

Simultaneous Reduction of NO_x and PM in Diesel Exhaust Based on Electrochemical Reaction

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ABSTRACT

The emission regulations for diesel engines are continually becoming stricter to reduce pollution and conserve energy. To meet these increasingly stringent regulations, a new exhaust after-treatment device is needed. Recently, the authors proposed the simultaneous electrochemical reduction (ECR) system for diesel particulate matter (PM) and NO_x. In this method, a gas-permeable electrochemical cell with a porous solid oxide electrolyte is used for PM filtering on the anode. Alkaline earth metal is coated on the cathode for NO_x storage. Application of voltage to both electrodes enables the simultaneous reduction of PM and NO_x by the forced flow of oxygen ions from the cathode to the anode (oxygen pumping).

In this study, the basic characteristics of the ECR system were investigated, and a disk-shaped electrochemical cell was evaluated. In addition, the chassis dynamometer test cycle for the JC08 mode (post new long-term regulation in Japan) was conducted to evaluate the practicality of a honeycomb electrochemical cell. Currently, the fabrication of the honeycomb cell requires further investigation. However, the overall results show that the ECR system has the potential to simultaneously reduce more than 90% of both NO_x and PM produced by diesel engines.

INTRODUCTION

Electrochemical reactions for the treatment of exhaust gas have been attempted since the 1960's^{(1),(2),(3),(4),(5),(6)}.

However, all of these attempts have suffered from low energy efficiency. Recently, the authors proposed the simultaneous electrochemical reduction (ECR) system for diesel particulate matter (PM) and NO_x by taking advantage of electrochemical reactions^{(7),(8)}. The concept of simultaneous reduction by the ECR system is shown in Fig. 1, where PM and NO_x are reduced electrochemically using a solid-state electrochemical cell. A gas-permeable electrochemical cell with a porous solid oxide electrolyte is used to trap PM on the anode. A NO_x storage material, such as alkaline earth metal, is coated on the cathode to selectively store NO_x. By applying voltage to both electrodes, the oxygen atoms in the adsorbed NO_x are extracted to form oxygen ions. As a result, NO_x is decomposed because of the reaction scheme toward the equilibrium state at temperatures close to the exhaust temperature. At the anode, oxygen ions have higher activity and can oxidize the trapped PM at relatively low exhaust temperatures. In addition, oxygen ions can be employed to oxidize CO and hydrocarbons contained in the exhaust.

The advantage of this ECR system over low-temperature activation is the ability to simultaneously reduce NO_x and PM with improved energy efficiency and without the need for Pt. The compactness of the device size, made possible by the simultaneous reduction, acts as a space-saver and enables close coupling of the system to the exhaust manifold.

In this study, both a disk type cell and a honeycomb type cell were used. Various disk cells using electrolytes such as YSZ (yttria-stabilized zirconia), SDC (samaria-doped ceria) and GDC (gadolinia-doped ceria) were tested and evaluated. The

basic characteristics of the ECR system were investigated using the disk-shaped electrochemical cell. In addition, a trial GDC honeycomb cell (28×28×50 mm) was developed to evaluate its potential for practical use. The JC08 mode test (a post new long-term regulation in Japan) was conducted using the partial-flow dilution tunnel system and a diesel engine meeting the EURO 4 standard.

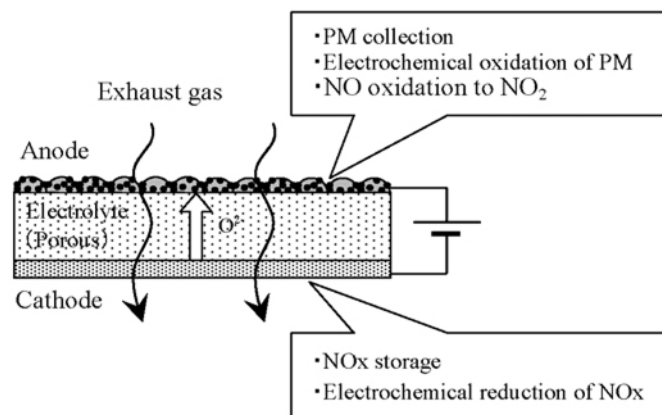


Figure 1. PM and NOx reduction mechanism of ECR

DISK CELL EXPERIMENT

EXPERIMENTAL SETUP AND METHOD

In the present study, $(\text{ZrO}_2)_{0.92}(\text{Y}_2\text{O}_5)_{0.08}$ (YSZ) and $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (GDC) were used as electrolytes. A cermet formed with the electrolyte and either Ag or Pt was used as the electrode to expand the three-phase boundary (electrolyte, electrode, and reactive gas). An Ag electrode was also used for comparison with the cermet electrode. The specifications for each cell used in the experiments are given in [Table 1](#). The appearance of the cell is shown in [Fig. 2](#). [Figure 3](#) shows a cross sectional micrograph of the porous electrolyte structure obtained by scanning electron microscopy (SEM).

