MEASUREMENTS OF HELIUM IN ELECTROLYZED PALLADIUM

COLD FUSION

TECHNICAL NOTE

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The results of a double-blind, cold fusion experiment are reported, in which six laboratories measured the helium content of five identically shaped 2-mm-diam × 10-cm-long palladium rods supplied by Fleischmann and Pons. Three rods were initially implanted with ^{4}He. Before analysis, three of the rods had served as cathodes during electrolysis in cold fusion experiments: two in 0.1 M LiOD, and one in 0.1 M LiOH. The other two, one implanted and one not, served as references. The major observations are as follows:

1. All the materials, including the as-received palladium stock, contained easily measured quantities of ^{4}He, well above amounts normally found in high-purity palladium.

2. The ^{4}He could be totally removed from at least two of the materials, including the as-received palladium stock, by surface etching the samples to a depth of ~25 μm.

3. Helium implanted by alpha-particle bombardment remained in the electrodes throughout the electrolysis.

4. No ^{3}He was measured above detection limits in any of the materials by any of the six laboratories.

It cannot be proven that the minimal excess heating in one of the rods reported by Fleischmann and Pons can be attributed to the formation of ^{4}He, although the possibility that some ^{4}He could have formed during electrolysis cannot be ruled out. If ^{4}He were generated, the mechanism must be surface related, not bulk related. No attempt was made to measure any helium or tritium that might have left the cathode surface as gas during electrolysis. The results presented cannot, unfortunately, confirm the existence or nonexistence of cold fusion via helium production. However, they provide a basis for follow-on experiments that should lead to a final conclusion.

BACKGROUND AND PROTOCOL

In the original paper describing the phenomenon that has since been commonly called "cold fusion," Fleischmann and Pons[1] stated that the bulk of the energy release during electrolytic reduction of D_2O on a palladium cathode must be due to "an hitherto unknown nuclear process or processes." Shortly thereafter, suggestions came from several sources[2] that fusion of two deuterium atoms to produce ^4He or the capture of a neutron by ^6Li to produce $^4He + {}^3H$ might account for the generation of energy without the simultaneous generation of profuse quantities of neutrons. Several investigators[3-9] have since reported the observation of tritium generation, but none has reported helium generation.

On June 12, 1989, the Fusion Research Project at the University of Utah requested that the Pacific Northwest Laboratory (PNL) coordinate a program in which palladium rods used in Fleischmann-Pons experiments would be tested for ^4He. As a result, the following protocol was developed and followed:

1. The University of Utah invited selected laboratories to analyze five palladium rods for ^4He.

2. PNL evaluated the capabilities of each responding laboratory and selected eight to participate in the double-blind search for ^4He.[a]

3. The University of Utah delivered five 2-mm-diam × 10-cm-long palladium rods[b] to PNL. According to prearranged agreement, the histories of the samples were not given to PNL when the samples were delivered.

4. PNL cut each of the rods into ten segments of approximately equal length and carefully packaged them to avoid surface contact with surroundings. The segments of each rod were randomly assigned with one segment from each rod being sent to each participating laboratory.

5. Each laboratory was encouraged to conduct measurements in its own chosen manner, with ^4He analyses receiving first priority. In addition, some laboratories analyzed for ^3He, ^1H, ^2H, and ^3H. One laboratory also studied the desorption heating spectrum of ^4He and another examined the surface morphology, surface chemistry, and microstructure of the palladium surfaces.

6. After PNL had received and assembled the results from the six laboratories, the data were given to the University of Utah in exchange for the histories of the rods. All of the data and the histories were then given to the participating laboratories.

7. After the histories of the rods were made known, some of the laboratories conducted additional studies on their palladium samples. These studies are also reported in this technical note.

DESCRIPTION OF RODS

When the information exchange took place on October 6, 1989, the University of Utah provided the following information on the five rods:

1. Rod 1 was ion implanted with 3×10^{-7} mol ^4He by Johnson-Matthey. It was then electrolyzed in the Fleischmann-Pons laboratory at 800 mA in 0.1 *M* LiOD for 28 days. The current was switched off, and the rod was left to outgas in solution. It was then removed from the cell, rinsed with pure D_2O, wiped dry with a clean piece of filter paper, and transferred to a N_2-filled tube. As observed at PNL, the rod was dry with a lead welded to the side ~5 mm from the top. It was quite straight but showed some discoloration.

2. Rod 2, the as-received stock, was removed from its original Johnson-Matthey packaging at the University of Utah, wiped dry with a clean piece of filter paper, and transferred to a N_2-filled tube. As observed at PNL, the rod was dry with a lead welded to the side ~2 mm from the top. It was straight and its surface was bright. This rod served as a reference.

3. Rod 3 was ion implanted with 3×10^{-7} mol ^4He by Johnson-Matthey. It was removed from its original Johnson-Matthey packaging by the University of Utah and packaged for PNL. As observed at PNL, the rod was dry with a lead welded to the side ~5 mm from the top. It was straight and had a bright surface.

4. Rod 4 was ion implanted with 3×10^{-7} mol ^4He by Johnson-Matthey. It was then electrolyzed in the Fleischmann-Pons laboratory at 800 mA in 0.1 *M* LiOH for 28 days. The current was switched off, and the rod was left to outgas in solution. It was then removed from the cell, rinsed with pure H_2O, wiped dry with a clean piece of filter paper, and transferred in dry condition to a N_2-filled tube. Two days later, the PNL group observed liquid on the surface of the rod. The top of the rod was discolored, the rod was warped, and it had a brown lead attachment mark near the top. Analysis of the liquid by PNL showed no tritium above normal background (~50 $d/m \cdot cm^3$).

5. Rod 5 was electrolyzed in the Fleischmann-Pons laboratory at 800 mA in 0.1 *M* LiOD for 28 days. The current was switched off and the rod was left to outgas in solution. It was then removed from the cell, rinsed with pure D_2O, wiped with a clean piece of filter paper, and transferred dry to a N_2-filled tube. When observed at PNL, as with rod 4, rod 5 was wet from weeping. The top of the rod was also discolored, the rod was warped, and it had a brown lead attachment mark near the top. Analysis of the liquid by PNL indicated that it was a mixture of H_2O and D_2O and did not contain tritium above background.

