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THE ROLE OF ALKALINE IONS IN DYNAMIC MOVEMENT OF HYDROGEN ISOTOPES IN Pd

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Abstract

Electrolysis in Pd-LiOD(H), NaOD(H) and KOD(H) systems was carried out to clarify the specific role of the lithium for tremendously high density and the dynamic movement of the deuterium on the surface of the Pd cathode. Only for LiOD system with pulse mode current electrolysis, anomalous high density of deuterium and lithium and the dynamic movement of deuterium are observed on the surface of the Pd cathode. A clear difference in absorption, desorption and depth profiles between LiOD(H) and NaOD(H) or KOD(H) system with the pulse mode current electrolysis is identified. This difference is attributed to the lithium accumulation structure on the Pd surface; only the pulse mode current electrolysis of Pd-LiOD system brings about the anomalous phenomena.

Introduction

The tremendously high density of deuterium and its dynamic movement have been discussed as some of the key factors of the deuterium based nuclear phenomena in condensed phase which have been reported by us [1] and SRI. [2] Three key points have been found necessary to produce anomalous nuclear phenomena: [3][4][5]

1. Low-High pulse mode current density (800-20mA/cm^2).
2. A 3-hour repetition time, which is enough to attain the equilibrium in the Pd bulk phase.
3. Lithium as the electrolyte.

The high density accumulations of deuterium and the lithium are not observed with the constant current electrolysis. The lithium ion is the smallest of the alkaline ions which can easily be absorbed in the Pd bulk phase and accumulated on the Pd surface. Lithium also generates the particular intermetallic compounds with Pd and D (H), as the Pd-Li-D(H) structure. The experimental conditions (except for the operation time) are just as same as our series of electrolysis experiments which gave anomalous deuterium based nuclear effects in Pd-Li-D. To realize the dynamic movement and the high density deuterium accumulation of deuterium based on the nuclear phenomena, the present series of experiment was carried out.

In the present study, the alkaline ions are used as the electrolyte. The loading ratio transition of absorption and desorption has been measured to clarify the roles of the lithium by comparing the data of the alkaline ions. The depth profiles analysis of the hydrogen isotopes and the alkaline ions has also been done by means of Secondary Ion Mass Spectrometer (SIMS) and Elastic Resonance Detection Analysis (ERDA).

Experimental

The same two sets of the experimental systems have been modified to perform separate operations. The electric resistance was measured using the milliohm meter (Hewlett Packard PH4338A) described in our previous report. [1] The electrolyte volume in the electrolysis cell has been kept to be 400ml employing the electrolyte level adjustment system. The configurations of the electrode and the electrolysis cell were also reported in our previous paper[1]. The size of the Pd electrode was 25mm × 10mm × 1mm. The Pd plates were polished mechanically and the Pd plates and the Pt wire were annealed at 850°C for 10 hours before electrolysis was started. Electrolysis was performed for 2 days. The concentration of the electrolyte was 1 mol/l in all cases. Two electrolysis modes, the constant current mode and the pulse current mode, have been adopted. The current density of the constant current was 800mA/cm^2 and those of the pulse mode were 800mA/cm^2 in the high mode and 20mA/cm^2 in the low mode, with 3 hours repetition in a square pulse. The loading ratios have been evaluated by use of the calibration curves reported by Kunimatsu et al[6], which is the same as our previous report. [1]

After finishing electrolysis, the Pd cathode was installed in the quartz glass holder. The amount of the hydrogen absorbed by the electrolysis was measured using the Gas Pressure Measurement System, which is illustrated in Fig. 4. The Gas Pressure Measurement System was evacuated before installing the Pd samples.

