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Selective decomposition of NO in the presence of excess O_2 in electrochemical cells

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Abstract

NO decomposition in solid electrolyte cells was investigated in the presence of excess O_2. The results show that NO is decomposed via an electrocatalytic mechanism rather than electrolysis in the range of 1–4 V of applied voltage. The NO is catalytically decomposed to N_2 on the cathode surface and O^{2-} produced *in situ* is transferred through the yttria-stabilized zirconia (YSZ) to the anode by direct current (d.c.) and then is evolved in the form of O_2, which helps to maintain the active state of the cathode. In a Pd/YSZ/Pd cell, the palladium metal surface is the active site for NO decomposition, while in the RuO_2/Pd/YSZ/Pd cell, the partially reduced RuO_x ($0 < x < 2$) is the main active site for NO decomposition. At 600 °C, the rate-determining step for the overall transportation of O^{2-} from cathode to anode in the RuO_2/Pd/YSZ/Pd cell is the transportation of O^{2-} at the cathode Pd/YSZ interface. The transportation rate of O^{2-} at the cathode M/YSZ interface decreases in the order of Ag > Au > Pd > Pt. Substitution of the Pd cathode by Ag leads to an increase in current density by a factor of 3.5. A higher NO decomposition parameter (α=13.4) is also achieved at a lower temperature of 500 °C.

1. Introduction

NO_x in exhaust gas from diesel and lean-burn engines has been known to be barely removed because the widely-used three-way catalysts are less active in the presence of excess O_2. To improve the efficiency for removal of NO_x, a number of methods including direct decomposition and selective catalytic reduction (SCR) have been developed, in which the catalyst is the central part. Of the catalysts tested so far, Cu-exchanged zeolite has attracted much attention because of its high catalytic activity for the reduction of NO_x in the presence of hydrocarbons under oxidizing conditions [1]. Nevertheless, its activity is significantly impaired in the presence of water vapour [2]. Huggins proposed the electrochemical reduction of NO in a solid electrolyte cell with platinum electrodes [3, 4]. By applying a direct electric potential, NO is decomposed to nitrogen and oxygen at the cathode, and the oxygen formed *in situ* is ionized and pumped to the anode through the solid electrolyte at a temperature higher than 700 °C.

Recently, Hibino et al. have reported the reaction of NO–CH_4–O_2 mixtures in a Pd/YSZ/Pd cell [5, 6], in which a high current density is required to attain substantial NO conversion because O_2 in the reactant gases is adsorbed and ionized by the cathode in preference to the oxygen released from the NO decomposition.

As the temperature of exhaust gases is generally in the range 300–500 °C, it is important to study the decomposition of NO in solid electrolyte cells at lower temperatures with higher current efficiency. The main purpose of this work is to design an effective electrochemical cell for decomposition of NO in the exhaust gas from diesel and lean-burn engines. The mechanism of NO decomposition in the presence of O_2 in the electrochemical cells is also addressed.

2. Experimental details

2.1. *Preparation of electrochemical cell*

A YSZ disc was prepared by pressing 8 mol % yttria-stabilized zirconia (YSZ) powder (Tosoh-Zirconia TZ-8YS) at 200 MPa and then sintering at 1400 °C for 4 h. Metal electrodes were obtained by smearing the metal paste on both sides of the YSZ disc of a diameter 14.00 ± 0.05 mm and calcining at 1200 °C for the Pd electrode and 800 °C for the Ag electrode. For the Ag / YSZ/ Pd cell, the Pd electrode was smeared and calcined first, and then the Ag electrode was made. The smearing process and calcination were repeated several times until the resistance along the disc diameter dropped to 0.2 Ω. The SEM study revealed that the Ag electrodes calcined at 800 °C and the Pd electrodes calcined at 1200 °C had net-like morphology, which agrees with literature results [7]. The thickness of the calcined YSZ disc was 0.30 ± 0.05 mm unless specifically stated otherwise. In order to study the effect of the thickness of YSZ on the properties of the cell, the YSZ discs with different thickness were tested. As a catalyst, RuO_2 coating layer was prepared on the Pd or Ag cathode by smearing the RuO_2 paste and then calcining at 800 °C.