Subsequently, on November 7, 1989, Pons reported that rod 5 had generated on the order of 5 to 8 mW continuously for 2.1×10^6 s (24.3 days). Although the rod had produced much less excess heat than anticipated, Fleischmann and Pons

[a]The original plan was to have eight laboratories participate in the study, but two withdrew after the rods were sectioned. One withdrew before analyses were attempted when it was made known that some of the rods could contain large quantities of helium that could contaminate other experiments that were under way. The second group analyzed the samples, but withdrew their results after they recognized that they had not heated their samples enough to drive out much, if any, helium. They reported heating to 550°C, but did not observe evolution of any gases in any of their samples above ~300°C. Hence, their results were inappropriate for comparison with the rest, who melted or vaporized their samples. The conclusions of this technical note are not altered by excluding their data.

[b]All palladium rods (99.98% pure) were originally prepared and delivered to Fleischmann and Pons by the Johnson-Matthey Technology Centre, Blount's Court, Sonning Common, Reading RG4 9NH, England, under their Loans Scheme.

elected to include this rod instead of one that had produced more excess heat because they felt that the replacement would not be consistent with the rest of the terms of the double-blind experiment. Whether the ~0.1% excess heat can be accurately measured can be questioned. Nevertheless, we have assumed this quoted number in the discussion that follows.

Johnson-Matthey prepared the palladium rods by melt-refining palladium sponge in a high-frequency induction furnace under 10% H_2/N_2 cover gas. The metal was cast into a square-section wire bar and hot forged at 1000°C in air. The forged bar was cold square-rolled before being drawn round to final size.

Rods 1, 3, and 4 were mounted parallel to each other in a gig such that half of the circumference of each rod was exposed. A clamp was placed on ~1 mm of the end of each rod. The assembly was outgassed overnight under a vacuum of 10^{-6} Torr. Helium-4 was implanted in the rods simultaneously by bombardment with 500-keV He^+ ions. Implantation was accomplished in five equidose stages along the length of the rods (~2 cm/stage) after which the rods were rotated 180 deg in the gig and the process was repeated. Thus, the concentration profile through the cross section would be expected to be elliptical, the highest concentration being at the surface normal to the beam of He^+ ions. Each rod received 3×10^{-7} mol ^4He (estimated uncertainty, ~25%) or $9.7 \pm 2.3 \times 10^{-7}$ mol/cm^3 Pd. Ion beam heating was limited so that the temperature of the rods was maintained <200°C. Monte Carlo range calculations indicated that the peak concentration of ^4He was at a depth of ~1 μm with virtually no penetration deeper than 1.2 μm.

ANALYTICAL PROCEDURES

Each laboratory used its own methods of analysis as described below.

Lawrence Livermore National Laboratory

At Lawrence Livermore National Laboratory (LLNL), each palladium sample was stored under vacuum in a Pyrex tube above a molybdenum crucible in a molybdenum basket resistance furnace. In performing the measurement, the sample was pushed into the crucible by a magnetic metal slug and heated by an element encased in a stainless steel vacuum jacket. The sample was heated to between 350 and 430°C for 1 h to outgas D_2. Finally, the sample was heated to 1600°C for 20 min to outgas helium.

The LLNL investigators were careful to remove D_2 from the samples by using a series of getters. Even then, they were not certain that they had successfully gettered all of the D_2 because some of the samples had such large quantities of D_2. However, when their results were compared with those of other laboratories, their concerns appeared not to have been warranted.

While the sample was heating and for 10 min after the crucible power had been turned off, chemically active gases were gettered by the combination of a Ti-Zr bulk getter at 800°C and a Cu-CuO getter at 450°C. These getters were then cooled for 10 min and the gaseous sample was exposed to an SAES® type 101 Zr-Al getter at 450°C and activated charcoal at 77 K. Subsequently, the residual chemically inert gases were analyzed in a noble gas mass spectrometer with low sensitivity and low mass resolution because there was much more helium in most of the rods than could be tolerated in the more sensitive instruments. Because of the low mass resolution, D_2 and ^4He could not be distinguished from each other. Thus, the investigators felt that their measurements only represented an upper limit of the ^4He content.

Calculations for high-concentration helium samples had to be extrapolated far beyond the calibration curve. Thus, errors of a factor of 2 or more could be possible. It was also evident that heating to 1600°C was necessary to extract all of the helium.

University of California–Santa Barbara

At the University of California–Santa Barbara (UCSB), small pieces (0.050 g) of each palladium sample were wrapped in molybdenum foil packets and melted in a tantalum crucible heated by resistance heating. While the sample was being heated, the extracted gases were exposed to a Cu-CuO getter at 550°C surrounded on either side by U-traps chilled to 77 K. The hydrogen isotopes were thereby converted to water and trapped in the U-traps. The remaining gases were pumped into the mass spectrometer cleanup line by condensing them onto a charcoal finger chilled to 10 K. The charcoal was then warmed to 140 K and the released gases were exposed to various getters to remove residual ^1H, ^2H, ^3H, argon, and neon. Finally, the helium sample was admitted into the spectrometer chamber through a charcoal trap at 77 K.

A hot furnace blank was run between each sample to ensure that each palladium sample had been completely extracted and that no leaks had appeared in the system. The HD peak was continuously monitored to ensure that neither HD nor D_2 interfered.

Rockwell International Rocketdyne Division

Following low-power optical microscopic examination to verify sample integrity, single small specimens were analyzed by mass spectrometry to determine the approximate helium levels in each sample. These samples were obtained by cutting a small piece from one end of the original sample using a newly purchased pair of 4-in. diagonal wire cutters. These first analyses were conducted with insensitive instrument settings to protect the instrument from damage in case the samples contained more helium than expected.

Following the preliminary analyses, additional specimens were then cut from each rod segment for accurate replicate helium analysis. The replicate specimens were ~1.3-mm-thick disks cut from near the midpoint along the length of the original sample using a miniature coping saw with a new wire blade. These samples were then cut in half with diagonal wire cutters to obtain multiple smaller specimens weighing ~15 mg, the optimum weight for high-sensitivity helium analyses. The sample disks that were known from the preliminary analyses to contain the most helium were cut using the original wire cutters. The low-helium-level disks were cut using a second new pair of wire cutters, starting with the disk containing the lowest level of helium and ending with the disk containing the highest level. Each specimen was then ultrasonically cleaned in acetone and dried in air under a heat lamp.

