Characteristics of $\text{LaCo}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$ Coated on Ni/YSZ Anode using CH_4 Fuel in Solid Oxide Fuel Cells

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ABSTRACT

Nickel-doped lanthanum cobalt oxide ($\text{LaCo}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$, LCN) was investigated as an alternative anode material for solid oxide fuel cells. To improve its catalytic activity for steam methane reforming (SMR) reaction, Ni^{2+} was substituted into Co^{3+} lattice in LaCoO_3 . LCN anode, synthesized using the Pechini method, reacts with yttria-stabilized zirconia (YSZ) electrolyte at high temperatures to form an electrochemically inactive phase such as $\text{La}_2\text{Zr}_2\text{O}_7$. To minimize the interlayer by-products, the LCN was coated via a double-tape casting method on the Ni/YSZ anode as a catalytic functional layer. By increasing the Ni doping amount, oxygen vacancies in the LCN increased and the cell performance improved. CH_4 fuel decomposed to H_2 and CO via SMR reaction in the LCN functional layer. Hence, the LCN-coated Ni/YSZ anode exhibited better cell performance than the Ni/YSZ anode under H_2 and CH_4 fuels. LCN with 12 mol% of Ni (LCN12)-modified Ni/YSZ anode showed excellent long-term stability under H_2 and CH_4 conditions.

Keywords : Solid Oxide Fuel Cell, Alternative Anode, $\text{LaCo}_{1-x}\text{Ni}_x\text{O}_{3-\delta}$, Interlayer by-Product, Methane Fuel

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1. Introduction

Solid oxide fuel cells (SOFCs) have received much attention as promising electrochemical conversion devices due to their high efficiency and environmental friendliness [1,2]. Due to their high temperature (700–900°C) operation, SOFCs can use various types of fuels including natural gas, biogas, liquid hydrocarbons, and pure H_2 . Fuel flexibility can lower system operating costs and improve overall efficiency by eliminating additional reformers and/or purifiers [3,4]. The hydrocarbon fuels, however, can degrade catalytic properties in anode, especially by carbon coking and sulfur poisoning, leading to degradation of cell performance. Nickel and yttria-stabilized zirconia (Ni/YSZ) cermet is one of the most typical anode materials in SOFCs because of its excellent catalytic activity for fuel oxidation and good electrical conductivity. The Ni/YSZ anode, however, permits only a few hundred parts per million levels of

sulfur compounds contained in commercial hydrocarbon fuels. In addition, Ni phase of the Ni/YSZ anode is easily deactivated by carbon deposition in hydrocarbon fuels resulting in severe degradation of cell performance [5-9].

To overcome the shortcomings of the Ni/YSZ cermet, many research groups have been developing alternative anodes for direct and practical utilization of hydrocarbon fuels [10-12]. However, alternative anodes of SOFCs must meet strict requirements such as good electrocatalytic activation, good electrical conductivity under reducing condition, chemical compatibility with electrolyte, and satisfied tolerance to carbon deposition and sulfur poisoning. Metal-based anodes including Cu, Co, W, etc., are not appropriate to utilize commercial hydrocarbon fuels, although they have exhibited excellent performance as alternative anodes. Noble metals including Ru, Pd, and Au are beyond consideration due to their high cost. Modification of the Ni/YSZ anode by mixed ionic and electronic conductive (MIEC) materials can be one approach to inhibit carbon deposition. A porous thin film of samarium-doped ceria (SDC) on the Ni/YSZ anode improves the cell performance and minimizes carbon deposition [13,14]. Due to MIEC

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properties exhibited by SDC, carbon deposited on the SDC coating layer of the Ni/YSZ anode reacts with O^{2-} ions to form CO or CO_2 via electrochemical oxidation given by

