Fabrication of Electrode-Supported Type Electrochemical Cell for NO_x Decomposition

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NO_x 分解用電極支持型電気化学セルの作製

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Bi-layers consisting of porous La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF) substrate and dense film of Ce_{0.9}Gd_{0.1}O_{1.95} (CGO) have been successfully fabricated using slurry-coating process. A CGO powder dispersed in acetone was deposited onto a pre-sintered LSCF (containing 50 mass% CGO) substrate, and then co-fired such that the thin electrolyte was fully densified and the substrate remains highly porous. Co-fired CGO film was well bonded to the substrate; crack- and pinhole-free, and exhibited very low ohmic resistance. The NO decomposition properties of electrode-supported type electrochemical cell, LSCF (substrate)|CGO (film)|LSCF (screen-printed) were investigated. A strong correlation between the structure of the working electrode and the NO decomposition characteristics were observed. By using electrode-supported thin electrolyte, the required electric power for NO decomposition could be remarkably reduced.

[Received February 8, 2002; Accepted March 25, 2002]

Key-words : NO decomposition, Electrode-supported, Thin-film electrolyte, CGO, LSCF

1. Introduction

The emission of NO_x from diesel and lean-burn engines, i.e. in the presence of excess oxygen, causes serious pollution problems such as acid rain and photochemical smog. Huggins et al.¹⁾ have proposed the electrochemical reduction of NO by using solid oxide electrolyte cells, yttria-stabilized zirconia (YSZ) coated with Pt electrodes. By applying DC potential to the cell, NO can be decomposed to nitrogen and oxygen ions on the cathode, and the oxygen ions can be pumped through the solid electrolyte to the anode.

Unfortunately, in the presence of oxygen, a high current density is required because coexisting oxygen is adsorbed by the cathode more preferably. As a result, the NO decomposition cell needs a high electric power. In the practical point of view, it is necessary that the electric power should be reduced. Additionally, in order to operate the electrochemical cell without an external heating, the working temperature of the electrochemical cell should also be lowered to 673–873 K, which is considered to be typical outlet temperatures of the car exhaust gas. However, electrolyte conductivity and electrode kinetics drop significantly with lowering the operating temperature.

Recently, many attempts to enhance a current efficiency for NO decomposition were performed by coating different metals or oxides onto the cathode for obtaining high NO selectivity.^{2)–6)} The electrochemical cell with the catalytic electrodes have shown better NO decomposition characteristics than with the conventional noble metal electrode such as Pt. Another way to reduce the electric power is to prepare the electrochemical cell with low resistance. Ohmic loss across the electrolyte can be minimized by the use of higher conductivity materials and/or the use of thin-film electrolyte. The electrode kinetics can be improved by increasing the electronic/ionic and catalytic properties of cathode and anode.

Sm₂O₃, or Gd₂O₃ doped CeO₂ electrolytes show higher ionic conductivity than conventional YSZ electrolyte, being expected to be a candidate as an alternative electrolyte

material for intermediate temperature solid oxide fuel cell (SOFC) and oxygen pump. In this study, we have focused on the application of thin-film electrolyte to the electrochemical cell in order to reduce the ohmic resistance. To deposit the electrolyte thin-film, various thin-film processes have been studied such as electrochemical vapor deposition,⁷⁾ sputtering,⁸⁾ physical vapor deposition,⁹⁾ electrophoretic deposition,¹⁰⁾ and slurry-coating¹¹⁾ by the various groups in SOFC community. We applied the slurry-coating process followed by co-firing because they are cost-effective and scalable. The electrode-supported type electrochemical cell, which consisted of CGO film as an electrolyte and LSCF electrode as a substrate was prepared. It is well known that La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF) is one of the most suitable electrode materials for intermediate temperature due to its high mixed (electronic and ionic) conductivity and excellent thermal and chemical compatibility to the Gd₂O₃-doped CeO₂ (CGO) electrolyte. This is the first report of the fabrication of CGO film on LSCF substrate by slurry-coating and its application to the electrochemical cell for NO decomposition. Microstructure of the prepared electrode-supported electrochemical cell and its NO decomposition characteristics were investigated.