Specimens from a single lot of high-purity control palladium from Rockwell-Rocketdyne stock were also prepared and analyzed along with the Fleischmann-Pons samples. Numerous analyses had previously shown this lot to contain no measurable ^3He or ^4He.

The helium content of each specimen was determined by static-mode mass spectrometry[10] after the specimen was completely vaporized in a resistance-heated tungsten wire crucible in a high-temperature vacuum furnace in the mass

spectrometry system. Except for two runs, the normal isotope dilution procedure (where a spike of ^3He or ^4He is added during vaporization) was not employed because of the desire to accurately measure both helium isotopes and because of potential interference from the relatively large levels of helium in the spikes ($\sim 10^{13}$ atoms). Instead, known quantities of ^3He and ^4He spikes were added to the furnace in subsequent runs. The absolute amount of helium released was then measured relative to these spikes. The spikes were obtained by expanding and partitioning known quantities of gas through a succession of calibrated volumes.[10,11] The mass spectrometer was calibrated for mass sensitivity during each series of runs by analyzing known mixtures of ^3He and ^4He.

To ensure that the helium measurements would not be confused with measurement of other gases, investigators connected the mass spectrometer to the sample vaporization furnaces through a series of physical and chemical getters, including liquid nitrogen-cooled activated charcoal and ambient-temperature SAES type 101 Zr-Al alloy. The getters purified the helium-containing gas released from the specimens and ensured that potentially interfering gases such as H_2, HD, D_2, HT, DT, and T_2 were not admitted to the spectrometer. As an added precaution to take care of deuterium potentially released during vaporization, an additional Zr-Al getter was added directly to the furnace used for specimen vaporization. Although the mass spectrometer did not have sufficient resolution to completely separate a potential D_2 peak from the ^4He peak, a number of factors made it possible to know with certainty that the release of D_2 during vaporization would not affect the helium analyses.

Helium concentrations reported by the Rockwell-Rocketdyne group represent the average of three or four independent replicate analyses for each sample; each had an absolute uncertainty of ~2%. Uncertainty in the measured ^3He data, which were all at background levels, was determined by the variability in helium released by control specimens analyzed in that furnace that day. For experiments reported here, the absolute sensitivity limit for ^3He was $\sim 4 \times 10^{-13}$ g·atom/cm^3 Pd.

Rockwell International Energy Technology Engineering Center

To determine whether significant helium concentration gradients existed across the diameter of the electrode, the Rockwell International Energy Technology Engineering Center (ETEC) used a jeweler's saw to hollow out the samples so that approximately the outer 50 to 70% remained. Samples were then sent to Rockwell-Rocketdyne for mass spectrometric analyses. The procedures for helium analysis were identical to those described in the previous section, but were performed by Rockwell-Rocketdyne independently and at a later time.

After the analyses for the double-blind experiment were completed by all of the participants and the results were reported back to Rockwell-ETEC, eight additional specimens were prepared from the original set of five rods delivered directly to Rockwell-Rocketdyne to determine if the measured ^4He in the unimplanted as-received material (rod 2) and in the unimplanted electrolyzed material (rod 5) was concentrated on the surface or spread throughout the bulk of the materials.

The Rockwell-ETEC group also used scanning electron microscopy to verify that no surface dendrites had formed. Such dendrites, if they had formed, would be expected to be very fragile. Thus, it is possible that dendrites could have been destroyed when the rods were wiped in the Fleischmann-Pons laboratory. There was no visible evidence of dendritic material on the filter paper used to wipe the rods.

Energy dispersive X-ray analysis was also used to determine chemical compositions to a depth of ~1 μm. Excepting the very top of rod 1, the surfaces of randomly selected sections of the rods were almost entirely free from impurities. The very top of rod 1 was covered by lead and tin to a depth between 0.25 and 0.75 μm (see Fig. 1), possibly originating from solder used to attach the lead to the electrode.

The Rockwell-ETEC group also examined each of the rods for entrained voids or gas bubbles by mounting the rod in plastic, polishing away half of its diameter, then swab etching the surface with aqua regia in glycerol to remove smeared metal. The sample was examined by the electron microscope at magnifications of 20 to 20 000 times. Voids or bubbles were numerous, in the neighborhood of 10^9 bubble/cm^3. The Rockwell-ETEC group suspected that the bubbles were created during ingot solidification and altered when the rod was drawn. The gas within was presumed to be nitrogen because subsequent analyses showed that the bubbles in the center of the rod contained essentially no helium.

Woods Hole Oceanographic Institution

The palladium samples (0.016 to 0.06 g) were heated in an ultra-high-vacuum resistance furnace equipped with a tantalum crucible. The procedure was similar to that reported by Kurz et al.,[12] except that a special extraction line with two flow-through titanium sponge getters was added to ensure that deuterium, hydrogen, and tritium were removed. Thus, the gases released were purified by four titanium sponge getters (three held at room temperature, and one at 600°C) and an SAES Zr-Al getter (operated at 150°C and room temperature). The helium content of an aliquot of the purified gas was measured by a quadrupole mass spectrometer to ensure against overloading the magnetic sector mass spectrometer. If the helium content exceeded the amount in the atmospheric standard aliquot (6.7×10^{-13} g·atom ^4He), the sample was appropriately split prior to the next step (in some cases by as much as 1300-fold). Helium was then adsorbed onto a charcoal trap and held at 13 K. The trap was subsequently warmed to 35 K to selectively desorb helium into the magnetic sector. Helium-4 was measured on a Faraday cup and ^3He

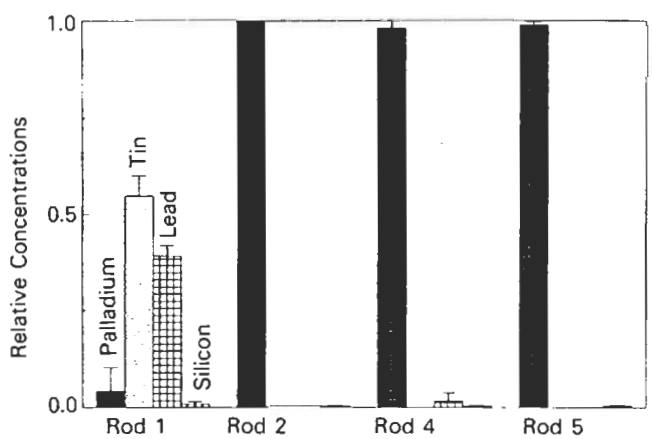

Fig. 1. Surface composition of palladium cathodes. All rods but the very top of rod 1 were exceptionally clean.

