Nitric oxide removal from simulated lean-burn engine exhaust using a solid oxide fuel cell with V-added (LaSr)MnO$_3$ cathode

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ABSTRACT

A solid oxide fuel cell (SOFC) unit cell is constructed by coating V-added La$_{0.8}$Sr$_{0.2}$MnO$_3$–Ce$_{0.9}$Gd$_{0.1}$O$_2$ as the cathode onto a disk of anode-supported bilayers of yttria-stabilized zirconia (YSZ) and Ni-YSZ. Various compositions of lean-burn engine exhaust components of O$_2$, H$_2$O, CO$_2$ and NO were tested over the cathode of SOFC unit cell operating at 700–800 °C. NO can be completely converted to N$_2$. All the exhaust components have beneficial effect on NO conversion. Increasing O$_2$ content from 2 to 10% increases NO conversion from 18% to about 70%; this enables us to increase the O$_2$ content by adding air in the exhaust to increase the NO conversion. Increasing NO concentration increases NO conversion. Adding H$_2$O, increasing CO$_2$ content and an increase of the generated voltage all increase NO conversion, although only slightly. These are beneficial for the application of SOFCs to NO removal from lean-burn engine exhaust.

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1. Introduction

The removal of nitric oxide (NO) from the lean-burn exhaust, such as the diesel engine exhaust, can be performed by the selective catalytic reduction (SCR) process, in which NO in the exhaust gases reacts with ammonia to produce nitrogen and water [1]. This SCR process has to use a reducing gas, usually ammonia; however, the residual ammonia can pose a problem. The technology of NO$_x$ storage-reduction (NSR) has also been considered for NO$_x$ removal. However, the NSR system needs to oxidize NO to NO$_2$ for storage and to periodically run the engine rich of stoichiometry for reduction [2]; this adds the complexity. Thus, the electrochemical NO reduction without a reducing gas has been studied extensively [3–8]. However, this process of electrochemical NO reduction is performed with applied current and the current efficiency is generally only a few percent because the reduction of O$_2$ occurs simultaneously to consume a substantial amount of the electrical current [8]. On the other hand, electrochemical NO reduction using a solid oxide fuel cell (SOFC) can remove NO and generate an electrical current instead [9–12]. Although this process needs an anode fuel, this fuel is consumed only when an electrical current is generated; thus, this SOFC-DeNO$_x$ process is very energy-efficient.

A process of DeNO$_x$ by SOFC means that the SOFC operation is performed with the exhaust gases passing the cathode side. For

the exhaust gases of the power plant or the nitric acid plant, the O$_2$ concentration is usually 4–6% and the NO concentration can be 1000–5000 ppm or higher. Recently, the problem of CO$_2$ emission has become very critical. The lean-burn engines are promising to decrease the fuel consumption for automotive use and thus decrease the CO$_2$ emission. However, for NO removal from the exhaust of the lean-burn engines, an efficient NO reduction at high oxygen concentrations is needed. Although the SOFC-DeNO$_x$ process can remove NO under high O$_2$ concentration, the reported experimental results until now have not shown its efficiency in the presence of water vapor; instead, it has been shown that the presence of 0.3% H$_2$O in a simulated exhaust has inhibited the NO activity considerably [11]. Notably, the lean-burn engine exhaust contains about 10% H$_2$O [13]. Therefore, suitable cathode materials in association with proper operating conditions are still to be studied for the SOFC-DeNO$_x$ process to become practical in automotive applications.

For the application of the SOFC-DeNO$_x$ process onto automobiles, the heating of SOFCs and thermal cycling may be problems; these may be solved using microtubular SOFCs with heating at the center of the tube that is on the anode side [14]. For microtubular SOFCs, quick heating can result in a startup time less than 10 s and thousands of thermal cycles can be operated [15]. This may be due to the mechanism that SOFC can become operational when only the electrolyte part of SOFC is heated to a temperature for startup of oxygen migration. Notably, SOFC is well known to produce more heat than needed to sustain its operating temperature. Additionally, the supply of the anode fuel may also be a problem; this has

been solved by the advance in the fuel processing technology, for example, SOFC-based auxiliary power unit for diesel trucks can use diesel as the fuel [16].

$(LaSr)MnO_3$ (LSM) perovskite is the commercial cathode material for SOFCs. The addition of gadolinia-doped ceria (GDC) into the perovskites can increase the oxygen reduction activity of the cathode [17]. Preliminary test in this work has shown that LSM-GDC is effective for NO conversion in the presence of 10% H_2O to allow us to simulate the lean-burn engine exhaust. Thus, the LSM-GDC composite is the choice of SOFC cathode material in this work. Additionally, V_2O_5 is the catalytic component of the commercial SCR catalyst [18]. The addition of this catalytic component into LSM is considered to be able to enhance the NO activity.

In this work, the current–voltage measurement and the fixed-voltage test were performed in an SOFC unit cell with V-added LSM-GDC cathode. Various compositions of lean-burn engine exhaust components of O_2, H_2O, CO_2 and NO were tested over the SOFC cathode at 700–800 °C. All these exhaust components have shown positive effect on NO conversion. This is beneficial for the application of the SOFC-DeNO$_x$ process to NO removal from the lean-burn engine exhaust.

