



Electrochemical Reduction of NO_x at Intermediate Temperatures Using a Proton-Conducting In³⁺-Doped SnP₂O₇ Electrolyte

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In³⁺-doped SnP₂O₇ was used as the electrolyte in an electrochemical cell for the reduction of NO between 150 and 300°C in the presence of excess O₂. NO was reduced to N₂ at a Pt/C cathode when current was applied to the cell. The electrocatalytic activity of the cathode for the reduction of NO was shown to be highest at 250°C. The addition of Ba species (an oxide/carbonate mixture) to the cathode further promoted the reduction of NO by adsorbing NO more selectively than O₂ on the surface. A resulting current efficiency of 5.81% was achieved in a 2% O₂ atmosphere.

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NO_x (NO and NO₂) produced by fuel combustion causes photochemical smog and acid rain. Various de-NO_x techniques have been studied, especially for diesel engines that emit exhaust with excess O₂,¹ wherein the commonly used three-way catalyst is not effective for the reduction of NO_x to N₂. Selective catalytic reduction (SCR) of NO_x is widely viewed as a promising de-NO_x technology. However, this reaction requires the use of hydrocarbons or urea as reducing agents, which necessitates storage tanks and frequent replenishment. In recent years, direct electrochemical reduction of NO_x has been attracting increasing interest, since it does not require the use of a reducing agent.^{2,3} Most electrochemical cells are constructed from zirconia-⁴⁻⁸ or ceria-based⁹⁻¹² electrolytes with different types of cathodes. NO is reduced to N₂ and O²⁻ by polarizing the cathode. O²⁻ ions are transported from the cathode to the anode through the electrolyte. A very important aspect of this method is the high-temperature operation (>400°C, 500-700°C in most cases) required to achieve sufficient oxide-ion conductivity of the electrolyte. Accordingly, the cell must be heated above the temperature of the exhaust (200-400°C), leading to energy losses. Recently, Machida et al. have reported that the electrochemical reduction of NO_x can occur at 70°C in a Nafion-based cell.¹³ In this case, hydrogen (H₂ or H) produced at the cathode is used as a reducing agent. However, this method also requires energy to cool down the cell to 70°C. On a more serious note, the Pt cathode electrocatalyst is poisoned by CO in actual applications, since exhaust from engines usually include several thousand ppm or higher of CO.

The above problems would obviously be avoided by using a proton or oxide-ion conducting electrolyte with conductivities >10⁻¹ S cm⁻¹ between 200 and 400°C. We recently found that an anhydrous proton conductor, 10 mol % In³⁺-doped SnP₂O₇, meets this criterion in the temperature range of interest.¹⁴ This material has a cubic structure, with SnO₆ octahedra and P₂O₇ units at the corners and the edges, respectively, so that the closely-packed P₂O₇ units can provide numerous proton bonding sites and associated transport pathways in the bulk. Figure 1 shows the total conductivity of this material in unhumidified air between 150 and 350°C. A H₂ concentration cell using this material as the electrolyte generated electromotive forces (EMFs) near the theoretical value calculated from the Nernstian equation, wherein the ionic (proton or oxide ion) transport number was estimated to be 0.97-0.98. On the other hand, the ionic transport number was reduced to 0.89-0.92 and 0.63-0.74 in a H₂-air

fuel cell and a steam concentration cell, respectively. This was due to the presence of electron holes in the bulk of the electrolyte at high partial pressure of O₂.

In this study, we have fabricated an electrochemical cell using 10 mol % In³⁺-doped SnP₂O₇ as the electrolyte in order to investigate the feasibility of reducing NO electrochemically at intermediate temperatures. The electrocatalytic properties of a Pt/C cathode for the reduction of NO have been evaluated between 150 and 300°C. In addition, the effect of Ba species as an additive to the Pt/C catalyst on the current efficiency for the reduction of NO has been examined at different O₂ concentrations (2-9%).

Experimental

Ten mole percent In³⁺-doped SnP₂O₇ was prepared in the same manner as previously reported.¹⁴ In brief, the corresponding oxides (SnO₂ and In₂O₃) were mixed with 85% H₃PO₄ and then held with stirring at 300°C until a paste with a high viscosity was formed. The paste was calcined in an alumina pot at 650°C for 2.5 h and then ground in a mortar with a pestle. The crystalline structure of the compounds was confirmed to be a single-SnP₂O₇ phase by X-ray diffraction (XRD) analysis, as shown in Fig. 2. Finally, the compound powders were pressed into pellets (diameter: 12 mm, thickness: 1.0-1.2 mm) under a pressure of 2 × 10³ kg cm⁻².

