

SEARCH FOR ^3He AND ^4He IN ARATA-STYLE PALLADIUM CATHODES II: EVIDENCE FOR TRITIUM PRODUCTION

NUCLEAR REACTIONS
IN SOLIDS

KEYWORDS: palladium cathodes, tritium, helium isotopes, mass spectrometry

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Measurements have been made of ^3He , ^4He , and ^3H in a sample containing 2.7% of the gas from the interior of an Arata-style hollow palladium electrode charged with ~ 5 g Pd-black that had undergone electrolysis in D_2O as a cathode for 90 days and then as an anode for a further 83 days. There is no evidence for the much larger amounts of ^4He observed by Arata and Zhang in similar experiments. However, a very large concentration has been found of ^3He , $2.3 \pm 0.5 \times 10^{12}$ atoms/cm³ standard temperature and pressure that apparently can all be attributed to the decay of tritium produced during electrolysis. No direct production of ^3He can be specified, a result that is also different from the conclusions of Arata and Zhang. The ^3He and tritium measurements and the results of a gas analysis using a Finnigan-type mass spectrometer show that at the end of the anodic electrolysis, the electrode void contained $5.8 \pm 0.7 \times 10^{13}$ atoms tritium in the gas phase as HT, DT, and T₂, and $1.7 \pm 0.3 \times 10^{15}$ atoms tritium in the aqueous phase as HTO,

DTO, and T₂O. At this stage, the gas phase pressure was ~ 18.8 atm in a free volume of 0.6 cm³, and the total mass of water was ~ 5.7 mg. The gas phase tritium value is viewed as a lower limit for gaseous tritium produced inside the electrode because some of that tritium must have been removed into the D_2O electrolyte during the anodic episode.

The ^3He and ^4He measurements were also made in the two samples of the Pd-black and in sections cut from the walls of both Pd electrodes. The H_2O electrolyzed samples did not show any evidence of unusually high ^3He and/or ^4He , but all the D_2O electrolyzed samples showed clear evidence of ^3He from tritium decay. A stepwise temperature heating experiment performed with a 24.9-mg sample of the D_2O Pd-black showed that the diffusion process for ^3He can be described by an equation of the form $D = D_0 \exp(-U/kT)$ with an activation energy U of 1.1 eV. It is also apparent that the ^3He from tritium is quantitatively retained in the Pd-black at room temperature.

I. INTRODUCTION

Observation of excess heat in D_2O electrolysis with Pd cathodes was first claimed in 1989 by Fleischmann and Pons, who attributed the effect to fusion of deuterium nuclei.¹ Subsequently, many attempts have been made to confirm this observation and to search for other

signatures of deuterium-deuterium (D-D) fusion under similar conditions. These attempts have met with varying degrees of success and failure. The reader is referred to detailed reviews presented by Storms² and Nagel,³ and to several books.⁴⁻⁶

In 1990, Arata and Zhang repeated the Fleischmann-Pons experiment and claimed that they had detected neutrons, "sometimes reaching 10^8 n/s, or more" from heavy water cells.⁷⁻⁹ In 1995, Arata and Zhang reported that

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after D₂O electrolysis, they had detected large amounts of ⁴He, ~10¹⁶ to 10¹⁷ atoms/mg, in Pd-black powder sealed under vacuum in specially prepared hollow Pd cathodes.¹⁰ These results were obtained by heating the Pd-black to 1500 K in a vacuum system attached to a statically operated quadrupole-type mass spectrometer. The results were stated to be "fully repeatable."¹⁰ In 1996, these authors reported that they had confirmed the aforementioned ⁴He observation, that they had also detected ³He with ³He/⁴He ~ 0.25, and that ³He and ⁴He were not detected in comparable electrolysis experiments using H₂O instead of D₂O (Ref. 11). In subsequent papers, Arata and Zhang¹²⁻¹⁵ reported additional data obtained with their mass spectrometric technique and restated their claims regarding production of excess ³He and ⁴He in Pd-black from the interior of Pd cathodes during D₂O electrolysis.

Although we have experienced some difficulties in understanding the details of the ³He and ⁴He observations of Arata and Zhang, that does not diminish their profound significance if the observations are confirmed. In this connection, Clarke,¹⁶ using techniques outlined by Clarke and Clarke,¹⁷ has described a recent search for ³He and ⁴He in four Pd-black samples that had been provided by Arata and Zhang. This search revealed no evidence for the very high ³He and ⁴He concentrations found by Arata and Zhang in similar specimens of Pd-black. However, it should be mentioned that in a recent paper,¹⁸ McKubre et al. have reported observations of significant excess heat generated during D₂O electrolysis using an Arata-style hollow palladium cathode.

This paper describes helium isotope investigations of gas samples and Pd-black samples from the interior of Arata-style Pd cathodes that had undergone electrolysis in H₂O and D₂O at Stanford Research International (SRI). The initial helium isotope measurements were made at Pacific Northwest National Laboratory (PNNL), and the samples were then sent to McMaster University (McM) for further analysis using a mass spectrometer that was more sensitive for ³He.

II. EXPERIMENTAL METHODS

II.A. Electrolysis

For the sake of clarity, it is desirable to give a brief description of the Arata-style cathode and the electrolysis as carried out at SRI. The cathode consists of a Pd cylinder of length = 6.0 cm, outside diameter = 1.4 cm, and inside diameter = 0.7 cm. The inner volume of 1.1 cm³ was charged with 5g Pd-black, leaving a free inner volume of ~0.6 cm³. The cathode was pumped out in a vacuum system, and the top piece and body were sealed by electron-beam welding. Two such sealed cathodes were provided by Arata. One was placed in D₂O and the other in H₂O. Sustained electrolysis commenced

on October 31, 1998, and ended on January 29, 1999. The electrodes remained in open circuit until February 27, 1999, when the electrode polarity was reversed, and electrolysis continued until May 11, 1999.

II.B. Gas Sampling

After electrolysis was completed, both palladium electrodes were sent to PNNL, where they were placed in a specially constructed vacuum device attached to the sample line of a Finnigan-type analytical mass spectrometer. The essential features of this device are shown in Figure 1. After an overnight pump, a sharp probe attached to a vacuum bellows was used to puncture the top of the electrode, releasing the trapped gas to the vacuum system. The H₂O electrode was observed to be broken following removal from the electrolysis system at SRI. At the time, it was assumed that high internal pressure had ruptured the circumferential weld near the electrode top. Later examination of the electrode, however, showed that the top of the electrode had not been welded to the body. However, the H₂O electrode was punctured as a test of the extraction system and the puncturing device. Following this test, the D₂O electrode was punctured on September 1, 1999. Because of a failure of a pressure sensor in the expansion volume, 90.6% of the electrode gas was pumped away after a 5-min equilibration time. After a second expansion and subsequent mass spectrometer analysis, 29% of the remaining sample, which represented 2.7% of the electrode gas, was stored in a 41.6 cm³ stainless steel cylinder with a high vacuum valve at one end. Pressure and temperature readings of

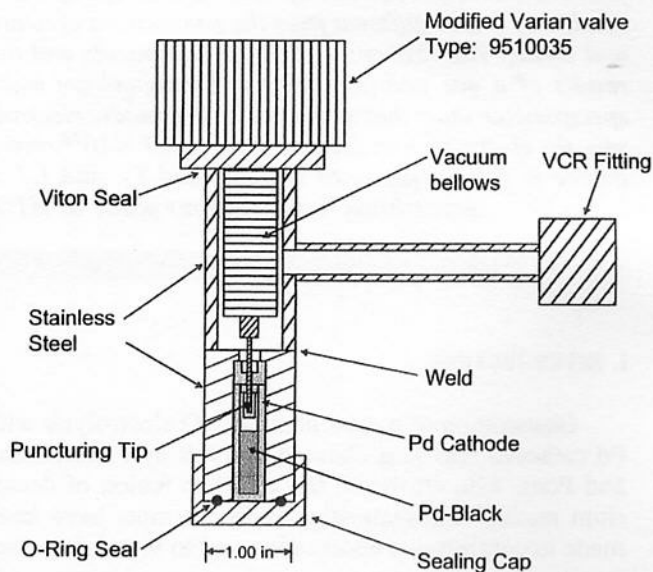


Fig. 1. Palladium electrode gas extraction device used at PNNL.

21.9 Torr and 26.5°C indicated that the steel cylinder contained 1.09 cm³ standard temperature and pressure (STP) gas. We estimate that the uncertainty of this number is ±2%.

