



High Selective deNO_x Electrochemical Cell with Self-Assembled Electro-Catalytic Electrode

TAKUYA HIRAMATSU,¹ SERGEI I. BREDIKHIN,¹ SHINGO KATAYAMA¹, OSAMU SHIONO,¹
KOICHI HAMAMOTO,² YOSHINOBU FUJISHIRO² & MASANOBU AWANO²

¹*Synergy Ceramics Laboratory, FCRA, Moriyama-ku, Nagoya 463-8687, Japan*

²*Synergy Materials Research Center, AIST Moriyama-ku, Nagoya 463-8687, Japan*

Submitted March 3, 2003; Revised March 22, 2004; Accepted March 22, 2004

Abstract. A new family of electrochemical cells for decomposition of NO gas in the presence of excess O₂, in which the cathode was covered with mixed oxide layer of NiO and YSZ (electro-catalytic electrode) were designed and investigated. The deNO_x properties were increased by microstructural and compositional control of the electro-catalytic electrode. Nano-size Ni grains were self-assembled at NiO/YSZ interfaces by oxidation-reduction reaction of the NiO during the cell operation. In order to use the reduced Ni for NO decomposition reaction effectively, the authors investigated multilayering of the electro-catalytic electrode. Through this process, the adsorption of coexisting O₂ was prevented and the deNO_x properties of the electrochemical cell were improved.

Keywords: electrochemical cell, NO decomposition, NiO-YSZ ceramics, NiO/YSZ interface, self-assembly

1. Introduction

Interest in lean-burn and diesel engines has spread from a viewpoint of the improvement in mileage-efficiency. However, since O₂ and NO_x coexist, the exhaust gases cannot be purified by the conventional three-way catalyst. The selective decomposition of NO_x from exhaust gases with coexisting O₂ becomes an important subject. Electrochemical cells have attracted attention as a new type of reactor that can permeate only a specific ion by applying a direct voltage to the cell. Recently, the electrochemical decomposition of NO_x using an electrochemical cell composed of a solid electrolyte and metal electrodes has been proposed [1, 2]. In these electrochemical cells, high current density is required for NO_x decomposition in the presence of excess O₂, which is adsorbed to the cathode in preference to NO_x. Furthermore, although low frequency AC electrolysis showed NO_x decomposition, a high applied voltage greater than 4 V was required [3, 4].

In our previous works, we designed and investigated a new family of electrochemical cells, in which the

cathode was covered with a mixed oxide layer of NiO and YSZ as shown below [5–9].

(Electro-catalytic electrode (NiO + YSZ)) | Cathode
(Pt + YSZ) | Electrolyte (YSZ) | Anode (Pt + YSZ)

A three-dimensional, nano-porous structure and network of electron and oxygen ion pathways are formed in the electro-catalytic electrode. The electro-catalytic electrode blocks direct penetration of gas molecules to the surface of the electrolyte and the NO and O₂ molecules are adsorbed and decomposed at different sites. Moreover, a strong correlation between NO decomposition properties and the microstructure and composition of the electro-catalytic electrode was observed, and the maximum efficiency of NO decomposition could be acquired when the ambipolar conductivity of the electro-catalytic electrode shows a maximum value [9].

In the present work, we have investigated the nano-size Ni grains that are self-assembled at NiO/YSZ interfaces by oxidation-reduction reaction of the NiO during the cell operation. We have proposed equations

for the NO decomposition in consideration of the oxidation-reduction reaction of the NiO. In order to use reduced Ni for NO decomposition reaction effectively, we have investigated multilayering of the electro-catalytic electrode.

