



Special Feature: Novel Catalytic Approach

Research Report

Electrochemical Automotive Exhaust Purification

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■ABSTRACT■ The following three criteria are of particular importance for automotive exhaust purification: low-temperature activity, purification of NO_x under excess oxygen (so-called lean conditions), and oxidation of particulate matter (PM). Traditional catalyst reactions are thermally activated and cannot be adequately initiated until the catalyst temperature is sufficiently high. Furthermore, it is impossible for a traditional catalyst to purify NO under lean conditions without a reductant such as urea, which is supplied from an on-board tank. The catalyst must also be heated sufficiently for PM oxidation, which requires an extra engine to supply fuel to the catalyst.

This paper summarizes the results of a study on electrochemical methods to improve automotive exhaust purification, including the temperature dependence of an electropromoted NO-HC-O_2 reaction, NO_x electrochemical reduction, a state analysis of an electropromoted electrode, a prototype monolith reactor, and NO permselective cells working at room temperature. Electrochemical automotive exhaust purification is expected to be one of the next generation of technologies for purifying automotive exhaust using electric power.

■KEYWORDS■ Automotive Catalyst, NO_x Reduction, Electrochemical Reaction, Solid Oxide Electrolysis Cell, Ionic Liquid

1. Introduction

Automotive exhaust purification is typically performed using a catalyst with small metal particles dispersed on metal oxides, such as three-way catalysts, selective NO_x reduction catalysts, and lean NO_x trap catalysts. Since their introduction in the 1970s, these traditional catalysts have been continuously improved to conform to new emission regulations.

The following three criteria are of particular importance for automotive exhaust purification: (1) low-temperature activity, (2) purification of NO_x under excess oxygen (so-called lean conditions), and (3) oxidation of particulate matter (PM) (**Fig. 1**). Traditional catalytic reactions are thermally activated and cannot be adequately initiated until the catalyst temperature is sufficiently high. Furthermore, it is impossible for a traditional catalyst to purify NO under lean conditions without a reductant such as urea, which is supplied from an on-board tank. The catalyst must also be heated sufficiently for PM oxidation, which requires an extra engine to supply fuel to the catalyst.

Traditional catalytic converter systems for exhaust

purification seem insufficient to meet increasingly strict emission regulations. To adhere to stricter regulations in the future, new methods of activating catalytic reactions using external energy have been proposed, e.g., plasma, ozone, light, or electric power. Among these external energy sources, electric power is a particularly promising candidate, as hybrid car technology has rapidly increased in popularity and has a readily available supply of electric power.

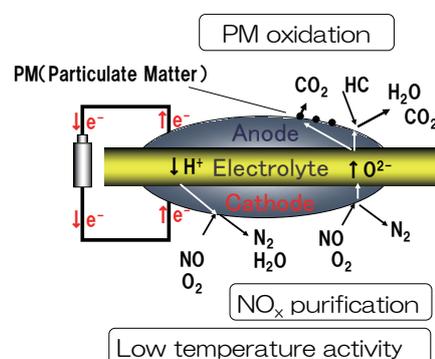


Fig. 1 Three key requirements for automotive exhaust purification and electrochemical methods that use a solid oxide electrolysis cell (SOEC).

Electrically heated catalysts (EHCs) are proposed to initiate catalytic reactions using electric power. However, EHCs only initiate the catalytic reaction and have not any functions to reduce NO under lean conditions. Another type of electric power activation method was proposed in the 1970s. This method uses a solid oxide electrolysis cell (SOEC) consisting of an electrolyte sandwiched between two electrodes. The ions within the SOEC activate catalytic reactions through Faradaic and non-Faradaic methods. The Faradaic method utilizes ions and electrons as reductants, and the reaction rate is proportional to the current (amount of ions and electrons). Huggins proposed a Faradaic NO reduction reaction in 1975.^(1,2) On the other hand, the non-Faradaic reaction rate is not proportional to the current and only uses ions to initiate the reactions. The non-Faradaic method proposed in the 1980s by Vayenas⁽³⁾ was studied for use with automotive exhaust purification, and is referred to as the non-Faradaic electrochemical modification of catalytic activity (NEMCA) or electrochemical promotion (EP). Since 2010, two notable review papers have been published on the Faradaic⁽⁴⁾ and non-Faradaic⁽⁵⁾ methods.

Although SOECs have not yet been commercialized for automotive exhaust purification, they are expected to form the next generation of catalyst technology. In this paper, research results in this field are introduced and reviewed.

2. Electrocatalysis for Automotive Exhaust Gas Purification

2.1 Temperature Dependence of SOECs for Automotive Exhaust Purification

This first section discusses the temperature dependence of SOECs for automotive exhaust purification.⁽⁶⁾ The reaction activity was evaluated using a Rh/YSZ (yttria-stabilized zirconia)/Au cell under 0.1% NO + 0.1% C₃H₆ + 0.4% O₂ at a flow rate of 60 cc/min, which simulated a stoichiometric gas composition. A 20-mm-diameter circular disc cell was set in a quartz tube. The C₃H₆ and NO conversion rates were evaluated as the temperature was decreased from 500 to 200°C, with and without an applied voltage (Fig. 2).

The rates of C₃H₆ and NO conversion were affected by the applied voltage, as shown in Fig. 3. Upon

applying +2 V to the Rh electrode, both conversion rates increased, relative to when no voltage was applied, (open circuit (OC)), with increasing temperature. This result indicated that the applied voltage of +2 V to the Rh electrode enhanced the both catalytic reactions of C₃H₆ oxidation and NO reduction. On the other hand, with the applied voltage of -2 V to the Rh electrode, the rate of C₃H₆ conversion was lower below 375°C and higher above 375°C compared to when no voltage was applied. The NO conversion rate showed a similar tendency; it was higher (lower) above (below) 310°C compared to when no voltage was applied.