2.2. *Electrochemical decomposition of NO*

The apparatus for electrochemical decomposition of NO is schematically shown in Figure 1. The experiments were carried out at a given temperature by applying a potential to the two electrodes. A mixture gas of 1000 ppm NO and 6 vol% O_2 in helium was passed through the quartz reactor at a rate of 50 ml min^{-1}. The outlet gases were analysed by gas chromatography (HP6890) with a capillary column (HP-PLOT/Zeolite 30 m × 0.32 mm × 12 μm) and TCD at 40 °C.

It should be noted that for the experimental set-up adopted in the present study, only half of the outlet gases passed by the cathode. This means that the maximum NO conversion is 50%. For each run, the applied potential was swept twice from 0 to 4.4 V in a terrace-pattern for 20 min at each voltage stage in one cell and the NO conversion data were collected in the second run. In the present study, a parameter α is adopted to define the selective conversion of NO, which is expressed as

$$\alpha = \frac{Conv_{\cdot NO}}{Conv_{\cdot O_2}}$$

where the $Conv_{\cdot O_2}$ is the ratio of O_2 decomposed on the cathode to that in the fed gases. The decomposed amount of O_2 on the cathode was calculated from the d.c. current according to Faraday's law. Obviously, NO is decomposed unselectively in the cell if α=1; in other words, when $\alpha > 1$ or $\alpha < 1$ then NO or O_2 is decomposed selectively. Moreover, the higher the value of parameter α, the greater the current efficiency for NO decomposition.

3. Results and discussion

3.1. *Properties of Pd/YSZ/Pd cell for NO decomposition*

When the circuit was open, no catalytic activity for NO decomposition in the Pd/YSZ/Pd cell was observed at 700 °C. When a potential was applied and the voltages were swept stepwise as described in the experiment section, the performances of the electrochemical cells varied in terms of the NO decomposition. As can be seen in Figure 2(a), in the first run, no detectable NO decomposition is observed in the Pd/YSZ/Pd cell, though a substantial d.c. current passes through the YSZ layer as shown in Figure 2(b). In the second run, the electrochemical promotion effect for the decomposition of NO can be observed but it becomes less gradually in the third and fourth runs. This means that an electrocatalytic mechanism is involved rather than an electrolysis one, simply because the NO decomposition initiates at different voltages and current densities.

It is well known that the oxide state of palladium is almost inactive for NO decomposition. With this in mind, in the as-prepared Pd/YSZ/Pd cell, the Pd electrode surface would be covered with the palladium oxides, which accounts for why no NO decomposition was observed when the circuit was open. In the first run, though the O^{2-} species were pumped from the cathode to the anode continuously, the Pd electrode still remained inactive due to insufficient Pd surface. During the second run, more O^{2-} species were pumped from the cathode to the anode, which causes more Pd surface to be exposed. Because of this, the Pd/YSZ/Pd cell showed a higher activity for NO decomposition in the second run. This finding can also be extended to explain why the Pd electrode calcined at 800 °C requires a larger current density than that calcined at 1300 °C for NO decomposition as reported by Nakatani [7]. The reason is that the Pd electrode calcined at 800 °C is porous and has a much larger oxidized surface than the Pd electrode calcined at 1300 °C. Hibino et al. [8] also suggested that

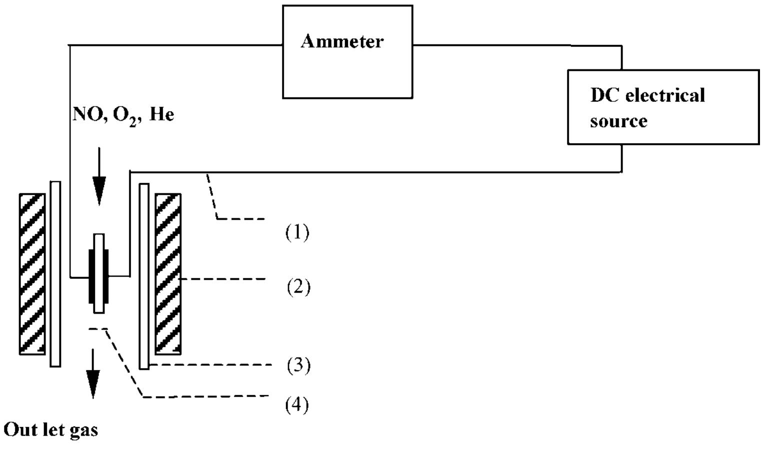

Fig. 1. Schematic illustration of the apparatus for NO electrochemical decomposition.Key: (1) electric leads, (2) electric furnace, (3) quartz reactor, (4) electrochemical cell.