Doped perovskites ($AA'BB'O_3$) may be appropriate candidates as alternative anode materials [15-20]. In our previous research, electrochemical properties of alternative anode materials including $Sr_{0.92}Y_{0.08}TiO_{3-\delta}$ [21], $Sr_{0.92}Y_{0.08}Ti_{1-x}Fe_xO_{3-\delta}$ [22], $Sr_{0.92}Y_{0.08}Ti_{1-x}Ni_xO_{3-\delta}$ [23], and Sr_2NiMoO_6 [24] were investigated under H_2 and CH_4 fuels. Due to good stability under high temperatures, perovskite with ABO_3 formula allows the substitution of alkaline, alkaline-earth, or lanthanide metals into A-sites and transition cations into B-sites such as Mn, Co, Fe, and Ti [25]. Multivalent state exhibiting transition metal cations as a function of oxygen partial pressure may provide electronic conductivity to the anode. Mis-valenced cations doped into B-sites can provide oxygen vacancies, leading to improved ionic conductivity. In addition, MIEC perovskites provide excellent compatibility with electrolyte and mechanical stability without thermal mismatch and/or structural failure during long-term operation. Because D. B. Meadowcroft group reports the use of lanthanum-based perovskite oxide as a catalyst, lanthanum-based perovskites have attracted increasing attention as bi-functional catalysts for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) [26]. Cobalt-based perovskites are one of the promising candidates for ORR activity. $LaCoO_3$ exhibits better electrocatalytic activity compared to other perovskite oxides [27]. Yoon et al. improved cell performance and maintained cell stability for 200 h by coating the $LaNi_{0.6}Co_{0.4}O_{3-\delta}$ catalyst layer on the $NiO-BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ ($NiO-BZCYb$) anode support through electron beam vapor deposition [28]. Zhang et al. reported that $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ nanoparticles modified on Ni-based anode exhibited excellent coking resistance and improved cell performance [29]. In this study, electrochemical characteristics of Ni/YSZ anode under methane fuel were studied by coating $LaCo_{1-x}Ni_xO_{3-\delta}$ (LCN). To improve oxygen ion conductivity and ORR catalytic activity in the anode, Ni^{2+} was substituted into Co^{3+} of $LaCoO_3$.

2. Experimental

2.1. Cell preparation

LCN was synthesized by the Pechini method in which the amount of nickel was changed to 1, 4, 7, and 12 mol%. Lanthanum (III) nitrate hydrate ($La(NO_3)_3 \cdot H_2O$, 99.9% trace metal, Sigma Aldrich) was mixed with 200 ml of distilled water, citric acid anhydrous ($C_6H_8O_7$, Daejung), and ethylene glycol ($HOCH_2CH_2OH$, Sigma Aldrich) to dissolve La as the A-site material. Cobalt (II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, ACS reagent, Sigma Aldrich) and nickel (II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, purum p.a., crystallized, Sigma Aldrich) were dissolved in 200 ml of ethanol (CH_3CH_2OH , Sigma Aldrich) to dissolve Co and Ni as B-site materials. The solution was adjusted to pH 6-7 by adding ammonium hydroxide solution (Sigma Aldrich). After solubilizing with some additives, the solution was dried at $120^\circ C$ and calcined at $350^\circ C$. Subsequently, the calcined sample was heated to $650^\circ C$ at the rate of $1^\circ C/min$ to form a perovskite structure. The synthesized crystal structure was analyzed by an X-ray diffractometer (XRD, Rigaku, RINT-5200). The formation of the LCN phase was analyzed using TGA/DTA (STA PT1600, TA, USA). The microstructure was analyzed using a scanning electron microscope (FE-SEM, Hitachi, S-4200, Japan). To investigate the electrochemical and electrocatalytic performances, button-type electrolyte substrates were prepared using 8 mol% of yttria-stabilized zirconia (8YSZ, Fuel cell materials) powder by uniaxial dry pressing and sintered at $1400^\circ C$ for 5 h. The 8YSZ electrolyte substrate was 0.9 and 25.2 mm in thickness and diameter, respectively. For the anode, Ni/YSZ slurry was tape-casted on the YSZ electrolyte and subsequently sintered at $1400^\circ C$ for 5 h. The LCN slurry was tape-casted on the Ni/YSZ electrode layer to form a catalytic functional layer and subsequently sintered at $1200^\circ C$ for 10 h. The thicknesses of the Ni/YSZ electrode layer and the LCN catalytic layer were about 35 and 25 μm , respectively. For the cathode, $La_{0.8}Sr_{0.2}MnO_3$ (LSM, Fuel cell materials) was tape-casted on the YSZ electrolyte and subsequently sintered at $1100^\circ C$ for 10 h.