The effect of applying voltage can be measured with two indicators; the reaction rate enhancement ratio (ρ) and the Faradaic efficiency (A):

$$\rho = r/r_0, \quad (1)$$

$$A = \Delta r/(I/2F), \quad (2)$$

where r and r_0 are the reaction rates with an applied voltage and in the OC condition, respectively, Δr ($= r - r_0$) is the change in reaction rate due to the applied voltage, I is the current, and F is Faraday's constant. For a Faradaic reaction, $|A| \leq 1$, and for a non-Faradaic reaction, $|A| > 1$. The reaction rate for non-Faradaic reactions can change drastically with a very small current.

The values of I , ρ , and A estimated from the results of Fig. 3 are shown in Fig. 4. From Figs. 4(d) and (e), it can be seen that below 375°C, $|A| > 1$ for C₃H₆ and NO conversion. Therefore, a non-Faradaic reaction occurred within this temperature range. This can be explained by the reactions taking place at the Rh electrode, as shown in Fig. 5. The Rh electrode surface is easily poisoned by oxygen. When a positive voltage (+2 V) was applied, chemical adsorption of oxygen at the electron acceptor was suppressed and C₃H₆ adsorption was enhanced. Applying a positive voltage increased both the C₃H₆ conversion and oxidation rates. When a negative voltage (-2 V) was supplied, oxygen poisoning increased, and the C₃H₆ conversion and oxidation rates decreased at lower temperatures. The reaction mechanism when a negative voltage is applied at higher temperatures is discussed in the following section.

At high temperatures, the current when -2 V was applied to the Rh electrode was larger than when +2 V

was applied. The Rh electrode resistance was found to decrease upon application of -2 V because the Rh electrode was reduced and metalized. The reduced Rh electrode could reduce NO, as shown in Figs. 3(b) and 4(c). This NO reduction is Faradaic because $|A| \approx 1$ (Fig. 4(e)). Therefore, NO was reduced by electrons in a Faradaic reaction and not by reductants in a non-Faradaic reaction.

2.2 NO_x Reduction Electrode

This section focuses on NO_x reduction by the cathode electrode,⁽⁷⁾ which is important not only for

applications to reduce NO_x, but also for amperometric NO_x sensors based on SOECs. Thus, it is worthwhile to analyze the mechanism for NO electrochemical reduction by electrodes. It was found that the NO reduction rate on a Pt electrode is affected by the addition of Au. The NO reduction mechanism was studied by transient analysis of the surface catalytic reactions (Fig. 6).

A multicell consisting of electrodes printed on zirconia plates separated by alumina plates was set in a quartz tube. A gas pulse of NO or O₂ was supplied at millisecond duration respectively. The NO reduction reaction rate was estimated from the

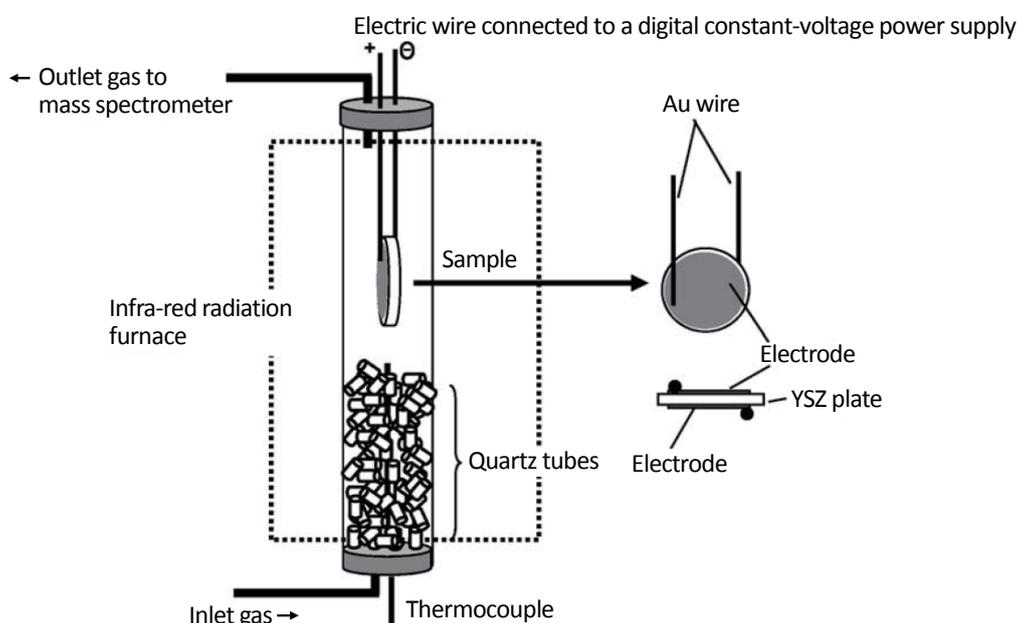


Fig. 2 Apparatus for measuring the temperature dependence of the performance of an SOEC for automotive exhaust purification.

