₃-based oxide. In any case, BLC cathode seems to be stable under the wet oxygen atmosphere because no significant increase in cathodic overpotential was observed and there was no change in XRD peaks after the term stability measurement was demonstrated. Therefore, it can be said that the addition of water to oxidant is effective for decreasing the overpotential of cathodes over a long period.

**Isotopic Oxygen Exchange and Diffusion Under the Coexistence of H₂O**

In order to study the mechanism for the positive effects of water on the surface reaction on BLC cathode, the isotopic exchange reaction of ¹⁶O₂-¹⁸O₂ was performed on BLC under the coexistence of H₂¹⁶O. Figure 7 shows the time dependence of the relative concentration of oxygen tracer in the gas phase when the gas mixture of ¹⁸O₂-¹⁶O₂-H₂¹⁶O was used for the reactant. Because ¹⁶O¹⁶O was exchanged with ¹⁸O¹⁸O, the concentration
of $^{16}$O$^{18}$O increased with the reaction time and attained a saturation concentration about 90 minutes after the exchange reaction started. Therefore, it is seen that the dissociative adsorption and surface recombination of oxygen occurs on BLC at 623K. On the other hand, a mass signal of 20, namely H$_2^{18}$O, also increased with the reaction time, though the signal was weak. This suggests that the dissociative adsorption of water also occurs on BLC oxide, and the exchange reaction between oxygen in water may be OH and the surface oxygen. Because the signal of the mass number 20 rapidly increased after the exchange reaction began, it seems that the exchange reaction between oxygen in water and the surface oxygen from O$_2$ is very fast.

It is known that the isotopic exchange reaction of oxygen molecule obeys the first-order reaction kinetics. The first-order reaction plots of the formation of $^{16}$O$^{18}$O and H$_2^{18}$O are shown in Figure 8. A good straight relationship is exhibited in the figure, suggesting that the isotopic exchange reaction between $^{18}$O$_2$-$^{16}$O$_2$ on BLC oxide under coexistence of H$_2$O was also well fit to first-order reaction kinetics. In Figure 8, the same plots of $^{18}$O$^{16}$O formation in the isotopic exchange reaction without H$_2$O coexistence was also superimposed for the comparison. It is seen that the isotopic exchange rate constant decreased six times by addition of water. Therefore, coexisting water greatly disturbs the simple surface exchange reaction between oxygen molecules. This is reasonably explained by the competitive adsorption of water and oxygen on the surface adsorption site of BLC. Because water is generally strongly adsorbed on the metal oxide, it seems likely that the simple surface exchange reaction of oxygen drastically decreased by coexistence of H$_2$O. In contrast, formation of H$_2^{18}$O is very fast, as shown in the figure. The estimated exchange constant of H$_2^{18}$O is almost the same as the oxygen exchange reaction constant without H$_2$O coexistence. Therefore, it became clear that the exchange rate of oxygen in water molecule with the surface oxygen is quite fast and that under humidified atmosphere the oxygen molecule may dissociate and diffuse into the bulk of BLC cathode or LSGMC electrolyte through oxygen in water or OH.

Tracer diffusion of $^{18}$O into the dense BLC sample was investigated. Because the Ba$_{0.3}$La$_{0.4}$CoO$_3$ disk with the relative density higher than 90% cannot be obtained, a tracer diffusion experiment was performed using Ba$_{0.7}$La$_{0.3}$CoO$_3$, which is an active composition for cathode similar to that of Ba$_{0.6}$La$_{0.4}$CoO$_3$ (3). It is also noted that the estimated relative density of Ba$_{0.7}$La$_{0.3}$CoO$_3$ is higher than 0.95. Table 1 summarizes the diffusion coefficient (D) and the surface exchange coefficient (k) at 1073K in Ba$_{0.7}$La$_{0.3}$CoO$_3$. It is seen that the D value is independent of the coexistence of oxygen. According to the theory, D value is dependent on the amount of oxygen vacancy and the mobility, so it is clear that the coexisting H$_2$O shows no influence on the concentration of the vacancy concentration in the bulk of BLC. On the other hand, k value increased by an order of magnitude when water coexisted. This is in good agreement with the results suggested by impedance measurements. Consequently, addition of a small amount of water to oxidant is effective for improving the surface activity of cathode oxide resulting in the decreasing the overpotential of cathode. This effect is appeared significant at intermediate temperatures. Therefore, coexisting water plays a catalytic role for the oxygen dissociation reaction, and it seems likely that the activation energy for cathodic reaction decreased drastically under the coexistence of water.
CONCLUSIONS

