

Electrochemical removal of both NO and CH₄ under lean-burn conditions

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An electrochemical cell, Pd|YSZ|Pd, was constructed in order to remove both NO and CH₄ in the presence of excess oxygen. When direct current was supplied to the cell with a flow of a mixture of NO, CH₄, O₂, H₂O and CO₂ at 700°C, NO was reduced to nitrogen at the cathode, and CH₄ was oxidized to CO_x at both the anode and cathode. At the cathode, the reduction of NO and the oxidation of CH₄ proceeded with the removal of chemisorbed oxygen species from the Pd surface, and at the anode, the oxidation of CH₄ was enhanced by forming an active oxygen atom.

1. Introduction

Three-way automotive catalysts are effective systems for cleaning exhaust gases from gasoline engines, when used with a specified air/fuel ratio. However, this system cannot reduce NO_x in exhaust streams containing several percent of oxygen, namely, under lean-burn conditions. This defect results in serious environment problems such as acid rain and air pollution. On the other hand, although V₂O₅–TiO₂ catalysts can selectively remove NO_x, even in the presence of excess O₂ using NH₃ as a reductant, there are some disadvantages, such as facility cost and leakage of unreacted NH₃. Therefore, many attempts to develop new converter systems have been made by various research groups: for example, the adsorption [1], absorption [2], electron-impact [3] and catalytic decomposition [4, 5] or reduction processes. Among them, Cu/ZSM-5 has attracted the greatest attention, because this catalyst shows high activity for the reduction of NO with hydrocarbons under oxidizing atmospheres [6–8]. However, the coexistent gases such as H₂O and SO_x decrease the catalytic activity significantly [9, 10], and the mechanical strength is not sufficient for long operation.

The electrochemical reduction of NO using zirconia-based solid electrolytes was proposed by Huggins and coworkers [11, 12]. NO was electrolysed to N₂ and O₂ by applying a voltage of above 1 V to the cell in the region of 600 to 800°C, and O₂ migrated through the solid electrolyte from the cathode to the anode. However, it has not been reported that the electrolysis of a trace amount of NO (1000 ppm) will occur in the presence of excess oxygen. Huggins *et al.* proposed that the decomposition of NO occurred on an electrochemically reduced surface, F-centre, of zirconia [11, 12]. If so, it will be difficult to form an F-centre on zirconia under oxidizing atmospheres. Moreover, since exhaust gases generally contain H₂O, CO₂, hydrocarbons, etc. besides NO and

O₂, there arise additional problems to be solved from a practical standpoint: (i) in the electrolysis process NO, H₂O and CO₂ will be competitively electrolysed. Therefore, the electrolysis of the latter two substances must be minimized. (ii) hydrocarbons, as well as NO, must be removed from exhaust gases.

The purpose of this research is, first, to remove both NO and CH₄ under oxidizing atmospheres in the region of 650 to 750°C and, second, to eliminate the effect of the presence of H₂O and CO₂ on the removal. Here, it is reported that an electrochemical cell of simple structure and small size, Pd|YSZ|Pd, satisfies the above demands and that the mechanism of the removal of both NO and CH₄ in the present system is elucidated.

2. Experimental procedure

YSZ ceramic was prepared by pressing TZ-8Y powder (Tosoh) at 2×10^3 kg cm⁻² and then calcining it at 1550°C for 10 h. The ceramic obtained was cut into disc form of 12 mm in diameter and 0.5 mm in thickness. Two porous palladium electrodes of 0.5 cm² area were baked on both sides of the disc at 700°C. Two platinum wires served as output terminals for the two electrodes, and these were connected to a galvanostat. The reaction experiment was carried out in a flow-type apparatus, as shown in Fig. 1(a). This is termed test cell (a). The composition of the reactant gas was 1000 ppm NO, 1000 ppm CH₄, 2–10% O₂, 5% H₂O and 5% CO₂, and the flow rate was 50 ml min⁻¹. The reaction temperature was in the region of 650 to 750°C, and direct current was supplied to the test cell (a) until the terminal voltage was 5 V. The outlet gas was analysed by gas chromatography (GC) and mass spectroscopy (MS).

