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Preparation of $LaCoO_3$ catalytic thin film by the sol–gel process and its NO decomposition characteristics

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Abstract

$LaCoO_3$ and $LaMnO_3$ gel films were deposited by dip-coating technique on yttria-stabilized zirconia (YSZ) substrate using the precursor solution prepared from $La(O\text{-}i\text{-}C_3H_7)_3$, $Co(CH_3COO)_2$ or $Mn(O\text{-}i\text{-}C_3H_7)_2$, 2-methoxyethanol, and polyethylene glycol. By heat-treating the gel films, electrochemical cells, $LaCoO_3|YSZ|LaCoO_3$ were fabricated. The effect of polyethylene glycol on the microstructure evolution of $LaCoO_3$ and $LaMnO_3$ thin films was investigated, and NO decomposition characteristics of $LaCoO_3$ powders and the electrochemical cells were investigated at 600–800°C. In the absence of oxygen, the $LaCoO_3$ powder was active both in decomposition of NO and reduction of NO by C_2H_4. It was found that they lost their catalytic activity in the presence of 2% oxygen. By applying a direct current to $LaCoO_3|YSZ|LaCoO_3$ electrochemical cell, a good NO conversion rate could be obtained at relatively low current value even if excess oxygen is included in the reaction gas mixture. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Chemical properties; Microstructure-final; Oxide superconductors; Perovskite; Sol–gel process

1. Introduction

NO_x emissions from diesel engines and a lean-burn condition of gasoline engines, i.e. in the presence of excess oxygen, are serious problems since NO_x compounds cause both acid rain and photochemical smog. Catalytic systems in which the pollutants including NO_x can be eliminated are required. Unfortunately, the catalytic systems used at present cannot sufficiently control the above pollutants. Only metal ion-exchanged zeolite-based catalysts are shown to be active for the selective reduction of NO_x by hydrocarbons.[1,2] However, since the zeolite-based catalysts exhibit a volcano-type dependence of the activity on temperatures, the catalytic activity decreases with temperature and it often limits their applications.

A different approach for NO_x decomposition has been proposed by Huggins et al.[3] The electrocatalytic cell consists of porous electrodes and a solid electrolyte. NO_x was decomposed to N_2 and O_2 at the cathode, for which noble metals are generally used, and O_2 can be pumped through the electrolyte to the anode by applying an electrical field. This electrocatalytic cell can be used even in the presence of excess oxygen. Recently, Hibino et al. have designed a single-compartment reactor, which is constructed from CeO_2 electrolyte with two palladium electrodes, and demonstrated its effectiveness on not only NO decomposition, but also CH_4 oxidation in the presence of excess oxygen, H_2O and CO_2.[4] However, the noble metal-based electrodes are too expensive, and the catalytic activity decreases at high temperature because of the grain growth as well as the poor adsorption against NO.

In this study, we developed a new-type of electrochemical cell, which consists of YSZ and perovskite-type oxide electrodes, $LaCoO_3$ or $LaMnO_3$. Perovskite-type oxides exhibit high electrocatalytic activity at higher temperatures than 500°C and are expected as a high temperature-type catalyst material for NO_x decomposition.[5] The thin films were deposited on YSZ substrate by dip-coating technique using alkoxide solutions. Microstructure evolution and NO decomposition characteristics of $LaCoO_3$ powders and $LaCoO_3|YSZ|LaCoO_3$ electrochemical cells were investigated.

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2. Experimental procedure

First, La(O-i-C_3H_7)$_3$ (Kojundokagaku Laboratory, Japan) was dissolved with 2-methoxyethanol (Wako Chemical Co. Ltd., Japan). A clear solution can be obtained by stirring the solution at room temperature for 30 min. $Co(CH_3COO)_2$ (Kishida Chemical Co. Ltd., Japan) or Mn(O-i-C_3H_7)$_2$ (Kojundokagaku Laboratory, Japan) was put into the La solution. By heating the solution at 60°C, clear solutions resulted. Then, 2-ethylacetoacetate ($CH_3COCH_2COOC_2H_5$) was added to La–Co or La–Mn solutions. La–Co or La–Mn precursor solutions were refluxed at 130°C for 2 h in a dried nitrogen gas atmosphere. After cooling the solution, H_2O, which was diluted with 2-methoxyethanol, was added to the solutions for a partial hydrolysis and a polymerization. The molar ratio of H_2O to the alkoxide was 1. Then, 15 wt.% of polyethylene glycol (MW = 2000) was added to the precursor solutions to modify the network structure of the solution and finally control the microstructure of thin films. The precursor solutions were further stirred at room temperature for 2 h.