on an electron multiplier. During the course of the experiment, complete procedural blanks were processed before and after each sample ($1.1 \pm 0.1 \times 10^{-15}$ g·atom ^{4}He with $<9 \times 10^{-21}$ g·atom ^{3}He). As evidenced by monitoring the HD peak in the magnetic sector and comparison of the ^{4}He peak heights obtained by the quadrupole and magnetic sector mass spectrometers, the procedure effectively removed all deuterium prior to the inlet to the quadrupole mass spectrometer. The samples were analyzed in bulk and also for surface concentrations by drilling out the centers, leaving a 0.5-mm-thick outside cylinder (44% of the total mass). All of the samples were handled by new cutters and forceps to avoid any cross contamination.

Delft University Laboratory

Samples were degassed in two stages: (a) from room temperature to 327°C to extract hydrogen isotopes and (b) from 327°C to above the melting point of 1600°C to extract ^{4}He. Over the lower range, quantities of H_2 and D_2 evolved and were measured after the released gas was oxidized to water. Over the upper range, ^{4}He was measured after traces of H_2 and D_2 had been gettered in a titanium evaporation trap.

Mass spectra of the low-temperature gases were obtained on a desorption spectrometer equipped with a Leyboldt residual gas analyzer (a Quadruvac™ Q100), a resistance-heated vacuum oven, a calibrated membrane manometer, and a device to burn the released H_2 gas. The water so formed was monitored in a Tri-carb 4000™ liquid scintillation counter.

During degassing in the second stage, samples were placed in a molybdenum crucible that was heated by electron bombardment. Released gases were monitored by a Balzers QMG 111B™ quadrupole mass spectrometer. The desorption system was calibrated for ^{4}He by admitting pulses of known amounts of helium.

Some of the first measurements were complicated by residual helium from the immediately previous samples that contained large amounts of helium. Subsequent measurements, however, were conducted in a sequence that negated memory effects.

The Delft group also examined the desorption behavior of helium from their samples of each of the rods. Parts of the rods (varying from 50 to 100 mg) that previously had been heated at 327°C for 1 h in a vacuum were inserted into their system, pumped, and baked at 220°C for 12 h, cooled for 4 h, then heated for 30 s at 280°C before proceeding to heat at a rate of 1.5°C/s to above the melting point. The evolved helium was measured at temperature increments of ~90°C.

RESULTS AND OBSERVATIONS

Helium-4

Figure 2 and Table I summarize the ^{4}He analyses; Fig. 2 gives the distribution of concentrations from the top to the bottom of each rod. For all participating laboratories, detection limits for the measurement of ^{4}He were far below the levels reported in the as-received rod 2. All five rods contained quantities of ^{4}He well above these limits and the contents of rods 1 and 4 generally agreed to within 1 standard deviation (1σ) with the quantities implanted. The reported ^{4}He content for rod 3 did not agree with the reported implantation value. There is also a strong suggestion that the helium content at the ends of the rods is higher than in the centers (e.g., rods 1, 4, and 5).

Sample heterogeneity is largely responsible for the analytical variances reported in this study. For example, Rockwell-Rocketdyne reported an absolute uncertainty of ~2% in individual analyses, yet their measured variability ranged from 10 to 50% for different samples from the same segment of rod. Considering the reported observations, this is not surprising given that concentrations may have varied radially

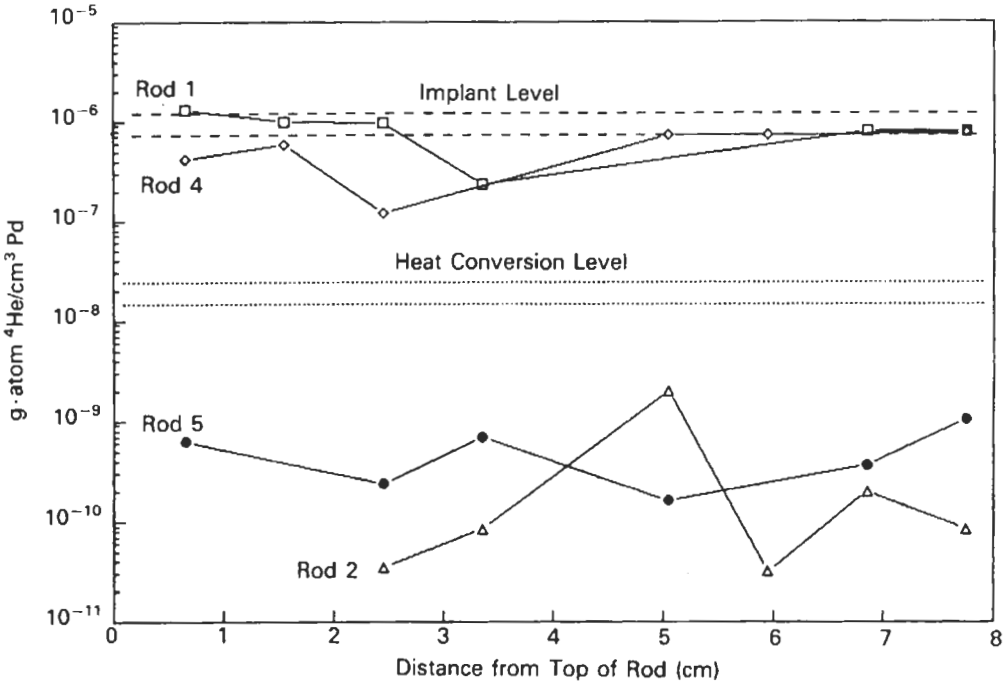

Fig. 2. Summary of ^{4}He results for rods 1, 2, 4, and 5.

