Preparation of $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$ Film by Pulse Laser Deposition (PLD) Method on Porous Ni–Fe Metal Substrate for CO_2 Electrolysis

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Preparation of metal supported $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$ (LSGM) thin film cell for CO_2 electrolysis was studied and by using selective reduction method of $\text{NiO-NiFe}_2\text{O}_4$, it was found that porous Ni–Fe(9:1) based substrate with ca.30% porosity was successfully prepared without large volume change resulting in the successful preparation of LaGaO_3 dense thin film on metal substrate. By using $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_2$ (SDC) thin film, Ni diffusion from Ni–Fe substrate was prevented. CO_2 electrolysis was performed on the prepared LSGM/SDC on Ni–Fe porous substrate. When $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (SSC) anode was prepared by screen print method using SSC powder, sintering of SSC powder was significantly occurred resulting in the large IR loss and overpotential. In contrast, when SSC anode layer was deposited by PLD (30 min) after LSGM/SDC layer deposition, tight contact between SSC anode and LSGM electrolyte film was obtained and the large CO_2 electrolysis current of 3 and 0.5 A/cm^2 were achieved at 973 and 773 K, respectively. Impedance analysis suggests that increased CO_2 electrolysis current was obtained by decreased IR loss and electrode overpotential.

KEY WORDS: CO_2 electrolysis; solid oxide electrolysis cell; LaGaO_3 thin film; metal support.

1. Introduction

Recently, solid oxide electrolysis cell (SOEC) is attracting much attention from the highly efficient electrolyzer by using heat energy. In order to reuse CO_2 , conversion of CO_2 into CO ($\text{CO}_2 \rightarrow \text{CO} + 1/2\text{O}_2$) is important issues by using electric power from renewable source or high temperature nuclear gas cool reactor (HTGR).^{1–3)} For this direct conversion of CO_2 into CO, high temperature CO_2 electrolysis using oxide ion conducting electrolyte is ideal because of simplicity of system and reliability of electrolyte. Two by-products, CO and O_2 , are produced in separate streams, which may be usefully applied for steel making processes. For instance, the generated CO can be used as a fuel gas or converted into hydrocarbon by reaction with H_2 or used for reducing iron oxide to pure iron in iron-making process, which has been proposed and developed so-called “Sustainable Iron and Steel Making System based on Material Recycling Technologies (SMART)”.³⁾ CO_2 produced in the iron-making process, can be converted into CO through a CO_2 reduction process (SOEC-based), therefore, cyclic utilization and low CO_2 emission can be realized. In addition, oxygen was produced as a byproduct in carbon

dioxide conversion and can be recycled to a combustor to supply heat demand for the reaction or used for several process in steel making process like a revolving furnace steel converter.⁴⁾ Furthermore, supplying additional heat energy such as waste heat can be decreased the electrical energy required for reducing CO_2 to CO, since the required electric energy (ΔG) for CO_2 electrolysis is decreased by increasing the operation temperature from the positive value of T ΔS (heat demand).⁵⁾ Therefore, CO_2 electrolyzer could be considered as an important system for converting waste heat to chemical energy, which could greatly reduce the cost for CO_2 electrolysis. Application of SOECs and the related technologies for an active carbon recycling energy system (ACRES) will potentially play a significant role in reducing greenhouse gas emissions from steel making process and progress towards a more sustainable economy.³⁾ When the electric power generated by wind or solar power is used for CO_2 electrolysis, CO_2 formation can be decreased overall (carbon neutral concept) and carbon can be assumed as energy carrier.⁵⁾

However, up to now, direct CO_2 electrolysis using SOEC is not comprehensively studied,^{6–10)} especially high current density in the CO_2 electrolyzer at intermediate temperature. For operating SOEC at intermediate temperature, decrease in IR loss by electrolyte should be achieved and for this, using LaGaO_3 based electrolyte which is fast oxide ion conduc-

