Hydrogen and Deuterium Absorption by Pd Cathode in a Fuel-Cell Type Closed Cell

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ABSTRACT

The hydrogen and deuterium loading ratio, H/Pd and D/Pd, in Pd cathode were measured during electrolysis of 1M LiOD, 1M LiOH, 2.8M H_2SO_4, 2.8M D_2SO_4, 14.7M H_3PO_4, 0.57M K_2CO_3 in a fuel-cell type closed cell. Cold worked pure Pd (ϕ 2- ϕ 5 rods) were used for cathodes. A gas-diffusion type fuel cell anode was used for ionization of hydrogen and deuterium gas. H/Pd or D/Pd was calculated from H_2 or D_2 gas pressure decrease and temperature during electrolysis under in-situ conditions.

The result is summarized as follows; the loading ratio depends on hydrogen overvoltage. D/Pd is smaller than H/Pd by 4~8% for a given overvoltage. The loading ratio does not depend on electrolyte, but the overvoltage depends on electrolyte for a given current density.

1. Introduction

After the reports on "Cold Fusion" by Fleischmann, Pons[1] and Jones et al[2], many groups have conducted experiments in order to reproduce either the excess heat generation or to detect nuclear products such as neutron, tritium, helium. In 2nd ACCF in Como, importance of achieving high loadimg ratio close to 0.9 was pointed out by a few groups[3] for successful detection of excess heat and the nuclear products. It has not been reported, however, how one can achieve such a high loading ratio by electrolysis of heavy water using a palladium cathode. The aim of the present study is to measure the loading ratio of both hydrogen and deuterium in Pd as a function of the hydrogen overvoltage at cathode in various media in order to find various factors which have influence on the loading ratio.

2. Experimental

The electrolysis was conducted in a closed cell schematically shown in Fig.1. The cell was pressurized by H_2 or D_2gas in which a gas diffusion electrode partially immersed in the electrolyte served as an anode in order to avoid oxygen evolution at the counter electrode and to determine the loading ratio from the pressure decrease during the electrolysis. A platinized platinum electrode served as the RHE(Reversible Hydrogen

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Electrode) for measurement of the hydrogen overvoltage at the Pd cathode. The overvoltage reported in the present report has been corrected for the Ohmic overvoltage due to the solution resistance which has been determined by galvanostatic transient method.

The determination of the loading ratio has been conducted in 1M LiOH, 1M LiOD, 2.8M H_2SO_4, 2.8M D_2SO_4, 14.7M H_3PO_4, 0.57M K_2CO_3 as a function of hydrogen overvoltage at either 10℃ or 30℃. The temperature inside the electrolyte, however, did change at the high current densities due to Joule heating of the electrolyte.

The palladium samples studied were rods of 99.99% purity with 2, 4 and 5mm in diameters. They have different Vicker's hardness, Hv, depending on their history of cold working. All the palladium samples were degassed at 200℃ in vacuum for 3 hours before the measurements. Two palladium wires of 0.5mm in diameter were spot-welded on the palladium rods to make the electrical lead from the cathode.

The initial pressure of H_2 or D_2 before the electrolysis was ca. 5～10kgf/cm^2, which decreased typically by 1～2kgf/cm^2 during the electrolysis. Temperature of the electrolyte as well as the gas phase changed at the high current densities, and the temperature change was corrected for by using the temperature measured by a thermocouple placed in the gas phase for the calculation of the loading ratio.

Electrolysis and data acquisition have been conducted by a computer controlled galvanostatic electrolysis system developed in our laboratory.

