Mass Spectroscopic Search for Helium in Effluent Gas and Palladium Cathodes of D₂O Electrolysis Cells Involving Excess Power

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Abstract
A heat burst equivalent to 360W per 1cm³ of Pd was observed in an open type electrolysis cell using Pd/0.1MLiOD/Pt. It happened, however, only once in all 5 cells ever tested. Although boiling has occurred many times in all cells, no direct correlation has been found between boiling and ⁴He production. By reducing the gas flow rate and properly adjusting the pressure gradient, the quantitative analysis of ⁴He could be realized in our Q-mass system with high detection sensitivity (17ppt) in continuous-flow mode and with high resolution in store mode. Two types of closed vacuum furnace were used to degas the Pd samples. An external-heater-type allowed permeation of ⁴He and H from air when heated above 1000°C. An internal-heater-type, on the other hand, enabled us to heat up the sample at 1200°C without any permeation. No traces of ⁴He were, however, detected probably due to one of three possible reasons: 1)There have been no ⁴He in the Pd sample from the beginning. 2)⁴He was degassed away during the 1st heating at 770°C, but could not be detected due to the then insufficient sensitivity. 3)⁴He still exists in the Pd lattice, but cannot migrate nor diffuse even at 1200°C, forming many trapped tiny bubbles.

1. Introduction
The low intensity of neutron and the small enrichment of tritium in cold fusion experiments have prompted proposals of nuclear processes that yield only heat and helium as products [1, 2]. Determination of the presence or the absence of ⁴He as a nuclear product became very essential. Until now we clearly observed a large heat burst equivalent to 110% of the input electric power in an electrolysis cell labeled "VI05(941016)". The cell was an open type using Pd/0.1MLiOD/Pt. The excess heat of 6.3W continued for 13min. It amounts to 360W per 1cm³ of palladium bulk. Neither increase of neutron emission nor that of tritium content in the cell was observed in this case [3].

The electrochemical cell used was a vacuum-insulated open type dewar that was made of Pyrex® glass and PTFE. Palladium cathode (99.80% pure, Johnson Matthey) was screwed together with 1mm Ø platinum wire and fixed in the center of the cell. Pt anode (1mmØ x 3m) was symmetrically wound around the cathode. Dimension, mass and surface area of the Pd cathode were 2mmØ x 7.05mm, 0.227g and 0.435cm², respectively. It was annealed in vacuo up to about 800°C and charged with D in the furnace just before installed in the cell.
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Observation through microscope revealed that Pt as well as Pd, near their interface in particular, had been seriously eroded. The Pyrex® glass was found to be cracked near the end of the cathode due to heat, which probably stopped the reaction. The heat of combustion (232J), the heat of absorption (16J) and any other chemical reaction can never account for the excess enthalpy of 53005 that comes from 6.8W lasting for 13min. If the nuclear reactions were assumed as: 1) \( \text{D} + \text{D} \rightarrow \text{He} + \gamma \) (23.8MeV), 2) \( \text{D} + \text{D} + \text{D} \rightarrow \text{He} + \gamma \) (23.8MeV), the number of nuclear products should be \( 2.62 \times 10^{11} \text{ s}^{-1} \) per Watt, that is, totally \( 1.39 \times 10^{15} \) in case of the heat excess of the VI05(941016) cell. It is very clear that the measurement of \( ^{4}\text{He} \) should be accomplished coincidentally with the heat burst as we observed.

2. Mass Spectroscopy System

A mass spectroscopy system was thus built to meet this special demand. Effluent gas during electrolysis as well as electrically charged solid palladium samples can be analyzed with high sensitivity and sufficiently good resolving power [4]. Three difficulties are met with, however, in this case: 1) Mass difference between \(^{4}\text{He} \) (4.0026031 amu) and \(^{2}\text{He} \) (4.0282044 amu) is very small (0.0256013 amu). 2) A large amount of \(^{2}\text{He} \) always exists as a background in both gas and solid phase samples. 3) System is very easy to be contaminated with \(^{4}\text{He} \) from other sources like laboratory air (5.24ppm). Special care should be taken to get reliable data by preparing elaborate gas collecting and analyzing systems. Shown in Figure 1 is the schematic drawing of our mass analyzer system.

The vacuum system is composed of three chambers separated by three manually operated gate valves (GV). The whole system can be evacuated by a main turbomolecular pump (TMP:500l/s) as well as by a modified cryopump (CP) at the top. The Q-mass and the cryopump (CP) chambers are usually separated by a CP-GV, but are bridged with two parallel non-evaporable getter (NEG) pump lines and one bypass line. Two NEG pumps (SAES: GP50-W2F installed with C50-ST101) can be used alternately, while the bypass line is opened only when the \(^{2}\text{He} \) signal is necessary for calibration. Pressures in the Q-mass and the CP chambers are measured with a Bayard-Alpert gauge (BA-G) and a cold cathode gauge (CC-G), respectively.