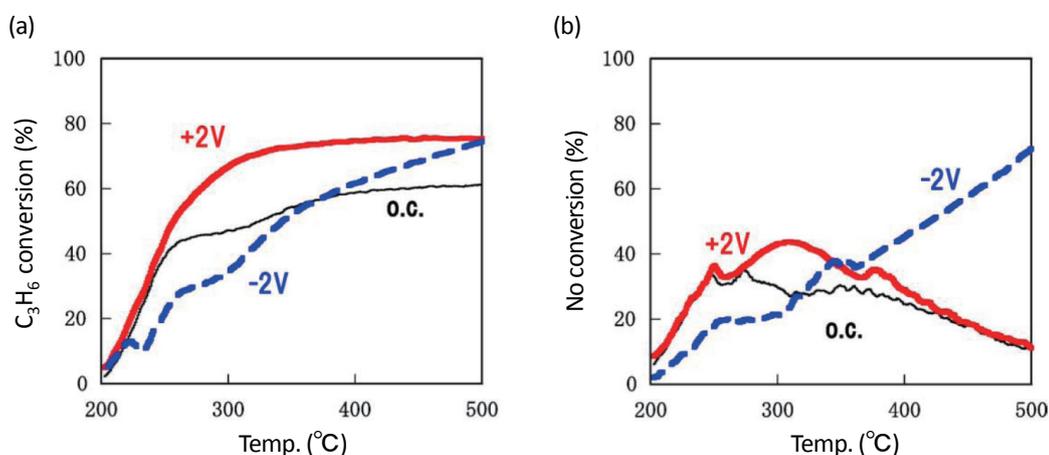


Fig. 3 Temperature and applied voltage dependence of (a) C₃H₆ conversion rate and (b) NO conversion rate.

N_2 generation rate, and the current response was measured simultaneously. The response analysis is important for not only the reaction analysis but also the development of automotive catalysts because the exhaust gas component usually fluctuates dynamically under transient engine operation.

A comparison of Pt and Pt–Au electrodes is shown

in Fig. 7. Increasing the applied voltage from 0 to 1 V increased the N_2 generation rate and the current for both electrodes, although the value were higher for the Pt electrode. The rate of N_2 generation was high and the reaction stopped within about 150 ms; however, the current flowed for over 5 s. This indicated that the gas reaction on the electrode surface was very fast

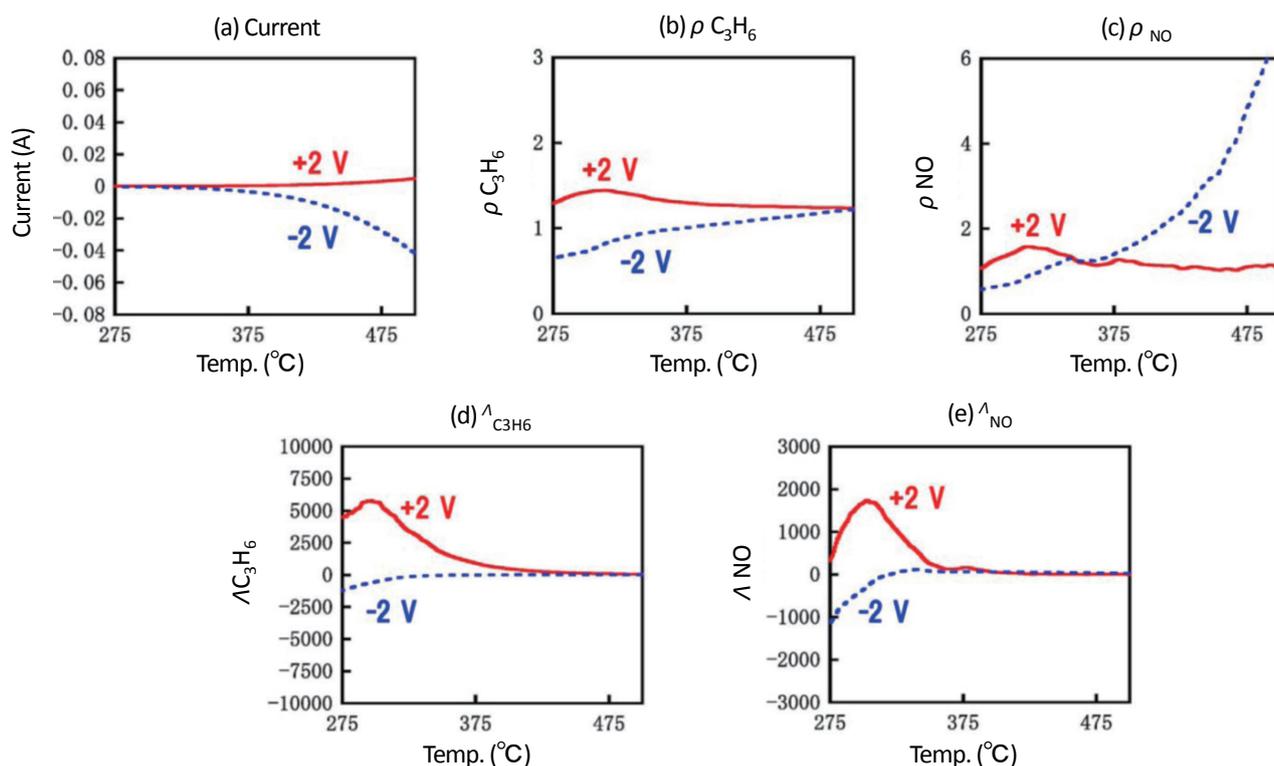


Fig. 4 Temperature and applied voltage dependence of current, reaction rate enhancement ratio (ρ), and Faradaic efficiency (Λ).