TABLE I

Summary of ^{4}He Analyses

Length from Top (cm)	Helium Concentration (ng·atom/cm^3 Pd)				
	Rod 1 (Implanted and Electrolyzed in LiOD)	Rod 2 (As-Received Stock)	Rod 3 (Implanted)	Rod 4 (Implanted and Electrolyzed in LiOH)	Rod 5 (Electrolyzed in LiOD)
0.2 to 1.1	1303 ± 257[a]	---	309 ± 150[a]	420[b]	0.63[b]
1.1 to 2.0	1000 ± 250[c]	---	57.8 ± 2.9[d]	580 ± 50[c]	---
2.0 to 2.9	957 ± 95[f]	0.035 ± 0.008[a]	---	120 ± 20[c]	0.23 ± 0.04[f]
2.9 to 3.8	236 ± 12[d]	0.085 ± 0.025[c]	7.8 ± 0.8[c]	---	0.7 ± 0.3[c]
3.8 to 4.6	---	---	---	---	---
4.6 to 5.5	---	2.0 ± 0.1[e,g]	5.3 ± 0.3[e]	725 ± 27.6[a]	0.16 ± 0.05[a]
5.5 to 6.4	---	0.032 ± 0.011[f]	1.1[b]	775 ± 42[d]	---
6.4 to 7.3	790 ± 80[e]	0.2[b]	12.2 ± 5.1[f]	---	0.368 ± 0.005[d]
7.3 to 8.2	790[b]	0.084 ± 0.001[d]	---	761 ± 79[f]	1.04 ± 0.05[e]
8.2 to 10	Archives	Archives	Archives	Archives	Archives
Average	846 ± 353	0.087 ± 0.068[g]	---	563 ± 255	0.52 ± 0.33
Heating equivalent					18.9 ± 4.6[h]

[a]Rockwell-ETEC.
[b]LLNL.
[c]Delft University.
[d]Woods Hole.
[e]UCSB.
[f]Rockwell-Rocketdyne.
[g]This result is probably compromised, either by an inordinately high surface-to-volume ratio or by cross contamination between rods, introduced when they were cut with nippers at PNL or UCSB. It is not included in the average because the value 2.0 ± 1 lies outside 2σ.
[h]Rod 5 is reported to have created $1.36 \pm 0.34 \times 10^{11}$ ergs of heat. The fusion reaction $2D \rightarrow {}^4He$ would generate 2.30×10^{19} erg/g·atom ^{4}He created. Thus, it would require the generation of $5.91 \pm 1.47 \times 10^{-9}$ g·atom ^{4}He ($18.9 \pm 4.6 \times 10^{-9}$ g·atom/cm^3 Pd) to generate the heat reported.

from 10^{-2} g·atom/cm^3 Pd on the surface to $<10^{-12}$ g·atom/cm^3 Pd in the center. Thus, the analyses of samples that contained varying ratios of surface-to-bulk quantities could vary quite significantly.

The third point in the lowest line of Fig. 2 is suspected to be biased (see footnote g in Table I). If this point is ignored, the ^{4}He content in the electrolyzed rod (rod 5) is nearly an order of magnitude greater than of the blank (rod 2).

The "heat conversion level" in Fig. 2 represents the level of ^{4}He that would be in rod 5 if the excess heat reportedly generated by rod 5 had resulted from the fusion of two deuterium atoms to produce ^{4}He (23.8 MeV) in the body of the rod. This value illustrates the excellent sensitivity of ^{4}He analyses in testing the helium generation postulate. As can be observed in Fig. 2, the quantity of ^{4}He found in rod 5 (non-implanted, D_2O electrolyzed) does not correlate well with the excess heat generated when the rod was electrolyzed. According to our calculations, it would take 36 ± 25 times as much ^{4}He as was measured to account for the reported excess heat. If rod 5 had produced somewhere near the amount of heat reported by Fleischmann and Pons for earlier experiments,[1] the proposed ^{4}He mechanism would have produced about the same amount as was implanted in rods 1, 3, and 4.

Several of the laboratories confirmed that the helium content in the rods was concentrated near the surface. According to the Rockwell groups, analyses of numerous specimens showed that all measurable helium could be removed from the as-received palladium stock (rod 2) and the electrolyzed unimplanted rod (rod 5) by surface etching to a depth of ~25 μm.

Helium-3

As indicated in Table II, none of the laboratories detected any ^{3}He, even though two of them were capable of detecting femtogram amounts. According to our calculations, detectable amounts of ^{3}He generated by the decay of tritium transferred into the rods along with deuterium during electrolysis ($\sim 10^{-17}$ g·atom/cm^3 Pd) would not have been evident in rods 1 and 5.

Helium Desorption Spectra

The group at Delft University examined the desorption behavior of helium from their sample of each rod in the fashion described above. Figure 3, which shows the accumulated released helium, summarizes the results for all of the Delft samples, including one of their own that had been implanted. Errors caused by simultaneous desorption of ^{4}He and D_2 were negligible for all five samples because desorption rates

TABLE II

Lower Detection Limits for ^3He

Laboratory	g·atom/cm^3 Pd				
	Rod 1	Rod 2	Rod 3	Rod 4	Rod 5
UCSB	8.6×10^{-15}	8.6×10^{-15}	4.6×10^{-17}	8.1×10^{-17}	5.9×10^{-15}
Woods Hole	2.8×10^{-15}	4.1×10^{-17}	5.1×10^{-16}	5.3×10^{-17}	5.3×10^{-17}
Expected[a]	2.3×10^{-17}				2.3×10^{-17}

[a]A typical $^3H(T)/^2H(D)$ ratio in D_2O is the order of 10^{-13}. If the palladium rod were charged to 0.67 g·atom D/g·atom Pd, [i.e., 0.67×10^{-13} g·atom T/g·atom Pd (7.6×10^{-15} g·atom/cm^3 Pd)] within the first 4 days and decayed to ^3He at the rate of 1.548×10^{-4} day^{-1}, the concentration of ^3He after 20 days of decay would be 7.6×10^{-15} [1 − exp(−0.00310)] = 2.3×10^{-17} g·atom/cm^3 Pd.

