Effect of Ni-based cathodic layer on intermediate temperature tubular electrolysis cell using LaGaO₃-based electrolyte thin film

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Abstract

NiO-YSZ tubular-type supported solid oxide electrolysis cell (SOEC) was prepared by dip-coating and co-sintering process for intermediate temperature steam electrolysis. To achieve a small overpotential, infiltration of Sm₀.₅Sr₀.₅CoO₃₋δ (SSC) powder into porous La₀.₉Sr₀.₁Ga₀.₈Mg₀.₂O₃₋δ (LSGM) layer on dense LSGM electrolyte film was performed for the air electrode. In this study, the effect of the Ni-Sm₀.₂Ce₀.₈O₂₋δ (Ni-SDC) and Ni-Fe₂O₃ (Ni-Fe) cathodic layer on steam electrolysis was further investigated. It was found that the Ni-based layer was effective for increasing electrolysis performance of the cell at low temperature in particular, but Ni-Fe layer was more effective. Impedance analysis suggests that this increased electrolysis performance of the cell using Ni-Fe layer was attributed to the decrease both in cathodic IR loss and overpotential. Electrolysis current density at 1.5 V was achieved to current density of 0.69, 0.47 and 0.28 A cm⁻² at 873, 823 and 773 K, respectively. In addition, the overpotential was also decreased by the insertion of Ni-SDC layer, which shows the mixed conductivity. The long-term stability of the cell when using Ni-SDC layer was also measured up to 150 h and stable electrolysis performance was demonstrated (degradation rate: around 1.9%/100 h).

1. Introduction

Solid oxide fuel cells (SOFCs) are being developed as a highly efficient power generator (>60% LHV) and are being put to commercial use [1, 2]. In contrast, solid oxide electrolysis cells (SOECs), which are the reverse operation of SOFCs, are still being developed as a highly efficient electrolysis method. It is expected that this will be an economical method of producing H₂ from steam, and in particular it is expected to be used as a storage method for renewable energy to be converted to chemical energy [3, 4]. Since the electrochemical reaction in SOECs is the reversible reaction of SOFCs, the components of SOECs are almost the same. However, the function of the anode and cathode are also opposite, resulting in many issues such as delamination and reoxidation [5]. Similarly, with SOFCs, two basic designs: planer and tubular-type are also considered for SOECs. The planar-type is popularly studied at present, since it has short current connecting lines, which contribute to a larger current density. However, the tubular-type SOECs have advantages such as stable mechanical property and easy gas sealing, which is one of the most difficult issues of high-temperature electrolyzer [3, 6]. High-temperature steam electrolysis using a tubular-type cell was reported recently [7, 8]. Li et al prepared a NiO-YSZ-supported tubular cell with YSZ electrolyte and an LSM-YSZ anode, with the current density at 1.5 V and 20 vol% H₂O is 0.79 A cm⁻² at 1073 K [7]. Mizusawa et al also fabricated a NiO-YSZ microtubular cell and reported reasonable performance at 1123 K [8]. However, there is limited study on the tubular-type solid oxide electrolysis cell operated at IT-temperature range, in particular at 773 K. In order to decrease the cost, and increase the durability, the operation of SOFCs and SOECs at intermediate temperature range is considered the most reasonable approach. Another issue is that the cell performance decreased due to the decrease in catalytic activity and kinetics of the electrodes or a sealing problem occurred as the temperature decreased [9]. Considering one of the aims in the development of steam electrolysis is to achieve high efficiency
and large current density for high H₂ productivity, tight gas sealing, which is needed more than in SOFC, is essential. Therefore, the development of a fuel-electrode-supported tubular cell at intermediate temperature range was urgently required for commercial steam electrolysis cells.

