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Improvement of CAPCIUS Cell Using $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ as a Solid Electrolyte

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The CAPCIUS cell was improved using $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ as a solid electrolyte. When the operating temperature was 950 ℃ and the thickness of $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ ceramic was 0.5 mm, the maximum power density was 21 mW cm^{-2}, which was about 10 times value observed in the CAPCIUS cell using YSZ with the same thickness as a solid electrolyte. The mechanism for the improvement was studied by various electrochemical techniques.

Novel electrochemical devices, which generate the voltage in the uniform atmosphere using two electrodes with different catalytic activities toward H_2, have been reported in both gas sensor and fuel cell fields. In the former case, a Au | antimonic acid film | Pt cell exhibits a quick response to dilute H_2 in air and changes the EMF in proportion to the logarithm of H_2 concentration at room temperature.[1a,b,c] Also, in the latter case, a $La(Co_{0.5}Ru_{0.5})O_3$ | hydronium β"-alumina | $LaMnO_3$ cell draws the short-circuit current of some decades of μA in H_2 + O_2 mixture at room temperature.[2)] These devices are independent of the need for a reference volume or for a separated gas supply.

On the other hand, we have proposed another type of cell for Chemical And Power Cogeneration In the Uniform-gas System (CAPCIUS).[3)] Ni-YSZ cermet or Pt | YSZ | Au cell can supply the stable electric power in CH_4 + air mixture (CH_4 : O_2 mole ratio = 2 : 1) at 950 ℃. The working mechanism of this cell is based on the difference in catalytic activity for partial oxidation of CH_4 between Ni-YSZ cermet or Pt and Au: Ni or Pt promotes the partial oxidation of CH_4 to form H_2 and CO, while Au dose not catalyze its reaction. This situation leads to a large gas concentration in the cell, allowing to give rise to the EMF. However, the power density of this cell is still low compared with the conventional SOFC, because the cathodic overpotential of Au electrode is some hundreds of mV mA^{-2}. Hence, it is necessary to reduce the cathodic overpotential in order to gain the satisfactory power density. It is often said that Au metal is inactive to the adsorption, diffusion or ionization of oxygen molecule or atom. If so, the polarization characteristic of Au electrode will be improved using a proton conductor. In addition, when the solid electrolyte slightly contains the electronic conduction, the electrolyte/electrode/gas interface area increases, and this effect brings about the low polarization.[4)] $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ is well-known to fill these demands.[5a,b)] Therefore, from these viewpoints, $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ has been applied to a solid electrolyte for the CAPCIUS cell in this study.

The structure of the CAPCIUS cell was the same as that described in the previous paper (Fig. 1 (a)).[3)] Porous Pt and Au electrodes were baked on each face of $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ ceramic specimen at 950 ℃, and these electrode areas were 0.20 cm^2. CH_4 + air mixture (CH_4 : O_2 mole ratio = 2 : 1) was introduced into the cell at 950 ℃, and the flow rate was 210 ml min^{-1}. In order to measure various electrochemical properties, an alternative cell was constructed (Fig. 1 (b)). CH_4 + air mixtures with the same composition (CH_4 : O_2 mole ratio = 2 : 1) were supplied to two electrode compartments. Porous Pt was attached around the side face of the ceramic specimen as a reference electrode. The overpotential of each electrode was measured by a current interruption method. Also, the hole conduction of the ceramic specimen was estimated from the dependence of the conductivity upon the partial pressure of O_2 in the Au electrode compartment. In this case, the partial pressure of CH_4 in the Au electrode compartment was kept constant, and the composition of CH_4 + air mixture in the Pt electrode compartment was the same as that described above.

