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PROPERTIES OF COPPER DOPED NEODYMIUM NICKELATE OXIDE AS CATHODE MATERIAL FOR SOLID OXIDE FUEL CELLS

Mixed ionic and electronic conducting K_2NiF_4 -type oxide, $Nd_2Ni_{1-x}Cu_xO_{4+\delta}$ ($x=0\sim 1$) powders were synthesized by solid state reaction technique and solid oxide fuel cells consisting of a $Nd_2Ni_{1-x}Cu_xO_{4+\delta}$ cathode, a Ni-YSZ anode and ScSZ as an electrolyte were fabricated. The effect of copper substitution for nickel on the electrical and electrochemical properties was examined. Small amount of copper doping ($x=0.2$) resulted in the increased electrical conductivity and decreased polarization resistance. It appears that this phenomenon was associated with the high mean valence of nickel and copper and the resulting excess oxygen (δ). It was found that power densities of the cell with the $Nd_2Ni_{1-x}Cu_xO_{4+\delta}$ ($x=0.1$ and 0.2) cathode were higher than that of the cell with the $Nd_2NiO_{4+\delta}$ cathode.

Keywords: Solid oxide fuel cells, $Nd_2Ni_{1-x}Cu_xO_{4+\delta}$, Copper, Electrical conductivity, Excess oxygen

1. Introduction

A solid oxide fuel cell (SOFC) is known to be an efficient energy conversion system that produces electricity by electrochemically combining a fuel and an oxidant across an ionic conducting oxide electrolyte. Generally, the SOFC stack has been designed to be operated at higher temperature than 800°C since the power density and efficiency increased with increasing temperature. However, the high-temperature operation, especially, for a long time can lead to the cell performance degradation which is resulted from the deterioration of the material or the reaction between the components. In this regard, the durability problem of the cell and stack is an obstacle that prevents the commercialization of SOFC [1, 2].

Therefore, it is necessary to lower the operating temperature of the SOFC to an intermediate temperature. When the SOFC stack is operated at the intermediate temperatures, the rate of the electrochemical reaction is rapidly decreased at electrodes, in particular, at cathode, which can results in the decrease in the performance of the cell. Recently, researches regarding the new cathode material showing high catalytic activity in the intermediate temperature range (650 to 800°C) have been actively carried out [3, 4].

Ruddlesden-Popper (RP) type oxides of general formula of $A_2BO_{4+\delta}$ particularly neodymium nickelate ($Nd_2NiO_{4+\delta}$) have attracted great attention as an alternative cathode material for intermediate temperature SOFCs due to their interesting transport, mechanical and catalytic properties [5-8]. $Nd_2NiO_{4+\delta}$ showed high electronic and oxygen ion conductivity due to the interstitial oxygen atoms located in rock salt layer. The interstitial oxygen can make the $Nd_2NiO_{4+\delta}$ -based oxide to be a good catalyst material for the oxygen reduction reaction [10-12]. In addition, $Nd_2NiO_{4+\delta}$

exhibits the phase compatibility with gadolinium doped ceria (GDC) or lanthanum strontium magnesium gallate (LSGM) electrolyte that are widely used for an intermediate temperature SOFC electrolyte material [9].

In this study, RP type $Nd_2Ni_{1-x}Cu_xO_{4+\delta}$ ($x=0\sim 1$) based oxides were synthesized by solid state reaction technique and the performance of the cell consisting of a scandia-stabilized zirconia (ScSZ) electrolyte, $Nd_2Ni_{1-x}Cu_xO_{4+\delta}$ ($x = 0, 0.1, 0.2$) cathode, and Ni-yttria-stabilized zirconia (YSZ) anode, were investigated in terms of the copper content. Also, we tried to evaluate the polarization losses with respect to oxygen ion oxidation over the $Nd_2Ni_{1-x}Cu_xO_{4+\delta}$ ($x = 0, 0.1, 0.2$) cathode.