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tor is required. In the present study, the cell using LaGaO₃ based electrolyte thin film deposited by pulse laser deposition (PLD) on porous Ni–Fe metal substrate was applied for CO₂ electrolysis at intermediate temperature (773–973 K). A cermet cathode (Ni–Fe–(La,Sr)(Fe,Mn)O₃) was found the high activity to CO₂ electrolysis at elevated temperatures (973–1 173 K) on the cell using La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O₃ (LSGM) electrolyte.^{11,12} Compared with Ni–Fe cathode in our previous work,^{11,12} mixing (La,Sr)(Fe,Mn)O₃ with Ni–Fe improves the activity for CO₂ electro-conversion with much smaller overpotential loss. A current density of 2.32 A/cm² at 1.6 V and 1 073 K was achieved for CO₂ electrolysis on the cell using the Ni–Fe–(La,Sr)(Fe,Mn)O₃ cermet cathode. For further increasing electrolysis current, application of LSGM thin film on Ni–Fe porous metal substrate was investigated in this study. Effects of deposition of anode oxide by PLD was also studied for decreasing the internal resistance.

2. Experimental

Dense NiO–Fe₂O₃ substrate was prepared with 10 wt% Fe₂O₃ coated NiO powder, which was prepared by a traditional impregnation method. The powder was pressed into disks (20 mm in diameter) at 20 MPa. After iso-statically pressing at 48 MPa, the obtained disks were sintered at 1 723 K for 5 h in air.¹³ On the dense substrate, thin La_{0.9}Sr_{0.1}Ga_{0.2}Mg_{0.2}O₃ (LSGM) and Sm_{0.2}Ce_{0.8}O₂ (SDC) film was deposited onto the dense substrate with a PLD method using a commercial system (PLD-7, PASCAL). Before deposition, the substrate was heated to 1 073 K with infrared heater. During the deposition, oxygen pressure was adjusted to 0.67 Pa by introducing commercial oxygen without purification. The power and frequency of excimer laser (Compex Co. Ltd.) were adjusted to 180 mJ/pulse and 10 Hz, respectively. In order to deposit the LSGM thin film, optimized LSGM target composition (La_{0.7282}Sr_{0.1}Ga_{0.6380}Mg_{0.4255}O_{3-δ}) was used. Before deposition of LSGM thin electrolyte film, SDC film was fabricated with commercial SDC (Sm_{0.2}Ce_{0.8}O_{2-δ}, Daiichi Kigenso Kagaku Kogyo Co. Ltd., Japan). After post-annealing in air at 1 073 K for 2 h, thin Sm_{0.5}Sr_{0.5}CoO_{3-δ} (SSC) layer was prepared by screen print method or fabricated via a PLD method with an optimized SSC target composition (Sm_{0.4}Sr_{0.6}Co_{1.6}O_{3-δ}) on the thin LSGM film. SSC powder anode was prepared using a slurry coating method on the deposited SSC film and then fired at 1 073 K for 30 min. A platinum wire was connected to the LSGM film near the cathode as the reference electrode.

X-ray diffraction (XRD) using Cu K α radiation (Rigaku Rint 2500) has been used for analysis of crystal structures of prepared film. Morphology and elemental distribution of the metal-supported SOECs were analyzed using a scanning electron microscope (SEM, VE-7800, Keyence) and energy dispersive X-ray spectroscopy (EDX, EDAX). The prepared single cell was set between two alumina tubes with molten Pyrex glass ring and ceramic sealant. Pt mesh was used as a current collector covering the surface of both anode and cathode. The electrodes were connected to the electrochemical equipment with Pt lead wire. The cathode feed gas is 50% CO₂ with a balance gas of Ar. Small amount of CO was added to fix OCV at the constant value. The

anode side was fed with air as a sweep gas. The total flow rate was always 100 mL/min for both electrode sides. CO₂ electrolysis measurements were conducted by a four probe method, with the applied DC voltage controlled by a galvanostat (Hokuto Denko, HA-301). Electrochemical impedance of the electrodes were measured with an impedance/gain-phase analyzer (Solartron SI 1260) combined with an electrochemical interface (Solartron SI 1287) at AC voltage amplitude of 10 mV. The frequency range was used from 10⁵ to 0.1 Hz. The measurement was performed under open circuit voltage (OCV). The electrochemical characterization was performed at temperature from 973 to 773 K. The rates of steady state CO₂ conversion and CO yield were analyzed by a gas chromatography (SHIMADZU, GC-8A) with a thermal conductive detector (SHIMADZU, C-R8A) after allowing at least 2 h equilibration times for each conditions.

