Characteristics of Sr$_2$Ni$_{1.8}$Mo$_{0.2}$O$_{6-\delta}$ Anode for Utilization in Methane Fuel Conditions in Solid Oxide Fuel Cells

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ABSTRACT

In this study, Sr$_2$Ni$_{1.8}$Mo$_{0.2}$O$_{6-\delta}$ (SNM) with a double perovskite structure was investigated as an alternative anode for use in the CH$_4$ fuel in solid oxide fuel cells. SNM demonstrates a double perovskite phase over 600°C and marginal crystallization at higher temperatures. The Ni nanoparticles were exsolved from the SNM anode during the fabrication process. As the SNM anode demonstrates poor electrochemical and electro-catalytic properties in the H$_2$ and CH$_4$ fuels, it was modified by applying a samarium-doped ceria (SDC) coating on its surface to improve the cell performance. As a result of this SDC modification, the cell performance improved from 39.4 mW/cm$^2$ to 117.7 mW/cm$^2$ in H$_2$ and from 15.9 mW/cm$^2$ to 66.6 mW/cm$^2$ in CH$_4$ at 850°C. The mixed ionic and electronic conductive property of the SDC provided electrochemical oxidation sites that are beyond the triple boundary phase sites in the SNM anode. In addition, the carbon deposition on the SDC thin layer was minimized due to the SDC’s excellent oxygen ion conductivity.

Keywords : Sr$_2$Ni$_{1.8}$Mo$_{0.2}$O$_{6-\delta}$, Double Perovskite Structure, Alternative Anode, Ce$_{0.8}$Sm$_{0.2}$O$_2$, Carbon Deposition

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1. Introduction

Solid oxide fuel cells (SOFCs) have been considered one of the most promising energy conversion devices due to their high efficiency and fuel flexibility. The high temperature operation (600°C-900°C) of the SOFCs facilitates the direct usage of commercial hydrocarbon fuels, such as syn-gas, natural gas, coal-gas, bio-gas, pure hydrogen and so on [1,2]. The hydrocarbon fuels provide many physiochemical advantages and characteristics over pure hydrogen fuels, such as easy transportation/storage and high energy density [3,4]. As hydrogen fuels are obtained from the hydrocarbon source through the reforming process, the direct utilization of the hydrocarbon fuels minimizes the necessity of additional system equipment, such as external reformers and/or purifiers, which improves the overall system efficiency and lowers the cost. The operation of several hydrocarbon fuels, however, cause carbon coking and sulfur poisoning in the nickel and yttria-stabilized zirconia (Ni/YSZ) anode, which is widely employed as the anode material in the SOFCs. Although the Ni-based cermet is considered an effective anode material in the SOFCs due to its excellent electrical conductivity and catalytic activity, it can tolerate only ppm levels of sulfur concentration [5,6]. Carbon deposition in the Ni/YSZ anode is also one of critical problems encountered due to the hydrocarbon fuel operation. Carbon deposition in the triple phase boundary (TPB), where the electrochemical reaction occurs, decreases the SOFC performance by covering the TPB sites. In addition, the bulk carbon deposition in the anode blocks the fuel gas flow causing an increase in the diffusion resistance.

Numerous alternative anodes that do not suffer from carbon deposition and sulfur poisoning have been developed for utilization in practical hydrocarbon fuels. Several stringent properties are required for an alternative SOFC anode [7,8]: (i) sufficient electro-catalytic activity for fuel oxidation, (ii) good electrical conductivity with ionic and electronic pathway, (iii) physical and chemical stability under the operating conditions of the SOFCs, (iv) chemical
compatibility with electrolytes at high temperatures, and (v) resistance to carbon deposition and sulfur poisoning.

