Measurements of Hydrogen Loading Ratio of Pd Electrodes
Cathodically Polarized in Aqueous Solutions

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Abstract

Various palladium and palladium alloy electrodes were prepared in order to compare their hydrogen loading ratios to be attained by cathodic polarization in alkaline aqueous solutions, 1 M LiOH or LiOD. Details of the loading ratio measurements are presented. No significant difference in H/Pd value was observed between the examined samples with different material processing histories. On the other hand the deuterium loading was very sensitive to the processing conditions. The determined D/Pd values are scattered over the experimental error in the measurement system. The loading ratios of Pd-Ag and Pd-Ce alloys were lower than those of Pd for both H/Pd and D/Pd. The loading ratios of Pd-Rh alloys were higher than those of Pd.

Introduction

Several research groups\(^1,2\) have claimed that one criterion for the observation of excess heat generation in heavy water electrolysis with a Pd cathode is the attainment of high deuterium loading of the Pd cathode. Much effort has been made to increase the loading ratio. It is well known that the loading ratio attained by electrolysis is higher than that attained by the gas loading method, when compared at the same pressure. Attempts to achieve higher loading ratios have been made by changing variables such as current density or temperature or by adding a number of so called "recombination poisons" or additives such as aluminum or silicon (in metallic and oxide form, respectively) to the electrolyte. Pulse electrolysis has also attracted attention, since Takahashi et al.\(^3\) reported anomalously large excess heat.

The reported loading ratios so far are considerably dispersed. Although the loading ratio is dependent on electrolysis conditions, it seems that the values determined in similar electrochemical conditions are still inconsistent. This dispersion in loading behavior might be the reflection of the difference in Pd material characteristics. In many cases, a failure to attain a high loading ratio has been ascribed to cracks of the Pd electrode during electrolysis. However, no detailed explanations of how the formation of cracks decreases the loading ratio have been given, although a
disruption of the local current density has been suggested to be the cause.

A main issue in this paper is whether the loading ratio is significantly influenced by material processing variables such as annealing temperature or mechanical processing ratio. The loading ratios of Pd-Ag, Pd-Ce, and Pd-Rh alloys are also presented. To pursue our objectives, we have developed reliable systems for loading ratio measurement. The error in loading ratio measurement with our systems is also discussed.

**Experimental**

**Pd Electrode Preparation**

**Pure Pd Electrodes.** Palladium grains (99.99 %, 3-5 mm in diameter) were arc-melted, and then cut into fine pieces. They were put in a quartz tube, melted by high frequency induction melting (1650 °C) under an argon atmosphere, and then cast into a rod 8 mm thick or 50 mm thick. The rods (8 or 50 mm in diameter) were swaged into 2 mm, and then cut into a final length of 10 mm. Another series of electrodes was prepared with annealing treatments. These electrodes were subjected to annealing in a vacuum (10⁻³ Torr) at three different stages, after casting into 8 mm, swaging into 4 mm, and swaging into a final diameter of 2 mm, for 1 hour each at three different temperatures 350, 450, or 650 °C. Following these steps, the following five different electrodes were prepared.

- **Sample A:** 50 to 2 mm swaging, no annealing.
- **Sample B:** 8 to 2 mm swaging, no annealing.
- **Sample C:** 8 to 2 mm swaging, annealing three times at 350 °C.
- **Sample D:** 8 to 2 mm swaging, annealing three times at 450 °C.
- **Sample E:** 8 to 2 mm swaging, annealing three times at 650 °C.

**Pd alloy electrodes.** Mother alloys of Pd-Ag, Pd-Ce, and Pd-Rh were prepared by arc-melting of palladium grains (99.99 %) and the respective metals (Ag: 99.9 %, Ce: 99.7 %, Rh: 99.9 %). The mother alloys were cast into rods (8 mm in diameter) by high frequency induction melting (1650 °C) under an argon atmosphere. Then the rods were swaged into 2 mm in diameter. During the swaging steps, annealing was made when necessary to keep the rods homogenous. No annealing was made after swaging into a final diameter of 2 mm. Taking these steps, the following eight different electrodes were prepared.

