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Study on electrode of solid electrolyte hydrogen (isotope) sensor for application to liquid blankets

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The control of hydrogen isotopes is one of the key issues for liquid blankets. For this purpose, monitoring of hydrogen isotopes using on-line sensors is the essential technology. In the present study, the hydrogen sensor using solid electrolyte ceramics was developed for fusion blanket application. Because of very corrosive environment of liquid breeders, Pd membrane electrodes, which will be more protective of the ceramics relative to the conventional porous Pt electrodes, were fabricated and tested. The Pd membrane electrode was shown to perform well in gaseous environment.

Keywords: Blanket, Hydrogen senor, Solid electrolyte, Electrode, Palladium, Flibe, Flinak, Pb-17Li, Li

1. Introduction

Molten salt LiF-BeF$_2$ (Flibe), molten lithium (Li), and molten lead-lithium (Pb-17Li) are candidate blanket tritium breeding materials for fusion reactors. For the blankets with those liquid breeders, control of tritium is the key issue. For this purpose, on-line sensing of tritium in the high temperature melts is the essential technology.

The hydrogen partial pressures of the three melts are extremely different, with very high pressure for Flibe, medium for Li-Pb and very low for Li [1].

Proton conductive solid electrolyte is the functional ceramics that can allow hydrogen to permeate selectively. It is used as the hydrogen sensor for molten aluminum, molten copper and so on [2,3]. The hydrogen sensors need electrodes on the ceramic surfaces. Porous platinum (Pt) has been used as the electrode. Though Pt electrodes show good performance, they do not protect well the ceramics from the atmosphere because of their open structure.

Palladium (Pd) has high conductivity and hydrogen permeation function and thus a candidate for the protective electrode if flawless coating on the ceramics is possible. Pd porous electrodes have been examined in the previous studies [4, 5]. However, application of Pd to the membrane electrodes has not been examined yet. In this study, fabrication and characterization of Pd membrane on proton conductive ceramics are carried out and the applicability to liquid blankets is examined.

2. The principle of hydrogen sensor

The principle of the hydrogen sensor for gaseous medium is shown in Fig.1. Proton conductive electrolyte ceramics partitions the sensor into two compartments in which flow of gases with different partial pressure of hydrogen is made. In this case, the electrode with higher hydrogen partial pressure acts as anode. The reactions of the electrodes are given bellow;

Anode: $H_2 \rightarrow 2H^+ + 2e^-$ (1)

Cathode: $2H^+ + 2e^- \rightarrow H_2$ (2)

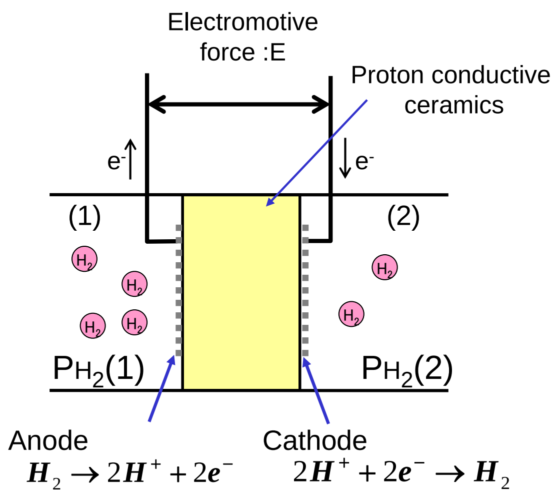

Fig.1 Principle of hydrogen sensor.

These reactions are induced by electromotive force (EMF) between the two electrodes. The EMF is given below according to the Nernst's equation

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$$E = \frac{RT}{2F} \ln \frac{PH_2(1)}{PH_2(2)} \quad (3)$$

where F is Faraday constant, R is a gas constant and T is absolute temperature. $PH_2(1)$ and $PH_2(2)$ are partial pressure of hydrogen in compartments (1) and (2), respectively.