Two homemade electrocatalysts (area: 0.5 cm²), Pt/C and PtM/C (M = Ca, Mg, Sr, and Ba), were tested as the cathodes. The Pt/C catalyst (30-90 wt % Pt) was prepared by a chemical reduction method. Carbon powders (Ketjen Black, EC600JD) were suspended in an ethanol/water (50 vol % ethanol) solution. A solution of 0.054 M H₂PtCl₆·6H₂O (Wako Pure Chemicals Co., Ltd.) in water and a solution of 0.460 M NaBH₄ (Wako Pure Chemicals Co., Ltd.) in water were added dropwise to the suspension at 70°C for 2 h. The suspension was washed with distilled water repeatedly. After drying at 50°C in air, the catalyst was reduced with a H₂/Ar (10 vol % H₂) atmosphere at 200°C for 1 h. The PtM/C catalysts were prepared by the precipitation of M(NO₃)₂ onto the 70 wt % Pt/C catalyst. The desired amounts of Pt/C and M(NO₃)₂ powders were mixed in an ethanol/water (50 vol % ethanol) solution. The precipitation process was carried out by the dropwise addition of a solution of 1.000 M NH₄CO₃ in water to the solution at 70°C for 2 h. Then, the solution was treated in a similar manner to the above approach. The weight ratio of M to Pt was in the range from 0.5 to 5.0. The Pt/C or PtM/C catalyst was mechanically mixed with 10% poly(vinylidene fluoride) (PVDF) binder in 1-methyl-2-pyrrolidinone (NMP) solvent with a mortar and a pestle. The mixture was applied homogeneously over a carbon paper (Toray TGPB-090). A commercial Pt/C anode

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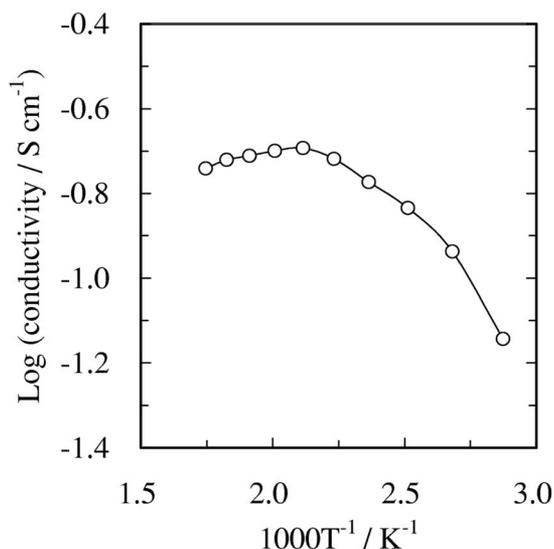


Figure 1. Temperature dependence of conductivity of 10 mol % In³⁺-doped SnP₂O₇ in unhumidified air.

(10 wt % Pt/C, 0.6 mg Pt cm⁻²) was purchased from E-TEK Inc. A Pt reference electrode was placed on the side face of the electrolyte pellet.

Two gas chambers were set up by placing the cell between two alumina tubes. Each chamber was sealed with an inorganic adhesive. The cathode chamber was supplied with a mixture of 800 ppm NO and 2-9% O₂ in Ar, and the anode chamber was supplied with wet air, which was saturated with water vapor at room temperature. The flow rate of these gases was 50 mL min⁻¹. The reference electrode was statically exposed to atmospheric air. Constant currents were applied to the cell using a galvanostat (Hokuto Denko HA-501). The potential of the cathode vs the reference electrode was recorded with an electrometer (Hokuto Denko HE-104). The concentration of NO in the outlet gas from the cathode was monitored using an on-line NO_x gas analyzer (Horiba PG-225). The conversion of NO and the current efficiency for the reduction of NO were calculated as below^{15,16}

$$\text{Conversion}(\%) = ([\text{NO}]_{\text{inlet}} - [\text{NO}]_{\text{outlet}}) / [\text{NO}]_{\text{inlet}} \times 100 \quad [1]$$

$$\text{Current efficiency}(\%) = \Delta\text{NO} / (It/nF) \times 100 \quad [2]$$

where ΔNO , I , t , n , and F denoted the number of moles of the reduced NO, current, time, electron number, and Faraday's constant,

