Chromium Poisoning of Neodymium Nickelate (Nd_2NiO_4) Cathodes for Solid Oxide Fuel Cells

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ABSTRACT

In this study, we investigated the long-term stability of Nd_2NiO_4 solid oxide fuel cell (SOFC) cathodes to evaluate their chromium poisoning tolerance. Symmetrical cells consisting of Nd_2NiO_4 electrodes and a yttria-stabilized zirconia electrolyte were fabricated and the cell potential and polarization resistance were measured at 850 °C in the presence of gaseous chromium species for 800 h. Up to 500 h of operation, the cell potential remained constant at 500 mA/cm². However, it increased slightly over the operation duration of 550–800 h. No appreciable increase was observed in the polarization resistance of the Nd_2NiO_4 cathode during the entire operation of 800 h. Physicochemical examinations revealed that the gaseous chromium species did not form chromium-related contamination not only in the Nd_2NiO_4 cathode but also at the cathode/electrolyte interface. The results demonstrated that Nd_2NiO_4 is resistant to chromium poisoning, and hence is a potential alternative to standard perovskite cathodes.

Key words : Nd_2NiO_4 , Chromium poisoning, Solid oxide fuel cells, Impedance spectra, Long-term stability

1. Introduction

High-temperature solid oxide fuel cells (SOFCs) have several advantages over polymer electrolyte membrane fuel cells, which operate at low temperatures.¹⁾ SOFCs exhibit multi-fuel capability, i.e., carbon monoxide or hydrocarbons can be directly supplied to the fuel electrode.²⁾ The operating temperature of SOFCs is 600–800°C. FCs with a high operating temperature exhibit high energy generation efficiency, particularly when they are coupled with a gas turbine. The electrical efficiency of SOFCs is 50–60%,³⁾ which increases up to 80% in combined heat and power applications.⁴⁾ In addition, since SOFCs are all-solid-state devices, they do not require liquid management and offer cell or stack design flexibility.⁵⁾

Solid ceramic electrolytes are used in SOFCs. The most popular SOFC electrolyte material is 8 mol% yttria-stabilized zirconia (8YSZ), which is a good oxygen ion conductor. Nickel-YSZ cermet and mixed ionic and electronic conducting (MIEC) ceramics are used as the SOFC anode and cathode materials, respectively. It has been reported that cathodic polarization is the major phenomenon that deteriorates the power density of SOFCs.⁶⁾ Thus, the choice of a good MIEC material and strategies for improving the catalytic activity of MIEC cathodes have been widely examined.⁷⁾ $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ (LSC), $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_{3-\delta}$ (LSCF), and

$\text{Ba}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_{3-\delta}$ (BSCF) have been studied as SOFC cathode materials because of their high catalytic activity for the oxygen reduction reaction and excellent electrical conductivity over a wide temperature range.^{8–10)}

Over the past few years, because of the decrease in the SOFC operating temperature, ferritic stainless steel has gained immense attention as an interconnecting material.¹¹⁾ Ferritic stainless steel is cost-effective and easy to manufacture and exhibits high electrical and thermal conductivities.^{12,13)} However, it requires effective oxidation protective coating and cathode materials that are inert and tolerant to chromium deposition and poisoning.¹⁴⁾ The oxidative scale reaction between oxygen and water vapor forms volatile Cr(VI) species, which poison SOFC cathodes.¹⁵⁾ The alkaline earth metal (particularly strontium among LSCF) cathodes are not suitable for long-term operation of SOFCs.¹⁶⁾ Therefore, various efforts have been made to develop novel cathode materials with high chromium resistance.¹⁷⁾

Recently, a novel $\text{A}_2\text{MO}_{4+\delta}$ (A: alkaline earth or rare earth metal, M: transition metal) oxide compound with a K_2NiF_4 -type structure has gained attention as a promising SOFC cathode material.^{18–20)} This compound is characterized by the stoichiometry of excess oxygen and a mixed valency of M. These structural characteristics can lead to high oxygen ion mobility and oxygen surface exchange coefficients.^{21,22)} Since $\text{NdNi}_2\text{O}_{4+\delta}$ -related materials do not contain strontium or manganese, unlike LSCF or lanthanum strontium manganite (LSM), they exhibit high chromium tolerance, and hence are considered as potential SOFC cathode materials.²³⁾

However, there is some controversy regarding the chromium poisoning tolerance of nickelate-based cathode mate-

