NO Decomposition in the Presence of Excess O_2 Using the Electrochemical Cells with Pd Electrodes Treated at High Temperature and Coated with $La_{1-x}Sr_xCoO_3$

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Decomposition of NO in the presence of oxygen was promoted by using an electrochemical cell composed of YSZ and non-porous Pd electrodes. The NO conversion into N_2 was successfully improved by coating the Pd electrodes with a perovskite oxide ($La_{1-x}Sr_xCoO_3$).

Direct catalytic decomposition of nitric oxides attracts much attentions because the reaction itself is quite simple so that no reducing agents are required. Actually, however, most of the catalysts are deactivated in the presence of oxygen, which has a pronounced inhibitive effect in the process of nitric monoxide decomposition. Huggin et al.[1] have proposed the electrochemical reduction of NO by using solid oxide electrolyte cells coated with Pt electrodes. By applying the direct electric potential, NO can be easily decomposed to nitrogen and oxygen on the cathode and the oxygen thus produced was ionized and pumped through the solid electrolyte to the anode. The NO decomposition in this kind of electrochemical cells also suffer from the inhibition by oxygen. For instance, Hibino[2] has recently reported the reaction of NO-CH_4-O_2 mixtures in an electrochemical cell consisting of porous Pd electrodes and a Y_2O_3-stabilized zirconia (YSZ) disk. In this system, a high current density is required to attain the substantial NOx reduction because the coexisting oxygens pass through the electrolyte more preferably than oxygen from NO decomposition.

In the present study, we have successfully developed the electrochemical cell consisting of non-porous Pd electrodes and a YSZ electrolyte, which can decompose NO at low current densities even in the presence of oxygen.

The electrochemical cell of this study was fabricated from tubular YSZ ceramics, which was produced by the following method. Mixtures of YSZ powders (8 mol% Y_2O_3), ethylene glycol, and water and binders (ShinEtu "metolose") were kneaded thoroughly and molded into a tube by extrusion. After drying and calcination at 1600 °C for 12 h, a solid oxide electrolyte tube (O.D. 4 mm x 240 mm, 0.7 mm thick) was obtained. Metal pastes, i.e. Pt, Ag, and Pd, were applied on the inside and outside of the tube to form electrodes (outside electrode area of 3.0 cm^2) after calcination at various temperatures. Table 1 shows five different types of cells thus obtained. Here, a Pd-1300F cell was prepared by coating the cathode surface of Pd-1300 with 2-propanol solution of mixed alkoxides of La, Sr and Co (mole ratio ; 0.4 : 0.6 : 1.0). The subsequent heating at 950 °C deposited perovskite oxide ($La_{1-x}Sr_xCoO_3$) particles on to the electrode surface as can be confirmed by X-ray diffraction measurement. The electrode morphology was observed by a field emission scanning electron microscope (FE-SEM: JEOL 6301F). NO decomposition were carried out in the apparatus as shown in Figure 1. Gas mixtures of NO (1000 ppm), O_2 (2%) and He (balance) was fed to the cathode (50 ml/min). Pure helium gas was supplied to the anode (50 ml/min). The reaction was carried out at 700 °C and at applied voltage of DC 2.2 - 3.5 V. The composition of effluent gases from both electrodes was analyzed by gas chromatography (GC) to determine the NO conversion into N_2.

Table 1. Electrochemical cells used in the present study

Cells	Electrodes		Calcination temp	Functional layer
	Cathode	Anode	(°C)	
Pt-1300	Pt	Pt	1300	none
Ag-800	Ag	Ag	800	none
Pd-800	Pd	Pd	800	none
Pd-1300	Pd	Pd	1300	none
Pd-Pt-1300	Pd	Pt	1300	none
Pd-1300F	Pd	Pd	1300	$La_{1-x}Sr_xCoO_3$

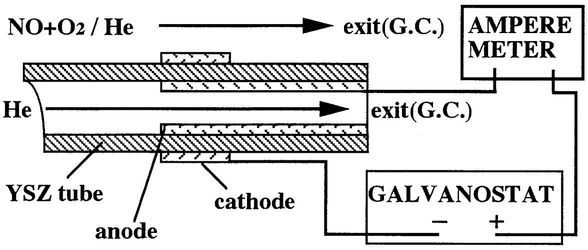

Figure 1. An electrochemical cell for NO decomposition.