Cell Y-1, used for the NOx reduction experiment, has pores of approximately 1 μm in the Pt/YSZ electrode. Y-2 has pores of approximately 4 μm in the Ag electrode. Y-3 and Y-4 have pores of approximately 1 μm in the Ag/YSZ electrode. Barium oxide (BaO) is coated on the cathode for NOx storage except in Y-3. Y-5 has a thickness of 160 μm and the other properties are the same as Y-4.

For decrease of the operation temperature, G-1 and G-2 were produced using the GDC electrolyte, which has suitable ion conductivity at a relatively low temperature. The electrolyte of the G-2 surface was polished before processing the electrode, while G-1 was not polished. A schematic of the experimental apparatus for evaluation of the disk cell is shown in [Fig. 4](#).

Table 1. Specifications for the electrochemical disk cells

Cell No.	Anode $\Phi = 58 \text{ mm}$ $t = 30 \text{ }\mu\text{m}$	Electrolyte $\Phi = 60 \text{ mm}$			Cathode $\Phi = 58 \text{ mm}$ $t = 30 \text{ }\mu\text{m}$
		Material	Porosity	Thickness	
Y-1	Pt+YSZ	YSZ	46%	500 μm	Pt+YSZ+Ba
Y-2	Ag				Ag+Ba
Y-3	Ag+YSZ				Ag+YSZ
Y-4	Ag+YSZ				Ag+YSZ+Ba
Y-5	Ag+YSZ			160 μm	Ag+YSZ+Ba
G-1	Ag+GDC	GDC	40%	400 μm	Ag+GDC+Ba
G-2	Ag+GDC			300 μm	Ag+GDC+Ba

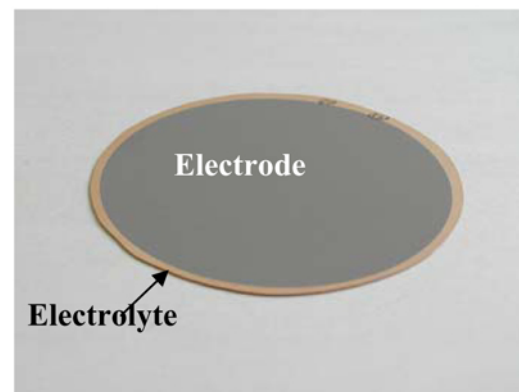


Figure 2. Electrochemical cell

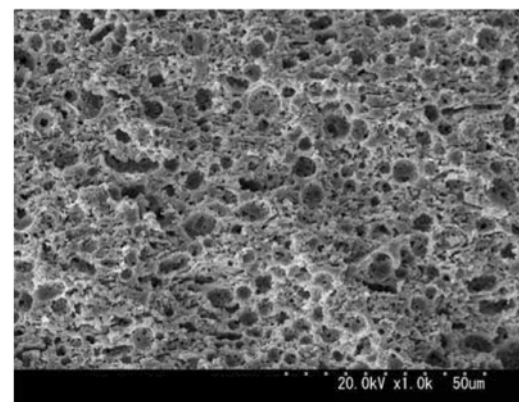


Figure 3. Electrolyte cross section

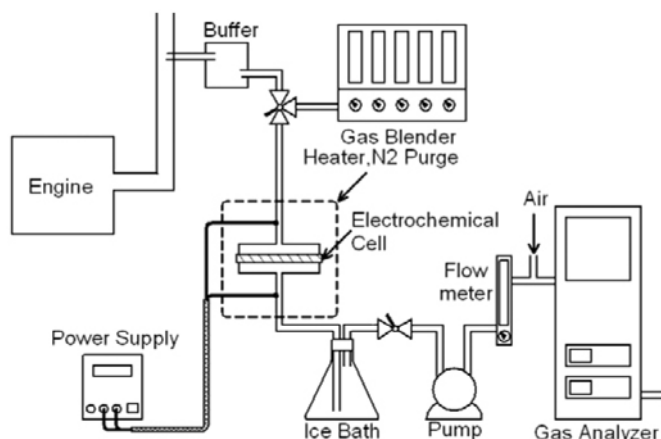


Figure 4. Experimental apparatus

RESULTS AND DISCUSSION OF THE DISK CELL EXPERIMENTS

NOx storage and NOx reduction

Figure 5 shows the NOx reduction ratio of the YSZ cells (Y-1- Y-5) at 400 °C for a simulated exhaust (450 ppm NO₂, 5% O₂, N₂ balance). Cell Y-3, without the Ba coating on the cathode, did not reduce NOx at all, which confirmed that the Ba coating is essential for NOx reduction. The Y-1 cell, with the Pt cermet electrode, showed a low reduction ratio compared to the Y-4 cell with the Ag cermet electrode. Comparison of Y-2 and Y-4 showed that the Ag cermet electrode is superior to the pure Ag electrode, due to the expanded three-phase boundary. A NOx reduction ratio of more than 90% was obtained with cell Y-4 “Ba coating quantity: 36 vol% of the electrode” at a current of 0.1 A (voltage: 4.9 V).