2. Experimental

The arrangement of the electrochemical cell is illustrated schematically in Fig. 1. A YSZ disc with a thickness of 500 μm and diameter of 20 mm was used as the solid electrolyte. The Pt-YSZ paste was screen-printed with an area of 1.77 cm^2 on one surface of the YSZ disc as the cathode and calcined at 1200°C for an hour. The NiO-YSZ paste was screen-printed with an area of 2 cm^2 over the cathode and sintered at 1500°C for 4 hours. The Pt-YSZ paste was then screen-printed with an area of 1.77 cm^2 on the other surface of the YSZ disc as the anode and calcined at 1200°C for an hour. Pt mesh and wire were attached to the cathode and the anode, for connection to the power supply unit.

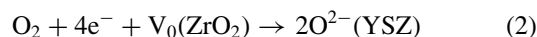
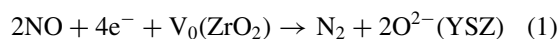
The electrochemical cell was set in a quartz reactor and connected to a potentiostat-galvanostat (SI1267/1255B, Solartron). The applied voltage and current dependence of NO decomposition behavior was investigated. The voltage was increased from 0 to 2.25 V in 0.25 V intervals. The electrochemical decomposition of NO was carried out at 600°C by passing a mixed gas of 1000 ppm NO ($[\text{NO}]_{\text{in}}$) and 3% O_2 in He through the cell at gas flow rate of 50 ml/min. The concentration of NO ($[\text{NO}]_{\text{out}}$) in the outlet gas from the reactor was monitored by a NO_x gas analyzer (BCL-100uH/BSU-

100uH, Best Instruments Co., Ltd.). The decomposition of NO (ΔNO), based on these measurements, was calculated as $\Delta\text{NO} = ([\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}})/[\text{NO}]_{\text{in}}$.

The microstructural features of the cell were observed by using a scanning electron microscope (SEM) (model JSM-6330F/JED-2140) and transmission and high-resolution electron microscopes (TEM) (models JEOL4000FX and JEOL2010F). The phases of the electrode were identified by X-ray diffraction (XRD) analysis using $\text{CuK}\alpha$ radiation (Rigaku RINT 2000).

3. Results and Discussion

NO decomposition reaction in the presence of excess oxygen using the electrochemical cell is shown in the following equations:



In the conventional electrochemical cell, since Eqs. (1) and (2) occur simultaneously, high current density is required for NO reduction in the presence of excess oxygen. The electrochemical cell for NO decomposition in which the cathode is covered with mixed oxide layer of NiO and YSZ has been proposed in our previous works [5–9]. Through our experiment, a change of the electro-catalytic electrode was observed during cell operation. The electro-catalytic electrode before cell operation showed a green color due to the NiO. Following cell operation in the voltage range 0–2.25 V for a total of 22 hours at a temperature of 600°C, the color of the electro-catalytic electrode changed from green to black.

The structure of the electro-catalytic electrode was studied by X-ray diffraction from the electro-catalytic electrode side. The X-ray diffraction patterns of the electro-catalytic electrode both before and after cell operation for 22 hours at a temperature of 600°C in the voltage range 0–2.25 V are shown in Fig. 2. The X-ray diffraction pattern of the cell before operation contains the reflections of YSZ, NiO and Pt, which are used for fabrication of the cell. In the X-ray diffraction pattern of the electro-catalytic electrode after cell operation, some new very weak reflections have been observed besides the reflections recognized in the cell before operation. These reflections belong to the FCC structure of Ni. Therefore, pure Ni was also present in the structure of the electro-catalytic electrode after cell operation.

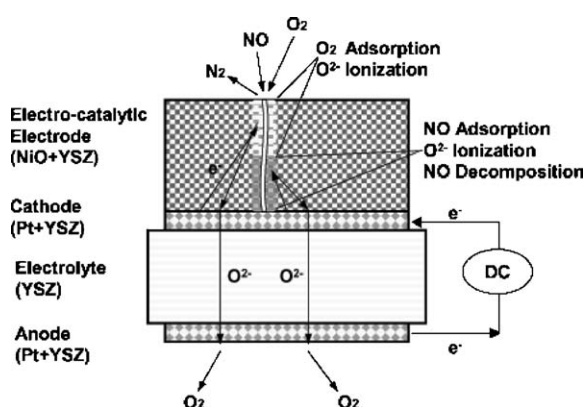


Fig. 1. Conceptual representation of the electrochemical cell for NO_x decomposition with electro-catalytic electrode.

