The behavior of SOEC was investigated as compared with that of solid oxide fuel cell (SOFC) using small cells prepared on yttria stabilized zirconia (YSZ) planar discs. Ni-YSZ cermet negative electrode showed asymmetric behavior indicating the existence of diffusion limited process in the electrolysis direction, although the behavior was strongly dependent on the electrode preparation. The behavior of positive electrodes made by using perovskite type oxides was also investigated. When polarized anodically, the positive electrode showed degradation behavior which ended up with electrode delamination from electrolyte. The degradation rate was remarkably decreased by improving the initial polarization performance of the electrode or by using a mixed ceria intermediate layer between YSZ and electrode. Polarization measurements of SOEC were conducted at 1173 K, 1223 K and 1273 K with various water content in hydrogen simulating the atmosphere of various water electrolysis rate. The cell was shown to work at a high current density and at high water electrolysis rate without suffering from diffusion limiting current.

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1. Introduction

Concerning the global environmental crisis, Agency of Industrial Science and Technology, MITI has started world energy network program in 1994. The objective of the program is to establish world-wide clean energy network where hydrogen which is produced by natural energies in the countries blessed with those is transported to areas where it is consumed. One of the keys of the project of the countries engaged in R & D of SOFC for many years, we have also been engaged in R & D of SOFC for many years, we have already published some papers concerning SOEC. In the papers the characteristics of solid oxide electrolysis cell (SOEC), heat balance and efficiency calculations, possible problems in SOEC development, etc. are mentioned. Also we have reported the potential advantages that SOEC has over the conventional electrolysis.

In this work, we experimentally tried to understand the outline of the current–voltage characteristics of SOEC. Also we tried to clarify the development problems which come from the difference of operation between SOEC and SOFC. Finally we tried to solve the problems found in the course of our experiments.
system was used when SOEC and/or SOFC characteristics as a whole were under investigation. These measurements were carried out using Solartron 1260 impedance analyzer and 1286 potentiostat. Polarization curves were measured with controlled voltage method at a voltage sweep rate of 1 mV/s using the potentiostat.

3. Results and discussion
3.1 Behavior of SOEC and negative electrode

$I-V$ curves of the SOEC fabricated on 1-mm thickness YSZ are shown in Fig. 2 as a function of temperature along with the contribution of ohmic polarization at 1273 K. Ohmic polarization data were estimated from ac impedance data obtained at the open circuit voltage. In the figure, the curves of the other direction (fuel cell direction) are also shown for the purpose of comparison. The steeper slope of the curves means higher internal cell resistance so the lower the operation temperature, the higher the internal resistance. Since there are only little asymmetry observed in the positive electrode $i-V$ characteristics, the asymmetry of the curves appeared in Fig. 2 around current equals zero point results mostly from the characteristics of the negative electrode side, i.e., hydrogen evolution and water formation reactions.

In order to clarify the origin of the asymmetry, the $i-V$ characteristics of SOEC was again measured using negative electrode of poorer performance which was prepared by controlling Ni content in the cermet electrode. The obtained curve is shown in Fig. 3. The rather exaggerated asymmetry clearly shows that it originates from hydrogen generation reaction. The curve shows diffusion limited current behavior in the direction of electrolysis while there can be seen no such a behavior in the fuel cell direction. The limiting current was later shown to have positive dependence on water vapor content in the feed gas. If the limiting current is attributable to the gaseous diffusion of water vapor in the electrode with only one reaction route, there can hardly be found any explanation for the current increase which follows in the higher voltage region. The limiting current behavior seen in Fig. 3 is a suggestive evidence of parallelly existing reaction path for the hydrogen evolution reaction on the solid electrolyte. The reaction path at the lower overvoltage region is strongly dependent on diffusion which is substantially dependent on the electrode morphology.

Kawada et al. have also pointed out the large difference of cermet electrode performance with different preparations in the SOFC direction, but their interpretation does not seem to apply in our case. Also Mizusaki et al. have reported the asymmetry of $i-V$ curve with Ni pattern electrode on YSZ. However, their observation is a little different from ours where Ni/YSZ porous electrode was used. Obviously, micro-pores in the electrode play an important role in the reaction scheme. Except for the parallel reaction path, another possible explanation for the diffusion limited type current behavior and the following increase in current would be the enlargement of the reaction site which initiates by applying overvoltage beyond certain point. But we would not go into any further works for the moment because it is beyond our present objective.