3. Results and Discussion

3.1. Preparation of Porous Ni–Fe Metal Substrate

In order to prepare the metal support cell using LSGM thin film, difference in reduction rate of NiO and NiFe₂O₄ was used as shown in **Fig. 1**. In this method, dense oxide substrate of NiO–Fe₂O₃ was prepared first and then LSGM film was deposited on the NiO–Fe₂O₃ substrate followed by reduction of NiO–Fe₂O₃ substrate with hydrogen. In general, size of substrate will be changed during reduction step resulting in the crack formation in film. However, because of first and slow reduction rate of NiO and NiFe₂O₄ respectively, size of NiO–Fe₂O₃ substrate can be kept same during reduction.^{13,14} For this purpose, preparation condition of dense NiO–Fe₂O₃ substrate is important parameter. Therefore, optimization of sintering temperature on porosity as well as shrinkage was studied first.

Table 1 summarized the porosity measured with the Archimedes method and the shrinkage estimated by comparing the size of the disk before and after reduction at 973 K. Effects of sintering temperature on porosity and shrinkage of the Ni–Fe alloy substrate after reduction at 973 K for 2 h are also shown in **Fig. 2**. Evidently, substrates sintered at higher temperature have larger porosity after reduction. The substrate prepared at 1 623 and 1 823 K had largest porosity but some cracks and bending of substrate were occurred. These cracks and bending in substrate lead to a gas leakage during

Fig. 1. Schematic image for making porous Ni–Fe metal supported LSGM cell by selective reduction method.

SOEC cell operation. Although the porosity of substrates sintered at lower temperature less than 1723 K was comparatively small, the porosity of substrates is sufficient for the porous substrate for SOECs. The volumetric shrinkage during the reduction should be small in order to prevent a formation of crack in the thin electrolyte film. The shrinkage decreased with elevating the sintering temperature because the substrate prepared at higher temperature was formed a dense structure during the sintering process. Therefore, the optimum sintering temperature of NiO-Fe₂O₃ is 1723 K.

Since porous metal substrate was prepared by in-situ reduction of NiO-NiFe₂O₄ oxide dense substrate, pore area was estimated using Amira software (FEI) after reduction with H₂. **Figure 3** shows a SEM image of Ni-Fe substrate, which was reduced at 973 K for 2 h. It is seen that small pores (less than 200 nm) are randomly dispersed on whole surface of Ni-Fe substrate. However, even after reduction, any micro-crack was not observed at grain boundary. Due to three phase boundary (TPB) is formed at the periphery of pores, the distribution of pore is quite important. Therefore, distribution of pores in bulk of Ni-Fe substrate was analyzed with FIB-SEM analysis. **Figure 4** shows the image of pore in Ni-Fe substrate. The formation of internal pore in the substrate has been confirmed via FIB-SEM. As shown in Fig. 4, the internal pore is fully developed in whole

substrate. Therefore, it can be expected that the Ni-Fe substrate have a role of not only current collector but also gas-diffusion layer. The estimated porosity of metal substrate was ca. 32% and so the Ni-Fe metal substrate can be used for substrate of SOFC using thin anode and electrolyte film.

Figure 5 shows the surface and cross section of the cell with LSGM layer after reduction at 973 K for 2 h. It is obvious that dense and smooth LSGM film was deposited on Ni-Fe porous metal substrate after reduction and the thickness of the LSGM films was about 10 μm in thickness. The

Fig. 2. Effects of sintering temperature on porosity and shrinkage of the Ni-Fe alloy substrate after reduction at 973 K for 2 h.

Table 1. Change of NiO-Fe₂O₃ substrate volume and density by reduction.