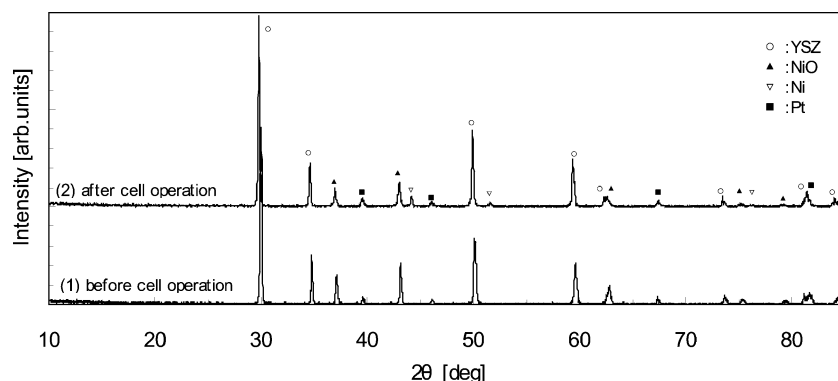


Fig. 2. X-ray diffraction patterns of the electro-catalytic electrode before cell operation (1) and after cell operation for 22 hours at a temperature of 600°C at voltages from 0–2.25 V (2).

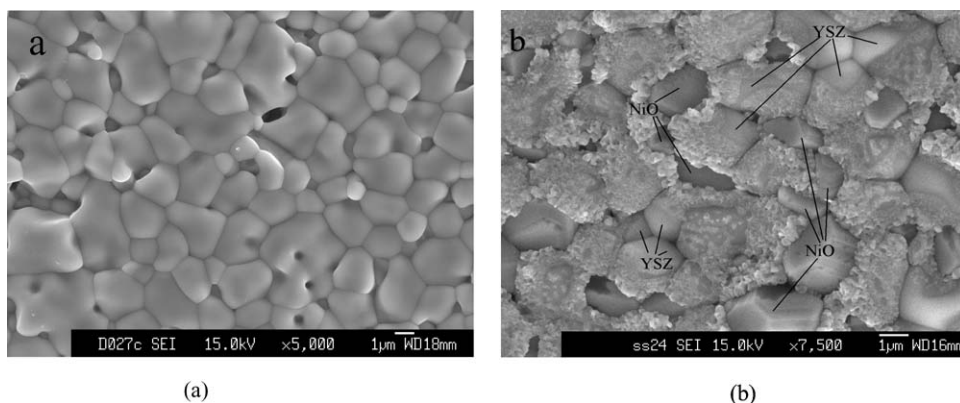


Fig. 3. The microstructures of the surfaces of the electro-catalytic electrode before cell operation (a) and after cell operation for 22 hours at a temperature of 600°C at voltages from 0–2.25 V (b).

The microstructures of the surfaces of the electro-catalytic electrode before and after cell operation are shown in Fig. 3(a) and (b), respectively. The surface of the electro-catalytic electrode before cell operation (Fig. 3(a)) is apparently dense and consists of NiO and YSZ grains with an average grain size of the order of 1 μm. The interfaces between the NiO/NiO, YSZ/YSZ, and NiO/YSZ grains are smooth. A structural change was observed in the surface of the electro-catalytic electrode after cell operation (Fig. 3(b)). The boundaries between the NiO/NiO and YSZ/YSZ grains remained smooth. New smaller grains have also been observed in the boundaries of the NiO/YSZ interfaces.