3. Fabrication of sensors with Pd electrodes

The hydrogen sensor used cap-shaped $CaZr_{0.9}In_{0.1}O_{3-a}$ as proton conductive ceramics. The sensor's dimension was 3.8mm for the outer diameter, 2.5mm for the inner diameter, and 37mm for the length. The outer surface of the sensor cell was coated with Pd paste and was baked twice at 1673K to make membranous electrode. Inner sensor cell was coated with Pt paste and was baked at 1273K to make a porous electrode. The ceramic sensor was fixed to an Al_2O_3 tube by low melting glass seal.

For measuring EMF of the sensor, Pt wires were fixed to the outer and the inner electrodes, and a stainless tube was inserted to flow the reference gas into the inner electrode. The same structures of the probes having Pt porous electrode or Pd membrane electrode on the both side of the sensor cell were also made. The system of measuring EMF is shown in Fig. 2. Three probes, a thermocouple and tubes for gas inlet to and outlet from the Al_2O_3 protection tube, were inserted and fixed to the silicon stopper. The protection tube was set into the electric furnace and the temperature was kept constant during the flow of H_2-Ar mixed gas.

The EMF was measured at 873K, 773K and 673K with 1%H_2-Ar gas as the reference gas flowing in the inner electrode. At the outer electrode, H_2-Ar mixed gases with several H_2 levels flowed. The 34970A data acquisition switch unit by Agilent was used to measure EMF of the three probes.

4. Characterization of the sensors

4-1 Microstructures

The surface and section of the outer electrode were observed using SEM. The images are shown in Fig. 3. The surface of Pt electrode showed grains of 1 to 5μm and with high density of pores. The diameter of the pores was below 10μm. There were, however, areas where the pore density was locally low. The cross section of Pt electrode showed porous structure with the thickness of 5 to 10μm. There were pores penetrating the electrodes.

The surface of Pd electrode showed grains of 10 to 50μm. The surfaces were smooth and contained very low density of pores. The sections of Pd electrode showed membrane structure with the thickness of 10 to 20μm. The pores observed in the membrane did not penetrate throughout the electrode.

4-2 Performance in gaseous environments

The results of the measurement of EMF are shown in Fig. 4. The dashed lines are the theoretical EMF by Nernst's equation for each H_2-Ar mixed gas with the reference 1%H_2-Ar gas at 873K.

The EMF of all probes changed immediately to the value observing Nernst's equation when the mixture of the flowing H_2-Ar gas was changed in the Al_2O_3 protection tube. The EMF of the three probes agreed with the theoretical values of Nernst's equation. The change of the gases in the Al_2O_3 protection tube was carried out twice and the reproducibility was confirmed.

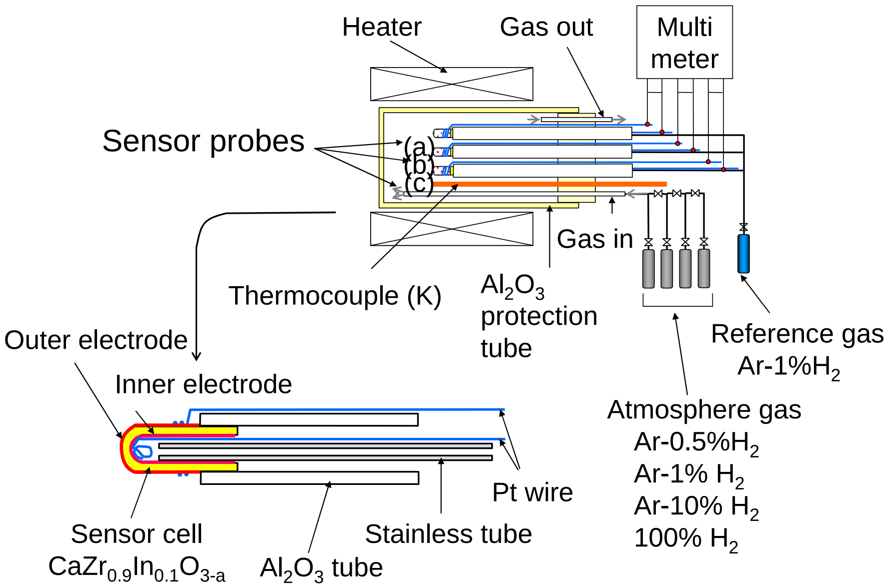

Fig. 2 System for measuring EMF and combination of outer electrode and inner electrode on sensor surface (a) Pt/Pt electrode, (b) Pd/Pt electrode, (c) Pd/Pd electrode