2.2. Cell characteristics

To investigate the electrochemical performance, a disk-type cell was mounted between double-layered

Fig. 1. Schematic representation of the experimental setup for cell housing in the reactor.

alumina tubes and sealed with Pyrex glass on the dense electrolyte, as shown in Fig. 1. A perforated Pt plate (1 cm² in area) and Ag paste were used as current collectors. For the anode, humidified hydrogen (~5 vol.% H₂O) and humidified methane (~5 vol.% H₂O) were used as fuel gases and supplied at a flow rate of 200 mL/min. For the cathode, O₂ was supplied at a rate of 200 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 from 10⁻²–10⁶ Hz at an excited voltage of 10 mV to ensure linear response. The impedance analyses were performed between 750 and 850°C, where the Nyquist plot indicated an equilibrium state.

3. Results and Discussion

3.1. Physical properties

Fig. 2 shows the TGA/DTA results for the LCN resin obtained at the rate of 10°C/min in air. The analytical results show four areas related to precursor decomposition for all samples due to removal of volatile compounds and decomposition of nitrate and citric acid as described by Lee et al. [30]. The first region below 200°C is due to the evaporation of weakly adsorbed water and volatiles. The rapid weight-degrading region between 200 and 400°C corresponds to the decomposition of nitrates and citrates. The region in the range of 400–650°C is due

Fig. 2. TGA and DTA curves of the precursor resin synthesized by the Pechini method using air at a flow rate of 10°C/min.

Fig. 3. X-ray diffraction (XRD) patterns of LaCo_{1-x}Ni_xO₃ calined at varying temperatures in air.

to the decomposition of nitrite and carbonate [31]. The small exothermic peak observed between 450 and 500°C in the DTA curves may be attributed to the crystallization of the LCN perovskite phase. The results correspond to the XRD data as shown in Fig. 3. The crystal structure of the synthesized perovskite oxide, LCN, was characterized by XRD at varying temperatures (400, 600, 650, 800, 1000, 1200, and 1400°C) in air. No noticeable peaks were detected for the sample calcined at 400°C, in which the perovskite

Fig. 4. XRD patterns of (a) $\text{LaCo}_{1-x}\text{Ni}_x\text{O}_3$ ($x = 0, 0.01, 0.04, 0.07$, and 0.12) with varying amounts of nickel: 0 mol% (LaCoO_3), 1 mol% (LCN01), 4 mol% (LCN04), 7 mol% (LCN07), and 12 mol% (LCN12) and (b) peak shifts with varying amounts of nickel.

crystalline structure was not formed. The perovskite structure of LCN was observed at 600°C and was prominent at 650°C. Up to 1400°C, no extra peaks emerged from any of the perovskite oxides, suggesting that there were no impurities and the perovskite phase is stable at high temperatures.