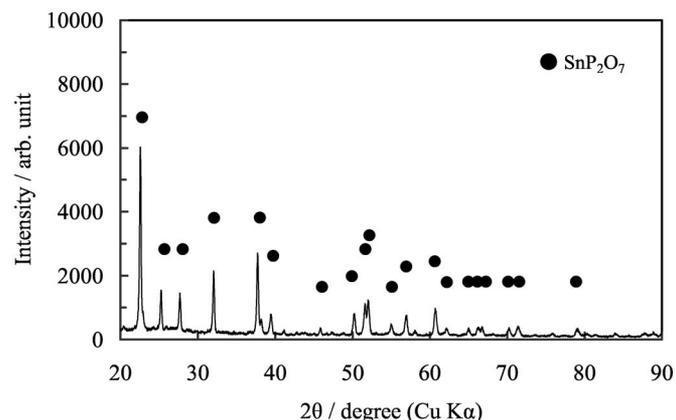


Figure 2. XRD pattern of 10 mol % In³⁺-doped SnP₂O₇.

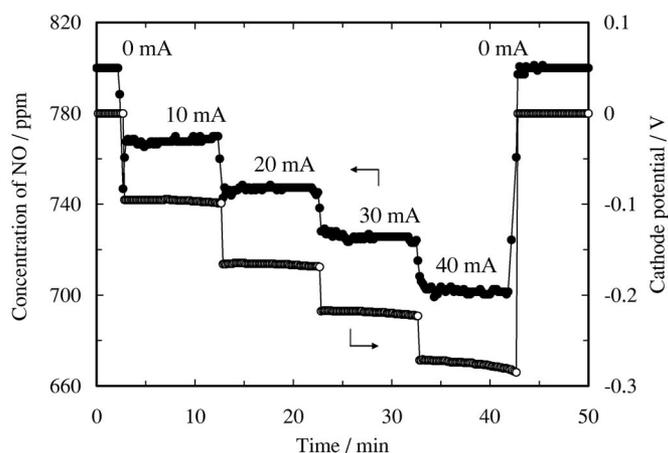
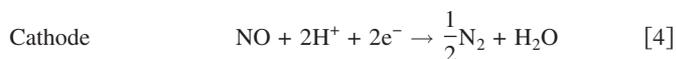
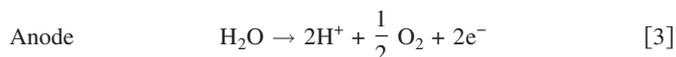


Figure 3. Transient change in cathode potential and NO concentration in the outlet gas from the cathode at 250°C. The reactant gas was 800 ppm NO and 5% O₂ in Ar at a flow rate of 50 mL min⁻¹.

respectively. Other gases (N₂O, NH₃, N₂, and H₂) were analyzed by on-line gas chromatography (Shimadzu GC-8A).

Results and Discussion

We first evaluated the electrocatalytic properties of a typical cathode, 70 wt % Pt/C, for the reduction of NO at 250°C in the presence of 5% O₂. Figure 3 shows the transient change in cathode potential and NO concentration in the outlet gas from the cathode during the application of current. The cathode potentials were almost stable for the range of currents investigated, indicating that steady fluxes of protons were established through the electrolyte. The reduction of NO did not occur over the Pt/C catalyst under open-circuit conditions. This is due to an inhibition of this reaction by oxygen adsorbed on the Pt surface from the gas phase.¹⁷ When a current density of 20 mA cm⁻² was applied, the NO concentration quickly decreased to about 765 ppm and then remained constant. The NO concentration further decreased with increasing current density. The major constituent of the product was N₂, with trace amounts of N₂O and NH₃. These results suggest that the following reactions mainly occurred in the cell



The NO conversion was similarly measured over the Pt/C cathodes with Pt contents of 30 to 90 wt %. It was found that the 70 wt % Pt/C cathode exhibited the highest NO conversions at all current densities tested, although the difference in NO conversion among the cathodes was not so large. Another important result is that NO was not reduced at all over a Pt-free carbon cathode, indicating that the Pt catalyst plays an important role in Reaction 4.