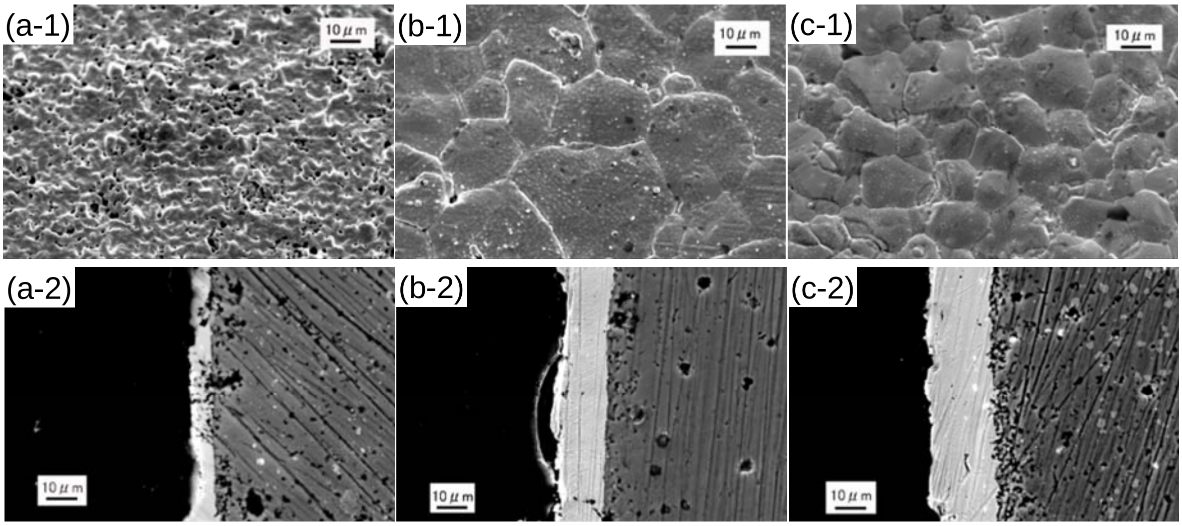

Fig. 3 The SEM images of the surface and the cross section of electrodes.

The measurement of EMF was also carried out at 673K and 773K. Fig. 5 shows the temperature dependence of the measured EMF for various gaseous environments. The probes using Pd electrode obeyed well the theory at all temperatures. The probe with Pt electrode, however, showed lower EMF than that of the theory at 673K.

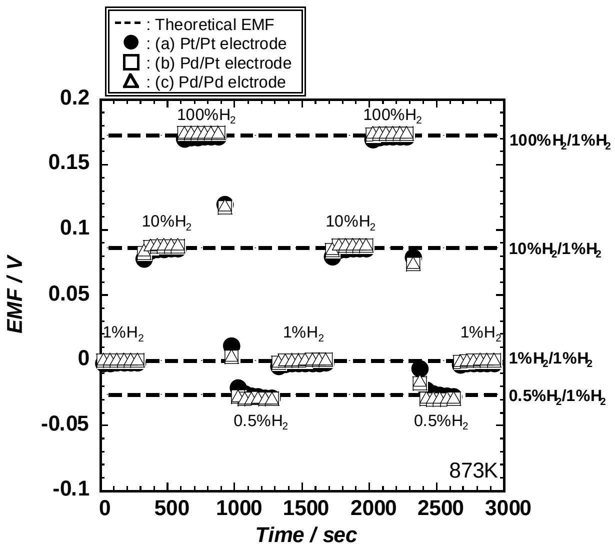

Fig. 4 The measurement of EMF in gaseous environments at 873K.

5. Discussion

In the case of porous Pt electrode, the environmental gas penetrates into the open pores and reaches the ceramics. The position where the surface of the ceramic cell contacts with Pt electrode and the atmospheric gas is called three-phase boundary [6]. The electrode reaction model at the three-phase boundary is schematically shown in Fig. 6(a).