$LaCoO_3$ or $LaMnO_3$ gel films were deposited by dip-coating technique on YSZ substrate. The withdrawn speed of the YSZ substrate from the solution was 1.5 mm/s. After the coating process, gelation occurred when the substrate was dried at 150°C for 10 min. Dried gel films were heat-treated at 600 and 800°C for 10 min in air. The coating and heat-treatment processes were repeated 10 times. Microstructures of thin films were observed by scanning electron microscope (SEM, JSM-6320FK, Jeol Co. Ltd., Japan)

NO decomposition characteristics were carried out at atmospheric pressure in a quartz microreactor. The typical gas mixture of 0.1% NO and 2% O_2 in He was passed through the microreactor containing 100 mg of the $LaCoO_3$ dried gel powder at a flow rate of 50 ml/min. A period of 30 min was allowed at each operating temperature (400 to 800°C) before any gas sample was taken. In the case of $LaCoO_3$|YSZ|$LaCoO_3$ electrochemical cell, it was connected with a galvanostat by Pt wires, and the direct voltage in the range between 0 and 4 V was applied to the cell for 15 min at 600, 700 and 800°C. The reactor effluent was analyzed with a gas chromatograph (GC, Chrompack CP-2002) and a chemiluminescent NO–NO_x gas analyzer (BSU — 100uH, Best Instrument).

3. Results and discussion

Microstructures of $LaMnO_3$ and $LaCoO_3$ thin films prepared from the precursor solution without and with polyethylene glycol heat-treated at 600°C are shown in Fig. 1. As is evident in Fig. 1 (a), a dense and inhomogeneous microstructure is observed in $LaMnO_3$ thin film without polyethylene glycol; large grains above 100 nm in size are observed, indicating that the abrupt grain growth of $LaMnO_3$ starts at around 600°C. On the other hand, the microstructure of $LaMnO_3$ thin film with polyethylene glycol heat-treated at 600°C was not only homogeneous but also porous. Pores of approximately 100 nm in size were observed in $LaMnO_3$ thin film. It is assumed that the observed porous microstructure in Fig. 1 (b) is induced by polyethylene glycol in the precursor solution, which leaves the pores in the microstructure of $LaMnO_3$ thin film when it is decomposed. A similar microstructure was observed in sol–gel derived TiO_2 thin film prepared from the alkoxide precursor solution that is modified with polyethylene glycol.[6] They reported that the porous microstructure could be controlled by the amount of polyethylene glycol.

Comparing with $LaMnO_3$ thin films, $LaCoO_3$ thin films heat-treated at the same temperatures shows different microstructures, especially in $LaCoO_3$ thin film with polyethylene glycol. As is evident in Fig. 1 (c), a dense and homogeneous microstructure was observed in $LaCoO_3$ thin film heat-treated at 600°C prepared from the precursor solution without polyethylene glycol. $LaCoO_3$ thin film without polyethylene glycol consists of grains larger than 100 nm. On the other hands, the microstructure of $LaCoO_3$ thin film with polyethylene glycol was porous, and its grain size was significantly decreased. Similar with $LaMnO_3$ thin films, it seems that the observed porous and fine microstructure is induced by polyethylene glycol. It was also found that $LaCoO_3$ thin film with polyethylene glycol kept its porous microstructure, even though the heat-treatment temperature was raised to 800°C. Hence, it can be concluded that the modification of the precursor solution by polyethylene glycol enables us to control the microstructure of $LaMnO_3$ and $LaCoO_3$ thin films.

