Intermediate Temperature CO₂ Electrolysis by Using La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O₃ Oxide Ion Conductor

Shijing WANG¹⁾ and Tatsumi ISHIHARA^{2)*}

1) Department of Automotive Science, Graduate School of Integrated Frontier Science, Kyushu University, Fukuoka, 819-0395 Japan. 2) International Institute for Carbon Neutral Energy Research (WPI-I2CNER), Kyushu University, Motooka 744, Nishi-ku, Fukuoka, 819-0395 Japan.

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Solid oxide electrolysis cell for electrolysis of CO₂ to CO was studied with the cell using LaGaO₃-based electrolyte at the intermediate temperature (*i.e.* 973–1 173 K). Various metal additives to Ni were examined for cathode to CO₂ reduction and it was found that Ni added with Fe shows high activity and the current density of 1.5 A/cm² was achieved at 1.6 V and 1 073 K on Ni–Fe (9:1) cathode. Improved electrolysis activity was explained by the expanded reaction site which may be assigned the fine particle of Ni. Furthermore, effects of additives to Ni cathode were studied and it was found that the electrolysis current could be much improved by addition of Fe to Ni. Effects of oxide ion conductor mixing with Ni–Fe were further studied and it was found that mixing La_{0.6}Sr_{0.4}Fe_{0.9}Mn_{0.1}O₃ with Ni–Fe bimetal is the most effective for achieving high electrolysis current of CO₂ of 2.07 A/cm² at 1.6 V and 1 073 K.

KEY WORDS: solid electrolysis cell; Ni–Fe cathode; LSGM cermet, CO₂ electrolysis; stability.

1. Introduction

Solid oxide electrolysis cell (SOEC) has been increasingly investigated as a high efficient electrolyzer and a green energy technology. At present, most research on solid oxide electrolyzers is focused on steam electrolysis (H₂O→H₂ + 1/2O₂) for the production of hydrogen,^{1–7)} however, the reduction of carbon dioxide (CO₂→CO+1/2O₂) using a highly efficient SOEC is also feasible^{2,8)} and this is attractive as a mean for reducing CO₂ emissions. Since the two by-products, CO and O₂, are produced in separate streams (due to their spatial separation by a dense electrolyte), they may be usefully applied in industrial processes; for example, a new carbon recycling energy system has been proposed and developed to reduce emissions of CO₂ into the atmosphere from iron production process, called the active carbon recycling energy system (ACRES).⁹⁾ The system is assumed to be an ideal iron production process powered by electricity and thermal energy generated from a high temperature gas reactor (HTGR). The regenerated carbon monoxide (CO) is recycled and used to reduce iron oxide to pure iron. CO₂ produced by the iron production process is regenerated into CO through a CO₂ reduction process (SOEC) using energy from the HTGR. In addition, the oxygen product stream can be recycled to a combustor to supply the heat demand for the reaction. For example, the CO product can be used as a fuel gas or made into syngas by reacting with H₂, or by co-electrolysis of CO₂ and H₂O. Furthermore, the oxygen product stream can be recycled to a combustor (in the case of

CO₂ electrolysis for mitigation of greenhouse gas emissions, the electrolyzer and the combustor are likely situated in close proximity), leading to an improved combustion efficiency due to the enriched oxygen content of the combustion gas. This would reduce the overall fuel demand of the process, whilst also decreasing the formation of NO_x.¹⁰⁾

By analogy with steam electrolysis, the required electric energy (ΔG) for CO₂ electrolysis also can be decreased by increasing the operation temperature because of the positive value of $T\Delta S$ (heat demand).⁴⁾ Therefore, supplying additional heat energy decreases the electrical energy required to reduce CO₂ to CO during the electrolysis cell (EC) operation. In this regard, the CO₂ electrolyzer becomes an important system for converting waste heat to chemical energy. With sufficient progress in other related technology, the heat and electricity energy required for the implementation of an integrated CO₂ electrolysis cell could be supplied by process waste heat, feed gas flow in the operation chimney and other resources, which could greatly reduce the cost for CO₂ electrolysis in SOEC. There are, however, to date only a limited number of studies on CO₂ electrolysis using SOECs;^{2,4,8,11–14)} most of these reports used Y₂O₃ stabilized ZrO₂ (YSZ) as the electrolyte because of its chemical stability and mechanical strength. However, the conversion rate of CO₂ in EC mode and the resistance to coke deposition in these YSZ-based cells have not been extensively reported; this aspect is important, as coke deposition on active surface sites or within the porous electrode could reduce electrolysis performance.