Due to the high catalytic activity for carbon formation exhibited in Ni, the carbon deposition easily occurs in the Ni/YSZ anode. Therefore, replacing Ni with other metals such as Cu, Co, Pd, and Ru that show relatively low catalytic activity for carbon formation be one of the solutions avoiding carbon deposition. The properties of such metal-based anodes, however, are still insufficient for the practical utilization of the commercial hydrocarbon fuels. Most metals are easily sintered and agglomerated at high temperatures during long-term operations. Noble metals are beyond consideration, as they are considerably expensive. The intrinsic limitation of a metal as an alternative anode material led to the consideration of the oxide-based materials, because most of the oxides are immune to carbon deposition. The desirable oxides possess the mixed ionic and electronic conductive (MIEC) property. An electrochemical reaction of the MIEC oxides can occur on the anode surface/fuel phase boundary (2PB) leading to an extension of the entire anode surface. Therefore, doped perovskites with the MIEC property can be considered excellent candidates for the alternative anode materials. Perovskites with the ABO$_3$ structure enables the substitution of rare-earth and/or lanthanide cations into the B-site. The multivalent function of $\text{P}_0\text{O}_2^-$ exhibited by the transition metal cations leads to the delocalization of electrons, resulting in good electronic conductivity. In addition, the misvalenced cations produce oxygen ion vacancies via the B-site transition metal cations into the A-site and transition metal cations into the B-site. The multivalent function of $\text{P}_0\text{O}_2^-$ for 10 h to form a perovskite. The viscous gel was swelled and ignited in a subsequent heating process at 400°C. After removing most of the organic compounds, it was calcined at 800°C for 10 h to form a perovskite structure. The synthesized crystal structures were analyzed using an X-ray diffractometer (XRD, Rigaku, RINT-5200). After grinding thoroughly, the SNM powder was blended with a binder, a solvent and some additives in a ball mill. The prepared SNM slurry was tape-casted on an electrolyte. In addition, the samarium-doped ceria ((CeO$_2$)$_{0.8}$(Sm$_2$O$_3$)$_{0.2}$, SDC) sol was prepared to modify the SNM anode. Samarium(III) nitrate hexahydrate (Sm(NO$_3$)$_3$$\cdot$H$_2$O, Aldrich) was diluted in deionized water with some additives in a ball mill. The prepared SNM slurry was tape-casted on the YSZ electrolyte and sintered at 1400°C for 5 h. The YSZ electrolyte was manufactured using the sol-gel method. Strontium nitrate (Sr(NO$_3$)$_2$·H$_2$O, Aldrich), nickel nitrate hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O, Aldrich), and ammonium heptamolybdate tetrahydrate ((NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O, Aldrich) were dissolved in ethylene diamine tetra acetic acid (EDTA), which is a chelating agent. The quantities of these compounds were determined using stoichiometric calculations. The sol-gel mixture was slowly evaporated on a hot plate equipped with a magnetic stirrer at 150°C. The viscous gel was swelled and ignited in a subsequent heating process at 400°C. After removing most of the organic compounds, it was calcined at 800°C for 10 h to form a perovskite structure. The synthesized crystal structures were analyzed using an X-ray diffractometer (XRD, Rigaku, RINT-5200). After grinding thoroughly, the SNM powder was blended with a binder, a solvent and some additives in a ball mill. The prepared SNM slurry was tape-casted on an electrolyte. In addition, the samarium-doped ceria ((CeO$_2$)$_{0.8}$(Sm$_2$O$_3$)$_{0.2}$, SDC) sol was prepared to modify the SNM anode. Samarium(III) nitrate hexahydrate (Sm(NO$_3$)$_3$$\cdot$H$_2$O, 99.9%, Aldrich) was diluted in deionized water with cerium(IV) oxide (CeO$_2$, 30-50 nm particles dispersion, Aldrich). The SNM anode was dip-coated in the prepared SDC sol and calcined at 700°C. The cathode side was masked completely during the anode coating process to minimize the cathode effects owing to the SDC modification. The coating process was repeated five times to ensure that the entire anode pore wall was coated. The microstructure and composition of the SNM anode were analyzed using a scanning electron microscope and an energy-dispersive X-ray spectroscopy (FE-SEM, EDS, Hitachi, S-4200, Japan).

The yttria-stabilized zirconia (YSZ, (ZrO$_2$)$_{0.92}$ (Y$_2$O$_3$)$_{0.08}$) (Fuelcellmaterials) electrolyte was prepared by uniaxial dry pressing and sintered at 1400°C for 10 h. The YSZ electrolyte with button-type was 25 mm in diameter and 1.0 mm in thickness. The prepared LSM slurry was tape-casted on the YSZ electrolyte and sintered at 1400°C for 5 h. The YSZ electrolyte was manufactured using the sol-gel method. Strontium strontium manganite (LSM, (La$_{0.8}$Sr$_{0.2}$)$_{0.95}$MnO$_{2.0}$, Fuelcellmaterials) was used as the cathode material. The prepared LSM slurry was tape-casted on the
YSZ electrolyte and co-fired at 1100°C for 10 h.