To clarify which electrode would reduce NO and oxidize CH₄, another test cell was constructed as shown in Fig. 1(b). This is termed test cell (b). The above described disc served as a diaphragm between

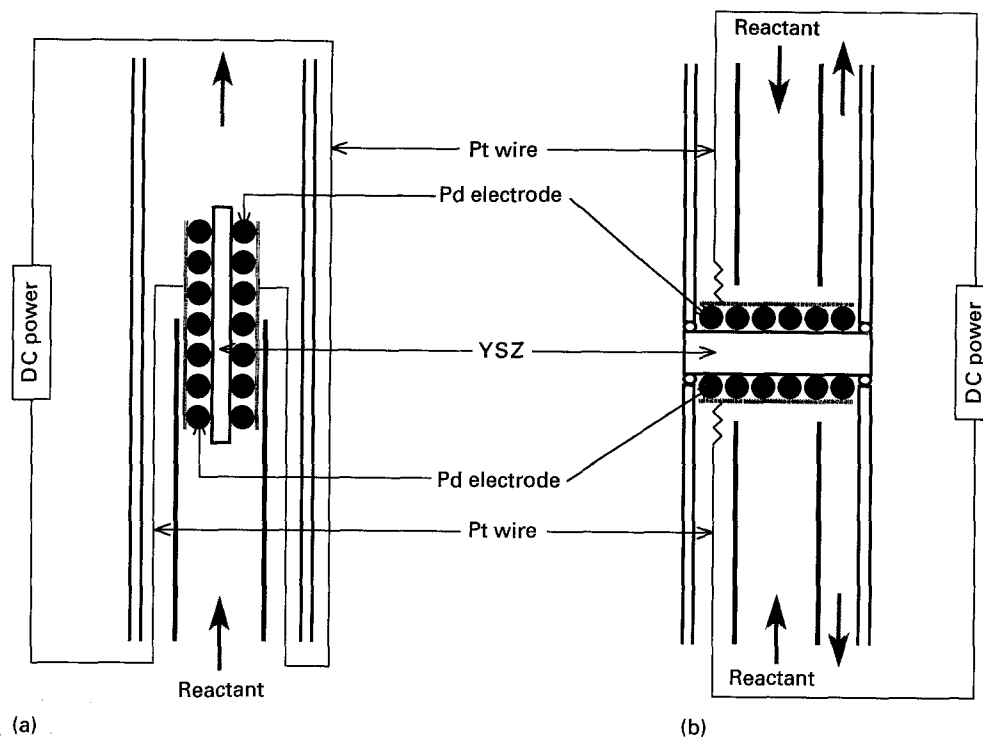


Fig. 1. Schematic illustrations of test cells (a) and (b).

two electrode compartments. Each electrode compartment was sealed by a glass ring gasket. The CH_4 -free and NO -free reactant gases were introduced into the cathode and anode compartments, respectively, or the anode and cathode compartments, respectively. The other reaction conditions were the same as above.

3. Results and discussion

3.1. Electrochemical removal of both NO and CH_4

Figure 2 shows the variations of NO and CH_4 amounts in the outlet gas from the cell (a) by switching on and off the current at 700°C . Here, the reactant amounts are calibrated to the inlet values. At open circuit, all NO was observed in the outlet gas, and CH_4 was consumed up to 26%. Thus, the palladium electrode is essentially inert to the reduction of NO , but active to the oxidation of CH_4 under oxidizing conditions. On supplying direct current of 800 mA cm^{-2} , the amount of NO was reduced by one-half from

its inlet concentration, and most of the CH_4 disappeared. In this case, the productions of N_2 and CO_x were confirmed by GC, but the productions of NO_2 and N_2O were not observed by MS. Finally, the amounts of NO and CH_4 were returned to the initial values by switching off the current. These results indicate that the present system can reduce NO to N_2 and oxidize CH_4 to CO_x electrochemically.