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rials. Park *et al.* investigated the chromium poisoning mechanism of LSM, $\text{Pr}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$, $\text{Nd}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$, and BSCF at 700°C and found that polarization increased with an increase in the deposition of chromium.²⁴ Schuler *et al.* showed that Nd-nickelate cathodes undergo degradation because of chromium poisoning.²⁵ In contrast, Yang *et al.* reported that gaseous chromium species have a minor effect on the surface exchange properties of $\text{Nd}_{1.95}\text{NiO}_{4.6}$.²³ This discrepancy may be associated with the composition variations or non-stoichiometry of the materials. In this study, we fabricated electrolyte-supported symmetrical cells consisting of a YSZ electrolyte and Nd_2NiO_4 electrodes and investigated the chromium poisoning of the Nd_2NiO_4 cathodes under open-circuit and constant current density conditions at 850°C for 800 h. Gaseous chromium species such as CrO_3 or $\text{CrO}_2(\text{OH})_2$ were produced from porous Cr_2O_3 powder compacts, and the humidifying air passing through Cr_2O_3 was delivered to the cell.

2. Experimental Procedure

Nd_2NiO_4 powder was synthesized using the solid-state reaction process. Nd_2O_3 (99.9%, Sigma-Aldrich, St. Louis, MO, USA) and NiO (99.9%, Sumitomo, Tokyo, Japan) were used as the starting materials. Stoichiometric amounts of Nd_2O_3 and NiO were mixed in ethanol (94.5%, Samchun Pure Chemicals, Pyeongtaek, Korea) using a planetary mill. After drying, the powder mixtures were calcined at 1100–1200°C for 12 h in air. Symmetrical cells consisting of a YSZ electrolyte and Nd_2NiO_4 electrodes were fabricated using a YSZ disk and Nd_2NiO_4 paste by screen-printing. The YSZ electrolyte disks were produced by sintering a 8YSZ (yttria-stabilized zirconia, Tosoh Corporation, Tokyo, Japan) powder compact at 1450°C for 5 h in air. The diameter and thickness of the YSZ disk were 20 and 0.2 mm, respectively. Before sintering, the YSZ powder compact was cold isostatic pressed at 200 MPa. Nd_2NiO_4 electrode films were coated on both sides of the 8YSZ disk by screen printing using the Nd_2NiO_4 paste. The Nd_2NiO_4 electrode films were dried at 150°C and subsequently sintered at 1050, 1100, and 1150°C for 2 h in air.

For the chromium poisoning test, two symmetrical cells were placed in an electric furnace, which was heated to 850°C, and 3% H_2O -humidified air was supplied to the furnace. Gaseous chromium species were produced using a chromium oxide (Cr_2O_3) powder compact. The Cr_2O_3 powder

(99.0%, Junsei Chemical Co., Ltd., Tokyo, Japan) was dry-pressed into a disk and sintered at 1000°C for 1 h. The temperature of the Cr_2O_3 powder compact was 700°C. Fig. 1 shows the schematic of the set up used for the chromium poisoning test. The test was carried out under open-circuit conditions and at a current load of 500 mA/cm^2 . An impedance analyzer was connected to the two cells to apply an electric current.

Phase identification of the synthesized Nd_2NiO_4 powder was carried out using an X-ray powder diffractometer (XRD, DMAX-2500, Rigaku, Tokyo, Japan) with Ni-filtered $\text{CuK}\alpha$ radiation. Microstructural and compositional analysis was carried out using a field emission scanning electron microscope (S-3200, Philips, Amsterdam, Netherlands). The electrochemical performance of the symmetrical cells was evaluated by electrochemical impedance spectroscopy. AC impedance spectra were obtained on an impedance analyzer (IM6e, Zahner, Germany) under open-circuit conditions at an excitation potential of 20 mV over a frequency range of 1 MHz–0.01 Hz.

3. Results and Discussion

In this study, the Nd_2NiO_4 powder was synthesized by calcining the mixture of Nd_2O_3 and NiO powders at various temperatures to obtain a single-phase Ruddlesden-Popper (RP) structure. Fig. 2 shows the XRD patterns of the powder samples calcined at 1100, 1150, and 1200°C for 5 h. The

Fig. 2. XRD patterns of the powder samples calcined at 1100, 1150, and 1200°C.

Fig. 1. Schematic of the set up used for the chromium poisoning test.

