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Fabrication of novel type solid electrolyte membrane reactors for exhaust gas purification

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Abstract

Three kinds of membrane reactors with different electrodes, LSCF, LSCF–GDC, and LSCF–Pt were fabricated for the purpose of application to a de-NOx device, and the electrocatalytic characteristic and NO decomposition behaviors of the reactors were investigated. Both the LSCF–GDC and LSCF–Pt composite electrodes seemed to have a better affinity against oxygen than LSCF. When electric current was applied to the membrane reactors, oxygen-gas reduction preferably occurred at the LSCF and composite electrodes rather than NO decomposition. Once oxygen in the reactant gas was completely pumped out from cathode to anode, the membrane reactors could decompose NO. The onset current for NO decomposition of the LSCF–Pt electrode was slightly lower than that required by the other two membrane reactors, which indicating that Pt shows better selectivity against NO than LSCF or LSCF–GDC electrode.

Keywords: Composites; Impedance; Membranes; Mixing; Perovskites

1. Introduction

Electrochemical removal of NO using a solid electrolyte membrane reactor consisting of porous electrodes and a solid electrolyte is a different approach for NO decomposition.[1] When a direct voltage is applied between the two porous electrodes, NO is directly decomposed at the cathode. At the same time, oxygen is also reduced to oxygen ions, which are pumped through the solid electrolyte before evolving as oxygen gas at the anode, with the formation of oxygen vacancies. Such a membrane reactor can be used even in the presence of excess oxygen, e.g., diesel engines and the lean-burn condition of gasoline engines, with no need for hydrocarbons as a reducing agent.

Iwayama et al.[2] fabricated the membrane reactor with a oxide catalytic layer, noble metal electrodes, and a yttria-stabilized zirconia, and they addressed the fact that the oxide catalytic layer coated on noble metal cathode makes it possible to enhance performance of the membrane reactors. Wachsman et al.[3] attempted to enhance the current efficiency of a membrane reactor using a perovskite-type electrode. However, relatively high voltage $>$ 2.0 to 2.5 V is still required to obtain a sufficient NO decomposition at lower temperature than 600 °C, and the membrane reactors need a large amount of noble metal as both cathode and anode materials. From a practical viewpoint, the electric power (voltage × current) of a membrane reactor must be decreased to obtain sufficient NO decomposition. Therefore, either the current or the voltage, or both, must be decreased to improve the performance of the membrane reactor.

For the present study, we fabricated membrane reactors consisting of a Gd_2O_3-doped CeO_2 ($Gd_{0.2}Ce_{0.8}O_{3-\delta}$, GDC) electrolyte and a $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{2-\delta}$, (LSCF)-based composite electrode with GDC or Pt particles. The GDC shows higher ionic conductivity than that of YSZ and is considered a candidate as electrolyte material for intermediate temperature (500–700 °C) applications.[4] LSCF is the most suitable electrode material because of its high mixed ionic and electronic conductivity and its excellent thermal and chemical compatibility with GDC electrolytes.[5] The electrocatalytic characteristics and NO decomposition behavior of the present membrane reactors were investigated.

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2. Experimental procedure

A commercially available GDC disk (22 mm in diameter and 0.5 mm thick) was used as the solid electrolyte for the present study. Three kinds of the symmetrical membrane reactors were produced by applying LSCF, LSCF-40 vol.% GDC, and LSCF-1 vol.% Pt composite electrodes (cathode and anode) on the GDC electrolyte. The LSCF and GDC or PtO_2 powders were mixed by ball-milling technique in ethanol. After the powder had been dried at 80 °C, the LSCF–GDC or LSCF–PtO_2 composite electrode paste was screen-printed onto both sides of the GDC disk. The membrane reactor was sintered at 1000 °C for 1 h. A current-collector platinum layer, consisting of 15 wt.% GDC, was further coated onto each of the LSCF–GDC or LSCF–Pt composite electrode. For comparison, a LSCF/GDC/LSCF membrane reactor was prepared by the same process.

