

Study of Pd Membrane Electrode in Solid Electrolyte Hydrogen (Isotopes) Sensor for Application to Liquid Blankets

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On-line measurement of hydrogen isotopes in corrosive environments is essential for the development of liquid blanket systems for fusion reactors. In the present study, a Pd membrane electrode for a solid electrolyte hydrogen sensor was developed. An electrode fabricated on the sensor surface was metallurgically analyzed and was found to be a compact layer with much lower porosity than conventional Pt electrodes. This compact electrode can serve as a protective layer against corrosion of the sensor material during measurement. The response and stability of the sensor with the Pd membrane electrode was investigated in an Ar-hydrogen gas mixture environment. The electromotive force of the sensor with the Pd compact electrode agreed with a theoretical calculation, assuming the same three-phase boundary as in the sensor with a porous Pt electrode.

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1. Introduction

The molten salt LiF-BeF₂ (Flibe), liquid metal lithium (Li), and molten lead-lithium (Pb-17Li) are candidates for tritium breeding materials for fusion blankets [1]. For blankets with these liquid breeders, control of tritium is commonly a key concern. Therefore, on-line sensing of hydrogen (isotopes) in high-temperature melts is essential. The hydrogen (isotopes) partial pressures of the three melts are extremely different, with a very high pressure for Flibe, medium pressure for Li-Pb, and very low pressure for Li [2, 3]. The application of hydrogen sensors made of proton-conductive solid electrolyte to the measurement of hydrogen (isotopes) in liquid blankets has been studied by authors [4, 5].

Proton-conductive solid electrolytes are functional ceramics and can selectively permeate protons. Solid electrolytes (e.g., CaZr_{0.9}In_{0.1}O_{3-a}) have been used as hydrogen sensors for molten aluminum and copper [6, 7]. Hydrogen sensors are equipped with electrodes on the surfaces to provide an electrode reaction and electrical collection. Porous platinum (Pt) has been used as the electrode [8, 9]. Though Pt electrodes show good performance, they do not protect the ceramics in a corrosive and reductive atmosphere because of their porous structure.

Pd metal has a high hydrogen diffusion coefficient of 1.1 m²/s at 873 K [10]. Therefore, hydrogen can diffuse in the matrix without pores, making Pd metal a candidate for a protective electrode if a compact layer can be formed on the sensor surface. Pd electrodes of porous structure

have been examined in previous studies [11, 12]. However, application of compact Pd membrane electrodes has not been examined yet.

In this study, fabrication and characterization of a Pd membrane on proton-conductive ceramics were carried out. The performance of a Pd membrane electrode was compared with that of a Pt membrane electrode by measuring hydrogen in an Ar-H₂ gas mixture. The purpose of this study is to investigate the availability of the Pd membrane electrode by metallurgical analysis of the electrode and an on-line sensing test in a gaseous environment.

2. Principle of hydrogen sensors using solid electrolyte

The principle of the electrode for a solid electrolyte sensor for hydrogen measurement [13–15] is shown in Fig. 1. The sensor consists of a proton-conductive solid

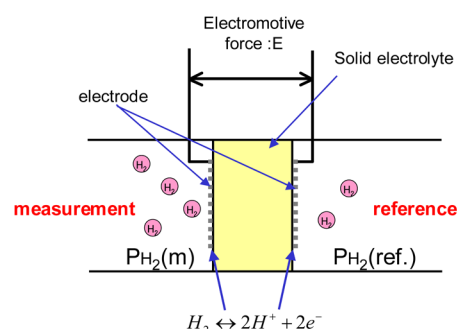


Fig. 1 Principle of the hydrogen sensor.

electrolyte, electrodes placed on both surfaces of the solid electrolyte, and an electrometer. The sensor is placed between two gas compartments (for reference and measurement) of an Ar-H₂ gas mixture at different partial pressures. The reference compartment is filled with a reference gas at a known hydrogen concentration, and the measurement one is filled with gas at an unknown concentration for measurement.