In this study, the intermediate temperature (973–1 173 K) electrolysis of CO₂ to CO using the cell with a LaGaO₃-based (LSGM) electrolyte was investigated, with particular

* Corresponding author: E-mail: ishihara@cstf.kyushu-u.ac.jp
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attention paid to the development of active cathode. Since the most critical reactions influencing the cell performance occur on the cathode side during CO₂ reduction in EC mode,¹⁵⁾ the anode material in this study was fixed as BLC (Ba_{0.6}La_{0.4}CoO₃), which was shown in a previous study to exhibits good activity as a cathode in fuel cell mode and anode in steam electrolysis mode cell.^{16–18)} The CO formation rate in this study was seen to obey Faraday's law; this suggests that the oxide ion transference number in LSGM perovskite oxide under a CO₂ electrolysis conditions is always unity.

2. Experimental

Ni-based metallic cathode (NiFe91, NiCu91, NiCo91, NiPt91 and NiRu91, 9:1 in weight ratio) were synthesized in oxide form by the precipitation method, and reduced immediately prior to electrochemical measurements by high temperature exposure to flowing H₂. The precursors were NiO (99.9% pure), Fe(NO₃)₃·9H₂O (99.9% pure), Cu(NO₃)₂·3H₂O (99.9% pure), Co(NO₃)₂·6H₂O (98% pure), H₂PtCl₆·6H₂O (99% pure) and RuCl₃ (99% pure), all obtained from Wako Pure Chemical Industries, Ltd. The additive precursor was dissolved in de-ionized water, and then NiO powder was added in a metal atom at the weight ratio of 9:1. After drying the suspension under stirring, it was precalcined in a ventilated furnace at 673 K for 2 h. The obtained powder was ground in a pestle and mortar for 30 min and then calcined again in a muffle furnace at 1273 K for 6 h in air. The calcined powder was ground again. Ba_{0.6}La_{0.4}CoO₃ (BLC) was used as the anode in all cases in this study. The starting reagents for the anode were BaCO₃ (99.9% pure, Wako), La₂O₃ (99.99% pure, Kishida Chemical Co., Ltd.) and Co₃O₄ (99.9% pure, Wako). Powder at stoichiometric ratio was mixed using an Al₂O₃ mortar and pestle. The powder mixture thus obtained was calcined at 1423 K for 6 h and then followed by grind for 30 min before measurement. The electrolyte of La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O₃ (LSGM) was prepared by a conventional solid state reaction method.¹⁹⁾

We chose the electrolyte-supported cell geometry and LSGM electrolyte disks were polished to a 0.3 mm thickness before measurement. 4 mm diameter (effective electrode area; 0.126 cm²) of BLC anode and Ni–Fe base cathode was prepared on each face of the sintered LSGM electrolyte by screen printing followed by calcination at 1423 K for 0.5 h. Then a cathode of the same diameter of the respective Ni-based composite powder was painted on the opposite face of the LSGM electrolyte with n-butyric acetate solvent as cathode. A platinum wire was applied with Pt paste on the cathode side as a reference electrode. The prepared single cell with all three electrodes was then calcined again at 1273 K for 30 min before the CO₂ electrolysis measurements. Pt mesh was used as a current collector covering the surface of both anode and cathode. The electrodes were connected to the electrochemical equipment using Pt leads. Before the measurement, the Ni-based cathode was reduced to a metallic state by feeding in a flow of H₂ at 1073 K for 2 h. The cathode feed gas is 50% CO₂ with a 1% CO and 49% Ar carrier gas. The small amount of CO was added to fix the OCV at the desired value. The anode side in EC mode 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 performed by a four probe method, with the applied DC voltage was controlled by a galvanostat (Hokuto Denko, HA-301). Potential for electrolysis was always expressed against counter electrode in this study. The internal resistance of the cell during the operation was measured by the current interruption method. The transient potential response to a current pulse (Hokuto Denko, HC 111) was monitored with a memory recorder (HIOKI 8835). Impedance spectra of the electrodes were measured with an impedance/gain-phase analyzer (Solartron FRA 1260) combined with an electrochemical interface (Solartron 1287). The rates of steady state CO₂ conversion and CO yield were analyzed by a gas chromatography (SHIMADZU, GC-8A) with a thermal conductive detector after allowing at least 2 h equilibration times for each set of new conditions. The electrochemical characterization was performed in a temperatures range from 973 to 1173 K.