The Pd electrode doesn’t have the open pores but has the membrane structure. In this case, the electrode reaction takes place at the interface of the electrode and the ceramic cell, which is called two-phase boundary [7]. The electrode reaction model at the two-phase boundary is schematically shown in Fig. 6(b).

Because no direct contact of the ceramics sensor cell with the environment is expected, the Pd membrane electrodes are thought to be more resistant to corrosion than the porous Pt electrodes.

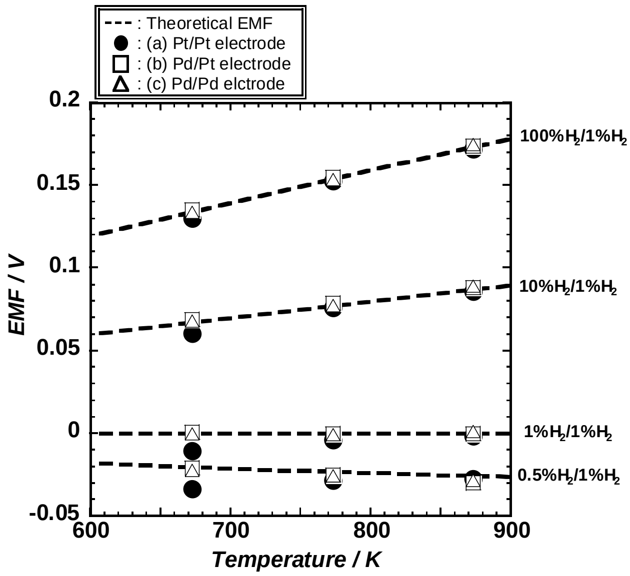

Fig. 5 The temperature dependence of EMF.

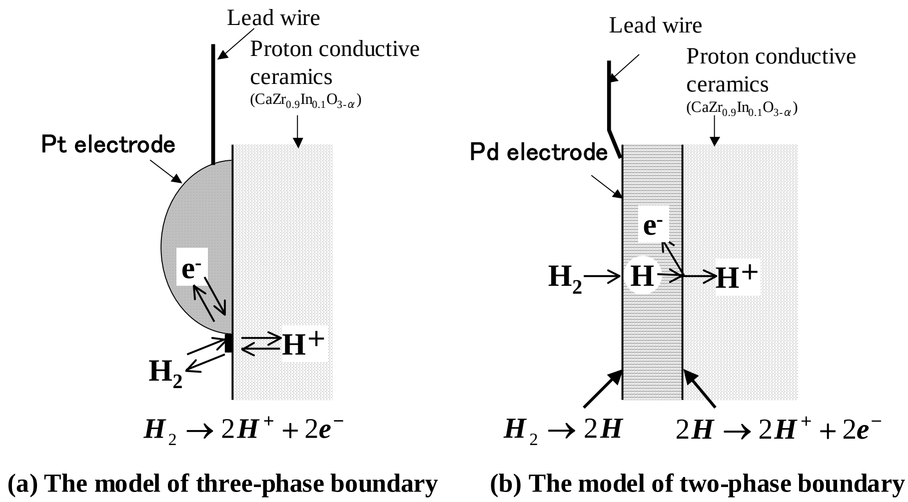

Fig.6 Electrode reaction model. (a) Three-phase boundary electrode, (b) Two-phase boundary electrode

6. Conclusion

The fabrication and the performance test of the Pd membrane electrodes for the hydrogen sensor for application to low oxygen or corrosive environments such as liquid breeders were carried out. The conclusions are as follows.

(1) The Pd membranes without open pores were fabricated successfully on the ceramics sensor cell.

(2) The sensor cells with the Pd membrane responded quickly to the change of hydrogen concentration of the flowing gas with high reproducibility.

(3) The EMF with the Pd electrodes was shown to be almost equal to that with the porous Pt electrode in the gaseous environment, indicating that the two-phase boundary of the Pd electrodes works similarly to the three-phase boundary of the Pt electrodes. Furthermore, since the EMF of the Pd electrode obeyed the Nernst's equation better than Pt electrode at lower temperature such as 673K, the sensor using Pd electrode may be used in lower temperature than Pt electrode as well as in the corrosive atmosphere.

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