Properties of $\text{La}_{2-x}\text{Pr}_x\text{NiO}_4$ cathode for intermediate-temperature solid oxide fuel cells

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A series of K_2NiF_4 -type compounds, $\text{La}_{2-x}\text{Pr}_x\text{NiO}_4$ ($x = 0, 0.6, 1.0, 1.4$, and 2.0), were synthesized by solid state reaction for use as cathodes in an intermediate-temperature ($500\text{--}700^\circ\text{C}$) solid oxide fuel cell (IT-SOFC). $\text{La}_{2-x}\text{Pr}_x\text{NiO}_4$ ($x = 0$ and 0.6) crystallize in the $Fmmm$ space group, while $\text{La}_{2-x}\text{Pr}_x\text{NiO}_4$ ($x = 1.0, 1.4$, and 2.0) belong to the $Bmab$ space group. The electrical conductivity increased by Pr doping and $\text{La}_{2-x}\text{Pr}_x\text{NiO}_4$ ($x = 0.6, 1.0$, and 1.4) exhibited electrical conductivities similar to one another while Pr_2NiO_4 had the highest. Single test-cells consisting of samarium oxide doped ceria (SDC) as an electrolyte, Ni-SDC cermet as an anode and $\text{La}_{2-x}\text{Pr}_x\text{NiO}_4$ as a cathode, were fabricated for measurements of cell performance at $500\text{--}700^\circ\text{C}$. Current interruption measurements revealed that the overpotential losses mainly decreased with increasing Pr content. Pr_2NiO_4 was found to exhibit the best cathode characteristics; maximum test-cell power densities of $14.1, 45.1$, and 104.4 mW/cm^2 were obtained at $500, 600$, and 700°C , respectively.

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1. Introduction

Lowering the operating temperature of solid oxide fuel cells (SOFCs) down to intermediate values ($500\text{--}700^\circ\text{C}$) is an important objective to realize the use of low-cost interconnectors and improve cell endurance. However, cathode resistance is still a limiting factor for operation at intermediate temperatures, because the cathode properties (e.g., electronic/oxide ionic conductivity^{1,2)} and catalytic activity for oxygen reduction reaction³⁾) strongly influence the performance of the SOFC. Therefore, high-performance cathode materials are required for the development of SOFCs operated at intermediate temperatures.

Recently, Ni-based layered perovskite compounds, $\text{Ln}_{2-x}\text{Ln}'_x\text{NiO}_4$ (Ln and $\text{Ln}' = \text{La, Pr, Nd, and Sm}$), with the K_2NiF_4 -type structure have attracted interest as SOFC cathodes, due to their excellent mixed ionic and electronic conducting properties.^{4–16)} Of particular note is that Pr_2NiO_4 exhibits the highest oxygen diffusion among the related perovskite oxides (Pr_2NiO_4 , Nd_2NiO_4 , La_2NiO_4 , $\text{Nd}_{1.8}\text{Ca}_{0.2}\text{NiO}_4$, and $\text{Nd}_{1.95}\text{NiO}_4$) at intermediate temperatures.¹³⁾ Previous investigations have already suggested the possibility of Pr_2NiO_4 as a prospective cathode material for an intermediate-temperature ($500\text{--}700^\circ\text{C}$) solid oxide fuel cell (IT-SOFC);^{14,15)} however, these were conducted by impedance spectroscopy measurements using symmetrical cells with the yttria-stabilized zirconia (YSZ) electrolyte, which is mostly used for high temperature (ca. 1000°C) SOFC. To develop high-performance cathode materials for IT-SOFC, it is necessary to investigate their performance using asymmetrical test-cells consisting of the cathode materials and electrolyte and anode materials that are appropriate for intermediate temperature applications. Moreover, previous re-

ports have also suggested that the rare earth elements of $\text{Ln}_{2-x}\text{Ln}'_x\text{NiO}_4$ influence the cathode properties. However, the electrode properties of the end members of a series of $\text{Ln}_{2-x}\text{Ln}'_x\text{NiO}_4$ have been mostly reported to date, and there have been few systematic studies on the substitution of the Ln site in $\text{Ln}_{2-x}\text{Ln}'_x\text{NiO}_4$ with other rare earth elements for the development of new cathode materials, except limited reports, such as that by Amow et al.¹⁰⁾ Accordingly, this study focused on the characterization of a series of $\text{La}_{2-x}\text{Pr}_x\text{NiO}_4$ ($x = 0, 0.6, 1.0, 1.4$, and 2.0) by the measurement of asymmetrical test-cells at intermediate temperature. The cathode properties of the $\text{La}_{2-x}\text{Pr}_x\text{NiO}_4$ series were systematically investigated using samarium oxide-doped ceria (SDC; $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_x$) electrolyte-supported test-cells.