The variation with time of NO and CH_4 conversions at 700°C is shown in Fig. 3. Although CH_4 conversion was kept constant, NO conversion decreased slightly and then became steady. No deterioration in the NO and CH_4 conversions was found, even after 10 h. These results, when considered with the stable terminal voltage, indicate that the present system is an active and steady reactor for removing both NO and CH_4 .

The influences of various reaction conditions on the removal in the present system were examined. The dependence of NO and CH_4 conversions on the partial pressure of O_2 in the reactant stream at

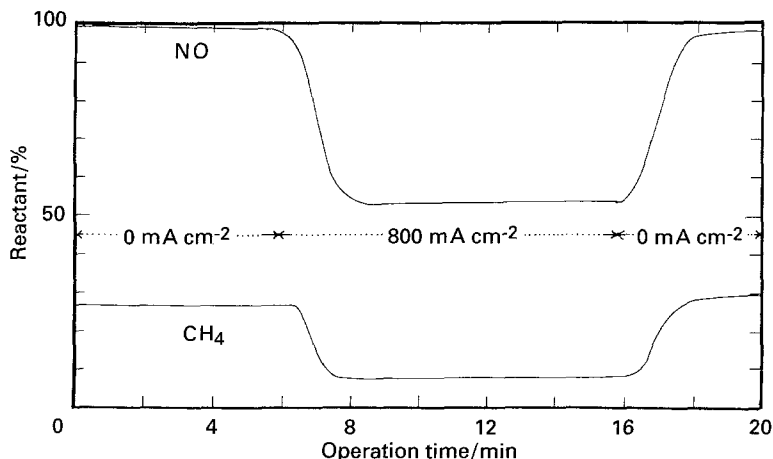


Fig. 2. Variation of NO and CH_4 reactants under direct current in the test cell (a): reaction temperature 700°C ; 1000 ppm NO , 1000 ppm CH_4 , 2% O_2 , 5% H_2O and 5% CO_2 .

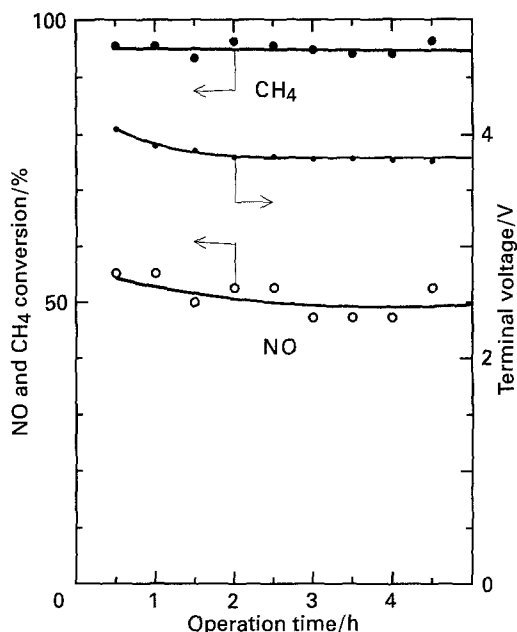


Fig. 3. Variation with time of NO and CH₄ conversions: reaction conditions as in Fig. 2.

700° C is shown in Fig. 4. In the range of 2–10%, CH₄ conversion increased with increasing current density in a similar manner. However, NO conversion was dependent on the partial pressure of O₂: NO conversion became smaller as the partial pressure of O₂ increased. This is due to the competitive electrolysis between NO and O₂ at the palladium cathode, as described later.