3. Results and Discussion

Figure 1 shows the I-V curves at different temperatures for CO₂ electrolysis using a cell with a nickel cathode. Since Ni is widely used for high temperature steam electrolysis and solid oxide fuel cells (SOFCs), the cathodic property of Ni was first studied. As shown in Fig. 1, the open circuit potential of 0.67, 0.72, and 0.8 V was observed at 973, 1073, and 1173 K and this open circuit potential is well corresponded to the theoretical value under the used condition (0.68, 0.74, and 0.82 V for 973, 1073 and 1173 K, respectively). Here, potential was expressed between cathode and anode. Although the current density is small, we observed the electrolysis current around 0.9 V which is much smaller than the CO₂ electrolysis potential at 273 K (1.342 V) and this is great advantage for high temperature CO₂ electrolysis. In Fig. 1, theoretical potential for CO₂ electrolysis is also shown and it can be seen that electrolysis current was observed at potential slightly higher than the theoretical one suggesting the high activity to cathode. The current density

Fig. 1. I-V curve for the cell using the Ni cathode (BLC/LSGM/Ni) for CO₂ electrolysis at 1173, 1073 and 973 K.

at 1.6 V is significantly increased with increasing operating temperature and at 1173 K, it attained to a value of 1.6 A/cm² which is reasonably high current density. However, at 973 K, it is only 0.25 A/cm² and so increase in cell performance at intermediate temperature is strongly required.

Figure 2 shows the internal resistance of the cell using Ni cathode and BLC anode under CO₂ electrolysis condition at 1073 K. Obviously, internal resistance, not only IR loss but also cathodic overpotential is much larger on cathode than that on anode. Therefore, main reason for internal resistance is assigned to IR loss in cathode. In particular, cathodic overpotential is much larger at low current density and this suggests that activation overpotential is large on Ni cathode. In contrast, anodic overpotential is small over all current density examined suggesting that BLC shows reasonable activity to oxygen recombination. Therefore, in order to improve the current density at intermediate temperature, improvement in cathodic activity is essentially requested.

The detail reaction mechanisms were studied with ac impedance measurement. **Figure 3** shows impedance spectra of Ni cathode and BLC anode under an open circuit conditions. In a similar manner with the results in Fig. 2, the cathodic impedance arc is larger than that of the anodic one by an order of magnitude. Resistance at the low frequency region is much larger than that at higher frequency. One reason for larger cathodic overpotential may come from the slow diffusion of gas through the narrow channels in Ni cathode due to the large molecular size of CO₂. Therefore,

a more porous cathode microstructure allows easier gas diffusion and effective for decreasing cathodic overpotential.

In order to improve the performance of Ni cathodes for CO₂ electrolysis, we studied the effects of metal additives to Ni cathode. **Figure 4** shows I–V curves for the cell using Ni-based metallic cathodes in electrolysis mode at 1073 K.

Fig. 4. I–V curve for the cells (BLC/LSGM/Ni-based metallic) for CO₂ electrolysis at 1073 K.

Fig. 2. IR drop and overpotential of the cell (BLC/LSGM/Ni) for CO₂ electrolysis at 1073 K. (a) Cathode (b) Anode.

Fig. 3. Impedance plots for the cathode (a) and anode (b) of the cell using the Ni cathode (BLC/LSGM/Ni) under an open circuit condition.

Obviously, the electrolysis performance is strongly influenced by metal additives. Comparing with Ni, the addition of Pt or Co decreases the electrolysis current density. Therefore, addition of these metals is not effective as an additive for CO₂ electrolysis. In contrast, the addition of Cu, Fe, or Ru was highly effective for increasing current density. The best performance was observed by the addition of Fe; for example, a cathodic current density of 1.84 A/cm² was achieved at 1.6 V and 1073 K. Therefore, addition of small amount of Fe is highly effective for CO₂ electrolysis. Positive effects of Fe addition on Ni are also observed for anodic activity of Ni for SOFC and cathodic property of Ni for steam electrolysis.

Figure 5 shows the internal resistances of the cells using Ni-based bimetallic cathodes for CO₂ electrolysis at 1073 K. The additives to the Ni cathode influence both the IR drop and the cathodic overpotential. Here, the Ni-Fe metallic cathode shows both the smallest IR loss as well as the smallest cathodic overpotential. As a result, positive effects of Fe addition could be assigned to the decreased IR loss and cathodic overpotential.