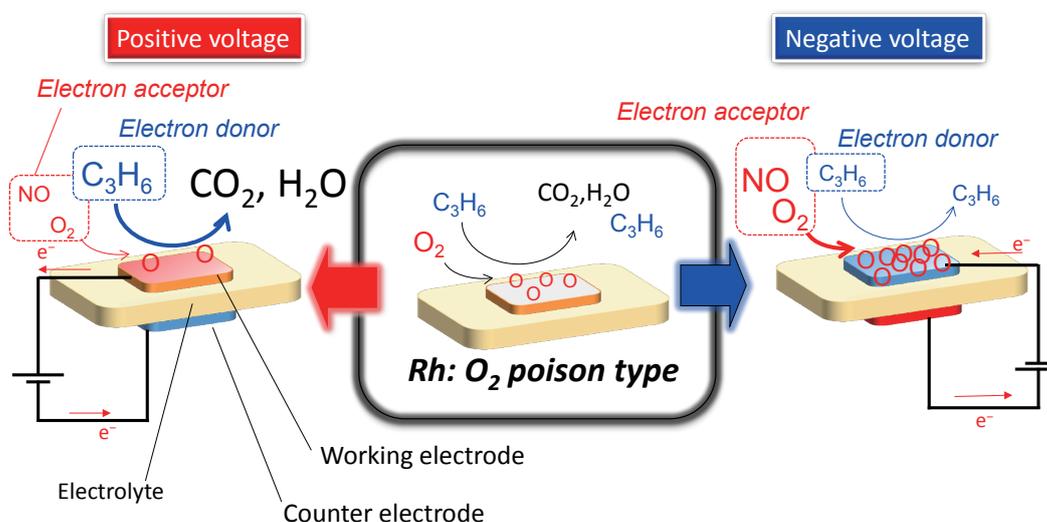


Fig. 5 Reactions occurring at the oxygen-poisoned Rh electrode surface for positive and negative applied voltages.

compared with the oxygen ion mobility in the cell, which is related to current flow. The increase in the current with increasing applied voltage was the same as when there was an oxygen supply.

Arrhenius plots for N_2 generation were determined for both electrodes (Fig. 8). The activation energy for the Pt–Au electrode (58 kJ/mol; 0.6 eV) was higher than that for the Pt electrode (24 kJ/mol; 0.25 eV). The higher activation energy for the Pt–Au electrode decreased the rate of N_2 generation. The applied voltage did not affect the activation energy for either electrode and changed only the frequency factor. This result indicates that increasing the applied voltage increases the number of active sites for NO reduction, but does not affect the NO reduction reactivity of either electrode.

2.3 Differences between Electropromoted Electrodes and Supported Metal Particles

The results described in Sec. 2. 1 imply that the Rh electrode catalytic reactivity can be controlled by the applied voltage. If the catalytic reaction is optimized in this way, the amount of precious metal required may be reduced. As practical catalysts utilize dispersed metal particles, it is relevant to compare the turnover

frequency (TOF) for the promoted electrode with that for a dispersed metal.⁽⁸⁾

The $NO-C_3H_6-O_2$ reaction was evaluated using an Rh electrode on a YSZ plate and Rh particles dispersed on YSZ powder (Fig. 9). The apparatus for evaluation was composed of three units: the gas feed, reactor, and gas analysis units. The Rh electrode on a YSZ plate was evaluated using the reactor unit shown in Fig. 9(a), whereas the Rh particles dispersed on YSZ powder were evaluated using the reactor unit shown in Fig. 9(b).

The surface area of the Rh electrode was estimated using a transient galvanostatic technique, and that of the dispersed Rh particles was obtained by H_2 chemisorption. The TOF of NO reduction for both samples was investigated. The oxygen concentration dependence of the TOF of NO reduction is shown in Fig. 10. For the dispersed Rh particles, the TOF was between that for the OC state and the NEMCA maximum state for the Rh electrode. Thus, the state of the dispersed Rh particles on YSZ powder was not fully optimized; however, the applied voltage could fully promote the Rh electrode. Utilization of a fully promoted electrode may allow a reduction in the amount of precious metal required compared with traditional precious metal dispersed catalysts.

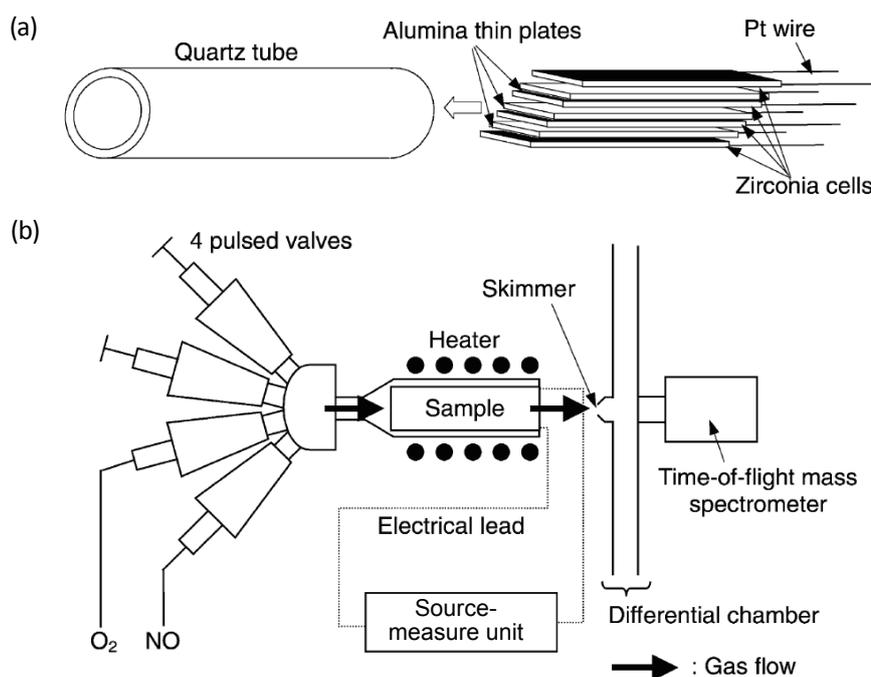


Fig. 6 Setup for analyzing the NO reduction performance of the electrodes. Printed zirconia plates were set in a quartz tube and separated with alumina plates.

