

ノート

## 電気抵抗測定から見た酸素存在下でのPdの水素吸収・放出挙動

赤丸悟士<sup>a,\*</sup>、古里咲輝<sup>a</sup>、原正憲<sup>a</sup>、松山政夫<sup>a</sup>

<sup>a</sup>富山大学 研究推進機構 水素同位体科学研究センター  
〒930-8555 富山市五福 3190

Hydrogen absorption-desorption behaviors on Pd in the presence of oxygen  
evaluated by electrical resistance measurements

Satoshi Akamaru<sup>a,\*</sup>, Saki Furusato<sup>a</sup>, Masanori Hara<sup>a</sup>, Masao Matsuyama<sup>a</sup>

<sup>a</sup>Hydrogen Isotope Research Center

Organization for Promotion of Research, University of Toyama

Gofuku 3190, Toyama 930-8555

\* aka@ctg.u-toyama.ac.jp

(Received February 2, 2016; accepted April 27, 2016)

### Abstract

To understand the hydrogen absorption and desorption behaviors of Pd under air, we performed real time measurements of the electrical resistance of Pd under gas mixture with various oxygen contents. The hydrogen absorption rate was independent of oxygen concentration. Conversely, the hydrogen desorption rate in the presence of oxygen was faster

than that without oxygen, suggesting that the additional desorption path including water formation reaction appears in the hydrogen desorption process in the presence of oxygen. The hydrogen concentration in Pd at equilibrium decreased with increasing oxygen concentration in gas phase because the hydrogen adsorption sites become partially occupied by oxygen atoms.

## 1. Introduction

Various hydrogen sensing systems have been developed for application within a future hydrogen energy system [1]. Pd metal and alloys are utilized in some hydrogen sensing systems as a detecting material, because the adsorption and absorption of hydrogen on/in Pd metal and alloys depends on the gas phase hydrogen partial pressure. In addition, the Pd metal and alloys have an advantage to absorb hydrogen at room temperature in atmosphere.

The existence of oxygen in the gas phase influences the hydrogen absorption and desorption properties of Pd [2]. It is important to understand quantitatively hydrogen absorption and desorption behavior for Pd metal and alloys in the presence of oxygen because the kinetics of hydrogen on/in Pd metal and alloys directly affects the characteristics of the hydrogen sensing system such as response speed and the detection limits. For Pd metal, this behavior has been investigated by many researchers [2,3]. However little has been reported regarding the behavior with Pd alloys. Moreover, the hydrogen kinetics were investigated through gas phase analysis technique, meaning that changes in the hydrogen concentration in Pd metal and alloys was only tracked indirectly [4,5]. As a result of these indirect probes, the quantitative analysis of the hydrogen absorption and desorption, especially the amount of hydrogen absorbed in Pd metal and alloys, quickly becomes complex.

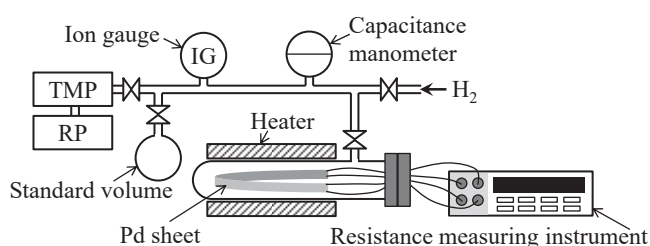
The electrical resistance is one way to estimate directly the hydrogen concentration in a hydrogen absorbing metal in real time [6]. It is well known that the hydrogen concentration in Pd is correlated with the electrical resistance of Pd [7], and this correlation can also be applied within a gas phase hydrogen sensing system [8].

In order to investigate directly the hydrogen absorption-desorption behavior of Pd metal and alloys in real time, an electrical resistance measuring system combined with a gas phase analysis system was constructed. We measured the electrical resistance of Pd in real time under a flowing gas mixture of hydrogen and oxygen-nitrogen gases, and evaluated the effect of the oxygen partial pressure on the hydrogen absorption-desorption behavior of Pd.

