Measurements of Hydrogen Loading Ratio of Pd Anodes Polarized in LiH-LiCl-KCl Molten Salt Systems

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Abstract

Hydrogen loading ratios of Pd anodes polarized in LiH-KCl-LiCl molten salt systems were measured at 430 °C using a volumetric method. The values determined at the current density of 300 mA/cm² are 0.057 and 0.030 for H/Pd and D/Pd, respectively. The electrochemical behavior of the Pd anodes in molten salt systems is presented.

Introduction

Cold fusion reaction in a molten salt system has been reported by Liaw et al.¹. For heavy water electrolysis, correlation between excess heat and deuterium loading of Pd has been pointed out by several research groups², ³. It has been reported that attaining high deuterium loading of Pd is essentially important to give rise to cold fusion reaction. It is known that the loading ratio (D/Pd) to be attained by electrolysis is higher than that attained by the gas loading method in which a Pd specimen is kept in contact with a deuterium gas, when compared at the same deuterium pressure. The deuterium loading ratios of 0.8 to 1 have often been reported for heavy water electrolysis. On the other hand, relatively few reports have been made for the behavior of Pd electrodes and for deuterium loading of Pd in molten salt systems.

The PTC diagram for a Pd-H system ⁴ shows that Pd absorbs hydrogen by H/Pd=0.02 at a hydrogen partial pressure of 1 atm at 400 °C, where molten salt electrolysis is to be carried out. It should be noted that the loading ratio at this temperature are much smaller than that at a room temperature (=0.7). Thus, if the attainment of higher loading ratio is one of the criteria for giving rise to cold fusion reaction, a loading ratio to be attained by molten salt electrolysis might be very high. This stimulated our current investigation to measure hydrogen loading ratio of Pd anodes polarized in LiH-LiCl-KCl molten salt systems. In this paper, hydrogen loading ratios (H/Pd, D/Pd) in molten salt systems are presented. Voltammetric data obtained with the Pd anodes in the molten salts are analyzed to understand the electrochemical reactions.
Experimental

An eutectic molten salt of LiCl-KCl (59 : 41 mole %, Wako Chemical) was used for an electrolyte. The LiCl-KCl mixture of the eutectic composition was dried under a vacuum at 200 °C, and then melted at 430 °C in an aluminum crucible placed in a separable flask. Then a suitable amount of LiD (Aldrich) or LiH (Wako Chemical) was added to the mixture. The electrolysis was carried out in an argon dry box with minimum oxygen and moisture content. A typical molten salt experimental setup is schematically shown in Fig. 1. Both Pd and Ni rods (1.5 - 2 mm in diameter, 3 - 10 mm in length, IMRA Material) are used as the anodes in separate experiments. An Al wire was used as the cathode. A Ni wire was used as the quasi reference electrode, whose potential was calibrated against a Li/Li⁺ equilibrium potential by measuring the potential difference between the Ni wire and another Ni wire on which Li was deposited electrochemically. The potential of the reference electrode was calibrated every time the experimental conditions were changed.

Voltammetry was conducted using a HAS01 potentiostat (Hokuto Denko) with a HB104 function generator. The measurements of hydrogen overvoltage were carried out using the current interrupt method.

The hydrogen loading ratios were determined by measuring the amount of the evolved gas during galvanostatic electrolysis using a mass flow meter (KOFLOC, Model-3710) or a gas burette (Fig. 1). The amount of the hydrogen absorbed into Pd was calculated by taking the difference between the amount of the evolved gas and the one from the quantity of electricity. The mass flow meter was mainly used to observe the gas evolution behavior and to estimate the loading ratio roughly. More accurate measurements were made using the gas burette.

Fig. 1. Hydrogen absorption measurement system for molten salt systems.
Results and Discussion

Prior to the measurements of the loading ratio we studied the electrochemical behavior of Pd anodes in a molten salt. Fig. 2 shows two cyclic voltammograms obtained with a Pd and a Ni electrode in a LiCl-KCl molten salt at 430 °C. The waves obtained for the Ni electrode correspond to the reduction and oxidation of Li. It should be noted for the Pd electrode that ambiguous cathodic waves appear at potentials positive with respect to the potential for Li deposition onto the Ni electrode. The electrochemical reactions corresponding to these waves have been found to be the formation of Pd-Li alloys with various compositions.

