Behavior of Key Elements in Pd for the Solid State Nuclear Phenomena Occurred in Heavy Water Electrolysis

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Abstract

The behaviors of some key elements in Pd cathodes used for study of solid state nuclear phenomena have been studied by means of a SIMS analysis of Li, D, Pd, Si, Na, and Al. The mechanism of the anomalous accumulation of deuterium in the surface of Pd electrodes is discussed based on the depth profiles of these elements obtained from the Pd cathodes which gave no nuclear effect, neutron emission, and neutron and excess heat, respectively.

Introduction

The behaviors of the key elements in Pd cathode have been discussed with respect to the occurrence of the solid state nuclear phanomena. As discussed in our previous report, (1)the anomalous accumulation of deuterium is the most significant process to realize the solid state nuclear phenomena. Lithium has been used as the most relevant electrolyte for the electrolysis method, but there is only one discussion on the role of the lithium for the occurrence of the solid state nuclear phenomena.(1) In this discussion, we proposed a hypothetical process for the anomalous accumulation of deuterium based on the intermetallic compounds of Li-Pd, and showed the clear correlation between the anomalous accumulation of deuterium in the surface region of Pd electrode and the neutorn emission. In the present work, we provided a set of Pd electrodes which can be classified into three categories:(1)Pd with no nuclear effects, (2)Pd with neutron emission , and (3)Pd with neutron emission and excess heat generation. The SIMS analysis has been carried out on the above Pd samples to clarify the process of the anomalous accumulation of deuterium and to discuss the excess heat evaluation method.

Experiment

The Pd samples were obtained by a High/Low pulse mode electrolysis described elsewhere in this proceedings by the present authors. The analysis of

the key elements was performed on a secondary ion mass spectrometer(Model IMS-4S, CAMECA/France). The primary ion used was oxygen(O_2^+) and its accelerated velocity was 15.1keV, and the resolution power (M/ Δ M)is more than 15,000.

Results and Discussion

SIMS results

The examples of the depth profiles of D, Li, Pd, Si, and Al are illustrated in Fig.1 and Fig.2. The profiles with bold line represent the depth profiles of each elements obtained from the Pd sample with the nuclear effect of neutron emission and excess heat generation, the medium line for Pd sample with only neutron emission, and the chain-line for Pd sample with no nuclear effect. The curves shown in these figures are normarized to the secondary ion intensity of Pd obtained in each analysis run to carry out the discussion on the concentrations on the same elements. Evidently from the figures, the depth profiles of the elements with no nuclear effects are monotonous as expected from the electrochemical point of view. (2)While, the depth profiles with some nuclear effects have some of irregular structures, especially in the surface within 2 μ m for every element. The depth profiles of lithium and deuterium are very similar in each. This fact indicates that there is a very strong chemical relation between the lithium behavior and the deuterium behavior as discussed in the previous paper.