## 2. Experimental

### 2.1. Dependence of the electrical resistance on hydrogen concentration in Pd

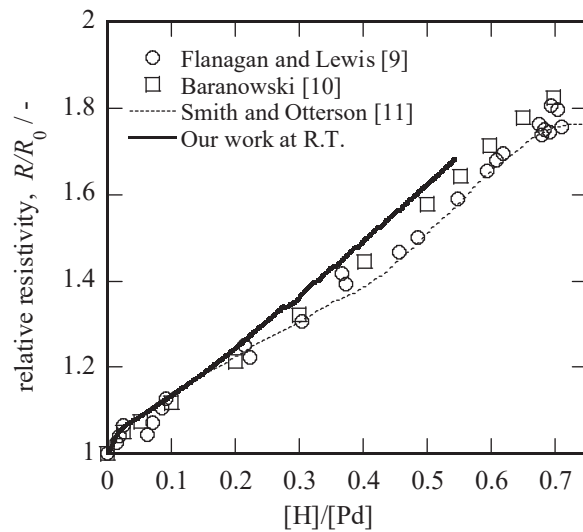
To obtain a relationship between the hydrogen concentration in Pd and the electrical resistance, the electrical resistance under a hydrogen gas environment was measured. The measuring system is shown schematically in Fig. 1. Pd sheet (5 mm width, 100 mm length, and 0.1 mm thickness) was purchased from Kojundo Chemical Laboratory Co. Ltd. The sample chamber to contain the Pd sheet was attached to a conventional pressure-composition isotherm measurement system. The atomic ratio of absorbed hydrogen in the Pd sheet (denoted as  $[H]/[Pd]$ ) was estimated by the volumetric method. Electrical wire leads were attached to each end of the Pd sheet, and the electrical resistance was measured continuously during the hydrogen absorption process using an electrical resistance measuring instrument (Keithley Instruments Inc., type 2401). The four-probe dc method was applied to measure electrical resistance.



**Fig. 1** Schematic view of the electrical resistance measurement system under pure hydrogen gas.

The dependence of the electrical resistance on  $[H]/[Pd]$  is shown in Fig. 2. At low  $[H]/[Pd]$ , the resistance steeply increased. A slope of the resistance was changed at  $[H]/[Pd] = 0.02$ , after which the resistance increased linearly with increasing value of  $[H]/[Pd]$ .

Previously obtained data by other researchers is also shown in Fig. 2 [8]. Although the resistance measured in this study was slightly larger than those measured by other researchers at higher  $[H]/[Pd]$  values, the resistance at  $[H]/[Pd] < 0.1$  was in good agreement with other datasets. This results means that the  $[H]/[Pd]$  value can be estimated directly from the electrical resistance of the Pd

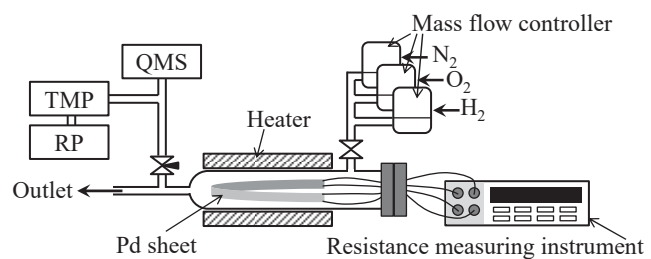


**Fig. 2** Dependence of relative electrical resistance on hydrogen concentration.

sheet in real time at  $[H]/[Pd] < 0.1$ . In general, the hydrogen sensing system requires the measurement of hydrogen concentration less than 4vol%. In measurements taken under a flowing mixture of hydrogen, nitrogen, and oxygen gases, therefore, the hydrogen concentration in the gas phase was fixed to 2vol%, which is equal to 2 kPa of partial pressure. The Pd-hydrogen system under 2 kPa of hydrogen partial pressure at 313 K shows a hydrogen dissolved phase ( $\alpha$  phase), within a region at about  $[H]/[Pd] < 0.05$ . This fulfills the required condition to estimate  $[H]/[Pd]$  from electrical resistance measurements in this study.

## 2.2. Measurement system

The system used in this study is schematically depicted in Fig. 3. The system consisted of mixing gas regulators, sample chamber, electrical resistance measurement instrument, and quadrupole mass spectrometer (QMS). A mixture of nitrogen and