2. Experimental

The mixture containing 40 mass% Ce_{0.9}Gd_{0.1}O_{1.95} (CGO, Anan Kasei), 40 mass% La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF, prepared in house by citric-acid process) and 20 wt% pore former (corn starch) was ball-milled in ethanol for 12 h. The mixture was then pressed into pellet, and then partially fired at 1173 K for 5 h in order to give a sufficient handling strength to the substrate. CGO slurry was prepared by dispersing CGO powder in acetone with 2 mass% Hypermer KD1 (ICI Chemicals, UK) as a dispersant. CGO electrolyte film was slurry-coated on the pre-fired substrate by repeating the dipping and drying three times. As-coated substrate (after drying) was subsequently co-fired at 1573 K for 2 h. After co-firing, the one side of CGO film was removed by

Fig. 1. Schematic configurations of electrochemical cell; (a) electrode-supported cell type-I and type-II, and (b) self-supported cell for NO decomposition.

lapping. The total thickness of the obtained bi-layer, CGO (film)|LSCF-CGO (substrate) was adjusted to about 1000 μm after lapping.

LSCF powder with 50 mass% CGO powder was mixed with organic vehicle (TMC-25TA, Tanaka Precious Metals, Jpappn) to prepare the electrode paste for screen-printing. An electrode-supported type electrochemical cell, LSCF-CGO (screen-printed)|CGO (film)|LSCF-CGO (substrate) has been completed by screen-printing the electrode paste on the surface of the CGO film. The paste was screen-printed onto CGO surface (1 cm^2), and it was then fired at 1273 K for 1 h. The thickness of the screen-printed electrode was approximately 10 μm after sintering. A self-supported type electrochemical cell, LSCF-CGO (screen-printed)|CGO (disk)|LSCF-CGO (screen-printed) was also prepared using a commercial 500 μm thick CGO disk ($\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$, Japan Fine Ceramics Co., Ltd.).

The schematic configurations of electrochemical cells and electrochemical test set-up for NO decomposition are represented in Fig. 1 and Fig. 2, respectively. The current collector was Pt mesh fixed to the electrode surfaces. Pt wires were connected to Pt mesh. A four-probe set-up was used to eliminate the ohmic losses in the lead wires. The electrochemical cell was mounted inside a quartz tube through which a mixture of 1000 ppm of NO and 2% of O₂ in He was passed at a flow rate of 50 ml/min. The tube was placed in a furnace and brought to the testing temperatures. AC impedance spectroscopy measurements (ac amplitude: 50 mV, frequency: 1 MHz–0.05 Hz) were carried out using Solartron 1260 FRA. NO decomposition characteristics were evaluated by applying a constant current (Galvanostatic) using Solartron 1287 Electrochemical Interface. The concentrations of NO_x and N₂ in the outlet gas were monitored using an on-line NO gas analyzer (Best instruments BCL-100 μH , BCU-1000 μH) and gas chromatography (Chrompack, Micro-GC CP 2002), respectively.

The conversion of NO were calculated as NO conversion (%) = $([\text{NO}]_\text{in} - [\text{NO}]_\text{out}) / [\text{NO}]_\text{in} \times 100$.

3. Result and discussion

Figure 3 shows the cross-section and as-fired surface of the co-fired bi-layer, CGO (film)|LSCF-CGO (substrate). It can be seen that the incorporation of a corn-starch as a pore-forming agent into the substrate made it possible to maintain sufficient porosity after co-firing. CGO films co-fired at 1573 K was sufficiently dense, crack- and pinhole-free with a thickness of 30 μm . No electronic leakages was observed, after screen-printing LSCF-CGO electrode onto CGO film as a counter electrode. It means that the slurry-coating process has produced a sufficiently dense electrolyte on porous LSCF-CGO substrate.

