

PRACTICAL ASPECTS OF HEAT AND HELIUM MEASUREMENTS IN DEUTERATED PALLADIUM

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ABSTRACT

Metal flasks were used to collect electrolysis gas samples in Pd/D₂O + LiOD and Pd/H₂O + LiOH experiments in order to minimize effects due to helium diffusion through glass. For five control experiments yielding no excess power, the mean value for the background helium concentrations in our system was 4.4 ± 0.6 ppb (parts per billion) or $5.1 \pm 0.7 \times 10^{13}$ ⁴He/500mL. For five experiments producing excess power, the measured helium concentration was higher than the background level in each case. Three different laboratories have been used for measurements of the helium concentrations in various electrolysis gas samples from our experiments during the past three years. The helium measurements from all three laboratories yield helium production rates of 10^{11} - 10^{12} ⁴He/s*W.

INTRODUCTION

Our previous results present a correlation between the measured excess power and helium production in D₂O-LiOD electrolysis cells using palladium cathodes. [1] The measured rate of ⁴He production (10^{11} - 10^{12} ⁴He/s*W) is the correct magnitude for typical deuteron fusion reactions that yield helium as a product. [2] Because helium is present in the atmosphere (5.22 ppm), it is essential that atmospheric contamination be prevented. It is indeed a very challenging experimental problem to clearly establish the production of ⁴He from Pd/D₂O electrolysis cells. This situation is compounded by difficulties in obtaining large excess power effects in these experiments.

Table I presents the theoretical relationship between the excess power and helium production assuming $^2\text{H} + ^2\text{H} \rightarrow ^4\text{He} + 23.8 \text{ MeV}$ as the major fusion reaction with the energy being deposited within the calorimeter. At low levels of excess power, the uncertainties in measurements of the helium and the excess power are rather large. When the excess power exceeds 0.2 W, however, it could be possible to correlate the rate of ⁴He production with proposed fusion reaction pathways. It should be noted that for any given excess power, the helium concentration in the electrolysis gas stream will be inversely proportional to the current. For example, an experiment producing 0.500 W of excess power when $I = 250$ mA would theoretically yield 112 ppb of ⁴He in the electrolysis gas stream.

EXPERIMENTAL

The electrolysis cells initially contained 16 cm³ of 0.1 M LiOD + D₂O (99.9% Cambridge Isotope Laboratories) or 0.1 M LiOH + H₂O. The design of the electrolysis cells and calorimeters were similar to previous reports. [1-4] The major difference was that electrolysis gas samples were collected in stainless steel, all metal flasks rather than the 500 mL Pyrex glass flasks used in previous experiments [1-3]. Four identical metal flasks (numbered 1-4) and four similar calorimetric cells (A, B, C, D) were used in this study. The helium concentrations in the metal flasks were measured by a Department of the Interior (DOI) laboratory (Helium Field Operations, Amarillo, Texas). The standard deviation (σ) for the

measurement of the helium concentration was generally about ± 1 ppb, meaning that there is a 67% confidence that the true concentration is within 1 ppb of the stated value and 95% confidence at 2σ ie. ± 2 ppb.

Most of the palladium rod cathodes investigated in this study were obtained from Johnson Matthey. The Pd-Ag alloy cathode (4mm x 1.6 cm) was loaned to us by Dr. Shinji Nezu of IMRA Japan. The palladium sheet cathode (1.0 mm x 3.2 mm x 1.6 cm) was cut from a sample loaned to us by Tanaka Metals (Japan). Two palladium rod cathodes (1mm x 1.5 cm and 2 mm x 1.2 cm) were produced by Johnson Matthey (UK) using the "original recipe" and were loaned to us by Dr. Haven E. Bergeson of the University of Utah.

The flasks were made by welding discs onto the ends of sections of stainless steel pipe and high temperature silver soldering two 0.25 inch stainless steel tubes into the side of the pipe. Nupro brand model SS-4-BK-TW valves were soft soldered to the tubes using Sn-Ag 96%-4% solder and stainless steel soldering flux. The valves were modified by replacing the standard bellows gasket with a copper gasket to effect a metal seal, while the normal Kel-F valve seat was retained in preference to a metal seat, to preclude seat galling induced mass transport leaks. To effect an all metal envelope, the valves were fitted with Cajon VCR fittings soft soldered in place and sealed with a nickel gasket and cap fitting for storage and shipping; the volume between the valve seat and VCR cap seal was flushed out with boil-off nitrogen as it was sealed, to preclude helium diffusing through the Kel-F valve seat.