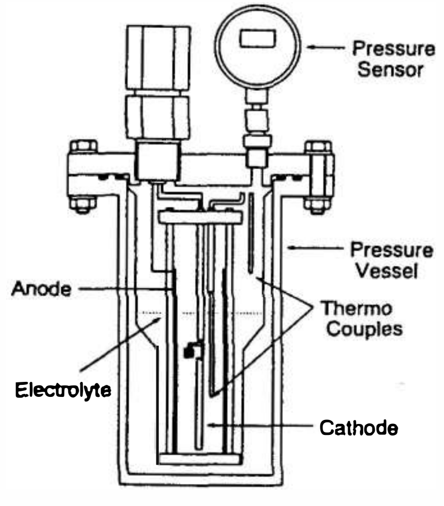

Fig.1 Electrolysis Cell

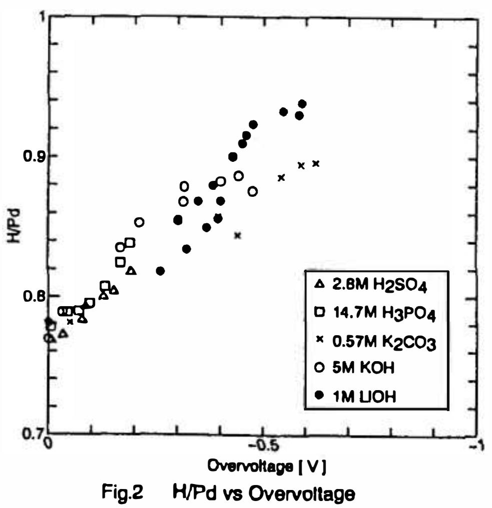

Fig.2 H/Pd vs Overvoltage for φ5 Pd at 30℃

3. Results and Discussion

Effect of the type of electrolyte on the loading ratio

Figure 2 shows the overvoltage dependence of the H/Pd observed in the various electrolytes. The results demonstrate that the loading ratio depends primarily on the hydrogen overvoltage, in other words the loading ratio for a given overvoltage is almost the same irrespective of the type of electrolyte. This means also that the alkaline electrolyte is a better choice for achieving the higher loading ratio simply because the overvoltage at the palladium cathode is higher in the alkaline solutions than in the acidic solutions for a given current density.

Isotope effect on the loading ratio

Figure 3 and 4 demonstrate the difference of the loading ratio between hydrogen and deuterium observed in LiOH, LiOD and H_2SO_4, D_2SO_4 respectively. The figures clearly show that the loading ratio for hydrogen is 4~8% larger than that of deuterium for a given overvoltage. This is interpreted in terms of the higher plateau pressure in the P-C-T curve observed commonly in the gas phase for the Pd/D_2 system than the pressure for the corresponding Pd/H_2 system. The relationship between the hydrogen overvoltage and it's equivalent hydrogen pressure was discussed by Enyo et al.[4] and the interpretation of the isotope effect on the overvoltage dependence of the loading ratio presented in Fig.3 and 4 is supported by their result.

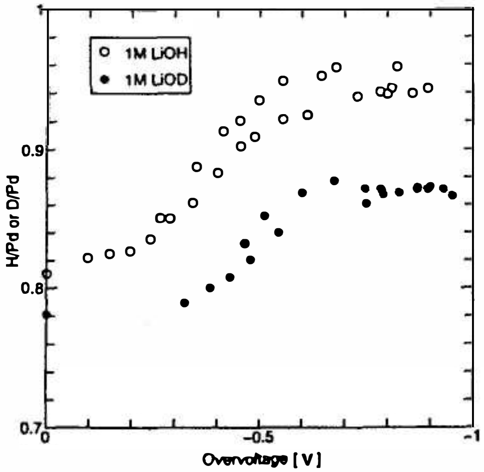

Fig.3 H/Pd or D/Pd vs Overvoltage for φ5 Pd at 10℃

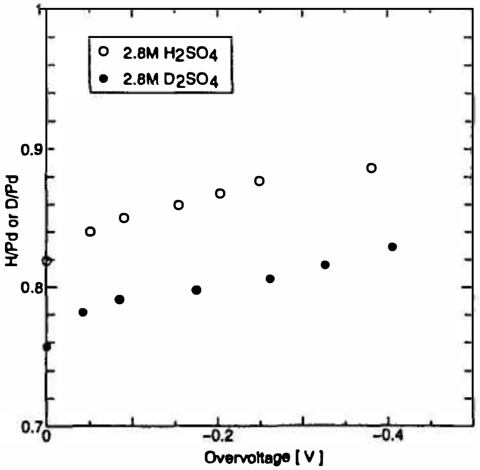

Fig.4 H/Pd or D/Pd vs Overvoltage for φ4 Pd at 10℃

Effect of Vicker's hardness of Pd on the loading ratio

Figure 5 demonstrates the overvoltage dependence of D/Pd for three kinds of palladium rods with different Vicker's hardness. The results suggest that the hardness of palladium has little effect on the loading ratio, although it is not clear at the moment if effect still remains small in the region of higher loading ratio than achieved in the present report. In view of the fact that the hardness is determined primarily by the history of the cold working of the palladium samples, we may conclude from the present data that the cold working of the sample has little effect at least on the loading ratio.