Figure 4 shows the Cole-Cole plots of AC impedance spectra of the electrode-supported type cell and self-supported type cell. The ohmic resistance (a low intercept of the real axis of the Cole-Cole plot) of the electrode-supported type cell was much lower than that of the self-supported type cell. The ohmic resistances of the electrode-supported cell and self-supported cell in the temperature range of 773–1073 K are summarized in Table 1. It was found that reducing the electrolyte thickness from the 500 μm to 30 μm could significantly lower the ohmic resistance of the electrochemical cell.

However, the electrode polarization (a difference between the high and low intercept of the real axis of the Cole-Cole plot) of the electrode-supported type cell was higher than that of the self-supported type cell. Generally, the electrochemical activity of the electrode is proportional to the amount of triple-phase-boundary. Figure 5 shows microstructure of LSCF-CGO electrode of the electrode-supported type cell co-fired with CGO film at 1573 K and

Fig. 2. Schematic image of experimental set-up for NO decomposition and electrochemical characterization.

Fig. 3. Scanning electron micrographs of (a) cross-section, CGO (film) | LSCF-CGO (substrate) and (b) as-sintered surface of CGO film, co-fired at 1573 K for 2 h.

self-supported cell sintered at 1273 K. Comparing the Figs. 5 (a) with (b), the microstructure of LSCF-CGO electrode in electrode-supported cell was coarser than that in self-supported cell because of the high sintering temperature of the electrode-supported type cell (1573 K). As a consequence, the amount of triple-phase-boundary, gas (pore) | CGO (electrolyte) | LSCF-CGO (electrode) of the electrode-supported type cell was much smaller than that of the self-supported type cell. This explains well the higher electrode polarization of the electrode-supported type cell. Nevertheless, the total resistance (the high intercept of the real axis) of the electrode-supported cell, i.e., sum of the ohmic and electrode polarization resistance was still lower than that of the self-supported type cell.

The terminal voltage change of the three different types of electrochemical cell was demonstrated in Fig. 6. (a) as a function of current. As can be expected from the highest total resistance of the AC impedance spectra, the self-supported type cell showed highest terminal voltage at a given

current, and terminal voltage of the electrode-supported cell type-I was much smaller than type II. The ohmic-free voltages of the cells, which were calculated on the basis of the ohmic resistance data from the AC impedance spectra, were represented in Fig. 6. (b) The ohmic-free voltage results from the electrode polarization resistance of the electrochemical cell. The electrode-supported cell type-I and the self-supported type cell showed little difference in the ohmic-free voltage. It means that the lowest terminal voltage of the electrode-supported cell type-I in Fig. 6. (a) was mainly due to its lowest ohmic resistance. On the contrary, electrode-supported cell type-II exhibited the highest ohmic-free voltage among the three different types of electrochemical cells, indicating that the co-fired LSCF-CGO substrate was poor cathode for oxygen pumping. In the electrode-supported cell type-I, the same LSCF-CGO substrate was used as an anode and the screen-printed LSCF-CGO layer was used as a cathode. The type-I cell showed much lower ohmic-free voltage than type-II, suggesting that

Fig. 4. Impedance spectra of the electrochemical cells at 873 K. Atmosphere: 1000 ppm of NO and 2% of O₂ in He at a gas flow rate of 50 ml/min, electrode area: 1 cm².

the electrode polarization of the co-fired LSCF-CGO substrate as an anode is much smaller than as a cathode.

As current flows, NO can be decomposed to nitrogen and oxygen ions on the cathode, and the oxygen ions can be pumped through the solid electrolyte to the anode. Hibino et

al.¹²⁾ reported that NO start to decompose after pumping out oxygen around the triple-phase-boundary below a certain level, and that the cathode having poor oxygen pumping properties, i.e., having the lower affinity against oxygen, easily came to such condition. This explains well the differences in NO decomposition behaviors as a function of current between the electrode-supported cell type-I and type-II demonstrated in Fig. 7. The current is proportion to the amount of oxygen which is pumped from the cathode side to the anode side. NO decomposition does not occur until reaching a certain current level, and the onset current of the electrode-supported cell type-II, which has less active cathode for oxygen pumping, is much lower than that of the electrode-supported cell type-I.