To investigate the electrochemical performance, the disk-type cell was mounted between two double-layered alumina tubes and sealed with Pyrex glass, as illustrated in Fig. 1. A perforated Pt plate and Ag paste were used as the current collectors. For the anode, humidified hydrogen (~3 vol% H₂) and humidified methane (~3 vol% H₂O) were used as the fuel gases, which were supplied at a flow rate of 200 ml/min. For the cathode, air was supplied at a rate of 300 ml/min as an oxidant gas. The electrochemical characteristics were analyzed using an impedance analysis device (SP-150, Biologic Science Instrument). The impedance spectra were recorded in the frequency range of 10⁻²-10⁶ Hz with an exciting voltage of 10 mV to ensure a linear response. The impedance analyses were performed at 750°C-850°C, where the Nyquist plot indicated an equilibrium state.

3. Results and Discussion

The double perovskite with A₂B₁₋ₓB’ₓO₆₋δ comprises BO₆/2 and B’O₆/2 corner-shared octahedra. An aliovalent substitution of the A lattice sites and/or B lattice sites can improve the physical and electrochemical properties of SNM rendering it suitable for utilization as an alternative SOFC anode. The divalent cation in the A sites enables various oxygen state combinations in the two B cations. In Sr₂Ni₁₋ₓMoₓO₆₋δ, the Ni²⁺ cations in the B sites alter the Mo⁶⁺ cations to Mo⁵⁺ by introducing oxygen vacancies. The mechanism of the oxygen vacancy formation can be provided as follows:

\[
O_o^{-} \leftrightarrow \frac{1}{2}O_2 + V'_O + 2e' 
\]  

\[
Mo^{6+} + 2e' \rightarrow 2Mo^{5+} 
\]  

At high temperature, the oxygen vacancies may be formed via reaction (1). The released electrons pair may react with Mo⁶⁺ to reduce the Mo⁵⁺ state via reaction (2). The Goldschmidt tolerance factor of Sr₂Ni₁₋ₓMoₓO₆₋δ is 0.962. It is defined as follows:

\[
\tau = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} 
\]  

where \(r_A\), \(r_B\), and \(r_O\) represent the Shannon’s radii [23] of the A-site cations, B-site cations and the oxygen ion. For the B-site cations, \(r_B\) is calculated as an average of the radii of Mo⁵⁺ (0.61 Å) and Ni²⁺ (0.69 Å) with six coordination numbers. The bigger radii of Ni²⁺ than that of Mo⁵⁺ Ni-O results to shorter band length of Ni-O than that of Mo-O. This leads to a reduction of the bonding angle of Ni-O-Mo from 180° and a decline in the tolerance factor to less than 1 in Sr₂Ni₁₋ₓMoₓO₆₋δ.

Fig. 2 shows the XRD patterns of the SNM powder at varying temperatures (400°C, 600°C, 800°C, and 1000°C). At 400°C, no specific peaks were detected indicating that the perovskite structure was not formed under 400°C. SNM demonstrates a single perovskite phase at 600°C and marginal crystalliza-

![Fig. 1. Schematic of the experimental setup of a cell housing in the reactor](image1)

![Fig. 2. X-ray diffraction (XRD) patterns of Sr₂Ni₁₋ₓMoₓO₆₋δ (SNM) after heat-treating at 400°C, 600°C, 800°C, and 1000°C for 10 h in air](image2)
tion at higher temperatures. The XRD patterns of YSZ, SNM and the SNM/YSZ mixture presented in Fig. 3 were used to investigate the chemical compatibility of the SNM anode and YSZ electrolyte. To verify the by-product formation between the SNM anode and YSZ electrolyte during the synthesis and/or operating process, the mixture of SNM and YSZ were co-fired at 1400°C for 10 h after the wet ball-milling. The XRD patterns of the SNM/YSZ mixture were compared to those of YSZ and SNM. No apparent peaks from the reaction of the by-products were detected other than the SNM and the YSZ phases.

Figs. 4(a) and 4(b) show the scanning electron microscopy images of the SNM anode and the interlayer between the YSZ electrolyte and the SNM anode, respectively. The average pore size was 2-5 μm in diameter and the pore volume was around 40 vol%. The SNM anode possessed a thickness of 50 μm on the dense YSZ electrolyte. The interlayer by-product between the SNM anode and the YSZ electrolyte was not detected. Fig. 5 shows the transmission electron microscopy images and EDS composition analysis of O, Ni, Sr and Mo in the SNM anode. Ni was exsolved and sintered in the perovskite structure in nanoparticle size in contrast to the uniform phase formation in Sr and Mo. This phenomenon is consistent with our previous research [22]. J.T.S Irvine Group also reported on the exsolution of Ni in the Ni-doped perovskite structure under reducing conditions at 800°C-900°C [24].