Two types of Q-mass analyzer are used in the Q-mass chamber: a high resolution type (ULVAC: HIRE SOM-2SM) and a high sensitivity type (Baklers: QMG112A). Tuning is fixed to mass 4 \( M/Z \) in the former, while that in the latter is adjusted in the range of 1-22 \( M/Z \) to monitor the change of gas balance of hydrogen, helium, carbon, water and neon. The differential evacuation is ensured by shutting off the CP-GV and an auxiliary bypass GV. The highest sensitivity can be obtained by putting the main GV in almost close position. As the charcoal absorber is removed from the cryo-panel, our CP has zero pumping speed for noble gases like \(^{3}\text{He}, ^{4}\text{He} \) and Ar. It keeps, however,
a large pumping speed for N₂, O₂ and for water in particular. The NEG pump has, on the other hand, a great pumping effect for hydrogen family. By passing the sample gas through this CP-NEG combined filter we can thus remarkably enrich helium content, if any.

To check the performance, a standard mixture of ⁴He (48.6%) and D₂ (51.4%) was prepared. First both signals were obtained by bypassing the NEG filter. Second one NEG pump line was opened with the CP-GV closed, and the same gas was introduced. The peak ratio \( \frac{I(⁴He)}{I(D₂)} \) was enhanced from \( 1.45 \times 10^{-9}A/4.55 \times 10^{-9}A = 0.319 \) to \( 3.65 \times 10^{-9}A/1.0 \times 10^{-11}A = 365 \) by virtue of a CP-NEG combined filter. An enhancement factor amounts to 1145. On the other hand, according to a factory test [5], the abundance sensitivity of ⁴He with respect to D₂ is over 50000, which means in this system we can distinguish 17 ppb of ⁴He from D₂ [4].

3. Improvement of Sensitivity

QMG112A is about a thousand times more sensitive to mass 4 M/Z than HIRESOM-2SM, although a resolution is insufficient to separate ⁴He and D₂ signal peaks. As the NEG filter works well to remove the hydrogen gas family (H, D, H₂, HD, T, HT, D₂, DDH, DT and T₂), it can, however, be used to detect a residue of ³He and ⁴He, in continuous-flow mode (See Fig.2(a)).

As shown in Fig. 1, we added needle valves in the NEG filter lines, forming a small but significant modifications to the system originally reported elsewhere [4]. Those needle valves are quantitatively controllable with micrometers. If they are throttled, the flow rate is reduced and the filtering efficiency is very much improved. Escaping probabilities of hydrogen gas family can be, therefore, far more suppressed. Shown in Fig 3 are the signal heights of the high resolution Q-mass versus the entrance pressure measured with CC-G in continuous-flow mode. By using the standard gas, both signals

![Figure 2. Schematic drawing of flow of sample gas. (a) Continuous-flow mode. NEG needle throttled and GV throttled. Pₐₓ-G is kept below Pₘ₋ₐₑ₋₉. and (b) Store mode. NEG needle throttled and GV almost closed. Pₐₓ-G is kept below 10⁻²Pa. Pₐₓ-G can become higher than Pₘ₋ₐₑ₋₉.](image-url)
can be obtained in (a) when the NEG bypass is opened, while D₂ signals are almost completely suppressed in (b) by virtue of the improved NEG filter.

\[ \text{D₂ : } ^4\text{He} = 1 : 1 \text{ by volume} \]

Figure 3. Signal heights of the high resolution Q-mass, HIRESOM-2SM, versus the entrance pressure measured with CC-G.

For comparison, the signal heights of the high sensitivity Q-mass under the same conditions are illustrated in Fig.4 with respect to CC-G pressure. As for M/Z 4, a similar straight line can be obtained over current range extending on three orders of magnitude higher level than that for the high resolution Q-mass. As shown in Fig.3(b) it is now clear that these M/Z 4 signals can be entirely attributed to \(^4\text{He}\). This means that, in combination with the NEG and NEG needle valves, the high sensitivity Q-mass provides a detection sensitivity for \(^4\text{He}\) a thousand times as high as that for the high resolution type. We can expect to distinguish a much smaller amount, only about 17ppb \( \times 10^{-3} = 17\text{ppt} \), of \(^4\text{He}\) from D₂. When high mass resolution is required as in case of calibration, the high resolution type can of course be used in store mode, almost closing the main GV, as shown in Fig.2(b).

