

Studies on Hydrogen Permeation Behavior into Pd, W, Cu by using Electrochemical Current Transient Technique

Myung-Hee Yun, Jei-Won Yeon, Hong-Joo Ahn*, Kyuseok Song
Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute,
Daeduk daero 989-111, Yuseong-gu, Daejeon 305-353, Korea
* Corresponding author: ahjoo@kaeri.re.kr

1. Introduction

Electrochemical hydrogen permeation has been a well established experimental technique for more than forty years [1-3]. It was first developed by Devanathan and Stachurski in 1962 [4]. Since then, this electrochemical technique has been widely used by other researchers to determine hydrogen permeation behavior due to its ease and simplicity.

In this study, we tried to investigate the electrochemical hydrogen permeation behavior to prepare the hydrogen implanted samples which was performed into metals such as tungsten, copper and stainless steel 316. They are considered as the first wall of ITER (International Thermonuclear Experimental Reactor).

2. Methods and Results

Electrochemical permeation cell was composed of two compartments [4]. In the first compartment, a constant cathodic potential was applied to generate hydrogen on the metal surface. The applied hydrogen generation potentials were determined from the potentiodynamic polarization curves measured at each metal specimen, respectively. In the other compartment, anodic potential was applied to maintain a zero hydrogen concentration on that surface.

0.1 N NaOH solution of pH 13 was used as the electrolyte and de-aerated by bubbling with argon gas before and during the experiments in both compartments. The surface area of the membrane specimen exposed to electrolyte was 1.766 cm^2 in both side. For the electrochemical measurement, the counter electrode used was a platinum wire (99.9% from Nilaco), while an Ag/AgCl electrode served as the reference electrode; both were placed directly in the cell and connected to a potentiostat (Bio-Logic SAS). All experiments were carried out at room temperature.

2.1 Potentiodynamic polarization behavior at Pd

It is well known that palladium membrane has good performance to permeate the hydrogen from the cathodic side. In order to investigate the possibility of hydrogen absorption into the metal, therefore, the current transient technique was performed on the palladium layers at a series of increasingly negative potentials before the experiment for materials such as

tungsten, copper and stainless steel used as the first wall of ITER.

Figure 2 shows the potentiodynamic polarization curve obtained from palladium membrane in a 0.1 N NaOH solution. The applied potential was scanned from -1.20 to $0.8 \text{ V}_{\text{Ag/AgCl}}$ in the anodic direction at a scan rate of 1 mV s^{-1} . There was one broad wave at $-0.59 \text{ V}_{\text{Ag/AgCl}}$ as shown in Fig. 2. This peak is related to oxidation of hydrogen on the palladium surface.

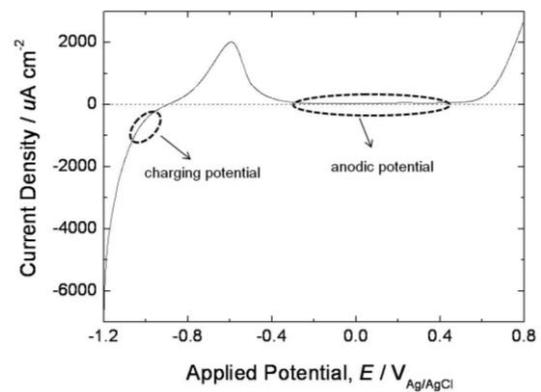


Fig. 2. Potentiodynamic polarization on Pd membrane in 0.1 N NaOH solution with a scan rate of 1 mV s^{-1} .

In order to perform the electrochemical permeation experiment, a charging potential has to be adjusted below $-0.9 \text{ V}_{\text{Ag/AgCl}}$ in cathodic compartment of palladium membrane, while the anodic potential to be oxidized to H^+ has to be applied in the range between -0.2 and $+0.4 \text{ V}_{\text{Ag/AgCl}}$.

2.2 Hydrogen permeation current as a function of the charging potential

Figure 3 shows typical hydrogen permeation current transients for the palladium membrane in 0.1 N NaOH solutions by current transient technique for 900 sec. In order to control the concentration of adsorbed hydrogen on the Pd surface, charging potentials were applied between -1.05 and $-1.15 \text{ V}_{\text{Ag/AgCl}}$ in the cathodic compartment, while the anodic side was potentiostatically kept at a constant potential of $-0.1 \text{ V}_{\text{Ag/AgCl}}$.

The steady-state permeation current increased as the applied charging potential negatively increased from -1.05 to $-1.15 \text{ V}_{\text{Ag/AgCl}}$ as shown in Fig. 3. This indicates that an increase of the negative charging potential leads

to an increase of the adsorbed hydrogen on the palladium surface, and then a fraction may diffuse into the metal substrate.