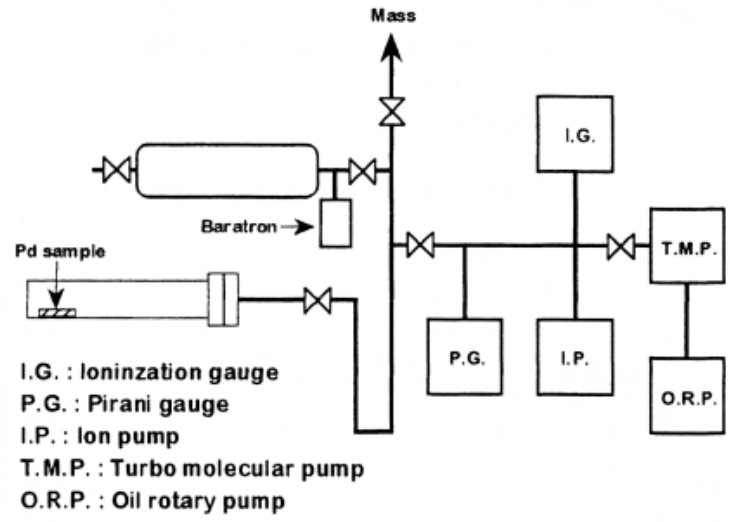

Figure 1. Gas pressure measurement system

The pressure data was acquired by a personal computer every thirty minutes for 2 days. After measuring of the pressure distribution for 2 days, the Pd plate has been annealed at 850°C for 15 minutes to measure the total amount of the absorbed hydrogen isotopes.

The depth profiles of the alkaline ions was analyzed using the Secondary Ion Mass Spectrometry (SIMS) (CAMECA Co. Ltd., France, IMS-4f). The O_2^+ ions have been employed as the primary ions and irradiated to the surface of the samples. The depth profiles of the hydrogen isotopes have also been examined by means of the Elastic Resonance Detection Analysis (ERDA).

Results and discussion

Dynamic movement of the hydrogen isotopes

The loading ratios using LiOD(H), NaOD(H) and KOD(H) electrolytes with the constant current electrolysis are shown in Fig. 2. The loading ratios obtained in the deuterium based systems are smaller than those obtained in hydrogen based systems. In constant current electrolysis, the loading ratio of hydrogen system is about 0.9 and that of deuterium system is about 0.8. This is a well-known hydrogen isotope effect. Fig. 3 shows the loading ratio with the pulse mode current electrolysis. The loading ratio achieved using LiOH with the pulse mode electrolysis is almost 0.9 and is higher than those of NaOH and KOH in the initial step. The absorption rates have been calculated from the initial slopes of each loading ratio with constant current electrolysis. There is no remarkable difference in the absorption rate in the hydrogen isotopes. Looking at the pulse mode current electrolysis, a loading ratio with deuterium of about 0.85 can be achieved. The loading ratios the pulse mode current electrolysis can acquire are higher than those of the constant current electrolysis, indicating that dynamic movement could be realized by the present pulse mode current electrolysis.