2. Experimental

$Nd_2Ni_{1-x}Cu_xO_{4+\delta}$ ($x=0\sim 1$) powders were prepared by solid state reaction technique using Nd_2O_3 (99.9%, Sigma Aldrich, USA), NiO (99.9%, Sigma Aldrich, USA) and CuO (99.9%, Sigma Aldrich, USA). The starting materials were mixed using planetary ball-mill and then calcined at 1150°C for 5 h.

An electrolyte supported Ni-YSZ/ScSZ/ $Nd_2Ni_{1-x}Cu_xO_{4+\delta}$ and $Nd_2Ni_{1-x}Cu_xO_{4+\delta}$ GDC/ $Nd_2Ni_{1-x}Cu_xO_{4+\delta}$ cells were fabricated from ScSZ (89 mole% ZrO_2 -10 mole% Sc_2O_3 -1 mole% Al_2O_3 , Daich Kigenso Kagau Kogyo Co. Ltd., Japan), Ni-YSZ (Fuel Cell Materials, USA) and gadolinium-doped ceria (GDC, Anan Kasei, Japan) powder. First, the GDC and ScSZ powders were uniaxially pressed into a pellet and sintered at 1450 and 1500°C for 5 h in air, respectively. $Nd_2Ni_{1-x}Cu_xO_{4+\delta}$ and Ni-YSZ pastes were prepared by mixing the powders and an organic vehicle. The $Nd_2Ni_{1-x}Cu_xO_{4+\delta}$ cathode and Ni-YSZ anode layers were coated on the ScSZ or GDC disk using screen printing technique followed by heat-

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treatment at 1000°C and 1400 °C for 2 h in air, respectively. The area of the electrode was 1 cm².

The alumina tubes on both the top and bottom sides of the cell were sealed with Pyrex glass rings. The cell was then placed inside a furnace and heated to 800°C to allow for the sealing glass to be softened. H₂ containing 3% H₂O and air were supplied to the anode and anode sides, respectively. The partial pressure of water vapor in the cathode gas mixture was determined by the temperature of the water bath inside the humidifier. The flow rates of H₂ and air were 100 ml·min⁻¹.

Phase identification of synthesized powders were performed with powder diffractometer (XRD, RU-200B, Rigaku Co. Ltd., Japan) with Ni-filtered CuKα radiation. The microstructures of the cathode were examined using a field emission scanning electron microscope (FE-SEM, JSM-6700F, JEOL, Japan).

The electrical conductivity was measured on sintered pellets in the temperature range 300–900°C using the four-probe method [20]. The current density-voltage curves were measured with a three probe method using electrochemical testing equipment (IM6e, Zahner, Germany). The three Pt wires from the anode, cathode, and reference electrodes were connected to the working, counter, and reference terminals of the testing equipment, respectively.

3. Results and discussion

XRD patterns for the synthesized Nd₂Ni_{1-x}Cu_xO_{4+δ} (x=0~1) powders are shown in Fig. 1. It was confirmed that the powder sample of Nd₂NiO_{4+δ} are orthorhombic phase, while it was transformed to tetragonal phase with the increase of the copper doping content in Nd₂Ni_{1-x}Cu_xO_{4+δ}. The crystalline structure of Nd₂Ni_{1-x}Cu_xO_{4+δ} strongly depends on excess oxygen (δ) [10, 11] and the tetragonal phase is more stable than the orthorhombic phase as the oxygen over-stoichiometry is increased. Thus, it can be inferred that the excess oxygen of Nd₂Ni_{1-x}Cu_xO_{4+δ} is increased with increasing the copper content [8, 14].