Fig. 4(a) shows the XRD patterns of the LCN sample with the degree of Ni substitution. The substitution amount of Ni as the B-site dopant was varied between 0 mol% (LCO), 1 mol% (LCN01), 4 mol% (LCN04), 7 mol% (LCN07), and 12 mol% (LCN12). No additional peaks were detected in LCO, LCN01, LCN04, LCN07, and LCN12 except in the lanthanum cobalt-based perovskite structure. It was observed that all peaks shifted slightly toward low angles with increase in nickel substitution amount as shown in Fig. 4(b). Replacement of Co with Ni led to lattice expansion due to the larger ionic radius of Ni^{2+} (0.69 Å for six coordination) as compared to that of Co^{3+} (0.61 Å for six coordination), resulting in the peak to shift to low angles. Over 12 mol% of Ni dopant, the LCN phase was unstable and NiO and Ni phase were detected. Due to the excellent catalytic performance shown in Ni phase, the cell performance can be improved in increasing Ni dopant amounts in the LCN. However, the chemical stability of LCN phase decreases in increasing Ni dopant amounts and NiO and/or Ni phase can be exsolved [32]. The NiO and Ni phase can serve as a major source of carbon deposition and significantly degrades cell performance.

Fig. 5. Chemical compatibility analysis based on the XRD patterns of (i) YSZ, (ii) LaCoO_3 (LCO), and YSZ/LCO mixture.

3.2. Chemical compatibility with YSZ electrolyte

Fig. 5 presents the XRD patterns of (i) YSZ, (ii) LCO, and (iii) YSZ-LCO mixture to investigate chemical compatibility between the LCO anode and YSZ electrolyte. LCO and YSZ powders were mixed in a 1:1 weight ratio by dry ball milling for 24 h. The LCO/YSZ mixture powder was co-sintered at 1200°C for 10 h, which is the temperature at which the anode can maintain sufficient adhesion to the electrolyte. In the case of the YSZ-LCO mixture, La reacted with Zr to form $\text{La}_2\text{Zr}_2\text{O}_7$, which is an electronic and ionic resistant material. The XRD results correspond to the SEM image as shown in Fig. 6. During sintering at high temperature, the interfacial reaction product, $\text{La}_2\text{Zr}_2\text{O}_7$, of 1–2 μm thickness, was formed between the LCO anode and YSZ electrolyte. Therefore, to minimize the unfavorable by-product formation, Ni/YSZ with 70 vol.% of Ni as an anode functional layer was located between the YSZ electrolyte and LCN layer as shown in Fig. 7. The LCN layer minimized the direct exposure of CH_4 to the Ni/YSZ anode, where carbon deposition could occur under CH_4 fuel. Due to the very high catalytic activity exhibited in the Ni/YSZ phase, hydrocarbon fuels including CH_4 would decompose rapidly to C and H_2 via pyrolysis, resulting in carbon deposition on the Ni/YSZ anode. However, the LCN layer tape-casted on the Ni/YSZ anode acted as a catalytic functional layer. H_2O from

Fig. 6. SEM image of cut-view between the YSZ electrolyte and LCN anode.

Fig. 7. SEM image of cut-view of the LCN-modified Ni/YSZ anode layer.

the humidified CH₄ and from the emitted gas via electrochemical oxidation reacted with CH₄ via steam methane reforming (SMR) on the LCN catalytic layer as follows:

Therefore, most of the CH₄ decomposed to H₂ and CO/CO₂ via SMR (reaction (2)) and water gas shift (WGS) reactions (reaction (3)) in the LCN catalytic layer. The produced H₂ and CO reacted with O²⁻ to produce H₂O and CO₂ electrochemically via reaction (4) and (5) in the Ni/YSZ layer. In addition, the undecomposed CH₄ reacted with O²⁻ via electrochemical oxidation (reaction (6)) in triple phase boundary (TPB) of the Ni/YSZ anode. Although La₂Zr₂O₇ was formed in the interlayer between the LCN and Ni/YSZ layers, 70 vol.% of Ni and 50 vol.% of porosity in the Ni/YSZ anode minimized the La₂Zr₂O₇ formation. In addition, small amounts of La₂Zr₂O₇ in the LCN and Ni/YSZ interlayer were negligible to the catalytic performance for SMR because most electrochemical reactions, which are critically affected by La₂Zr₂O₇, occur in the Ni/YSZ anode functional layer, especially near the YSZ electrolyte.