To investigate the new small grains existing on the boundaries of the NiO/YSZ interface, we have carried out a transmission electron microscopy study. A typical image of the grain boundary of the NiO/YSZ interface

after cell operation is shown in Fig. 4. It is seen from this figure that the 10–100 nm size new NiO grains have appeared on the NiO side of the boundary region of NiO/YSZ.

To describe these morphological/microstructural changes at the grain boundary of the NiO/YSZ interface, we considered the oxidation-reduction reaction of NiO, and the NO and O₂ gas adsorption and decomposition. The oxidation-reduction mechanism of the NiO is schematically illustrated in Fig. 5. It is well known that NiO can be easily reduced to Ni under reducing atmospheres and Ni can be easily oxidized to NiO under oxidizing atmospheres in the temperature region of 600 to 900°C. Through the external voltage applied to an electrochemical cell, oxygen vacancies in YSZ are generated, near the cathode region of the YSZ solid electrolyte. NO and O₂ gas molecules

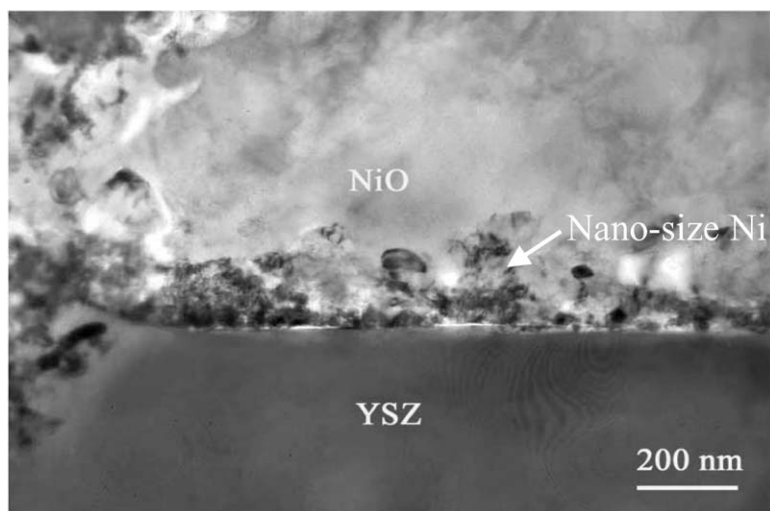


Fig. 4. A typical TEM image of the grain boundary of the NiO/YSZ interface after cell operation for 22 hours at a temperature of 600°C at voltages from 0–2.25 V.

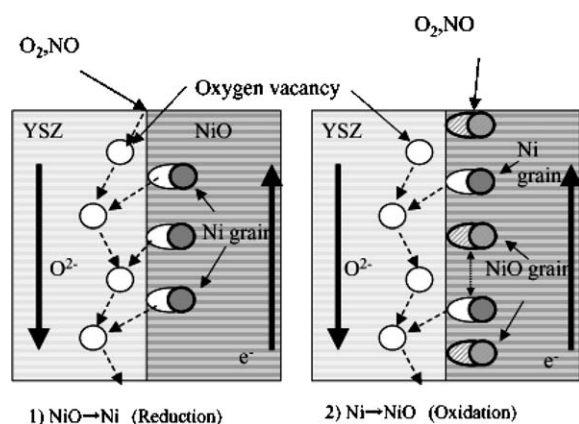
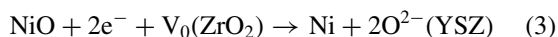
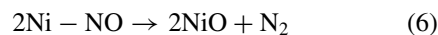


Fig. 5. Schematic illustration of the oxidation-reduction mechanism of the NiO.

receive an electron and are ionized at the NiO/YSZ interface. The ionized-oxygen is then transferred to the YSZ electrolyte because the YSZ in the electrocatalytic electrode is connected with the YSZ solid electrolyte through the YSZ in the cathode. Moreover, it is thought that the oxygen constitutes of NiO that exists near the NiO/YSZ interface is ionized and transferred to the YSZ grains and then reduced. Conversely, Ni is oxidized to NiO easily by O₂ gas adsorption.