Figure 5 shows the dependence of NO and CH₄ conversion on the presence of H₂O and CO₂ in the reactant stream at 700° C. Neither the reduction of NO nor the oxidation of CH₄ was affected by the presence of H₂O and CO₂. Although the catalytic activity of Cu/ZSM-5 is greatly decreased by adding

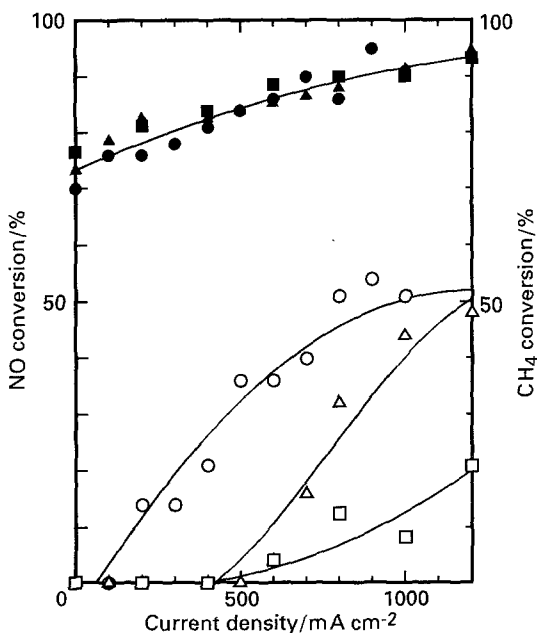


Fig. 4. Dependence of NO and CH₄ conversions in the test cell (a) on partial pressure of O₂: reaction temperature 700° C; 1000 ppm NO, 1000 ppm CH₄, 5% H₂O and 5% CO₂; 2% O₂ (O●), 6.6% O₂ (Δ▲), 10% O₂ (□■), the open and closed symbols are NO and CH₄ conversions, respectively.

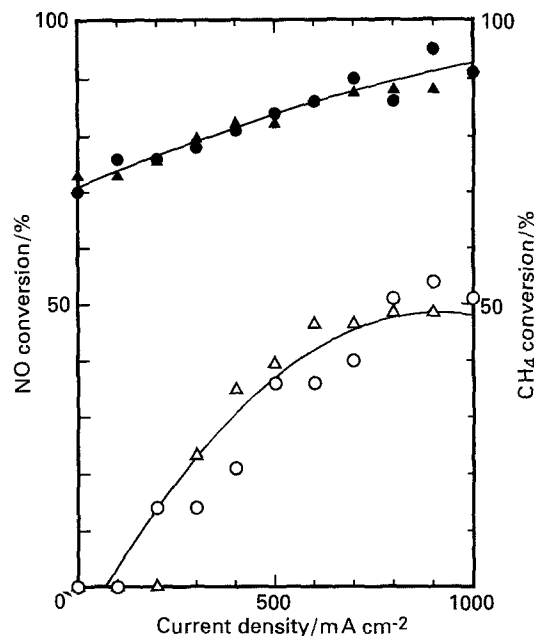


Fig. 5. Dependence of NO and CH₄ conversions in the test cell (a) on presence of H₂O and CO₂: reaction temperature 700° C; 1000 ppm NO, 1000 ppm CH₄ and 2% O₂; 5% H₂O and 5% CO₂ (O●), 0% H₂O and 0% CO₂ (Δ▲), the open and closed symbols are NO and CH₄ conversions, respectively.

H₂O in the reactant gas [9, 10], the present system is independent of such a problem. This can be explained by the fact that, since H₂O is not appreciably electrolysed at the palladium cathode, this molecule does not interfere with the electrolysis of NO, as described later.

