ABSTRACT

In order to overcome the problems of SOFC anode such as carbon deposition and microstructural change by oxidation, it is desired to develop a reliable substitute for nickel/yttria stabilized zirconia cermet. Several kinds of oxide materials were tested as fuel electrode by means of impedance spectroscopy and steady state polarization measurements. These measurements confirmed that anode performance of Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ and Ce$_{0.992}$Nb$_{0.008}$O$_2$ was good in humid hydrogen atmosphere. On the other hand, La$_{0.9}$Ca$_{0.1}$Cr$_{1-x}$Al$_x$O$_3$ (x=0.2, 0.8), SrZr$_{0.825}$Y$_{0.1}$Ru$_{0.075}$O$_3$ showed much poorer performance. The reaction kinetics of doped ceria was also investigated and it was revealed that doped ceria has almost the same dependence on gaseous partial pressure and temperature. A possible kinetic equation is proposed, though unclear points still remain.

INTRODUCTION

The advantages of solid oxide fuel cells (SOFC) are high energy conversion efficiency and internal reforming due to a high operating temperature. However, the most familiar anode, Ni/YSZ cermet, has problems such as deterioration by carbon deposition in hydrocarbon atmosphere and microstructural change caused by nickel oxidation under startup/shutdown operation. To widen application field of SOFCs, more reliable anode should be developed. One of the possible solutions is using oxide materials for anode. It has been reported that several oxide anodes have a tolerance against carbon deposition (1, 2). There are a few studies on high performance oxide anode. Tao et al. reported that (La, Sr)(Cr, Mn)O$_3$ system had a high anode performance in both wet hydrogen and wet methane atmospheres (3). Van herle et al. reported that the performance of Nb doped ceria was good in methane (4). It has been reported that the anode of gadolinium doped ceria had high performance (5). Some researchers also tested other oxide materials (6-9).

The reaction mechanism of oxide anodes is, however, still unclear. In this paper, the anode performance of several oxide materials was investigated with variation in gas partial pressure and temperature to elucidate the oxide anode reaction mechanism.
EXPERIMENTAL

Sample Preparation

Sample powders were synthesized as follows: Lao.9Ca0.1Cr1-xAlxO3 (x=0.2, 0.8: LCCA9182, LCCA9128) were made by a citric acid method. Starting materials such as La(NO3)3·6H2O, Ca(NO3)2·4H2O, Cr(NO3)3·9H2O and Al(NO3)3·9H2O were dissolved into water, respectively. The concentration of each solution was determined by chelatometric titration. Then, these solutions were mixed together in proper ratios of the metal ions. An excess amount of citric acid was added to the mixed solutions. The precursors were obtained by heating the solution to remove water and nitric oxides. They were fired in air at 1173 K.

SrZro.825Yo.1Ru0.075O3 (SZYR) was prepared by a conventional ceramic method. Starting materials were SrCO3, ZrO2, Y2O3 and RuO2. These materials were precisely weighed and thoroughly ball-milled with ethanol. The mixed powder was fired at 1673 K for 10 h.

Ce0.9Gdo.1O1.95 (GDC) and Ce0.992Nb0.008O2 (NbDC) were synthesized by a co-precipitation method. Cerium oxide and gadolinium oxide were precisely weighed and dissolved into nitric acid; while niobium pentachloride was dissolved into hydrochloric acid. These solutions were mixed in proper metal ratios. Then, the mixed solution was introduced into oxalic acid solution by micro drop to obtain a fine precipitate. The precipitate was calcined at 1273 K for 2 h. X-ray diffraction confirmed that all of the resultant powders were single phase.

Electrochemical Measurements

As an electrolyte, 8 mol% yttria stabilized zirconia was pressed into a pellet and sintered at 1673 K for 3 h. The dimensions of the pellet were φ15 mm × t 2 mm. Each oxide powder was screen-printed on the dense 8YSZ pellet as a working electrode (WE) of 6 mm in diameter and fired at 1573 K for 3 h. Platinum paste was used as counter (CE) and reference electrodes (RE). The configuration of a test cell is depicted in Fig. 1. A gold mesh was chosen as a current corrector of WE. To check the catalytic activity of gold mesh, Au mesh/porous 8YSZ/dense 8YSZ cell was fabricated as a reference.
Electrochemical measurements were conducted via a three terminal method by potentiostat/galvanostat (Toho Technical Research, 2000) and frequency response analyzer (NF Corp., 5080). The anode performance was tested by d.c. steady state polarization method and impedance spectroscopy in humid hydrogen atmosphere at high temperatures. The partial pressure of hydrogen and temperature were controlled in the ranges of 0.01 to 1 bar and 973 to 1173 K, respectively. IR compensation of steady state polarization measurement was done by estimated ohmic resistance from equivalent circuit fitting of impedance spectra.