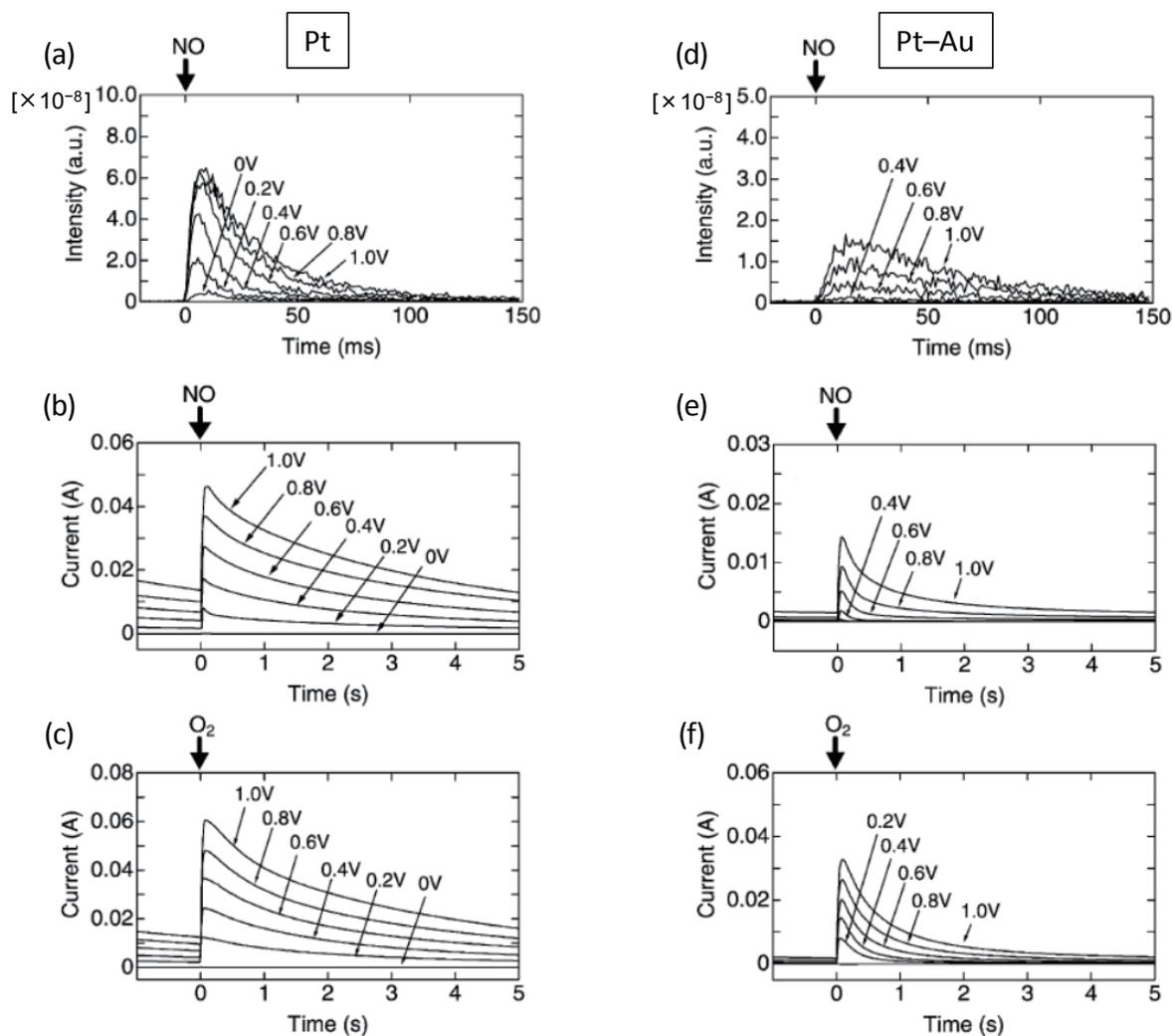


Fig. 7 Time dependence of N_2 generation rate (a) (d) and current for NO (b) (e) or O_2 (c) (f) gas pulses under a constant applied voltage.

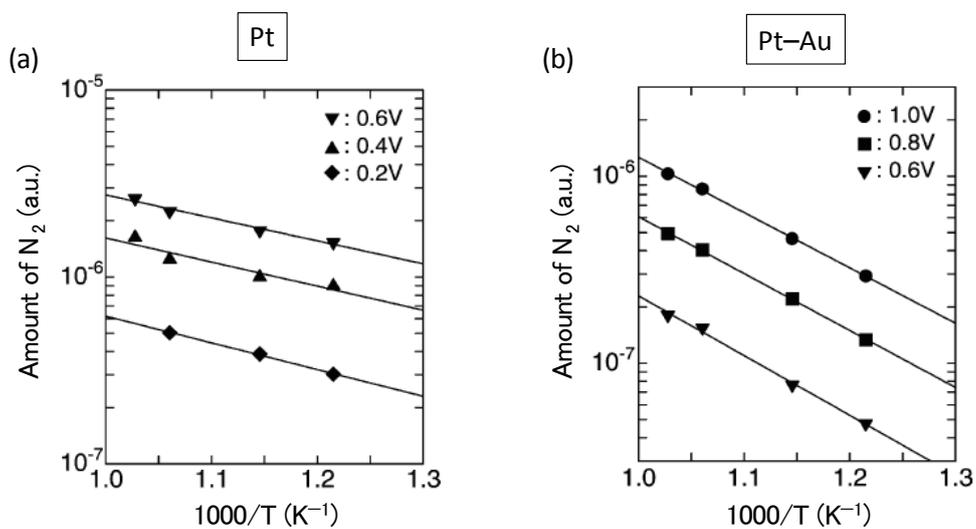


Fig. 8 Arrhenius plots for the amount of N_2 generated on (a) a Pt electrode and (b) a Pt-Au electrode.