2. Experimental

All cathode samples were prepared by solid state reaction of La_2O_3 (99.99%, Kanto Chemical, Tokyo, Japan), Pr_6O_{11} (99.9%, Kojundo Chemical Lab., Saitama, Japan), and NiO (99.9%, Kanto Chemical). The La_2O_3 powders were pre-heated at 900°C for 5 h in air to remove adsorbed water prior to weighing. Stoichiometric amounts of the starting materials were first mixed and ground with a ball mill for 24 h, and then calcined at 700°C for 10 h in air followed by further grinding for 24 h. The calcined powders were pressed into pellets under a uniaxial pressure of 5 MPa. $\text{La}_{2-x}\text{Pr}_x\text{NiO}_4$ ($x = 0, 0.6, 1.0, 1.4$, and 2.0) were then sintered at 1350°C for 4 h. The sintered pellets were reground with a ball mill for 24 h. The crystalline phases in the samples were identified using powder X-ray diffraction (XRD; Rigaku RINT2100/PC, Tokyo, Japan) with monochromated $\text{Cu K}\alpha$ radiation. The electrical conductivity of sintered sample bars was measured using the standard DC four-probe method with Pt wire probes. The density of the sintered samples was measured by Archimedes method, and the theoretical density was estimated, assuming the

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stoichiometric compositions for $\text{La}_{2-x}\text{Pr}_x\text{NiO}_4$ ($x = 0, 0.6, 1.0, 1.4, \text{ and } 2.0$) samples.

Single test-cells were fabricated as follows. Commercial SDC (AGC Seimi Chemical, Kanagawa, Japan) powder was pressed into a pellet (20-mm diameter) under a uniaxial pressure of 10 MPa followed by sintering at 1400°C for 24 h. The thickness of the electrolyte pellet was approximately 800 μm . Commercial Ni (50 mass %)- $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_x$ (Ni-SDC) powder, prepared by Hosokawa Powder Technology Research Institute, was applied as an anode material by screen-printing a paste of polyethylene glycol and Ni-SDC powder onto the SDC-sintered electrolyte pellet (14.9-mm diameter) followed by heating at 1300°C for 2 h. A cathode paste of polyethylene glycol and the prepared cathode powder samples was then screen-printed on the opposite side of the Ni-SDC-coated SDC electrolyte, followed by heating at 1000°C for 2 h, which resulted in cathode thicknesses of approximately 20–30 μm . The area of these respective electrodes was 28.3 mm^2 . The single test-cell was mounted into an alumina tube with a 9-mm inner diameter and a 13-mm outer diameter and heated in situ at 700°C in a reducing atmosphere to reduce NiO in the anode to metallic Ni. Commercial soft glass rings were used for sealing the test-cells. Measurements of cell performance were carried out at 500–700°C with humidified (3% H_2O) hydrogen and air supplied as fuel and oxidant, respectively, at a controlled gas-flow rate of 50 cm^3/min . Pt mesh current collectors were used for both electrodes. Current–voltage curves were measured using an electrochemical analyzer (IviumStat, Ivium Technologies, Eindhoven, The Netherlands). The current interruption technique was used to separately estimate the ohmic and overpotential losses in the test-cell, and measurements were conducted in parallel with the current–voltage curve measurements using a two-electrode configuration. When a constant-current load on the single test-cell was abruptly interrupted, the resulting voltage-time response was monitored. The ohmic and overpotential losses were estimated from the instantaneous rebound and time-dependent rebound in the voltage, respectively. The cross-sectional microstructures of the single test-cells were examined before and after the electrochemical tests using a scanning electron microscope (SEM; Jeol JSM-6380, Tokyo, Japan).

3. Results and discussion

XRD revealed that all samples were single-phase and identified as orthorhombic crystal structures (Fig. 1). As previously reported,¹⁷⁾ a phase transition occurs in the $\text{La}_{2-x}\text{Pr}_x\text{NiO}_4$ solid solution; $\text{La}_{2-x}\text{Pr}_x\text{NiO}_4$ ($x = 0$ and 0.6) crystallizes in the $Fmmm$ space group, while $\text{La}_{2-x}\text{Pr}_x\text{NiO}_4$ ($x = 1.0, 1.4, \text{ and } 2.0$) belong to the $Bmab$ space group. Furthermore, the lattice parameters of all samples, as shown in Fig. 2, were also consistent with those in the previous report.¹⁷⁾ Therefore, the cathode powder samples were confirmed for use in the test-cells.