The experimental setup for the electrocatalytic and NO decomposition measurements is shown in our previous paper.[6] The reactant gas, a mixture of 1000 ppm NO and 2% O_2 (balance helium), from a premixed gas cylinder, was supplied to both the cathode and the anode compartments at a flow rate of 50 ml/min. Platinum wires were connected to the cathode and anode of the membrane reactor. AC impedance spectroscopy was conducted, with excitation potentials of 50 mV, over a frequency range from 1 MHz to 0.1 Hz, generated by a frequency analyzer, and the NO decomposition characteristics were evaluated by applying a constant current to the membrane reactor, using a galvanostat. The resulting gas species emitted from the cathode compartment were analyzed by gas chromatography and NO–NO_x gas analyzer. The microstructures of the composite electrodes were observed by SEM.

3. Results and discussion

Fig. 1 shows SEM micrographs of LSCF (a), LSCF–GDC (b), LSCF–Pt (c), and LSCF–GDC–Pt (d) composite electrodes sintered at 1000 °C for 2 h. All the electrodes show porous microstructure and are in good interfacial contact with a GDC electrolyte, with no signs of delamination. In the case of the LSCF–GDC composite electrode, it seems that relatively large LSCF grains are surrounded by fine GDC grains. Sintering the LSCF-based electrodes at high temperature > 900 °C increases their grain sizes and, thus, decreases the length of the triple-phase boundaries (tpb), resulting in high polarization resistance. As is evident in Fig. 1 (b), an addition of the GDC (40 vol.%) into the LSCF can suppress the growth of LSCF particles, and as a consequence, it sustains the porosity of the LSCF electrode and increases the tpb.

During the sintering process, a starting PtO_2 is completely reduced to Pt at around 650 °C. Although Pt particles cannot be seen in Fig. 1(c), it could be confirmed by high resolution SEM that Pt particles are dispersed in the LSCF. It seems that the Pt addition

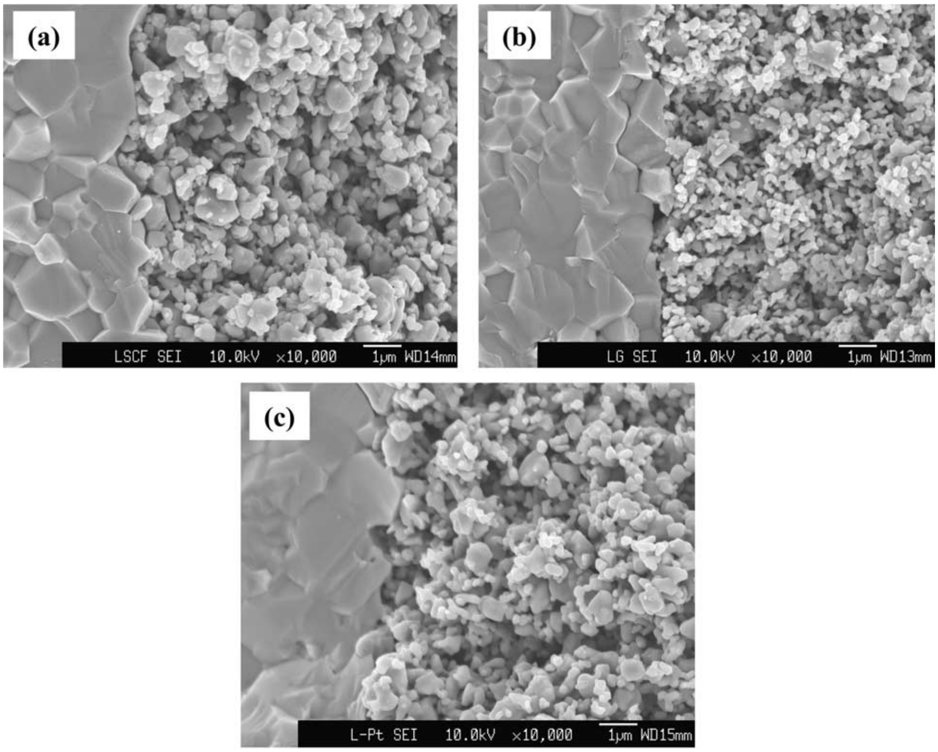

Fig. 1. Cross-section view of the LSCF (a), LSCF–GDC (b), LSCF–Pt (c), and LSCF–GDC–Pt (d) composite electrodes sintered at 1000 °C for 2 h.

does not affect the microstructure evolution of the LSCF. The microstructure of the LSCF–Pt composite electrode is almost the same as that of the LSCF electrode. This phenomenon is not surprising because the amount of Pt was very small (1 vol.%).