- **Pd-Ag alloys:** Pd₉₀Ag₁₀, Pd₈₀Ag₂₀, Pd₇₀Ag₃₀
- **Pd-Ce alloys:** Pd₉₇Ce₃, Pd₉₅Ce₅, Pd₉₀Ce₁₀
- **Pd-Rh alloys:** Pd₉₇Rh₃, Pd₉₅Rh₅

**Electrode Pretreatment.** After cutting into 10 mm in length, the electrodes were washed with acetone using a ultrasonic cleaner. The electrodes not subjected to annealing were treated at 200 °C (lower than the recrystallization temperature of Pd)
for 3 hours under an vacuum for a degassing purpose. After drying in the air, the electrodes were weighed. Then lead wires (Teflon coated Ag wire) were attached by using spot welding. The connection spots were sealed by resin sealants.

**Loading Ratio Measurements**

**Gas Burette Method.** Figure 1 schematically shows the loading ratio measurement system using gas burettes. In this system, both of the evolved gases, O$_2$ and H$_2$, were collected together in the burettes for the measurement of the gas volume. In Principle, the difference between the amount of the collected gas and the one calculated from the quantity of electricity for water electrolysis corresponds to the hydrogen absorbed into the Pd electrode, assuming that the recombination of the evolved gases does not occur and the current efficiency is 100 %. 200 ml of D$_2$O (ISOTEC inc., 99.9 %) containing 1 M LiOD (by dissolving Li metal) or H$_2$O (ion exchanged, resistivity > 15 MΩ·cm) containing 1 M LiOH (by dissolving analytical grade LiOH·H$_2$O) was used as the electrolyte. The Pt helical anode was placed symmetrically, surrounding the cathode. The cell body was made of acrylic, and had double side walls so that water (25 °C) for cell temperature control could flow between the walls. The funnel placed reversely in the electrolyte solution was used to introduce the evolved gases into the gas burettes (a capacity of 300 ml each). The two burettes were used alternately to collect more than 300 ml of gas by switching the valves. The gas pressure in the burettes was made equal to atmosphere pressure by adjusting the height of the levelling bottle containing water. The gas temperature was maintained at 25 °C by circulating water through the jackets of the burettes. The gas volume measured on the burettes was corrected for the water vapor pressure in the burettes, and then converted into moles of hydrogen atoms to calculate the loading ratio. Electrolysis was carried out galvanostatically at 300 mA/cm$^2$ throughout this study using a HA-151 galvanostat (Hokuto Denko). Although the electrolysis was carried out galvanostatically, the current was recorded every 5 seconds for better accuracy, and integrated into the quantity of electricity.

Prior to the measurements of the loading ratio, the following two examinations were carried out to estimate the accuracy of this method. Firstly, the current efficiency for the electrolysis was checked by measuring the rate of gas evolution using a Pt cathode (2 mm in diameter, 10 mm in length). During several hours after starting the galvanostatic electrolysis at 300 mA/cm$^2$, the gas recovery efficiencies (the ratio of an actual collected gas amount to the theoretical amount from the quantity of electricity) determined for the period of 1 hour were less than 99.5 %. They increased with time. After 12 hours continuous electrolysis, however, those determined for the period of 8 hours (typical time required for measurements in this study) were in the range 99.9 to 100.1 % in 20 separate measurements. The lower efficiencies of gas recovery at the beginning of the electrolysis were due to the dissolution of gas into the electrolyte, as fresh electrolyte solutions always gave lower efficiencies. Secondly, the degree of the dissolution of the collected gas into the water in the burettes was checked. This was found to be negligible in the time-scale for this method. Considering these facts, we assumed that the current efficiency with respect to water electrolysis was 100 % even if a Pd cathode was used.
and that the error in collecting the gases was ±0.1% in 8 hours. For example, if 700 ml of the gases (typical volume in this study) is collected, the error will be smaller than ±0.7 ml. Since about 35 ml (0 °C, 1 atm) of the hydrogen gas is typically absorbed into a Pd rod 2 mm thick and 10 mm long, the estimated error in loading ratio would be ±2% in the worst case.

