Steam Electrolysis Using LaGaO$_3$ Based Perovskite Electrolyte for Recovery of Unused Heat Energy

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Application of LaGaO$_3$ based electrolyte for steam electrolysis was studied for the useful utilization of unused heat energy from steelmaking process. It was found that the $H_2$ formation rate almost obeys the Faraday's law suggesting unity of oxide ion transport number in LaGaO$_3$ perovskite under an electrolysis condition up to 2.0 V applied potential. Among the examined cathode catalyst, nickel shows the smallest cathodic overpotential and the addition of Fe to Ni is highly effective for increasing the $H_2$ formation rate in the steam electrolysis at 873 K. The highest $H_2$ formation rate is obtained at the composition of Ni : Fe = 9 : 1. Short stack of the steam electrolysis cell consisting of 25 cells in series connection was also studied and the formation rate of $H_2$ was achieved as large as 70 L/min at 1.8 V applied potential. Heat balance was calculated based on the developed stack level. It became clear that the heat source of 223 K level is enough for sustaining cell temperature because of large Joule heat.

KEY WORDS: solid oxide electrolyzer; LaGaO$_3$ perovskite; energy balance.

1. Introduction

Fuel cells directly convert a chemical energy of fuel to electricity by the electrochemical oxidation. Because there is no mechanical conversion of energy, the efficiency of fuel cell is not limited by the Carnot efficiency and can be achieved much higher value than that of current internal combustion engines. On the other hand, opposite operation of fuel cell becomes an electrolyzer. In particular, steam electrolyzer is attracting much interest recently as a highly efficient electrolyzer for production of $H_2$ and is called a solid oxide electrolysis cell (SOEC). Steam electrolysis is principally endothermic reaction and so required electricity for electrolysis can be much decreased by using thermal energy (TDS). Therefore, the steam electrolyzer is an important system for converting heat energy to chemical energy and useful method to storage heat energy as hydrogen; however, comparing with solid oxide fuel cell (SOFC), number of study on steam electrolysis is limited up to now. When unused heat energy from various process is used for heat source, SOEC is a new method to useful utilization of unused heat energy at present. Up to now, $Y_2O_3$ stabilized $ZrO_2$ (YSZ) is the most popular used electrolyte for both SOFC and SOEC at high temperature. Chemical stability and also mechanical strength of YSZ are reasonably high for the electrolyte of SOFC and SOEC. However, because of the insufficient oxide ion conductivity in YSZ, the formation rate of $H_2$ in SOEC is not high at intermediate temperature. Because of the operating temperature higher than 1 073 K, application of SOEC is considered to a high temperature process like a high temperature nuclear reactor. However, when the operating temperature could decrease down to 873 K, many heat sources from industrial process such as steelmaking processes can be used for SOEC and in this point, SOEC is highly interesting as an energy recovery process for unused heat energy. In addition, formed oxygen is not always used efficiently in the conventional electrolyzer; however, steam electrolyzer operates always with the heat sources, namely, combustor. Therefore, if the formed oxygen is used for enriching oxygen content in air and fed to a combustor, then the combustion efficiency could be much improved resulting in reducing the fuel amount. In particular, since steelmaking industry pay large cost and energy for production of oxygen, development of the intermediate temperature steam electrolyzer is suitable for heat recovery system for steelmaking industry. In order to achieve the high $H_2$ formation rate at intermediate temperature, cathode catalyst and electrolyte with high ion conductivity is essentially requested. At present, Ni or Ni-YSZ cermet is generally used for SOEC, however, activity of Ni is not high for intermediate temperature SOEC. In this study, we investigated the Ni–Fe bimetallic electrode for cathode of SOEC using LaGaO$_3$ based oxide electrolyte, which is considered as the most promising oxide ion conductor for the intermediate temperature SOFC. 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 much improved by addition of Fe to Ni. The improved power density is assigned to the decreased anodic overpotential. Therefore, in this study, steam electrolyzing performance of the cell using LaGaO$_3$ electrolyte, which is one of the most
promising oxide ion conducting electrolyte was mainly studied and we found that high 
H₂ formation rate was achieved on SOEC using LaGaO₃ electrolyte at interme-
tiate temperature. Cell stack using 25 cells was successfully demonstrated. Furthermore, energy source for SOEC is also considered based on the energy balance of the single cell performance.