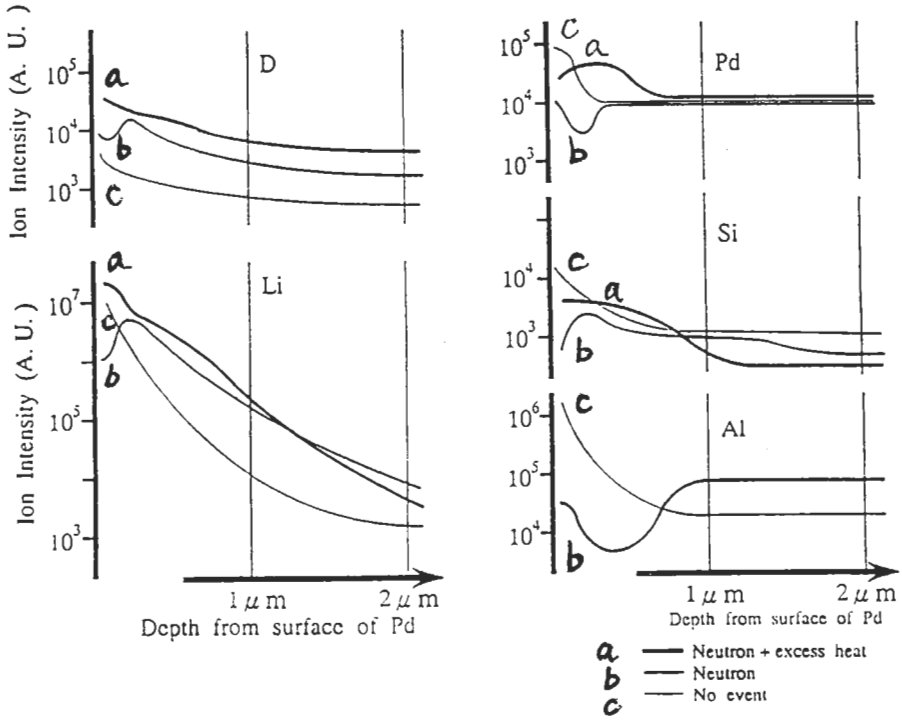

Fig.1 Examples of Depth Profiles for Each Element

The depth profiles of the deuterium are very interesting not only in the structures but also in the concentrations. The deuterium absorbed into the Pd by the electric force releases easily to the solution phase when the force is off. The sample Pd plates were stocked for more than one week or for three months till the element analysis by SIMS, in the present study. The SIMS analysis gave us only the traces of deuterium accumulation like an archeology. Even so, the significantly large amount of deuterium remained in the surface area of the sample Pd. From this consideration, it can be concluded that the more deuterium had been accumulated when the electrolysis was carried on. The anomalous accumulation of the deuterium should be recognized to have an important correlation to the occurrence of the nuclear effects.

Accumulation process of deuterium

As shown schematically in Fig.3, the cell voltage increased with the increase of the H/L pulse cycle in the present constant current operation. This indicates that the electric resistance of the Pd electrode increased in the way of the electrolysis. We have a hypothesis based on the chemistry of Pd-Li intermetallic compounds and Pd-Li-D compound reported by O.Loebich and J. Raub, and by B.Nacken and W. Bronger, respectively.(3,4) The hypothesis is that by the electrolysis of the D_2O-LiOD solution lithium also migrates into tne metallic Pd and formes the very stable intermetallic compounds, so the electric resistance of Pd surface increases, resulting the increase of the cell voltage. As illustrated in Fig.4, the intermetallic compound layer works as the barrier for the back migration of the deuterium when the current density is reduced from the high mode to the low mode. The depth profiles at the equilibrium state of the high mode operation and low mode operation can be illustrated as shown in the lefthand side of Fig.5. When the operation mode changed from the high mode to the low mode, the equilibrium depth plofile of the high mode should be changed to the low mode operation by the back migration of the deuterium. However, the intermetallic compound layer works as the barrier the amount of the deuterium corresponded to the shaded area in the high mode operation retaines at the righthand side of the intermetallic compound layer as illustrated in Fig.5. The next high mode operation starts with this depth profile. The repeating of the high mode and the low mode operations, the layer of the intermetallic compound becomes thicker and the concentration of the deuterium increases with increase of the cycle number of the high and low mode operation. The concentraitons observed [archeologically] in the above Pd electrodes with the nuclear effects are higher almost one order than that of no nuclear effect. It can be concluded that the present high and low mode operation enables us to provide an