Fig. 2 shows impedance spectra, measured at 600 and 500 °C, in 20% oxygen atmosphere (balance helium), for several membrane reactors. The membrane reactors with composite electrodes showed better electrocatalytic activity than the LSCF/GDC/LSCF. The polarization resistance of the membrane reactor with the LSCF electrode was 0.5 Ω and 6.4 Ω at 600 and 500 °C, respectively. Considering that the polarization resistances of the LSCF–GDC or LSCF–Pt electrodes were ~0.2 and 2.5 Ω at 600 and 500 °C, the composite electrode is a candidate as an electrode material for oxygen reduction and NO decomposition, a finding consistent with reports by other researchers.[7]

At high temperature > 600 °C, the Pt addition seems to be more effective than GDC in enhancing the catalytic activity against O_2 reduction, while, at low temperature <600 °C, e.g., at 500 °C the LSCF–GDC was found to be a better oxygen electrode. This result means that the Pt and GDC addition would contribute to the catalytic activity improvement of the LSCF electrode in a different manner. Watanabe et al.[8] found that fine Pt particles had a significant depolarizing effect on LSM electrode. It was proposed that Pt promotes the dissociative adsorption of O_2 or the exchange reaction with oxygen vacancies. At low overpotential (impedance results), the LSCF–Pt composite electrode shows low polarization resistance than the LSCF electrode. However, at high overpotential (I $>$ 200 mA), the total resistance (ohmic + polarization) of the LSCF–Pt/GDC/LSCF–Pt membrane reactor was higher than that of the other two membrane reactors with pure LSCF or LSCF–GDC composite electrode, as will be described in Fig. 3. Therefore, the improvement of the catalytic activity of the LSCF–Pt composite electrode might be mainly due to the catalysis of the charge–transfer reaction, which is a rate-determining step of oxygen reduction at high temperature.[9]

The composite of LSCF and GDC showed its catalytic activity better at low temperature <600 °C rather than at high temperature. Comparing Fig. 1(a) with Fig. 1(b) suggests that GDC can serve as a grain growth inhibitor of LSCF. It is well known that the oxygen reduction process strongly depends on the microstructure of the electrode, in particular, the grain size of the electrode material. The low polarization resistance obtained in the LSCF–GDC composite electrode might be associated with the microstructural change by an addition of GDC. In addition, GDC not only can produce triple phase boundaries (tpb), but also provide rapid mass transport (the interface between LSCF and GDC) and enhance performance of the membrane reactor.[10]

As current flows through a membrane reactor, NO decomposes into nitrogen and oxygen ions on the cathode, and the oxygen ions can be pumped through the solid electrolyte to the anode. However, much more oxygen (2%) than NO (1000 ppm) is present in the reactant gas mixture, and the excess oxygen is preferably adsorbed and reduced in the cathode. Fig. 3 shows NO conversion rate (a) and terminal voltage (b) change as a function of current for three membrane reactors. No change in NO conversion rate occurred with an electric current <200 mA, indicating that, in the current range <200 mA, only oxygen is pumped from cathode to anode. The current, at which oxygen partial pressure becomes sufficiently lower than NO at the cathode, is the onset current at which NO conversion starts. The NO conversion rate increased abruptly as the current increased in the range 200–220 mA; thereafter, the increase in NO conversion rate slowed with further increases in current.

As is evident in Fig. 3 (a), the current required to initiate NO decomposition decreases in the following