When LiH was added to the LiCl-KCl molten salt, the rest potential of the Pd electrode changed from +2400 to +580 mV (vs. Li/Li⁺). This potential, 580 mV corresponds to the starting potential for the Pd-Li alloy formation as described above. This means that the Pd electrode is chemically reduced to form Pd-Li alloys by the addition of LiH. Thus this rest potential should originate from the equilibrium potentials of the following reactions:

\[
x \text{Pd} + a \text{Li}^+ + b \text{H}^+ \rightleftharpoons Pd_xL_yH_z + (a-y) \text{Li}^+ + (b-z) \text{H}^+ + (z-y) e^- \\
\text{H}^+ \rightleftharpoons \frac{1}{2} \text{H}_2 + e^-
\]

Figure 3 shows cyclic voltammograms obtained by scanning anodically from the rest potentials for a Pd and a Ni electrode. For the Ni electrode, it is seen that one wave which corresponds to the oxidation of hydride ions appears. For the Pd electrode, on the other hand, overlapping with several waves can be seen. The electrochemical reactions corresponding to the waves should be as follows:

\[
Pd_xL_yH_z \rightarrow Pd_xL_y-xH_z + a \text{Li}^+ + a e^- \\
Pd + x \text{H}^+ \rightarrow PdH_x + x e^- \\
\text{H}^+ \rightarrow \frac{1}{2} \text{H}_2 + e^-
\]

Fig. 2. Cyclic voltammograms obtained with a Pd and a Ni electrode in a LiCl-KCl molten salt at 430°C.
(a) WE : Ni (S = 0.31 cm²), (b) WE : Pd (S = 0.13 cm²).
Scan rate : 100 mV/sec.
Fig. 3. Cyclic voltammograms obtained with a Pd and a Ni electrode in a LiH-LiCl-KCl molten salt at 430°C.
(a) WE : Ni (S = 0.31cm²); (b) WE : Pd (S = 0.13cm²).
Scan rate : 100 mV/sec; LiH : 4.03 mole %.

Figure 4 shows typical mass flow meter responses to switching on and off constant current electrolysis for a Pd and a Ni anode. For the Ni anode, the gas evolution began and stopped immediately on switching on and off the electrolysis, respectively. For the Pd anode, on the other hand, delays in the response were observed on switching on and off, as shown in Fig. 4, indicating the hydrogen absorption and desorption. The hydrogen absorption was saturated in 15 minute with a Pd rod 2 mm thick and 10 mm long at the current of 500 mA. From the steady state gas flow rate, it was confirmed that the current efficiency was —100 %. The estimated loading ratio with this technique were 0.07 (H/Pd) and 0.06 (D/Pd).

Fig. 4. Typical responses of the mass flow meter for a Pd and a Ni electrode upon switching on and off the electrolysis.
LiH : 12.2 mole %; current : 500 mA.
Separate experiments using a gas burette were made to determine the loading ratio more accurately. The numbers of measurements were 25 and 9 for H/Pd and D/Pd, respectively. The results are summarized in Table 1. In these experiments, we must consider the influence of the Pd-Li alloy formation described above. Upon the addition of LiH to the molten salt, \( \text{Pd}_x\text{Li}_y\text{H}_z \) may form before electrolysis, hydrogen being incorporated into the alloy. This hydrogen cannot be taken into account in our method. This leads to an underestimate of the loading ratio. In addition, the formed Pd-Li-H alloy may be oxidized to form Pd-H and Li\(^+\) at the early stage of the electrolysis, lithium coming off the alloy. If this is the case, hydrogen evolution might be suppressed. This leads to an overestimate of the loading ratio. However, since these reactions should take place only at the surface, we ignored these effects in estimating the loading ratios. The data in Table 1 show that the loading ratios attained by electrolysis is slightly higher than that of the gas loading method. Fig. 5 shows the relationship between current density and hydrogen loading ratio. An increase in loading ratio with current density, as has been reported for aqueous systems, was not found within the accuracy of our experiment for this molten salt system.

Hydrogen overvoltages in this molten salt system and in a 1 M LiOH aqueous system were then determined. For this experiment, we needed to choose a reference electrode which shows the hydrogen equilibrium potential in the molten salt. We found that a Ni electrode worked as RHE satisfactorily. Fig. 6 shows that the total overvoltages in this molten salt system are smaller than in the 1 M LiOH system.
Table 1. Hydrogen loading ratios of Pd in a molten salt and an aqueous system.

<table>
<thead>
<tr>
<th></th>
<th><strong>Molten salt system</strong></th>
<th><strong>Aqueous system</strong></th>
<th><strong>H2 gas system</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Method</strong></td>
<td>Gas burette</td>
<td>Mass flow meter</td>
<td>Gas burette</td>
</tr>
<tr>
<td><strong>Electrolyte</strong></td>
<td>LiH</td>
<td>LiD</td>
<td>LiH</td>
</tr>
<tr>
<td><strong>Loading ratio H(D)/Pd</strong></td>
<td>0.057  ** 0.030</td>
<td>0.07  ** 0.06</td>
<td>0.84  0.76</td>
</tr>
</tbody>
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* Mean value in 25 measurements.
** Mean value in 9 measurements.

References