2. Experimental

2.1. Preparation of LSM and GDC and V addition

LSM was prepared by the glycine-nitrate process with a composition of $La_{0.8}Sr_{0.2}MnO_3$. Appropriate amounts of reagent-grade (Showa, Japan) metal nitrates $La(NO_3)_3 \cdot 6H_2O$, $Sr(NO_3)_2$, and $Mn(NO_3)_2 \cdot 4H_2O$ were dissolved in de-ionized water. Glycine (Sigma, USA) was also dissolved in de-ionized water. Then, these two solutions were mixed together with a glycine to NO_3^- ratio of 0.8:1. The mixture was then heated under stirring at 110 °C until combustion occurred. The product was ground to powders. Then, the powders were calcined by heating to 500 °C and held for 2 h, then to 900 °C and held for 4 h, and then slowly cooled down to room temperature. In this work, the heating of the powders was always done in air at a rate of 5 °C min^{-1}.

GDC was prepared by the co-precipitation method with a composition of $Ce_{0.9}Gd_{0.1}O_2$. The details of the method have been described elsewhere [19]. The GDC powders were calcined by heating to 900 °C and held for 4 h.

The LSM-GDC composite was prepared by mixing the above-prepared LSM and GDC powders at a ratio of LSM:GDC being 1:1 in weight. The mixture was ground for 24 h, then calcined by heating to 500 °C and held for 2 h, and then to 800 °C, held for 4 h.

Adding V to LSM-GDC powders was done by impregnation. The V cation solution was prepared by dissolving NH_4VO_3 (Merck, Germany) in de-ionized water. After drying, the powders were calcined by heating to 800 °C and held for 4 h before cooling down to room temperature. Notably, after calcination at 800 °C when O_2 can be dissociated to oxygen atom over V added LSM-GDC, V can be fully oxidized to V_2O_5 [20]. The weight of V_2O_5 in calcined V-added LSM-GDC was 1 wt.% in terms of the weight of LSM.

2.2. Construction of SOFC unit cell

A commercial disk of anode-supported bilayers of yttria-stabilized zirconia (YSZ) and Ni-YSZ (NexTech, USA) was used to make an anode-supported cell. The disk has a diameter of 2 cm. The cathode side of the disk was spin-coated with a thin interlayer of LSM-GDC to enhance adhesion; the thus-coated disk was dried at 50 °C for 6 h, then heated in air at 10 °C min^{-1} to 500 °C and held for 2 h, and then heated at 5 °C min^{-1} to 1200 °C and held for 2 h before cooling down. Then, the disk was spin-coated with V-added

LSM-GDC as the cathode functional layer; the thus-coated disk was dried at 50 °C for 6 h, then heated at 10 °C min^{-1} to 500 °C and held for 2 h, and then heated at 5 °C min^{-1} to 900 °C and held for 2 h. Then, the disk was spin-coated with LSM as the current collecting layer to complete the SOFC unit cell; the heat treatment was the same as that for the cathode functional layer.

2.3. Current–voltage measurement

The measurement of current–voltage curve was performed at 700–800 °C with pure hydrogen flowing on the anode side and various gas mixtures, all balanced by helium, on the cathode side. The overall flow rate was 150 Nml/min and that on the anode side was the same as that on the cathode side. The voltage was varied by an adjustable resister, and both the voltage and the current were measured by a Multimeter (TES 2730).

2.4. Fixed-voltage test

The fixed-voltage (constant-voltage) tests were performed at 800 °C with the generated voltage kept constant at 0.6 V, except noted otherwise. The anode gas was pure hydrogen. The inlet cathode gas was a mixture of NO, O_2, H_2O and/or CO_2, balanced in helium, with the composition designated in the figure and table legends. The overall flow rate was always 150 Nml/min.

The tests were conducted with introducing a designated gas mixture to the cathode side of the SOFC unit cell until a steady state was obtained for a certain period of time. Throughout the test, the electrical current, the voltage, and the outlet gas compositions were always measured. The NO and NO_2 contents in the outlet cathode gas were measured by NO and NO_2 analyzers (NGA 2000, Emerson, Germany), respectively. The N_2 content was measured by a gas chromatograph (GC) equipped with a thermal conductivity detector (China Chromatography 8900, Taiwan).
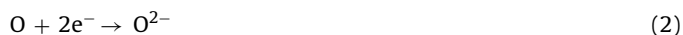
3. Results and discussion

3.1. Effect of O_2 concentration on NO conversion

Fig. 1 shows that an electrical current is generated with 6% NO as the cathode gas at 700–800 °C. This indicates the occurrence of electrochemical NO reduction—that is, the occurrence of NO decomposition:

$$NO \rightarrow N + O \tag{1}$$

followed by the charge transfer reaction to form the oxygen ion:

$$O + 2e^- \rightarrow O^{2-} \tag{2}$$

Notably, electrochemical NO reduction is completed and generates an electrical current only after the oxygen ion produced in reaction (2) has been transported to the anode and consumed by electrochemical oxidation with the fuel.

Table 1 shows that, with 6% NO as the cathode gas, the maximum power density increases with increasing temperature from 700 to 800 °C, being a same trend as that with 20% O_2; however, the open circuit voltage (OCV) decreases with increasing temperature; this is also a same trend as that with 20% O_2 but at a much larger extent. Notably, the OCV with 20% O_2 as the cathode gas is close to the theoretical value, indicating that the SOFC setup of this work operated properly—that is, no gas leakage or cross over the electrolyte layer.

Table 2 shows a comparison of SOFC performance with various O_2 content in simulated exhaust gas containing 10% H_2O, 10% CO_2 and 5000 ppm NO and that in a gas mixture containing only O_2 in He. Both the OCV and the maximum power density differ only