II.C. Gas Analysis

Three mass spectrometers were employed in the present study. The Finnigan instrument at PNNL is used for rapid analysis of major components of gas samples. The helium mass spectrometer at PNNL is a statically operated machine used for isotopic analysis of small helium samples at a mass resolution of 1 part in 100 (Refs. 19 and 20). The helium mass spectrometer at McM is also statically operated and has a mass resolution of 1 part in 620, which is sufficient to clearly separate ³He from the isobaric species HD and H₃ (Refs. 16, 21, and 22). The detection limits for ⁴He in the PNNL and McM instruments are comparable, ~10⁸ atoms, but the ³He detection limit of the McM instrument, ~10⁴ atoms, is several orders of magnitude lower than that for the PNNL instrument because of the difference in mass resolution and other factors. The detailed sequence of analyses using these three mass spectrometers will be described in the following sections.

III. RESULTS AND DISCUSSION

III.A. Finnigan Data

The Finnigan gas analysis results are given in Table I. The percentage as H₂O, HOD, and D₂O is 74.5%, which at first glance is surprisingly large. As mentioned previously, pressure and temperature were 21.9 Torr and 26.5°C in the Finnigan vacuum system at the time the sample cylinder was isolated. Using this information and the known volumes of the puncturing device and those in

the Finnigan vacuum system, and assuming no serious H-D fractionation during gas expansion, we calculate that before the electrode was punctured, its free volume of ~0.6 cm³ contained ~5.7 mg liquid water, 0.015 mg water vapor, and gas (H₂ + HD + D₂ + N₂ + O₂ + N₂O) in the proportions given in Table I at a pressure of ~18.8 atm.

It is apparent that the gas sample analyzed by the Finnigan mass spectrometer was not in isotopic equilibrium for H and D. If we insert the measured values for H₂, HD, and D₂ into the isotopic formulas given by Fischer et al.²³ and by Kirshenbaum,²⁴ the predicted equilibrium concentration for D in the water is 60 mol%. The measured value is 43 mol%, which indicates that D is depleted in the water or that D is enhanced in the gas relative to H. It does not seem possible to attribute this effect to partial pressure differences between H₂O, HOD, and D₂O during the expansion steps in the Finnigan vacuum system. Although the sequence and timing of sample handling may have caused minor enhancement of D in the water, this is in the opposite direction to the observed effect. We believe that the observed disequilibrium is mainly due to H-D isotopic fractionation that occurred during partial removal of H₂, HD, and D₂ from the electrode interior during the anodic electrolysis due to the higher rate of H absorption at the inner wall. At the end of this process, D/H in the gas phase inside the electrode must have been considerably higher than the value before the anodic phase began. It is possible that the apparent H-D water-gas disequilibrium is due to incomplete establishment of H-D isotopic equilibrium during the time between the end of the anodic electrolysis on May 11, 1999, and puncturing the electrode on September 1, 1999.

III.B. Initial Helium Measurements in the Electrode Gas Sample

The 41.6 cm³ stainless steel cylinder containing 1.09 cm³ STP sample gas was attached to the inlet line of the PNNL helium mass spectrometer. A 2.4 cm³ aliquot volume was formed between the cylinder valve and an adjoining metal valve in the inlet system. This volume was accurately measured by determining the ⁴He content in air trapped at known pressure and temperature between the two valves using a standard isotope dilution procedure with the addition of a known quantity of ³He "spike." A small fraction of the gas mixture was chemically cleaned of active gases with Zr-Al getters (at room temperature) and liquid N₂-cooled charcoal, and then the fraction was admitted to the mass spectrometer for determination of the ³He/⁴He ratio. From measurements of the isotopic ratio, the amount of ³He spike, and the known ⁴He concentration in the atmosphere, the aliquot volume was determined. After the aliquot volume measurement, the system was thoroughly pumped out, and two aliquots of sample gas were admitted separately to

TABLE I

PNNL (Finnigan) Analysis of Electrode (D₂O) Interior Gas

Species	Percentage of Total
H ₂	13.2
HD	8.9
D ₂	2.3
H ₂ O	24.6
HOD	35.5
D ₂ O	14.4
N ₂	0.6
O ₂	0.2
N ₂ O	0.1

the mass spectrometer using the same procedure described earlier except that the sample ^3He and ^4He ion currents were first measured in a small fraction ($\sim 1.4\%$) of each aliquot. Then, a ^3He spike was added to the remaining fraction ($\sim 98.6\%$) of each aliquot, and a small fraction ($\sim 1.4\%$) of this mixture was analyzed. This procedure allowed an absolute "peak height" calibration of the mass spectrometer. The ^4He was below the detection limit for both aliquots, which is equivalent to an upper limit of $\sim 7 \times 10^{11}$ atoms $^4\text{He}/\text{cm}^3$ STP in the sample cylinder. For one aliquot, the ^3He signal in the unspiked sample was below the detection limit, i.e., $\leq 7 \times 10^{11}$ atoms $^3\text{He}/\text{cm}^3$ STP in the sample cylinder. The other aliquot showed evidence of a barely detectable amount of ^3He that was equivalent to $\sim 1.1 \times 10^{12}$ atoms $^3\text{He}/\text{cm}^3$ STP in the cylinder. When these measurements were complete, the cylinder containing 0.98 cm^3 STP gas was sent to McM for further analysis using the more sensitive ^3He mass spectrometer.

III.C. Initial Helium Isotope Measurements in the Pd-Black Samples

Samples weighing 13 to 17 mg were vaporized in resistance-heated graphite crucibles on-line to the PNNL helium mass spectrometer. Details of the procedures including isotope dilution with ^3He are given by Farrar and Oliver.²⁰ The results of the helium isotope measurements on duplicate samples are given in Table II. It appears that in this sense there is no difference between the Pd-black samples used during H_2O and D_2O electrolysis. It is also apparent that there is no evidence for the large amounts of ^3He and ^4He claimed by Arata and Zhang in Pd-black from similar D_2O electrolysis experiments.¹⁰⁻¹⁵ When these measurements were completed, the Pd-black samples were sent to McM for further helium isotope analysis.

TABLE II
PNNL Measurements of ^3He and ^4He in Pd-Black from Arata-Style Pd Cathodes

Sample ^a	Mass (mg)	^4He Atoms/mg ^b ($\times 10^9$)	^3He Atoms/mg ^b ($\times 10^6$)
94A (a)	17.39	0.03 ± 0.13	-23 ± 52
94A (b)	13.50	0.23 ± 0.17	67 ± 67
94B (a)	15.09	0.15 ± 0.15	60 ± 60
94B (b)	13.36	-0.04 ± 0.17	37 ± 67
Weighted mean ^c		0.09 ± 0.12	35 ± 45

^aAll samples were analyzed on September 12, 1999. The 94A and 94B samples were from H_2O and D_2O electrodes, respectively.

^bUncertainties are estimates of random and systematic errors at a level of 1σ . They do not include the effect of sample inhomogeneity.

^cUncertainties for weighted means are twice the standard error.

III.D. Helium Isotope and Tritium Measurements in the Electrode Gas Sample

Soon after arrival from PNNL, the sample cylinder was attached to the McM helium isotope mass spectrometer inlet system. After pump down, the instrument performance was checked carefully by analysis of several standard air aliquots and inlet system blanks as described previously.^{16,17} The sample cylinder valve was cracked open and a small fraction of the gas admitted at 22°C to a 34.7 cm^3 volume at a pressure of 1.5 ± 0.3 Torr, as determined by a small mercury manometer in the inlet line. The amount of sample admitted to the inlet line was $0.063 \pm 0.013 \text{ cm}^3$ STP. This sample was treated in the usual way by exposure to two activated charcoal traps at liquid N_2 temperature, and to Ti sponge at room temperature.²² Because of the results obtained in the PNNL analyses described earlier and in the previous study of Pd-black from Arata-style cathodes,¹⁶ it was expected that the sample would contain only very small amounts of ^3He and ^4He . When the sample was admitted to the mass spectrometer volume, it was shocking to observe a very large signal of ^3He due to 1.4×10^{11} atoms in the static volume. Simultaneous measurement of the ^4He ion current gave a value of 1.6×10^{10} atoms for ^4He . It should be noted that the ^3He sample admitted to the mass spectrometer is large only by comparison with the usual ^3He samples of 10^5 to 10^8 atoms, and the instrument detection limit of $\sim 10^4$ atoms. The McM measurements gave the following values for the gas in the stainless steel container: $^3\text{He} = 2.3 \pm 0.5 \times 10^{12}$ atoms/ cm^3 STP and $^4\text{He} = 2.5 \pm 0.7 \times 10^{11}$ atoms/ cm^3 STP. The uncertainties are mainly due to the large error in measurement of pressure.