2. Experimental

Ni–Fe bimetallic cathode was prepared by reduction of oxide precursor and the oxide precursor of NiO–Fe₃O₄ mixed oxide was prepared by the conventional impregna-
tion method. Firstly Fe(NO₃)₂·H₂O was dissolved into de-ionized water and then NiO powder was added into the solution. After drying the suspension under stirring, it was precalcined in a ventilated furnace at 673 K for 4 h. The obtained powder was calcined again in a muffle furnace at 1 073 K for 4 h in air. Electrolyte of LaₓSr₀.₁Ga₀.₈Mg₀.₂O₃ (LSGM) was prepared by using a conventional solid state reaction method. The precursors of the electrolyte were La₂O₃ (99.99% pure, Kishida), SrCO₃ (99.5%, Wako), MgO (99.5%, Wako), and Ga₂O₃ (99.99%, Kishida). Pow-
ders of the precursors in stoichiometric ratio were mixed using Al₂O₃ mortar and pestle. Thus obtained powder mixture was precalcined at 1 273 K for 4 h and then it was iso-
statically pressed into a disk at 274.6 MPa for 30 min (φ=2.0 cm). The disk was then sintered at 1 753 K for 6 h in air and the sintered disks were polished to a 0.5 mm thickness before measurement. In case of stack, LSGM disk with 50 mm was prepared by using tape casting method. LSGM slurry was prepared by using ethanol for solvent and after drying a tape casted slurry, calcination of the dried slurry was performed at 1 773 K for 3 h.

NiO–Fe₂O₄ powder and Ba₀.₆La₀.₄CoO₃ (denoted as BLC), which was also prepared by a solid state reaction method, were painted on each face of the obtained LSGM disk with n-butyric acetate solvent for anode and cathode, respectively, at 5 mm diameter. The prepared single cell was calcined at 1 273 K for 0.5 h before measurement of the electrolysis property. Platinum electrode was used for a refer-
ence electrode and put on the cathode side. Pt mesh was covered on the surface of anode and cathode, respectively, as current collector. Pt lead wire was used to connect the electrodes to electrochemical equipments. Before measure-
ment, Ni–Fe cathode was reduced by feeding H₂ at 1 273 K, 1 h. Steam diluted with N₂ (steam : N₂ = 1 : 3) was fed to the cathode side and air was fed to the anode side as a sweep gas and the total flow rate was always set to 80 mL/min for both sides.

Steam electrolysis property of the cell was measured by a four-probe method. The current across the cell was con-
trolled by using a galvanostat (Hokuto Denko, HA-301) and the terminal voltage was measured using a digital multimeter (Advantest R6451A). Formation rate of H₂ and O₂ was analyzed with gas chromatographs with thermal con-
ductive detector (TCD).

3. Results and Discussions

3.1. Steam Electrolysis Performance of the Cell Using LaGaO₃ Based Electrolyte

In the previous study, we optimized the anode and cath-
ode for steam electrolysis cell using LaGaO₃ based oxide. Among the examined anode and cathode materials, Ni–Fe (9 : 1) and Ba₀.₆La₀.₄CoO₃ (BLC) show the smallest overpoten-
tial. Figure 1 shows the comparison of H₂ and O₂ formation rate on the cell using LSGM electrolyte and the optimized electrode at 873 K and that using YSZ electrolyte with Pt, the most common electrolyte, at 1 273 K. Evi-\ndently, on both cells, the observed H₂ and O₂ formation rate well obeys the Faraday’s law. Comparing the formation rate of H₂ on the cell using YSZ electrolyte, that of LSGM cell shows much larger H₂ formation rate in spite of 400 K lower operating temperature. This suggests that the opti-

mized LSGM cell is highly effective for producing hydro-
gen by the steam electrolysis at intermediate temperature. Figure 2 shows the I–V curves of the cell at 1 073 and 873 K. Evidently, with increasing operating temperature, current density at the same potential increased drastically and at 1.75 V, the current density was achieved a value as high as 800 mA/cm².