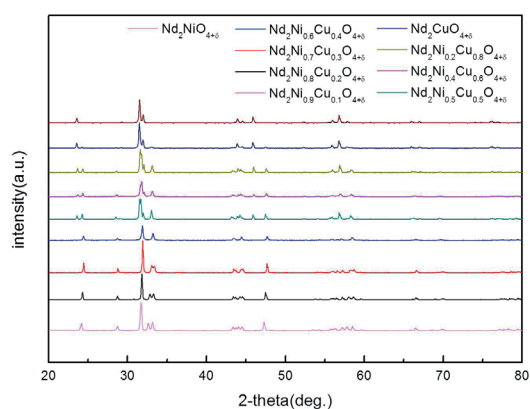


Fig. 1. XRD patterns of Nd₂Ni_{1-x}Cu_xO_{4+δ} (x=0~1)

Figure 2 presents the electrical conductivities of the Nd₂NiO_{4+δ}, Nd₂Ni_{0.8}Cu_{0.2}O_{4+δ} and Nd₂CuO_{4+δ} [13] samples measured in air as a function of temperature. The conductivity of the Nd₂NiO_{4+δ} and Nd₂Ni_{0.8}Cu_{0.2}O_{4+δ} samples increased

as the temperature increased in the low temperature range (300~500°C) and thereafter decreased. It appears that this phenomenon results from the typical semiconductor-to-metal transition at the high temperature [15-18]. On the other hand, the Nd₂CuO_{4+δ} sample exhibited the typical temperature dependence which can be observed in oxide semiconductors, i.e., the conductivity increased with increasing the temperature.

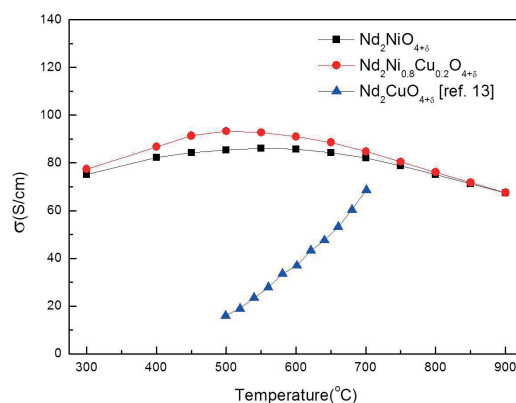


Fig. 2. Electric conductivity of Nd₂Ni_{1-x}Cu_xO_{4+δ} (x=0, 0.2, 1) with temperature

As is evident in Fig. 2, the conductivity of the Nd₂Ni_{0.8}Cu_{0.2}O_{4+δ} sample is slightly higher than that of the Nd₂NiO_{4+δ} sample and also much higher than that of Nd₂CuO_{4+δ} sample. This result suggests that adding a small amount of copper into Nd₂NiO_{4+δ} effectively contributes to the electrical conductivity enhancement. Generally, electronic and ionic conduction of K₂NiF₄-type oxide was associated with the metal mixed valency and the excess oxygen (oxygen over-stoichiometry), respectively [19]. Thus, it can be considered that copper doping in the Nd₂NiO_{4+δ} structure can result in the increased Ni³⁺/Ni²⁺ and Cu³⁺/Cu²⁺ ratios, which allows the Nd₂Ni_{0.8}Cu_{0.2}O_{4+δ} sample to have good electronic and ionic conductivity.

Polarization resistances determined from impedance spectra of the Nd₂Ni_{1-x}Cu_xO_{4+δ}/GDC/ Nd₂Ni_{1-x}Cu_xO_{4+δ} symmetric cells were shown in Fig. 3 (a) and (b). Polarization resistance was decreased with increasing the copper doping content and show the minimum at x=0.2. The further addition of copper resulted in the increased polarization resistance. It seems that the copper doping effect on the polarization resistance is complicated and the observed phenomenon is associated with the electrical conductivity, excess oxygen and crystal structure in terms of copper doping content.

