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Application of LaGaO$_3$ based electrolyte for steam electrolysis at intermediate temperature was studied for the generation of hydrogen and oxygen by using the unused heat energy from steelmaking process. It was found that H$_2$ formation rate was much improved by combination of oxygen ion conducting oxide with NiFe (9:1) bimetallic alloy. In particular, combination with La$_{0.6}$Sr$_{0.4}$Fe$_{0.9}$Mn$_{0.1}$O$_3$ (LSFM) or Ce$_{0.8}$Sm$_{0.2}$O$_2$ (SDC) is highly effective for increasing current density. Impedance plots for cathode were consisted of two semicircles, which could be assigned to a diffusion and an activation overpotential in low and high frequency region, respectively. Comparing with NiFe, mixing with SDC is much effective for decreasing the diffusion overpotential. This might be assigned to increase in three phase boundary and porosity of cathode. Effects of steam partial pressure was further studied and because of slow diffusivity of water in porous cathode, increase in humidity pressure decreased H$_2$ formation rate. Humidity utilization of 56% was achieved by using 81 ml/min (29% P$_{H_2O}$) steam flow rate.

KEY WORDS: Solid Oxide Electrolyzer; LaGaO$_3$ perovskite; hydrogen; oxygen.

1. Introduction

Fuel cells directly convert a chemical energy of fuel to electricity by the electrochemical oxidation.1–3) On the other hand, opposite operation of fuel cell becomes an electrolyzer which generates hydrogen and oxygen. At present, steam electrolyzer is attracting much attentions because of a high efficiency for production of H$_2$ and O$_2$, and this cell is called a solid oxide electrolysis cell (SOEC).4–8) Steam electrolysis is principally endothermic reaction and so required electricity for electrolysis can be much decreased by using thermal energy (T$_\Delta$S).9,10) Therefore, the steam electrolyzer is an important system for converting heat energy to chemical energy10) and useful method to storage heat energy as hydrogen; however, comparing with SOFC, number of study on steam electrolysis is limited up to now.

On the other hand, large amount of heat energy was exhausted in steel making industry. When unused heat energy from these energy consumption industry is used for heat source, SOEC is a new method to recovery of unused heat energy at present and the recovered heat energy can be stored as a chemical energy of H$_2$ and O$_2$. Since large amount of O$_2$ is also produce in steelmaking industry and electric energy is used for O$_2$ production, simultaneously generated O$_2$ in steam electrolysis is also useful and so SOEC also contributes the energy saving of O$_2$ production. Up to now, Y$_2$O$_3$ stabilized ZrO$_2$ (YSZ) is the most popular used electrolyte for both SOFC and SOEC at high temperature.5) 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 like 1 073 K. Because of the operating temperature higher than 1 073 K, heat source of SOEC is considered to be a limiting high temperature process like a high temperature nuclear reactor.11) However, when the operating temperature could decrease down to 873 K, many heat sources, in particular, from steelmaking processes can be used for SOEC and in this point, SOEC is highly attractive as an energy recovery and H$_2$/O$_2$ generation process. 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 back to a combustor, then the combustion efficiency could be much improved resulting in reducing the fuel amount.12) In particular, since production of oxygen in steelmaking industry requires a significant cost and electricity, 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, active cathode catalyst and electrolyte with high ion conductivity is essentially requested. At present, Ni or Ni-YSZ cermet is generally used for cathode of SOEC.13,14) however, activity of Ni is not high for intermediate temperature SOEC. In our previous study, we reported that the Ni–Fe bimetallic electrode is

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active 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 this study, further increase in cathodic activity was investigated with combination of oxygen ion conducting oxide. Furthermore, reversibility of electrode reaction, namely, overpotential of cathode and anode in SOEC and SOFC respectively, was studied. On the other hand, up to now, effects of humidity partial pressure on electrolysis have not been reported in details, however, humidity utilization is also highly important for considering the efficiency of electrolyzer. In this study, effects of humidity partial pressure are also investigated.