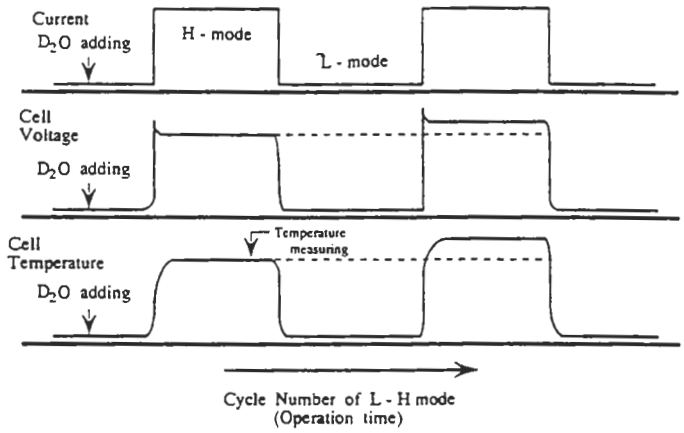

Fig.3 Schemes of Electrolysis

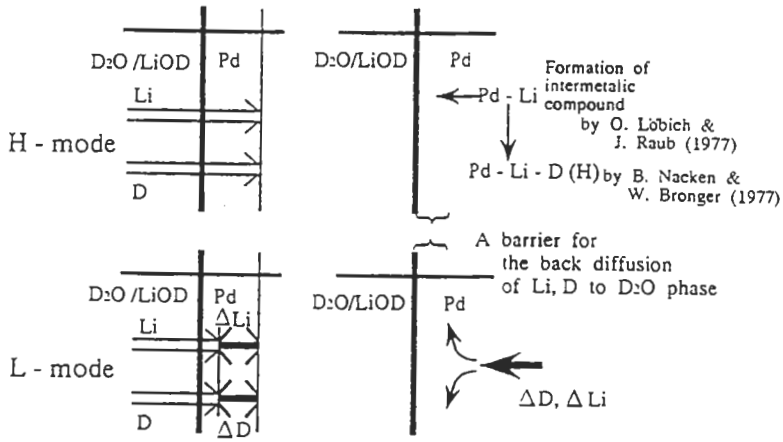

Fig.4 Role of Metallic Layer

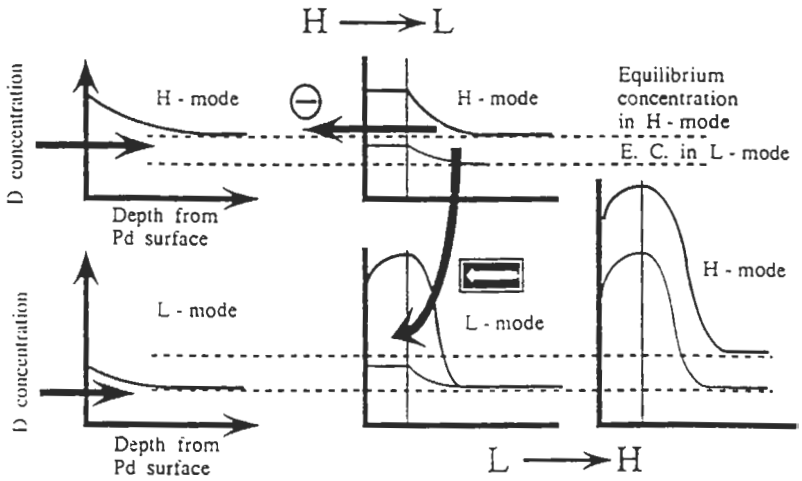

Fig.5 Model of D Accumulation Process

anomalously high density zone of the deuterium in Pd electrode occasionally. The depth profiles of Si and Al have the irregular structures but just reversal each other. When these elements coexist, Al can be excluded by Si which formes more stable intermetallic compound with Pd. The profiles are the trace of the above chemistry.

The irregular structures of Si and Al were observed only in the Pd electrode with the neutron emission and the excess heat generation(Run No.3). These two elements seems to have some key roles to the occurrence of the nuclear effects in D_2O electrolysis through the anomalous accumulation of deuterium.

The excess heat evaluation

In the present high and low mode operation, the electrical resistance of the Pd electrode increases with the increase of the number of the pulse mode cycles. The calibration of the cell temperature as a function of the input power should be changed along with the electrolysis operation, unlikely discussed by Mizuno and Takahashi et al.(5,6) The excess heat has been evaluated from the upper deviation of the cell temperatures from the calibration curve obtained before the full-operation of the electrolysis or by use of inert metal electrodes. When the cell temperature depends on the cycle number of the high and low mode operation as mentioned above, the calibration should not be the same before and after the full-operation of the electrolysis. A typical example of the dependency is illustrated in Fig.6 along with the cell voltage dependency on the input power. The calibration curve obtained after the full-operation should deviate upward because of the increase of the electrical resistance of the Pd electrode in the high and low mode of electrolysis . We have confirmed this in our electrolysis cell equipped an excess heat monitoring system. In Fig.7, a couple of typical examples of calibration curves before and after the operation are shown as a function of the input power. An upward diviation is observed in the calibration curve after the electrolysis as expected above. In this case, the upward deviation of the cell temperature of $\sim 0.2^{\circ}C$ from the calibration curve before the full-electrolysis can not be concluded as the excess heat generation. Based on the fact, for the evaluation of the excess heat in the present open system, the calibration curves should be obtained at least two times, before and after the full operation. In the excess heat evaluation from the present cell temperature measurement, a linear function was introduced as a corrected calibration curve by connecting the last point of the calibration curve after the full-operation and the first point of the calibration curve before the full-operation. The plots of the cell temperature are shown in Fig.8. These cell temperatures are average values obtained from the three thermocouples placed around the electrodes as described in other paper by

the present authors in this proceedings. In this electrolysis, it can be said that we detected the excess heat clearly, but the feature of the excess heat generation is not continuous unlikely to the previous report.