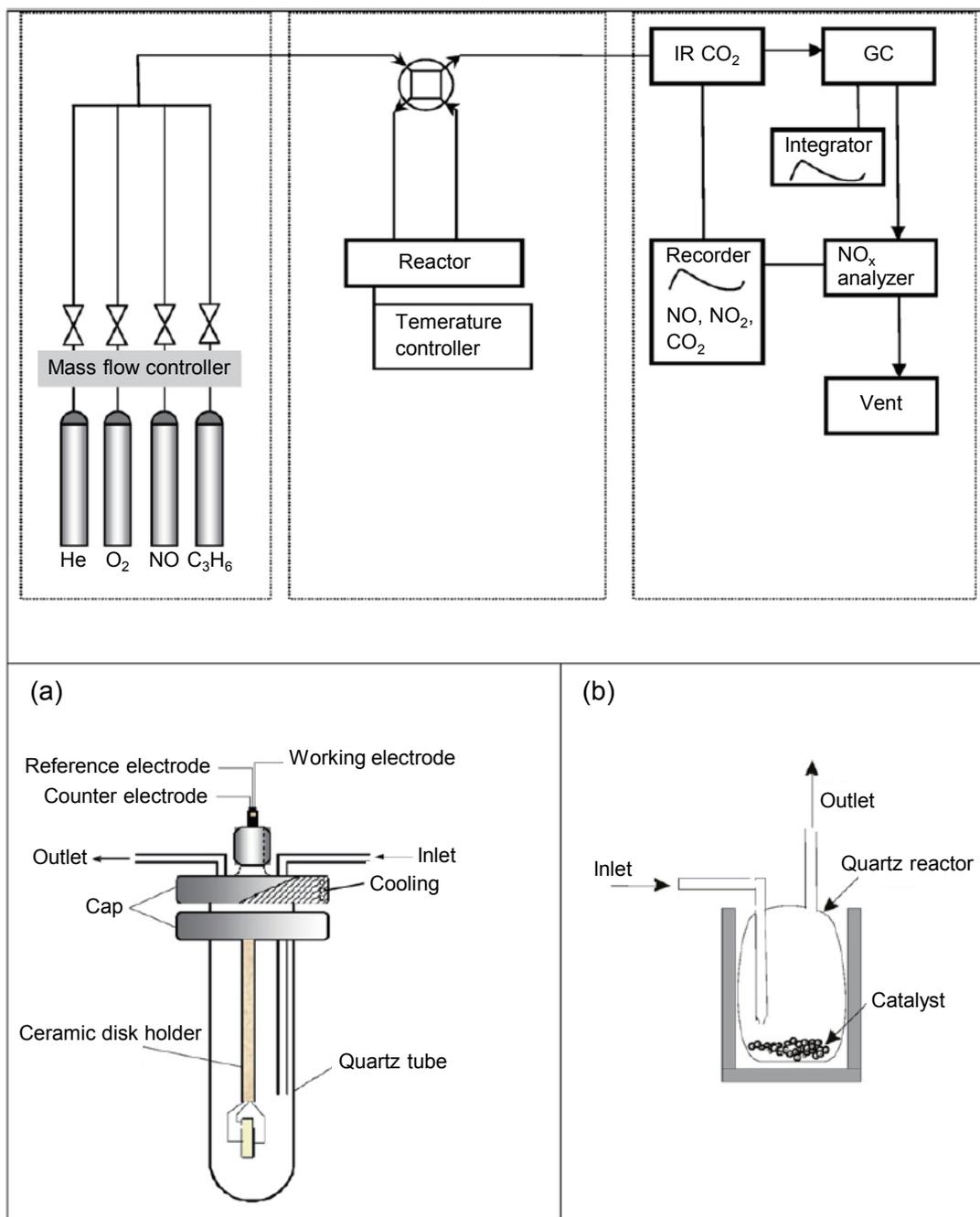


Fig. 9 Schematic of the measurement apparatus and quartz reactors (a) for an SOEC with an Rh electrode on a YSZ plate and (b) dispersed Rh particles on YSZ powder.

This result indicates the practical usefulness of electrochemical promotion.

2.4 Monolithic Electropromoted Reactor

One may consider that the SOEC shows remarkable performance as an automotive exhaust purifier with only a single cell and a low gas flow rate.⁽⁹⁾ However, for practical use in automotive applications, scaling

up the SOEC and adjustment for high gas flow rates should be considered. Therefore, a monolithic electropromoted reactor (MEPR) was developed and its catalytic performance was investigated under high gas flow rates (**Fig. 11**).

The MEPR was composed of eight 50×50 mm square plates, which were stacked in the grooves of a monolithic ceramic holder. Each plate was a Pt-Rh (1:1)/YSZ/Au-type cell, which consisted

of a thin (0.25 mm) parallel solid electrolyte plate, sputter-coated with thin (40 nm) porous catalyst electrodes. The catalytic reaction of $\text{NO}-\text{C}_2\text{H}_4-\text{O}_2$ under excess oxygen was evaluated at a high gas flow rate of 1000 cc/min.