Figs. 6(a) and 6(b) show the electrochemical impedance spectroscopy (EIS) results of the SNM symmetric cell with the YSZ electrolyte in H₂ (~3 vol% of H₂O) and CH₄ (~3 vol% of H₂O) at 750°C-850°C, respectively. H₂ and CH₄ were humidified in a bubbler before entering the reactor. Nyquist plots with Z_real (Re Z') versus Z_imaginary (Im Z") as the functions of frequency (0.01-10⁶ Hz) were obtained under the open circuit voltage (OCV) conditions. The high frequency intercepts of the arcs with Z_real axis were corrected to compare the electrode polarization resistance values of the anodes. The polarization resistances of the SNM anode were 40.9 Ωcm², 20.1 Ωcm², and 12.1 cm² at 750°C, 800°C and 850°C, respectively in H₂. The anode polarization resistance of the SNM anode was much higher than that of the Ni/YSZ anode, which was typically 1 Ωcm² at
The marginal intrinsic catalytic activity of SNM for $H_2$ oxidation can increase the polarization resistance. In $CH_4$, the anode polarization resistances increased to 75.8 $\Omega$cm$^2$, 30.7 $\Omega$cm$^2$, and 18.4 $\Omega$cm$^2$ at 750°C, 800°C and 850°C, respectively. The diffusion of $CH_4$ was slower than that of $H_2$ leading to an increase in the polarization resistance of mass transport. In addition, the exsulated Ni nanoparticles can provide sufficient active sites for the $CH_4$ pyrolysis to form the carbon depositions resulting in deactivating the electrochemical reaction in the SNM anode. The bulk carbon deposition on the Ni nanoparticles blocks the anode pore leading to an increase in the mass transfer resistance.

Figs. 7(a) and (b) show the IV-characteristics of the single cell with the SNM anode/YSZ electrolyte/LSM cathode in $H_2$ and $CH_4$ at 750°C, 800°C, and 850°C. The maximum power densities of the $H_2$ fuel were 18.6 mW/cm$^2$, 30.3 mW/cm$^2$, and 39.4 mW/cm$^2$ at 750°C, 800°C, and 850°C, respectively. The maximum power densities of the $CH_4$ fuel were 9.6 mW/cm$^2$, 13.2 mW/cm$^2$, and 15.9 mW/cm$^2$ at 750°C, 800°C, and 850°C, respectively. The $CH_4$ fuel can be decomposed to CO and $H_2$ in the presence of $H_2O$ through a steam methane reforming reaction. However, this formation
would be limited, because the humidified CH\textsubscript{4} contains only \(~3\) vol\% of water. CH\textsubscript{4} could be decomposed to CO and H\textsubscript{2} via an electrochemical oxidation, which is defined as follows:

\[
\text{CH}_4 + \text{O}^{2-} \rightarrow \text{CO} + 2\text{H}_2 + 2\text{e} \tag{4}
\]

A relatively low OCV and cell performance in CH\textsubscript{4} could be due to the poor catalytic/electro-catalytic activity of the SNM anode. In addition, the Ni nanoparticles exsolved from the SNM phase can accelerate the pyrolysis of CH\textsubscript{4} so that it can be decomposed to carbon and hydrogen. The carbon deposition via the pyrolysis of CH\textsubscript{4} can increase the anode polarization resistance leading to a decline in the cell performance. Therefore, the SDC surface modification of the SNM anode can be effective in improving the catalytic and/or electro-catalytic performance of the SNM anode surface resulting in an improved cell performance.

Figs. 8(a) and 8(b) show the microstructure cut-view images of the unmodified SNM anode and the SDC-modified SNM anode, respectively. SDC has been studied as an alternative electrolyte material for the SOFCs due to its high ionic conductivity. The MIEC property in the reducing conditions is also a beneficial characteristic for the alternative anode materials. The MIEC property exhibited by the SDC can provide electrochemical oxidation sites that are beyond the triple phase boundary (TPB). In addition, the SDC has been recognized as an oxygen storage and transfer material. The electrochemical oxidation of CH\textsubscript{4} and the deposited carbon can likely occur on the SDC surface. In our previous research, we
reported that the SDC-modified cells demonstrated an improvement of 30-50% in the cell performance due to the MIEC property and good ionic conductivity of the SDC. In the present study, the SNM anode was modified by the SDC sol-gel coating to minimize the carbon deposition and improve the cell performance. The SDC layer with 10-50 nm in thickness was formed on the SNM anode surface. The SDC was chemically compatible with the SNM anode. No noticeable peaks of by-products in the SDC-coated SNM anode were detected other than SNM and SDC phase shown in Fig. 9. The SDC thin layer can provide the catalytic active sites for the chemical and electrochemical decomposition of CH$_4$. In addition, the deposited carbon can be oxidized to CO or CO$_2$ electrochemically due to the oxygen storage property of the SDC.