In order to ensure the saturation of the electrolyte with hydrogen, pre-electrolysis was carried out using a Pt cathode which had the same size as the Pd ones at 300 mA/cm² for at least 12 hours. Then the Pt cathode was changed to a examined Pd cathode within 10 minutes after stopping the electrolysis with the Pt cathode. In 10 minutes after stopping the pre-electrolysis, electrolysis with the examined Pd cathode was started. Reading of the burette was made every 15 minutes. After the gas volume collected in 1 hour reached 99.9 to 100.1% of the theoretical volume, the electrolysis was further continued for another 1 hour, and then terminated. The total amount of the hydrogen reduced in the electrolysis was then calculated from the amount of the gases collected in the last 1 hour by multiplying by the number of the hours required for the electrolysis. It should be noted that this amount is slightly different from the one calculated from the amount of electricity (less than ±0.1% as mentioned above), but could lower the error in loading ratio. Then the amount of the collected gas was subtracted from this amount to determine the amount of the hydrogen absorbed into the Pd cathode.

Fig. 1. Hydrogen loading ratio measurement system using gas burettes.
Mass Flow Meter Method. Although we mainly used the measurement system described above in this study, the loading ratios of the Pd-Rh alloys were measured using the system shown in Fig. 2. This system features the use of a mass flow meter and automatic operation. The principle of the measurement is the same as that of the system using gas burettes except that the flow rate is recorded to be integrated into the gas volume. Several improvements were made on the system reported in our previous paper\textsuperscript{4}. In our previous system, the cathode compartment was separated from the anode one with a glass separator to introduce only the evolved hydrogen gas into the mass flow meter, and the electrolyte in the anode compartment was open to the air. Since with this configuration there is a pressure drop inherent in the mass flow meter (less than 9 mmH\textsubscript{2}O), a flow of the gas is suppressed at the beginning of electrolysis until the pressure difference between the anode and the cathode compartment reaches the pressure drop. This results in the loss in gas collection. Typically this loss volume varied in the range 3 ml to 6 ml with our cell design and was difficult to control. Thus a blank run with a Pt cathode was necessary before each of Pd electrodes was examined. The other problem in our previous system was that the current distribution was not uniform because of the existence of the separator. The new design shown in Fig. 2 solved these problems. In this system, both the evolved hydrogen and oxygen gases are together introduced into the mass flow meter. The loss volume due to the pressure drop was decreased by minimizing the space above the electrolyte. The helical Pt anode was placed symmetrically, surrounding the Pd cathode. The mass flow meter was calibrated for the mixture of a hydrogen and a oxygen gas.

![Diagram of Hydrogen loading ratio measurement system using a mass flow meter.](image)

Fig. 2. Hydrogen loading ratio measurement system using a mass flow meter.
Results and Discussion

Table 1 lists the results of the measurements. For the pure Pd electrodes, 2 separate measurements for each of the various samples were carried out except for 13 separate measurements of H/Pd for sample A. For sample A, the mean loading ratio (H/Pd) in the 13 measurements was 0.846 with the maximum of 0.866 and the minimum of 0.828. Fig. 3 shows typical output of the mass flow meter. In the Figure, the hatched area corresponds to the absorbed hydrogen. It should be noted that the output rises very quickly to one third of the final value at the start of the electrolysis. This is due to the evolution of the oxygen gas, demonstrating the very quick response of the mass flow meter with the pressure drop minimized by the improved cell design. Fig. 4 shows the change of the loading ratios (D/Pd, D/Pd+Rh) with time for a Pd and a Pd95Rh5 electrode.

As shown in Table 1, significant difference in H/Pd was not observed between the examined pure Pd electrodes with different processing conditions. The slight difference should be considered as experimental error inherent in this method, as explained in the experimental section. The observed scattering in loading ratio in 13 measurements for sample A is consistent with the estimated error, ± 2%. For the heavy water system, on the other hand, we observed significant difference in D/Pd. Even if the samples were taken from the same batch, those loading ratios were scattered over the experimental error. The results show that the electrode with higher processing ratio and without annealing gives the highest loading ratio and annealing at 650 °C significantly decreases the loading ratio.