The reaction was carried out at 650–750° C (±1° C). The results are summarized in Fig. 6. CH₄ conversion increased with increasing temperature, while NO conversion was almost independent of temperature. In other words, the electrolysis rate of NO was dependent only on the transfer flux of oxide ion

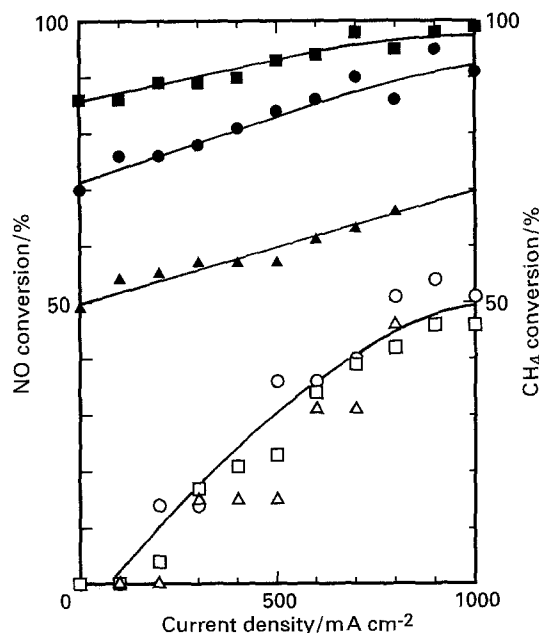


Fig. 6. Dependence of NO and CH₄ conversions in the test cell (a) on reaction temperature: 1000 ppm NO, 1000 ppm CH₄, 2% O₂, 5% H₂O and 5% CO₂; 650° C (Δ▲), 700° C (O●), 750° C (□■), the open and closed symbols are NO and CH₄ conversions, respectively.

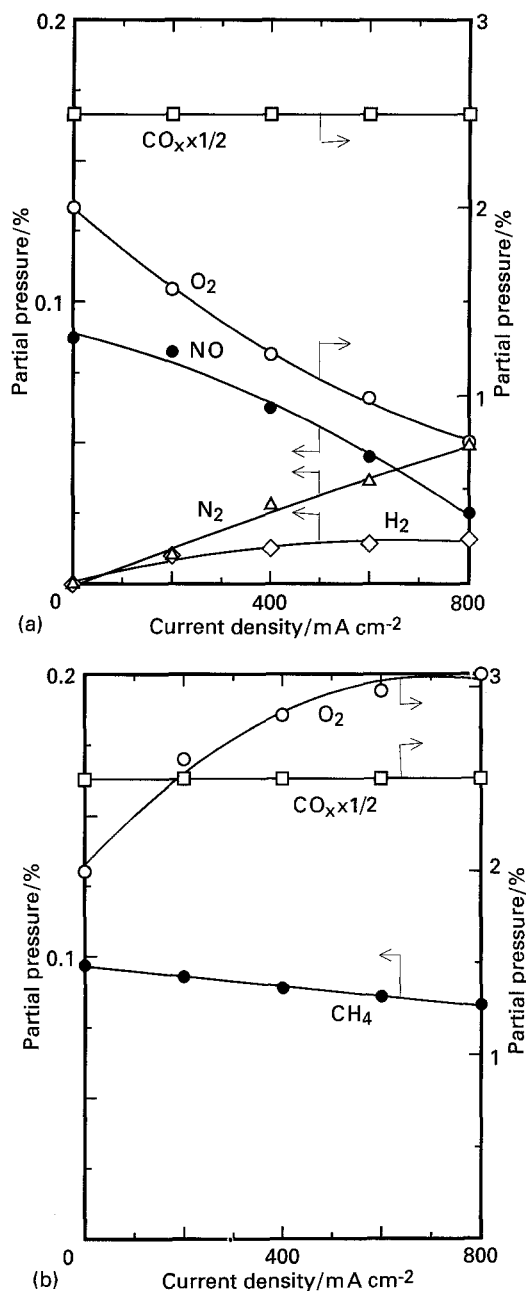


Fig. 7. Composition of the outlet gases: (a) at the cathode in the test cell (b) with reaction temperature 700°C, 1000 ppm NO, 2% O₂, 5% H₂O and 5% CO₂; and (b) at the anode in the test cell (b) with reaction temperature 700°C, 1000 ppm CH₄, 2% O₂, 5% H₂O and 5% CO₂.

from the cathode to the anode. However, according to Huggins *et al.*, the electrolysis rate of NO showed Arrhenius-type behaviour under O₂-free conditions [11, 12]. This disagreement suggests that the mechanism of NO reduction in the present system is different from that proposed by Huggins *et al.* The present mechanism will be discussed below.