Metal sample flasks are fragile and must be handled, packaged and shipped with care. The soft solder is easily broken using the leverage available from the valve knob and tubes. For best results, the flasks are routinely baked out at $\approx 100^\circ\text{C}$ for four hours while dynamically evacuated to 5μ vacuum, and stored filled with boil-off nitrogen to avoid contamination by residual helium that might otherwise be trapped in any pores present in the flask metal.

RESULTS

Helium measurements in D_2O and H_2O control experiments are presented in Table II. Stainless steel metal flasks were used to collect the electrolysis gas samples in order to minimize atmospheric contamination due to helium diffusion.^[2] The helium concentrations in Table II support a detection limit of approximately 10^{13} $^4\text{He}/500\text{mL}$ in these experiments as reported previously.^[2] The measured helium concentrations in these control experiments yield a mean value of 4.4 ± 0.6 ppb or $5.1 \pm 0.7 \times 10^{13}$ $^4\text{He}/500\text{mL}$.

For experiments producing excess power, five helium measurements using these same metal flasks have been completed. These experiments are shown in Table III and yield a mean value of $1.4 \pm 0.7 \times 10^{11}$ $^4\text{He}/\text{s}^*\text{W}$ after correcting for background levels of helium measured in control studies (Table II), ie. 45 Mev per ^4He atom. This value is the correct magnitude for typical deuteron fusion reactions that yield ^4He as a product^[2]. It is interesting to note from Table III that the two palladium rods produced by Johnson Matthey using the "original recipe" yielded excess power. The palladium sheet from Tanaka Metals also produced excess power. The excess power density is greater than $1 \text{ W}/\text{cm}^3 \text{ Pd}$ for each of these three cathodes. However, the excess power levels measured during the collection of the gas samples in these new experiments were only 0.1 W or less, hence experimental errors are rather large (Table I). Further experiments using metal flasks are needed that involve equal numbers of control cells and cells producing large excess power effects. This should provide additional statistical evidence regarding helium production in Pd/ D_2O electrolysis cells.

Table II shows that no measurable differences occur in background levels of ^4He over a time period

exceeding four months. Nearly identical ^4He concentrations are obtained for the electrolysis cell C gas sample collected on 24 February 1993 and then again in a different experiment on 7 July 1993. Furthermore, Table II illustrates that the particular metal flask used produces no significant difference in the ^4He result. The lowest ^4He concentration (3.4 ± 1.1 ppb) was obtained using metal flask #4. However, the highest ^4He concentration (9.7 ± 1.1 ppb) was obtained using this same metal flask in an experiment producing excess power (Table III).

Discussion

The strategy of the experimental work was to preclude atmospheric contamination by a system of overlapping and redundant precautionary measures. Cell, gas lines and D_2O were flushed with nitrogen, and then the electrolysis off-gas itself was allowed to flush the entire system and the flask (usually over night). Because of the self flushing feature of open cell operation, contamination by in-diffusion of helium reached a steady state value, allowing a reasonable background correction.

By contrast, closed cell operation would have collected the sum of all contamination sources. Thus, a closed cell experiment requires the use of all-metal apparatus with all metal seals and high vacuum electrical feedthroughs, lest the ingress of atmospheric helium cause the concentration to equilibrate to that of air, followed then by the egress of any helium produced in the experiment to maintain the equilibrium helium concentration. Given impermeable sealing, quantitation of the closed cell build-up experiment for energy versus helium would require that the sum of all energy produced be measured.

Thus, open cell operation provides a much more tractable and reliable experimental method than the closed cell build-up experiment, for the purpose of heat versus helium correlation. The open cell method when upgraded to an impermeably sealed apparatus provides for direct quantification, within instrumental resolution.

The likely source of the measured helium concentration in the control experiments (Table II) is the diffusion of atmospheric helium through the glass in the system and through the thick-walled rubber tubing that connects the electrochemical cell, collecting flask, and oil bubbler [3]. The contribution of atmospheric helium that diffuses through the glass in a system can be calculated by the equation

$$q = KP/d \quad (1)$$

as discussed previously [1,2]. For Pyrex glass with surface area of 300 cm^2 and thickness (d) of 1.8 mm , Equation 1 yields $2 \times 10^{11} \text{ } ^4\text{He}/500\text{mL}$ when $I = 500 \text{ mA}$ (500 mL of $\text{D}_2 + \text{O}_2$ gas is generated in 4870 seconds at 23°C and 700 torr). This amount of ^4He is more than two orders of magnitude smaller than the measured helium levels in the control experiments (Table II). Thus diffusion of atmospheric helium through the thick-walled rubber tubing is the major source of helium in our control experiments. This conclusion is supported by measured diffusion rates of helium through rubber tubing [5].