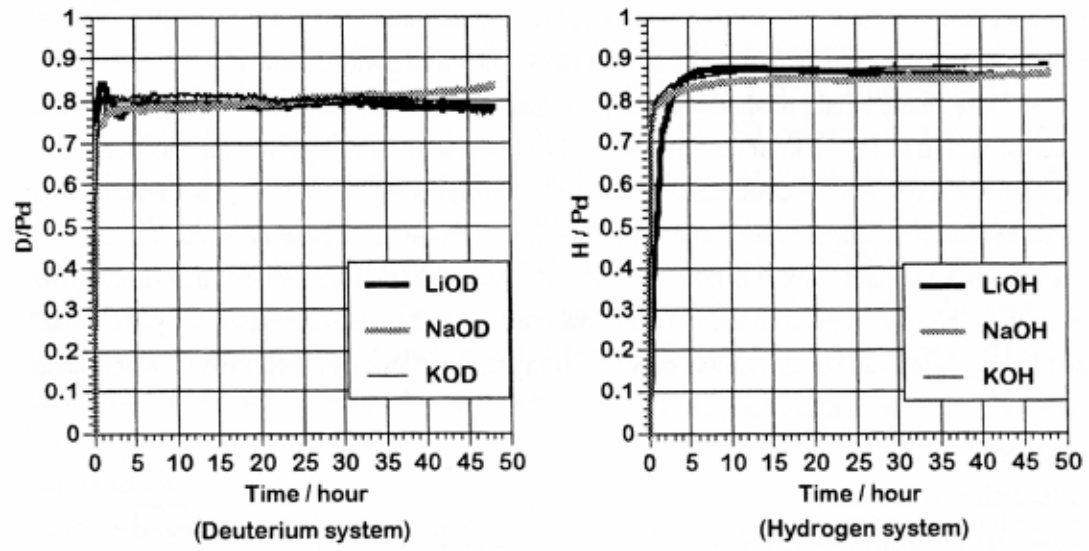

Figure 2. The loading ratio transition with constant current electrolysis

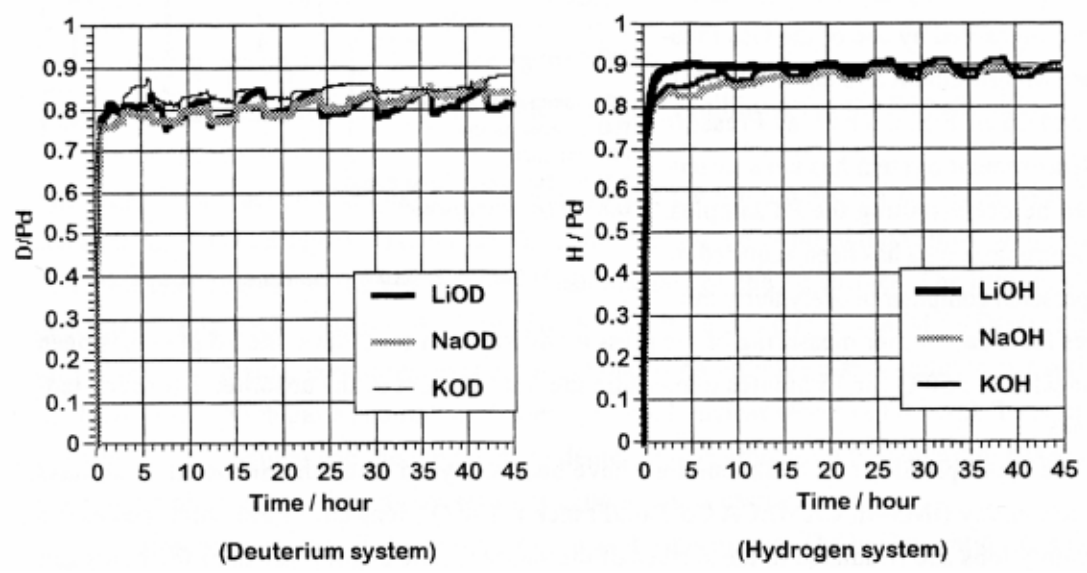

Figure 3. The loading ratio transition with pulse mode current electrolysis

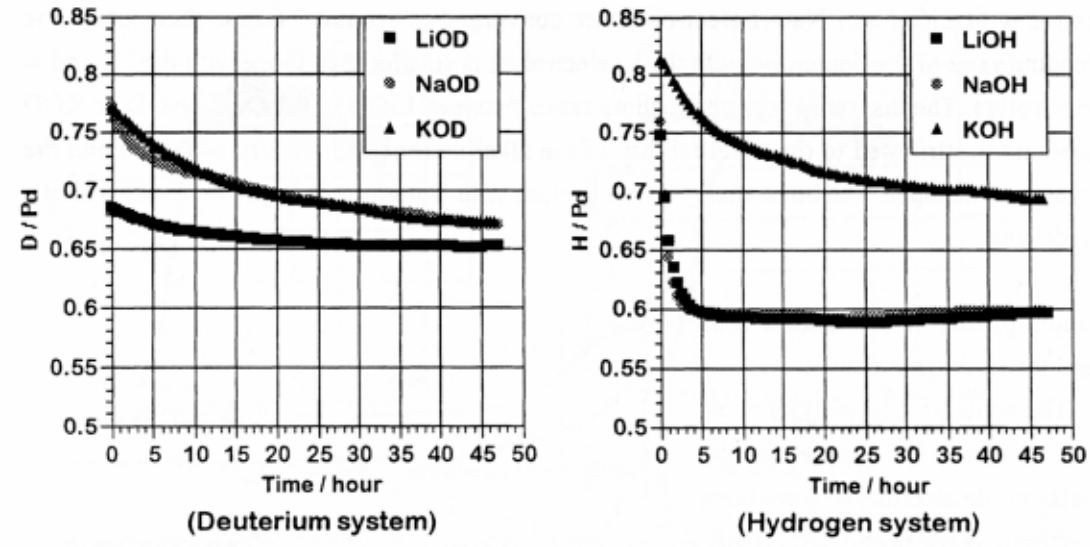

Figure 4. The loading ratio transition after constant current electrolysis

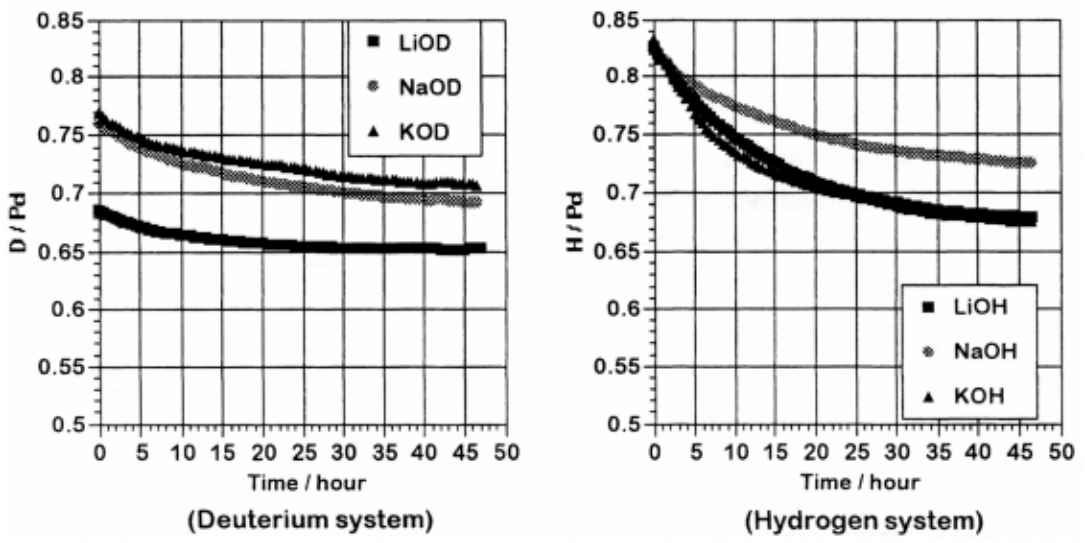

Figure 5. The loading ratio transition after pulse mode electrolysis

The loading ratio of the hydrogen isotopes after constant current electrolysis are shown in Fig. 4 and 5, respectively. In the constant current electrolysis system, the loading ratios with LiOH and NaOH electrolyte converged to around 0.6 in a short time. The loading ratio of the deuterium with the Li electrolyte is smaller than those with the Na and K electrolyte. The discrepancy of the loading ratios between LiOD system and NaOD or KOD systems is attributed to the absorbability of the alkaline ions and affinity of the Pd and the hydrogen isotopes. The bond energy of the lithium with deuterium is larger than that with the hydrogen.

Depth profile of the alkaline ions and the hydrogen isotopes

As depth profile analysis of alkaline ions in Pd samples for the pulse mode electrolysis were performed with SIMS. Fig. 6 and 7 show the depth profiles of the alkaline ions in Pd samples with LiOD(H), NaOD(H) and KOD(H) electrolysis, respectively. Comparing these three profiles of the alkaline ions, the tendency of the lithium curve is clearly different from those of sodium and potassium curve. Only lithium ions appear to accumulate on the near surface area (~1 μm) of the Pd samples.