La₀.₉Sr₀.₁Ga₀.₈Mg₀.₂O₃·δ (LSGM) is considered a promising alternative electrolyte material for IT-SOFCs/SOECs with fast and stable oxide ionic conductivity [10]. Reasonably high steam and CO₂ electrolysis performance was also reported by using LSGM-electrolyte-supported planar-type cells [11–13]. In our previous work, reasonably high current density in steam electrolysis and stable durability after 30 cycles of reversible SOFC/SOEC operation at 973–773 K was achieved by using the NiO-YSZ (NiO-Y₂O₃ stabilized ZrO₂) tubular substrate and Sm₀.₅Sr₀.₅CoO₃−δ (SSC) air electrode deposited on the thin and porous LSGM functional layer [14]. The electrolysis current density was increased at low temperature (773 K) by the introduction of porous LSGM electrolyte layer. However, the electrolysis performance was still not as sufficient as expected due to the relatively large IR loss and overpotential. Therefore, the decrease in the cathodic overpotential was investigated in this study. Considering the change in diffusion resistance of the cell depending on cathodic cermet materials, the cathodic activity could be further increased by the addition of Ni mixed alloy. In our previous study, it was found that Ni-Fe bimetallic catalyst is highly active for the anodic reaction of SOFC and the maximum power density is significantly increased by the addition of Fe to Ni [15]. Oppositely, Ni-Fe can also be effective as an active cathode in electrolysis [16, 17]. On the other hand, mixing mixed ion–electron conductor (MIEC) such as Ni mixed with Sm or Gd-doped CeO₂ with metal, so-called cermet, to the fuel electrode side is also effective for increasing the fuel electrode activity because of the increased triple phase boundary (TPB) length. Since the surface of Sm or Gd-doped CeO₂ phase is considered as electrochemically active due to the MIEC properties and high surface activity to oxygen dissociation, both the TPB length of Ni-YSZ and surface activity could be increased by combination with doped CeO₂ [18, 19].

Therefore, in this study, Ni-SDC and Ni-Fe layer were deposited on the NiO-YSZ tubular substrate as the cathode functional layer, and the steam electrolysis property of prepared cells at 873–773 K was investigated. In addition, the durability of steam electrolysis of the cell using Ni-SDC was assessed.

2. Experimental

2.1. Synthesis of powders and preparation of dip-coating slurry

The electrolyte material prepared in this study was La₀.₉Sr₀.₁Ga₀.₈Mg₀.₂O₃·δ (LSGM), which was synthesized by using a conventional solid-state reaction technique of ball milling. La₂O₃ (Kishida), SrCO₃ (Rare Metallic), Ga₂O₃ (Wako) and MgO (Wako) powders were ball milled in ethanol with a 100 ml ZrO₂ pot for one day in order to obtain small particle size (less than 1 μm). After being dried under the IR lamp, the prepared powder was calcined at 1373 K for 6 h. Ce₀.₉Mn₀.₁Fe₀.₆O₃−δ (CMF), TiO₂-added La₀.₅Ce₀.₅O₂−δ (Ti-LDC) and Sm₀.₅Sr₀.₅CoO₃−δ (SSC) powders were also prepared by solid-state reaction method, and starting powders of Ce(NO₃)₃·6H₂O, Mn(NO₃)₂·H₂O and Fe(NO₃)₃·9H₂O, TiO₂ (High Purity Materials), La₂O₃ (Kishida) and GeO₂ (Wako); Sm₂O₃ (Wako), SrCO₃ (Rare Metallic) and Co₂O₃ (Wako) were first mixed with a planetary ball mill mixer and then calcined for 6 h in air at 1273 K for CMF, 1623 K for Ti-LDC, and 1473 K for SSC, respectively. In addition, Ni-SDC and Ni-Fe cathode functional layers were applied in this study. NiO-SOEC (6:4 wt%) and NiO-Fe₂O₃ (9:1 wt%) powders were prepared by the traditional impregnation method and calcined at 1373 K for 6 h. All calcined powders were ball milled again to further decrease the particle size. In addition, 15 wt% cellulose mixed LSGM powder was used for the preparation of porous LSGM layer. The prepared powders were mixed with polyvinylbutyral (PVB) as a binder and dispersed into 2-Propanol solvent for the dip-coating slurry.