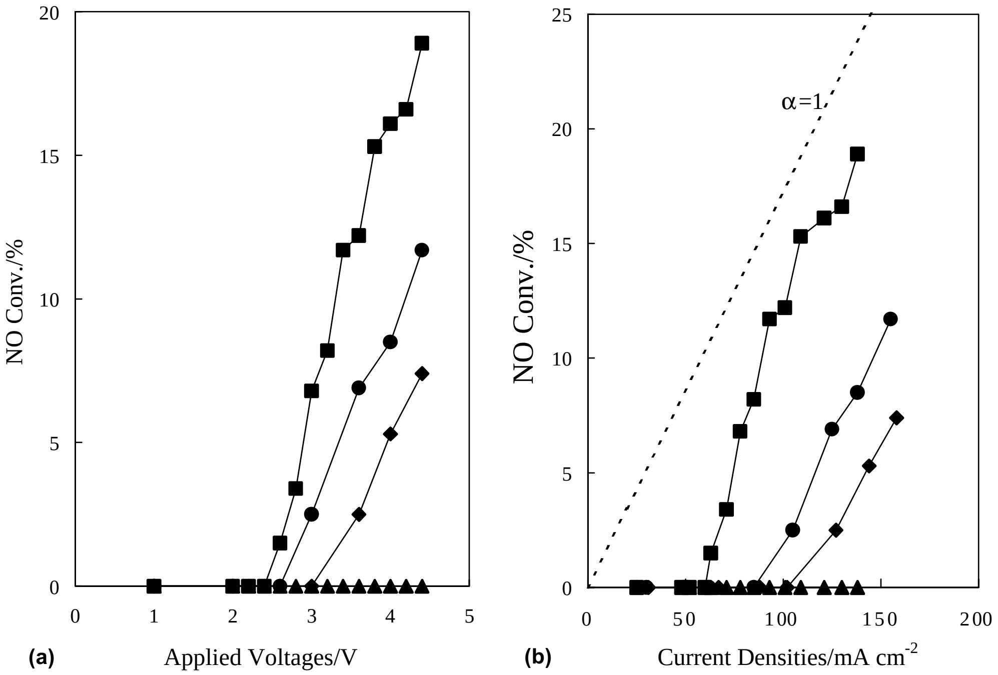

Fig. 2. Dependence of NO conversion on voltages (a) and on current densities (b) in the Pd/YSZ/Pd cell. Key:(▲) in the first run; (■) second run; (●) third run;(◆) fourth run. Reaction conditions: temperature, 973 K; fed gas, NO 1000 ppm and O_2 6 vol% in He; total flow rate 50 ml min^{-1}. Dashed line in Figure 2(b) corresponds to an unselective reaction of NO and O_2 in the cell (α=1).

the calcinations of Pd electrode at 1450 °C depressed the oxidation of Pd to PdO at temperatures below 800 °C.

In the Pd/YSZ/Pd cell, it has been found that for a given voltage, the current density tended to increase and became constant as the test was repeated. Thus, a new mechanism must be involved in this process, which is schematically shown in Figure 3. When the voltage exceeds a certain value at which the rate of O^{2-} being pumped from YSZ electrolyte to anode equals the diffusion rate of O^{2-} from the cathode Pd surface to the three-phase (Pd phase, YSZ phase and gas phase) interfaces (abbreviated as TPI), the zirconia near the TPI in the YSZ cell would be reduced partially. Similar results were reported by Guillou [9] and Casselton [10], but in their cases no oxygen was used. They found that zirconia became black at high applied voltage, which was attributed to electroreduction of the zirconia in the solid electrolyte. Huggins and coworkers studied a scandia stabilized zirconia solid state electrochemical cell in NO free of O_2 at 900 °C [3, 4], in which the partial reduction of zirconia; was also observed when a high potential was applied. They believed that for the NO decomposition in the Pt/ScSZ/Pt cell, the NO decomposition took place on the surface of solid electrolyte that was partially reduced. In our case, O_2 is used and it is more active than NO for the partially reduced zirconia; we believe that the excess O_2 would be preferably adsorbed on the partially reduced zirconia near the TPI. The voltage-sweeping at high voltages results in a wider partially-reduced area that surrounds the Pd cathode. Consequently, the NO conversion would be decreased in the same Pd/YSZ/Pd cell at a given current density as the test runs were repeated.