Figs. 10(a) and 10(b) show the EIS results of the SDC-modified SNM anode symmetric cell with the YSZ electrolyte at 750°C, 800°C, and 850°C in the humidified H$_2$ and humidified CH$_4$ fuel conditions, respectively. The anode polarization resistances were 3.98 Ωcm$^2$, 3.01 Ωcm$^2$, and 1.30 Ωcm$^2$ at 750°C, 800°C, and 850°C in H$_2$, respectively. The SDC thin layer can provide high oxygen ion conductivity and expanded electrochemical reaction sites beyond the TPB to the SNM anode, leading to a significant decrease in the anode polarization resistance. In addition, the anode polarization resistance decreased from 75.8 Ωcm$^2$, 30.7 Ωcm$^2$, and 18.4 Ωcm$^2$ to 5.96 Ωcm$^2$, 4.87 Ωcm$^2$, and 2.91 Ωcm$^2$ at 750°C, 800°C, and 850°C in CH$_4$, respectively. In addition to the MIEC characteristics exhibited by the SDC, its excellent catalytic property towards CH$_4$ decreased the anode polarization resistance of the SDC-modified SNM anode. The carbon deposited on the anode surface can oxidize to CO or CO$_2$ due to the oxygen storage and transfer properties of the SDC. Fig. 11(a) and 11(b) show the IV-characteristics of the SDC-modified SNM anode in H$_2$ and CH$_4$ at 750°C, 800°C, and 850°C.
The maximum power densities improved from 18.6 mW/cm², 30.3 mW/cm², and 39.4 mW/cm² to 51.8 mW/cm², 69.8 mW/cm², and 117.7 mW/cm² in the H₂ fuel at 750°C, 800°C, and 850°C, respectively. They improved from 9.6 mW/cm², 13.2 mW/cm², and 15.9 mW/cm² to 39.2 mW/cm², 49.7 mW/cm², and 66.6 mW/cm² in the CH₄ fuel at 750°C, 800°C, and 850°C, respectively. As the Ni particles were exsolved from the SNM anode, CH₄ would not only decompose chemically and electrochemically to form H₂ and CO but also decompose to C and H₂ via the CH₄ pyrolysis. The carbon deposition, however, can be minimized on the SDC thin layer due to the SDC’s excellent oxygen ion conductivity. The SDC coating layer on the pore surface of the SNM anode would minimize the direct exposure of the CH₄ fuel with Ni particles by exsolution, leading to limiting the pyrolysis of CH₄ on the anode surface. The deposited carbon can likely oxidize to CO or CO₂ electrochemically. In addition, the electrochemical reaction site would expand to 2PB (gas/anode) beyond the TPB leading to an improved cell performance.

4. Conclusions

In this study, Sr₂Ni₁.₈Mo₀₂O₆₋₄₋ was investigated as an alternative anode material for utilization in methane fuels in the SOFCs. At high temperature and reducing conditions, the Ni²⁺ cations in the double perovskite structure substituted the Mo⁶⁺ cations with Mo⁵⁺ cations by introducing oxygen vacancies. SNM demonstrates a double perovskite phase at 600°C and marginal crystallization at higher temperatures. The SNM anode was compatible with the YSZ electrolyte under the SOFCs operating conditions. The SNM phase was not stable during the fabrication process. Ni was exsolved on the SNM anode, which was detected using the EDS mapping images. As the SNM anode demonstrates poor electrochemical and electro-catalytic property for H₂ and CH₄, the SNM anode was modified with an SDC coating on the anode surface to improve the cell performance. The anode polarization resistances significantly decreased from 12.1 Ωcm² to 1.30 Ωcm² in H₂ and 18.4 Ωcm² to 2.91 Ωcm² in CH₄ at 850°C. In addition, the maximum power densities improved from 39.4 mW/cm² to 117.7 mW/cm² in H₂ and from 15.9 mW/cm² to 66.6 mW/cm² in CH₄ at 850°C. The MIEC property exhibited by the SDC provided electrochemical oxidation sites that are beyond the TPB sites in the SNM anode. In addition, the carbon deposition on the SDC thin layer was minimized due to the excellent oxygen ion conductivity of the SDC.

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