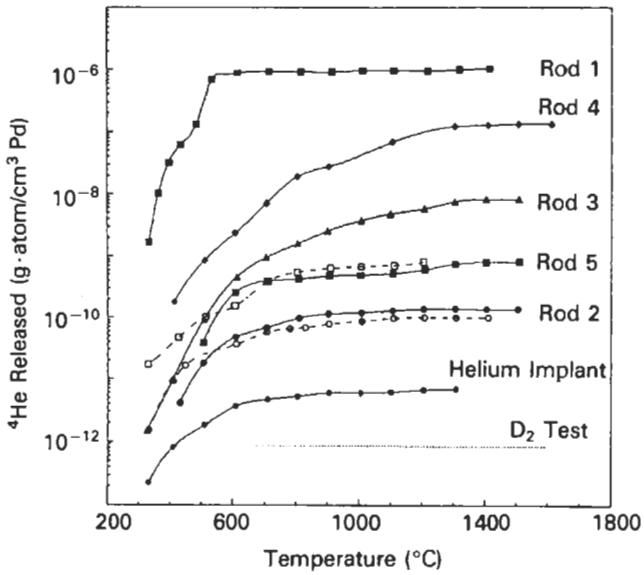

Fig. 3. Accumulated helium release. Measurements were made between heating increments of ~90 to 150°C. Minimum detection is $<10^{-12}$.

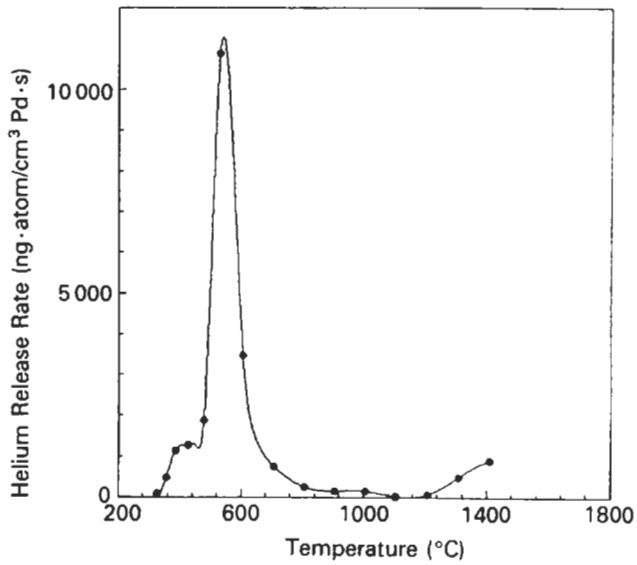

Fig. 4. Helium-4 desorption spectrum of rod 1 (total cross section).

were at least two orders of magnitude above the rate at which errors could become important (10^{-13} g·atom/cm^3·s). Duplicate analyses on samples of rods 1, 2, and 5 indicate reasonable reproducibility in total helium release. The total amount of ^4He evolved correlates qualitatively with other investigators (Fig. 2).

Figures 4, 5, and 6 show the corresponding differential desorption spectra. Differences in detail between duplicate runs again emphasize the heterogenous distribution of helium in the samples. The global characteristics of the desorption spectra, however, are described by a low-temperature desorption component centered at ~725°C (A), and a high-temperature component, centered at ~1325°C (B). Samples of rods 1, 2, and 5 showed significant A-type release, and samples of rods 4 and 5 showed significant B-type release.

Several factors play a role in desorption: (a) the binding of helium to traps, (b) the depth distribution of the helium, (c) the mobility of helium in the presence of more or less heterogeneously distributed point defects, and (d) the number of extended lattice defects.

Low-temperature degassing occurs when helium is released from small defects, e.g., monovacancies. Agglomeration of helium into bubbles increases binding. Therefore, a higher temperature release is expected when helium agglomerates as bubbles. However, the formation of cracks in the material, such as those caused by deuterium charging, may create pathways along which part of the helium can desorb at low temperature. Spectra from rods 1 and 5 suggest that this has happened to these rods but not to rod 4.

After the Delft group had received the history and results of experiments by other laboratories, they performed a series of measurements to determine the behavior of helium in palladium charged with deuterium. Palladium rods (1-mm-diam) were exposed to a deuterium-helium gas mixture (3% helium) at 30 bars and 425 and 507°C for 30 min. Desorption spectra for such rods (Fig. 7) show that major desorption occurs at ~1325°C as observed for rod 5. By contrast, the same charging experiments performed without D_2 in the charging

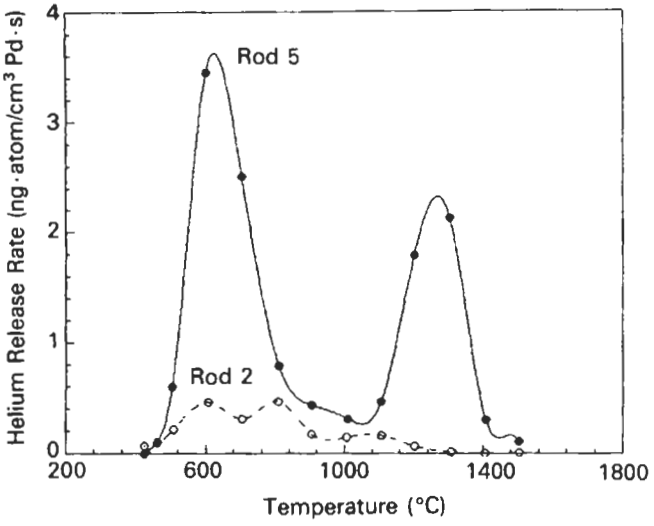

Fig. 5. Evolution rates from rods 2 (as-received stock) and 5 (electrolyzed in D_2O, unimplanted). Notice the distinct difference in the spectra.

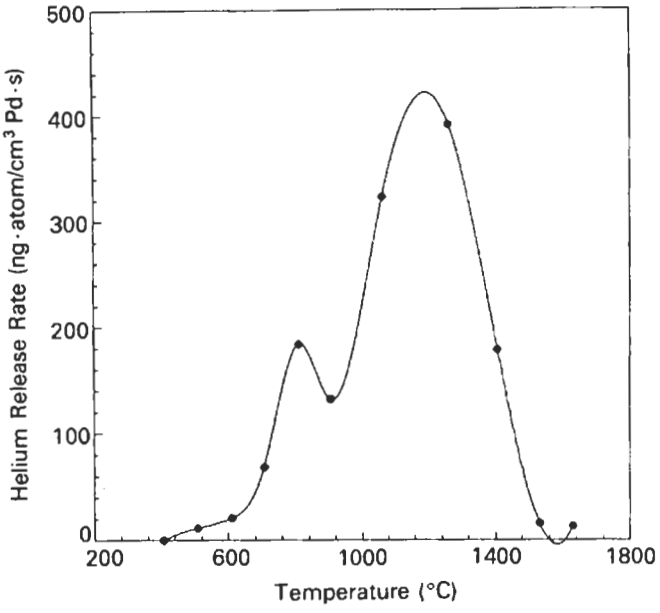

Fig. 6. Helium desorption spectrum for rod 4 (electrolyzed in H_2O).

gas did not yield any helium release. Electropolishing samples previously exposed to deuterium and helium by the method outlined by Kushner[13] completely removed the dissolved helium, evidencing only surface penetration of helium.