3.3. EIS analysis

Fig. 8 shows the electrochemical impedance spectroscopy (EIS) results of Ni/YSZ and LCN-modified Ni/YSZ with the YSZ electrolyte and LSM cathode with varying Ni amounts in (a) H₂ (~5 vol.% of H₂O) and (b) CH₄ (~5 vol.% of H₂O) at 800°C. H₂ and CH₄ were humidified in a bubbler before being inserted into the reactor at the rate of 200 ml/min and pure O₂ was used as an oxidant gas at the same rate. EIS results were obtained under open circuit voltage (OCV) conditions. Nyquist plots of Z_{real} (Re Z') vs. Z_{imaginary} (Im Z'') as a function of frequency (0.01 to 10⁶ Hz) under 10 mV current conditions were drawn to ensure linear response. Because analysis of the impedance spectra of a multi-layered fuel cell is very complicated and mostly uncertain, we discuss and explain the overall polarization resistance of the sample. The effects of impedance spectra can be attributed to the anode because the cathode and the electrolyte are the same in all the samples. In our experimental, the SMR can be limited because of low amounts of H₂O (~ 5wt%). Therefore, the electrochemical oxidation of H₂ via the reaction (4) will compete to CH₄ oxidation via the reaction (6), which also occurs CH₄ pyrolysis. Because of the slower reaction of CH₄ electrochemical oxidation than H₂ electrochemical oxidation and carbon deposition by CH₄ pyrolysis, the overall polarization resistance increased in CH₄ fuel condition. Under H₂ conditions, the polarization resistances of the bare,

LCN01-modified, LCN04-modified, and LCN12-modified Ni/YSZ anodes were 4.52, 3.88, 0.88, and $0.56 \Omega\text{cm}^2$, respectively. The polarization resistances decreased with increasing amounts of Ni substitution in the LCN. Under CH_4 conditions, the polarization resistances of the bare, LCN01-modified, LCN04-modified, and LCN12-modified Ni/YSZ anodes were 54.3, 38.7, 31.2, and $6.9 \Omega\text{cm}^2$, respectively. Lower reaction kinetics and slower gas diffusion were exhibited under CH_4 conditions than those under H_2 , thereby increasing the polarization resistance under CH_4 . The polarization resistance of the bare Ni/YSZ anode was significantly increased compared to that of the LCN12-modified Ni/YSZ anode under CH_4 conditions. CH_4 decomposed to C and H_2 via pyrolysis of methane in the Ni phase of the Ni/YSZ anode leading to carbon deposition. The deposited carbon deactivated the TPB area and increased the mass transport resistance in the anode, resulting in the increase of low frequency arc ($>1 \text{ Hz}$) in the impedance spectra. However, in the LCN12-modified Ni/YSZ anode, CH_4 decomposed to H_2 and

CO via SMR in the LCN12 layer, and subsequently, the decomposed H_2 and CO reacted with O^{2-} electrochemically in the Ni/YSZ layer. H_2O for the SMR was obtained from humidified CH_4 and the electrochemical reaction of H_2 in the Ni/YSZ anode. In addition, CH_4 reacted with CO_2 from the electrochemical reaction of CO in the Ni/YSZ anode and WGS reaction via reaction (3). The existence of dry methane reforming ($\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$) in the LCN12-modified Ni/YSZ anode will contribute to our further research.

3.4. I-V characteristics

Fig. 9 shows the I-V characteristics of the electrolyte supported single cell with the bare and LCN-modified Ni/YSZ anodes in (a) H_2 and (b) CH_4

Fig. 8. Impedance spectra of bare, LCN01-modified, LCN04-modified, and LCN12-modified Ni/YSZ anodes at 800°C in (a) H_2 and (b) CH_4 .