2. Experimental

Ni–Fe bimetallic cathode was prepared by reduction of oxide precursor and the oxide precursor of NiO–Fe$_2$O$_3$ mixed oxide was prepared by the conventional impregnation method.\(^1\)\(^2\) Firstly Fe(NO$_3$)$_3$·H$_2$O was dissolved into deionized water and then NiO powder was added into the solution. After drying the suspension under stirring, it was precalcined in a vented furnace at 673 K for 4 h. The obtained powders was calcined again in a muffle furnace at 1 073 K for 4 h in air. The obtained NiFe oxide was mixed again with oxide ion conductor like stabilized ZrO$_2$, LaGaO$_3$, or doped CeO$_2$, or mixed conductor by ball milling mixer with composition of NiFeFe(9:1):oxide=9:1 at weight basis. Mixed conductor of La$_{0.6}$Sr$_{0.4}$Fe$_{0.9}$Mn$_{0.1}$O$_3$ was prepared by the conventional solid state reaction method.\(^3\)\(^4\) The precursors of the electrolyte were La$_2$O$_3$ (99.99% pure, Kishida), SrCO$_3$ (99.5%, Wako), MgO (99.5%, Wako), and Ga$_2$O$_3$ (99.99%, Kishida). Powders of the precursors in stoichiometric ratio were mixed using Al$_2$O$_3$ mortar and pestle. Thus obtained powder mixture was precalcined at 1 273 K for 6 h and then it was isostatically pressed into a disk at 274.6 MPa for 30 minutes ($\phi$=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.

NiO–Fe$_2$O$_3$ powder and Ba$_{0.6}$La$_{0.4}$CoO$_3$ (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-butric 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 reference 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 measurement, Ni–Fe cathode was reduced by feeding H$_2$ at 1 273 K, 1 h. Steam diluted with N$_2$ (Steam:N$_2$=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 controlled by using a galvanostat (Hokuto Denko, HA-301) and the terminal voltage was measured using a digital multimeter (Advantest R6451A). Formation rate of H$_2$ and O$_2$ was analyzed with gas chromatographs with thermal conductive detector (TCD). Effects of steam partial pressure was estimated at 1 073 K with the 50 mm $\phi$ cell using NiFe(9:1) and BLC cathode and anode respectively. Ar was used as carrier gas with flow rate of 203 ml/min and constant current of 6 A was applied.

3. Results and Discussions

3.1. Cathodic Activity of NiFe Base Cermet for Steam Electrolysis

In the previous study, we optimized the anode and cathode for steam electrolysis cell using LaGaO$_3$ based oxide. Among the examined anode and cathode materials, Ni–Fe (9:1) and Ba$_{0.6}$La$_{0.4}$CoO$_3$ (BLC) show the smallest overpotential. In this study, effects of oxygen conducting oxide on cathodic overpotential was further studied. In Fig. 1, I–V curves in SOEC and SOFC mode was shown on the cell using various NiFe base cermet electrode. Evidently, not only SOFC but also SOEC performance was strongly affected by oxide mixed with NiFe for both SOEC and SOFC. Among the examined oxide combined with NiFe, it was found that current density was decreased by mixing with BaCe$_{0.9}$Y$_{0.1}$O$_{3}$ (BCY) and Ce$_{0.6}$Mn$_{0.3}$Fe$_{0.1}$O$_{2}$ (CMF), but much increased by mixing with Ce$_{0.8}$Sm$_{0.2}$O$_{2}$ (SDC), La$_{0.8}$Sr$_{0.2}$Ga$_{0.8}$Mg$_{0.2}$O$_{3}$ (LSGM), or La$_{0.8}$Sr$_{0.2}$Fe$_{0.8}$Mn$_{0.2}$O$_{3}$ (LSFM). In particular, evidently, largest current density of 1.8 A/cm$^2$ was achieved at 1.6 V on NiFe/SDC cermet cathode. This current density is almost twice larger than that of single NiFe cathode. Therefore, mixing SDC or LSFM is highly effective for enlarging the current density in SOEC mode. On the other hand, in Fig. 1, opposite operation of electrolysis, namely, fuel cell mode is also shown. Here, it is noted that open circuit potential of SOFC is different from that of SOEC because H$_2$ with 3 vol% H$_2$O is used for fuel in SOFC. In similar manner with that of SOEC, current density of the cell is also strongly affected by using oxide mixed with NiFe for anode. The largest current density was achieved on NiFe–LSFM cermet anode and

![Fig. 1. I-V curves in SOEC and SOFC mode of the cell using various NiFe-oxygen conducting oxide at 1 073 K. SOEC is measured with 40%H$_2$O–1%H$_2$/air fed to cathode and SOFC is 97%H$_2$–3%H$_2$O for anode. Ba$_{0.6}$La$_{0.4}$CoO$_3$ is used for counter electrode and air is always used for counter electrode gas.](image-url)
the maximum power density is close to 0.7 W/cm² at 1 073 K. Therefore, considering high current density in SOEC and SOFC mode, NiFe-SDC or NiFe-LSFM shows the most superior performance of electrode in both reactions.