In the Pd/YSZ/Pd cell, at any d.c. density for all runs, the values of the parameter α were less than 1, for instance, the maximum value of α at 109 mA cm^{-2} in the

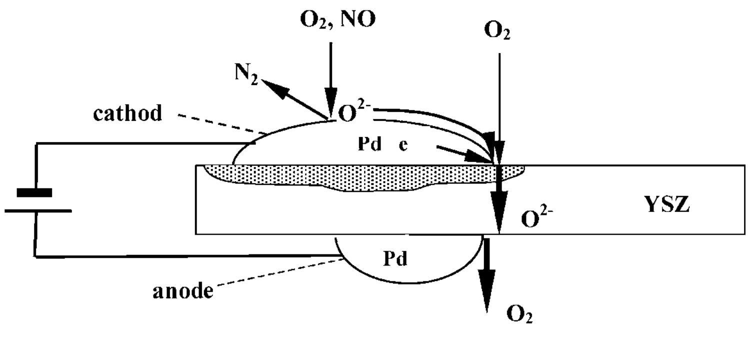

Fig. 3. Schematic mechanism of the NO electrochemical decomposition in the Pd/YSZ/Pd cell in excess O_2. (The shaded area denotes partially reduced zirconia in the YSZ by the DC potential).

second run was 0.8, implying that in comparison to NO in the reaction system, O_2 would be preferably adsorbed on the Pd cathode surface. Similar results were reported by Huggins and coworkers who suggested that the catalytic decomposition of NO in Pt/ScSZ/Pt cell was inhibited by O_2, which was believed to be due to the preferential chemisorption of O_2 over NO and the possible formation of inactive platinum oxide surface on the cathode [3, 4].

3.2. *Properties of RuO_2/Pd/YSZ/Pd cell for NO decomposition*

The RuO_2/Pd/YSZ/Pd cell was obtained by coating RuO_2 on the Pd/YSZ/Pd cathode. At 700 °C, the RuO_2/Pd/YSZ/Pd cell in the NO–O_2–He fed gases showed no catalytic activity for NO decomposition, which is similar to the Pd/YSZ/Pd cell discussed above. The NO conversion at different reaction temperature is correlated to the voltages and the current densities, as shown in Figure 4(a) and (b), respectively. By coating RuO_2 layer on the Pd/YSZ/Pd cell, the parameter α over 1 for NO decomposition can be obtained at appropriate current densities. At 700, 650 and 600 °C, the α value reaches 1.2 at 129 mA cm^{-2}, 2.4 at 55 mA cm^{-2}, and 2.0 at 24 mA cm^{-2}, respectively. This implies that for NO decomposition, the partially reduced ruthenium oxide is more active than the palladium metal. For the RuO_2/Pd/YSZ/Pd cell, the variation tendency of the parameter α in the temperature range 650 °C to 750 °C is as follows: The lower the reaction temperature, the higher the α value. Here it should be noted that at 600 °C, no larger value of parameter α is observed, as can be seen in Figure 4(b), which is probably due to the lower current densities. In other words, the resistance to the O^{2-} transportation from the cathode to the anode is so great that the partially reduced ruthenium oxide could not be sufficiently generated on the cathode. This means that the lower reaction temperature is beneficial to the chemisorption of NO on the partially reduced ruthenium oxide rather than to the adsorption of O_2.

In the RuO_2/Pd/YSZ/Pd cell, as the applied voltage was increased from 0 to 4 V, a maximum NO conversion was obtained both at 650 °C and 700 °C. Moreover, at the higher reaction temperature, a higher applied voltage is necessary to obtained the maximum conversion, as shown in Figure 4(a). This implies that for NO decomposition, the most active species are the oxides of ruthenium with a valence between 0 and 4 that are retained by a balance of oxidation and electric reduction. Because the oxidation rate of the Pd cathode and ruthenium oxide coating layer is a certain value at a given temperature, the active state of ruthenium cannot be maintained, either at higher or lower voltages. The Pd cathode and ruthenium oxide coating layer in reactant gases are oxidized more rapidly at higher temperatures, and thus, the higher voltage is necessary for the removal of the excess O^{2-}.