"Memory effects" for the inert gases are well known to mass spectroscopists, and helium is a special case. In sample handling systems, helium memory is often due to diffusion of remnants of previous samples from glass sections or Viton O-rings. This effect is usually easy to remove by heating the inlet line or by waiting a few days for the effect to disappear. Another type of memory effect is due to ions imbedded from previous samples in interior sections of the instrument. Release of imbedded atoms can cause significant drifts in ion currents when a sample is admitted to the static volume. The bias can be difficult or impossible to correct for when a "dirty" inert gas sample is admitted, i.e., one that contains large amounts of H_2 , D_2 , or other gases not removed during chemical cleanup of the sample. For such samples, until the getter(s) in the static mass spectrometer volume has removed the noninert gases, instrumental mass resolution is seriously degraded, and the experimenter may be unaware of enhanced release of imbedded helium from previous samples. In most cases, the problem is minimized or eliminated by the use of efficient getters in the inlet system and/or in a separate vacuum system and by extrapolating helium ion currents to the time of sample

admission to the static volume. In some cases of serious memory, a large sample of N_2 is admitted to the mass spectrometer and the instrument is "scrubbed" by magnetically sweeping the N_2 ion beam back and forth across the tube while using higher than normal ion-accelerating voltage.

After the helium isotope analysis of an aliquot of the electrode gas was completed, 3He memory in the mass spectrometer volume was cleaned as described earlier, but the 3He memory in the sample inlet system could not be completely removed even after several episodes of heating. After a time, it was realized that the memory effect was mainly due to tritium present as HT, DT, and TT and/or HTO, DTO, and TTO in the sample. The charcoal traps at liquid N_2 temperature and the Ti sponge trap effectively prevent any tritium from entering the mass spectrometer volume, but a small fraction of tritium must have diffused into the metal sections of the inlet system. Tests showed that the 3He memory was almost entirely due to release of the tritium decay product 3He from certain metal sections in the inlet line. After these sections were replaced, it was decided to make measurements of tritium in the gas and water components of the D_2O electrode gas sample.

These measurements were carried out by a method^{22,25} wherein samples are sealed in low helium permeability^a containers for suitable decay times prior to assay of accumulated 3He . For this purpose, the cylinder containing the electrode gas sample was attached to a separate vacuum system that had not been previously used for samples high in 3He or tritium. Aliquots of the sample were processed in the following way: After sealing the cylinder to the vacuum system and evacuating, an aliquot of the sample at known temperature and pressure was admitted. The aqueous fraction ($H_2O + HOD + D_2O$) was condensed in a U-trap at liquid N_2 temperature and the gas fraction (mostly $H_2 + HD + D_2$) pumped quantitatively with a mercury toepler pump into a 1720 glass sample tube that was flame sealed. The liquid N_2 was removed from the U trap and ~ 30 mg of degassed laboratory distilled water was admitted to the line via a side arm. This water acted as a carrier to allow quantitative recovery of the water in the sample by freezing at liquid N_2 temperature in a 1720 glass sample tube that was flame sealed. The water carrier introduced a negligible additional amount of tritium because of its low mass and low tritium content ($T/H \sim 30 \times 10^{-18}$). Several aliquots were treated in this way. For some of these, the gas and liquid samples were easily resealed into new 1720 glass sample tubes after the first measurements of accumulated 3He . Decay times varied from 3 to 6 days. Measurements of the tritium concentrations in aliquots of the electrode gas sample received from PNNL gave the following values:

^aOf Corning 1720 aluminosilicate glass.

1. In the H_2 , HD, and D_2 , tritium = $1.56 \pm 0.20 \times 10^{12}$ atoms/cm³ STP ($N = 2$).

2. In the $H_2O + HOD + D_2O$, tritium = $2.04 \pm 0.40 \times 10^{14}$ atoms/cm³ STP ($N = 2$).

The measured values (in November 1999) were decay corrected to reflect the tritium concentrations on September 1, 1999. The uncertainties are estimates of random and systematic errors at a level of 1σ , and N is the number of aliquots analyzed.

As mentioned previously, we have estimated that before the electrode was punctured, its free volume of ~ 0.6 cm³ contained ~ 5.7 mg ($H_2O + HOD + D_2O$)_{l+g} and ($H_2 + HD + D_2$)_g at a total pressure of 18.8 atm. Thus, we calculate that the amounts of tritium inside the electrode before puncturing were as follows:

1. In the H_2 , HD, and D_2 , $T_g = 5.8 \pm 0.7 \times 10^{13}$ atoms.

2. In the $H_2O + HOD + D_2O$, $T_l = 1.7 \pm 0.3 \times 10^{15}$ atoms.

3. From which, $T_g/T_l = 0.03$, and total tritium is $T_t = 1.8 \pm 0.3 \times 10^{15}$ atoms.

If we assume that the relative amounts of H and D in the various hydrogen and water species were approximately the same as found by the Finnigan analysis described previously, then we also find that $H_g/H_l = 0.6$ and $D_g/D_l = 0.3$.

During the time between sampling in the steel cylinder on September 1, 1999, and helium isotope analysis at McM on September 19, 1999, we calculate that the 3He production from tritium decay was $6.0 \pm 1.1 \times 10^{11}$ atoms/cm³ STP, and therefore, the 3He concentration in the cylinder was $1.7 \pm 0.6 \times 10^{12}$ atoms/cm³ STP on September 1, 1999. The cylinder initially contained 1.09 cm³ STP gas on that date, which represented 2.7% of the gas phase sample in the electrode. Thus, the electrode contained $6.9 \pm 2.4 \times 10^{13}$ atoms 3He immediately before puncturing on September 1, 1999. We have estimated that the total tritium content in the electrode at this time was $1.8 \pm 0.3 \times 10^{15}$ atoms. If we assume that the 3He was produced as a result of a single-event injection of tritium, then it is easy to calculate that the event occurred 251 ± 100 days before September 1, 1999, or sometime between September 15, 1998, and April 3, 1999. This calculation indicates that the tritium was produced during cathodic or anodic electrolysis, which lasted from October 31, 1998, to May 11, 1999. This result also indicates that tritium was not removed to a large extent from the electrode interior during anodic electrolysis, which lasted from February 17, 1999, until May 11, 1999. We believe that this was because a very large fraction of the tritium was bound as HTO, DTO, and TTO, and as such it could not escape through the Pd wall into the electrolyte.

III.E. The Possibility of Contamination by Tritium and/or ^3He

Although every aspect of the sample handling and analysis at McM was checked carefully by performing many appropriate blank runs etc., we were acutely aware of the (remote) possibility that the large ^3He concentration found in the stainless steel sample cylinder was due to some sort of contamination. For a time, we considered that this may have occurred during initial helium measurements at PNNL. Several procedural blanks were carried out with the PNNL mass spectrometer inlet system, and these ruled out the possibility of contamination at this stage. In addition, several other gas samples in similar containers and valves had been processed in the mass spectrometer inlet system at PNNL at the same time and in the same way as the D_2O electrode gas sample. Subsequent analyses of these samples at McM did not show any evidence of contamination by ^3He or tritium. For a time, we entertained the possibility that contamination had been introduced in the Finnigan mass spectrometer inlet system when the electrode was punctured. The records were checked and showed that immediately before analyzing the samples from the H_2O and D_2O electrodes some "blanks" and a nitrogen calibration were performed to test the Finnigan system, and no trace of tritium was observed. In addition, samples that were high in ^3He or tritium had not been processed in this system during several months prior to these experiments. As previously mentioned, a gas sample could not be collected from the H_2O electrode because the two sections of this electrode had not been welded. However, as will be described later, McM analyses of the Pd-black inside this electrode and in a section of the Pd wall did not show any unusual concentrations of ^3He similar to those observed for the D_2O electrode. We believe that these facts rule out the possibility of any significant contamination of tritium and/or ^3He in the Finnigan inlet system.

III.F. Further Helium Measurements in the Electrode Gas Sample

After the aforementioned McM analyses were completed, the remainder ($0.75 \text{ cm}^3 \text{ STP}$) of the electrode

gas sample was transferred by a mercury toeppler pump to a new leak-tested and helium-blank-tested stainless steel container with a new high-vacuum valve, which was then shipped to PNNL for further ^3He and ^4He analyses using the most sensitive technique wherein $\sim 60\%$ of the helium in a gas aliquot is admitted to the mass spectrometer volume. Two aliquots were analyzed on December 19, 1999, and a third aliquot was analyzed on February 10, 2000. The results are given in Table III along with the McM result of September 19, 1999, for comparison. The observed increase of ^3He with time clearly confirms the presence of tritium, although the actual rate of increase should be carefully examined.