A large current cannot be sent to the test cell below 600°C, because of the large ohmic resistance. It is necessary to reduce the thickness of the YSZ disc by a means of EVD (Electrochemical Vapor Deposition) method [13] to lower the reaction temperature.

3.2. Mechanism of electrochemical removal

Cell (b) was used to explain the mechanism of NO and

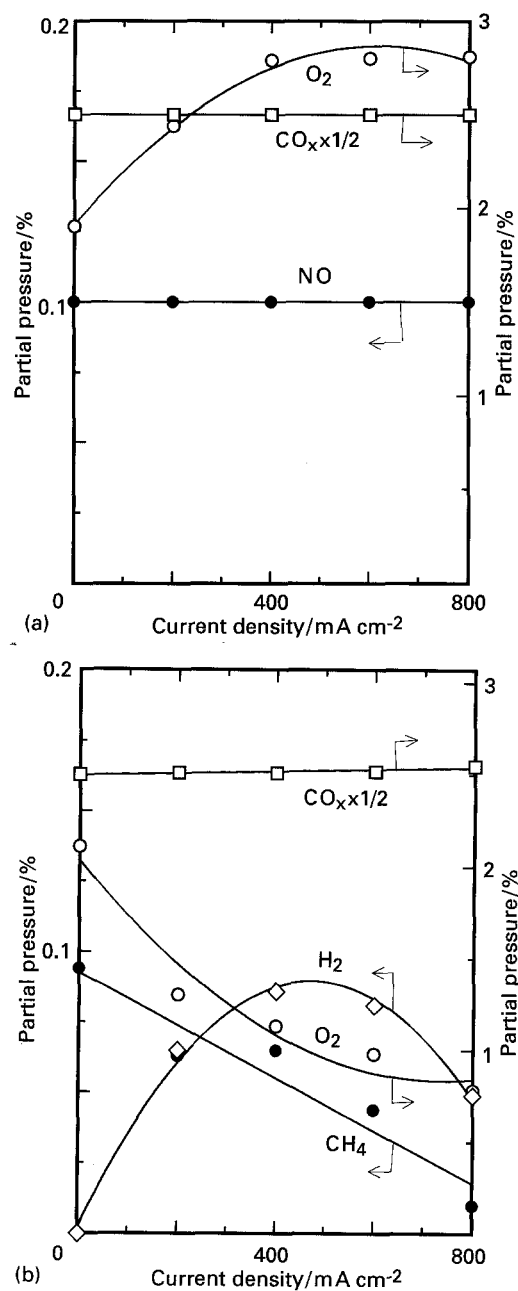
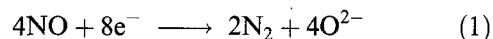


Fig. 8. Composition of the outlet gases: (a) at the anode in the test cell (b) with reaction temperature 700°C, 1000 ppm NO, 2% O₂, 5% H₂O and 5% CO₂; and (b) at the cathode in the test cell (b) with reaction temperature 700°C, 1000 ppm CH₄, 2% O₂, 5% H₂O and 5% CO₂.

