DEVELOPMENT OF SOFC-TYPE REACTOR FOR NO\textsubscript{X} DECOMPOSITION AND GRAPHITE OXIDATION

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ABSTRACT

Direct oxidation of solid state graphite particles was carried out using a 10 mol% Gd-doped CeO\textsubscript{2} (CGO) based electrochemical reactor with an oxidative porous anode consisting of 12CaO7Al\textsubscript{2}O\textsubscript{3}. A ceramic electrochemical cell was prepared by screen-printing Ag, NiO-CGO and 12CaO7Al\textsubscript{2}O\textsubscript{3}-Ag pastes on CGO plates. Simultaneous decomposition of NO\textsubscript{x} and oxidation of graphite particles was investigated in 1000 ppm NO\textsubscript{x}-He gas flowing at 475°C. Graphite particles on the surface of the 12CaO7Al\textsubscript{2}O\textsubscript{3}-Ag composite anode were oxidized by applying 1.5 V DC voltage at 475°C. The coated graphite particles on the anode were removed directly with 80% decomposed NO\textsubscript{x} by electrochemical reaction.

INTRODUCTION

Regulation of toxic substances, such as NO\textsubscript{x} and particulate matter (PM), in automobile exhaust gas is progressing rapidly because of global environmental problems. For example, Japanese government hopes to curtail NO\textsubscript{x} in vehicle exhaust gas by 80% compared to present concentrations by 2005. This is difficult to achieve with conventional catalyst technology, such as the Pt-Pd-Rh three-way catalyst. Therefore, the development of an innovative technology is urgently needed. Electrochemical reaction is promising for active reduction and oxidation of electrodes using electric power. NO\textsubscript{x} decomposition using a solid state electrochemical cell system was reported by Mason et al. in 1975 [1]. They showed NO\textsubscript{x} decomposition using O\textsubscript{2} pumped through ion conducting materials such as Y-doped ZrO\textsubscript{2} at high voltage. Recently, low voltage electrochemical decomposition of NO\textsubscript{x} was achieved successfully using an asymmetric catalytic cathode in the electrochemical reactor [2,3]. Ionic conducting electrochemical cells with O\textsubscript{2} pumping also show oxidation reaction on the anode side. When graphite particles in the particulate matter are placed on the anode side, they react with active oxygen coming out through the electrolyte. This technology simultaneously decomposes NO\textsubscript{x} and oxidizes PM using one electrochemical cell. Therefore, we carried out NO\textsubscript{x} decomposition using an electrochemical cell and investigated direct oxidation of graphite particles using electrochemical cells with 12CaO7Al\textsubscript{2}O\textsubscript{3} as a catalyst for oxidation. 12CaO7Al\textsubscript{2}O\textsubscript{3} is a strong oxidative material, which forms active oxygen, O* by electrochemical reaction [4]. Furthermore, Gd-doped CeO\textsubscript{2} (CGO) is oxygen ion conducting material, possessing high conductivity at low temperatures. For the purpose of decreasing reaction temperature, CGO electrolytes were characterized for the properties of the electrochemical reactors.
EXPERIMENTAL

The structure of the 10 mol% Gd-doped CeO$_2$ (CGO)-based cell is shown in Fig.1.

![Figure 1. Schematic of the prepared electrochemical cell.](image)

A CGO ceramic disk of 20φ x 0.5 mm thick (Japan Fine ceramics Co.) was used. 50 vol% NiO - CGO composite paste was screen printed as the cathode (1.77 cm$^2$) and sintered at 1500°C for 4 h. Ag paste (Tanaka Kikinzoku Co. TR-7097) was printed on the surface of the cathode in a mesh pattern (0.5 mm wide lines at intervals of 1 mm). 12CaO7Al$_2$O$_3$ (C12A7) was prepared by solid state reaction using a mixture of CaCO$_3$ and gamma-Al$_2$O$_3$ (Ca:Al=12:14) at 1000°C in flowing O$_2$ [5]. C12A7 was mixed with 50 wt% Ag paste to decrease resistance of the cathode. After screen printing Ag paste in a mesh pattern, the C12A7-Ag composite paste mixed with 40 vol% polyethylene glycol was printed as the anode and sintered at 1000°C for 4 h.