The molecules of hydrogen in both compartments are dissociated on the electrode and ionized on the surface of the solid electrolyte, and protons are selectively diffused in the solid electrolyte. The electrode reaction can be expressed as



The intensity of the reaction in eq.(1) depends on the chemical potential of the hydrogen in the gas, which is proportional to the partial pressure of hydrogen in the gas. Thus, the difference in electrical work done by the reaction on the electrodes in both compartments is obtained as the electromotive force (EMF). The theoretical EMF is given

according to the Nernst equation, and expressed as

$$2FE = RT \ln \frac{C(m)}{C(ref.)} = RT \ln \frac{PH_2(m)}{PH_2(ref.)} \quad (2)$$

where, E is the EMF in units of V, F is the Faraday constant in units of C/mol, R is a gas constant in units of J/K·mol, and T is the absolute temperature in units of K. $C(m)$ is the mole ratio of the hydrogen concentration of the gas in the measurement compartment, and $C(ref.)$ is that in the reference one. $PH_2(m)$ is the partial H₂ pressure of the gas in the measurement compartment in units of Pa, and $PH_2(ref.)$ is that in the reference one.

When a porous electrode is placed on a solid electrolyte, the reaction takes place at the three-phase boundary, as shown in Fig. 2. In this case, the EMF is given by eq.(2). In the case of a compact membrane electrode, the reaction can take place either at the plane interface between the electrode and the solid electrolyte (two-phase boundary), as shown in Fig. 3 (A), or at the three-phase bound-

Nomenclature

F	Faraday constant, 96485 C/mol
E	Electromotive force, V
R	Gas constant, 8.314 J/K·mol
T	Absolute temperature, K
k	Sievert's constant, mole ratio/Pa ^{0.5}
$C(m)$	Hydrogen concentration of measurement compartment, mole ratio
$C(ref.)$	Hydrogen concentration of reference compartment, mole ratio
$PH_2(m)$	Hydrogen partial pressure of measurement compartment, Pa
$PH_2(ref.)$	Hydrogen partial pressure of reference compartment, Pa
$Ce(m)$	Hydrogen concentration in Pd electrode of measurement compartment, mole ratio
$Ce(ref.)$	Hydrogen concentration in Pd electrode of reference compartment, mole ratio

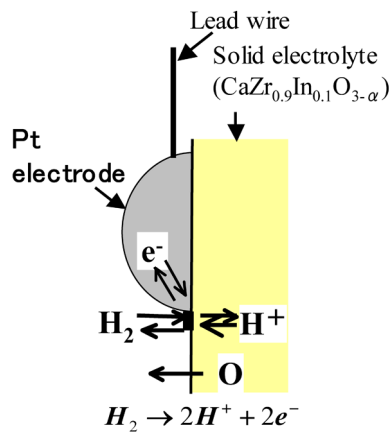
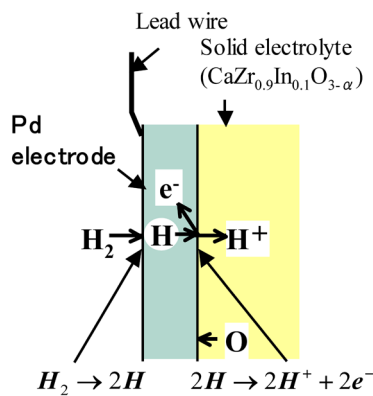


Fig. 2 Three-phase boundary electrode reaction model for the porous electrode.

(A)



(B)

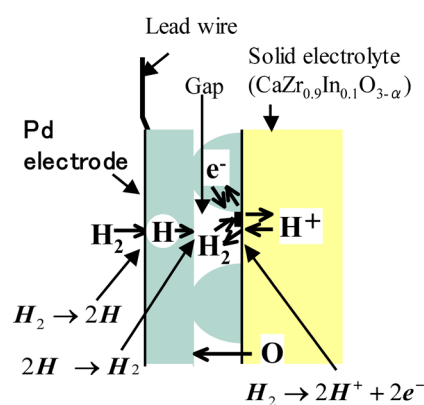


Fig. 3 Electrode reaction models for the compact membrane electrode. (A) Two-phase boundary model, (B) Three-phase boundary model.

ary formed by the electrode, the solid electrolyte, and the gap formed at the interface, as shown in Fig. 3 (B). In the case of the three-phase boundary, the recombination of hydrogen atoms into molecules occurs in the gap. Then, the electrode reaction takes place at the three-phase boundary, where the hydrogen molecules were dissociated to atoms and the hydrogen atoms were ionized to protons, which diffused to the solid electrolyte.