3.3. *Factors influencing current density*

Based on the results discussed above, it is clear that for NO decomposition, it is important to keep the reaction temperature as low as possible to increase the value of the parameter α, and it is also crucial to reduce the transportation resistance of O^{2-} in the cell, which helps to maintain the current density. The total transportation resistance of O^{2-} from cathode to anode can be considered as a sum of three parts: the resistance from the cathode to the YSZ layer, the resistance of the YSZ

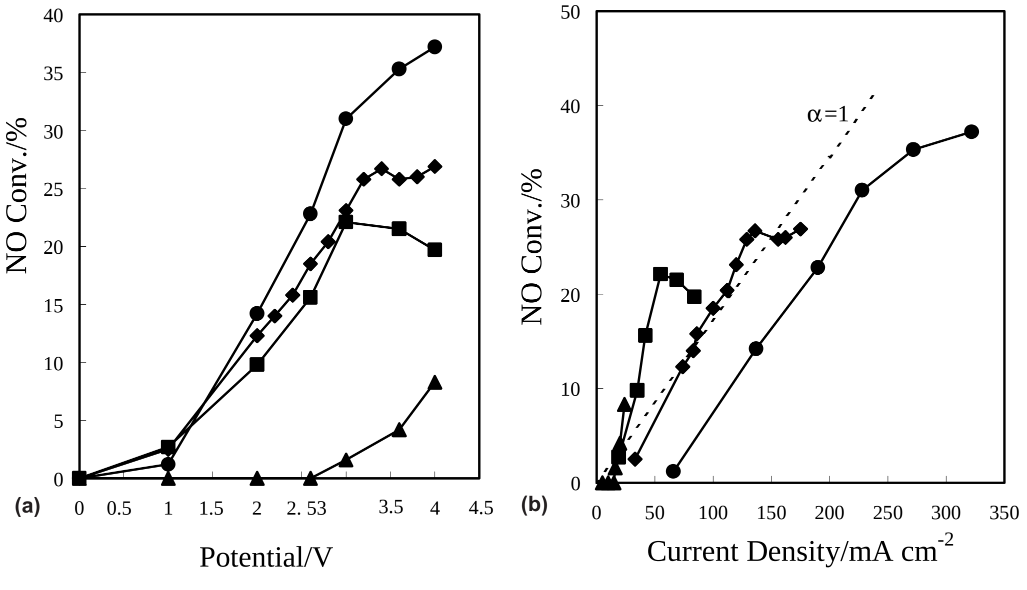

Fig. 4. Dependence of NO conversion on voltages (a) and current densities (b) in RuO_2/Pd/YSZ/Pd cell. Key: (▲) 600 °C, (■) 650 °C, (◆) 700 °C and (●) 750 °C. Other conditions: fed gas, NO 1000 ppm and O_2 6 vol% in He; total flow rate, 50 ml min^{-1}. Dashed line in the Figure 4(b) corresponds to an unselective reaction of NO and O_2 in the cell (α=1).

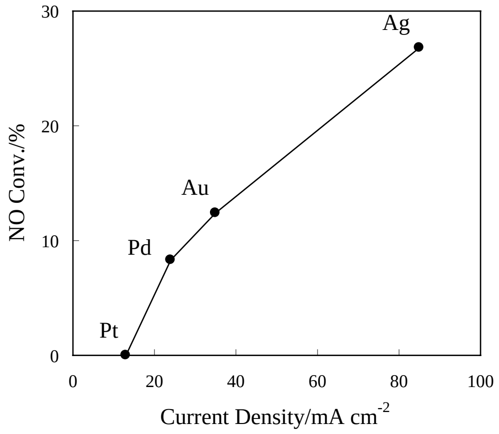

Fig. 5. NO conversion as a function of current densities in the RuO_2/metal/YSZ/Pd cells. Reaction conditions: 1000 ppm of NO and 6 vol% of O_2 in He with the total flow rate of 50 ml min^{-1} at 600 °C and at an applied voltage of 4.0 V.

layer, and the resistance from the YSZ layer to the anode.

As shown in Table 1, the thickness of YSZ has little influence on both the current density and NO conversion, therefore it can be concluded that the transportation of O^{2-} in the YSZ layer is not the rate-determining step in the whole process of O^{2-} transportation in the cell. Based on the relationship between the activity change for NO decomposition in the Pd/YSZ/Pd cell and the voltage sweeping times, we suggested in Section 3.1 that some palladium atoms still existed in oxidized state on the cathode when the YSZ surrounding Pd cathode had been partially reduced by the electric potential. This suggests that the rate-determining step is the transportation of O^{2-} from the cathode into the YSZ layer.