Fig. 2 shows NO conversion rate over $LaCoO_3$ powder as a function of temperature. In the absence of oxygen (open and closed circles in Fig. 2), direct NO decomposition starts at 400°C, whereas the temperature which NO decomposition starts, shifted to a lower temperature by adding C_2H_4 as a reducing agency, which suggests that the addition of hydrocarbon accelerates NO decomposition. NO conversion rate sharply increases in the temperature range between 400 and 500°C, and is saturated at above 600°C. Therefore, it is evident that the $LaCoO_3$ powder processes sufficient catalytic activity against NO not only in reduction of NO by C_2H_4, but also in direct NO decomposition. The maximum conversion rate in direct NO decomposition (about 100%) was similar to that in NO reduction by C_2H_4.

However, the situation is completely different in the presence of excess oxygen (2%). It appears that the catalytic activity against NO over the $LaCoO_3$ powder decreases remarkably because the activation sites, which are known to be oxygen vacancies in the perovskite crystal structure, may be preferentially covered by

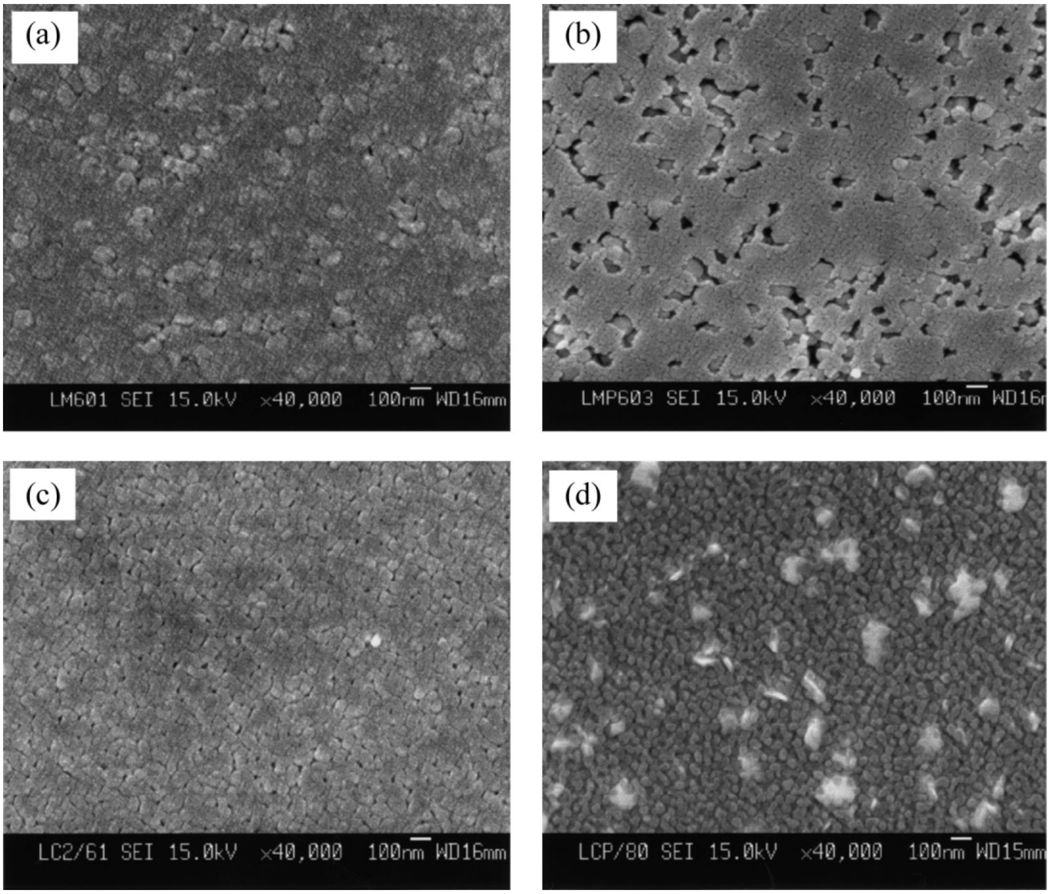

Fig. 1. Microstructure of $LaMnO_3$ thin film without polyethylene glycol (a), with polyethylene glycol (b), $LaCoO_3$ thin film without polyethylene glycol (c), and with polyethylene glycol (d) heat-treated at 600°C.

excess oxygen and, as a consequence, NO couldn't be adsorbed over $LaCoO_3$. NO conversion rate has been significantly reduced, and the maximum conversion rate is at most 10% at 800°C in reduction of NO by C_2H_4.