**Figure 2** shows the cathodic overpotential in SOEC as a function of current density at 1 073 K. The estimated cathodic overpotential increased in the following order, none>Zr0.92Y0.08O2 (YSZ)>BaCe0.9Y0.1O3 (BCY)>Ce0.6Mn0.3Fe0.1O2 (CMF)=Ce0.8Sm0.2O2 (SDC)>La0.6Sr0.4Fe0.9Mn0.1O3 (LSFM)>La0.9Sr0.1Ga0.8Mg0.2O3 (LSGM). Therefore, at higher current density, cathodic overpotential of NiFe-LSFM is the smallest and the estimated overpotential is smaller than 100 mV up to 1.4 A/cm². Therefore, NiFe-LSFM is suitable cathode for SOEC at high current density in high temperature range. However, when operating temperature became lower, current at 1.6 V on NiFe-LSFM drastically decreased and this may be related with the low electrical conductivity of LSFM at lower temperature. Therefore, at 873 K, cathodic overpotential of NiFe-SDC became the smallest among the examined NiFe base cermet.

**Figure 3** shows the anodic overpotential of NiFe cermet in SOFC mode as a function of current density at 1 073 K. NiFe bimetal anode principally exhibited a small anodic overpotential and so combination with oxygen conducting oxide generally increased the anodic overpotential. Evidently, anodic overpotential decreased when SDC was mixed with NiFe bimetal. Although the largest power density was achieved on NiFe-LSFM, anodic overpotential was not smaller than that of NiFe. Therefore, increased power density could be explained by decreased IR loss. Therefore, NiFe-SDC shows high activity to both SOEC and SOFC and suitable for cathode and anode, respectively.

In order to identify the decreased cathodic overpotential in SOEC mode by mixing with SDC and LSFM, impedance measurement was performed on NiFe, NiFe-SDC, and NiFe-LSFM under open circuit condition (**Fig. 4**). In case of NiFe bimetal, impedance plots were consisted of depressed two semicircles, which can be assigned to the activation and the diffusion overpotential. Detail discussion for assignment of impedance semicircle was reported in our previous study and also discussed later. Since the semicircle at lower frequency is large, large diffusion resistance was observed for NiFe, and this large diffusion resistance could be assigned to the lower diffusion rate of water in cathode pore. On the other hand, evidently, the large semicircle at lower frequency, which could be assigned to a diffusion resistance became smaller by mixing with oxide ion conductor. Therefore, decreased cathodic overpotential could be explained by extending reaction site into three dimensions, which is similar phenomena with cermet anode for SOFC. On the other hand, comparing with NiFe-SDC, impedance semicircle at
high frequency region was smaller when LSFM was mixed with NiFe. LSFM is reported as an active oxide anode for SOFC,\(^1\) LSFM may also contribute to steam electrolysis reaction resulting in the decreased activation overpotential. Although overpotential of NiFe-LSFM is much smaller than that of Ni-SDC in Fig. 1, resistances estimated from impedance semicircle in Fig. 4 are similar for both NiFe-SDC and NiFe-LSFM. This difference is explained by the different current density for measurement. As shown in Fig. 4, NiFe-LSFM shows small diffusion overpotential and so large positive effects by mixing with NiFe bimetal were observed for LSFM at high current density.

**Figure 5** shows the formation rate of H\(_2\) in steam electrolysis of the cell using various NiFe base cemet cathode. In this figure, H\(_2\) formation rate estimated with Faraday’s law were also shown as a dashed line. Evidently, H\(_2\) formation rate are almost obey the theoretical formation rate and so coulomb efficiency is almost 100% on all cells studied. Therefore, apparently, NiFe-SDC or NiFe-LSFM is highly active to steam electrolysis and the improved activity could be explained by extended active site. This is because large resistivity in cathode reaction of steam electrolysis was diffusion resistance. Details on diffusion overpotential in steam electrolysis are further studied in the following part of this study.