4. Helium in Effluent Gas?

Preliminarily \(^4\text{He}\) was observed in the effluent gas collected after the heat burst phenomenon. The detection was, however, not 100% sure due to the possible contamination through PTFE from air [3]. To make it clearer, improvements were made in the gas sampling system as shown in Fig.5 and a new series of electrolysis was started. All PTFE tubing, cocks and glass bottles with plastic caps were replaced by stainless steel flexible hoses, bellow valves, and all-metal or glass-metal combined vessels with Kovar-glass seals. Before use every component was helium leak tested and connected with VCR\(^\circledR\) joints using nickel gaskets. PTFE and Viton\(^\circledR\) O rings were only left in a
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tee piece, a cock in D2O feeding line and a double flange of the dewar. On the downstream of the 2nd bubbler, two parallel branches were prepared, consisting of several metal valves, one metal vessel about 130ml in volume and a 3rd bubbler. Before use air in each branch was purged with >99.9999% pure nitrogen. Each line can be used alternately to ensure successive batch sampling of the effluent gas.

A very small residue of 4He can still be detected with our high sensitivity Q-mass system probably due to the contamination from air caused by limited use of PTFE and Viton® as well as by prolonged electrolysis period. Our target is, however, to detect a large amount of 4He coincidentally. No direct correlation between boiling and 4He has been found so far. Another heat burst phenomenon is now being expected to make decisive conclusions.

5. Helium in Palladium Cathode Samples?
Soon after the excess heat burst, the Pd cathode sample of the V105(941016) cell was degassed up to 770°C in a closed vacuum furnace. Then the extruded gas was analyzed in the Q-mass system. No trace of 4He could be, however, detected in that sample as reported before [3], partly due to the insufficient sensitivity of the old system and the old way of Q-mass analysis. Whether 4He would be extruded from this Pd sample or not, if it were heated up at much higher temperature, aroused our great interest recently [6].

Experiment was first performed, using an external-heater-type furnace, on another Pd sample that showed boiling several times. The sample was pinched off in a small SUS316 vessel with pure nitrogen gas of 1atm. The vessel was then set in a furnace and connected to a pre-evacuated buffer tank. Furnace temperature was increased up to 1180°C. Results of heat processing with this furnace are summarized in Table I.

The difference of starting pressure is due to volume difference of vessels as well as of buffer tanks used. Pressure minimum observed during heat processing in one of the blank experiments was probably caused by nitriding of inner surface of SUS316. Formation of ammonium radicals might promote this reaction that must be very sensitive to temperature and gas pressure of N2 and H2. Above 1000°C pressure began to increase and large amount of 4He was surely observed in the extruded gas.

![Figure 5. Newly improved gas sampling system.](image)

<table>
<thead>
<tr>
<th>Table I. Summary of heat processing with external-heater-type furnaces</th>
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<tbody>
<tr>
<td><strong>Sample</strong></td>
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<tr>
<td><strong>Type of Furnace</strong></td>
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<tr>
<td><strong>Carrier Gas</strong></td>
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<tr>
<td><strong>Temperature</strong></td>
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<tr>
<td><strong>Before heat processing</strong></td>
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<tr>
<td><strong>Pressure during h.p.</strong></td>
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<td><strong>After heat processing</strong></td>
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ICCF-6 October 13-18, 1996 Japan
The pressure increase, however, could be mostly attributed to permeation of hydrogen from moisture in air through furnace body made of stainless steel (SUS316). 4He itself could also be attributed to this permeation.

According to a literature [7], activation energy for helium migration is estimated to be very large, \((2.06 \pm 0.08)\) eV, for the AISI316 steel (SUS316). Due to the high temperature, however, the SUS316 steel became unstable and changed its structure and properties. Presence of He in it can also induce helium embrittlement. 4He and H could thus penetrate the wall (See Fig.G(a)). Palladium treated in this furnace showed an interesting faceting structure. Ablation of Pd could be observed, too (See Fig.9(a)).

![Diagram](image)

**Figure 6.** Improvements in heat processing. (a) External-heater-type furnace with N2 as a carrier gas. Although H2 content in air is one order of magnitude smaller than He, H can be made by dissociation of H2O from moisture in air. Nitriding of SUS can be realized by ammonium radicals formed by N and H at high temperatures. (b) Internal-heater-type furnace with Ar as a carrier gas. Wall temperature of SUS can be kept low by several layers of heat shields.