The MEPR performed well in terms of its response

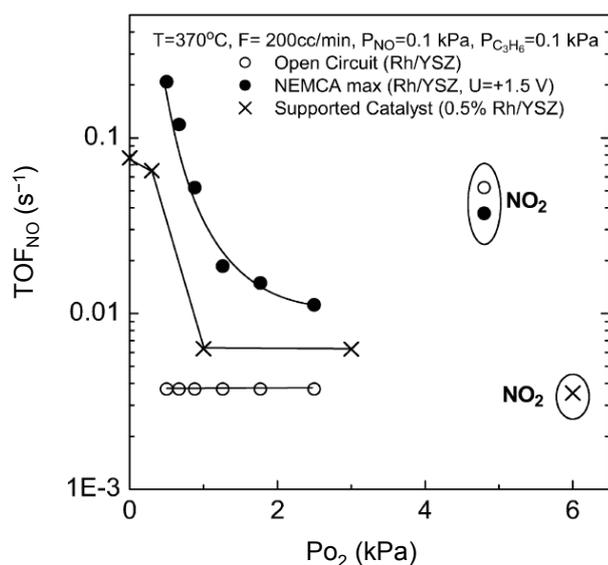


Fig. 10 Dependence of the TOF for NO reduction on the oxygen concentration (partial pressure). Here, a partial pressure of 1 kPa is equivalent to an O_2 concentration of 1%.

to the applied voltage and its stability under a high gas flow rate. **Figure 12** shows the effect of the applied voltage on the rates of CO_2 production (r_{CO_2}), NO reduction (r_{NO}), C_2H_4 conversion ($X_{\text{C}_2\text{H}_4}$), and NO conversion (X_{NO}). This was investigated under stable gas composition and gas flow rate conditions. The reaction rate enhancement ratio (ρ) and Faradaic efficiency (A) for NO reduction and C_2H_4 oxidation were calculated using Eqs. (1) and (2). The C_2H_4 conversion rate corresponding to the CO_2 production rate is shown by solid lines in Fig.12, whereas the NO conversion rate corresponding to the NO reduction rate is shown by dotted lines.

The applied voltage affected all of the reaction and conversion rates. A positive potential increased the conversion rate for both C_2H_4 and NO, and a negative potential decreased both conversion rates. In addition, it was confirmed that the performance of the MEPR was stable throughout the two-week experiment. This is a promising result for the practical utilization of the SOEC for automotive exhaust purification.

2.5 NO Permselective Cell Working at Room Temperature

Finally, we introduce a first attempt to electrochemically remove NO from excess oxygen at low temperatures using a novel electrochemical

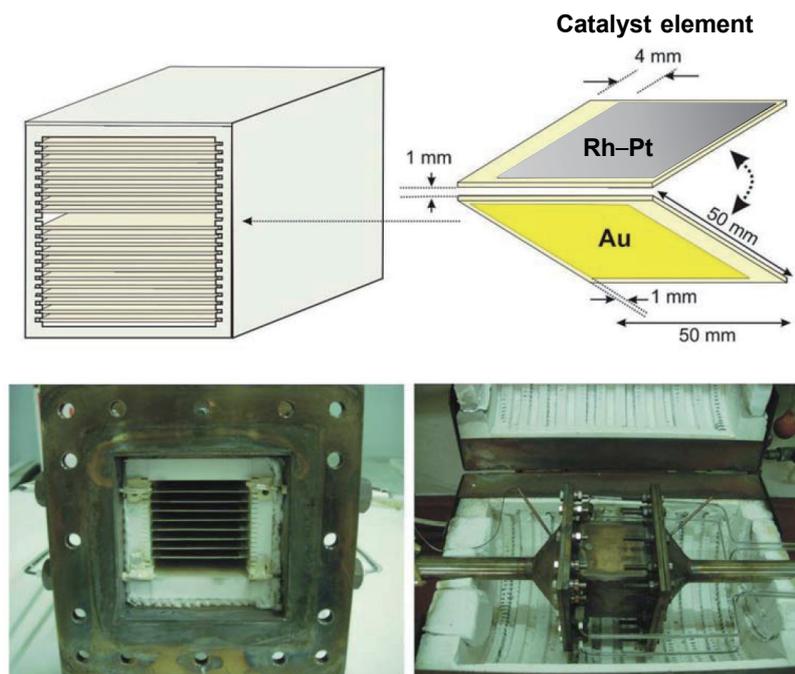
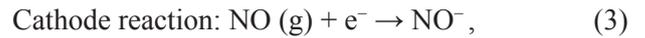


Fig. 11 Monolithic electropromoted reactor (MEPR) using 8 of a maximum of 22 cells.

ionic liquid membrane reactor (EMR).⁽¹⁰⁾ The EMR was made of a thin anodized alumina film with Pt electrodes on both sides, which was dipped into the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([C₂mim][NTf₂]).

Under an applied voltage, the EMR could transport NO selectively from the cathode side, which was subjected to a NO + O₂ gas flow, to the anode side, which was subjected to an inert He gas flow (Fig. 13). The following simple reactions are expected to occur at each electrode:



As shown in Fig. 14, during the period from 15 to 25 min, the NO concentration on the cathode side decreased and that on the anode side increased. However, O₂ on the cathode side did not pass through the EMR, either with or without the applied voltage. If we assume that the transport reaction involves one electron per NO molecule (as shown in the above reactions), the current efficiency is estimated