Also, it is well known that adsorption and decomposition of NO gas molecules occur on Ni grain surfaces. NO gas molecules are adsorbed on Ni. This adsorbed NO decomposes to N₂ and Ni is oxidized to NiO.



It is thought that a large amount of nano-size Ni and NiO grains were self-assembled at the grain boundary of the NiO/YSZ interface through these oxidation-reduction reactions and the high NO decomposition properties are affected by the self-assembled nano-size Ni grains.

In order to use reduced Ni for NO decomposition reaction effectively, it is required to control the reaction of Eq. (4). To control this reaction, the new electrochemical cell structure schematically illustrated in Fig. 6 has been designed and investigated. The electro-catalytic electrode is multilayered with a thin YSZ layer, which does not have electronic conductivity, as the upper layer. By covering the electrocatalytic electrode with the upper layer, the oxidation of the reduced Ni by coexistence O₂ adsorption can be prevented. Moreover, since taking in the O₂ to oxygen vacancies in the YSZ grains in the electrocatalytic electrode is also prevented by multilayering, it is thought that both the rate of the reduction of the

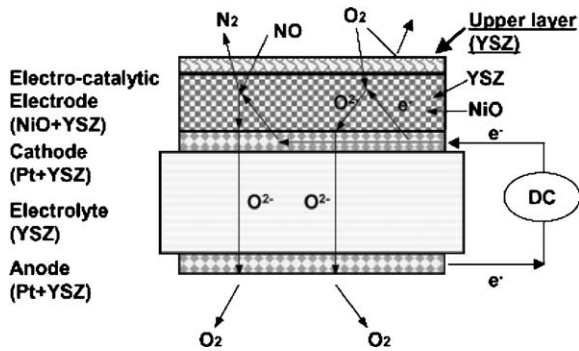


Fig. 6. Conceptual representation of the electrochemical cell for NO_x decomposition with multilayered electro-catalytic electrode.

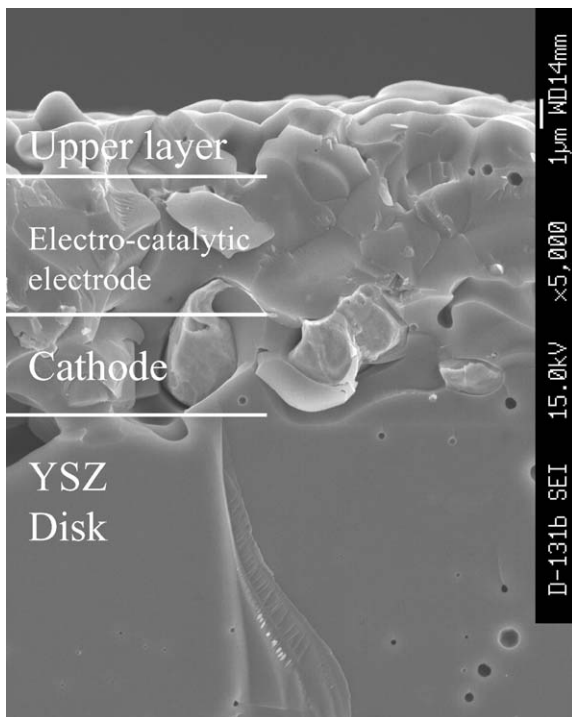


Fig. 7. The cross-sectional view of the multilayered electrochemical cell with the thin upper YSZ layer.