In addition to the Pd metal, other metals such as Pt, Au and Ag metals were also tested as cathode with an aim of improving the transportation of O^{2-} at the cathode/YSZ interface. As shown in Table 2, the current density is strongly affected by the cathode metal. At 600 °C, the current density at 4 V is 35 mA cm^{-2} in the RuO_2/Au/YSZ/Pd cell, and 85 mA cm^{-2} in the RuO_2/Ag/YSZ/Pd cell, which are 1.5 and 3.5 times as high as that in the RuO_2/Pd/YSZ/Pd, respectively. However, in the case of the RuO_2/Pt/YSZ/Pd cell, the current density is only 50% in comparison to the cell with Pd cathode under the same conditions. These results further suggest that the transportation of O^{2-} from the cathode into the YSZ layer is the rate-determining step. Of the metals tested, Ag is the most effective one to transport O^{2-} from cathode into the YSZ phase. At the same time, the NO conversion is greatly increased as expected by enhancing the current density.

In comparison to the RuO_2/metal/YSZ/Pd cells, metal/YSZ/Pd cells exhibited no NO conversion at 600 °C regardless of metal cathode tested at 4 V. Even though the current density in the Ag/YSZ/Pd cell reached 40 mA cm^{-2}, no activity for NO decomposition was observed. The results indicate that the RuO_2 coating layer plays a key role for NO decomposition.

For all the metal/YSZ/Pd cells, the current density increases obviously after the cathode is coated with RuO_2 as shown in Table 2. All of the metal cathodes tested have a net-like morphology and RuO_2 is an electron conductive material. Accordingly, the increase in current density in the cell with the RuO_2 coating layer can be attributed to the transportation of O^{2-} in RuO_2 to the YSZ layer. The difference in current density between the RuO_2/metal/YSZ/Pd cell and the counterpart metal/YSZ/Pd cell was greatly influenced by the metal cathode, though there was not much difference in

Table 1. Performance of RuO_2/Pd/YSZ/Pd cells with different YSZ thickness in NO decomposition

Coating layer	Cathode	Anode	YSZ thickness /mm	Current densities /mA cm^{-2}	NO conv. /%
RuO_2	Pd	Pd	0.53	22	7.1
RuO_2	Pd	Pd	0.32	24	8.3
RuO_2	Pd	Pd	0.18	28	10.2

Reaction conditions: 600 °C, 1000 ppm of NO and O_2 6 vol% in helium with the total flow rate of 50 ml min^{-1} at applied voltage of 4.0 V

Table 2. Performance of different electric cells in NO decomposition

Coating layer	Cathode	Anode	YSZ thickness /mm	Current densities /mA cm^{-2}	NO conv. /%
RuO_2	Pd	Pd	0.32	24	8.3
RuO_2	Pt	Pd	0.28	13	0
RuO_2	Au	Pd	0.35	35	12.4
RuO_2	Ag	Pd	0.33	85	26.8
none	Pd	Pd	0.30	12	0
none	Au	Pd	0.35	28	0
none	Ag	Pd	0.34	40	0

Reaction conditions: 600 °C, 1000 ppm of NO and 6 vol% of O_2 in helium with the total flow rate of 50 ml min^{-1} at 4.0 V.

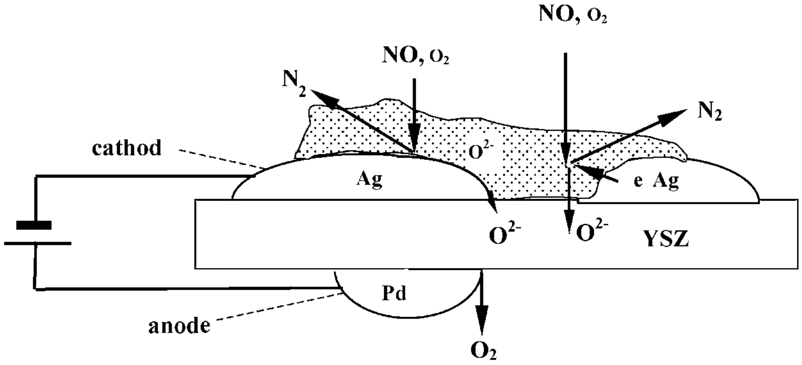

Fig. 6. Schematic mechanism of NO electrochemical decomposition in the RuO_2/Ag/YSZ/Pd cell in the presence of O_2. (Shaded area denotes RuO_2 coating layer.)