Figure 4 shows the dependency of $i-V$ curve in SOEC and SOFC directions on the composition of negative electrode gaseous atmosphere. Each curves were obtained with different water vapor/hydrogen mixture ratio fed into the negative electrode compartment. Open circuit voltage increases as water content decreases, which is consistent

![Fig. 2. Current-voltage characteristics of the cell, O₂, LSM/YSZ/Ni-YSZ, H₂(60% H₂O), at various temperatures. a: 1273 K, b: 1223 K, c: 1173 K, d: ohmic contribution at 1273 K.](image2)

![Fig. 3. Current-voltage characteristics of the cell, O₂, LSM/YSZ/Ni-YSZ, H₂+H₂O, at 1273 K when the negative electrode has a poor performance. a: 20%H₂O, b: 40%H₂O, c: 60%H₂O.](image3)

![Fig. 4. Current-voltage characteristics of the cell, O₂, LSM/YSZ/Ni-YSZ, H₂+H₂O, at 1273 K with various steam content in hydrogen. a: 18%H₂O, b: 26%H₂O, c: 50%H₂O, d: 66%H₂O.](image4)
with the theoretically predicted value. In the case of the practical SOEC where almost pure water vapor is fed to the cell and the water is decomposed into hydrogen and oxygen, the water content in the negative electrode compartment is the index of water decomposition rate. Therefore, in the case of Fig. 4, the curves are summative at water decomposition rate of 82, 74, 50 and 34% (100% steam fed minus denoted remaining steam content).

One of the problems, we have pointed out in our previous report1), was possible appearance of diffusion limited current in the higher current region which arises in the consequence of lack of water supply to the electrode/electrolyte interface where the electrochemical reaction takes place. The reasons for our apprehensions are that SOEC is expected to work at the higher current density than SOFC and that the water molecules are less diffusive than any other gas species included in SOEC reaction. The figure shows that we can work on more than 1 A/cm² without any interference of concentration polarization even at the water decomposition rate of 82%. The negative electrode used in the study has the thickness of ca. 100 µm which is sufficiently enough to obtain the conductance required for the in-plane electronic conduction. The remaining work is to design and to make porous substrate which is pervious enough to permit the easy diffusion of water molecules if the SOEC is to be fabricated like the type we have adopted for SOFC application, i.e., substrate type tubular structure with water vapor fed inside the tube.5)

Recent paper pointed out the damage of YSZ at the negative electrode side caused by the reduction of SiO₂ existing in YSZ grain boundaries.6) The authors have reported that at the voltage of less than −1.4 V (vs. air, iR free) the degradation takes place. Using the data shown in Fig. 2 the cell voltage without iR drop at 1 A/cm² can be calculated to be less than 1.3 V at 1273 K. This value means the negative electrode potential of more positive than −1.25 V vs. air considering the positive electrode polarization as well. These experimental data are the evidence that we can safely avoid the YSZ intergranular degradation reported even at 1 A/cm² of SOEC operation at 1273 K.

Furthermore, Gibbs free energy of ZrO₂ formation at 1273 K (860 kJ/mol) gives us the decomposition voltage of higher than 2 V which is far higher than the optimum SOEC operation voltage (1.48 V) we have previously calculated1) considering the heat balance. Our recent data suggest that 2 A/cm² SOEC operation could well be achieved within the optimum operation voltage if we could make YSZ layer as thin as possible. Besides, in the optimum operation voltage, anodic and ohmic polarizations as well as cathodic polarization are involved. So the potential of the negative electrode can be kept within −1.4 V and hence the possible YSZ intergranular degradation can be avoided.

3.2 Positive electrode performance
When the cell was operated under constant current, considerable voltage increase with time was observed. This voltage shift was later found to be attributable to the degradation of positive electrode which ended up with its delamination from YSZ. On the other hand, when the cell was operated in the SOFC direction these phenomena were hardly observed. The degradation was hence concluded to be a unique phenomena for the electrolysis operation, i.e., anodic polarization.

3.2.1 Effect of initial polarization resistance
There are several direct causes which can possibly explain the destructive deterioration. However, it is quite clear that the primary factor is the anodically applied overvoltage for the reason mentioned above. Hence the simplest method to avoid the degradation is to suppress the anodic overvoltage as low as possible. Because SOEC is required to work at high current density as is mentioned in the previous chapter, we cannot decrease the current level in order to get lower overvoltage. Instead, by properly controlling the microstructure of the electrode, overvoltage can be made lower.

In Fig. 5 three shifts of overvoltage with time curves are shown. Each curve was obtained with the electrode whose polarization resistance is quite different from each other. The initial polarization resistances were determined by ac impedance spectroscopy before making any other measurement. As was expected the degradation rate is remarkably dependent on the electrode polarization resistance; the larger the polarization resistance the faster the degradation rate. Hence it was proved that we can improve the degradation behavior by making the initial polarization resistance lower, i.e., by improving the initial electrode performance. Nevertheless, even with the electrode having polarization resistance of 0.06 ohm·cm², the degradation was not completely suppressed. The improvement of the long term performance by mixing YSZ into the electrode reported in the literature6) also seems to come from this initial polarization resistance decreasing effect.

Thus it was concluded that the anodic overvoltage is the primary cause of the degradation of LSM anode. The anodic overvoltage brings about what causes the degradation directly.