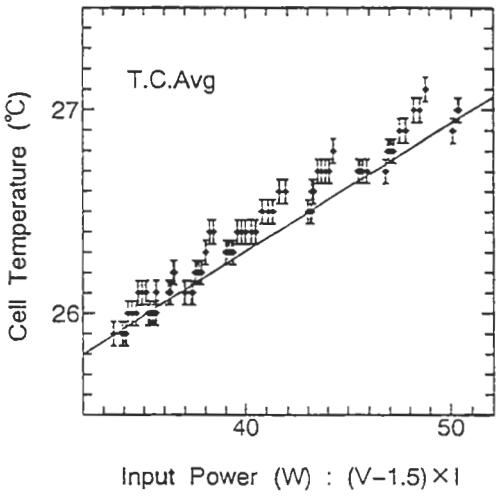

Fig.6 Typical Example Plots of Excess Heat Evaluation

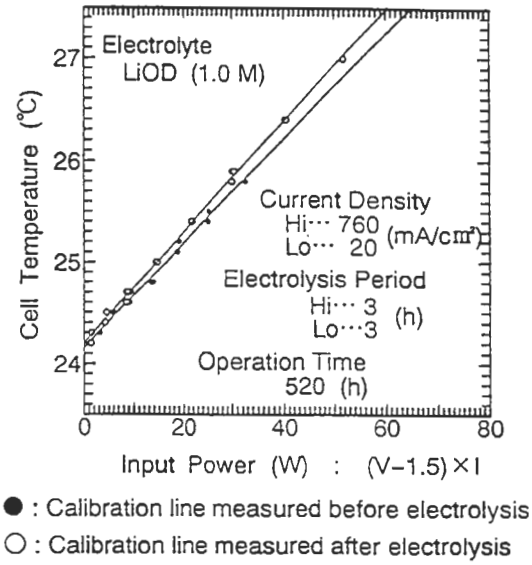

Fig.7 A Couple of Calibration Curves

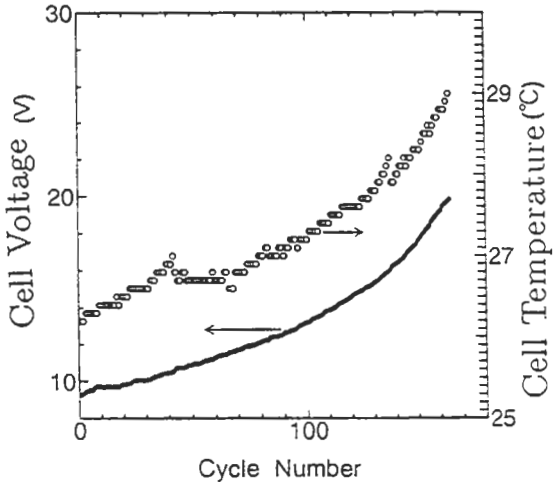

Fig.8 Cell Voltage and Cell Temperature vs. Input Power

Conclusion

Based on the SIMS analysis data, the anomalous deuterium accumulation in the surface area of the Pd electrodes which gave the nuclear effects including the excess heat generation has been confirmed and the deuterium concentration was

found to be in the sequence of

Pd with the excess neutron emission with the excess heat generation

∨

Pd with the excess neutron emission

∨

Pd with no nuclear effect.

The process of the anomalous accumulation of deuterium was discussed based on the formation of the Pd-Li intermerallic compound in the surface area of Pd electrode. According to the formation of the intermetallic compound, the electric resistance of the Pd electrode increases, the calibration curve for the evaluation of the excess heat in the open cell system should be obtained not only before the full-operation but also after the full operation. The calibration curves obtained by use of inert metals as the electrodes give an over estimation of the excess heat, because, even if they form some intermatallic commpounds, the electric resistance by the formation may be smaller than the case of Pd. For further quantitative discussion of deuterium based on nuclear phenomane in the solid state, the absolute concetration of the deuterium should be determined in real time and the evidences attributed to the nuclear phenomena also should be detected in real time with the excess heat monitoring.

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