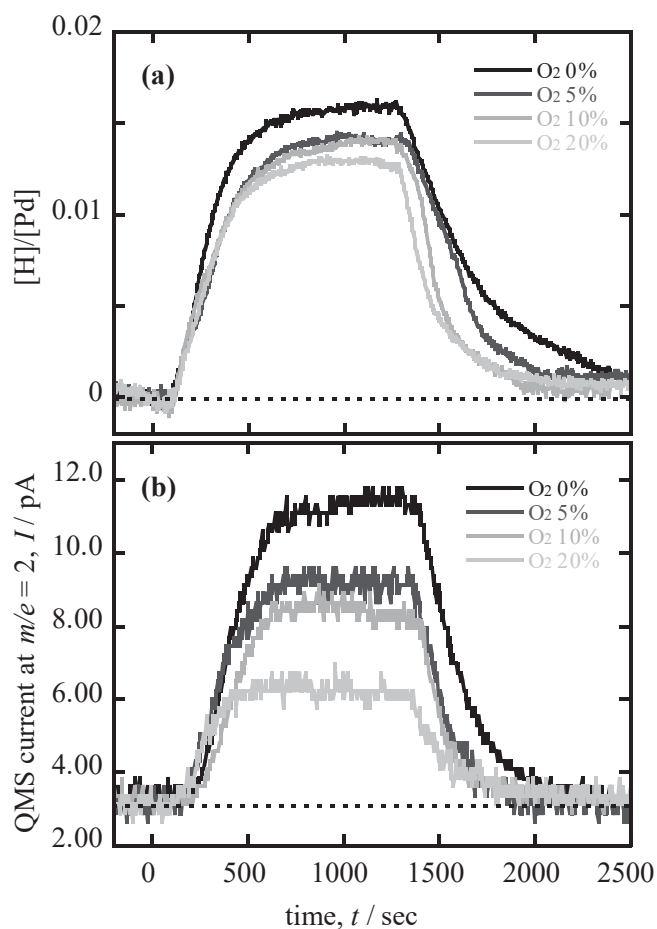
**Fig. 3** A schematic view of the electrical resistance measurement system, usable in real time under flowing gas mixtures.

oxygen gases was flowed as a carrier gas at the rate of 50 cm<sup>3</sup>/min. The flow rate and the volume ratio between N<sub>2</sub> and O<sub>2</sub> for the carrier gas were controlled using mass flow controllers (Fujikin Co. Ltd., FCS-T1000L). Hydrogen gas was added to the carrier gas, and the hydrogen gas concentration was adjusted to 2vol% while the flow speed of the total mixture was kept at 50 cm<sup>3</sup>/min. The mixture was flowed into the sample chamber constructed of heat-resistant glass. The Pd sheet in the chamber was the same as that used in the electrical resistance measurements shown in Fig. 2. The electrical resistance of the sheet was measured continuously during the gas mixture flow. The temperature of the chamber was kept at 313 K using a ribbon heater covering the outside of the chamber. The mixture was exhausted to atmosphere through an outlet, indicating that the pressure in the chamber was kept at atmospheric pressure. A part of the exhaust mixture was introduced into quadrupole mass spectrometer (ANELVA, M-100QA-M), and measured continuously the amount of mass number  $m/e = 2$  in the mixture, which corresponds to the mass of a hydrogen molecule.

### 3. Results and Discussion

Fig. 4(a) shows the electrical resistance of the Pd sheet under a flowing mixture at room temperature. The electrical resistance is already converted to  $[H]/[Pd]$ . After 2vol% of hydrogen was added at  $t = 0$  in pure N<sub>2</sub> as the carrier gas, the  $[H]/[Pd]$  began to increase linearly at 100 s. The delay time is due to the substitution time of the gas in the chamber. The  $[H]/[Pd]$  reached a constant value of 0.016 at about 500 s, indicating that the  $[H]/[Pd]$  came to an equilibrium with hydrogen in the gas phase. The addition of hydrogen in the carrier gas was stopped at 1200 s. The  $[H]/[Pd]$  decreased gradually, and returned to approximately zero at 2500 s, indicating that hydrogen desorption from the Pd sheet was nearly completed at 2500 s. Fig. 4(b) shows the QMS current at  $m/e = 2$  in the exhaust gas at various oxygen concentrations. In pure N<sub>2</sub> (oxygen 0%), the QMS current was also similar in behavior to the

[H]/[Pd]; the QMS current increased smoothly after addition of hydrogen into the carrier gas and reached a saturated value. After the addition of hydrogen was stopped, the QMS current decreased gradually and returned to an initial value at 2100 s. It should be noted that the time for the hydrogen desorption estimated by QMS was faster than that estimated by the electrical resistance. The discrepancy is probably due to the differences in the detection limit for each measurement, namely the electrical resistance measurement could detect smaller change in hydrogen than the QMS analysis.



**Fig. 4** Time dependence on (a) hydrogen concentration in Pd and (b) QMS current at  $m/e = 2$  under various oxygen concentrations.