To prevent contamination by 4He and H from air, improvements have been made in heat processing apparatus. External heater was changed to internal heater made of tungsten that was surrounded by several layers of heat shields. The sample was contained in a ceramic crucible placed in a spiral-shaped W heater. As a carrier gas, \(99.9999\%\) pure Ar was used instead of pure N2. Nitriding of tungsten heater can be thus avoided even during heat process lasting for about 24h. Before use every component in hot area including crucible was degassed in vacuo by using another conventional vacuum furnace.

6. **Experimental Results and Discussions**

Signal heights of the high sensitivity Q-mass, QMG112A, versus CC-G pressure are illustrated in Fig.8 semi-logarithmically. First a blank experiment was
performed by heating up the furnace, installed with a vacant crucible, up to 1200°C for 24h (6). Second the Pd/Pt cathode sample of VI05(941016) cell was loaded in and heated up under the same conditions. Q-mass analysis has been done twice consecutively (2 and 3). Lastly the carrier Ar gas itself was analyzed after being prepared in the same manner but without heat processed (6). Repeated run in 2 presents smaller signal heights only due to the gas consumption. No significant difference is seen in the data except 3. We can thus conclude that no 4He could be detected in the gas sample extruded from the cathode of VI05(941016) cell.

In a non-defective lattice, if helium is trapped at an interstitial site, the transport will be controlled by the activation energy for migration between interstitial sites. Although we could not find the very data just on He in Pd, the barrier for this process is generally very high. For example, in case of Ni (fcc), W (bcc) and Mo (bcc), the activation energy for migration of interstitial He and the activation energy for dissociation of He out of a vacancy are 0.1, 2.2 eV; 0.3, 4.2 eV; and 0.2, 3.0 eV, respectively [8]. The significance of such a high value is that migration of He in this manner will be slow even at elevated temperatures.

According to literature [8, 9], helium in metals precipitates into bubbles due to its insolubility. It means that there is a possibility that 1200°C for 24h is still insufficient for degassing He out of our Pd cathode samples. Microscopic view of the sample that was heat-processed in the internal-heater-type furnace shows clearly a 120° grain growth of Pd and something like tiny bubbles in each grain (See Fig. 9(b)).

![Figure 9](image)

**Figure 9.** Pd heat processed (a) in N2 by external-heater-type furnace and (b) in Ar by internal-heater-type furnace.

**7. Conclusion**

A heat burst equivalent to 110% of the input was observed in an open type electrolysis cell using Pd/0.1M LiOD/Pt. It happened, however, only once in all 5 cells ever tested and seems very difficult to be reproduced. Although boiling has occurred many times in all cells, mainly caused by build-up of cell...
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Voltage in constant current mode, no direct correlation has been found so far between boiling and \(^4\)He production.

By reducing the gas flow rate through the NEG filter, the detection sensitivity for \(^4\)He could be a thousand times increased. By properly adjusting the pressure gradient, the quantitative analysis of \(^4\)He could be realized with high detection sensitivity (17ppt) in continuous-flow mode and with high resolution in store mode.

Two types of closed vacuum furnace were used to degas the Pd samples. In case of an external-heater-type using SUS316 body, analysis proved to be difficult owing to permeation of \(^4\)He and H, as well as material instability of SUS316 when the furnace was heated above 1000°C up to 1180°C.

In case of an internal-heater-type, heat processing at 1200°C proved to be possible. No traces of \(^4\)He were found in Pd cathode samples showing several times of boiling or involving the heat burst. As the latter sample was once degassed up to 770°C and analyzed with less sensitivity before, three possibilities can be conjectured: 1) There have been no \(^4\)He in the Pd sample from the beginning, 2) \(^4\)He was degassed away during the 1st heating at 770°C, but could not be detected due to the then insufficient sensitivity, 3) \(^4\)He exists in the Pd sample, but cannot move nor diffuse even at 1200°C by forming trapped tiny bubbles in the Pd lattice.

To make it clearer a parallel study of \(^4\)He in Pd is now being prepared by ion implantation technique. Another option is of course to process the Pd sample again at much higher temperatures above 1200°C. Anyway to determine the presence or absence of \(^4\)He as a nuclear product in effluent gas and/or palladium cathode, it becomes far more essential to reproduce the another excess heat burst as clearly observed before [3].

**Acknowledgements**

Continuing encouragement of Professors H. Sugawara, Y. Kimura and K. Takata are gratefully acknowledged. Thanks are also due to E. Komoda of Hakuto Co. Ltd. for kindly lending a high-sensitivity 9-mass analyzer for this experiment. This work is partially supported by the Thermal & Electric Energy Technology Foundation.

**References**