the morphology or structure of these metal cathodes. For example, the difference between the RuO_2/Ag/YSZ/Pd cell and the Ag/YSZ/Pd cell is 45 mA cm^{-2}, while the difference between the RuO_2/Pd/YSZ/Pd cell and the Pd/YSZ/Pd cell is 12 mA cm^{-2}. Therefore, it can be concluded that there are interactions between the metal cathode and the RuO_x, which include the transportation of electrons from the metal to the oxides and the O^{2-} species from the oxides to YSZ along the interfaces between the metal and the oxides, as shown schematically in Figure 6.

3.4. *Mechanism of NO decomposition in the cells*

To elucidate the mechanism of NO decomposition in the cell, the effect of pretreatment voltage (pre-voltage) was also investigated. As shown in Table 3, the NO conversion in the RuO_2/Pd/YSZ/Pd cell pretreated at 3.4 V is obviously higher than that in the cell pretreated at 2.0 V, though both reactions were carried out at the same applied voltage of 2.8 V. Furthermore, it is interesting to note that in the RuO_2/Pd/YSZ/Pd cell, as high as 13.6% of the NO conversion is obtained at open circuit when the pre-voltage is 3.6 V, as shown in Table 3. The N_2 analysed at open circuit can be excluded from that of the reactor remaining, because very different results were observed in the other cells. For instance, a 23.7% of NO conversion in the Pd/YSZ/Pd cell at 4.8 V drops to 3.3% when the circuit was cut off for the same period of 5 min. This shows that the NO decomposition proceeds via an electrocatalytic mechanism rather than an electrolytic one. The electrocatalytic mechanism is strongly supported by the facts that the cells still decompose NO with considerable activity even though the circuit has been cut off. All the results discussed above can be satisfactorily elucidated by this mechanism. In the RuO_2/Pd/YSZ/Pd cell, the partially reduced ruthenium oxide species, which are responsible for catalysing NO decomposition, loses its activity gradually when the O^{2-} in ruthenium oxide is no longer pumped to the anode by the potential. The cell pretreated at the higher voltages (expected to be covered with less O^{2-}) maintains its activity for a longer time than that pretreated at lower voltages. If the NO decomposition in the cell follows an electrolysis scheme, the NO conversion would increase continuously with increasing applied voltage, but this is not the case. As can be seen in Figure 4(a), the NO conversion passes through a maximum as the applied voltage increases under the reaction conditions.

3.5. *Properties of RuO_2/Ag/YSZ/Pd cell for NO decomposition*

The performance of the RuO_2/Ag/YSZ/Pd cell for NO decomposition was tested in the temperature range 500 °C–600 °C. As shown in Figure 7, there is a maximum NO conversion at each temperature in the voltage region of 0–4 V, which is similar to the RuO_2/Pd/YSZ/Pd cell. Moreover, the maximum value of the

Table 3. Effect of pretreatment voltages on the NO decomposition in the cells

Cells	Pre-voltages /V	Applied voltages /V	Current densities /mA cm^{-2}	NO conv. to N_2 /%*
RuO_2/ Pd/YSZ/Pd	2.6 min for20	2.8	112	20.4
RuO_2/ Pd/YSZ/Pd	2.0 min for20	2.8	108	16.3
RuO_2/ Pd/YSZ/Pd	3.4 min for20	2.8	117	25.8
RuO_2/ Pd/YSZ/Pd	3.4 min for20	3.6	156	25.8
RuO_2/ Pd/YSZ/Pd	3.6 min for20	0 (circuit open)	0	13.6
Pd/YSZ/Pd	4.8 min for20	0 (circuit open)	0	3.3

* The NO conversion was measured at the time that the potential had been changed from the pre-voltages to the applied voltages in reaction for five minutes at 700 °C

