

# Effects of Water on The Cathodic Performance of $\text{Ba}_{0.6}\text{La}_{0.4}\text{CoO}_3$ on The Cell Using $\text{LaGaO}_3$ Based Oxide for Electrolyte

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Development of the intermediate temperature solid oxide fuel cell is an important subject. In order to achieve a high power density at intermediate temperature, development of an electrolyte with low electrical resistance and an active electrode is essentially requested. In our previous study, it was found the  $\text{LaGaO}_3$  based oxide exhibits a high oxide ion conductivity and the high power density can be achieved by using  $\text{LaGaO}_3$  based oxide for electrolyte. On the other hand, it was also found that the overpotential of cathode can be sustained to a small value even at 873 K by using  $\text{Ba}_{0.6}\text{La}_{0.4}\text{CoO}_3$  (BLC). Recently, Sakai et al. reported that the surface reaction can be accelerated by addition of water(1). In this study, effects of water on the cathodic performance of BLC under operating condition of SOFC were investigated.

Preparation of  $\text{Ba}_{0.6}\text{La}_{0.4}\text{CoO}_3$  cathode and  $\text{LaGaO}_3$  based oxide was performed by using the conventional solid state reaction. For the preparation of  $\text{LaGaO}_3$  based oxide, commercial oxide of  $\text{La}_2\text{O}_3$ ,  $\text{Ga}_2\text{O}_3$ ,  $\text{SrCO}_3$ ,  $\text{MgO}$  and  $\text{CoO}$  was mixed in ball mill mixer. The composition of  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.15}\text{Co}_{0.05}\text{O}_3$  (LSGMC) was always used in this study. The thickness of the electrolyte was always set to 0.3 mm. The prepared cathode and commercial  $\text{NiO}$  were painted on each surface of the LSGMC disk with screen-printing method. Power generating property of the cell was measured with four-probe method and 3 vol% humidified  $\text{H}_2$  and  $\text{O}_2$  were fed to the anode and cathode side respectively. The overpotential of anode and cathode was estimated by using the complex impedance method and the current interruption method.

Figure 1 shows the power generating property of the cell using dry and humidified oxygen at 1073 K. It was seen that the power density of the cell increased by addition of humidity to oxygen. In particular, increase in the power density at high current density is significant. Detail analysis of the internal resistance of the cell demonstrated that the improved power density by addition of  $\text{H}_2\text{O}$  to the oxidant was assigned to the decreased overpotential of cathode. Since the main internal resistance of the present cell is the electrical resistance which is mainly assigned to that of electrolyte, improvement in power density is not significant. However, it is obvious that the activity of BLC cathode for oxygen dissociation could increase by addition of  $\text{H}_2\text{O}$  to oxidant. This is in good agreement with that reported by Sakai et al. on YSZ cell. Detail analysis of the improved activity of BLC cathode by  $\text{H}_2\text{O}$  addition was further studied.

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  $\text{O}_2$ . In dry atmosphere, apparent activation energy for the cathodic reaction on BLC is estimated to be ca. 0.45 eV. However, in wet atmosphere, although the same BLC was

used for cathode, temperature dependence of the cathodic polarization becomes small and the apparent activation energy is as small as 0.03eV, which is smaller than that in dry atmosphere by an order of magnitude. Therefore, it is seen that the cathodic activity can be improved by coexistence of water. Impedance analysis suggested that the cathodic reaction contains at least two slow steps and the semicircle appeared at high frequency region, which could be assigned to the surface reaction, mainly decreased by coexisting of water. Therefore, it is considered that the coexisting water in the cathodic side plays a catalytic like work to accelerate the dissociation of oxygen molecule into oxide ion.

In order to confirm the positive effects of water on the dissociation reaction of oxygen on BLC cathode, tracer diffusion of  $^{18}\text{O}$  into the dense BLC sample was investigated. Table 1 shows the diffusion coefficient (D) and the surface exchange coefficient (k) at 1073 K in BLC. It is seen that the D value is independent of the coexisting oxygen. Therefore, in agreement with the theory, D value is only dependent on the amount of oxygen vacancy and the mobility, and it is clear that the coexisting  $\text{H}_2\text{O}$  shows no influence on the concentration of the vacancy concentration in BLC. On the other hand, k value increased drastically when water was coexisted. This is in good agreement with that by impedance results. Consequently, addition of small amount of water to oxidant is effective for improving the surface activity of cathode oxide for oxygen dissociation resulting in the decreasing the overpotential of cathode.

## References

- 1) N. Sakai, K. Yamaji, H. Negishi, T. Horita, H. Yokokawa, Y. Xiong, M. B. Phillips, *Electrochemistry*, 68, 499 (2000).

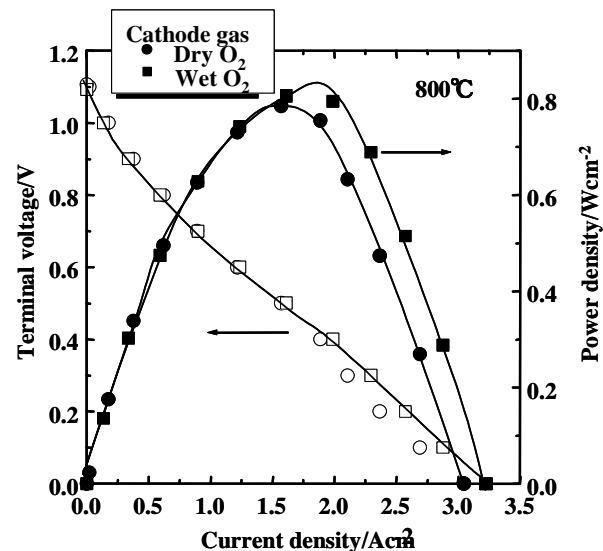


Fig.1 Effects of water in cathodic site on the power generating property.

Table 1 Effects of water on self diffusion constant (D) and surface exchange coefficient (k) of  $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{CoO}_3$  at 973K.

	Self diffusion coefficient D /cm <sup>2</sup> /s	Surface exchange coefficient k /cm/s
Dry $^{18}\text{O}_2$	$2.23 \times 10^{-7}$	$3.90 \times 10^{-7}$
$\text{H}_2^{18}\text{O} + ^{18}\text{O}_2$	$3.20 \times 10^{-7}$	$3.82 \times 10^{-6}$