CONCLUSIONS

The integrated data from the six laboratories support the following statements.

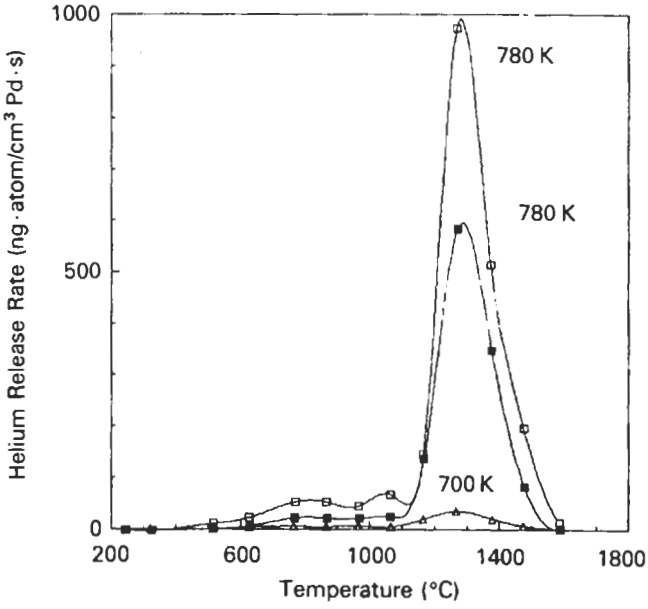

Fig. 7. Studies on the desorption behavior of helium in deuterium-charged palladium. The desorption is type B, even though the helium was shown to be on the surface.

1. All palladium rods supplied by Fleischmann and Pons, including the as-received stock, contained significant and easily measured quantities of helium, much above the amounts normally found in high-purity palladium.

2. No ^4He was generated in the center of rod 5 during electrolysis. All of the helium was shown to be concentrated within ~25 μm of the surface.

3. Much or all of the helium implanted by alpha-particle bombardment remained in rods 1 and 4 through the electrolysis.

4. No ^3He was detected in any of the materials by any of the six laboratories (detection limits down to 3 to 8 $\times$ 10^{-17} g·atom/cm³ Pd).

From these observations, we draw the following conclusions.

1. The as-received palladium stock (rod 2) had undergone some treatment during or after its fabrication that deposited a significant amount of ^4He in the surface layers of the rod. It is possible that the same process also deposited ^4He in the surface layers of the other rods.

2. The fact that alpha-particle implanted ^4He was retained on the surface of rods throughout the electrolysis confirmed the generally accepted notion that once helium is trapped in the palladium matrix it will not be released easily, even from the surface layers. This suggests that, if electrolysis had generated helium, most of the ^3He or ^4He generated within the palladium by electrolysis would have remained in the matrix for measurement afterwards. It would not have been released by electrolysis.

3. It is not possible from the data at hand to determine whether electrolysis produced helium by a fusion process. We

have considered a number of possibilities to explain the helium content found in rod 5: (a) The rod was contaminated with helium at a higher level than the as-received rod 2 and there was no production of helium during the electrolysis; (b) electrolysis produced helium by a surface reaction but only a small fraction of the helium was retained in the rod; (c) electrolysis produced helium but most of the heating came from another mechanism; and (d) electrolysis produced helium but the excess heat was less than reported. Unfortunately, none of these explanations can be confirmed.

4. No detectable ^{3}He was generated within the palladium by electrolysis.

RECOMMENDATIONS

An inordinately large number of contributors to this technical note have performed many extensive, careful, and expensive tests that provide valuable insights. We fully recognize, however, that, were it possible, additional measurements should be made on electrodes that have produced much more heat than the heat-producing electrode measured in this experiment. Consequently, we suggest a rather obvious sequel experiment that could be used to unambiguously determine whether ^{4}He can be generated by a fusion mechanism when excess heat is produced during electrolysis of D_2O. First, measurements should be made on a rod that has been shown to contain no ^{4}He prior to electrolysis. Second, the rod should have generated significant quantities of excess heat during electrolysis. Third, sequential mass spectrometric analyses should be performed on single samples, alternating with controlled removal of surface layers of the single samples to obtain a radial distribution of ^{4}He. Simultaneously, and at appropriate stages, elemental analysis of the surface could be conducted to determine whether there is a correlation of surface condition, e.g., content of ^{6}Li, to deduce a possible mechanism of ^{4}He production. Appropriate getters, as described in this technical note, should be used to ensure that unwanted gases, e.g., D_2, do not interfere with the analyses. It is preferable to resistance heat samples to minimize the memory effects of ^{4}He desorption that is sometimes caused by electron bombardment.[14]

APPENDIX

GENERAL COMMENTS

The Rockwell-Rocketdyne Laboratory reports that the sample containing the least amount of ^{4}He contained ~40 times the limit of detection. Whenever this has occurred in the past, the elevated concentrations have always been subsequently attributed to the use of helium somewhere in the material's processing. D. T. Thompson of Johnson-Matthey expresses in private communication that he is virtually certain that only the implanted rods, rods 2, 3, and 4, contained ^{4}He when they left Johnson-Matthey. On the other hand, investigators who measured the ^{4}He content of the samples are just as certain that their measurements were not flawed. Small amounts of background ^{4}He released by the furnaces and from high-purity control samples supplied by Rockwell-Rocketdyne were negligible in comparison with the helium released from any of the Fleischmann-Pons samples.

According to the Delft analysis, all of the rods contained $<2 \times 10^{-14}$ g·atom ^{3}H/cm^3 Pd. Also, the evolution curves for ^{4}He differed substantially from one rod to another. The implanted rod that had been electrolzyed in LiOD (rod 1) seemed to release its ^{4}He more easily than the others.

