

## Fabrication of (La, Sr)MO<sub>3</sub> (M = Mn or Co)/YSZ Nanocomposite Thin Film Electrodes for the Exhaust Gas Purification by a Chemically-Modified Sol-Gel Process

H. J. Hwang, J. W. Moon, M. Awano and K. Maeda\*

*Synergy Materials Research Center, National Institute of Advanced Industrial Science and Technology, Nagoya 463-8687, Japan*

*\*Synergy Ceramics Laboratory, Fine Ceramics Research Association, Nagoya 463-8687, Japan*

(Received August 9, 2001)

**Abstract** LaMnO<sub>3</sub>, (La, Sr)MnO<sub>3</sub>, and (La, Sr)MnO<sub>3</sub>/YSZ gel films were deposited by spin-coating technique on scandium-doped zirconia (YSZ) substrate using the precursor solution prepared from La(O-i-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>, Co(CH<sub>3</sub>COO)<sub>2</sub> or Mn(O-i-C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>, 2-methoxyethanol, and polyethylene glycol. By heat-treating the gel films, the electrochemical cells, (La, Sr)MnO<sub>3</sub>/ScSZ|Pt were fabricated. The effect of polyethylene glycol on the microstructure evolution of LaCoO<sub>3</sub> and LaMnO<sub>3</sub> thin films was investigated, and NO<sub>x</sub> decomposition characteristics of the electrochemical cells were investigated at 500°C to 600°C. By applying a direct current to the (La,Sr)MnO<sub>3</sub>/ScSZ|Pt electrochemical cell, good NO<sub>x</sub> conversion rate could be obtained relatively at low current value even if excess oxygen is included in the reaction gas mixture.

**Keywords :** Thin film electrode, (La, Sr)MnO based nanocomposite, Sol-gel process, NO<sub>x</sub> decomposition

### 1. Introduction

NO<sub>x</sub> emissions from diesel engines and a lean-burn condition of gasoline engines, i.e., in the presence of excess oxygen, are the serious problems since NO<sub>x</sub> compounds cause both acid rain and photochemical smog. Catalytic systems in which the pollutants including NO<sub>x</sub> can be eliminated are required. Unfortunately, the catalytic systems used in the 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<sub>x</sub> by hydrocarbons.<sup>1,2)</sup> However, since the zeolite-based catalysts exhibit a volcano-type dependence of the activity on temperatures, the catalytic activity decrease with temperature and it often limits their applications.

A different approach for NO<sub>x</sub> decomposition has been proposed by R. Huggins et al.<sup>3)</sup> The electrocatalytic cell consists of porous electrodes and a solid electrolyte. NO<sub>x</sub> was decomposed to N<sub>2</sub> and O<sub>2</sub> at the cathode, for which noble metals are generally used, and O<sub>2</sub> 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<sub>2</sub> electrolyte with two palladium electrodes, and demonstrated its effectiveness on not only NO decomposition, but also CH<sub>4</sub> oxidation in the presence of excess oxygen, H<sub>2</sub>O and CO<sub>2</sub>.<sup>4)</sup> 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 electrochemical cell, which consists of scandium-doped zirconia (ScSZ) and perovskite-type oxide catalyst electrodes, (La, Sr)MnO<sub>3</sub> or (La, Sr)CoO<sub>3</sub>. 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<sub>x</sub> decomposition.<sup>5)</sup> In particular, (La, Sr)MnO<sub>3</sub>/Y<sub>2</sub>O<sub>3</sub> (8%)-stabilized ZrO<sub>2</sub> nano composite electrodes were also prepared from (La, Sr)MnO<sub>3</sub> and YSZ precursor solutions. The thin films were deposited on ScSZ substrate by spin-coating technique using the alkoxide solutions. Microstructure evolution and NO<sub>x</sub> decomposition characteristics of (La, Sr)MnO<sub>3</sub> or (La, Sr)

$\text{MnO}_3/\text{YSZ}/\text{ScSZ}/\text{Pt}$  electrochemical cells were investigated.