Table 1 summarizes the effects of additives on CO yields during CO₂ electrolysis at a potential of 1.6 V at 1073 K on Ni cathode. A high selectivity for the reduction of CO₂ to CO is observed for all bimetallic cathodes studied. In particular, the Ni-Fe cathode exhibits the highest selectivity and almost no carbon deposition was observed because CO₂ conversion rate is corresponded with CO formation rate within experimental errors. Furthermore, the amount of CO₂ converted is in good agreement with that from Faraday's law. Therefore, addition of Fe shows positive effects for not only cathodic overpotential but also preventing coke formation during CO₂ electrolysis.

Figure 6 shows Arrhenius plots for cathodic reaction, *i.e.*, current density at cathodic overpotential plotted against temperature. In this figure, same plots for Ni are also shown. Evidently, apparent activation energy for Ni and Ni-Fe is almost the same and difference is only observed at Y axis interception, namely, pre-exponential term. This suggests that activity for cathodic reaction on Ni is hardly changed by Fe addition and the difference is mainly observed on reaction area. Increase in pre-exponential term by addition

of Fe suggests the enlarged reaction area. **Figure 7** shows SEM image of Ni and Ni-Fe after CO₂ electrolysis. Obviously, much smaller Ni particle size was observed after CO₂ electrolysis and so, the increased pre-exponential term in Arrhenius plots in Fig. 6 may be related with the small particle size of Ni, and thus a larger active area for the dissociative adsorption and surface diffusion processes of the active species during CO₂ electrolysis. On the other hand,

Table 1. Gas conversion amount for the cells (BLC64/LSGM9182/ Ni-based metallic) at the potential of 1.6 V for CO₂ electrolysis at 1073 K.

BLC64/LSGM9182/Cathode	1.6 V/Current density (A/cm ²)	Converted CO ₂ amount (μmol/min·cm ²)	Yielded CO amount (μmol/min·cm ²)	Formed C amount (μmol/min·cm ²)
NiFe91	1.84	561	549	12
Ni	0.76	224	213	11
NiCu91	1.21	366	357	9
NiCo91	0.52	149	137	12
NiPt91	0.61	179	168	11
NiRu91	1.55	471	461	10

Fig. 6. Arrhenius plots for cathodic reaction of Ni and Ni-Fe for CO₂ electrolysis.

Fig. 5. Internal resistance of the cells (BLC/LSGM/Ni-based metallic) for CO₂ electrolysis at 1073 K. (a) IR loss, (b) Cathodic overpotential.

Fig. 7. SEM image of Ni (a) and Ni-Fe (b) cathode after CO₂ electrolysis.

contact between the Ni electrode and LaGaO₃-based oxide electrolyte also be improved by the addition of Fe, because of the change in the thermal expansion property^{18,20)} and the large contact area of Ni.

For further increase in electrolysis current and preventing coke deposition, we investigated effects of oxide mixed with Ni-Fe bimetal. For SOFC application, combination of ion conducting oxide with Ni is widely adopted because of expanding reaction area. Therefore, in this study, combination of mixed conducting ceramics with Ni-Fe was studied. **Figure 8** shows the I-V curves of CO₂ electrolysis on the cell using Ni-Fe based oxide composites (BLC64/LSGM/Ni-Fe-based cermet) as the cathodes at temperatures higher than 973 K. It was found that mixing a small amount of mixed conductor with Ni-Fe is highly effective for further increasing the current for CO₂ electrolysis. Particularly, among the examined Ni-Fe cermet, Ni-Fe-La_{0.6}Sr_{0.4}Fe_{0.9}Mn_{0.1}O₃ (LSFM) exhibited the highest activity for CO₂ conversion and cathodic current density of 1.42 Acm⁻² was obtained at 1.6 V and 1073 K, which is the highest value for the studied cells using LSGM electrolyte and the reported value in the open literature. For the Ni-Fe-LSFM cermet cathode, the oxygen vacancy in LSFM could be contributed to dissociation of oxygen from CO₂ because of the reduced state of La(Sr)Fe(Mn)O_{3-δ} under electrolysis. In any case, these results suggest that the addition of mixed conductor to Ni-Fe is an effective strategy for increasing cell performance for CO₂ electrolysis.