Although the effects of coexistence of water on the cathodic reaction have not been studied in detail, this study reveals that the surface oxygen dissociation reaction on cathode oxide could be greatly accelerated by the addition of water to oxidant. Consequently, the overpotential of Ba$_{0.5}$La$_{0.4}$Co$_3$O$_7$ decreased greatly, and the power density of the cell increased by addition of H$_2$O to oxygen. Humidification of oxidant can be easily done by recycling the exhaust gas. Addition of water to oxidant is also effective for removing the excess heat from the cell. In addition, stability of Ba$_{0.5}$La$_{0.4}$Co$_3$O$_7$ seems to be reasonably high in the humidified atmosphere. Therefore, addition of small amount of water to the oxidant is desirable for increasing the power density of the cell.

ACKNOWLEDGMENT

The authors acknowledge the financial support from Grant-in-Aid for Science Promotion (No. 11102006) from Ministry of Education, Culture, Sports, Science, and Technology.

REFERENCES

1. B. C. H. Steele, *Solid State Ionics*, 134, 3 (2000).
2. T. Ishihara, H. Matsuda, Y. Takita, *J. Am. Chem. Soc.*, 116, 3801 (1994).
3. T. Ishihara, T. Shibayama, M. Honda, H. Nishiguchi, and Y. Takita, *Chem. Comm.*, 1227 (1999).
4. T. Ishihara, S. Fukui, H. Nishiguchi, and Y. Takita, *J. Electrochem. Soc.*, 149, A828 (2002).
5. N. Sakai, K. Yamaji, H. Negishi, T. Horita, H. Yokokawa, Y. Xiong, M. B. Phillipps, *Electrochemistry*, 68, 499 (2000).
6. I. Akikusa, K. Adachi, K. Hoshino, T. Ishihara, Y. Takita, *J. Electrochem. Soc.*, 148, A1275 (2001).

| Table 1. Effects of Water on Self-Diffusion Constant and Surface Exchange Coefficient of Ba$_{0.5}$La$_{0.4}$Co$_3$O$_7$ at 700°C |
|---------------------------------------------------------------|
| **Self-Diffusion Coefficient** | **Surface Exchange Coefficient** |
| D(cm$^2$/s) | k/cm/s |
| Dry $^{18}$O$_2$ | $2.23\times10^{-7}$ | $3.90\times10^{-7}$ |
| $H_2^{18}$O+$^{18}$O$_2$ | $3.20\times10^{-7}$ | $3.82\times10^{-6}$ |
Effects of water in cathodic site on the power generating property. Wet O₂ means 2.8 vol% H₂O containing O₂.

Cathodic overpotential of Ba₀₅La₀₆CoO₃ in a dry and wet atmosphere as a function of operating temperature.
Figure 3. Arrhenius plots of the current density at the cathodic overpotential of 5 mV in dry and 2.8 vol% H₂O added O₂.

Figure 4. Impedance plane plot of the BLC cathode at open circuit condition in dry and wet oxygen.
Figure 5. Stability of power-generating characteristics of SOFC using wet O₂ for oxidant.

Figure 6. Time dependence of the internal resistance under the wet oxygen used for oxidant.
Figure 7. Time dependence of the relative concentration of oxygen tracer in the gas phase when the gas mixture of $^{18}$O$_2$-$^{16}$O$_2$-H$_2^{16}$O was used for the reactant.

Figure 8. First order reaction plots of the formation of $^{16}$O$^{18}$O and H$_2^{18}$O in $^{18}$O$_2$-$^{16}$O$_2$ under co-existing H$_2^{16}$O at 623 K.