In our preliminary experiment, we have found further lower loading ratios of 0.2 to 0.3 (D/Pd) for the samples annealed at 1000 °C for 24 hours. The loading ratio for the light water system was not changed significantly. This is quite interesting finding. Although we had evaluated our Pd electrodes using light water, this reminded us to use heavy water. It is noted that these lower loading ratios were determined at the time when the gas recovery efficiencies reached in the range 99.9 to 100.1%. Since this range is the limit of our measurement, there is a possibility that slow loading (less than 0.1%) was still continued at that time. Therefore, the lower loading ratios may have resulted from unsaturation. We first suspected the effect of the oxide on the surface of the Pd electrodes. However, the EPMA for oxygen did not show any significant difference in the oxygen content between the annealed and the unannealed samples. A study to explain this interesting result is in progress.

A visible crack on a Pd electrode subjected to electrolysis was observed once in a series of sample B. The loading ratio (H/Pd) was 0.802. Although this lower value may be ascribed to the cracking, further accumulation of data is needed to conclude the relationship between cracking and loading ratio.

The loading ratio of Pd-Ag and Pd-Ce alloys decreased with increasing Ag or Ce content for both H/Pd and D/Pd. On the other hand, the loading ratios of the Pd-Rh alloys were higher than those of pure Pd. As shown in Fig. 4, the loading rate of the Pd-Rh alloy was smaller than that of pure Pd.
Table 1. Hydrogen loading ratios observed for various Pd and Pd alloy electrodes at the current density of 300 mA/cm².

<table>
<thead>
<tr>
<th>Sample</th>
<th>Processing ratio (%)</th>
<th>Anneal temp.(°C)</th>
<th>H/Pd 1st run</th>
<th>H/Pd 2nd run</th>
<th>H/Pd mean</th>
<th>D/Pd 1st run</th>
<th>D/Pd 2nd run</th>
<th>D/Pd mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd100 (A)</td>
<td>99.8</td>
<td>no anneal</td>
<td>0.834</td>
<td>0.843</td>
<td>0.846**</td>
<td>0.817</td>
<td>0.819</td>
<td>0.818</td>
</tr>
<tr>
<td>Pd100 (B)</td>
<td>93.8</td>
<td>no anneal</td>
<td>0.835</td>
<td>0.839</td>
<td>0.837</td>
<td>0.823</td>
<td>0.757</td>
<td>0.775</td>
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<tr>
<td>Pd100 (C)</td>
<td>93.8</td>
<td>350</td>
<td>0.802</td>
<td>0.865</td>
<td>0.834</td>
<td>0.798</td>
<td>0.731</td>
<td>0.765</td>
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<tr>
<td>Pd100 (D)</td>
<td>93.8</td>
<td>450</td>
<td>0.831</td>
<td>0.854</td>
<td>0.843</td>
<td>0.803</td>
<td>0.782</td>
<td>0.793</td>
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<tr>
<td>Pd100 (E)</td>
<td>93.8</td>
<td>650</td>
<td>0.836</td>
<td>0.850</td>
<td>0.843</td>
<td>0.734</td>
<td>0.704</td>
<td>0.719</td>
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<tr>
<td>Pd90Ag10</td>
<td>93.8</td>
<td>-</td>
<td>0.628****</td>
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<td>Pd80Ag20</td>
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<td>-</td>
<td>0.469</td>
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<td></td>
<td>0.477</td>
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<tr>
<td>Pd70Ag30</td>
<td>93.8</td>
<td>-</td>
<td>0.333</td>
<td></td>
<td></td>
<td>0.315</td>
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<tr>
<td>Pd97Ce3</td>
<td>93.8</td>
<td>-</td>
<td>0.660</td>
<td></td>
<td></td>
<td>0.629</td>
<td></td>
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<tr>
<td>Pd95Ce5</td>
<td>93.8</td>
<td>-</td>
<td>0.582</td>
<td></td>
<td></td>
<td>0.526</td>
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<tr>
<td>Pd90Ce10</td>
<td>93.8</td>
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<td>0.311</td>
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<td>0.340</td>
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<tr>
<td>Pd97Rh3</td>
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<td>0.839</td>
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<tr>
<td>Pd95Rh5</td>
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* Defined as (1 – final cross section area / initial area) × 100, without considering the effect of annealing.

** Mean value in 13 experiments.

*** For the alloys, refer to the experimental section.

**** For the alloys, D(or H)/(Pd+Ag, Ce, Rh) values are given.

Fig. 3. Typical output of the mass flow meter.
Fig. 4. Loading ratio vs. time plot for Pd100 and Pd95Rh5.

References