NO conversion rate (a) and current efficiency (b) of the proposed $LaCoO_3|YSZ|LaCoO_3$ electrochemical cell in the presence of 2% oxygen are shown in Fig. 3 as a function of temperature. As is evident in Fig. 3 (a), NO could be decomposed by applying a direct current to the electrochemical cell. Regardless of temperature, no NO decomposition occurs at low current. Thereafter, NO starts to decompose and NO conversion rate gradually increases as the current increases. These results mean that NO does not decompose until oxygen in the cathode ($LaCoO_3$ thin film) disappears. The current that is required to initiate NO decomposition depends on temperature, and it decreases from 80 mA at 800°C to 7 mA at 600°C. Therefore, it can be inferred that the selectivity against NO at 600°C is higher than at 800°C, and NO rather than oxygen can be preferentially adsorbed over $LaCoO_3$ thin film of the electrochemical cell.

Current efficiency is an important parameter to be considered when one constructs the electrochemical cell. The current efficiency is the ratio of the current consumed to decompose NO to N_2 to the overall current flowed through the electrochemical cell. The former can be theoretically calculated according to the Faraday's law. The current efficiency curve at 600°C against current

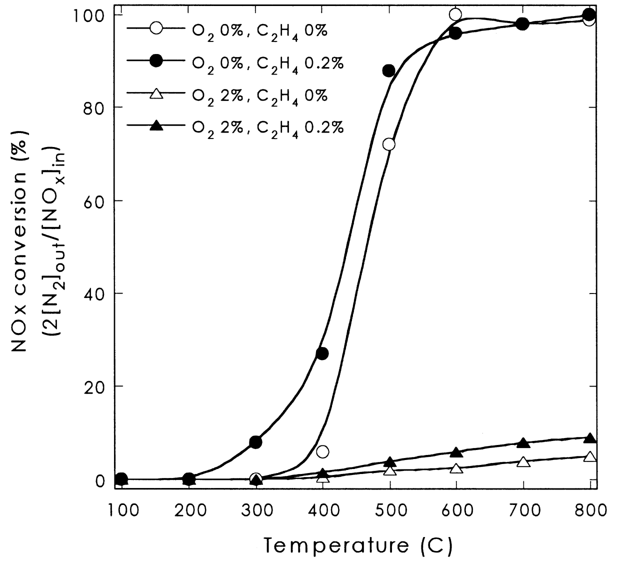

Fig. 2. NO conversion vs. temperature over $LaCoO_3$ powder prepared from the precursor solution with polyethylene glycol; NO 1000 ppm, balance He.