Assuming the presence of $^3\text{H}_0$ atoms of tritium at $t = 0$, the amount of radiogenic ^3He is given by $^3\text{He}_r = ^3\text{H}_0(1 - e^{-\lambda t})$, where λ is the decay constant of ^3H (Ref. 26), assuming that the system was closed with respect to ^3He and tritium. Thus, a plot of $^3\text{He}_r$ versus $(1 - e^{-\lambda t})$ as shown in Fig. 2 should yield a straight line. We have used the method of least-squares fitting of points with experimental uncertainties as given by York²⁷ to determine the best straight line fit, and we find that the slope indicates a tritium content (on September 1, 1999) of $1.08 \pm 0.20 \times 10^{14} \text{ atoms/cm}^3 \text{ STP}$, which may be compared with the value of $2.06 \pm 0.40 \times 10^{14} \text{ atoms/cm}^3 \text{ STP}$ found from the actual tritium measurements (via accumulated ^3He) on aliquots of the sample in the 41.6 cm^3 steel container. We believe that the apparent discrepancy between these two tritium values is due to the very different absorption characteristics of ^3He and tritiated water, i.e., calculated depletion factors after aliquots are removed from the cylinder are valid for ^3He but not for tritium.

III.G. Total Production of Tritium

Our measurements indicate that the D_2O electrode contained $5.8 \pm 0.7 \times 10^{13}$ atoms T as HT, DT, and TT, and $1.7 \pm 0.3 \times 10^{15}$ atoms T as HTO, DTO, and TTO at the end of the anodic episode, assuming that no loss occurred between then and when the electrode was punctured. We have calculated that the gas pressure at that

TABLE III
 ^3He and ^4He in Electrode (D_2O) Gas Sample

Analysis Date—Laboratory	^4He Atoms/ $\text{cm}^3 \text{ STP}^a$ ($\times 10^{11}$)	^3He Atoms/ $\text{cm}^3 \text{ STP}^a$ ($\times 10^{12}$)
Sep. 19, 1999—McM	2.5 ± 0.7	2.3 ± 0.5
Dec. 18, 1999—PNNL	3.6 ± 1.0	3.52 ± 0.18
Dec. 18, 1999—PNNL	4.1 ± 0.6	3.71 ± 0.19
Feb. 10, 2000—PNNL	4.3 ± 0.3	4.67 ± 0.23

^aUncertainties are estimates of random and systematic components at a level of 1σ . In most cases, pressure measurements were the major source of error.

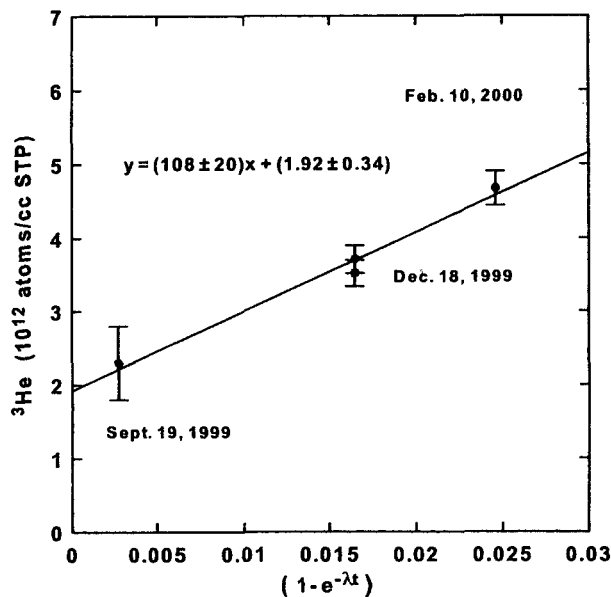


Fig. 2. The ^3He concentration versus $(1 - e^{-\lambda t})$ for aliquots of the sample of electrode gas collected on September 1, 1999, at PNNL. The line is a least-squares fit, and zero time is September 1, 1999.

time was ~ 18.8 atm in a free volume of 0.6 cm^3 . Arata and Zhang have quoted a pressure of 1000 atm attained in similar electrodes during electrolysis.²⁸ For the purpose of illustration, we will assume that the gas pressure in our experiment was between 100 and 1000 atm at the end of cathodic electrolysis. Thus, we calculate that at this stage the electrode contained between 0.31×10^{15} and 3.1×10^{15} atoms T in the gas phase. We will also assume that the amount of T in the aqueous phase did not change significantly during the anodic episode because during this time only gaseous hydrogen is removed from the interior of the electrode. Thus, as a preliminary estimate, we conclude that the total production of tritium during cathodic electrolysis was between 2.0×10^{15} and 4.8×10^{15} atoms, and that 81 to 98% of the T in the gas phase escaped from the electrode during the anodic electrolysis. It should be emphasized however that we do not know what pressure was reached in the electrode during normal electrolysis. The only reasonably hard number we have at present is the estimated pressure of ~ 18.8 atm in the electrode before it was punctured.

III.H. Tritium in the Electrolyte

Before electrolysis began, the tritium content in the D_2O electrolyte was $50 \pm 1 \text{ dis/min} \cdot \text{ml}^{-1}$, which is equivalent to $\sim 1.2 \times 10^{12}$ atoms in the $0.5\text{-}\ell$ electrolyte volume. After electrolysis was completed, the tritium content was measured at $67 \pm 1 \text{ dis/min} \cdot \text{ml}^{-1}$, indicating that at least 4×10^{11} atoms of tritium had entered the electro-

lyte and exchanged with D and H in D_2O and H_2O during the anodic phase. The actual amount was probably larger than this because the cell was not well isolated from the atmosphere during electrolysis as shown by the fact that the H_2O concentration increased from $\sim 0.1\%$ at the beginning to $\sim 10\%$ at the end. The total amount of tritium increase measured in the electrolyte is only 0.7% of the gaseous tritium as HT, DT, and TT estimated to have remained in the electrode void at the end of the anodic phase of electrolysis. While the observed $\sim 30\%$ increase of tritium in the electrolyte appears small in this sense, it is worth noting that it constitutes the only statistically significant case in more than 500 similar assays of tritium associated with Pd cathodes and D_2O electrolysis performed at SRI.

III.I. The ^3He - ^4He Measurements in the Pd-Black and Al-Foil

In a previous paper, Clarke¹⁶ has described ^3He - ^4He measurements in 2- to 6-mg samples of Pd-black provided by Arata and Zhang from the interior volumes of Pd cathodes that had demonstrated excess heat during D_2O electrolysis in their laboratory. Similar ^3He - ^4He measurements and techniques have also been described by Clarke and Clarke.¹⁷ These methods were used with minor modifications for the SRI Pd-black powders. The previous McM measurements¹⁶ had showed that there were small and variable amounts of ^3He and ^4He in the Arata-Zhang Pd-black powders, which included one sample that had not been used in any electrolysis experiment. It should be noted, however, that the amounts of ^3He and ^4He were factors of 10^6 to 10^9 lower than Arata and Zhang have observed in similar specimens of Pd-black.¹⁰⁻¹⁴

During previous McM work, it was found that pieces of Al foil used to wrap the Pd-black samples also contained small and variable amounts of ^3He and ^4He (Ref. 16). Before the Pd-black measurements described herein commenced it was decided to examine other samples of Al foil in the hope of finding a foil containing lower and less-variable helium. To this end, a new roll was purchased from a local hardware store and a 1.0 cm^2 piece analyzed on August 4, 1999, was found to contain $570 \pm 32 \times 10^3$ atoms ^3He , at a concentration of $141 \pm 8 \times 10^3$ atoms/mg. This may be compared with the highest value of $1096 \pm 21 \times 10^3$ atoms/mg found previously¹⁶ for the Pd-black sample A-3. In a further search for a "better" Al foil, helium isotope analyses were carried out on seven pieces of Al foil that had been used in the small sample helium work of Farrar and Oliver since ~ 1966 and found by them to contain especially low amounts of ^4He . The ^3He and ^4He results obtained at McM are shown in Figs. 3 and 4. It is apparent that in these respects, the Farrar-Oliver foil is superior to the foil used in the previous McM study.¹⁶ Although we do not pretend to understand fully the origin of these sporadic

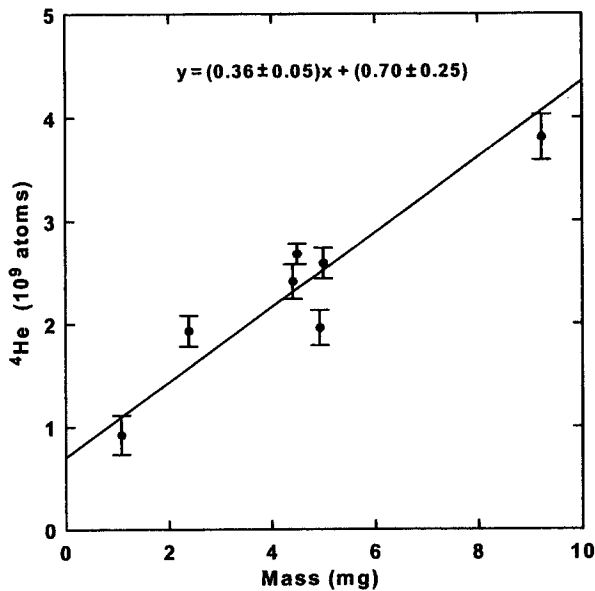


Fig. 3. The ^4He measured in seven pieces of Farrar-Oliver Al foil at McM (see the text). The ^4He intercept of 0.70×10^9 atoms represents a constant amount of atmospheric ^4He released from the inside of the furnace wall due to radiant heating by the hot W furnace coil. These measurements were carried out before the liquid N_2 jacket was installed on the furnace.