## 2. Experimental Procedure

The procedure for preparing a chemically modified precursor solution and fabricating  $(\text{La, Sr})\text{MnO}_3$  and  $(\text{La, Sr})\text{MnO}_3/\text{YSZ}$  thin films are illustrated in Fig. 1. Firstly,  $\text{La}(\text{O-i-C}_3\text{H}_7)_3$  (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.  $\text{Co}(\text{CH}_3\text{COO})_2$  (Kishida Chemical Co. Ltd., Japan) or  $\text{Mn}(\text{O-i-C}_3\text{H}_7)_2$  (Kojundokagaku Laboratory, Japan) was put into the La solution. By heating the solution at  $60^\circ\text{C}$ , clear solutions resulted. Then, 2-ethylacetoacetate ( $\text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5$ ) was added to La-Co or La-Mn solutions. La-Co or La-Mn precursor solutions were refluxed at  $130^\circ\text{C}$  for 2 h in a dried nitrogen gas atmosphere. After cooling the solution,  $\text{H}_2\text{O}$ , which was diluted with 2-methoxyethanol, was added to the solutions for a partial hydrolysis and a polymerization. The molar ratio of  $\text{H}_2\text{O}$  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 solu-

tions were further stirred at room temperature for 2 h.

The precursor solution for  $(\text{ZrO}_2)_{0.92}(\text{Y}_2\text{O}_3)_{0.08}$  was prepared from  $\text{Zr}(\text{O-i-C}_3\text{H}_7)_4$ ,  $\text{Y}(\text{O-i-C}_3\text{H}_7)_3$ , and 2-methoxyethanol. The coating solution for the  $(\text{La, Sr})\text{MnO}_3/40 \text{ vol}\% \text{YSZ}$  nanocomposite electrode was obtained by mixing the above  $(\text{La, Sr})\text{MnO}_3$  and YSZ precursor solutions.  $(\text{La, Sr})\text{MnO}_3$  or  $(\text{La, Sr})\text{MnO}_3/\text{YSZ}$  gel films were deposited by spin-coating technique at a speed of 2000 rpm for 30 s, followed by drying at  $150^\circ\text{C}$  for 10 min on  $10\% \text{Sc}_2\text{O}_3\text{-}1\% \text{CeO}_2\text{-}89\% \text{ZrO}_2$  (ScSZ) substrate. The dried gelled film was heat-treated at a prescribed temperature ( $300^\circ$  to  $800^\circ\text{C}$ ) for 1 h in air. The above coating and heat-treatment process were repeated 10 times. Microstructures of thin films were observed by scanning electron microscope (SEM, JSM-6320FK, JEOL Co. Ltd., Japan).

Figure 2 shows the schematic figure of the typical electrochemical cell for  $\text{NO}_x$  decomposition used in this study, and characterization system.  $\text{NO}_x$  decomposition characteristics were carried out at atmospheric pressure in a quartz microreactor. The typical gas mixture of 0.1%  $\text{NO}$  and 2%  $\text{O}_2$  in He was passed through the microreactor at a flow rate of 50 ml/min. The  $(\text{La, Sr})\text{MnO}_3/\text{ScSZ}/\text{Pt}$  or  $(\text{La, Sr})\text{MnO}_3/\text{YSZ}/\text{ScSZ}/\text{Pt}$  electrochemical cell was connected with a galvanostat by Pt wires, and the direct voltage in the range between 0 to 4 V was applied to the cell for 20

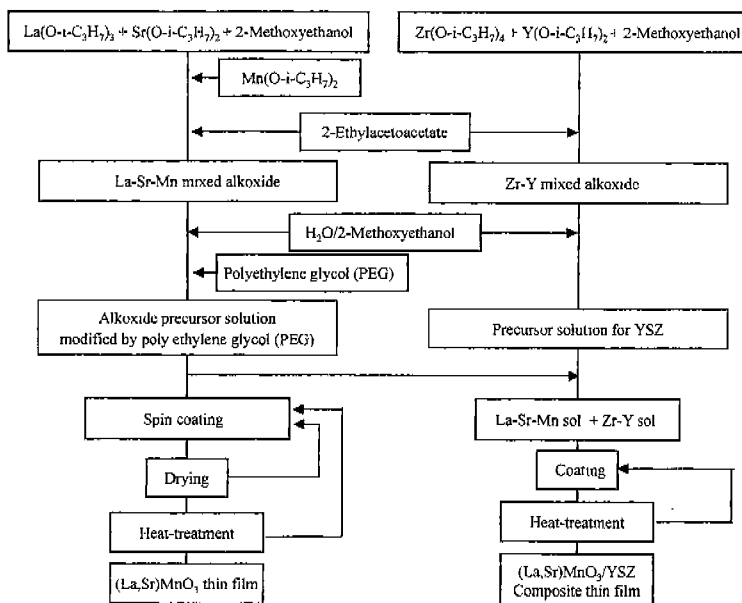


Fig. 1. The procedure for preparing a chemically modified precursor solution and fabricating  $(\text{La, Sr})\text{MnO}_3$  and  $(\text{La, Sr})\text{MnO}_3/\text{YSZ}$  thin films.