The relatively large uncertainties following each value in Table I do not in general reflect uncertainties in the experimental precision. They are, instead, the standard deviations (1σ) in the distribution of these replicate values, reflecting heterogeneity in the ^{4}He content of the samples and not the absolute accuracy of the individual measurements.

ROD 1—IMPLANTED AND ELECTROLYZED IN 0.1 *M* LiOD

The Delft group found that the rod initially contained 0.67 mol D/mol Pd and virtually all of the ^{4}He was evolved from the rod before the temperature reached 625°C. Evolution of ^{4}He continued through the heating range up to 1600°C. If all of the helium (3×10^{-7} g·atom) were in the first 1.2 μm, the concentration would be 4×10^{-2} g·atom/cm^3 Pd; if within the total bulk volume, 9.5×10^{-7} g·atom/cm^3 Pd. The Woods Hole analysis for surface and bulk volumes suggests that the total ^{4}He content was at least within the outer 8.7% of the volume. The Delft results indicate that 99.5% of the helium had been deposited in the surface layer (<200 μm deep).

ROD 2—AS-RECEIVED STOCK

The Rockwell groups found that two specimens from the as-received stock etched to a depth of ~25 μm showed no measurable ^{4}He ($<8 \times 10^{-13}$ g·atom/cm^3), whereas five similar unetched specimens, some of which were analyzed at the same time, showed an average ^{4}He level of 320 ± 110 (1σ) $\times 10^{-13}$ g·atom/cm^3. Neither hydrogen nor deuterium were found in this rod. The Delft group found no hydrogen or deuterium (detection limit = 10^{-3} mol/cm^3 Pd). Evolution of ^{4}He continued through the heating range up to 1600°C. Prior to analyzing the Fleischmann-Pons samples, Kurz of Woods Hole analyzed two pieces of palladium obtained commercially from the English laboratory of Johnson-Matthey (1-mm-diam, puratronic grade 1, batch W1393). He analyzed one sample before the analysis of the Fleischmann-Pons samples ($6.95 \pm 0.26 \times 10^{-13}$ g·atom/cm^3 Pd) and one after ($21.8 \pm 2.0 \times 10^{-13}$ g·atom/cm^3 Pd). In each case, the amount was significantly lower than his measurement for rod 2 ($842 \pm 120 \times 10^{-13}$ g·atom/cm^3 Pd). Lupton of UCSB also analyzed several pieces of unreacted 0.5-mm-diam palladium wire (lot 1028 from Mathey-Bishop) and found $<8.3 \times 10^{-13}$ g·atom ^{4}He/cm^3 Pd and $<1.5 \times 10^{-18}$ g·atom ^{3}He/cm^3 Pd in each piece.

ROD 3—IMPLANTED, NONELECTROLYZED ROD

There is no obvious reason why this rod did not contain the expected level of implanted helium. Possibly some of the surface layer was either mechanically or chemically removed during its handling, or for some unknown reason, this rod failed to be uniformly exposed to ^{4}He$^+$ during implantation. The Delft group found neither hydrogen nor deuterium in the rod (detection limit = 10^{-3} mol/cm^3 Pd). Evolution of ^{4}He continued through the heating range up to 1600°C.

ROD 4—IMPLANTED, ELECTROLYZED IN 0.1 *M* LiOH

According to the Delft analysis, the rod contained 0.05 mol H/mol Pd and a significant amount of helium. Evolution of ^{4}He continued through the heating range up to 1600°C.

ROD 5—NOT IMPLANTED, ELECTROLYZED IN 0.1 *M* LiOD

According to the Woods Hole analysis, measurement of surface and bulk ^{4}He concentrations suggested that the helium was deposited at least within the outer 40% of the rod. According to the Rockwell groups, analyses of two specimens etched to a depth of ~25 μm showed no measurable ^{4}He ($<8 \times 10^{-13}$ g·atom/cm^3), whereas five similar unetched specimens, some of which were analyzed at the same time, showed an average ^{4}He level of 2310 ± 400 (1σ) $\times 10^{-13}$ g·atom/cm^3. The Delft group found 0.12 mol D/mol Pd. Evolution of ^{4}He continued through the heating range up to 1600°C. After receiving the history and analyses from the other participating laboratories, the Delft group performed a measurement on a piece of rod 5 that had ~30 μm of surface removed by electropolishing[14] (electrolyte: 50 vol% methanol, 33 vol% HNO_3, and 17 vol% H_3PO_4). Only 0.2×10^{-13} g·atom ^{4}He/cm^3 Pd were extracted up to 1525°C.

The ^{3}He data clearly demonstrate that the excess heating reported by Fleischmann and Pons cannot be due to deuterium fusion via the ^{3}He or tritium branches. If rod 5 created $1.36 \pm 0.34 \times 10^{11}$ ergs of excess heat, then by conventional D-D reactions (assuming equal production of ^{3}He and tritium), the excess heat production corresponds to the generation of 6.2×10^{-8} mol ^{3}He/cm^3 Pd, which is 10^8 to 10^9 times higher than observed by the UCSB or Woods Hole groups. A significant fraction of any fusion-produced ^{3}He should have been retained by rod 5 even if the fusion reaction had occurred at the surface of the palladium, given that electrolysis failed to remove helium implanted in rods 1 and 4. Suggestions have been made, on the other hand, that the tritium branch predominates over the ^{3}He branch for the D-D reaction occurring in palladium.[15] Even assuming 100% tritium production, the rod 5 results imply the production of 1.1×10^{-7} mol T/cm^3 Pd. Considerable buildup of ^{3}He should have occurred in the palladium due to the decay of tritium ($t_{1/2} = 12.3$ yr) during the 10 to 30 days that elapsed between the electrolysis experiment and the measurement of helium in the rods. The resulting ^{3}He would still have been 10^5 to 10^7 times higher than observed. It is hard to imagine tritium or helium losses by diffusion that would explain such discrepancies. Thus, conventional D-D fusion reactions are unlikely to be the source of the 5- to 8-mW excess heating reported for rod 5.

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S. J. Pons and M. Fleischmann participated in this study, but elected not to be coauthors of this paper. Their comments will appear in a future issue.

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