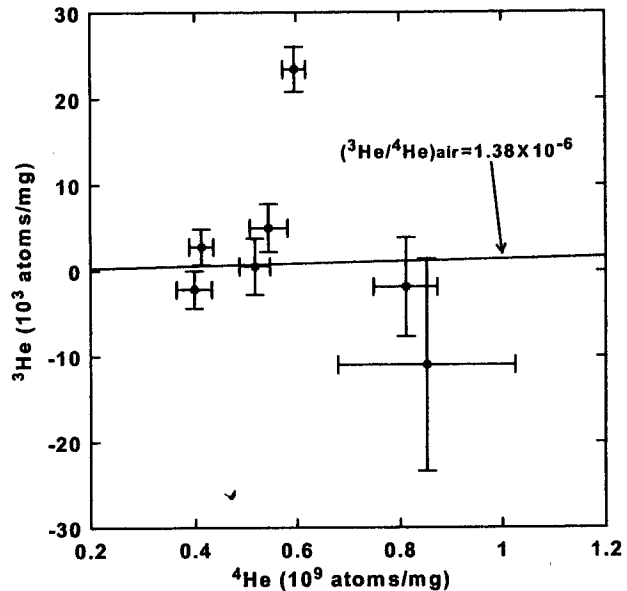


Fig. 4. The ^3He and ^4He concentrations in seven pieces of Farrar-Oliver Al foil.

small amounts of anomalous ^3He and ^4He trapped in metals such as aluminum, we will use the average values as valid corrections for the Pd-black samples wrapped in such foil and vaporized on-line to the mass spectrometer.

Another technical improvement as compared to the previous study¹⁶ was effected near the end of the McM

Pd-black measurements reported in this paper. A jacket cooled to liquid N_2 temperature was added to surround the Pyrex glass sample container on-line to the mass spectrometer. In this way, the "hot blank" of atmospheric helium due to radiant heating of the furnace wall by the W coil and heating due to condensation of vapor from the Al foil wrapping and the Pd samples was significantly reduced.

A summary of ^3He and ^4He measurements made at McM on Pd-black samples from the H_2O and D_2O

TABLE IV

McM Measurements of ^3He and ^4He in Pd-Black from Arata-Style Pd Cathodes

Sample ^a	Analysis Date ^b	Mass (mg)	^4He Atoms/mg ^c ($\times 10^9$)	^3He Atoms/mg ^c ($\times 10^3$)
94A (1)	Nov. 20, 1999	0.72	-0.3 ± 2.2	481 ± 68
94A (2)	Nov. 29, 1999	2.14	1.0 ± 0.7	-34 ± 35
94A (3)	Dec. 02, 1999	1.97	1.2 ± 0.8	15 ± 44
94B (1)	Nov. 20, 1999	1.51	2.6 ± 1.0	4781 ± 64
94B (2)	Nov. 25, 1999	2.59	0.4 ± 0.6	4288 ± 41
94B (3)	Nov. 28, 1999	7.82	-0.13 ± 0.19	4198 ± 24
94B (4)	Nov. 29, 1999	4.27	-0.10 ± 0.36	5023 ± 38
94B (5)	Feb. 29, 2000	1.46	0.31 ± 0.13	7734 ± 97
94B (6)	Mar. 15, 2000	3.55	0.21 ± 0.03	8341 ± 41

^a94A and 94B samples were from the H_2O and D_2O electrodes, respectively.

^bAfter Feb. 2, 2000, samples were vaporized in the improved vacuum chamber with liquid N_2 cooling (see the text).

^cUncertainties are estimates of random and systematic errors at a level of 1σ . They do not include the effect of sample inhomogeneity.

electrodes is given in Table IV. Several features are immediately apparent:

1. The ^4He results for the samples of Pd-black from the D_2O electrode are in good agreement with the independent PNNL results (see Table II) and previous McM results,¹⁶ and as before, they do not confirm the very much higher concentrations found in similar specimens by Arata and Zhang.

2. As mentioned earlier, improved (lower) hot blanks were secured for 94B (5) and 94 B (6). Accordingly, we believe that the weighted mean ^4He concentration of $0.22 \pm 0.05 \times 10^9$ atoms/mg for these two samples is a reliable indicator of ^4He in the Pd-black. However, because we cannot eliminate the possibility that the Pd-black contains a trace of trapped atmospheric helium, we believe that the aforementioned ^4He concentration should be regarded as a high upper limit for production of ^4He in the Pd-black during the D_2O electrolysis at SRI.

3. The ^3He results for Pd-black from the H_2O electrode are comparable to previous results for the specimen of Pd-black (D), which had not been used in any electrolysis experiment.¹⁶

4. The ^3He results for Pd-black from the D_2O electrode appear to be anomalous in a similar sense to the ^3He results in the gas sample obtained by puncturing the electrode at PNNL. The data for D_2O samples 94B (1) to 94B (4) analyzed during a few days at the end of November 1999 indicate that the ^3He concentration is very roughly constant but with definite variation beyond analytical uncertainty as if due to sample inhomogeneity. Samples 94B (5) and 94B (6), which were analyzed in February and March 2000, show clear evidence of enhancement of ^3He due to tritium decay.

As done previously in the case of the electrode gas sample, we will assume a single-event injection of $^3\text{H}_0$ atoms of tritium at $t = 0$, and that the system was closed with respect to ^3He and tritium. Figure 5 shows a plot of ^3He versus $(1 - e^{-\lambda t})$. We have again used the method of least-squares fitting of points with experimental uncertainties as given by York²⁷ to determine the best straight line fit to the data, and we find that the "zero time," i.e., the date when $^3\text{He} = 0$, was July 30, 1999, with an estimated uncertainty of ± 12 days.

It is very puzzling that the least-squares fit line extrapolates to $^3\text{He} = 0$ on July 30, 1999, which is several months *after* the key date of May 11, 1999, which marked the end of anodic electrolysis, or January 29, 1999, when cathodic electrolysis was completed. It appears that the tritium responsible for the observed growth of ^3He in the D_2O Pd-black from the end of November 1999 to April 20, 2000, did not reside in the Pd particles for several months after its production. A possible explanation is that the tritium produced during electrolysis exchanged rapidly with H and D in H_2O or D_2O on the surfaces of

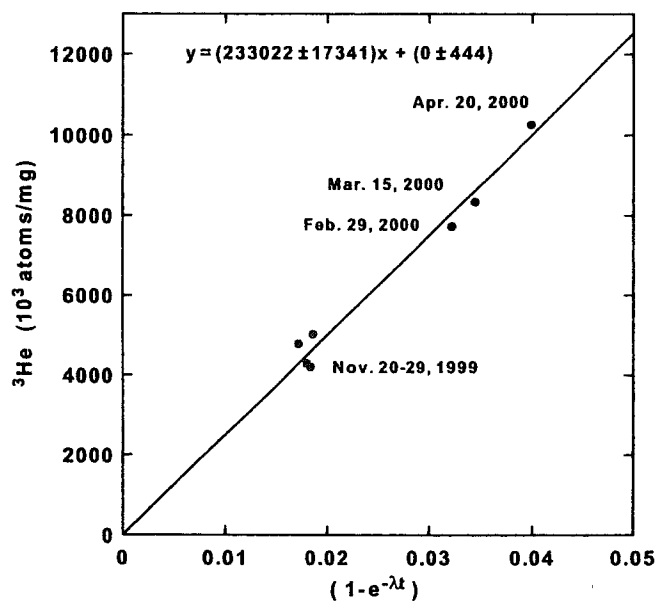


Fig. 5. The ^3He versus $(1 - e^{-\lambda t})$ for 2- to 8-mg samples of Pd-black from inside the Pd electrode used during D_2O electrolysis. Also included is the total ^3He result obtained in the stepwise heating experiment on April 20, 2000, and the subsequent vaporization of part of the sample. The least-squares fit line is drawn through (0,0) with zero time determined to be July 30, 1999 (± 12 days) (see the text).

the Pd particles in preference to residing as T inside the Pd particles, and/or some factor such as the presence of Pd oxide on the particle surfaces inhibited diffusion of tritium back into the Pd particles once it had escaped to the gas phase. In addition, although it may seem plausible to assume that the observed tritium was produced inside the Pd particles, this may not be the case. It is expected that further measurements, which we are continuing, will shed some light on this problem.