Sample (Shrinkage, Vol.%)		Weight (g)	Volume (cm ³)	Density (g/cm ³)	Apparent Density (g/cm ³)	Relate density (%)	Porosity (%)
NiFe1623 (19.99)	Before reduction	1.99	0.35	5.88	6.11	96.30	3.70
	After reduction	1.57	0.28	5.78	8.47	68.24	31.76
NiFe1673 (19.45)	Before reduction	1.93	0.30	5.88	6.02	97.62	2.38
	After reduction	1.52	0.24	5.77	8.46	68.17	31.83
NiFe1723 (18.77)	Before reduction	2.02	0.35	5.88	5.98	98.33	1.67
	After reduction	1.59	0.29	5.75	8.46	67.97	32.03
NiFe1773 (17.62)	Before reduction	1.95	0.36	5.76	5.83	98.86	1.14
	After reduction	1.53	0.29	5.69	8.90	63.97	36.03
NiFe1823 (15.58)	Before reduction	2.03	0.37	5.73	5.78	99.12	0.88
	After reduction	1.59	0.31	5.49	8.59	63.87	36.13

Fig. 3. SEM image of Ni-Fe substrate reduced at 973 K for 2 h. (a) Low magnification (b) High magnification.

contact between LSGM/SDC film is also tight and contact between LSGM/SDC bilayer to Ni-Fe porous substrate is quite high and no delamination was observed. Therefore, it can be said that LSGM/SDC bilayer electrolyte on porous Ni-Fe metal substrate was successfully obtained by selective reduction method followed by the deposition of LSGM film on the oxide dense substrate.

3.2. CO₂ Electrolysis Performance of the Cell

Figure 6 shows I-V curves of 50%CO₂-Ar electrolysis on the cell; SSC/LSGM/SDC/Ni-Fe(9:1). CO₂ electrolysis current was started to flow at potential higher than ca. 0.9 V, although small current was observed at potential lower than 0.9 V. This was more significantly observed at 973 K. At present, this current at potential lower than 0.937 V which is theoretical potential for CO₂ electrolysis was not clear, however, it might be explained by electrochemical pumping current of oxygen which comes into CO₂ stream by gas leakage at sealing part. In any way, under applied potential higher than 0.9 V, CO₂ electrolysis is mainly occurred. It is evident that reasonable electrolysis current was observed at temperature higher than 773 K. The electrolysis current at

1.5 V of this cell was 0.6, and 0.5, 0.15, and 0.05 A/cm² at 973, 873, and 773 K, respectively. This current density was much smaller than that expected from a thickness of LSGM electrolyte (10 μm). In order to confirm the CO₂ electrolysis occurred in this cell, formation rate of CO was plotted in Fig. 7 as a function of current density. Formation of CO was only observed and CO formation rate was increased with

Fig. 6. I-V curves of 50%CO₂-Ar electrolysis on the cell; SSC/LSGM/SDC/Ni-Fe(9:1).

Fig. 4. 3D image of pore in Ni-Fe substrate after reduction. (Online version in color.)

Fig. 7. Formation rate of CO as a function of current density on the cell shown in Fig. 6.

Fig. 5. Surface and cross section of the cell with LSGM layer after reduction at 973 K for 2 h.

increasing current density. In Fig. 7, formation rate of CO from Faraday's law was also shown as a dashed line. It was obvious that at low current density, CO formation rate was slightly larger, however, well agreed with that of Faraday's law at high current density. The larger amount of CO formation rate than the theoretical value could be assigned to analytical error by gas chromatograph. However, considering the increase in CO formation rate, CO₂ reduction into CO was mainly occurred on this cell.

Figure 8 shows impedance plots of the cell at open circuit condition and it is obvious that IR loss is quite large and two semicircles were observed for overpotential, one higher frequency may be assigned to cathode and other at lower frequency may be anode. Since the overpotential of anode is larger than that of cathode at 973 K. Decrease in IR loss as well as anodic overpotential is strongly required for the present cells. One reason for large IR loss and overpotential of SSC anode was assigned to the partial delamination of SSC cathode because of smooth surface of LSGM film deposited by PLD.

Figure 9 shows SEM image of the cross-section of the LSGM electrolyte after electrolysis measurement. From the cross-section of LSGM/SDC layer prepared by FIB processing, LSGM/SDC bilayer electrolyte is highly dense and no interface was observed and also electrolyte layer was tightly deposited on the Ni-Fe substrate. It is also noted that thickness of electrolyte layer was around 10 μm .