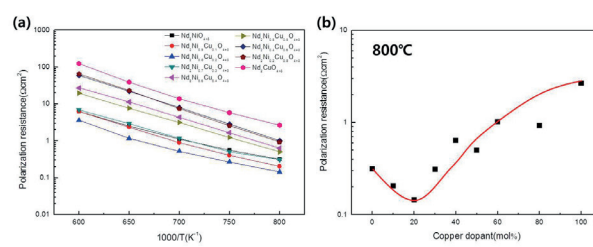


Fig. 3. Polarization resistance of Nd₂Ni_{1-x}Cu_xO_{4+δ} (x=0~1) with (a) temperature, (b) copper dopant at 800°C

The electronic state of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4+\delta}$ becomes a localized or itinerant state depending on the copper mean valence. The transition of the electronic state takes place at the copper mean valence of around 2.05 at 800 and 900°C, and the electronic state of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ takes place at the nickel mean valence between 2.1 and 2.4 at 600 and 800°C [8, 17, 21]. Thus $\text{Nd}_2\text{NiO}_{4+\delta}$ will have more excess oxygen content than $\text{Nd}_2\text{CuO}_{4+\delta}$, because Ni mean valence is higher than Cu. Therefore, $\text{Nd}_2\text{NiO}_{4+\delta}$ have higher electronic and ionic conductivity than $\text{Nd}_2\text{CuO}_{4+\delta}$. However, it is not clear why the $\text{Nd}_2\text{Ni}_{0.8}\text{Cu}_{0.2}\text{O}_{4+\delta}$ sample have higher conductivity than other two samples. Small amount of copper doping can increase the mean valence of nickel and copper in the $\text{Nd}_2\text{Ni}_{0.8}\text{Cu}_{0.2}\text{O}_{4+\delta}$ sample [22].

High temperature XRD patterns of $\text{Nd}_2\text{Ni}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$ ($x=0, 0.2, 1$) were shown in Fig. 4. At $x=0$ ($\text{Nd}_2\text{NiO}_{4+\delta}$), the crystal structure was orthorhombic and tetragonal at room temperature and at high temperature (600 to 800°C), respectively. In the case of $x=0.2$, the structure was tetragonal at room temperature and the tetragonality was increased with increasing the temperature. The $\text{Nd}_2\text{CuO}_{4+\delta}$ sample showed a similar behavior to $x=0.2$ sample. Therefore, the phase transformation with respect to the temperature may affect the polarization resistance of $\text{Nd}_2\text{Ni}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$ samples.

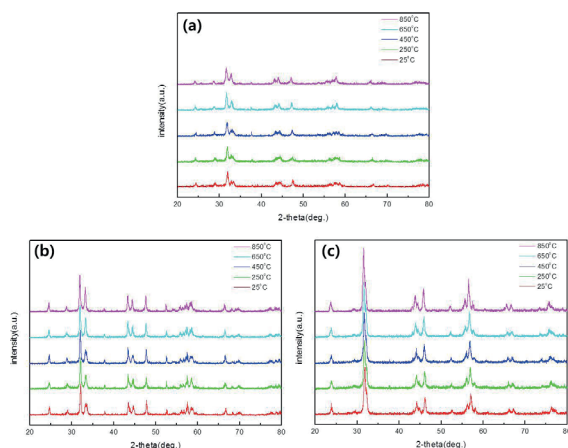


Fig. 4. XRD patterns of $\text{Nd}_2\text{Ni}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$ on high temperature (25~850°C), (a) $x=0$, (b) $x=0.2$, (c) $x=1$

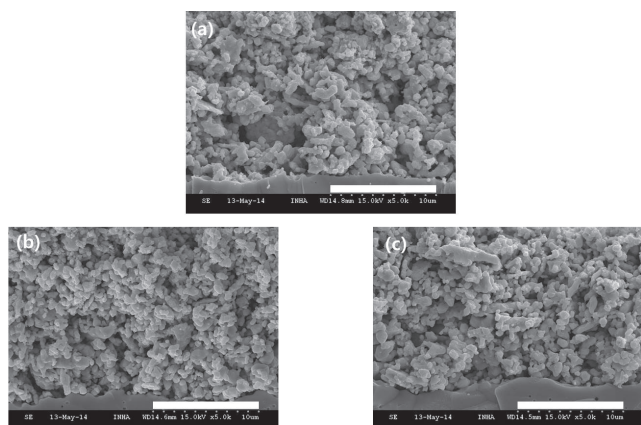


Fig. 5. Microstructures of $\text{Nd}_2\text{Ni}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$ cathode on ScSZ, (a) $x=0$, (b) $x=0.1$, (c) $x=0.2$