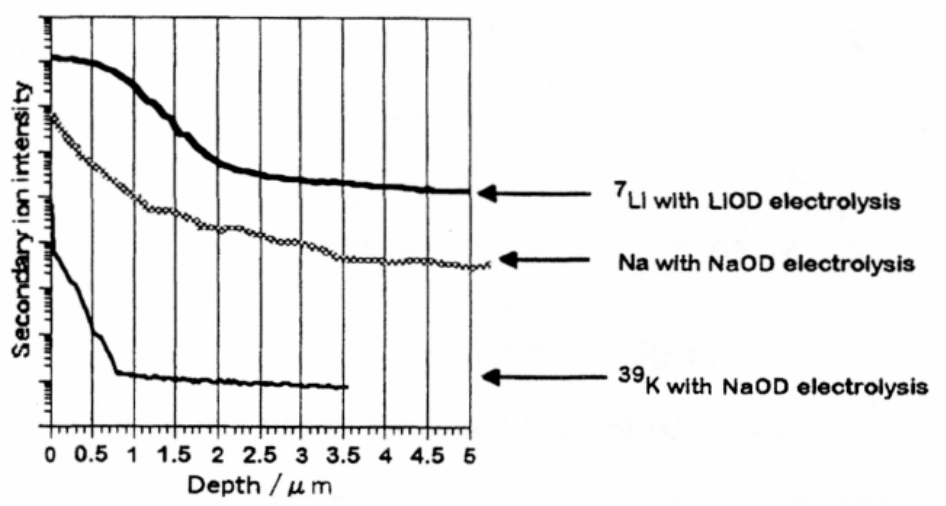

Figure 6. The depth profile of alkaline ions in electrolysis (deuterium based system)

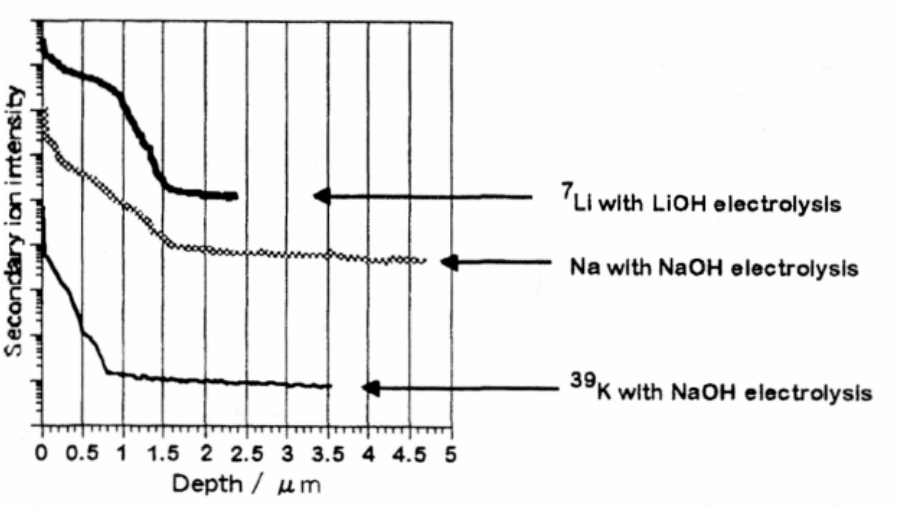

Figure 7. The depth profile of alkaline ions in electrolysis (hydrogen based system)