For the purpose of increasing H₂ formation rate, increase in cell size was also studied by using tape casting method for preparation of LaGaO₃ electrolyte. Figure 3(a) shows photographs of the prepared LSGM disk with 0.25 mm

![Fig. 1. Comparison of H₂ and O₂ formation rate on the cell using L₉/Ga₉/SrGa₀.₈Mg₀.₂O₃ (LSGM) electrolyte with Ni–Fe cathode and Ba₀.₆La₀.₄CoO₃ (BLC) anode at 873 K and that using Zr₀.₈Y₀.₂O₂ (YSZ) electrolyte with Pt elec-

trode for both cathode and anode.](image1)

![Fig. 2. I–V curves of the cell using LaGaO₃ based oxide electrolyte at 1 073 and 873 K. Ni–Fe and Ba₀.₆La₀.₄CoO₃ were used for cathode and anode, respectively.](image2)
thickness. The effective electrode area was 12.56 cm². The electrode was coated with a screen printing method followed by calcination at 1273 K for 1 h. Figure 3(b) shows XRD pattern of the LSGM disks (50 mm in diameter) made by tape casting method after sintering at 1773 K for 3 h. Although small peaks assigned to a secondary phase were observed, all strong diffraction peaks were assigned to those from LaGaO₃ based oxide. Therefore, La₀.₉Sr₀.₁Ga₀.₈Mg₀.₂O₃ (LSGM) based oxide disk with 50 mm in diameter and 0.25 mm in thickness was successfully prepared by tape casting method.

Figure 4 shows the I–V curves for steam electrolysis on the cell with 50 mm diameter at 1073 and 873 K. Comparing the I–V curves shown in Fig. 2, current density of the larger cell at 1073 K is almost the same and the current density at 1.7 V was almost 800 mA/cm². However, at 873 K, current density becomes much smaller than that of 20 mm size cell, i.e., at 1.8 V, current density of 20 mm size cell is ca. 380 mA/cm², however, it decreased to a value of ca. 180 mA/cm², that is almost half. At present, the detail reason for decrease current density at 873 K is not clear, however, partial pressure for steam was much higher on the 50 mm size cell (30% for 20 mm diameter cell and 70% for 50 mm diameter cell). Degradation of the cell may occur at higher steam partial pressure resulting in the small current density at 873 K. The detail reason for small current density at 873 K is now under investigated and the results will be reported in future. Since the reasonably high H₂ formation rate was achieved at 1073 K, stacking the cells was performed by using the cell with 50 mm diameter.

**Figure 5** shows the scheme of the stack structure adopted in this study. In case of steam electrolysis, gas sealing is the most difficult but important issues. We used silver paste for fixing the cell onto the metal plate so-called cell holder and the compressed design was used for the gas sealing of the cell. Height of the one cell unit is ca. 3 mm and the total height of the cell stack was around 80 mm, which is consisted of 25 cells in series connection. **Figure 6** shows the photographs of the cell stack developed in this study. The diameter and thickness of the stack are ca. 80 and 84 mm, respectively and each cell can be monitored independently by a digital multimeter. The stack has internal manifold and steam diluted with N₂ was fed one side of the cell with stainless tube (6 mm in diameter) and the formed hydrogen was exhausted from another end of the cell with stainless tube with 12 mm in diameter. On the other hand, because of the reliability of the gas seal, we did not seal oxygen side and so the formed oxygen was exhausted directly from the cell with a narrow hole.

**Figure 7** shows the H₂ formation rate at 1073 and 873 K in the single cell unit. In this figure, theoretical formation rate which is estimated by Faraday’s law, was shown as a dashed line. It is seen that the formation rate of hydrogen at
1073 K is corresponded with that of Farady’s law, however, slightly smaller at 873 K. Therefore, gas sealing of the unit cell in the stack is reasonably tight and so gas sealing of the compressed structure seems to be acceptable in spite of the simple structure. It is also noted that the increase in operating temperature is effective for increasing \( \text{H}_2 \) formation rate. This also suggests that IR loss assigned to the electrolyte resistance dominated the internal resistance of the cell. Therefore, increase in \( \text{H}_2 \) formation rate could be further improved by using thin film of LaGaO\(_3\) based electrolyte. This will be reported in future.

Since the formation rate of \( \text{H}_2 \) is slightly smaller than that of the theoretical value at 873 K, steam electrolysis performance was measured with 25 cell stack at 1073 K. **Figure 8** shows the \( I-V \) curves of the stack consisting of 25 cells. \( I-V \) curves for 25 cell stack is very close to that of the single cell one multiplied with 25 and the estimated formed hydrogen was also well agreed with that of Faraday’s law suggesting the small gas leakage. At 39 V, the estimated formation rate of hydrogen was ca. 70 L/min. Therefore, the stack studied in this study was well functioned and it can generate reasonable amount of hydrogen. It is also noted that the theoretical potential for water electrolysis is 30.2 V and so it is seen that the production of hydrogen is observed at the potential lower than the theoretical one for water electrolysis. This is typical advantage of steam electrolysis as discussed above.