III.J. The ^3He - ^4He Measurements in Sections of the Pd Electrodes

Two sections ~ 0.8 mm thick were sliced from the center of each electrode at SRI and sent to McM for analysis. Small slices ~ 2 mm wide were cut from the H_2O and D_2O sections. First, a slice was cut out from the D_2O section with a steel knife, and the slice was then chopped into two pieces with the knife. Then, a slice was cut out from the H_2O section with a thin diamond saw, and the slice was chopped into two pieces with another steel knife. Another slice was cut from the D_2O section with the diamond saw using a new blade, and then this slice was chopped into four approximately equal-length pieces with a steel knife. After the analyses of these samples were completed, the remainder of the D_2O section was filed on the inner and outer edges with a coarse

TABLE V

McM Measurements of ^3He and ^4He in Sections from the Arata-Style Pd Cathodes

Sample ^a	Analysis Date	Mass (mg)	^4He Atoms/mg ^b ($\times 10^9$)	^3He Atoms/mg ^b ($\times 10^3$)
12261-96B (1)	Jan. 21, 2000	4.18	0.32 ± 0.14	16 ± 15
12261-96B (2)	Jan. 23, 2000	3.43	0.28 ± 0.12	-25 ± 23
12261-96E (1)	Jan. 15, 2000	5.57	0.25 ± 0.20	467 ± 16
12261-96E (2)	Jan. 16, 2000	2.99	0.23 ± 0.20	1532 ± 32
12261-96E (3)	Feb. 3, 2000	6.91	0.04 ± 0.03	261 ± 9
12261-96E (4)	Feb. 5, 2000	7.72	0.10 ± 0.03	486 ± 9
12261-96E (5)	Feb. 6, 2000	6.62	0.04 ± 0.03	1061 ± 11
12261-96E (6)	Feb. 7, 2000	5.36	0.11 ± 0.04	1563 ± 21
12261-96E (7)	Feb. 10, 2000	10.43	-0.01 ± 0.03	307 ± 10
12261-96E (8)	Feb. 13, 2000	4.22	-0.04 ± 0.05	2656 ± 30

^a12261-96B and 12261-96E sections shaped like ordinary metal washers were cut from the H_2O and D_2O electrodes, respectively. Samples labeled (1) and (2) were outer and inner half (approximately) pieces chopped from 2-mm-wide slices cut from the sections. Samples labeled (3) to (6) were quarter (approximately) pieces from outside to inside. Samples labeled (7) and (8) were obtained from filings scraped from the outside and inside edges of the D_2O section (see the text).

^bStated uncertainties are estimates of random and systematic errors at a level of 1σ .

metal file, and the chips were recovered to make two more samples. Weighing the chips and the section before and after filing allowed rough estimates of the thickness of Pd removed by filing. These were 0.10 ± 0.04 and 0.05 ± 0.02 mm for the outer and inner edges, respectively. The ^3He - ^4He results and descriptions of the locations of pieces are given in Table V.

It is apparent that the H_2O section does not show any credible evidence for excess ^3He or ^4He , but the D_2O section shows very clear evidence for excess ^3He but essentially no evidence for excess ^4He . If we assume that the ^3He data for the four quarter pieces cut from the D_2O slice are representative of the whole Pd electrode (mass ~ 78.7 g excluding the Pd-black), the total inventory of ^3He was $\sim 6.6 \times 10^{10}$ atoms on or about February 5, 2000. At present, we do not have sufficient information to determine the actual concentration of the tritium parent or when it was injected into the wall of the electrode. However, the ^3He concentration gradient through the wall shown in Fig. 6 clearly indicates that the source of tritium was inside the electrode or in the Pd-black, rather than inside the Pd wall. If we suppose that the tritium diffused through the Pd wall with a constant concentration at the inner surface, then the equation describing the steady-state concentration of tritium through the electrode wall is that for radial diffusion through the wall of a long cylinder given by Crank,²⁹ which is

$$C = [C_1 \ln(b/r) + C_2 \ln(r/a)] / \ln(b/a),$$

where C_1 and C_2 are concentrations at the inner and outer surfaces, and a and b are inner and outer radii. In our

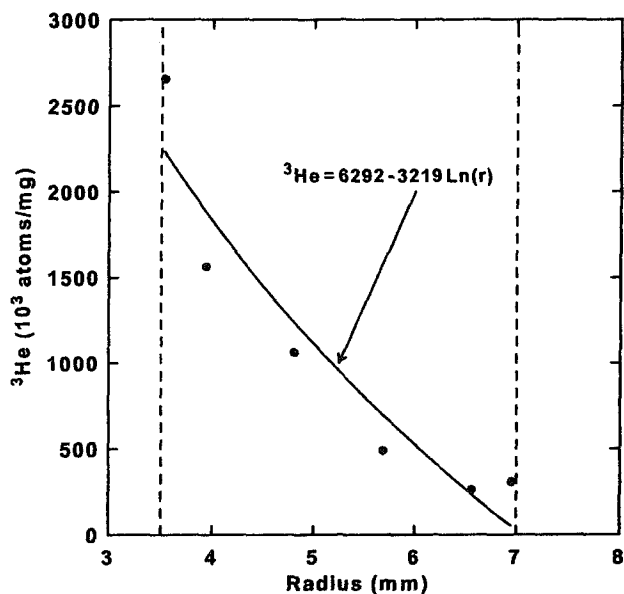


Fig. 6. The ^3He concentrations through the wall of the Pd electrode used during D_2O electrolysis as determined from analyses of pieces cut from a 0.8-mm-thick section from the middle of the electrode. The line drawn through the points is a least-squares logarithmic fit (see the text).

electrode, $a = 3.5$ mm and $b = 7.0$ mm, so the aforementioned equation becomes

$$C = 2.81C_1 - 1.81C_2 - [(C_1 - C_2)/\ln(2)]\ln(r).$$

An equation of the form $C = A + B \ln(r)$, where A and B are constants determined by the boundary conditions, should also be valid for ^3He produced in the wall from tritium decay provided that a steady-state condition is achieved for tritium and there is no diffusion loss of ^3He .

A logarithmic least-squares fit to the ^3He data points shown in Table V and Fig. 6 is given by

$$^3\text{He} = 6292 - 3219 \ln(r) ,$$

where ^3He is in units of 10^3 atoms/mg and r is in millimetres. From this equation, we obtain $C_1 = 2259 \times 10^3$ atoms/mg and $C_2 = 28 \times 10^3$ atoms/mg.

III.K. Stepwise Heating Experiment

A sample of 24.9-mg Pd-black from the D_2O electrode was placed in a thin-wall Ni tube that had been outgassed under high vacuum overnight at $\sim 1000^\circ\text{C}$. The Ni tube was placed in a stainless steel tube resistance furnace attached to the McM mass spectrometer inlet system. After calibration of the instrument with standard air aliquots and measurement of two inlet line blanks, the furnace temperature was raised in a series of steps from room temperature to 980°C . Each temperature was

held for 30 min, and analysis of the helium isotopes released in one temperature step was completed before the gas in the next step was processed. The sequence of measurements was carried out in a continuous series on April 20, 2000. The ^3He and ^4He results are given in Table VI and illustrated in Figs. 7 and 8.

For the purpose of analysis, we consider that the Pd-black is an assembly of uniform spheres of radius a . To obtain a solution, the following equation must be solved:

$$\partial C/\partial t = (D/r^2)\partial/\partial r(r^2\partial C/\partial r) ,$$

with the boundary conditions $C = C_0$ at $t = 0$ and $C = 0$, $r > a$ for $t \geq 0$.