The cross-sectional SEM images of the $\text{Nd}_2\text{Ni}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$ ($x=0, 0.1, 0.2$) cathode samples were shown in Fig. 5. All

sample exhibited homogeneous microstructures and the cathode layers were well adhered to the ScSZ electrolyte. In addition, there was no delamination or chemical reaction between electrode and electrolyte.

Figure 6 shows current density-voltage (j - V) and power density vs. voltage (P - V) curves of the $\text{Nd}_2\text{Ni}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$ ($x=0, 0.1, 0.2$)/ScSZ/Ni-YSZ cell operated at 750, 800, and 850°C. The cell performance was improved as the operating temperature was increased. This observed phenomenon is associated with enhanced electrochemical reaction rates on the electrodes and high oxygen ion conductivity at high temperatures. Power densities of 160, 260, and 300 mWcm^{-2} were reached at 850°C for the cells with the $\text{Nd}_2\text{NiO}_{4+\delta}$, $\text{Nd}_2\text{Ni}_{0.9}\text{Cu}_{0.1}\text{O}_{4+\delta}$, and $\text{Nd}_2\text{Ni}_{0.8}\text{Cu}_{0.2}\text{O}_{4+\delta}$ cathode, respectively. Power densities could be significantly improved in the copper-doped samples, which might be due to the reduction in the polarization resistance.

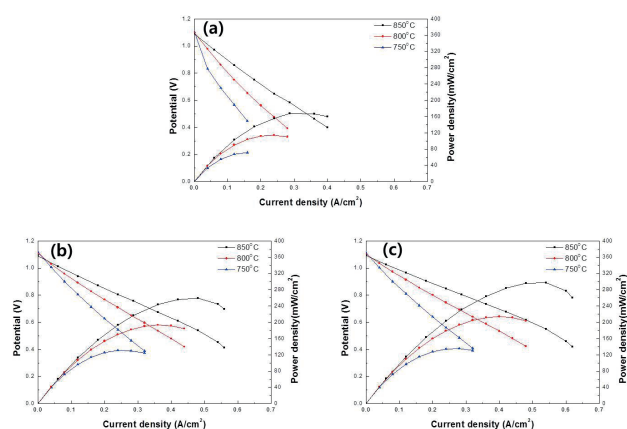


Fig. 6. j - V curve and power density of $\text{Nd}_2\text{Ni}_{1-x}\text{Cu}_x\text{O}_{4+\delta} \parallel \text{ScSZ} \parallel \text{Ni-YSZ}$ cell, (a) $x=0$, (b) $x=0.1$, (c) $x=0.2$

4. Conclusions

Ruddlesden-Popper (RP) type single phase $\text{Nd}_2\text{Ni}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$ ($x=0\sim 1$) powders were successfully synthesized by solid state reaction and the ScSZ electrolyte-supported cells with the $\text{Nd}_2\text{Ni}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$ cathode and Ni-YSZ anode were fabricated. The electrical conductivity of the $\text{Nd}_2\text{Ni}_{0.8}\text{Cu}_{0.2}\text{O}_{4+\delta}$ sample were higher than those of the $\text{Nd}_2\text{NiO}_{4+\delta}$ and $\text{Nd}_2\text{CuO}_{4+\delta}$ samples and it might be due to the higher mean valence of nickel and copper in the $\text{Nd}_2\text{Ni}_{0.8}\text{Cu}_{0.2}\text{O}_{4+\delta}$ sample. Polarization resistances show the minimum at $x=0.2$ sample and this results can be explained by the increased excess oxygen and crystal structure transformation in the $\text{Nd}_2\text{Ni}_{0.8}\text{Cu}_{0.2}\text{O}_{4+\delta}$ sample. On the other hand, further addition of copper resulted in the decreased conductivity and as a consequence, increased polarization resistance. Thus, the cell performance was enhanced in $x=0.1$ and $x=0.2$ samples and the polarization resistance reduction might be responsible for the high power density observed in two samples.