2.2. Fabrication of NiO-YSZ-supported cell using the dip-coating process

The green NiO-YSZ (NiO:YSZ = 66:34%) cathode-supporter tubular substrate was supplied by NGK Spark Plug Co. Ltd. The pre-calcined temperature of the NiO-YSZ substrate was optimized to 1423 K before dip-coating in order to match the thermal expansion/shrinkage rate of the LSGM electrolyte in co-sintering. The pre-calcined substrate was dip-coated into the Ni-SDC or Ni-Fe slurry to form the cathodic functional layer. Then, the substrate was further dip-coated into CMF and Ti-LDC slurry to form the buffer layer, dip-coated into LSGM slurry and porous LSGM slurry to form around 50 μm thickness electrolyte film. After being dried overnight at room temperature, the prepared half cell was co-sintered at 1623 K for 3 h to obtain the single-phase LSGM electrolyte. Finally, the cell was dip-coated into the SSC slurry to form the porous anode, then calcined at 1373 K for 1 h. The dip-coating speed was 1 mm s⁻¹ with a 10 s immersion in slurry. The detailed preparation process was provided in our previous report [14, 20].

The schematic image and photograph of the prepared cells are shown in figure 1. In this study, we used double layers consisting of CMF and Ti-LDC for the buffer layer, which prevents reaction of LSGM and NiO in the substrate. It is reported that CMF was an active anode of SOFC and also the cathode of SOEC. It was found...
that CMF is also effective for preventing Ni diffusion by reaction of Mn in CMF with Ni [21, 22]. In addition, Ti-LDC is also effective for preventing Ni diffusion into LSGM electrolyte by reaction of Ti with NiO in gas phase [23]. Therefore, CMF and Ti-LDC layer were used in this study for the buffer layer to prevent Ni diffusion in the LSGM electrolyte. A detailed analysis such as energy-dispersive x-ray (EDX) mapping has been reported in our previous study [14, 20].

2.3. Characterization and performance testing
The diameter of the NiO-YSZ cell after co-sintering was around 9.8 mm. The coated length of the SSC anode layer was 5 mm. Therefore, the obtained effective electrode area of the cell was around 1.53 cm². The platinum mesh was covered on the surface of the SSC anode layer for the current collector and the four platinum probes were used as connecting lines. The molten Pyrex glass and glass paste were used as the sealing material between the single tubular cell and Al₂O₃-supported tubes at 1073 K. After confirming the negative gas leakage, the cell was reduced at 973 K with humidified H₂ first. Then, the steam electrolysis property of the cell was tested at the intermediate temperature (873–773 K) by using 20% steam-30% H₂ in Ar (100 cc min⁻¹). The SSC anode was exposed to the open air. The concentration of supplied steam was calculated from the saturated vapor pressure by adjusting the temperature of the water in the tank of the evaluation vessel.

The current applied to the cell was controlled by using a galvanostat (HAL-3001, Hokuto Denko) and the terminal voltage was monitored with a digital multimeter (R6451A, Advantest). In the case of the durability test, the electrochemical measurement system (HZ-7000, Hokuto Denko) was used to control the applied current and record the change of potential. The steam was supplied and controlled by using the fuel cell evaluation system (Mini Test 3000, Toyo Technica Corporation). The H₂ formation amount was measured by a gas chromatograph (GC-8A, Shimazu). The complex impedance analysis, which evaluated the inner resistance of the cell was measured by using the impedance/gain-phase analyzer (Solartron type 1260, Solartron) with an electrochemical interface (Solartron type 1287, Solartron). The microstructure and elemental distributions of the cells were analyzed using a field-emission scanning electron microscope (FE-SEM, Versa 3D, FEI) equipped with an EDX detector (EDX, Oxford).