Fig. 3. Polarization resistance of the Nd_2NiO_4 electrodes sintered at 1050, 1100, and 1150°C.

powder sample calcined at 1100°C consisted of the Nd_2O_3 phase. This indicates that the calcination temperature of 1100°C was too low to obtain a single-phase RP structure. In contrast, the powder samples calcined at temperatures above 1150°C had the single-phase RP structure and did not contain Nd_2O_3 , NiO , or unwanted reaction phases. The obtained Nd_2NiO_4 powders showed an orthorhombic structure. Nd_2NiO_4 is orthorhombic at room temperature and becomes tetragonal at temperatures $\geq 800^\circ\text{C}$.²⁶⁾

To investigate the effect of the sintering temperature on the catalytic activity of the Nd_2NiO_4 cathodes, their impedance spectra were obtained. The polarization resistances of the cells were determined from their impedance arcs. The temperature-dependent polarization resistance of the cells is shown in Fig. 3. The polarization resistance decreased with an increase in the operating temperature. This phenomenon was expected because the activation energies of electrode reactions decrease exponentially with temperature.²⁷⁾ In general, the polarization resistance of SOFC cathodes increases with an increase in the sintering temperature. This can be explained by the reduced triple-phase boundary caused by the grain growth of the electrode when sintering

is carried out at high temperatures. This was not observed in this study. In this study, high-temperature sintering enhanced the interfacial adhesion of the porous Nd_2NiO_4 electrodes to the YSZ electrolyte, thus reducing the polarization resistance of the cell.²⁸⁾

The effect of chromium poisoning on the long-term stability of the Nd_2NiO_4 electrodes was investigated. The cell potential and polarization resistance of the $\text{Nd}_2\text{NiO}_4/\text{YSZ}/\text{Nd}_2\text{NiO}_4$ symmetrical cell as a function of time at 500 mA/cm² are shown in Fig. 4. The resistance values shown in Fig. 4(b) were obtained from the impedance analysis results shown in Fig. 5. The Nd_2NiO_4 electrode sintered at 1150°C for 5 h was used. As shown in Fig. 4, stable and slightly improved cell performance was observed over the 500 h of operation. The initial decrease in the potential occurred because of the activation of the cathode. The cell required time to reach a steady-state condition, indicating that the voltage or current readings did not change over time.²⁹⁾ This delay occurred because of the changes in the microstructure of the electrode and in the reaction atmosphere. After the activation, the potential became rather stable and did not change (~ 0.6 V) even after 500 h of operation. In contrast, during 500–540 h of operation, the potential showed an unexpected increase with time. This can be attributed to the chromium poisoning of the Nd_2NiO_4 cathode or the contact problems between the Nd_2NiO_4 cathode and the YSZ electrolyte.

Figure 5 shows the impedance spectra of the Nd_2NiO_4 electrode after 84, 492, and 788 h of operation under gaseous chromium species. The impedance spectra showed two arcs; a large arc in the medium-frequency range ($\sim 10^3$ Hz) and a small arc in the low-frequency range ($\sim 10^0$ Hz). No significant change was observed in the polarization resistance (difference between the high- and low-frequency arc intercepts with the real axis) even after 788 h of operation. This suggests that the catalytic activity of the Nd_2NiO_4 electrode did not degrade appreciably in the presence of gaseous chromium species. However, the ohmic resistance showed a two-fold increase with an increase in the operation time from 788 to 492 h (high-frequency arc intercept with the

Fig. 4. (a) The cell potential and (b) polarization resistance as a function of time of the $\text{Nd}_2\text{NiO}_4/\text{YSZ}/\text{Nd}_2\text{NiO}_4$ symmetrical cell under gaseous chromium species at 500 mA/cm². The cell temperature was 850°C.

Fig. 5. Impedance spectra of the Nd_2NiO_4 electrode after 84, 492, and 788 h of operation.

real axis). We believe that this increase in the resistance resulted in the abrupt voltage decrease (increase in potential) during 500–540 h of operation, as described in the previous section (Fig. 4).

With an increase in the operation time, the shape of the impedance arc changed slightly. The low frequency arc increased after 884 h of operation. The medium frequency arc can be attributed to the charge transfer during the oxygen reduction reaction at the cathode, while the low frequency arc can be attributed to the mass transfer or interface between the electrolyte and the electrode.³⁰⁾ The

subtle change in the structure of the YSZ/ Nd_2NiO_4 interface might have increased the low frequency arc.