### 3.2. Effects of Steam Partial Pressure on Electrolysis

**Figure 6** shows I-V curves in steam electrolysis on NiFe, and NiFe-SDC at 873 K and different steam partial pressure. Current density increased with decreasing steam partial pressure. However, at both steam partial pressure, current density at the same potential is much smaller on NiFe-SDC than that of NiFe. **Figure 7** shows the H\(_2\) formation rate as a function of current density at 873 K. In similar manner with Fig. 4, H\(_2\) formation rate on all cells examined is well corresponded with the theoretical value at 873 K and so coulomb efficiency is almost 100%. Therefore, H\(_2\) formation rate is always larger on NiFe-SDC than that of single NiFe.

**Figure 8** shows comparison of impedance plots of NiFe cathode in SOEC and anode in SOFC. Obviously, impedance semicircles mainly consist of two semicircles; one is large semicircle observed at lower frequency, which could be assigned to a large diffusion resistance and the second one is small one at high frequency and assigned to the activation overpotential. In case of SOEC, large overpotential for cathode could be assigned to the large diffusion overpotential. Two diffusion processes are generally considered, i.e., one is gas diffusion process and the other is surface diffusion process of adsorbed or activated species to three phase boundary (TPB). In case of surface diffusion process, diffusion rate could be much improved with elevating temperature. However, effects of steam partial pressure on steam electrolysis performance were significantly observed at 673 K as shown in Fig. 7. Therefore, diffusion overpotential becomes more significant with increasing temperature. It is well known that gas diffusion rate in narrow channel becomes slower with increasing temperature. Furthermore, considering the large molecular size and weight of H\(_2\)O than those of H\(_2\), diffusion of water in narrow pores in cathode seems to reasonably explain a large overpotential and so cathodic overpotential of SOEC becomes much larger than that of anode in SOFC.

**Figure 9** shows impedance plots of NiFe cathode at 20 and 40 vol\% H\(_2\)O. In both H\(_2\)O partial pressures, impedance semicircles mainly consist of two semicircles. Evidently, at 40 vol\%, semicircle at lower frequency is much larger than that of 20 vol\% and this could suggest that lower current density is assigned to the increased diffusion resistance into cathode. Therefore, at lower steam partial pressure, larger H\(_2\) formation rate can be assigned to a smaller diffusion
Effects of steam feeding rate on the cell potential at current 6 A, 1073 K. Ar gas was used for balance gas. Flow rate in figure is steam feeding rate and Ar was used as carrier gas with 203 ml/min.

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overpotential. Therefore, from these results, higher steam partial pressure is preferable for system, but not suitable from electrolysis performance.

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Fig. 10 shows effects of steam feeding rate on the cell potential at current 6 A, which is corresponded with current density of 0.48 A/cm² and 45.6 ml/min H₂ formation rate. At higher steam partial pressure, cell potential was stable, however, with decreasing steam partial pressure, the cell potential increased and became unstable and stable current was observed at steam flow rate higher than 100 ml/min. This could be assigned to the insufficient steam amount and the cell can not be stably operated at lower steam partial pressure because of the limiting gas diffusion. For the examined cell structure, the lower limit of steam seems to be 81 ml/min which is corresponded to be ca. 0.29 atm of steam partial pressure and under this condition, steam electrolysis utilization (steam conversion into H₂ and O₂) is estimated to be 56%. Therefore, for the current cell design, steam seems not to be uniformly supplied over the cell and so slightly lower steam utilization may be assigned to an insufficient gas diffusion to three phase boundary (TPB). One reason for insufficient gas diffusion could be related with a large diffusion overpotential of cathode and so improvement of porosity of cathode and also cell structure seems to further improve steam utilization efficiency.

4. Conclusion

Electrolysis performance of the cell using LaGaO₃ based oxide electrolyte was studied and it is seen that both H₂ and O₂ formation rate almost obey the theoretical value estimated by Faraday’s law and the current density up to 1.8 V applied. On the other hand, IR loss and cathodic overpotential, in particular, concentration overpotential, dominated the internal resistance of the cell and so it is found that the steam utilization of ca. 70% is achieved at 1 073 K under 0.4 A/cm² constant current density. Further optimization of cathode porous structure and cell steam diffusion is highly requested for further improvement in steam electrolysis. This study reveals that steam electrolysis is highly interesting process to produce hydrogen and oxygen by using unused heat, in particular, for steel making industry.