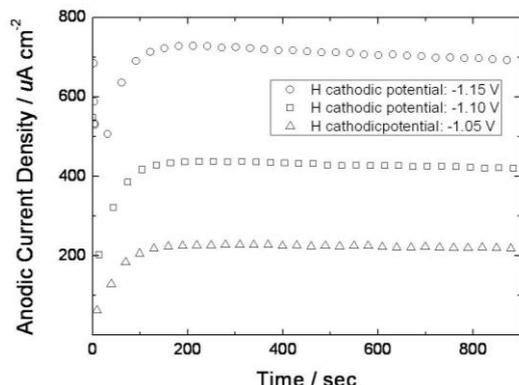


Fig. 3. Typical permeation current transients obtained from the palladium electrode specimen in 0.1 N NaOH solutions at hydrogen charging potentials from -1.05 to -1.15 V_{Ag/AgCl}

2.3 Evaluation of hydrogen permeation parameters

Hydrogen permeation behavior depends on both the hydrogen diffusion coefficient and surface hydrogen concentration [6]. The hydrogen diffusion coefficient determines the ability for hydrogen to permeate through a material. In order to calculate hydrogen permeation parameters such as the diffusion coefficient, hydrogen concentration and permeability, we obtained the hydrogen permeation current transient from materials such as W, Cu and STS 316 by current transient technique as shown in Fig. 4. The steady state current density obtained from the current transient was used in the well known mathematical equations [6-7] and the calculated permeation parameters were summarized in Table 1.

From the comparison between the hydrogen permeation parameters, it was recognized that the metal with the long bond length between atoms has a good performance for the hydrogen permeation since hydrogen tends to diffuse to interstitial sites in metallic microstructures.

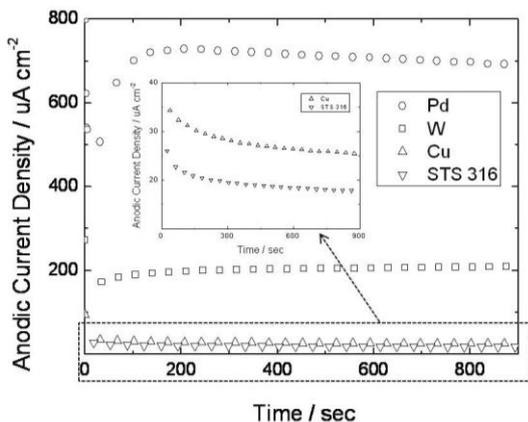


Figure 4. Permeation current transients obtained from the Pd, W, Cu and STS 316 in 0.1 N NaOH solutions.

Table I: Calculated permeation parameters in Pd, W, Cu and STS 316

Metal	Diffusion coefficient, $\text{cm}^2 \text{s}^{-1}$	Hydrogen concentration, mol cm^{-3}	Permeability, $\text{mol cm}^{-2} \text{s}^{-1}$
Pd	2.97×10^{-8}	4.0×10^{-4}	1.18×10^{-11}
W	1.86×10^{-8}	5.6×10^{-4}	1.04×10^{-11}
Cu	1.15×10^{-8}	1.2×10^{-4}	1.39×10^{-12}
STS316	9.8×10^{-9}	1.0×10^{-4}	9.95×10^{-13}

3. Conclusions

Hydrogen permeability was reduced as the hydrogen diffusion coefficient decreased at each metal. On the other hand, permeability of Pd and W showed better performance than that of Cu and STS 316, respectively. From experimental results, it was realized that the flux of hydrogen entering the metal depends on the element composition and microstructure of the metal and on the applied charging potential. Consequently, we can easily control the hydrogen concentration into metal by using electrochemical hydrogen permeation technique for hydrogen implantation.

Acknowledgements

This work was supported by the R&D program of the International Thermonuclear Experimental Reactor (ITER).

REFERENCES

- [1] J.O'M. Bockris and D.F.A. Koch, J. PHYS. Chem., 64, pp. 1941, 1961.
- [2] M.A.V. Devanathan, Z. Stachurski, J. Electrochem. Soc., 111, pp. 6193, 1964.
- [3] K.J. Vetter, 'Electrochemical Kinetics, Academic Press, New York, pp. 525, 1967.
- [4] M. A. V. Devanathan, Z. Stachurski, Proc. Roy. Soc.(London), 270A, pp. 90, 1962.
- [5] K.B. Kim, K. Park, J.S. Lee, J. Kor. Inst. Met. & Mater., 4, 5, pp. 1013-1016, 1998.
- [6] E. Gileadi, M.A. Fullenwider, J.O'M. Bockris, J. Electrochem. Soc., 113, pp.926, 1996.
- [7] J. McBreen, L. Nanis, W. Beck, J. Electrochem. Soc. 113, pp. 1218, 1966.