To better understand the reduction of NO over the Pt/C cathode at intermediate temperatures, we measured the NO conversion over the 70 wt % Pt/C cathode between 150 and 300°C in 5% O₂. A relatively large temperature dependence of the NO conversion can be seen in Fig. 4. The NO conversion at a given current density increased with increasing temperature and reached a maximum at 250°C. This temperature dependence can be explained by a combination of two factors: (i) a more selective adsorption of NO at lower temperatures, and (ii) an increasing rate of Reaction 4 with increasing temperature. At 150°C, NO is more predominantly adsorbed than O₂ on the Pt surface, whereas Reaction 4 proceeds at a very slow rate over the Pt catalyst. In contrast, at 300°C, although the rate of Reaction 4 is very fast, NO and O₂ are adsorbed competitively on

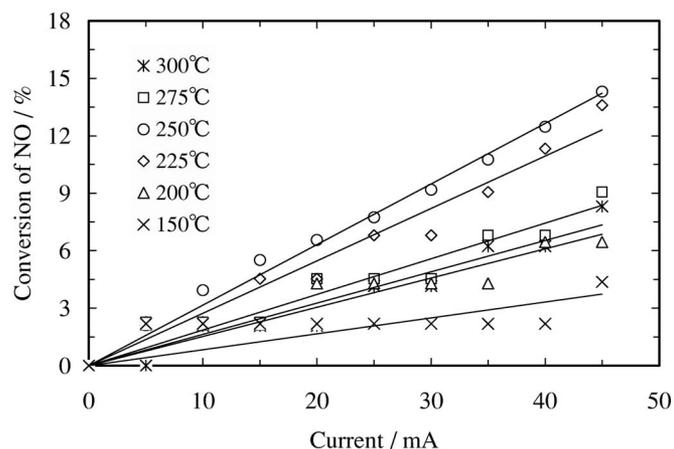


Figure 4. Dependence of NO conversion on the operating temperature. The reactant gas was 800 ppm NO and 5% O₂ in Ar at a flow rate of 50 mL min⁻¹.

the Pt surface. As a result, the highest current efficiency of 1.83% was obtained at 250°C. We note that this value is higher than the current efficiency of 0.79% calculated by assuming that 800 ppm NO and 5% O₂ are nonselectively reduced to N₂ and H₂O, respectively, depending on their concentrations. It is thus proposed that the Pt/C cathode shows a certain selectivity toward the reduction of NO at 250°C, which is based on the selective adsorption of NO on the Pt surface, as described above.

The selective adsorption of NO would be further improved by the addition of a basic material such as alkaline earth oxides or carbonates to the Pt/C cathode, since NO is an acidic molecule. This concept is similar to that reported for a series of NO_x storage-reduction (NSR) catalysts.¹⁸ We thus precipitated different alkaline earth species (Mg, Ca, Sr, and Ba) onto the Pt/C catalyst. It can be seen from Fig. 5 that the Ba species is the most promising adsorbent among the materials tested, with an optimal Ba/Pt weight ratio of 4. (The results for the PtBa/C catalysts with the other Ba/Pt weight ratios are omitted in Fig. 5.) The current efficiency of this best catalyst was enhanced up to 2.48%. XRD measurement of the PtBa/C catalyst showed that the Ba species was present in the form of an oxide/carbonate mixture on the surface of carbon. Based on the mechanism reported for the NSR catalysts,¹⁹ NO is likely oxidized by O₂ over the Pt catalyst to form NO₂, which is stored as

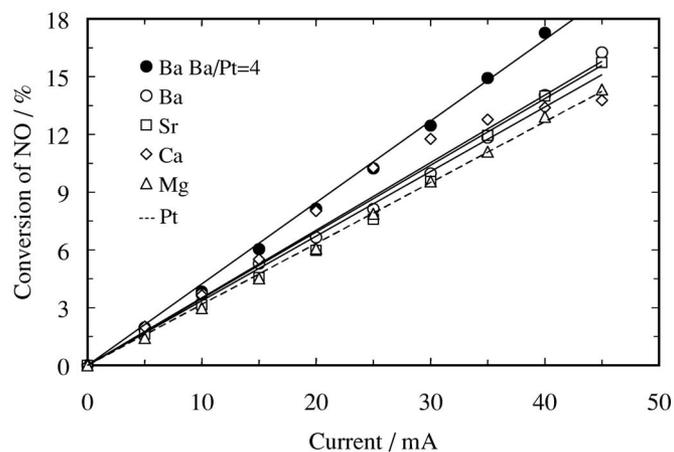


Figure 5. Effects of the addition of alkaline earth species (Mg, Ca, Sr, and Ba) to the Pt/C cathode at 250°C. The reactant gas was 800 ppm NO and 5% O₂ in Ar at a flow rate of 50 mL min⁻¹. The Ba/Pt weight ratios are 1 and 4, and the weight ratio for the other alkaline earth species was 1.