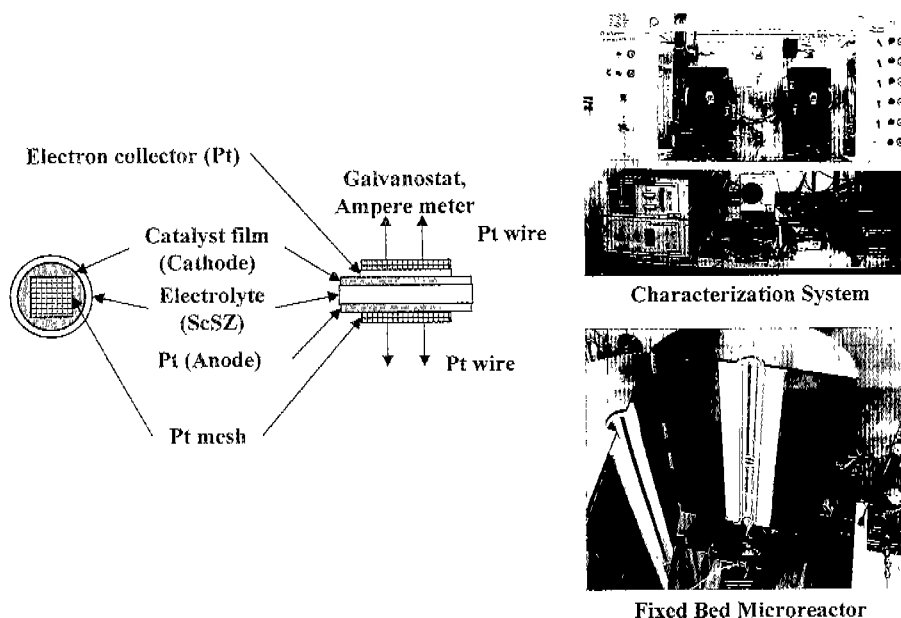


Fig. 2. Schematic figure of the typical electrochemical cell for NO<sub>x</sub> decomposition used in this study, and characterization system.

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<sub>x</sub> gas analyzer (BSU-100uH, Best Instrument).

### 3. Results and Discussion

#### 3.1. Microstructure of the thin films

Microstructures of LaMnO<sub>3</sub> and LaCoO<sub>3</sub> 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. 3(a), a dense and inhomogeneous microstructure is observed in LaMnO<sub>3</sub> thin film without polyethylene glycol; large grains above 100 nm in size are observed, indicating that the abrupt grain growth of LaMnO<sub>3</sub> starts at around 600°C. On the other hands, the microstructure of LaMnO<sub>3</sub> 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<sub>3</sub> thin film. It is assumed that the observed porous microstructure in Fig. 3(b) is induced by polyethylene glycol in the precursor solution, which leaves the pores in the microstructure of LaMnO<sub>3</sub> thin film when it is decomposed. Similar microstructure was observed in sol-gel derived TiO<sub>2</sub> thin film prepared from the alkoxide precursor solution that is modified

with polyethylene glycol.<sup>6)</sup> They reported that the porous microstructure could be controlled by the amount of polyethylene glycol.

Comparing with LaMnO<sub>3</sub> thin films, LaCoO<sub>3</sub> thin films heat-treated at the same temperatures shows different microstructures, especially in LaCoO<sub>3</sub> thin film with polyethylene glycol. As is evident in Fig. 3(c), a dense and homogeneous microstructure was observed in LaCoO<sub>3</sub> thin film heat-treated at 600°C prepared from the precursor solution without polyethylene glycol. LaCoO<sub>3</sub> thin film without polyethylene glycol consists of grains larger than 100 nm. On the other hands, the microstructure of LaCoO<sub>3</sub> thin film with polyethylene glycol was porous, and its grain size was significantly decreased. Similar to LaMnO<sub>3</sub> thin films, it seems that the observed porous and fine microstructure is induced by polyethylene glycol. It was also found that LaCoO<sub>3</sub> 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<sub>3</sub> and LaCoO<sub>3</sub> thin films.