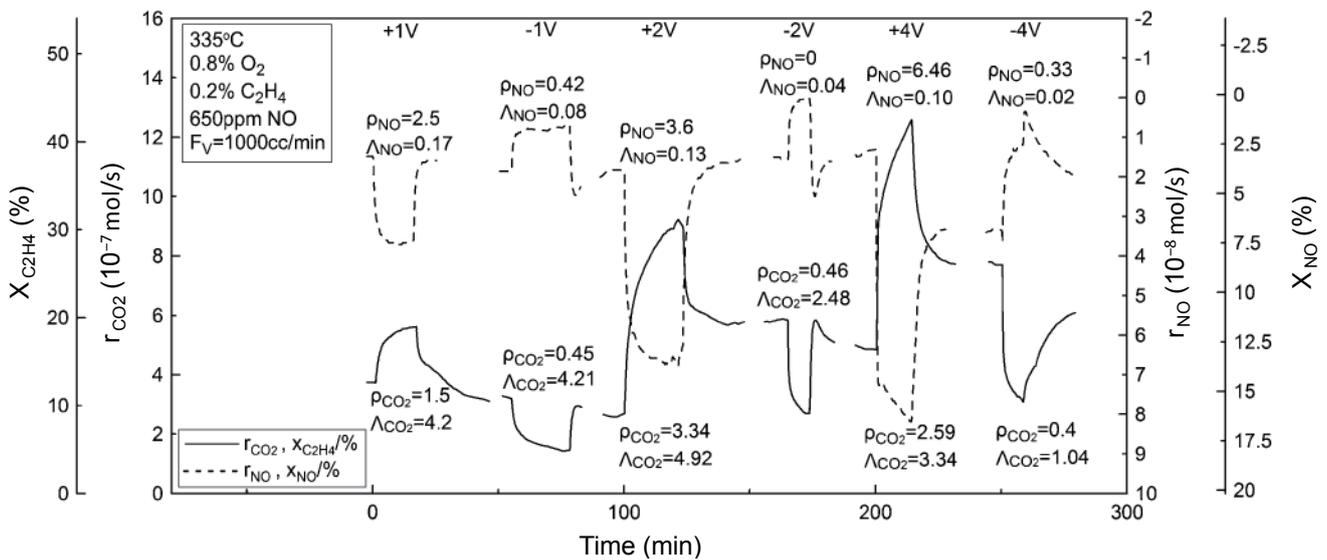


Fig. 12 Effect of the applied voltage on the NO-C₂H₄-O₂ reaction using an MEPR.

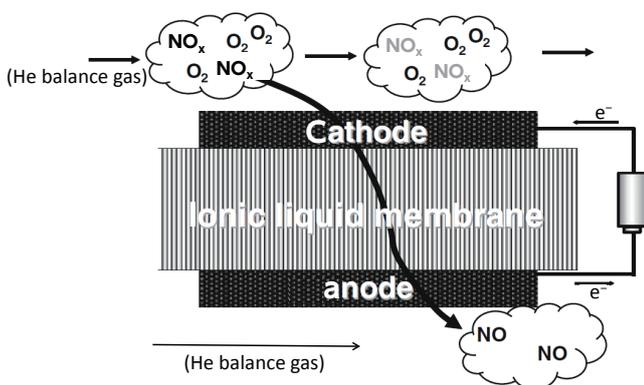


Fig. 13 An electrochemical ionic liquid membrane reactor (EMR) for selective NO permeation.

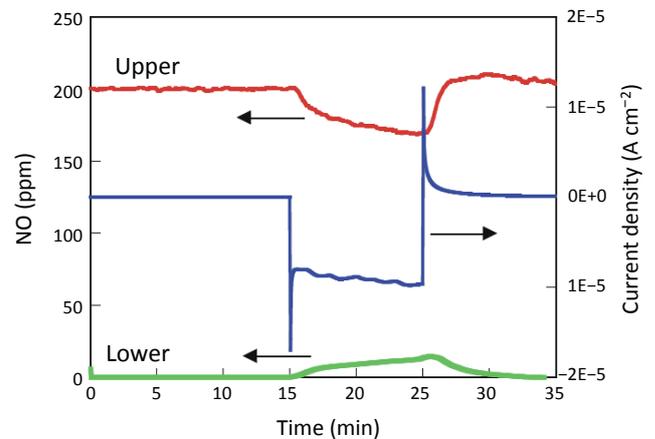


Fig. 14 Selective electrochemical NO transportation from an excess oxygen mixed gas using an EMR. The upper (anode) side gas contains 200 ppm NO + 10% O₂, and the lower (cathode) side gas contains 100% He.

to be about 20%. This indicates the possibility of operating with a higher current efficiency and at lower temperatures than conventional electrochemical reactors, such as the SOEC.

3. Conclusion

The catalytic reactor device electrochemically promoted by an electric power supply is expected to be a next-generation technology for automotive exhaust purification. Automotive exhaust conditions such as temperature, composition, and gas volume, fluctuate with the use and condition of the automobile. The results described in Sec. 2. 1 show that the catalytic performance of the device can be optimized by tuning the applied voltage. In addition, as shown in Sec. 2. 2, NO can be reduced by electrons rather than by reductant materials, which has not previously been achieved with traditional commercially available catalysts. The results described in Sec. 2. 3 imply that the device could allow a reduction in the quantity of precious metals consumed, because the TOF for the electropromoted precious metal exceeds that for traditional catalysts. The high performance of the MEPR under a high gas flow rate, as shown in Sec. 2. 4, demonstrates the easy, practical utilization of the MEPR. Furthermore, the EMR device described in Sec. 2. 5 will produce the desired NO reduction at room temperature.

We believe that this technology has the potential for use in automobiles to help overcome the serious problems with automotive exhaust purification that cannot be solved with traditional catalysts.

Acknowledgement

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Figs. 2, 3 and 4

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Figs. 9 and 10

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Yoshiyuki Sakamoto

Research Fields:

- Automotive Exhaust Catalyst
- Transient Reaction Analysis
- Electrochemical Reaction

Academic Degree: Ph.D.