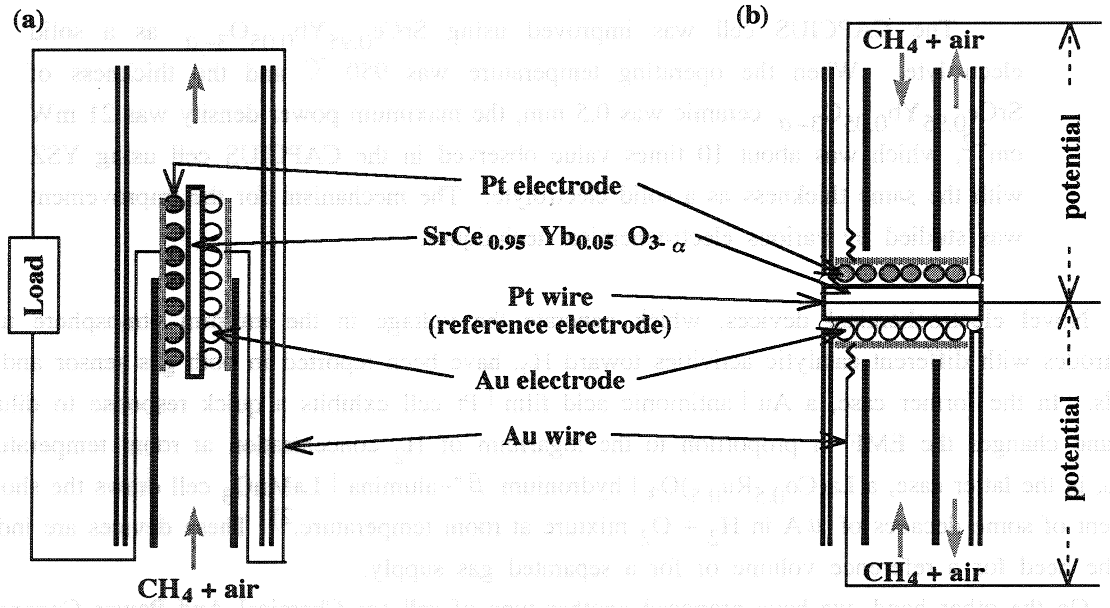

Fig. 1. The schematic illustrations of the test cells.

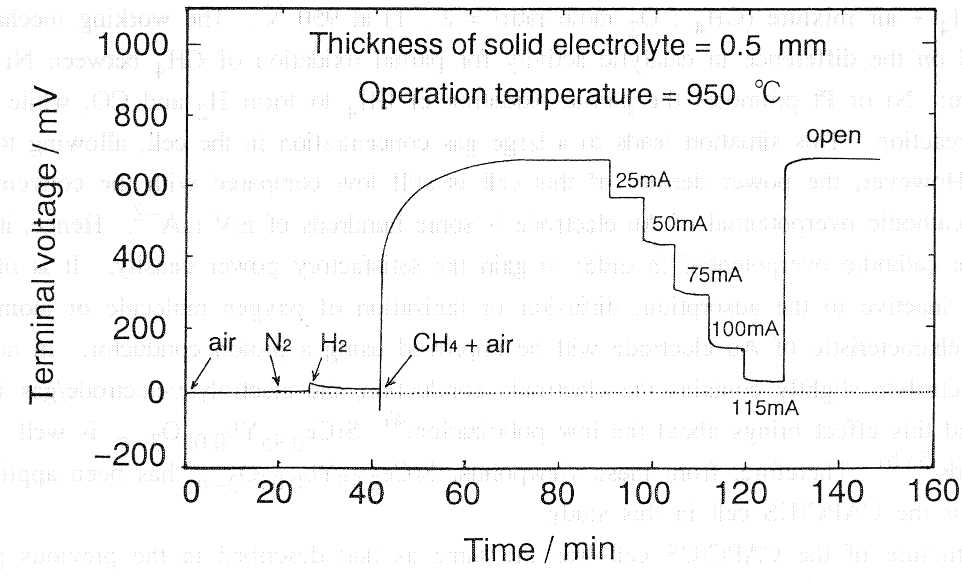

Fig. 2. The EMF response and discharge characteristic of the CAPCIUS cell using $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ as a solid electrolyte: the numbers in the figure indicate the current density (mA cm^{-2}).

When air, N_2 or H_2 was introduced into the CAPCIUS cell at 950 ℃, the cell voltage was almost zero as shown in Fig. 2. However, the CAPCIUS cell gave a stable EMF of 660 mV in the flow of CH_4 + air mixture. In this case, the potential of Au electrode was positive against Pt electrode. This direction suggests that the EMF is generated according to the above-mentioned mechanism. The current could be stably drawn from the CAPCIUS cell. The maximal power output was 21 mW cm^{-2} at 50 mA cm^{-2} current density and 420 mV terminal voltage. This value, which is comparable to that observed in the conventional H_2-air SOFC using $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ with the same thickness as a solid electrolyte, is about 10 times that observed in the CAPCIUS cell using YSZ (8 mol % Y_2O_3) as a solid electrolyte. Therefore, $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ is a promising material as a solid electrolyte for the CAPCIUS cell.

In order to understand the difference in the discharge characteristics between $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ and YSZ, the overpotential of each electrode was measured with the cell shown in Fig. 1 (b). These results are summarized in Fig. 3. The difference in cathodic overpotential between two electrolytes was extremely large compared with that in their anodic overpotential: 126 mV at 140 mA cm^{-2} in the case of $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$, and 113 mV at 2 mA cm^{-2} in the case of YSZ. Hence, it is found that the voltage drop during the discharge of the CAPCIUS cell using $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ mainly results from the ohmic resistance of the electrolyte, while using YSZ it is mainly indebted to the cathodic polarization of Au electrode.