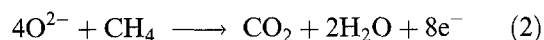
CH₄ removal in the present system. First, the CH₄- and NO-free reactant gases were introduced into the cathode and anode compartments, respectively. The results are summarized in Fig. 7(a) and (b). In the outlet gas of the cathode compartment, on imposing direct current to cell (b), the partial pressures of O₂ and NO decreased at the same time, and N₂ and a small amount of H₂ were produced. This suggests that NO, as well as O₂, is electrolysed at the cathode as follows:



Here, the electrolytic amounts of NO and O₂ at any current density were roughly in the ratio of 1 to 40, which was equal to the proportion of their constituent oxygen atoms in the reactant gas. This means

that NO is electrolysed in competition with O₂. On the contrary, from the observation of a small amount of H₂ and CO, one would expect that H₂O and CO₂ scarcely interfere with the electrolysis of NO. The above mechanism clearly differs from that based on the F-centre on zirconia. At least, the decomposition of NO at low current densities, where the partial pressure of O₂ is still high, cannot be explained by the formation of the F-centre. Aminarzmi *et al.* proposed that the decomposition of NO was enhanced by removing O₂ from the platinum surface [14]. Assuming that this is also the case for the palladium electrode, the mechanism of NO decomposition in the present system is ascribed to the electrolytic removal of O₂ from the palladium surface.

In the outlet gas of the anode compartment, with direct current to cell (b), the partial pressure of O₂ increased, and that of CH₄ decreased. Consequently, oxygen atoms are formed at the anode, and some oxidize CH₄ as follows:



Here, it seems reasonable to consider that CH₄ reacts with oxygen atoms rather than molecules, because CH₄ conversion is not dependent on the partial pressure of O₂, as shown in Fig. 4.

Next, the CH₄- and NO-free reactant gases were introduced into the anode and cathode compartments, respectively. The results are summarized in Fig. 8(a) and (b). In the outlet gas of the anode compartment, there was no change, except for the partial pressure of O₂. This suggests that NO is reduced to N₂ only at the cathode of the cell (a). Consequently, NO conversion cannot exceed 50% in the cell (a), because only half of the reactant gas passes the cathode.

By contrast, in the outlet gas of the cathode compartment, large changes were observed: the partial pressure of CH₄, as well as O₂, drastically decreased, and H₂ and CO_x were produced. Taking into account that the electrolytic amounts of H₂O and CO₂ were very small at the cathode, as shown in Fig. 7(a), H₂ and CO_x would be formed not by electrolysis of H₂O and CO₂, respectively, but by oxidizing CH₄. These results indicate that CH₄ is oxidized at the cathode according to a mechanism different from Equation 2. In the presence of excess O₂, the palladium electrode will be partially oxidized, and its catalytic activity will be lowered. In fact, the ohmic resistance of the cell (a) was decreased by replacing the reactant gas with Ar or N₂. As a result of the cathodic discharge, the oxygen-species on the palladium electrode are removed, and its catalytic activity is enhanced. However, since the partial pressure of O₂ in the

neighbourhood of the palladium electrode is low, CH₄ is partially oxidized to CO and H₂, as shown in Fig. 8(b). Therefore, it is concluded that CH₄ is oxidized to CO_x at both the anode and cathode of the cell (a).

4. Conclusions

The principal conclusions can be summarized as follows:

- (i) When a Pd|YSZ|Pd cell of simple structure and small size is placed in a flow of a NO and CH₄ mixture around 650–750°C with direct current, both NO and CH₄ can be removed, even under an oxidizing atmosphere. No deterioration of activity is found in the presence of H₂O and CO₂.
- (ii) NO is reduced to N₂ at the cathode. In this case, the decomposition of NO is enhanced by removing the oxygen-species from the palladium surface electrochemically. CH₄ is oxidized to CO_x at both the anode and cathode. CH₄ is subject to combustion at the anode and partially oxidized to CO and H₂ at the cathode.

This simple cell, which eliminates two electrode compartment geometries, is practical for application to converter systems. If a cascade of such cells is constructed, the present system will further remove both NO and CH₄ from exhaust gases under oxidizing atmospheres.

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