The changes in the NOx concentration during electrochemical reduction using the Y-4 cell at a current of 0.05 A are shown in Fig. 6. In this figure, t=0 indicates the time when a voltage was applied to both electrodes. The concentrations of NO and NO₂ decreased gradually, due to the dead volume of the measuring system. Here, NO₂ was supplied to the simulated exhaust gas as NOx, and at t=0 almost the same concentrations of NO and NO₂ were detected. This indicates that the supplied NO₂ may be converted to NO by the catalytic effect of the Ag electrode. With this condition, both NO₂ and NO were reduced by application of the voltage, and 80% NOx reduction was achieved. Figure 7 shows the result when 450 ppm of NO is supplied in the simulated exhaust gas. In this case, 40% of NO was oxidized to NO₂ by the catalytic effect of the Ag electrode, and 70% NOx reduction was achieved by application of the voltage. N₂O was not detected during the experiments. From these results, the ratio of NO to NO₂ in

the exhaust gas seems to affect the NOx reduction; therefore, it may be possible to increase the NOx reduction ratio by optimizing the ratio of NO to NO₂.

The voltage and the current are also shown in Figs. 6 and 7. The electrochemical reaction takes place as the result of ion flow. The current increases sharply as the voltage is applied, which indicates that NOx decomposition by electrochemical reaction proceeds at a sufficient rate. However, NOx reaction in the ECR system will also depend on the NOx storage process. The overall reaction rate will be discussed in the section “Improvement of cell performance.”