Fig. 9. I-V characteristics of a single cell with bare, LCN01-modified, LCN04-modified, and LCN12-modified Ni/YSZ anodes at 800°C in (a) H_2 and (b) CH_4 .

at 800°C. After stabilizing the cell in H₂ or CH₄ at 800°C, the I-V characteristics were measured with 200 mL/min of humidified H₂ (5 vol.% of H₂O) or humidified CH₄ (5 vol.% of H₂O) as the anode fuel and O₂ as the cathode gas. The OCV was 1.1 V in H₂ and increased to 1.15~1.3 V in CH₄ due to the increasing chemical potential (ΔG) of methane oxidation, which reported in our previous research [33]. Even though many possible mechanisms could be coupled to determine the OCV, the governing mechanism under the high ratio of CH₄/H₂O conditions likely involved the electrochemical oxidation of methane via reactions (6). The maximum power density of the bare, LCN01-modified, LCN04-modified, and LCN12-modified Ni/YSZ anodes were 92.3, 111.1, 84.1, and 172.6 mW/cm², respectively, under H₂ conditions. Owing to the extended surface area by the LCN modification on the Ni/YSZ anode, the cell performance tended to improve in the LCN-modified Ni/YSZ anode. For the LCN12-modified Ni/YSZ anode, the cell performance significantly improved compared to the LCN01 and LCN04-modified Ni/YSZ anodes. The aliovalent substitution of Ni²⁺ into Co³⁺ increased the oxygen vacancies in the LCN phase resulting in improved ionic conductivity given by

This aliovalent substitution via reaction (7) forms lattice defects to maintain electrical neutrality of the crystals. Co³⁺ (0.61 Å in ionic radii for six coordination) in the B-site of LaCoO₃ was substituted by Ni²⁺ (0.69 Å in ionic radii for six coordination) resulting in the creation of oxygen vacancies with a pair of electron holes. In addition, the existence of the mixed valence states of Ni²⁺/Ni³⁺ and Co³⁺/Co⁴⁺ in the reducing atmospheric condition could affect to the improvement of electrical conductivity and cell performance. In CH₄, the maximum power density decreased to 32.68 mW/cm² (65% decrease) for the Ni/YSZ anode and 125.56 mW/cm² (27% decrease) for the LCN-modified Ni/YSZ anode. Due to the LCN catalytic functional layer, CH₄ was decomposed to H₂ and CO. The decomposed gas reacted with oxygen ion electrochemically to produce H₂O, CO₂, and electrons in the Ni/YSZ electrode functional layer. The low intrinsic catalytic activity exhibited in the LCN phase reduced CH₄ pyrolysis and minimized carbon deposition in the anode. Oxygen vacancies formed by Ni²⁺ substitution via reaction (7) improved the catalytic properties of CH₄ oxidation.

Fig. 10. XPS spectra of Co 2p_{3/2} and representative fitting for (a) LCN01, (b) LCN04, (c) LCN07, and (d) LCN12.

Fig. 11. XPS spectra of O 1s and representative fitting for (a) LCN01, (b) LCN04, (c) LCN07, and (d) LCN12.

3.5. XPS analysis

X-ray photoelectron spectroscopy (XPS) was used to investigate the chemical binding characteristics of the LCN surface element composition. Fig. 10 shows the XPS spectra in the Co 2p_{3/2} regions. The peak located around 780 eV corresponds to the binding energy of Co 2p_{3/2}. The peak can be deconvoluted into two peaks with binding energies of 779.6 and 781.8 eV, which are attributed to Co³⁺ and Co²⁺ ions, respectively. By increasing the amount of Ni²⁺ substitution, the Co³⁺/Co²⁺ ratio increased. New active sites of Ni²⁺/Ni³⁺ formed by Ni substitution were difficult to detect because Ni 2p peaks were overlapped by La 3d peaks. Different surface oxygen states were identified by O 1s XPS spectra shown in Fig. 11. Three clear sub-peaks were observed in the samples. The largest sub-peak, observed around 528.6 eV (blue peak in Fig. 11), is associated with lattice oxygen or highly oxidative oxygen species (O_L). The sub-peak that was observed around 530.8 eV (red peak in Fig. 11) represents the contribution of chemically adsorbed oxygen on the oxygen vacancies (O_V). The smallest sub-peak, observed around 532.5 eV (green peak in

Table 1. Summary of XPS peak deconvolution results of Co 2p_{3/2} and O 1s from Fig. 10 and Fig. 11.