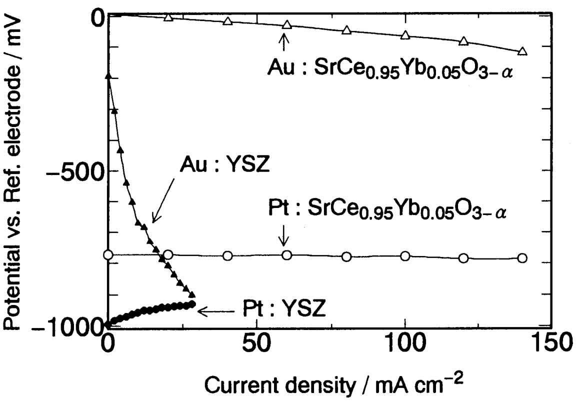

Fig. 3. The polarization characteristics of Pt and Au electrodes of two CACIUS cells at 950 ℃ (IR free).

Next, we have clarified which conduction, proton or hole conduction, is operating in determining the observed small polarization of Au electrode in the present cell. From the previous study, it has been found that $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ exhibits the oxide ionic conduction in dry air.[5a,b] So, if air and Ar are introduced into Au and Pt electrode compartments, respectively, and the direct current is sent to the cell, O_2 can be electrochemically pumped from the Au- to the Pt electrode compartment. The cathodic overpotential of Au electrode during such a pump is shown in Fig. 4. In this case, the transport number of oxide ion can be determined by comparing the evolution rate of O_2 from Pt electrode with theoretical value, and the ionic current density can be obtained by multiplying the total current

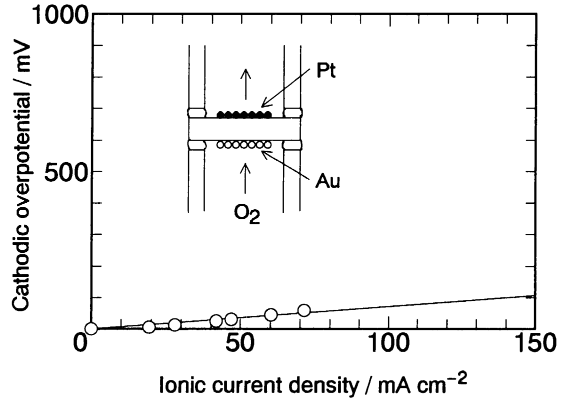

Fig. 4. The polarization characteristic of Au electrode on $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ during the O_2 pump at 950 ℃.

density by the transport number of oxide ion. Evidently, the cathodic overpotential during the O_2 pump was rather low, indicating that the polarization characteristic of Au electrode was independent of the protonic conduction.

The contribution of the hole conduction to the polarization can be thought as another possibility. So, we estimated whether $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ exhibited the hole conduction under the operating condition. The dependence of the conductivity upon the partial pressure of O_2 is shown in Fig. 5, where the closed symbol corresponds to the partial pressure of O_2 under the operating condition. Although the conductivity of YSZ was essentially constant irrespective of the partial pressure of O_2, the conductivity of $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ at high pressures increased with increasing partial pressure of O_2. This means that the conduction in the latter oxide is partly electronic due to the hole under the operating condition. It can therefore be assumed that such a hole conduction increases the area of three phases interface, resulting in the small polarization of Au electrode. This assumption is supported by the fact that the small cathodic polarization is observed when CeO_2-based electrolyte, which is partly electronic due to the electron, is used for the CAPCIUS cell.

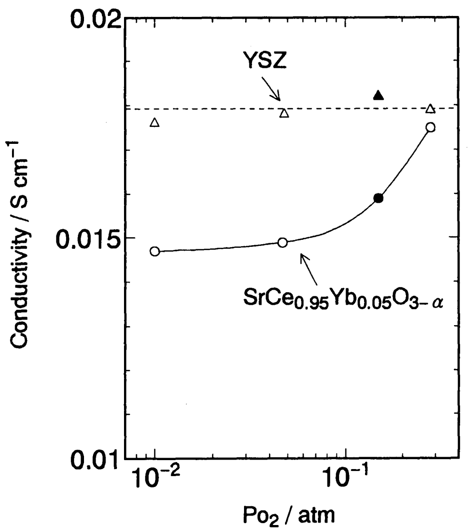

Fig. 5. The dependences of conductivities of two electrolytes on the partial pressure of O_2 at 950 ℃.

Since the power density of the CAPCIUS cell is approached to the practical level using $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ as a solid electrolyte, this system will be useful to make the structure of SOFC simple and to lower its cost. Furthermore, since synthesis gas (H_2 + CO) is produced with supplying the electric power, this system will be applied to a cogeneration for electric power and chemicals.

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