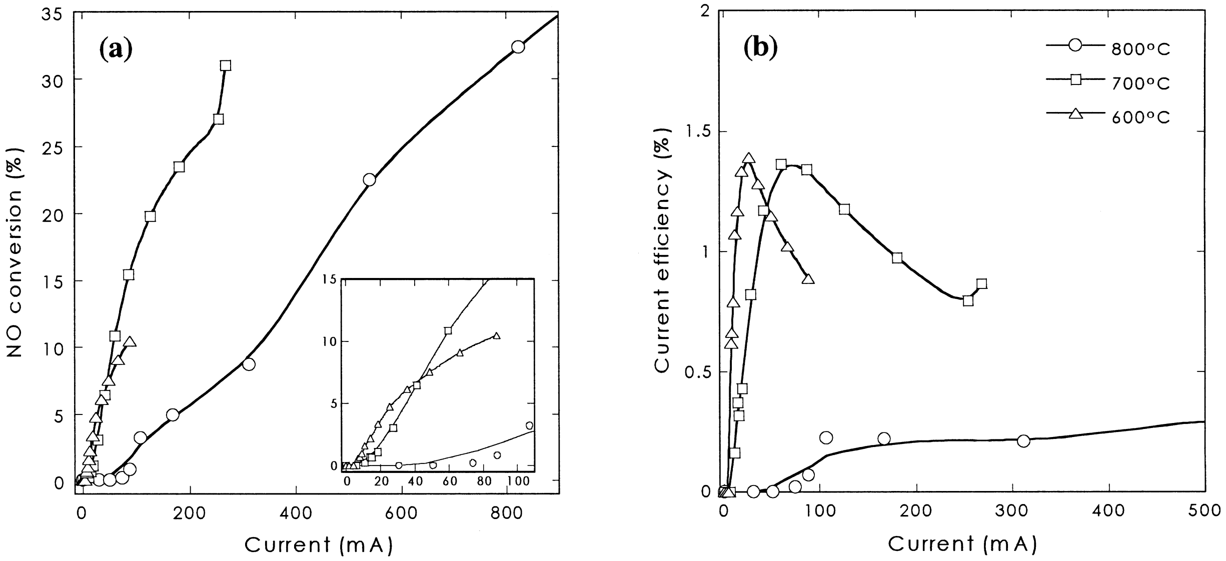

Fig. 3. NO conversion vs. current (a) and current efficiency (b) of $LaCoO_3|YSZ|LaCoO_3$ electrochemical cell; NO 1000 ppm, O_2 2%, balance He.

is almost the same as at 700°C. It sharply increases at the current that is lower than a few tens of mA, shows a maximum value, and decreases with the current. On the other hand, the current efficiency at 800°C is much lower than those at 600 and 700°C. This result might be associated with the selectivity against NO. It seems that both NO and oxygen adsorption behavior as a function of temperature change at around 700°C. The maximum current efficiency is approximately 1.5% at 600 and 700°C.

Fig. 4 shows NO conversion rate of the $LaCoO_3|YSZ|LaCoO_3$ electrochemical cell as a function of voltage. NO conversion rate is higher at 800°C than at 700 and 600°C, since the resistance of $LaCoO_3|YSZ|LaCoO_3$ electrochemical cell increases with decreasing temperature. This means that as the temperature decreases, much higher voltage should be required to obtain the same NO conversion rate. Maximum NO conversion rates at 800 and 600°C are 43 and 10%, respectively. The resistance of the $LaCoO_3|YSZ|LaCoO_3$ electrochemical cell depends on the conductivity of both the $LaCoO_3$ thin film and YSZ electrolyte. Since the conductivity of YSZ is much higher than that of $LaCoO_3$ thin film, low conversion rate at 700 and 600°C may be responsible for low conductivity of $LaCoO_3$ thin film.

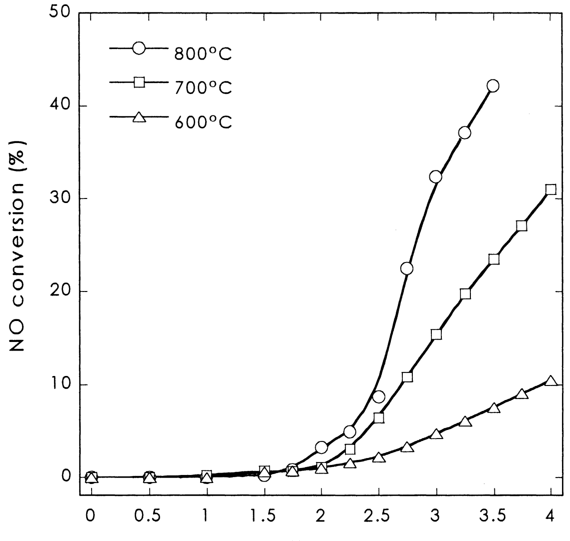

Fig. 4. NO conversion vs. voltage $LaCoO_3|YSZ|LaCoO_3$ electrochemical cell; NO 1000 ppm, O_2 2%, balance He.

4. Conclusions

$LaCoO_3$ and $LaMnO_3$ catalytic thin films with porous and homogeneous microstructures could be successfully prepared by the sol–gel route. An addition of polyethylene glycol played an important role in crystallization and microstructure evolution of the thin films. The proposed electrochemical cell, $LaCoO_3|YSZ|LaCoO_3$ could effectively decompose NO in the presence of 2% oxygen by applying a direct current to the cell. It was found that the selectivity against NO was better at low temperature (600°C), however, much higher voltage was needed to obtain sufficient NO conversion rate because of low conductivity of $LaCoO_3$ thin films. Applying high voltage to the cell for a long time would result in the deterioration of NO decomposition activity. Therefore, the overall resistance of the cell needs to be reduced.

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