§8. Study on Electrode of Solid Electrolyte Hydrogen (Isotope) Sensor for Application to Liquid Blankets

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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 these liquid breeders, control of tritium is the key issue.

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 and so on. 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. 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. 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 and inner electrodes were used Pd or Pt. Pd paste was coated on the surface of ceramics and baked twice at 1673K to make membranous electrode. Pt paste was coated and baked at 1273K to make porous electrode. The combinations of outer and inner electrode are Pt/Pt, Pd/Pt and Pd/Pd. The structure of sensor probe is shown in Fig. 1.

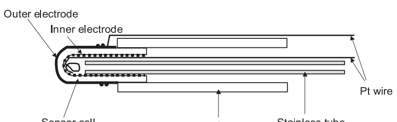

Fig. 1 The structure of sensor probe

Three probes, a thermocouple were inserted into the Al_2O_3 protection tube and set into the electric furnace and the temperature was kept constant during the flow of H_2-Ar mixed gas.

The sensor 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.

3-1 Microstructures

The surface and cross section of the outer electrode were observed using SEM. The images are shown in Fig. 2. The surface of Pt electrode showed high density of pores(Fig.2(a)). The surfaces of Pd were smooth and contained very low density of pores(Fig.2(b)).

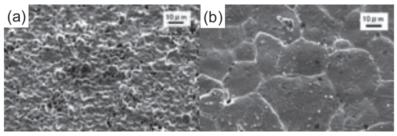

Fig. 2 The SEM images electrodes of surface

The electrolytic dissociation models of Pt and Pd are shown in Fig. 3. The Pt electrode has three-phase boundary(Fig. 3(a)), Pd electrode has two-phase boundary or mixed layer structure(Fig. 3(b),(c)).

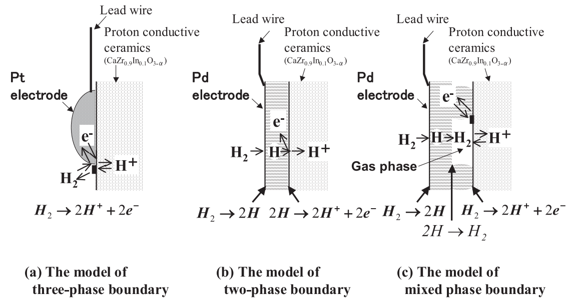

Fig. 3 The models of electrode structure and electrolytic dissociation

3-2 Performance in gaseous environments

The results of the measurement of EMF at 873K, 773K and 673K 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.

$$E = \frac{RT}{2F}\ln\left(\frac{PH_2(m)}{PH_2(r)}\right) \tag{1}$$

here, R is gas constant, T is temperature K, F is Faraday constant, $PH_2(m)$ and $PH_2(r)$ are hydrogen partial pressure of measure side and reference side.

The probes using Pd electrode obeyed well the theory at all temperatures.

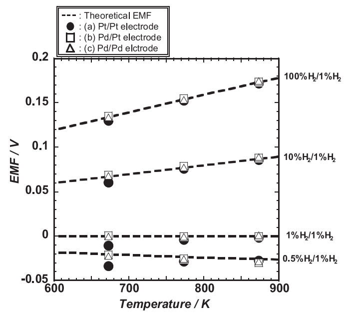

Fig. 4 The temperature dependence of EMF

4. Conclusion

Major conclusions are follows;

(1) The Pd membranes without open pores were fabricated successfully on the ceramics sensor cell.
(2) The EMF with the Pd electrodes was shown to be almost equal to that with the porous Pt electrode in the gaseous environment.