Figure 4 shows the microstructure of La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3</sub> (a) and La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3</sub>/40 vol%YSZ nanocomposite (b) thin films, which were dried at 300°C and sub-

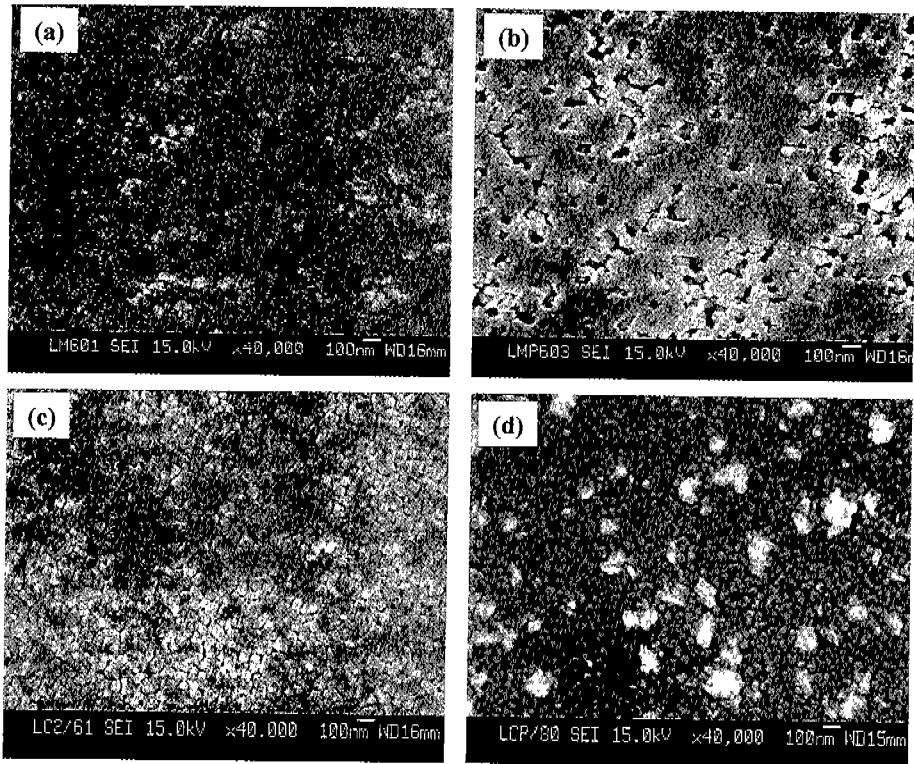


Fig. 3. Microstructure of  $\text{LaMnO}_3$  thin film without polyethylene glycol (a), with polyethylene glycol (b),  $\text{LaCoO}_3$  thin film without polyethylene glycol (c), and with polyethylene glycol (d) heat-treated at  $600^\circ\text{C}$ .

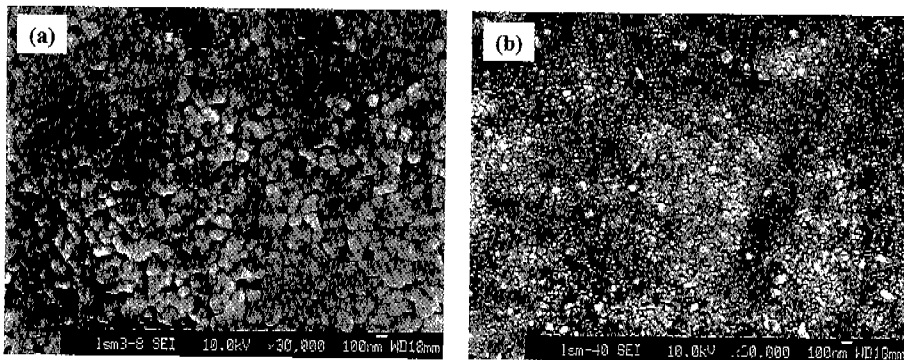


Fig. 4. Microstructure of  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  (a) and  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3/40 \text{ vol}\% \text{YSZ}$  nanocomposite (b) thin films, which were dried at  $300^\circ\text{C}$  and subsequently heat-treated at  $800^\circ\text{C}$ .

sequently heat-treated at  $800^\circ\text{C}$ . The coating process was repeated by 10 times. As is evident in Fig. 4(a), the  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  thin film consists of interconnected round particles with diameter of about 100 to 200 nm, showing a highly porous microstructure. Although the surface morphology of the  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3/40 \text{ vol}\%$

YSZ nanocomposite thin film is similar to that of the  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ , the grain size was significantly reduced and the porosity of the composite thin film was enhanced. Such a microstructure that is obtained in the composite thin film would increase the three-phase boundary of the thin film electrode, at which  $\text{O}_2$  can be

absorbed and ionized to diffuse as the form of O<sup>2-</sup> through the ScSZ electrolyte, and NO<sub>x</sub> is simultaneously reduced to N<sub>2</sub> and O<sub>2</sub>. Therefore, the La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3</sub>/40 vol%YSZ nanocomposite thin film electrode works well as a good cathode of the electrochemical cell for NO<sub>x</sub> decomposition and also for a solid oxide fuel cell (SOFC). Although not shown in the present paper, we can control the microstructure of the thin film electrode, such as grain size, morphology, and pore size by modifying the coating processes, for example, the concentration of the precursor solution, drying or heat-treating temperature, and so on.