3. Results and discussion
3.1. Effect of Ni-based cathodic layer on steam electrolysis property
Since a good electrolyte-cathode laminated layer was required for achieving superior electrolysis performance, the effect of the Ni-SDC and Ni-Fe functional layer between the NiO-YSZ cathode substrate and CMF buffer layer was investigated. The cells with the Ni-SDC and Ni-Fe layer were prepared, respectively, with dip-coating, and the electrolysis performance was measured. Figure 2 shows the SEM image of the cross-section of a NiO-YSZ cell with the Ni-SDC cathodic layer after co-sintering. The tight structure of the deposited functional films was confirmed and dense LSGM electrolyte was also obtained. This was also similar in the case where the Ni-Fe layer was used. Therefore, gastight electrolyte film was obtained in this study. After reduction, the steam electrolysis performance was tested under fuel of 20% steam-30% H₂ in Ar from 873–773 K.
Figure 3 shows the temperature dependence of the $I$–$V$ curves of the NiO-YSZ cells with the Ni-SDC and Ni-Fe cathodic layer in steam electrolysis, respectively. Theoretical open circuit voltage was achieved on both prepared cells. The achieved electrolysis current density of the cell with the Ni-SDC anodic interlayer was 0.5, 0.26 and 0.13 A cm$^{-2}$ at 873, 823 and 773 K, respectively, at the potential of 1.5 V. In the case of the cell with the Ni-Fe layer, much higher electrolysis performance was presented. The current density was 0.69, 0.47 and 0.28 A cm$^{-2}$ at 873, 823 and 773 K, respectively, at the potential of 1.5 V. Figure 4 shows the comparison of electrolysis current density of cells without the Ni-based layer, and with the Ni-SDC layer and Ni-Fe layer, respectively, at 873 and 773 K. The result suggested that the Ni-Fe cathode layer was significantly effective for increasing the electrolysis property in the entire tested temperature range. On the other hand, the cell without the Ni-based layer shows higher current density than that of Ni-SDC at 873 K. However, it was noted that the slope of the $I$–$V$ in the cell using the Ni-SDC layer was obviously larger than that of the cell without the Ni-based layer at low temperature of 773 K. Thus, higher current density was achieved in the cell using the Ni-SDC layer at electrolysis potential above 1.5 V. Considering the thermal neutral operation voltage in the steam electrolysis was near 1.3 V, the reference values of tested cells at 1.3 V were compared. The current density at 773 K was 0.056, 0.042 and 0.137 A cm$^{-2}$, in the case of the cell without the Ni-based layer, and with the Ni-SDC layer and Ni-Fe layer, respectively. The results clearly indicated that the cell-inserted Ni-Fe layer played an active role in the realistic application for steam electrolysis.

Figure 5 shows the $H_2$ formation rate in steam electrolysis on the LSGM tubular cell using the Ni-Fe and Ni-SDC cathode layer as a function of current density at 873 K, respectively, measured by gas chromatograph.
this figure, the theoretical H₂ formation rate estimated by Faraday’s law (n = It/(2F), n: H₂ formation amount, I: current, F: Faraday constant) was also shown. The H₂ formation rate was monotonically increased with increasing current density. In the case of the cell using the Ni-Fe layer, the H₂ formation amount was close to the theoretical amount from Faraday’s law at low current density range because of small gas leakage. The observed H₂ formation rate was slightly smaller than that of the theoretical amount with current increasing, while the Coulomb efficiency at 1.5 V of the cell with the Ni-Fe and Ni-SDC layer was estimated to be around 88% and 91%, respectively. Deviation of the observed H₂ formation rate from the theoretical one became larger with increasing current density and so this deviation might be assigned to the gas leakage at the gas sealing part of the cell because almost theoretical EMF was observed at open circuit condition and the gas leakage became larger with the increasing difference in H₂ concentration.

Figure 6 (left) shows temperature dependence impedance plots of the cell with the Ni-Fe cathode interlayer under open circuit condition from 873–773 K. Figure 6 (right) shows a comparison of the impedance of cells without the Ni-based layer, and with the Ni-SDC and Ni-Fe layer, respectively. The fitting of an equivalent circuit was also performed. On both cells, at least two semicircles were observed and they could be attributed to the activation and concentration overpotential at the high- and low-frequency region, respectively. Obviously, both IR and overpotential were decreased by the insertion of the Ni-Fe layer. Ni-Fe bimetallic catalyst is significantly active in increasing the cathodic activity, which seems to be effective for increasing the higher
current density in steam electrolysis. When the Ni-based layer was not inserted, diffusion resistance of R2 at the low-frequency region was estimated to be around 9.1 Ω cm², which became significantly large at 773 K. In contrast, when the Ni-SDC layer was inserted, the concentration of overpotential was sustained at a smaller value (7.8 Ω cm²) than that of the cell without the Ni-based layer. This resulted in the small cathodic overpotential at 773 K, which could be attributed to the mixed conductivity of SDC at the cathode site. However, the impedance semicircle at lower frequency, which was attributed to the diffusion resistance was still larger than expected, and for further increase in electrolysis performance, decrease in cathodic overpotential is still required. Considering the current density of the cell using the Ni-SDC layer below 1.5 V, the decreased potential drop, in particular, the overpotential seems to be still strongly required. Compared with the deposited functional layer on the electrode surface, another method of fabricating electrodes by liquid infiltration has also been proposed [24–26]. This is because liquid infiltration enables the formation of nanostructured phases at temperatures as low as 773 K [24]. Gonzalez et al and Barnett et al infiltrated GDC into NiO-YSZ substrate by the liquid infiltration method, and the polarization resistance was significantly decreased [25, 26]. This increase in cathodic performance by the infiltration method is now under investigation in order to further increase the performance of NiO-YSZ-supported SOFC/SOEC.