NiO to Ni and the amount of nano-sized Ni grains increased. Consequently, it is thought that both the adsorption rate of NO molecule to Ni and the decomposition rate of NO to N₂ increased. The YSZ paste was screen-printed with an area of 2 cm² over the electro-catalytic electrode and sintered at 1450°C for 4 hours. Figure 7 shows the cross-sectional view of the multilayered electrochemical cell with the thin upper YSZ

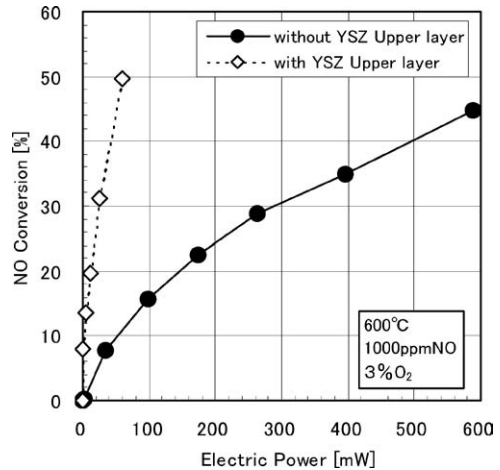


Fig. 8. The dependence of NO conversion on electrical power value at a temperature of 600°C. ●: electrochemical cell without YSZ upper layer, ◇: electrochemical cell with YSZ upper layer, Reactant gas: 1000 ppm NO and 3% O₂ in He at gas flow rate of 50 ml/min.

layer sintered at 1450°C. A YSZ layer with a thickness of about 3 µm was deposited over the electro-catalytic electrode.

The NO decomposition properties were evaluated at a temperature of 600°C in the voltage range 0–2.25 V. The reactant gas was 1000 ppm NO and 3% O₂ in He at gas flow rate 50 of ml/min. The dependence of NO conversion rate on current value was improved and exceeded the theoretical value calculated from the current efficiency based on the electrode reaction [5, 6]. The dependence of NO conversion on electrical power is shown in Fig. 8. The electric power was also decreased sharply and the required electric power at 50% of NO conversion was 60 mW. This electric power decreases to the level of 1/10 of the electric power of the electrochemical cell without the YSZ upper layer. The deNO_x properties of the electrochemical cell were improved by multilayering as mentioned above, and the electrochemical cell with YSZ upper layer can be operated at low electric power.

4. Conclusions

The microstructure and chemical changes in the electro-catalytic electrode of electrochemical cells for NO_x decomposition after cell operation were evaluated. Nano-size Ni grains were self-assembled at NiO/YSZ interfaces by oxidation-reduction reaction of

the NiO during the cell operation. In order to use the reduced Ni for NO decomposition reaction effectively, we investigated multilayering of the electro-catalytic electrode. The NO decomposition properties of the cell were improved dramatically by multilayering techniques, and the electric power decreases to the level of 1/10 of the electric power of the electrochemical cell without YSZ upper layer.

Acknowledgments

This work has been supported by 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.

References

1. T. Hibino, *Chem. Lett.*, 927 (1994).
2. J. Nakatani, Y. Ozeki, K. Sakamoto, and K. Iwayama, *Chem. Lett.*, 315 (1996).
3. T. Hibino, T. Inoue, and M. Sano, *Solid State Ionics*, **130**, 19 (2000).
4. T. Hibino, T. Inoue, and M. Sano, *Solid State Ionics*, **130**, 31 (2000).
5. S. Bredikhin, K. Maeda, and M. Awano, *Solid State Ionics*, **144**, 1 (2001).
6. S. Bredikhin, K. Maeda, and M. Awano, *J. Electrochem. Soc.*, **148**, D133 (2001).
7. S. Bredikhin, K. Matsuda, K. Maeda, and M. Awano, *Solid State Ionics*, **149**, 327 (2002).
8. A. Aronin, G. Abroshimova, S. Bredikhin, K. Matsuda, K. Maeda, and M. Awano, *J. Ceram. Soc. Jpn.*, **110**, 722 (2002).
9. K. Matsuda, S. Bredikhin, K. Maeda, and M. Awano, *Solid State Ionics*, **156**, 223 (2003).