In case of a thicker and less porous cathode such as co-fired LSCF-CGO substrate, the supply of oxygen from the electrode surface to the electrochemical reaction site came to insufficient with increasing the oxygen-pumping rate, i.e., the concentration polarization easily occur. As a result, oxygen partial pressure around the triple phase boundary dropped down to such a level as the NO can be electrolyzed to nitrogen gas and oxygen ion, at a given current. However, the NO decomposition of the electrode-supported cell type-II cannot exceed over 50%. This phenomenon is considered that the supply of NO gas was also limited with increasing the oxygen-pumping rate. On the contrary, in case of the electrode-supported cell type-I, which used 10 μm thick screen-printed LSCF-CGO as a cathode, such a situation is relatively hard to occur because the supply of both oxygen and NO gases is sufficiently rapid. Therefore, onset current of the electrode-supported cell type-I is much higher than that of the type-II, and the maximum NO decomposition of the thin-film cell type-I has been readily reached to over 70%.

Table 1. Summary of the Ohmic Resistances of Electrochemical Cells Measured by AC Impedance Spectroscopy. Atmosphere: 1000 ppm of NO and 2% of O₂ in He at a Gas flow Rate of 50 ml/min, Working Electrode Area: 1 cm²

Temperature K	Electrode-Supported (30-μm)	Self-Supported (500-μm)
773 K	0.50 Ω	
873 K	0.25 Ω	2.34 Ω
973 K	0.18 Ω	1.05 Ω
1073 K	0.16 Ω	0.61 Ω

Fig. 5. Scanning electron micrographs of the cross sections of the LSCF|CGO interface.

(a) Bi-layer, LSCF-CGO (substrate) | CGO (film) co-fired at 1573 K for 2 h. (electrode-supported)

(b) Screen-printed LSCF-CGO electrode (left side) on commercial CGO disk (right side) sintered at 1273 K for 1 h. (self-supported)

Fig. 6. Current-voltage characteristics of the electrochemical cells at 873 K.

Atmosphere: 1000 ppm of NO and 2% of O_2 in He at a gas flow rate of 50 ml/min, working electrode area: 1 cm^2

(a) Dependence of terminal voltage (V_{terminal}) on the value of the current passing through the cell. (b) Dependence of $V_{\text{terminal}} - V_{\text{ohmic}}$ on the value of the current passing through the cell.

Fig. 7. Dependence of NO conversion on the value of the current passing through the thin-film electrochemical cells at 873 K. Reacting gas: 1000 ppm of NO and 2% of O_2 in He at a gas flow rate of 50 ml/min, working electrode area: 1 cm^2 .

Fig. 8. Dependence of NO conversion on the value of the required electric power at different types of electrochemical cells prepared in this study. Reacting gas: 1000 ppm of NO and 2% of O_2 in He at a gas flow rate of 50 ml/min, working electrode area: 1 cm^2 .

Figure 8 demonstrates the electric power required for NO decomposition at 873 K. It is clearly observed that the electrode-supported cells prepared in the present study could remarkably reduce the required electric power for NO decomposition. The structure of the cathode strongly influenced the NO decomposition behaviors of the electrode-supported type electrochemical cells for NO decomposition.

4. Conclusion

In order to put an electrochemical NO decomposition into

practice, it is necessary to reduce the consuming of electric power and lower working temperature. Lowering the resistance of by using thin-film electrolyte is a straightforward way to reduce a required electric power for NO decomposition. Electrode-supported NO decomposition cell prepared in this study exhibited high NO decomposition rate at relatively low electric power, comparing with the conventional self-supported electrochemical cell. The correlation between the structure of the electrode and the NO decompo-

sition characteristics suggests that further improvement of the electrode-supported type cell will be realized through the microstructure control of the cathode and the substrate.

Acknowledgments This work has been supported by AIST, METI, Japan, as part of the Synergy Ceramics Project. Part of the work has been supported by NEDO. The authors are members of the Joint Research Consortium of Synergy Ceramics.

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