3.2. Long-term stability measurement
The long-term stability of steam electrolysis performance was another important issue. Figure 7 shows the long-term stability of the steam electrolysis performance of the prepared tubular cell with the Ni-SDC layer at 873 K and current density of 0.15 A cm⁻². The initial terminal potential was 1.3 V at 0.15 A cm⁻² and after 100 and 150 h later, the measured terminal potential was 1.328 and 1.341 V, respectively, which indicated that the prepared NiO-YSZ cell with the Ni-SDC functional layer was quite stable in long-term electrolysis operation. The average degradation rate was estimated to be 1.7% after the initial 100 h and 1.9% after 100–150 h. Since the prepared cells in this study deposited with almost similar structure and composition, reasonable stability was shown on the prepared NiO-YSZ tubular-type cell using the LSGM electrolyte film and SSC anode.

Figure 8 shows the impedance plots of the cell before and after 150 h electrolysis measurement at 873 K. IR loss, which is estimated by X-axis intercept of impedance arc at the high-frequency region in the impedance plots and also the diffusion resistance, which is estimated by the impedance arc at the low-frequency region, became larger after 150 h electrolysis. Therefore, aggregation of the electrode, in particular, the anode may have occurred during the long-term stability measurement. An increase in tolerance of the anode could be effective for further increasing the long-term stability of the electrolysis in this study.

Figure 9 shows the SEM image of the cross-section of the cell after 150 h electrolysis. The dip-coated LSGM film was reasonably dense, with no crack or delamination observed. This was also the same with other functional layers. Since porosity as well as Ni aggregation was not observed, degradation in the Ni-YSZ substrate may not have occurred during the initial 150 h long-term stability measurement.

Figure 10 shows the XRD pattern of the Ni-YSZ inner surface after the long-term test. Single phases of Ni and YSZ without NiO were detected. This result also indicated that Ni was hardly re-oxidized into NiO due to the mechanical density of the prepared film structure being still well attached to the substrate in the 150 h long-term electrolysis test. As a result, this study reveals that the prepared NiO-YSZ tubular cell with the Ni-SDC cathode
Figure 7. Time dependence of the potential of the cell with the Ni-SDC layer at applied current density of 0.15 \( \text{A cm}^{-2} \) at 873 K.

Figure 8. Impedance plots of the NiO-YSZ cell with the Ni-SDC layer at 873 K before and after the 150 h long-term electrolysis test.

Figure 9. SEM image of the cross-section of the cell with the Ni-SDC cathode layer after the 150 h long-term electrolysis test.
layer presented a better steam electrolysis performance at low temperature and stable durability over the 150 h steam electrolysis test.

4. Conclusion

The NiO-YSZ cathode-supported tubular cells using LSGM dense and porous electrolyte film were prepared with the dip-coating method by using Ni-SDC or Ni-Fe, CMF and Ti-LDC functional layer in the cathode side. The cell depositing Ni-Fe cathodic layer on the NiO-YSZ substrate showed much larger current density, in particular, at low temperature. This was attributed to the high activity of Ni-Fe bimetallic catalyst and high electrical conductivity, which led to the decrease in both IR loss and overpotential. In addition, the cathodic overpotential at 773 K was decreased by the Ni-SDC interlayer. This could be attributed to the mixed conductivity of Ni-SDC under electrolysis condition. The long-term stability in steam electrolysis at 873 K was also measured, and the cell exhibited reasonably stable performance over 150 h, although degradation of the SSC anode layer was observed. Thus, the prepared tubular cell using the LSGM electrolyte film shows reasonable steam electrolysis performance and stability at intermediate temperature range.

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Figure 10. XRD pattern of the Ni-YSZ inner surface after the 150 h long-term test.
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