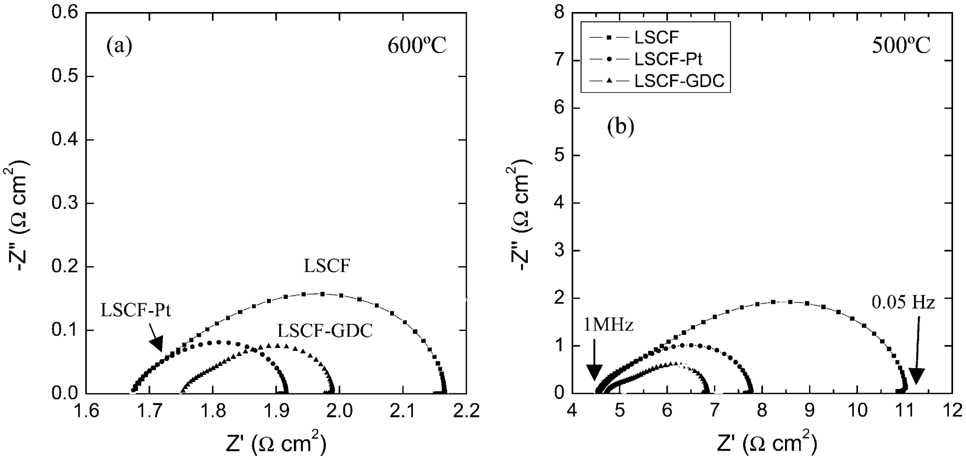

Fig. 2. AC impedance spectra of LSCF/GDC/LSCF, LSCF–GDC/GDC/LSCF–GDC, and LSCF–Pt/GDC/LSCF–Pt membrane reactors. The operating temperature of the reactors is 600 (a) and 500 °C (b).

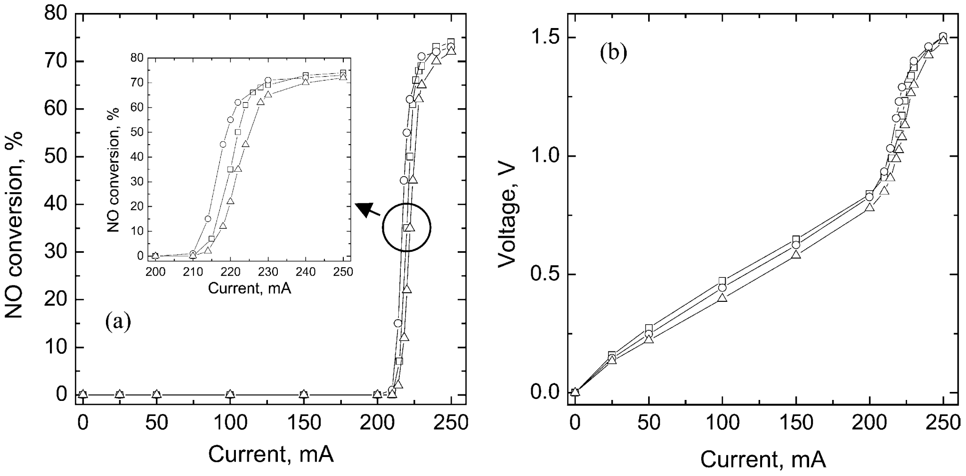

Fig. 3. Applied current vs. NO conversion rate (a) and terminal voltage (b) at 600 °C of LSCF/GDC/LSCF (squares), LSCF–Pt/GDC/LSCF–Pt (circles), and LSCF–GDC/GDC/LSCF–GDC (triangles) membrane reactors.

order: LSCF–Pt > LSCF > LSCF–GDC. On the other hands, the terminal voltage of the membrane reactors was lowest at a given current in the LSCF–GDC, and highest in the LSCF at $I<200$ mA or in the LSCF–Pt at $I > 200$ mA [Fig. 3 (b)]. This phenomenon means that at high overpotential ($I > 200$ mA) the LSCF–Pt electrode shows a slightly lower affinity against oxygen (relatively higher selectivity against NO) than the other two electrodes and, based on current, is a better electrode for NO decomposition. Because LSCF–GDC is a good electrode material for oxygen reduction at high overpotential, oxygen in the cathode, rather than NO, would be reduced preferably, until all of the oxygen had been pumped to the anode compartment.

4. Conclusions

Electrochemical removal of NO using the membrane reactor which consists of a solid electrolyte covered by porous catalytic electrodes has potentiality for use even in an excess-oxygen atmosphere, without the aid of reducing agents. However, in practice, electrochemical NO decomposition requires a decrease in electric power consumption and a lower working temperature. In this study, we fabricated a membrane reactor by using a GDC electrolyte and LSCF–GDC and LSCF–Pt composite electrodes. The LSCF–Pt electrode showed good electrocatalytic activity against O_2 at low overpotential and high temperature > 600 °C. In the microstructural viewpoint, an addition of GDC is more effective than Pt, and fine-grained microstructure can be obtained in the LSCF–GDC composite electrode. The resultant LSCF–GDC/GDC/LSCF–GDC membrane reactor exhibited 70% of NO conversion rate at a current density of 230 mA/cm^2.

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