Figure 9 shows the cathodic overpotential for the cell using the Ni-Fe-based cermet cathodes during CO₂ electrolysis at 1073 K. Clearly, Ni-Fe-LSFM exhibited a much lower overpotential than Ni-Fe and the lowest overpotential of all of the examined Ni-Fe-based cermet cathodes for CO₂ electrolysis. Thus, LSFM is a highly effective additive for decreasing the cathodic overpotential of Ni-Fe. The resistance for some of the intermediate reactions on the cathode

Fig. 8. I-V curves of CO₂ electrolysis on the cell using Ni-Fe based oxide composites.

Fig. 9. Cathodic overpotential for the cell using the Ni-Fe-based cermet cathodes during CO₂ electrolysis at 1073 K.

and at the interface between the cathode and the electrolyte during CO₂ electrolysis was significantly reduced in the Ni-Fe-LSFM cermet. Cathodic performance was studied in further detail with impedance measurement.

For identifying the reason of the decreased cathodic overpotential in Ni-Fe-LSFM cermet, impedance measurements were performed. **Figure 10** shows the complex impedance plots for the cells using Ni-Fe-LSFM and Ni-Fe cathodes under open circuit conditions in electrolysis mode at 1073 K. On the basis of reports in the literature,^{18,47)} the observed impedance dispersion at the low frequency range (1–10 Hz) could be assigned to the chemical surface adsorption/desorption equilibration and/or surface diffusion processes for CO₂ reduction. Both the cathodic ohmic (the intercept of the impedance arc with the real axis in the high frequency regime) and polarization resistances (from the low frequency regime) were reduced by mixing the oxide ion conductor (LSFM) with Ni-Fe in the cell, which could be assigned to the formation of much smaller Ni-Fe particles, defect chem-

Fig. 10. Complex impedance plots for the cells using Ni-Fe-LSFM and Ni-Fe cathodes under open circuit conditions in electrolysis mode at 1073 K.

Fig. 11. I-V curves for CO₂ electrolysis at 973–1173 K using a cell with a Ni-Fe-LSFM cathode in electrolysis mode.

istry of LSMF at low P_{O_2} and high temperature, and better contact with the LSGM electrolyte in the Ni-Fe-LSFM cathode during the electrolysis reaction. On the other hand, cathodic overpotential, in particular, diffusion resistance appeared at lower frequency in impedance plots, became smaller by mixing with LSMF. Therefore, introduction of mixed conductor like LSMF is highly effective for decreasing the diffusion resistance.

Figure 11 shows I-V curves for CO₂ electrolysis at 973–1173 K using a cell with a Ni-Fe-LSFM cathode in electrolysis mode. At higher temperatures, higher current was achieved at the same potential because of the improved kinetics and cathodic activity. The current density at 1.6 V significantly increased with operating temperature, reaching a value of 2.07 A/cm² at 1073 K, which is the highest current density we have observed and higher than that in Fig. 4. Furthermore, at 973 K, the current density was 0.85 A/cm², which is also a remarkable value for CO₂ electrolysis at intermediate temperatures for a cell with 0.3 mm electrolyte.

Therefore, the cell based on LSGM electrolyte and the Ni-Fe-LSFM cathode exhibited much higher catalytic activity for CO₂ electrolysis at elevated temperatures (973–1173 K). As a result, it was found that Ni-Fe-LSFM composite cathode shows high activity to CO₂ electrolysis and LSGM shows the pure oxide ion conductivity under electrolysis condition. Therefore, CO yield well obeyed the Faraday's law suggesting that transport number of LSGM is always unity under CO₂ electrolysis condition.

4. Conclusions

Electrochemical reduction of CO₂ to CO at intermediate temperature (973–1173 K) was studied with LSGM used for the electrolyte. Compared with pure Ni and other Ni based metallic cathodes, it was found that Ni-Fe cathode shows a superior performance for CO₂ electrolysis. This can be assigned to Fe suppress Ni particle growth, thus retaining smaller metal particles. A cell consisting of BLC64/LSGM9182/NiFe91 exhibited the highest CO₂ electrolysis activity (e.g. a current density of 1.84 A/cm² at 1.6 V and 1073 K) of all metal cathodes investigated in this study, and CO₂ electrolysis current can be further increased by mixing with LSMF for composite cathode. Electrolysis current of CO₂ on the optimized cell was achieved a value of 2.07 A/cm² at 1173 K. As a result, this study revealed that Ni-Fe-LSFM is highly interesting as a new cathode material for CO₂ electrolysis on LSGM-based electrolyte.

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