In the case of the two-phase boundary [Fig. 3 (A)], the EMF is given by

$$2FE = RT \ln \frac{Ce(m)}{Ce(ref.)}, \quad (3)$$

where $Ce(m)$ and $Ce(ref.)$ are the concentration of hydrogen (mole ratio) in the Pd electrode on the measurement and the reference side, respectively. Based on Sievert's law,

$$Ce = k \sqrt{PH_2}, \quad (4)$$

where k is Sievert's constant in units of mole ratio/ $\text{Pa}^{0.5}$, and thus

$$2FE = RT \ln \frac{\sqrt{PH_2(m)}}{\sqrt{PH_2(ref.)}}. \quad (5)$$

For the three-phase boundary [Fig. 3 (B)], the EMF is given by eq. (2).

3. Experimental procedure

3.1 Experimental conditions

The hydrogen sensor was prepared for the experiment to investigate its performance with the Pd electrode.

Pt and Pd electrodes were coated on the solid electrolyte ceramics of the sensors, which were made of $\text{CaZr}_{0.9}\text{In}_{0.1}\text{O}_{3-a}$. The ceramics were cap-shaped with an outer diameter of 3.8 mm, an inner diameter of 2.5 mm, and a length of 37 mm. The sensor was fixed to Al_2O_3

tubes with an outer diameter of 6.0 mm, an inner diameter of 4.0 mm, and a length of 450 mm by a low-melting glass seal. Pt lead wires 0.3 mm in diameter were fixed to the electrodes of the measurement and reference compartments. A stainless steel tube was inserted to inject the reference gas into the inner electrode to control the partial pressure in the reference compartment. The details of electrode coating are explained in the next section. The surface and cross section of the electrodes were observed by scanning electron microscopy (SEM).

The EMF of the sensors was measured in the Ar-H_2 gas mixture using the experimental setup shown in Fig. 4. Two sensors, a thermocouple, and tubes for a gas inlet and outlet were inserted into the Al_2O_3 crucible, which was placed in an electric furnace. The electrometer used in the present study has a high impedance of $10\text{ M}\Omega$.

EMF measurements using the sensor containing the electrodes was performed at 673 K, 773 K, and 873 K, which correspond to typical blanket operation temperatures. The reference gas was an $\text{Ar-1}\%\text{H}_2$ gas mixture and was continuously introduced into the reference compartment. Ar-H_2 mixed gases flowed from the inlet gas tube to the Al_2O_3 crucible as the measurement gas. $\text{Ar-0.5}\%\text{H}_2$, $\text{Ar-1}\%\text{H}_2$, $\text{Ar-10}\%\text{H}_2$, and $100\%\text{H}_2$ were prepared as measurement gases to check the validity of the output EMF signal by comparison with theoretical calculation using eq. (1). The measurement gas was replaced with these Ar-H_2 gases.

3.2 Fabrication of Pt and Pd membrane electrodes on solid electrolyte cell

The Pt electrode was coated on the solid electrolyte using Pt paste. The Pt paste was painted on the solid electrolyte and coated by baking in air at a temperature of 1273 K for 0.5 hr. The Pt paste coating and baking were performed twice. The surface was observed by SEM. Fig. 5 (A) shows a surface image of the Pt electrode, indicating porous structure.