### 3.2. NO<sub>x</sub> decomposition behavior

Figure 5 shows NO<sub>x</sub> conversion rate vs. applied current curves (a) and NO<sub>x</sub> conversion vs. applied power (b) at 500, 550, 600°C of La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3</sub> (cathode)|ScSZ|Pt (anode) electrochemical cell heat-treated at 800°C. For comparison, the NO<sub>x</sub> decomposition behavior of the electrochemical cell with Pt cathode, Pt|ScSZ|Pt, is also shown in Fig. 5. Because the area of the working electrode (cathode), i.e., La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3</sub> thin film is small (*ca.* 3 × 10<sup>-4</sup> m<sup>2</sup>) and the reactant gas mixture contains 2% oxygen, it was found that there is no NO<sub>x</sub> conversion when a direct current is zero (open circuit). By applying the direct current to the electrochemical cells, NO<sub>x</sub> started to decompose to N<sub>2</sub> and O<sub>2</sub> at the interface between

La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3</sub> thin film electrode and ScSZ electrolyte, i.e., three-phase boundary according to the reaction: 2NO → N<sub>2</sub> + O<sub>2</sub>. For instance, 70~80% NO<sub>x</sub> can be decomposed at the current smaller than 400 mA in the case of the electrochemical cell with La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3</sub> thin film electrode. In Fig. 5, NO<sub>x</sub> conversion curves show three different behaviors against the current, depending on operation temperatures and whether the working electrode is La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3</sub> thin film or Pt. When the electrochemical cells operate at higher temperature, for example, 600°C, no significant NO<sub>x</sub> decomposition happens at the lower current than *ca.* 100 mA and 300 mA for the La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3</sub> thin film electrode and Pt electrode, respectively. This phenomenon is mainly due to a poisoning of the electrode by oxygen.<sup>4,7</sup> Oxygen rather than NO<sub>x</sub> preferably adsorbs the active sites of the electrode. As a result, NO<sub>x</sub> decomposition does not happen until all of the adsorbed oxygen were electrolyzed and pumped through the ScSZ electrolyte to the Pt anode. As the current exceed the above values, NO<sub>x</sub> decomposition gradually appears, and it sharply increases with increasing the current. In addition, at > 300 mA and 500 mA for the La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3</sub> thin film electrode and Pt electrode, respectively, the increase of NO<sub>x</sub> decomposition as a function of the current is modest.

The activity for NO<sub>x</sub> decomposition was better in the electrochemical cell with La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3</sub> thin film

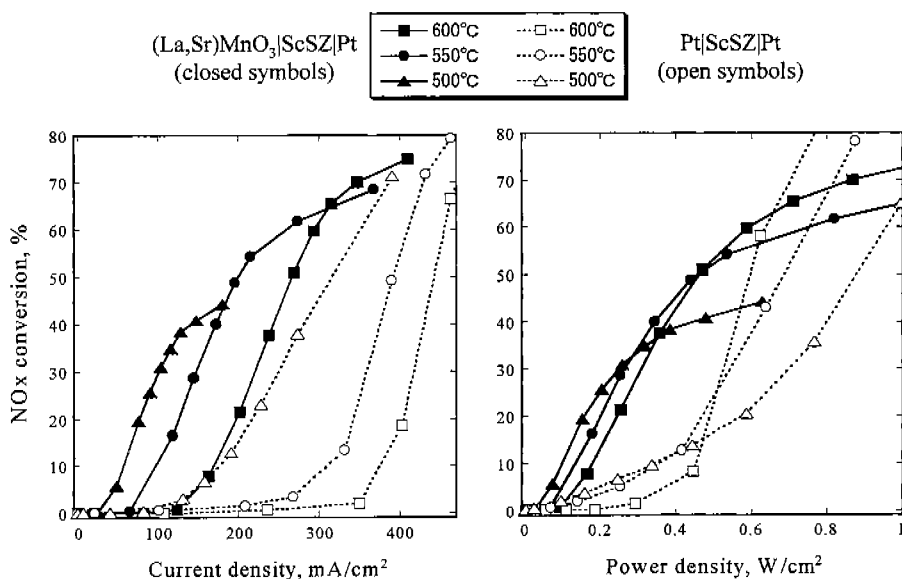


Fig. 5. NO<sub>x</sub> conversion rate vs. current (a) and power (b) of La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3</sub>|ScSZ|Pt electrochemical cell; NO 1000 ppm, O<sub>2</sub> 2%, balance He.