Electrochemical cells were connected by a Pt wire and mounted into quartz tubes through a 1000 ppm of NO gas in He(balance) at a flow rate of 50 ml/min. Glassy carbon paste was screen-printed on the surface of the anode and dried at 500°C for 2 h in air. Products in the test gas were analyzed by gas chromatography (Varian Co. Micro-GC CP2002 and Chromatopack Co. Molesive-5A). The degree of NOx decomposition was measured by a NOx analyzer (Best Instruments, BCL-100uH.).

RESULTS AND DISCUSSION

The coated graphite particles on the surface of the cathode remained after being calcined at 500°C in air for 2 h. The coated graphite was fired at >600°C in air. The photographs of the cathode side of the prepared electrochemical cell at 1.5 V are shown in Fig. 2.

Graphite particles on the surface of the C12A7-Ag composite anode were directly oxidized by applying 1.5 V DC voltage at 475°C for 2 h. The electrochemical oxidation of graphite on the anode was detected at 475-550°C. Degree of the electrochemical oxidation decreased with decreasing temperature because of the increasing resistance of the cell. The value of the open circuit current was about 50 mA during the reaction at 475°C. The oxidation rates of the coated graphite particles on the surface of various anode materials are shown at various stages in Table 1. When Pt or Ag was used as the anode material for the electrochemical cell, graphite particles remained after oxidation at 475°C for 2 h. These results indicate that an improvement in graphite oxidation on the anode side contributed to the catalytic effect of the C12A7-Ag composite anode because C12A7 may be an active
species for oxidation as reported in [5]. Furthermore, CO₂ formation was detected in the test gas when DC voltage was applied.

![Figure 2](image_url)

**Figure 2.** Photographs of electrochemical oxidation of graphite particles at 475°C and 1.5 V after (a) 0 h, (b) 1 h, and (c) 2 h.

**Table 1.** Amount of electrochemical oxidation of graphite on the surface of anode at 2 V and 475°C.

| Anode material | Decomposed graphite (mol/cm²-h) |
|----------------|----------------------------------|
| Pt             | 0.3x10⁻⁵                         |
| Ag             | 0.7x10⁻⁵                         |
| Ca₁₂Al₂O₃³⁺Ag  | 1.3x10⁻⁵                         |

\[
2O₂^{2⁻}(CGO) = Vo(CeO₂) + O₂ + 4e⁻ \quad (1)
\]

\[
O₂^{2⁻} (\text{cage in C12A7}) + O₂ \rightarrow O'(\text{cage in C12A7}) + O₂^{2⁻}(\text{cage in C12A7}) \quad (2)
\]

\[
2O^- + C = CO₂ + 2e^- \quad (3)
\]

The relationship between the degree of NO decomposition, formation of CO₂ and applied voltage is shown in Fig. 3. The degree of NO decomposition \(\equiv ([\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}})/[\text{NO}]_{\text{in}}\) increased with an increase in applied voltage at 475°C. By applying 2 V of voltage, about 80% of the NO was decomposed at the cathode by electrochemical reaction of O₂ being pumped though the electrolyte at 457°C. The degree of NOx decomposition in the CGO based electrochemical reactor was lower than that of NiO-8 mol%Y₂O₃ doped ZrO₂ based cell as reported in [3]. However, the reaction temperature decreased with decreasing resistance of CGO based cells, such as electrolytes. The amount of CO₂ formation by oxidation of graphite particles also increased by increasing the applied voltage. About 15 ppm of CO₂ was formed at 2 V at 475°C.

\[
2\text{NO} + Vo(CeO₂) + 4e^- = N₂ + 2O₂^{2⁻}(CGO) \quad (4)
\]
This is the first report of simultaneous decomposition of NOx and oxidation of graphite particles by electrochemical reaction. However, the quantitative amount of direct oxidation of graphite particles by the activated oxygen from the anode side was not clear in this paper because of the complicated oxidation mechanism at the anode. Catalytic effects of the added 12CaO7Al2O3 appeared in the experimental data. Our next research project will study the effects of active oxygen.

CONCLUSIONS

Direct oxidation of graphite particles by an electrochemical cell was successfully obtained using a C12A7-Ag composite anode at 457°C. About 80% of the NOx was decomposed on the NiO-CGO anode by oxidizing graphite particles on the cathode at 1.5-2.0 V DC. A novel gas purification system in exhaust gas will enable the development of catalytic electrodes in electrochemical reaction cells.

ACKNOWLEDGEMENTS

This work was supported by METI, Japan, as part of the Synergy Ceramics Project. Part of the work was supported by NEDO.

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