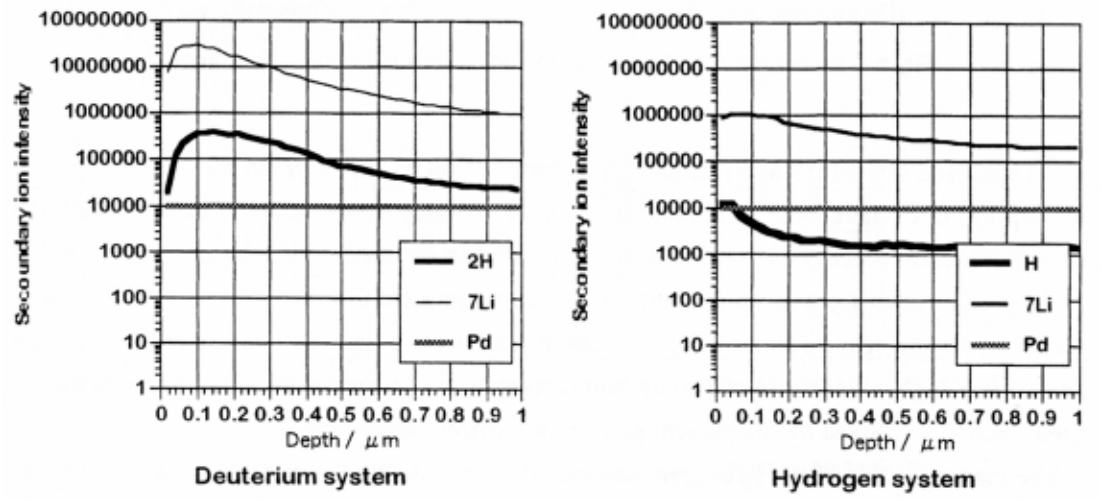

Figure 8. The depth profile of the elements in the Pd surface

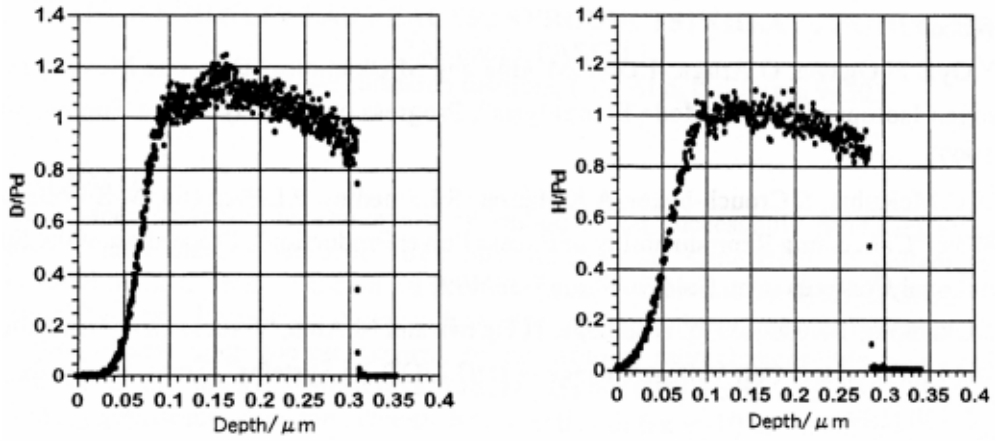

Figure 9. The depth profile of hydrogen isotopes by ERDA

In the lithium system, the deuterium ions also accumulate in the Pd surface, as shown in Fig. 8. The amount of the hydrogen absorbed is not so large compared to that of the deuterium.

To determine the absolute quantity of the hydrogen isotopes in the Pd surface, the ERDA technique was applied. The depth profiles of the hydrogen isotopes in Pd surface using LiOD(H) by ERDA are shown in Fig. 9. The loading ratios of LiOD and LiOH electrolysis reach 1.1 and 1 on the Pd surface, respectively. The total loading ratio of the hydrogen isotopes determined by the electroresistance measurement is around 0.85. The loading ratio is also converged to 0.6 for 2 days after the electrolysis. These facts indicate that the loading ratios of the Pd surface are higher than those of the Pd bulk and the accumulations of the hydrogen isotopes are clearly confirmed.

Conclusion

The electrolysis of the constant and the pulse mode current has been performed with three electrolyte solutions: Pd-LiOD(H), NaOD(H), and KOD(H). The depth profiles of the alkaline ions as well as those of the hydrogen isotopes near the surface of the Pd electrode have been measured and analyzed using the SIMS and ERDA techniques. Only for the Pd-LiOD experiment carried out by the pulse mode current electrolysis, we have observed that the lithium ions and the hydrogen isotopes, especially the deuterium, are accumulated markedly on or near the Pd surface. It is concluded that the three-element Pd-Li-D system appears to be an extremely interesting combination initiating the anomalous phenomena in dynamic electrochemistry.

Acknowledgments

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