The temperature dependence of the electrical conductivity for $\text{La}_{2-x}\text{Pr}_x\text{NiO}_4$ ($x = 0, 0.6, 1.0, 1.4, \text{ and } 2.0$) is shown in Fig. 3. The relative density of all samples ranged from 95 to 97%, and there is no significant difference in the values between the samples. The overall electrical conductivities of the end members (Pr_2NiO_4 and La_2NiO_4) at intermediate temperature (500–700°C) were similar to those reported by Boehm and coworkers,¹⁴⁾ and Pr_2NiO_4 exhibited the highest electrical conductivity in the $\text{La}_{2-x}\text{Pr}_x\text{NiO}_4$ ($x = 0, 0.6, 1.0, 1.4, \text{ and } 2.0$) series. Furthermore, the electrical conductivity increased by partial Pr doping and $\text{La}_{2-x}\text{Pr}_x\text{NiO}_4$ ($x = 0.6, 1.0, \text{ and } 1.4$) exhibited electrical conductivities similar to one another. Although this result is not yet clearly understood at this time, similar behavior, in which the

Fig. 1. X-ray diffraction patterns of (a) La_2NiO_4 , (b) $\text{La}_{1.4}\text{Pr}_{0.6}\text{NiO}_4$, (c) LaPrNiO_4 , (d) $\text{La}_{0.6}\text{Pr}_{1.4}\text{NiO}_4$, and (e) Pr_2NiO_4 .

Fig. 2. Cell parameters a , b , and c as a function of x in $\text{La}_{2-x}\text{Pr}_x\text{NiO}_4$ ($x = 0, 0.6, 1.0, 1.4, \text{ and } 2.0$).

Fig. 3. Temperature dependence of the electrical conductivity for $\text{La}_{2-x}\text{Pr}_x\text{NiO}_4$ ($x = 0, 0.6, 1.0, 1.4, \text{ and } 2.0$).

Ohmic loss vs. current density

Overpotential loss vs. current density

Fig. 4. Cell performance (left: ohmic loss vs. current density and right: overpotential loss vs. current density) at 500, 600, and 700°C for La_2NiO_4 (square), $\text{La}_{1.4}\text{Pr}_{0.6}\text{NiO}_4$ (circle), LaPrNiO_4 (diamond), $\text{La}_{0.6}\text{Pr}_{1.4}\text{NiO}_4$ (inverted triangle), and Pr_2NiO_4 (triangle).

electrical conductivity varies nonsystematically with the amount of doping, was reported for the $\text{La}_{2-x}\text{Sm}_x\text{NiO}_4$ system.¹⁰⁾ Consequently, it was revealed that Pr_2NiO_4 was suitable as the best cathode material for IT-SOFC in the $\text{La}_{2-x}\text{Pr}_x\text{NiO}_4$ system, in terms of the electrical conductivity. Furthermore, the electrical conductivities of $\text{La}_{2-x}\text{Pr}_x\text{NiO}_4$ ($x = 0.6, 1.0$, and 1.4) were also acceptable, assuming a conductivity requirement of approximately 100 S/cm at the operating temperature (700°C).

The single-cell performance of the $\text{La}_{2-x}\text{Pr}_x\text{NiO}_4/\text{SDC}$ (800 μm thick)/Ni-SDC cell configurations was examined at intermediate temperatures. The cell performance characteristics

(ohmic loss vs. current density and overpotential loss vs. current density) measured at 500, 600, and 700°C are shown in Fig. 4. All test-cells exhibited similar ohmic resistance over the entire temperature range. In contrast to the difference in the ohmic resistance between the test-cells, the difference in the overpotential resistance varied with Pr content and increased with decreasing operation temperature. The overpotential resistance at 500°C decreased significantly with increasing Pr content. The cathode properties (e.g., electronic/oxide ionic conductivity^{1),2)} and catalytic activity for oxygen reduction reaction³⁾) strongly influence the overpotential resistance. SEM observation revealed

Fig. 5. Scanning electron microscope micrographs of (a) La_2NiO_4 , (b) $\text{La}_{1.4}\text{Pr}_{0.6}\text{NiO}_4$, (c) LaPrNiO_4 , (d) $\text{La}_{0.6}\text{Pr}_{1.4}\text{NiO}_4$, and (e) Pr_2NiO_4 of $\text{La}_{2-x}\text{Pr}_x\text{NiO}_4/\text{SDC}/\text{Ni-SDC}$ cells. Inset: the enlarged cross-sectional view of the $\text{La}_2\text{NiO}_4/\text{SDC}/\text{Ni-SDC}$ cell.