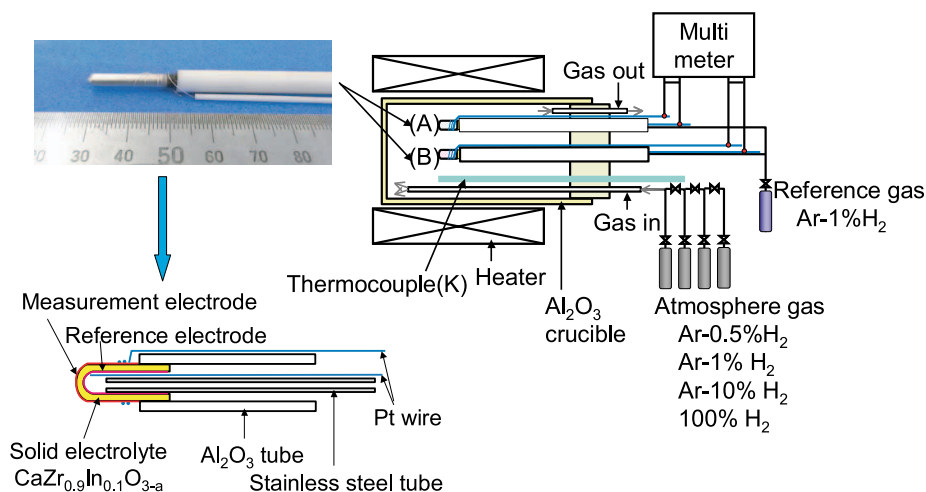


Fig. 4 Hydrogen sensor and experimental apparatus for performance test.

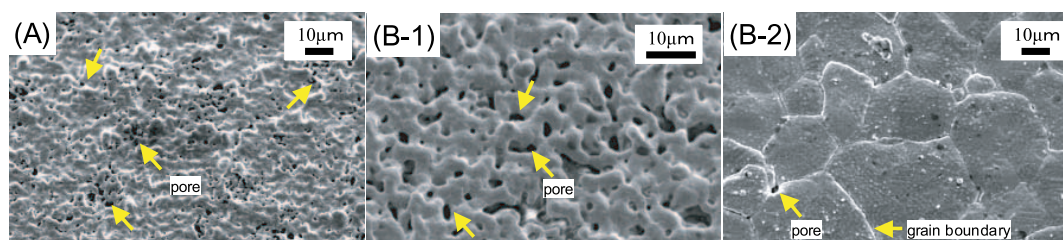


Fig. 5 SEM images of the surface of electrodes. (A) The surface of Pt electrode, (B-1) The surface of Pd electrode baked at 1173 K and (B-2) The surface of Pd electrode baked at 1673 K.

The Pd electrode was coated on the solid electrolyte using Pd paste. The Pd paste was painted on the solid electrolyte and coated by baking in air at a temperature of either 1173 K or 1673 K for 0.5 hr. This procedure was performed twice, as it was for the Pt electrode.

The effect of the baking temperature on the membrane structure was investigated, as shown in Fig. 5 (B-1) and (B-2). A Pd electrode with porous structure was obtained after baking at 1173 K, as shown in Fig. 5 (B-1). After baking at 1673 K, the compact membrane structure was obtained, as shown Fig. 5 (B-2).

4. Results and discussions

4.1 Electrode structure

Figure 6 shows the cross-sectional microstructure of the Pt and compact Pd electrodes. The surface of the Pt electrode showed 1- to 5- μm grains with a high density of pores [Fig. 6 (A)]. The diameter of the pores was less than 10 μm . The thickness of the electrode was 5 to 10 μm . However, in some areas the pore density was locally low. The electrode reaction on the porous Pt electrode occurs at the three-phase boundary of solid electrolyte, electrode, and gas (Fig. 2) [16].

The cross sections of the Pd electrode showed a membrane with less porous structure than the Pt electrode, as shown in Fig. 6 (B). The thickness was 10 to 20 μm . The Pd membrane is expected to protect the solid electrolyte from corrosion by the environment. However, the electrode reaction may occur at either the two-phase or three-phase boundary.

A gap between the membrane and substrate was not observed by SEM.

4.2 Electrode performance

Examples of EMF measurements are shown in Fig. 7. The EMF output of the sensors changed immediately to the new value when the mixture of the injected Ar-H₂ gas was changed in the Al₂O₃ crucible. The gas change was carried out twice, and the reproducibility of the sensors was confirmed.

Figure 8 shows the temperature dependence of the measured EMF for various gaseous environments. The probe with the Pt electrode showed stable output. The

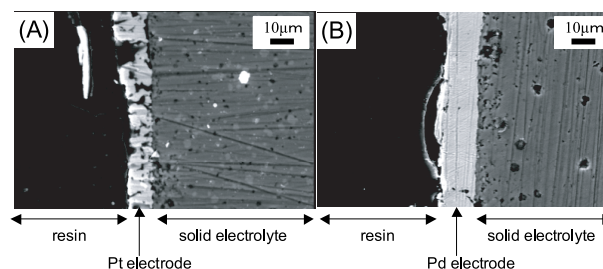


Fig. 6 SEM images of the cross section of electrodes. (A) The cross section of Pt electrode, (B) The cross section of Pd electrode.