RESULTS AND DISCUSSION

Anode Performance of Various Oxides and Catalytic Activity of Gold Current Collector

Figure 2 shows performance of the oxide anodes in 97.7% H₂-2.3% H₂O at 1173 K. At first, to check the catalytic activity of gold mesh, let us compare the results. The impedance spectra of LCCA9128, LCCA9182 and SZYR were much higher than the porous YSZ reference cell. This means that gold current collector has a higher catalytic activity than LCCA9128, LCCA9182 and SZYR under humid hydrogen atmosphere, though it has been generally considered that gold is inactive material against oxidation of hydrogen. The same tendency was also observed in the steady state polarization results. One should be careful to evaluate anode performance precisely by use of gold current collector.

On the other hand, NbDC and GDC showed higher performance than the reference cell. It means that these are the materials worth measuring the performance in detail.

Figure 2. The performance of oxide anodes in 97.7% H₂-2.3% H₂O at 1173 K: (a) impedance spectra under open circuit condition and (b) steady state polarization results.

On the other hand, NbDC and GDC showed higher performance than the reference cell. It means that these are the materials worth measuring the performance in detail.
Therefore, the dependence of anode performance on gaseous partial pressure and temperature was investigated to elucidate the reaction mechanism. The results are shown in the next section.

**Dependence of the Anode Performance on Time, Gas Partial Pressure and Temperature**

I-V curves of doped ceria gradually improved until I-V relations became almost linear (Fig. 3). This is an interesting phenomenon, though the reason is still unclear. The data for the following analyses were obtained after the performance became stable.

![Figure 3. Time dependence of anode performances of GDC and NbDC.](image)

![Figure 4. Steady state polarization results of GDC and NbDC under various hydrogen partial pressures at 1173 K.](image)
Figure 5. Steady state polarization results of GDC and NbDC under various hydrogen partial pressures at 1073 K.

Figure 6. Steady state polarization results of GDC and NbDC under various hydrogen partial pressures at 973 K.

The dependence of the performance on hydrogen partial pressure and temperature was measured (Figs. 4, 5, 6). Here, electromotive force, $E$, can be interpreted as oxygen activity, $a_0$, at electrolyte/working electrode interface by the following equation:

$$ a_0 = P(O_2)^{1/2} \exp \left( \frac{2FE}{RT} \right) $$

[1]
where $P(O_2)$ is oxygen partial pressure of gaseous phase; $F$ is Faraday constant; $R$ is the gas constant; $T$ is temperature of the sample. The calculated oxygen activity is displayed on the top axis of the figures. While absolute value of current was different between NbDC and GDC, the slopes of cathodic and anodic currents against the interface oxygen activity were almost the same. The possible relationship between current density and interface oxygen activity is the following:

$$I_{\text{anodic}} \propto a_0^{0.25}$$

$$I_{\text{cathodic}} \propto a_0^{-0.5}$$

The current density at the constant EMF was estimated by means of Lagrange's interpolation technique. The estimated values were plotted against hydrogen partial pressure (Fig. 7). Consequently, the relationship between hydrogen partial pressure and current was also derived:

$$I_{\text{anodic}} \propto P(H_2)^{0.5}$$

$$I_{\text{cathodic}} \propto P(H_2)^{0}.$$  

Considering that the reaction order of both anodic and cathodic directions should be equal, one possible candidate for the overall kinetic equation is deduced as follows,

$$I_{\text{overall}} = k P(H_2)^{0.5} - k P(H_2O)^{0.5} a_0^{-1/2}.$$  

However, as temperature becomes higher, the value estimated by Eq. 6 remarkably deviated from the experimental data. It is likely that several elementary reactions are superimposed and the rate limiting process changes with change in temperature.

Figure 7. Dependence of anodic and cathodic currents on hydrogen partial pressure at constant electromotive force: (a) GDC, (b) NbDC.

The current density at the constant EMF was estimated by means of Lagrange's interpolation technique. The estimated values were plotted against hydrogen partial pressure (Fig. 7). Consequently, the relationship between hydrogen partial pressure and current was also derived:

$$I_{\text{anodic}} \propto P(H_2)^0$$

$$I_{\text{cathodic}} \propto P(H_2)^0.$$  

Considering that the reaction order of both anodic and cathodic directions should be equal, one possible candidate for the overall kinetic equation is deduced as follows,

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However, as temperature becomes higher, the value estimated by Eq. 6 remarkably deviated from the experimental data. It is likely that several elementary reactions are superimposed and the rate limiting process changes with change in temperature.
CONCLUSIONS

Several kinds of oxide materials were tested as fuel electrode of SOFC by means of impedance spectroscopy and steady state polarization measurement. The anode performance of Ce0.9Gd0.1O1.95 and Ce0.992Nb0.008O2 was good in humid hydrogen atmosphere. On the other hand, La0.9Ca1-xAlxO3 (x=0.2, 0.8), Zr0.825Y0.1Ru0.075O3 showed much poorer performance. The reaction kinetics of doped ceria was also investigated. Possible kinetic equation is proposed.

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