The saturated value of [H]/[Pd] decreased with increasing oxygen concentration in the carrier gas as shown in Fig. 4(a). The hydrogen concentration in the carrier gas was kept to be a constant 2vol% for all experiments. When the oxygen concentration in the carrier gas was 5vol%, the saturated value reduced by a factor of about 0.9 in comparison with that in oxygen 0%. The saturated value of [H]/[Pd] decreased with increasing oxygen concentration because of adsorption of oxygen atoms on the Pd surface. The concentration of hydrogen atoms on the Pd surface depended on the ratio between hydrogen and oxygen partial pressures in the gas mixture. Because the oxygen atoms occupy the adsorption sites of hydrogen, the

concentration of hydrogen atom on the Pd surface decrease with the oxygen partial pressure. In the saturated  $[H]/[Pd]$  region, the hydrogen atoms in the Pd bulk are equilibrated with those on the Pd surface. As the result, the saturated value of  $[H]/[Pd]$  depended on the oxygen concentration in the gas phase.

The hydrogen desorption rate from Pd increased with increasing oxygen concentration. This indicated that an additional pathway for hydrogen desorption to the gas phase appears in the presence of oxygen; water molecules are formed on the Pd surface. In the desorption process, hydrogen atoms in the Pd bulk diffuse to the Pd surface and become adsorbed hydrogen on the surface. The adsorbed hydrogen easily reacted with adsorbed oxygen atom to form  $H_2O$ , and the adsorbed  $H_2O$  leaves the surface to the gas phase. The formation of  $H_2O$  on the Pd surface is inferred by the QMS analysis. The saturated value of the QMS current reduced with increasing oxygen concentration, meaning that a considerable amount of hydrogen was consumed to form  $H_2O$ . If  $H_2O$  formation reaction rate was comparable to hydrogen atom recombination on the Pd surface at ambient temperature, the hydrogen desorption rate from the Pd bulk could be accelerated by the water formation reaction. In contrast,  $H_2O$  formation did not affect the speed of hydrogen absorption. This can likely be attributed to the surface coverage of adsorbed hydrogen being larger than that of the adsorbed oxygen under a flowing gas mixture of hydrogen and oxygen-nitrogen gases.

#### 4. Conclusions

The hydrogen absorption and desorption behavior in the presence of oxygen was investigated through electrical resistance measurements of a Pd sheet in real time. The time dependence of the hydrogen concentration in the Pd sheet was clearly observed using the developed system. Under the existence of oxygen, the hydrogen concentration in the Pd sheet at equilibrium decreased with oxygen concentration, and the hydrogen desorption rate was

accelerated by the water formation reaction.

### Acknowledgement

This study was partially supported by JSPS KAKENHI (25820353).

### References

- [1] T. Hübert, L. Boon-Brett, G. Black, and U. Banach, *Sensors and Actuators B*, **157** (2011) 329-352.
- [2] Y. Fukai, K. Tanaka, and H. Uchida, *Hydrogen and Metals*, Uchida Rokakuho, Tokyo, 1998, 109-152. (in Japanese)
- [3] M. Johansson, I. Lundstrom, and L.-G. Ekedahl, *Journal of Applied Physics*, **84** (1998) 44-51.
- [4] L. Piccolo, A. Piednoir, and J.-C. Bertolini, *Surface Science*, **600** (2006) 4211-4215.
- [5] D. Wang, J.D. Clewley, Ted B. Flanagan, R. Balasubramaniam, and K.L. Shanahan, *Journal of Alloys and Compounds*, **298** (2000) 261-273.
- [6] G. Reisfeld and M. Strongin, *Chemical Physics Letters*, **246** (1995) 85-89.
- [7] R. C. Hughes and W. K. Schubert, *Journal of Applied Physics*, **71** (1992) 542-544.
- [8] F. Di Pascasio, D. Gozzi, B. Panella, and C. Trionfetti, *Intermetallics*, **11** (2003) 1345-1354.
- [9] Ted B. Flanagan and F. A. Lewis, *Zeitschrift für physikalische Chemie Neue Folge*, **27** (1961) 104-111.
- [10] B. Baranowski, F. A. Lewis, W. D. McFall, S. Filipek, and T. C. Witherspoon, *Proceedings of the Royal Society of London A*, **386** (1983) 309-332.
- [11] R. J. Smith and D. A. Otterson, *Journal of Physics and Chemistry of Solids*, **31** (1970) 187-189.