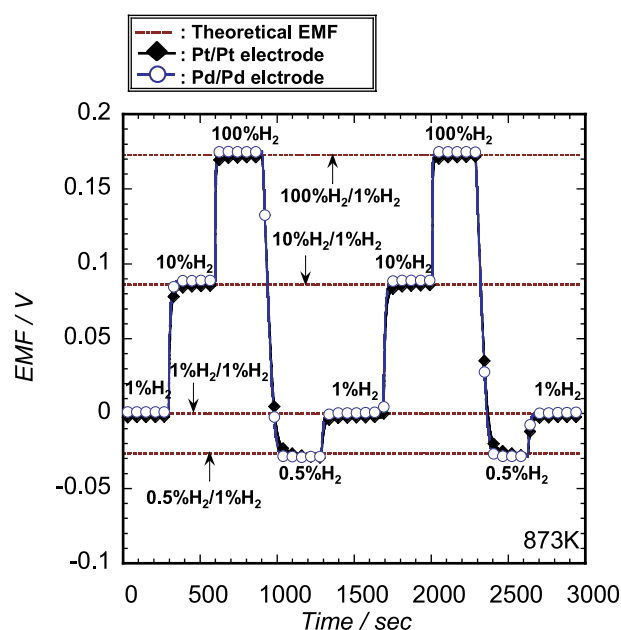


Fig. 7 Examples of the EMF tests with the gas mixture change.

theoretical EMF was obtained using eq. (2) for the three-phase boundary and eq. (5) for the two-phase boundary, which are shown by dotted and broken lines, respectively, in Fig. 7. The experimental output agreed with the estimated values within the error level, assuming the three-phase boundary in all conditions.

Therefore, the Pd membrane electrode causes the electrode reaction at the three-phase boundary in the small gap between the compact membrane and the substrate.

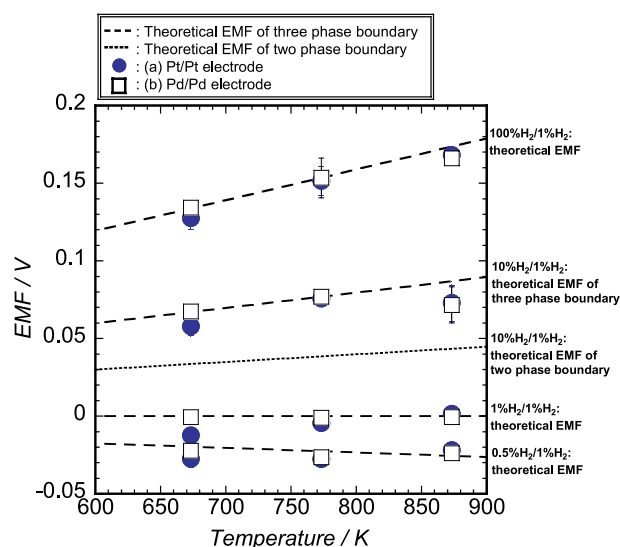


Fig. 8 Temperature dependence of EMF.

5. Conclusion

Compact membrane electrodes made of Pd for a hydrogen sensor were developed for application to hydrogen (isotopes) sensors in corrosive environments such as liquid blankets in fusion reactors. The metallurgy and basic performance of the electrodes were investigated. The major conclusions are as follows:

(1) Pd membranes without open pores were fabricated on the ceramic sensor cell. Compact membranes could be formed with a small number of pores by heat treatment. Heat treatment at a temperature of 1673 K was especially effective.

(2) The hydrogen sensor with a compact Pd membrane showed reliable performance, similar to that of a sensor with a porous Pt membrane. The electromotive force output by the sensor with the Pd electrode agreed with that given by theoretical estimation based on the Nernst equation, assuming the three-phase boundary as in the case of a

porous Pt electrode. This suggests that the reaction occurred at the three-phase boundary formed by the electrode, the solid electrolyte, and the gap formed at the interface.

Acknowledgments

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