In the opening-circuit reaction, the formation of N_2 was not detected at all and the concentration of O_2 at the cathode did not change. On the other hand, when applying the DC voltage between the two electrodes of the cell, substantial current was detected as the a result of the transfer of oxygen ions. Figure 2 shows the relationship between the NO conversion into N_2 and the current density for different types of cells. The amount of pumped oxygen ions, which was calculated from the current densities, is also indicated as an upper abscissa. A broken line indicates the calculated relation assuming that electrochemically reduced NO : O_2 ratio is equal to that of the supplied gas mixture (1:20), corresponding to the completely unselective cathodic reduction to occur. In the case of Ag-800 and Pt-1300 cells, NO decomposition was not observed up to 60 and 80 mA/cm^2, respectively. Above this critical current densities, the NO conversion increased steeply with an increase of the current density. These results indicate that the electrochemical reaction at relatively low current densities is dominated by the transfer of oxygen ions from gaseous O_2. The reaction of NO decomposition on these electrodes takes place only when the gaseous oxygen near the cathode surface is removed at high current densities. The highest NO decomposition activity among three precious metal electrodes was attained on the Pd, which initiated the N_2 formation below 40mA/cm^2. The NO conversion strongly depends on the heating temperature of the electrode; decomposition rates over Pd-1300 was higher than those over Pd-800. Further improvement of the NO conversion was attained by the Pd electrode coated with the perovskite oxide(Pd-1300F). The almost proportional relationship between the NO conversion and the current density for these cells suggests that the electrochemical reduction of NO proceeds in the whole range of the current density. As can be judged from simple comparison between Pd-Pt-1300 and Pd-1300 cells, NO decomposition on these cells is not affected by the anodes. The catalytic activity of cathodes for NO decomposition plays a key role in electrochemical NO reduction. Figure 2 also shows that coating of the Pd cathode with perovskite oxides is effective in promoting the electrochemical reduction of NO. But actually, it was difficult to achieve more than 25% NO conversion with Pd-1300F because of the internal resistance. This high resistance is considered to be originated from the difficulty of gas diffusion through the electrode to three-phase boundary.

As described above, electrochemical reduction of NO was enhanced by heating the Pd cathode at increasing temperatures.

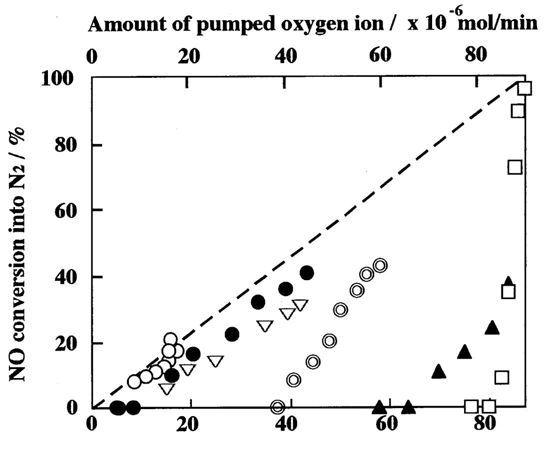

Figure 2. Relationships between NO conversion and current density flowed in the cells using Pt-1300 (□), Ag-800 (▲), Pd-800 (◎), Pd-1300 (●), Pd-Pt-1300 (▽), and Pd-1300F (○).
Reaction conditions: NO 1000 ppm, O_2 2%. Reaction temperature: 700 ℃. DC power supply: 2.2-3.5 V.

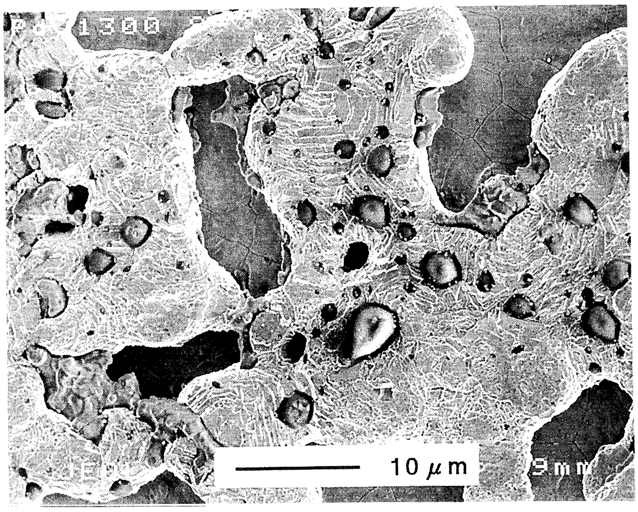

Figure 3. SEM photograph of Pd-1300 electrode.

SEM photographs showed that the difference of electrode morphology between Pd-800 and Pd-1300. The electrode of Pd-800 was porous as reported by Hibino[2], but that of Pd-1300 was significantly sintered into a non-porous layer and part of the solid electrolyte surface was exposed. Upon heating at 1300 ℃, a lot of grain boundaries in Pd-800 electrode almost disappeared and many steps were generated on the electrode surface. Observation of the cross section of the Pd-1300 electrode showed that the thickness of the densely packed Pd layer was 3 μm. Such reduced three-phase boundary structure of the electrode brings about not only the high internal resistance of the cell but also suppresses preferential reduction of O_2.

Consequently, the results of this study represents that the non-porous Pd electrode after heating at 1300 ℃ produces higher activity for electrochemical NO reduction in the oxidizing atmosphere. Further research is directed towards the elucidation of effects of the morphology and surface modification of electrodes on the electrochemical reactions.

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References and Notes

1 S. Pancharatnam, R. A. Huggins, and D. M. Mason, *J. Electrochem. Soc.*, **122,** 869(1975).
2 T. Hibino, *Chem. Lett.*, **1994**, 927.