good contact between the cathode and electrolyte, and the microstructure and thickness of the cathodes were approximately the same among the test-cells (Fig. 5). Therefore, it was considered that Pr doping caused the differences in cathode properties. It has been reported that Pr_2NiO_4 exhibits higher oxygen diffusion than La_2NiO_4 ,¹³⁾ therefore, it is highly possible that the difference in overpotential resistance is due to the difference in the oxygen diffusion of the cathode materials. Moreover, Huang et al.¹⁸⁾ and Takahashi et al.¹⁹⁾ have reported that catalytic activity could be related with the redox couples of the transition metal B site cation in perovskite compounds (ABO_3) and layered perovskite compounds (A_2BO_4 , $\text{A}_3\text{B}_2\text{O}_7$, and $\text{A}_4\text{B}_3\text{O}_{10}$), respectively. For example, the following reactions might occur in the case of the M(IV)/M(III) redox couples on a cathode surface:

where $\square$ represents an oxygen vacancy. Therefore, it is considered that the increase of the redox couples increases the catalytic activity, so that another possible explanation is that Ni(IV)/Ni(III) redox couples produced by introducing Pr^{4+} species, which can be present on the cathode surface and can increase with increasing Pr doping amount, may enhance the catalytic activity.

It should be noted that the test-cell with $\text{La}_{1.4}\text{Pr}_{0.6}\text{NiO}_4$ showed anomalously low overpotential resistance at 700°C. Although the reason for this result is still unclear, the result for the $\text{La}_{2-x}\text{Pr}_x\text{NiO}_4$ series is interesting. Figure 6 shows the cell performance characteristics (power density vs. current density) measured at 500, 600, and 700°C. The open-circuit voltage (OCV) values for all cathodes were lower than the theoretical electromotive force values estimated from the Nernst equation, due to the electronic leakage of the SDC electrolyte. Thus, these results suggest that from the $\text{La}_{2-x}\text{Pr}_x\text{NiO}_4$ ($x = 0, 0.6, 1.0, 1.4$,

Fig. 6. Power density vs. current density at 500, 600, and 700°C for La_2NiO_4 (square), $\text{La}_{1.4}\text{Pr}_{0.6}\text{NiO}_4$ (circle), LaPrNiO_4 (diamond), $\text{La}_{0.6}\text{Pr}_{1.4}\text{NiO}_4$ (inverted triangle), and Pr_2NiO_4 (triangle).

and 2.0) series, Pr_2NiO_4 is the best candidate for use as an IT-SOFC cathode material. In addition, $\text{La}_{1.4}\text{Pr}_{0.6}\text{NiO}_4$ possesses cathode properties comparable to Pr_2NiO_4 at 700°C. The maximum power densities for the test-cell with a Pr_2NiO_4 cathode were 14.1, 45.1, and 104.4 mW/cm² at 500, 600, and 700°C, respectively.

4. Conclusions

A series of $\text{La}_{2-x}\text{Pr}_x\text{NiO}_4$ ($x = 0, 0.6, 1.0, 1.4$, and 2.0) K_2NiF_4 -type compounds were prepared and comparatively evaluated as IT-SOFC cathodes. $\text{La}_{2-x}\text{Pr}_x\text{NiO}_4$ ($x = 0$ and 0.6) crystallized in

the $Fmmm$ space group and $\text{La}_{2-x}\text{Pr}_x\text{NiO}_4$ ($x = 1.0, 1.4$, and 2.0) crystallized in the $Bmab$ space group. The electrical conductivity increased by Pr doping and $\text{La}_{2-x}\text{Pr}_x\text{NiO}_4$ ($x = 0.6, 1.0$, and 1.4) exhibited electrical conductivities similar to one another while Pr_2NiO_4 had the highest. Cell performance measurements conducted at $500\text{--}700^\circ\text{C}$ with $\text{La}_{2-x}\text{Pr}_x\text{NiO}_4/\text{SDC}/\text{Ni-SDC}$ single test-cell configurations indicated that the cell performance mainly increased with Pr content, due to enhancement of the cathode properties. In the series of $\text{La}_{2-x}\text{Pr}_x\text{NiO}_4$ materials, Pr_2NiO_4 was determined to be the best candidate for an IT-SOFC cathode. $\text{La}_{1.4}\text{Pr}_{0.6}\text{NiO}_4$ possessed comparable cathode properties to Pr_2NiO_4 at 700°C . The maximum power densities for the test-cell with a Pr_2NiO_4 cathode were $14.1, 45.1$, and $104.4\text{ mW}/\text{cm}^2$ at $500, 600$, and 700°C , respectively.

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