Acknowledgments

This work was supported by the New & Renewable Energy Core Technology Program of the Korea Institute

of Energy Technology Evaluation and Planning (KETEP), granted financial resource from the Ministry of Trade, Industry & Energy, Republic of Korea. (No. 20113020030050)

Acknowledgments

This work was supported by the Fundamental R&D Program for Core Technology of Materials (No.10051006) of the Korea Evaluation Institute of Industrial Technology (KEIT), Republic of Korea.

REFERENCES

- [1] J. Huijsmans, F. Van Berkel, G. Christie, *Journal of Power Sources*. **71**, 107 (1998).
- [2] N.Q. Minh, *Solid State Ionics*. **174**, 271 (2004).
- [3] F. Mauvy, C. Lalanne, J. Bassat, J. Grenier, H. Zhao, P. Dordor et al, *J. Eur. Ceram. Soc.* **25**, 2669 (2005).
- [4] V. Kharton, A. Viskup, A. Kovalevsky, E. Naumovich, F. Marques, *Solid State Ionics*. **143**, 337 (2001).
- [5] T. Ishihara, K. Nakashima, S. Okada, M. Enoki, H. Matsumoto, *Solid State Ionics*. **179**, 1367 (2008).
- [6] J.B. Smith, T. Norby, *J. Electrochem. Soc.* **177**, 639 (2006).
- [7] J. Guo, H. Lou, Y. Zhu, X. Zheng, *Mater. Lett.* **57**, 4450 (2003).
- [8] T. Nakamura, K. Yashiro, K. Sato, J. Mizusaki, *Materials Chemistry and Physics*. **122**, 250 (2010).
- [9] A. Aguadero, J. Alonso, M. Escudero, L. Daza, *Solid State Ionics*. **179**, 393 (2008).
- [10] V. Vashook, S. Tolochko, I. Yushkevich, L. Makhnach, I. Kononyuk, H. Altenburg et al, *Solid State Ionics*. **110**, 245 (1998).
- [11] V.V. Kharton, A.V. Kovalevsky, M. Avdeev, E. V. Tsipis, M. V. Patrakeev, A. A. Yaremchenko et al, *Materials Chem. Mater.* **19**, 2027 (2007).
- [12] E. Boehm, J. Bassat, P. Dordor, F. Mauvy, J. Grenier, P. Stevens, *Solid State Ionics*. **176**, 2717 (2005).
- [13] A. Khandale, S. Bhoga, *Solid State Ionics*. **262**, 416 (2014).
- [14] K. Ishikawa, K. Metoki, H. Miyamoto, *Journal of Solid State Chemistry*. **182**, 2096 (2009).
- [15] S. Nishiyama, D. Sakaguchi, T. Hattori, *Solid State Commun.* **94**, 279 (1995).
- [16] N. Poirot, P. Odier, P. Simon, F. Gervais, *Solid State Sci.* **5**, 735 (2003).
- [17] J. Bassat, P. Odier, J. Loup, *J. Solid State Chem.* **110**, 124 (1994).
- [18] T. Nakamura, K. Yashiro, K. Sato, J. Mizusaki, *Phys. Chem. Chem. Phys.* **11**, 3055 (2009).
- [19] M. Greenblatt, *Solid State & Materials Science*. **2**, 174 (1997).
- [20] A. Khandale, S. Bhoga, *Journal of Power Sources*. **195**, 7974 (2010).
- [21] A.M. George, I.K. Gopalakrishnan, M.D. Karkhanavala, *Mat. Res. Bull.* **9**, 721 (1974).
- [22] A.P. Khandale, S.S. Bhoga, R. V. Kumar, *Solid State Ionics*. **238**, 1(2013).