electrode than in Pt|ScSZ|Pt electrochemical cell for all the operating temperatures. At 600°C, the  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ |ScSZ|Pt electrochemical cell is able to decompose 50%  $\text{NO}_x$ , when the applied current exceeds 250 mA. Whereas, Pt|ScSZ|Pt cell can decompose  $\text{NO}_x$  less than 5% at the same current value. It seems that the good NO decomposition behavior observed in  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ |ScSZ|Pt cell can be explained by the porous microstructure with fine grain size and good catalytic activity against the  $\text{NO}_x$  decomposition of  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  thin film electrode. As described previously in Fig. 4, the  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  thin film showed porous microstructure with nano-sized grains.

Another important feature observed in Fig. 5 is that the current that is required to initiate  $\text{NO}_x$  decomposition shifted to lower current both in  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ |ScSZ|Pt and Pt|ScSZ|Pt cells. In the case of  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ |ScSZ|Pt cell, 120, 70 and 40 mA are required to initiate  $\text{NO}_x$  decomposition at 600, 550, and 500°C, respectively. This result means that  $\text{NO}_x$  selectivity of the  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  thin film relative to oxygen is much higher at lower operating temperature, in other words, the  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  thin film is more active for  $\text{NO}_x$  decomposition at low temperature than high temperature. Therefore, at low temperature  $\text{NO}_x$  was preferably adsorbed on the  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  thin film to easily decompose to  $\text{N}_2$ .

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  $\text{NO}_x$  to  $\text{N}_2$  to the overall current flowed through the electrochemical cell. Thus, the current efficiency of the electrochemical cell should be increased to reduce the power, which needs to operate the electrochemical cell. The former can be theoretically calculated according to the Faraday's law. The current efficiency value is about 1.5% for the  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ |ScSZ|Pt and 0.2% for the Pt|ScSZ|Pt cell. As is shown in Fig. 5(b), the power, which needs to apply to the electrochemical cell is even lower in the  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ |ScSZ|Pt cell than in the Pt|ScSZ|Pt cell.

#### 4. Conclusion

(La, Sr) $\text{MnO}_3$  catalytic thin films and (La, Sr) $\text{MnO}_3$ /

YSZ nanocomposite thin film electrode 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, (La, Sr) $\text{MnO}_3$ |ScSZ|Pt could effectively decompose  $\text{NO}_x$  in the presence of 2% oxygen by applying a direct current to the cell. It was found that the selectivity against  $\text{NO}_x$  was better at low temperature (500°C), however, much higher voltage was needed to obtain sufficient  $\text{NO}_x$  conversion rate because of low conductivity of the thin film electrode. Applying high voltage to the cell for a long time would result in the deterioration of  $\text{NO}_x$  decomposition activity. Therefore, the overall resistance of the cell needs to be reduced.

**Acknowledgement.** 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.

*This paper is dedicated to Professor Dr.  
Koichi Niihara on the occasion of  
his 60<sup>th</sup> birthday*

#### References

1. M. Iwamoto and H. Hamada: *Catal. Today*, **10** (1991) 57.
2. Y. Li and J. N. Armor: *Appl. Catal.*, **B2** (1993) 239.
3. S. Pancharatnam, R. A. Huggins and D. M. Mason: *J. Electrochem. Soc.*, **122** (1975) 869.
4. T. Hibino, K. Ushiki, Y. Kuwahara and M. Mizuno: *J. Chem. Soc., Faraday Trans.*, **92** (1996) 4297.
5. L. G. Tejuka, J. G. Pierro and J. M. D. Tascon: *Adv. Catal.*, **36** (1989) 237.
6. K. Kato, A. Tsuzuki, Y. Torii, H. Taoda, T. Kato and Y. Butsuman: *J. Mat. Sci.*, **30** (1995) 837.
7. A. Mirnazmi, J. E. Benson and M. Boudart: *J. Catal.*, **30** (1973) 55.