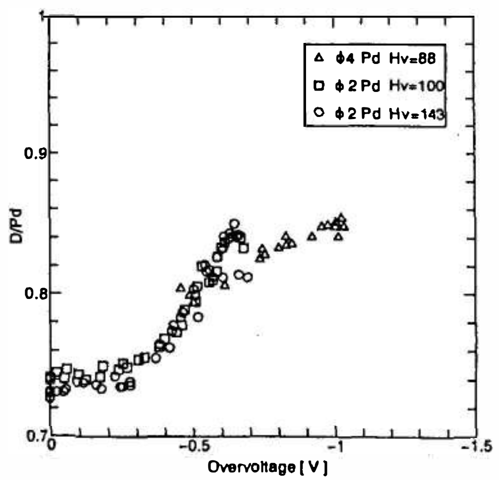

Fig.5 D/Pd vs Overvoltage for φ2 and φ4 Pd in 1M LiOD at 30℃

Dependence of the loading ratio on the current density

The overvoltage dependence of the loading ratio can be converted to the corresponding dependence of the loading ratio on the electrolysis current density using the relation between the current density and the overvoltage. Figure 6 shows the dependence of the overvoltage on the current density in 2.8M H_2SO_4, 1M LiOH and 1M LiOD. The dependence of the loading ratio on the current density is shown in Fig.7.

The role of the current density demonstrated in Fig.7 strongly suggests that high current density is necessary to achieve and maintain the high loading ratio. The dependence of excess heat generation on the current density reported originally by Fleischmann and Pons and later by Storms[5] can be interpreted in terms of the role of the current density described above.

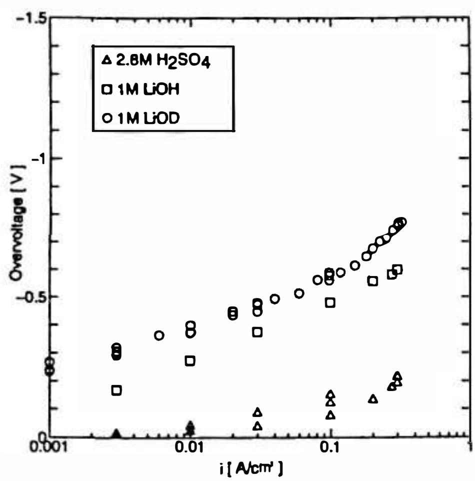

Fig.6 Overvoltage vs Current density for ϕ 2 Pd at 30℃

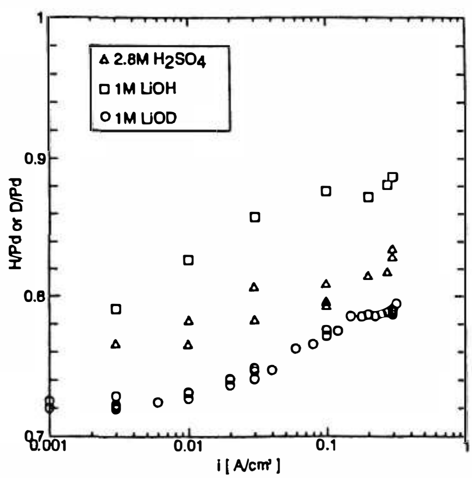

Fig.7 H/Pd or D/Pd vs Current density for ϕ 2 Pd at 30℃

4. Conclusion

The loading ratio does not depend on the type of electrolyte, but depends primarily on hydrogen overvoltage at Pd cathode. D/Pd is smaller than H/Pd by 4～8% for a given overvoltage. The difference of the hardness of Pd cathode have little effect on the loading ratio.

5. Reference

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