**Figure 9** shows the degradation of electrolysis performance of 25 cell stack under constant current condition of 1.5 A at 1073 K. Although the terminal potential was gradually increased with period, however, it is seen that the stable potential was observed over 300 h examined. Therefore, it can be said that the stability of LaGaO\(_3\) is reasonably high under steam electrolysis condition and the stack structure, namely, seal less one, is also worked for the examined period.

### 3.2 Energy Balance of the Cell Using LaGaO\(_3\)

Energy balance for the SOEC system was calculated based on the single cell performance. Steam electrolysis is principally endothermic reaction, however, because of the internal resistance, Joule’s heat was generated with increasing the current density, namely, increasing hydrogen formation rate, and so the total reaction will result in the exothermic one. Therefore, in similar manner with SOFC, SOEC cell is also thermally self-stood at high current density. Therefore, in spite of low temperature steam used, steam electrolysis can be self-stood thermally. **Figure 10** shows the energy balance for the SOEC cell using LaGaO\(_3\) based oxide electrolyte. The internal resistance of the cell was estimated to be 1.1 \( \Omega \) cm\(^2\) from slope of \( I-V \) curves as shown in Fig. 4 and at 1.8 V, the amount of formed \( \text{H}_2 \) was 280.0 mmol/cm\(^2\) min (0.9 A/cm\(^2\)). The electrolysis efficiency can be defined as follows.

\[
\eta = \frac{(\Delta H \text{ for } \text{H}_2 \text{ oxidation at } 298 \text{ K})}{(\text{electricity for steam electrolysis})}
\]
The estimated electrolysis efficiency at 1.8 V applied potential for the developed cell was 82.3% LHV and the estimated Joule heat under this condition is $\dot{F}R = 0.89 \text{ J/cm}^2\text{s}$. It is also noted that current efficiency of electrolysis ($=\text{H}_2$ formation rate/(2×current×Faraday’s constant)) is ca. 100% for the present cell. Therefore, steam electrolysis was performed under exothermic condition for producing hydrogen as the compact hydrogen generator. The heat energy under steam electrolysis can be used for heating steam to operating temperature of the cells and also for keeping the temperature of the cells at operating one. For example, heat energy requested for heating steam from 423 (which is widely obtained from the current industrial process) to 1073 K is estimated to be 0.293 J/cm² s by using the steam feeding rate (3.81 mmol/cm² min) under the present condition and specific heat value of steam, $C_p = 35.5 \text{ J/K mol}$. Considering the conversion of steam of the present cell at 1.8 V is ca. 37%, further smaller feeding rate of steam will be sufficient and so the requested energy for heating steam will further decrease. Comparing the Joule heat and energy for heating steam to operating temperature, the present cell can be sustained thermally even though the steam at 423 K level is used for the heat source of SOEC. Furthermore, temperature of the formed hydrogen and oxygen from the steam electrolysis reactor is 1073 K, which can be also recovered and used for heating of steam. Therefore, heat energy is still excess and so low quality heat like 423 K level could be used for the heat source of steam electrolyzer. Consequently, this study reveals that the steam electrolysis process using LaGaO₃ for electrolyte is highly attractive as a new and reliable technology for converting unused heat energy to chemical one, i.e., hydrogen and oxygen.

4. Conclusion

Electrolysis performance of the cell using LaGaO₃ based oxide electrolyte was studied and it is seen that both $\text{H}_2$ and $\text{O}_2$ formation rate almost obey the theoretical value estimated by Faraday’s law and the current density up to 1.8 V. Therefore, the chemical stability of LaGaO₃ based oxide is acceptably high under a steam electrolysis condition. On the other hand, IR loss and cathodic overpotential dominated the internal resistance of the cell and so it is found that the addition of Fe to Ni cathode is effective for improving the electrolysis performance by decreasing the IR loss and the cathodic overpotential. Calculation on energy balance of the cell based on the present cell performance suggests that low quality heat, which is not effectively used at present, can be used for the heat source of the steam generation, and SOEC is highly interesting new technology for converting heat energy to chemical energy and so new method as the heat recovery system.

REFERENCES