Samples	Co 2p _{3/2}		O 1s		
	Co ³⁺	Co ²⁺	O _L	O _V	O _C
LCN01	63.7%	36.3%	45.5%	35.9%	18.6%
LCN04	66.3%	33.7%	44.0%	37.9%	18.1%
LCN07	64.4%	35.6%	49.1%	41.2%	9.7%
LCN12	69.0%	31.0%	38.8%	51.8%	9.4%

Fig. 11), corresponds to physically adsorbed oxygen species (O_C) on the surface such as H₂O. The relative amounts of the different states of cobalt and oxygen species, estimated from the relative area in the fitted peaks (Fig. 10 and 11), are listed in Table 1. The atomic ratio (%) of the chemically adsorbed oxygen to the oxygen vacancies were 35.9, 37.5, 41.2, and 51.8% in LCN01, LCN04, LCN07, and LCN12, respectively. This indicates that the oxygen vacancies were formed due to oxygen loss by Ni²⁺ substitution via reaction (7).

Fig. 12. Long-term test of a single cell with bare [22] and LCN12-modified Ni/YSZ anodes at 800°C.

3.6. Long-term stability

To analyze the long-term stability of the LCN12-modified Ni/YSZ anode, which exhibited the best performance in terms of the I-V characteristics, the performance of the 8YSZ electrolyte-supported single cell was measured under a constant current of 120 mA/cm² at 800°C, as shown in Fig. 12. The performance was compared to that of the Ni/YSZ anode reported previously [22]. After 10 h of stabilizing the cell in humidified H₂, humidified CH₄ was introduced as the anode fuel. The cell performance of the LCN12-modified Ni/YSZ anode decreased in a few hours after introducing CH₄ and subsequently stabilized at 0.685 V. For the Ni/YSZ anode, the cell performance rapidly decreased in the presence of CH₄ because of carbon deposition [21-24]. Otherwise, the cell performance of the LCN-modified Ni/YSZ anode showed no significant degradation for 200 h. The LCN12 catalytic functional layer minimized the direct exposure of CH₄ to the Ni phase, where most of the carbon deposition occurred. Therefore, CH₄ reacted with H₂O from the bubbler and/or the electrochemical reaction in the Ni/YSZ layer to form H₂ and CO via SMR reaction. In addition, the oxygen vacancies by Ni²⁺ substitution via reaction (7) improved the catalytic activity for the SMR reaction.

4. Conclusions

LCN was modified on the Ni/YSZ anode as a catalytic functional layer to evaluate its feasibility as an alternative anode. To improve the catalytic activity for SMR reaction, Ni²⁺ was substituted into Co³⁺ lattice in LaCoO₃. By increasing the Ni doping amount, oxygen vacancies in the LCN increased and the cell performance improved. CH₄ fuel decomposed to H₂ and CO via SMR reaction in the LCN functional layer. In addition, oxygen vacancies by Ni substitution improved the catalytic activity for the SMR reaction. The decomposed H₂ and CO reacted with O²⁻ electrochemically in the Ni/YSZ layer. Consequently, the maximum power densities of the bare and LCN12-modified Ni/YSZ anodes under H₂ conditions were 92.3 and 172.6 mW/cm², respectively. The maximum power densities under CH₄ condition were 32.7 mW/cm² (65% performance decrease) for the Ni/YSZ anode and 125.6 mW/cm² (27% performance decrease) for the LCN12-modified Ni/YSZ anode. The LCN12-modified Ni/YSZ anode showed excellent long-term stability under H₂ and CH₄ conditions. Otherwise, the cell performance of the LCN-modified Ni/YSZ anode showed no significant degradation for 200 h.

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