The deposition of chromium on the Nd_2NiO_4 electrode during the chromium poisoning test was confirmed by energy-dispersive spectroscopy (EDS) analysis. The analysis was carried out under open-circuit conditions and at a current load of 500 mA/cm^2 . For comparison, we also carried out the EDS analysis of the cell before chromium poisoning under the same conditions. Fig. 6 shows the concentration profiles of nickel, neodymium, and chromium obtained from the EDS line scan from the cross-section of the Nd_2NiO_4 cathode/YSZ electrolyte interface. Although some fluctuations were observed in the cathode region, the nickel and neodymium concentrations decreased sharply at the interface and became nearly zero in the YSZ region, suggesting that the diffusion of nickel or neodymium into the YSZ electrolyte was negligible. The chromium concentration remained almost constant throughout the electrode before and after the chromium poisoning test. Chromium deposition was not observed at the cathode or the interface between the electrode and the electrolyte.

To further examine the chromium deposition on the Nd_2NiO_4 cathode, its transmission electron microscopy-EDS (TEM-EDS) analysis was carried out after removing it from the electrolyte. Fig. 7 shows the TEM images and the corre-

Fig. 6. EDS analysis of the Nd_2NiO_4 electrode and YSZ electrolyte after the chromium poisoning test; (a) before the chromium poisoning test, (b) under open-circuit conditions, and (c) at a current load of 500 mA/cm^2 .

Fig. 7. TEM images and EDS analysis of the Nd_2NiO_4 cathode operated at 850 °C for 1000 h; (a) before the chromium poisoning test, (b) under open-circuit conditions, and (c) at a current load of 500 mA/cm².

sponding EDS analysis results of the Nd_2NiO_4 cathode. It can be observed that the increase in the chromium concentration after the chromium poisoning test was nearly negligible. Interestingly, Figs. 7(b) and 7(c) show that the chromium concentration was nearly the same for the cells operated under open-circuit conditions and at the current load of 500 mA/cm². This suggests that the electrochemical deposition of chromium compounds was negligible and that the Nd_2NiO_4 cathode was highly resistant to gaseous chromium species.

Figure 8 shows the XRD patterns of the YSZ electrolyte surface and Nd_2NiO_4 cathode before and after the chromium poisoning test. Fig. 8(b) shows that the Nd_2NiO_4 cathode had an orthorhombic structure before the chromium poison-

ing test, as was also shown in Fig. 2. In contrast, peaks corresponding to the tetragonal structure were detected at $2\theta = 31$ and 32° after the chromium poisoning test. This phenomenon was more remarkable when a current of 500 mA was applied. This indicates that after the chromium poisoning test, the Nd_2NiO_4 sample showed mixed phases with the orthorhombic and tetragonal structures. Generally, the crystal structure of R-P phases such as Nd_2NiO_4 depends on factors such as oxygen vacancy and thermal history.^{31–33} Hence, Nd_2NiO_4 samples exposed to high temperatures and potentials for long durations can experience crystal structural changes.

As shown in Figs. 8(a) and 8(b), chromium-related compounds were not detected in the cells operated under the

Fig. 8. XRD patterns of (a) YSZ electrolyte surface and (b) Nd_2NiO_4 cathode powder before and after the chromium poisoning test.

open-circuit conditions and at the current load of 500 mA/cm² even after 800 h of operation. Therefore, only small amounts of chromium-related compounds were deposited on the electrode surface. Additionally, the electrochemical deposition of chromium did not occur at the Nd_2NiO_4 /YSZ interface.

4. Conclusions

In this study, we investigated the electrochemical performance and chromium poisoning of symmetrical cells consisting of Nd_2NiO_4 electrodes and a YSZ electrolyte. The sintering temperature significantly affected the catalytic activity of the Nd_2NiO_4 cathode. High-temperature sintering resulted in a strong adhesion between the cathode and the YSZ electrolyte, thus decreasing the polarization resistance of the cell. Up to 500 h of operation, the cell showed a constant potential of 500 mA/cm² in the presence of gaseous chromium species. The potential increased over the operation duration of 540–550 h. This can be attributed to the electrode/electrolyte interface and not chromium poisoning. The impedance spectra of the cells showed no significant increase in the polarization resistance after the chromium poisoning test. In addition, the XRD and EDS results suggested that no chromium-related compound was found in either the Nd_2NiO_4 cathode or the cathode/YSZ interface. Therefore, Nd_2NiO_4 is a promising material for SOFC cathodes because of its high catalytic activity and chromium poisoning tolerance.

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