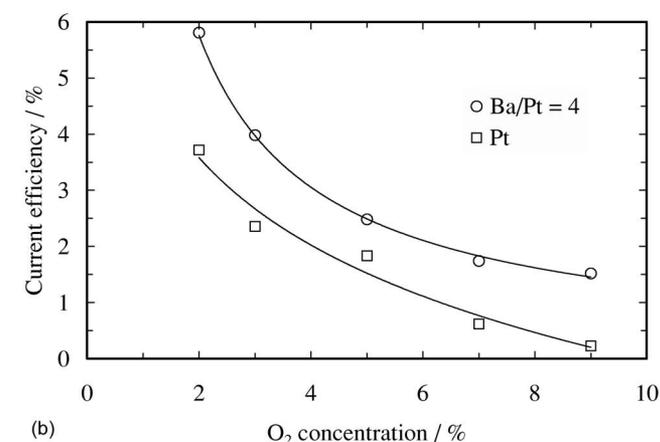
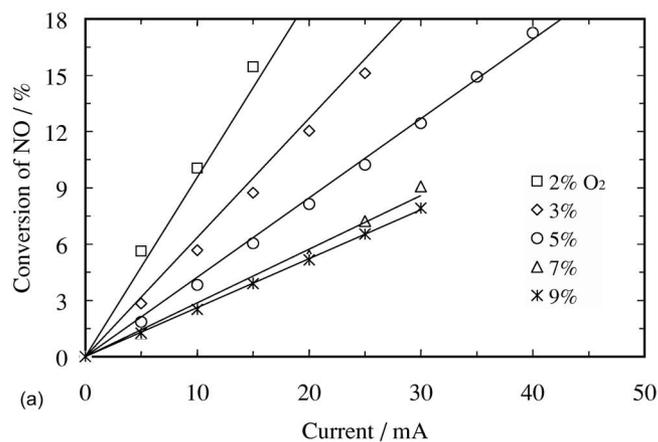


Figure 6. (a) Dependence of NO conversion on O₂ concentration at 250°C. The reactant gas was 800 ppm NO and 2-9% O₂ in Ar at a flow rate of 50 mL min⁻¹. The cathode was the PtBa/C catalyst with a Ba/Pt weight ratio of 4. (b) Current efficiency for reduction of NO as a function of O₂ concentration at 250°C. Experimental conditions are the same as in Fig. 6a.

NO₃⁻ on the BaO or BaCO₃ surface. The NO₃⁻ species are subsequently reduced by H₂ or H produced at the cathode.

The O₂ concentration in the outlet gases from diesel engines is usually in the range from 2 to ~10%. Hence, the reduction of NO over the PtBa/C cathode was examined at different O₂ concentrations. The dependence of the NO conversion on the O₂ concentration is shown in Fig. 6a. The NO conversion was significantly influenced by the O₂ concentration. This is common behavior observed for the electrochemical reduction of NO at low or high temperatures. Nonetheless, the decrease in current efficiencies of the PtBa/C cathode with increasing O₂ concentration was much less than that for the Pt/C cathode, as shown in Fig. 6b. Moreover, comparing the current efficiencies of the PtBa/C cathode with the current efficiencies of the other cathodes allows us to further understand the advantages of the present technique. Most of the current efficiencies reported thus far were around 2% in 2% O₂,³ which is lower than the current efficiency of 5.81% shown for the same concentration in Fig. 6b. Another interesting comparison was made between hydrogen produced electrochemically at the cathode and gaseous hydrogen supplied from the outside of the system. The cathode chamber was supplied with a mixture of 0.4% H₂, 800 ppm NO and 5% O₂ in Ar, wherein the H₂ concentration of 0.4% was equivalent to the H₂ amount produced by passing a current of 30 mA to the cell. The NO conversion at the open-circuit voltage was shown to be 1.31%, which is lower than the NO conversion of 12.5% at 30 mA shown in Fig. 6a. The difference observed between the two hydrogen species

is not surprising. The hydrogen produced at the cathode shows higher H₂ activity at the electrode surface or inside the electrode than gas-phase hydrogen.

In conclusion, the use of the In³⁺-doped SnP₂O₇ electrolyte made the operation of the cell between 150 and 300°C possible, which is close to the temperature range of exhaust from diesel engines. The mechanism for the reduction of NO was based on the reaction of NO with hydrogen produced at the cathode. The addition of the Ba species to the cathode improved the selectivity towards reduction of NO, yielding a higher current efficiency compared to the current efficiencies for other cathode materials reported. This was shown to be due to selective adsorption of NO on the surface of the Ba species.

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