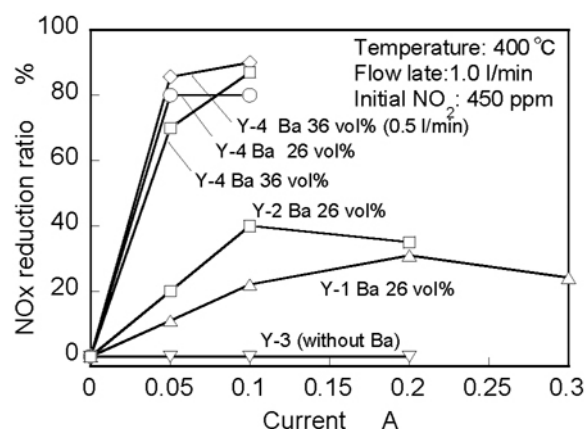


Figure 5. NOx reduction ratios for the simulated exhaust gas

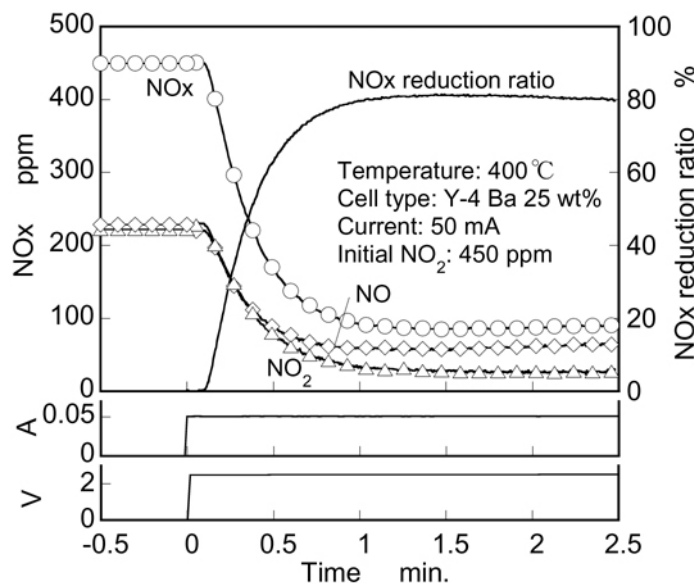


Figure 6. NOx reduction ratio for in the case of NO₂ as the NOx input gas

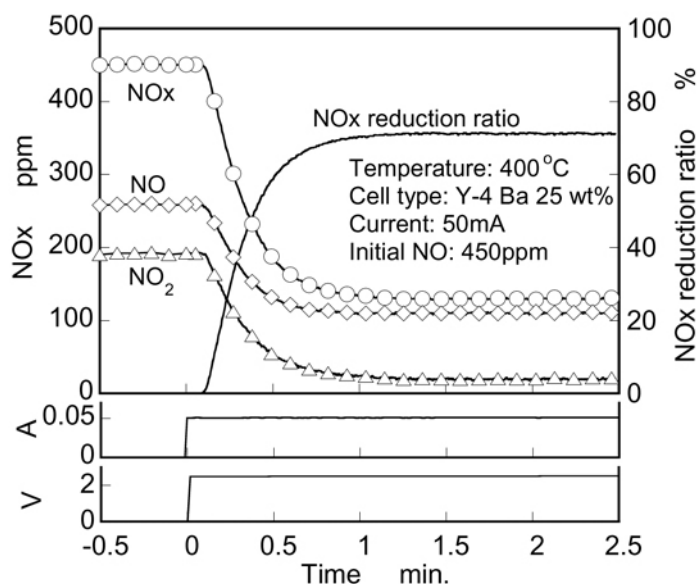


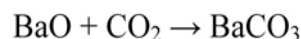
Figure 7. NOx reduction ratio in the case of NO as the NOx input gas

Simultaneous reduction

The simultaneous reduction of PM and NOx was investigated using actual diesel exhaust. The exhaust includes 450 ppm of NOx and 50 mg/m³ of PM at a brake mean effective pressure (BMEP) of 0.36 MPa (50% engine load) at an engine speed of 1800 rpm. Figure 8 shows the change in the NOx concentration when 1.0 L/min of exhaust is supplied to the Y-4 cell at 400 °C and 100 mA of current is applied for 10 min. During application of the current, the NOx concentration decreased from 456 ppm to 193 ppm, which is a 60% NOx reduction ratio.

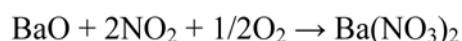
The effect of the current on the reduction ratios of NOx, PM, CO, and hydrocarbons (methane equivalent) is shown in Fig. 9. The reduction ratio of NOx is saturated at 0.1 A. Because the current is proportional to the flux of oxygen ions in the electrolyte, the current indicates the throughput speed of the electrochemical reaction. Saturation of the NOx reduction ratio may be due to the limitation of NOx absorption on Ba. As for PM, the 70% reduction at zero current shows the catalytic effect of Ag. By applying a current of 100 mA, a PM reduction ratio of more than 95% can be achieved. Figure 9 also shows that not only NOx and PM, but also CO and hydrocarbons are reduced by the ECR system. Figure 10 shows a photograph of the electrochemical cells after the experiment, with and without application of current. The weight of the backup filter installed downstream of the cell was not increased. Therefore, almost all of the PM was trapped by the cell. Figure 11 shows the effect of CO₂, which is a coexistent gas in the exhaust, on the NOx reduction ratio. With no CO₂ in the simulated exhaust gas, the NOx reduction was 85%, but with 5.5% CO₂, the NOx reduction ratio

decreased to 60%. From these results, it is concluded that CO₂ in the exhaust gas impedes the NOx reduction (9). This may be due to the reaction of CO₂ with Ba to form BaCO₃.



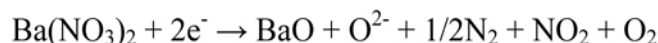
R(1)

In the ECR process, NOx storage on Ba is an essential process for the electrochemical reduction of NOx. Ba is usually present in the BaO form and reacts with NOx as indicated by reaction R(2).



R(2)

NOx reduction is then achieved by decomposition of Ba(NO₃)₂ with applied voltage according to R(3).



R(3)

Consequently, NOx decomposes to N₂ and O₂. However, CO₂ is also stored by Ba, as shown in R(1). Although Ba(NO₃)₂ is more stable than BaCO₃, a much higher concentration of CO₂ causes fast production of BaCO₃. BaCO₃ is finally converted to (NO₃)₂, as shown by R(4).



R(4)

However, the reaction rate of R(4) is slower than R(2), so that the rate of NOx storage is slower in the presence of CO₂. The decrease in the NOx storage rate is compensated by expansion of the reaction surface or NOx storage sites in the cathode. Electrochemical reduction of NOx takes place at the three-phase boundary (Ag-GDC-Ba(NO₃)₂). Therefore, effective NOx storage sites extend the three-phase boundary. This detail is discussed in the following section, "Improvement of cell performance."

Experiments were then conducted using the Y-5 cell with a thin electrolyte (160 μm thickness) to clarify the energy operation, and the results are shown in Fig. 12. Almost the same PM and NOx reduction ratios occur in the Y-4 cell (500 μm thickness) at the same current, as shown in Fig. 9, which confirmed that the ECR process depends on the current value or the flux of oxygen ions. In contrast, the applied voltage of the Y-5 cell is almost one-third that of the Y-4 cell. Therefore, the energy consumed, the product of the current and voltage for simultaneous PM and NOx reduction, can be reduced by employing a thin electrolyte cell. The energy consumption for an actual system was evaluated to be