The solution given by Barrer³⁰ is

$$C = -2C_0 a/\pi r \sum (-1)^n/n \exp(-n^2\pi^2 Dt/a^2) \sin n\pi r/a .$$

Boyd et al.³¹ have shown that

$$F = 1 - 6/\pi^2 \sum (1/n^2) \exp(-n^2\pi^2 Dt/a^2) ,$$

where F is the fraction diffused out of the sphere in time t . The foregoing series has been numerically evaluated

TABLE VI

^3He and ^4He Evolved From 24.9-mg Pd-Black (D_2O Electrode) as a Function of Temperature

Temperature ($^\circ\text{C}$)	^4He Atoms ($\times 10^9$)	^3He Atoms ($\times 10^3$)	$\sum ^3\text{He}$ Atoms ($\times 10^3$)	F	Dt/a^2
25	0.11 ± 0.08	15 ± 29	15	0.00006	---
35	-0.05 ± 0.08	-5 ± 23	11	0.00004	---
45	-0.20 ± 0.08	-12 ± 29	-2	-0.00001	---
70	0.20 ± 0.08	0 ± 30	-2	-0.00001	5.37×10^{-12}
105	0.03 ± 0.08	7 ± 32	5	0.00002	2.93×10^{-11}
150	0.00 ± 0.08	73 ± 27	78	0.0003	8.10×10^{-9}
190	-0.19 ± 0.08	513 ± 61	591	0.002	4.67×10^{-7}
240	0.02 ± 0.08	776 ± 66	1368	0.005	2.50×10^{-6}
295	0.03 ± 0.08	2105 ± 89	3473	0.014	1.62×10^{-5}
360	0.00 ± 0.08	5500 ± 84	8973	0.035	1.09×10^{-4}
425	0.27 ± 0.08	17082 ± 129	26054	0.102	9.57×10^{-4}
490	0.12 ± 0.08	68205 ± 251	94260	0.368	1.49×10^{-2}
555	0.39 ± 0.08	49839 ± 218	144099	0.563	4.11×10^{-2}
620	0.31 ± 0.08	37095 ± 168	181194	0.708	7.70×10^{-2}
690	0.22 ± 0.08	15287 ± 159	196481	0.768	9.89×10^{-2}
755	0.50 ± 0.08	4431 ± 81	200912	0.785	1.07×10^{-1}
870	0.23 ± 0.08	5137 ± 95	206050	0.805	1.16×10^{-1}
915	-0.05 ± 0.08	4150 ± 79	210200	0.822	1.25×10^{-1}
980	0.11 ± 0.08	4248 ± 80	214448	0.838	1.33×10^{-1}
Reheat ^b	$(2.06 \pm 1.14)^a$ 3.77 ± 0.25	41395 ± 270	255843	1.000	

^aTotal ^4He released from room temperature to 980°C .

^bAfter the stepwise temperature experiment was completed, a portion of the Pd-black was vaporized to determine the total inventories of ^3He and ^4He (see the text).

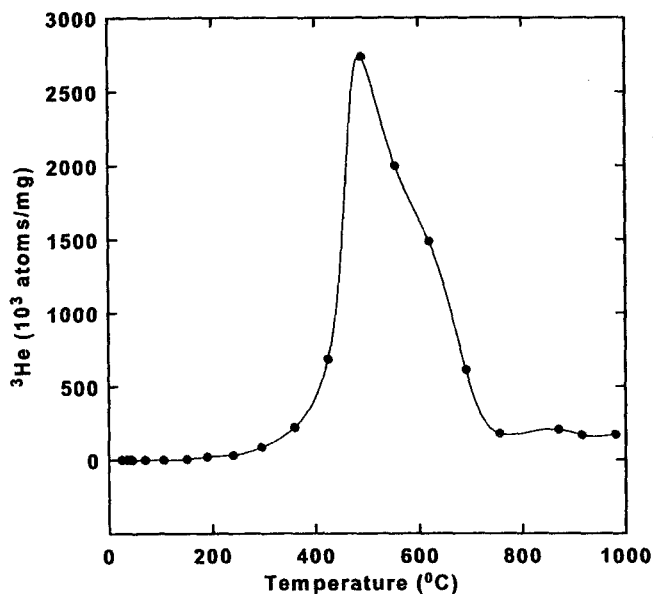


Fig. 7. Release of ^3He from Pd-black used during D_2O electrolysis as a function of temperature.

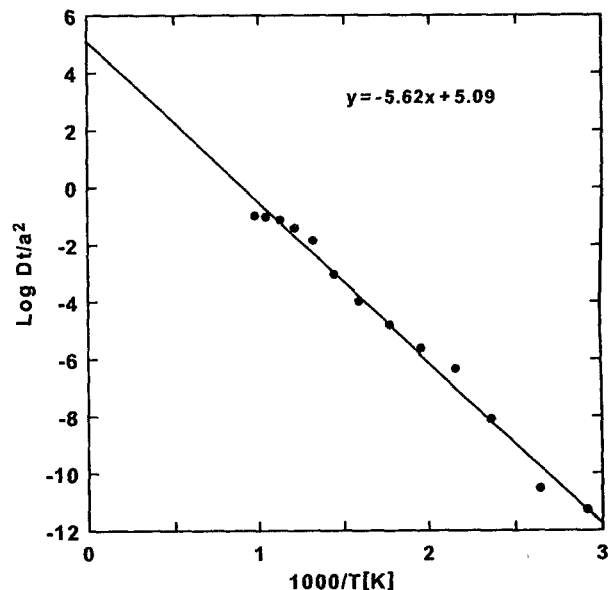


Fig. 9. The relationship between the diffusion coefficient D and $1/T$ for ^3He in the Pd-black used during D_2O electrolysis. The activation energy is $1.1 \text{ eV} = 25\,500 \text{ cal/mol}$.

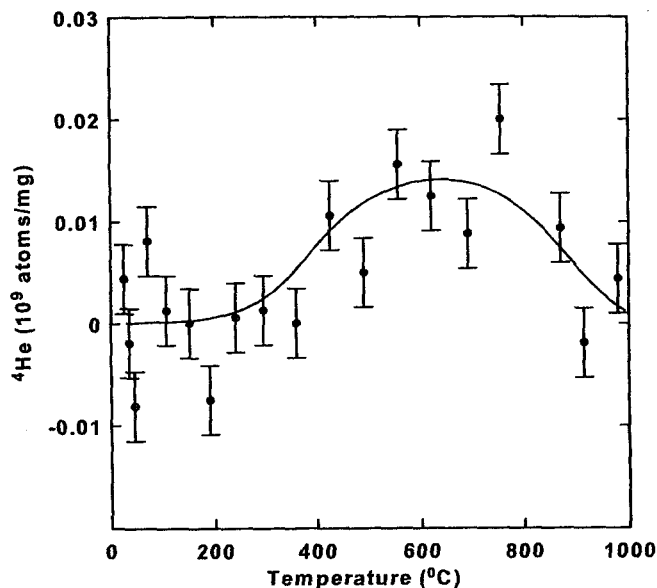


Fig. 8. Release of ^4He from Pd-black used during D_2O electrolysis as a function of temperature. The curve has been drawn by eye through the points to indicate the apparent release of trapped ^4He from 500 to 980°C .

by Reichenberg³² for values of F from 0.01 to 0.99. Table VI gives our experimental F values and the corresponding calculated values of Dt/a^2 .

If the diffusion process can be described by an equation of the form $D = D_0 \exp(-U/kT)$ then a plot of $\log(Dt/a^2)$ versus T^{-1} should give a straight line, and

the slope should allow a calculation of the activation energy U . A graph of the ^3He data plotted in this way is shown in Fig. 9. The first three low-temperature points were omitted because evolved ^3He was at or below detection. The last three high-temperature points were omitted because the ^3He release became approximately constant with increasing temperature. We thought that this was due to a sintering of the Pd-black, which caused a sudden increase in effective particle radius. After the stepwise temperature series was completed, the Ni container was removed from the furnace and the Pd-black was examined with a low-power microscope. The color had changed from black to light grey, and the Pd particles had indeed stuck together in a sinter.

It is apparent from Fig. 9 that the diffusion process can be adequately described by an equation of the form $D = D_0 \exp(-U/kT)$ and that only one activation energy of $1.1 \text{ eV} = 25\,500 \text{ cal/mol}$ exists. It is also apparent that the ^3He formed from tritium is quantitatively retained in the Pd-black at room temperature. If we use the approximation for diffusion from a sphere given by Booth,³³ i.e., that $F = 6(Dt/\pi a^2)^{1/2}$ for $F \leq 0.1$, it is easy to show that the loss of ^3He due to diffusion is only $\sim 6\%$ per million years at 25°C .