Fig. 8. Impedance plots of the cell at open circuit condition.

Fig. 9. SEM image of the cross-section of the LSGM electrolyte after electrolysis measurement. Cross-section was prepared by FIB processing in SEM.

No delamination was observed after CO₂ electrolysis. The thickness of the electrolyte was about 10 μm , which is the expected thickness considering the PLD period for LSGM film preparation. It was observed the SSC anode layer on the top of the LSGM/SDC film and it is seen that SSC particle was changed from porous powder to dense morphology, and the size of particles was increased around 5–10 μm in diameter. Therefore, large IR loss and anodic overpotential were assigned to sintering the anodic SSC powder and poor contact between anode and electrolyte film.

In order to further increase in anodic contact and stability against sintering, deposition of SSC anode as a film shape was prepared by using PLD for 30 min. **Figure 10** shows SEM image of cross-section of SSC film deposited on LSGM/SDC electrolyte film. Similar dense LSGM film was obtained and SSC film with 200 nm thickness of the rough morphology was successfully deposited on LSGM electrolyte film. Contact between SSC and LSGM layer is also quite tight and so it is expected that stability of SSC layer could be much improved.

Figure 11 shows I-V curves of CO₂ electrolysis of the cell which is prepared SSC anode by PLD. In our previous study, we also deposited SSC air electrode interlayer for improvement attachment strength¹⁵⁾ by PLD method. Comparing with I-V curve in Fig. 6, obviously, much larger electrolysis current can be flown by preparing SSC anode by PLD deposition, *i.e.*, CO₂ electrolysis current at 973 K

Fig. 10. SEM image of cross-section of SSC film deposited on LSGM/SDC electrolyte film.

Fig. 11. I-V curves of CO₂ electrolysis of the cell with SSC anode film prepared by PLD.

was increased from 0.55 to 3 A/cm². Even at 773 K, much larger electrolysis current was observed and it seems that anodic overpotential was much decreased at 773 K considering from the I-V curve as shown in Fig. 11. This could be explained by the increased stability and contact of the SSC anode. It is also noted that stable electrolysis current was observed. In Fig. 8, impedance plots at open circuit potential of this cell was also shown at 973 K. As discussed, on the cell using SSC film anode, it is obvious that much smaller IR loss and also overpotential of electrode was confirmed. Therefore, much increased CO₂ electrolysis current could be assigned to the decreased IR loss as well as the electrode overpotential, in particular, anodic overpotential. Due to gas leakage through porous metal support, the observed amount of CO formation was deviated from Faraday's law with increasing current density, however, coke deposition was not observed after cell test, and so CO₂ reduction to CO seems to be dominant reaction. As a result, this study reveals that the metal supported LSGM cell was successfully prepared by selective reduction method of dense oxide substrate on which LSGM/SDC bilayer electrolyte film was deposited by PLD method and the cell deposited SSC layer by PLD as well shows reasonable large current density at decreased temperature, 3A/cm² at 973 K.

4. Conclusion

CO₂ electrolysis on LSGM thin film cell supported on porous Ni-Fe bimetallic substrate was studied. LSGM/SDC bilayer electrolyte film was successfully deposited on Ni-Fe porous metal substrate with selective reduction method. About 30% porosity of metallic substrate with few 100 nm diameter pore was prepared and by optimizing the sintering temperature, change in volumetric change was suppressed and the shrinkage of the NiO-NiFe₂O₄ was smaller than 20% shrinkage when sintering was performed at 1 723 K. The LSGM thin film cell with screen printed SSC anode shows CO₂ electrolysis with reasonable electrolysis current.

However, SEM observation suggested that sintering of SSC anode was significantly occurred and so large IR loss as well as overpotential of electrode were observed. Stability of SSC anode was much improved by deposition of SSC film by PLD method and CO₂ electrolysis current at 973 K was increased from 0.55 to 3 A/cm². This suggests that CO₂ electrolysis on Ni-Fe porous substrate was achieved at intermediate temperature around 773–973 K and contributes the achievement of sustainable iron and steel making system based on material recycling technologies (SMART).

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