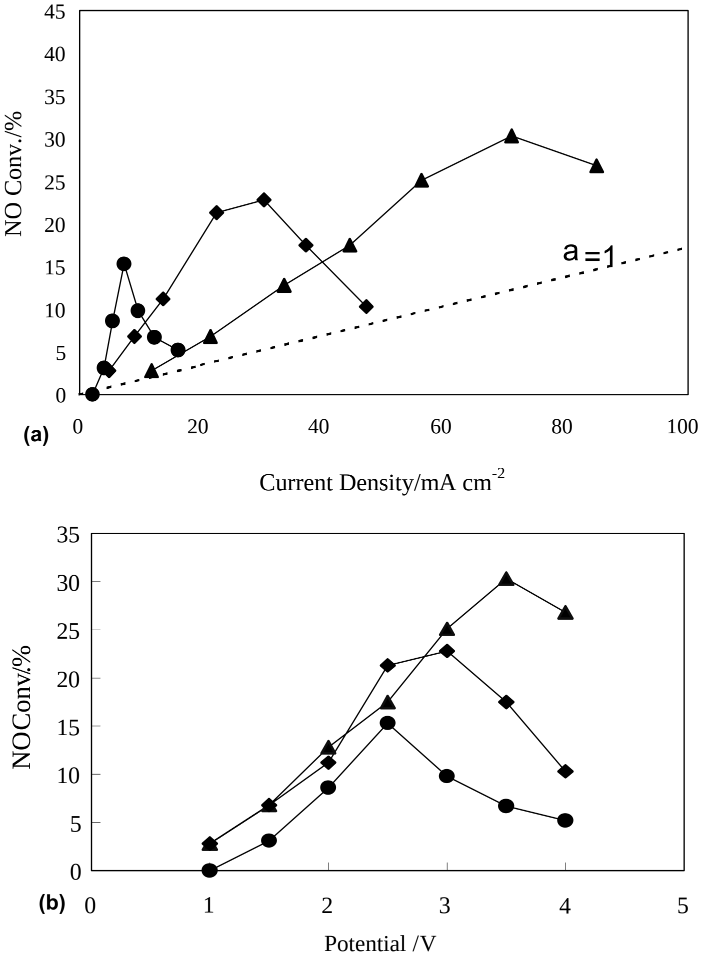

Fig. 7. Dependence of NO conversion on current densities (a) and on voltages (b) in RuO_2/Ag/YSZ/Pd cell. Dashed line in the Figure 7(a) corresponds to an unselective reaction of NO and O_2 in the cell (α=1). Key: (●) 500 °C, (◆) 550 °C, (▲) 600 °C. Other conditions: fed gas, NO 1000 ppm and O_2 vol 6% in He; total flow rate 50 ml min^{-1}.

NO conversion appears at a higher voltage when the reaction proceeds at a higher temperature. The α value is 2.5 with 30.3% of NO conversion at 600 °C, 5.7 with 21.3% of NO conversion at 550 °C, respectively. And at 500 °C, the α value of 13.4 with 15.3% of NO conversion is achieved in the RuO_2/Ag/YSZ/Pd cell at an applied voltage of 2.5 V.

4. Conclusions

NO decomposition has been effectively carried out in the RuO_2/Pd/YSZ/Pd and RuO_2/Ag/YSZ/Pd cell using 1–4 V d.c. voltage in the presence of excess O_2. In particular, the main results are summarized as follows:

(i) At 700 °C, O_2 is selectively decomposed in the Pd/YSZ/Pd cell, while at lower temperatures, NO can be selectively decomposed in the RuO_2/Pd/YSZ/Pd cell.

(ii) At 600 °C, the O^{2-}transportation at the cathode Pd/YSZ interface is the rate-determining step in the overall transportation process of O^{2-} from cathode to anode. Before O^{2-} on the cathode being completely pumped to the anode, the solid electrolyte zirconia near the three-phase interface is partially reduced at higher applied voltages. The ionization of O_2 in the cell is enhanced notably due to the preferential decomposition of O_2 over NO on the partially reduced solid electrolyte.

(iii) On the partially reduced ruthenium oxides, the lower reaction temperature is favorable to NO in the competition for electrons with O_2, therefore decreasing reaction temperature is essential to improve the selective decomposition of NO.

(iv) The transportation resistance of O^{2-} at the cathode Ag/YSZ interface is much less than at the cathode Pd/YSZ interface. For the RuO_2/Pd/YSZ/Pd cell, when the Pd cathode is replaced by a Ag cathode, its current density at lower temperatures is increased. At 500 °C, the NO conversion in the RuO_2/Ag/YSZ/Pd cell can reach 15.3% with the NO decomposition parameter α being 13.4.

(v) NO decomposition takes place via an electrocatalytic mechanism rather than an electrolytic scheme, as previously reported.

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