III.L. The ^4He Results

The weighted mean value for ^4He in the sample of gas released by puncturing the D_2O electrode is $4.0 \pm 0.9 \times 10^{11} \text{ atoms/cm}^3 \text{ STP}$ (see Table III). Thus the amount of ^4He in the cylinder when it was analyzed at McM on September 19, 1999, was $3.9 \pm 0.9 \times 10^{11}$

atoms. As mentioned previously, after McM analyses were completed, the sample gas was transferred to a new stainless steel container, which was shipped to PNNL for further analysis. The original container was pumped out and the valve was tightly closed. After 7 days, the cylinder was attached to the McM mass spectrometer, and helium isotopes were measured in the usual way. The results gave an upper limit of 1.2×10^8 atoms $^4\text{He}/\text{day}$ for leakage of atmospheric helium into the cylinder, which indicated that no more than 2.3×10^9 atoms ^4He could have leaked into the cylinder during the time between sample collection on September 1, 1999, and the McM analysis on September 19, 1999. However, the Finnigan measurements on September 1, 1999, showed that the gas in the sample cylinder contained 0.6% N_2 and 0.2% O_2 . If these amounts are due to a previous air leak or a residue of air because of incomplete pumping of the electrode prior to welding, then the N_2 and O_2 should be accompanied by $\sim 1.1 \times 10^{12}$ atoms $^4\text{He}/\text{cm}^3$ STP, or more than that if the leak was fractionating with respect to ^4He versus N_2 . This is more than enough to account for the observed ^4He in the cylinder.

As mentioned previously, we believe that the weighted mean value of 0.22×10^9 atoms $^4\text{He}/\text{mg}$ for Pd-black samples 94B (5) and 94B (6) (see Table IV) is a high upper limit for any production of ^4He in the Pd-black during D_2O electrolysis. The weighted mean ^4He value for the six electrode section samples processed using liquid N_2 cooling of the furnace envelope, 12261-96E (3) to 12261-96E (8), is $0.05 \pm 0.04 \times 10^9$ atoms $^4\text{He}/\text{mg}$, where the uncertainty is twice the standard error. Although we do not know the original concentrations of ^4He in the Pd-black used or in the Pd electrode before electrolysis, it should be mentioned that we have recently measured amounts of ^4He from 0.03×10^9 to 0.06×10^9 atoms/mg in several specimens of ordinary Pd wire.^b These amounts should be compared with literature values for ^4He in ordinary Pd wire using comparable laboratory equipment to that used in this work. Values of 0.008×10^9 and 0.026×10^9 atoms/mg were measured for two pieces of Pd wire^c by Kurz (see Ref. 34) and a value of $<0.010 \times 10^9$ atoms/mg was found during analyses of several pieces of Pd wire^d by Lupton (see Ref. 34).

The ^4He data from the stepwise heating experiment (see Fig. 8) indicate that ^4He is released from the Pd-black from ~ 400 to 980°C , with a maximum at $\sim 700^\circ\text{C}$. The sum of all the ^4He released from room temperature to 980°C from the 24.9-mg sample is $2.1 \pm 1.1 \times 10^9$ atoms, which corresponds to $0.08 \pm 0.05 \times 10^9$ atoms/mg. The ^4He released from the Pd-black when the sample was removed from the furnace after the stepwise heat-

ing experiment, and a portion was vaporized, amounted to $0.15 \pm 0.01 \times 10^9$ atoms/mg. Thus, total ^4He is $0.23 \pm 0.06 \times 10^9$ atoms/mg. This value is in good agreement with the weighted mean value of $0.22 \pm 0.05 \times 10^9$ atoms/mg for the Pd-black samples 94B (5) and 94B (6). Our measurements therefore indicate that there is indeed some ^4He trapped in the Pd-black after it was used in the D_2O electrolysis experiment. However, we consider that such a small amount of ^4He is probably due to atmospheric helium present in microscopic bubbles of air or tank helium in the cover gas used during manufacture of the Pd-black. To put the conclusion in another way, we see no compelling reason(s) to assume any other origin than the earth's atmosphere or crust for the small quantities of ^4He seen in our experiments.

Measurement of ^4He in a 0.1-mm layer filed from the outer edge of the section cut from the D_2O electrode gave a value of $-0.01 \pm 0.03 \times 10^9$ atoms/mg (see Table V). This value can be used to set a limit on near-surface production of ^4He via the reaction $\text{D} + \text{D} = ^4\text{He} + \gamma$. If we take the upper limit for near-surface ^4He to be 0.05×10^9 atoms/mg (2σ) and the surface area of the electrode as 9.0 cm^2 , then the inventory of ^4He in the 0.1-mm-thick layer was no more than 5.5×10^{10} atoms. Because 50% of the total ^4He produced via classical D-D fusion would be expected to recoil into the Pd with a range $<0.1 \text{ mm}$, and the other 50% into the electrolyte, 5.5×10^{10} atoms ^4He is also a valid upper limit for the amount of ^4He that entered the D_2O electrolyte in our experiment during 90 days of cathodic electrolysis. This limit, expressed per unit time and per unit electrode area, is many orders of magnitude below the observed amounts of ^4He of 10^{14} to 10^{15} atoms produced in 3.1 days of D_2O electrolysis for a Pd electrode area of 2.6 cm^2 as claimed by Miles et al.³⁵ Therefore, it would appear that these observations require some other explanation than conventional D-D fusion near the Pd electrode surface.

III.M. Tritium Versus Heat

We have estimated that the amount of tritium produced in the cathode was between 2.0×10^{15} and 4.8×10^{15} atoms. If we assume that the tritium was produced by the reaction $\text{D} + \text{D} = ^3\text{H} + ^1\text{H} + 4.03 \text{ MeV}$, then the total released energy was between 1.3 and 3.1 kJ. These numbers should be compared with the excess energy of $64 \pm 6 \text{ MJ}$ measured at SRI (Ref. 18) and the value of $\sim 100 \text{ MJ}$ indicated by Arata and Zhang¹¹ for similar cathodes and D_2O electrolysis times as in our experiment. Clearly, if ^3H is produced within the cathode void by the aforementioned nuclear reaction, it does not contribute significantly to the observed excess heat. If there are any other products of D-D fusion (such as ^3He and ^4He) associated with the observed heat production, they must be generated and released at the cathode surface in such a way that practically none of the products recoil into the Pd.

^bFrom Aithaca, 1 mm diameter.

^cFrom Johnson-Matthey, 1 mm diameter.

^dFrom Mathey-Bishop, 0.5 mm diameter.

IV. CONCLUSIONS

The following can be concluded:

1. During electrolysis of an Arata-style electrode in D_2O for 90 days as a cathode and 83 days as an anode, at least 1.8×10^{15} atoms of tritium were generated inside the electrode, and the estimated pressure was ~ 18.8 atm at the end of anodic electrolysis. If the internal pressure was 100 to 1000 atm, the total production of tritium was between 2.0×10^{15} and 4.8×10^{15} atoms.

2. Estimates of tritium and 3He inside the electrode at the time it was punctured indicate that if the tritium was injected in a single event, this occurred sometime during cathodic or subsequent anodic electrolysis.

3. There is definite evidence of excess 3He from tritium decay in all samples of Pd-black from the D_2O electrode, whereas three samples of Pd-black from the H_2O electrode show much lower and variable 3He similar to previous McM results for Pd-black.¹⁶ Analysis of the D_2O Pd-black data indicates that the tritium parent of 3He was not introduced into the interior of the particles until several months after electrolysis was completed.

4. Measurements of the 3He concentration gradient through the 3.5-mm wall of the D_2O electrode clearly indicate that the 3He is the decay product of tritium that diffused from a source inside the electrode. Further measurements are needed to determine when the tritium was injected and how much remains at present.

5. There is no evidence for any significant production of 4He either in the gas phase sample from the D_2O electrode, the Pd-black inside the two electrodes, or in pieces of Pd cut from sections of the electrodes and thin samples scraped from the inner and outer surfaces. The upper limits found for 4He in Pd-black are many orders of magnitude below corresponding values published by Arata and Zhang,¹⁰⁻¹⁵ who used identical electrodes and D_2O electrolysis for similar times. The upper limit for 4He production near the electrode surface (assuming conventional D-D fusion and recoil of 50% of the 4He into the electrode) is many orders of magnitude lower than observed amounts of 4He evolved during D_2O electrolysis using Pd electrodes by Miles et al.³⁵

6. A stepwise heating experiment from room temperature to 980°C was carried out on-line to the McM mass spectrometer using 24.9 mg of the Pd-black that had been inside the Pd electrode during D_2O electrolysis. The results showed that the diffusion process for trapped 3He can be described by an equation of the form $D = D_0 \exp(-U/kT)$, where $U = 1.1$ eV, and that loss of trapped 3He due to diffusion is only $\sim 6\%$ per million years at 25°C.

7. These experiments have suggested many avenues of investigation that should be explored to achieve a detailed understanding of the observed effects.

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