When the positive electrode is polarized anodically, oxygen gas is produced at the electrode/electrolyte interface. The evolved oxygen molecules will then be released into the gaseous phase which exists in the electrode as pores. The oxygen molecules which were released into the closed pores existing in electrode/electrolyte interface may produce extremely high pressure because of the overvoltage; ca. 60 mV of overvoltage can make the pressure difference ten times as large at 1273 K. This pressure could make an enough reason for the degradation.

In order to check the hypothesis, Pt paste electrode was used for the oxygen electrode. If the big pressure was created by the overvoltage, the same phenomena would be to be observed with the Pt porous electrode. However, in the long term experiment using Pt anode, no such rapid degradation was observed even though the polarization resistance of the Pt anode was not so good. Although there may be large difference between the microstructure of Pt electrode and that of LSM electrode used in our study, the high pressure may not be concluded to be the direct cause of the delamination.

3.2.2 Performance of LC electrodes
Because of their highly catalytic activities, lanthanum cobalites are very attractive materials for oxygen electrode at high temperatures. Sr-doped and non-doped lanthanum
cobaltite electrodes (LSC and LC, respectively) were then examined as for the positive electrode of SOEC. The reason we chose these materials is as follows.

When LCs are used as cathode for SOFC, they are tend to be reduced accompanying the reduction of cobalt ion because the electrode is polarized cathodically. This is one of the reasons that LCs are not usually adopted for SOFC applications. However if LCs are used as anode of SOEC, there should be less tendency for their reduction.

Figure 6 shows the change of overvoltage with time at the anodically polarized conditions. With Sm-doped ceria in cathode, the electrode is polarized cathodically. This is one of the cases of the intermediate layer compositions in SOEC.

The intermediate layer was prepared at different temperature having Sm-doped ceria at 500mA/cm². The intermediate layer together with the electrode was prepared at different temperature as a: 1323K, b: 1423K, c: 1523K. The intermediate layer which is the mixture of doped or non-doped ceria and of LSM is located between YSZ and electrode layer. The idea is that since any stable compound between CeO₂ and LSM is known, better durability could be expected providing that the degradation is caused by the reaction product between LSM and YSZ under anodically polarized conditions. With Sm-doped ceria intermediate layer the best performance ever observed was almost the same and it is about twice as much in the case of the electrode using non-doped ceria intermediate layer.

Although the contact area between LSM and YSZ was drastically reduced by applying the intermediate layer, there still remains some contact area between them. We think the remaining contact area between LSM and YSZ causes these gradual degradation observed in Fig. 7. To confirm this idea we are planning to prepare the specimen having dense Sm-doped ceria layer which avoids the two materials from the direct contact. The layer is to be deposited by means of magnetron sputtering between LSM electrode and YSZ in order to avoid their direct contact.

Finally, the effect of electrode firing temperature was also examined. If the degradation is caused by the reaction product such as La₂Zr₂O₇, the higher firing temperature was expected to bring poorer performance. In Fig. 8 the voltage shift vs. time curves are shown using electrode prepared at different firing temperature having Sm-doped ceria intermediate layer. The one fired at 1523K showed remarkably poor performance as compared to the other two electrodes fired at lower temperatures. The initial polarization resistances of the three electrodes in this case were also almost identical. The result of the durability was consistent with our expectation while the result of the initial performance was not. It could be that the reaction product which was like an embryo at as-fired state makes it impossible to detect the difference in the initial behavior because of the experimental detection limitations and that the amount of initial reaction product makes the large difference in the long run. Microscopic analysis of the interface by Raman spectroscopy will be planned. As a conclusion, the firing temperature is concluded to be a key factor in the intermediate term electrode performance, although it only makes minor difference in the long term performance.

4. Summary

The behavior of solid oxide electrolysis cell was investigated as follows.

(1) The asymmetry of i-V performance indicated the existence of the parallel reaction path in the hydrogen evolution reaction.

(2) It is possible to operate the cell at high water decomposition rate (>82%) without a remarkable interference of concentration polarization maintaining the effective electronic conductance of the electrode.

(3) The polarization behavior revealed that the operation current density of 2 A/cm² can well be achieved within the optimum cell voltage of 1.48 V at 1273 K.

(4) The degradation rate of LSM anode was decreased by improving the initial polarization resistance.

(5) The degradation of LSC anode was accelerated by improving the initial polarization resistance.

Fig. 6. Overvoltage vs. time curves with Sr-doped and non-doped LCs at 1273 K in oxygen. Current density: 500 mA/cm², a: La₀.₆Sr₀.₄CoO₃, b: La₀.₈Sr₀.₂CoO₃, c: LaCoO₃.

Fig. 7. Shift of overvoltage vs. time with LSM electrode having different intermediate layer composition at 500 mA/cm². The components of the intermediate layer were a: non-doped ceria + LSM, b: Gd-doped ceria + LSM, c: Sm-doped ceria + LSM.
Sr.

(6) The use of ceria-based electrolyte as an intermediate layer is effective in decreasing the degradation rate of LSM anode. The complete inhibition of the degradation could be achieved by avoiding the direct contact between LSM and YSZ.

References
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