The background helium concentration of 4.4 ± 0.6 ppb or $5.1 \pm 0.7 \times 10^{13} \text{ } ^4\text{He}/500 \text{ mL}$ places our helium production rate at 10^{11} - $10^{12} \text{ } ^4\text{He}/\text{s} \cdot \text{W}$ as reported previously [2,6]. Furthermore, this background level of helium in our system explains why the effect of atmospheric helium diffusing into our glass flasks during storage and shipment was not observable in experiments involving the analysis of our electrolysis gas samples at the University of Texas [1-3]. The experimental rate of atmospheric helium diffusion into our Pyrex glass flasks when filled with H_2 or $\text{D}_2 + \text{O}_2$ is $1.96 \pm 0.34 \times 10^{12} \text{ } ^4\text{He}$ atoms/day as measured by Rockwell International^[2]. Based on this result, it would require 26 days before the atmospheric diffusion of helium into our glass flasks would equal the minimum helium detection limit for those studies^[1-3]

In our initial study, wherein the glass flask samples were analyzed at the University of Texas⁽¹⁻³⁾ ⁴He was found in 8 out of 8 experiments generating significant excess power, while no ⁴He was found in 6 out of 6 control experiments not generating excess power; no ³He was detected. In a later study the helium diffusion rate for typical glass sample flasks was determined, and showed that our earlier findings were in fact quite reasonable; and further, that the quantity of helium produced was of the right order of magnitude to indicate a nuclear fusion reaction [6]. In the study described here, we approach direct identification of nuclear fusion as the heat producing process, by quantitative helium analysis (see Table III).

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Table I. Theoretical Relationship Between Excess Power and Helium Production. Magnitude of Expected Experimental Errors.

Px (W)	⁴ He ^a (ppb)	⁴ He (atoms/500mL)	⁴ He Error ^b (%)	Colorimetric ^c Error (%)
0.050	5.6	6.38 X 10 ¹³	18.0	40
0.100	11.2	1.28 X 10 ¹⁴	8.9	20
0.200	22.4	2.55 X 10 ¹⁴	4.5	10
0.500	56.0	6.38 X 10 ¹⁴	1.8	4
1.000	112.0	1.28 X 10 ¹⁵	0.9	2

^a For I = 500 mA assuming ²H + ²H → ⁴He + 23.8 MeV is the fusion reaction.

^b ±1 ppb.

^c ±0.020 W.

Table II. Helium Measurements in Control Experiments Using Metal Flasks. No excess power was measured.

Electrode	Flask / cell (date)	⁴ He ^a (ppb)	⁴ He (atoms/500mL)
Pd Rod ^b (4mm x 1.6 cm)	1/C (2/24/93)	4.8 ± 1.1	5.5 x 10 ¹³
PdAg Rod ^b (4mm x 1.6 cm)	2/D (2/24/93)	4.6 ± 1.1	5.2 x 10 ¹³
Pd Rod ^b (4mm x 1.6 cm)	3/C (2/28/93)	4.9 ± 1.1	5.6 x 10 ¹³
PdAg Rod ^b (4mm x 1.6 cm)	4/D (2/28/93)	3.4 ± 1.1	3.9 X 10 ¹³
Pd Rod ^c (1mm x 1.5 cm)	3/C (7/7/93)	4.5 ± 1.5	5.1 X 10 ¹³
(Mean)		(4.4 ± 0.6)	(5.1±0.7 X 10 ¹³)

^a Helium analysis by U.S. Bureau of Mines, Amarillo, Texas.

^b D₂O + LiOD (I = 500 mA).

^c H₂O + LiOH (I = 500 mA).

Table III. Helium Measurements Using Metal Flasks. Experiments Producing Excess Power.

Electrode	Flask / Cell (date)	⁴ He ^a (ppb)	P _x (W)	⁴ He/s*W ^b	MeV/ ⁴ He
Pd Sheet ^c (1.0mm x 3.2 mm x 1.6cm)	3/A (5/21/93)	9.0 ± 1.1	0.055	1.6 x 10 ¹¹	39
Pd Rod ^c (1mm x 2.0cm)	4/B (5/21/93)	9.7 ± 1.1	0.040	2.5 X 10 ¹¹	25
Pd Rod ^c (1mm x 1.5cm)	1/C (5/30/93)	7.4 ± 1.1	0.040	1.4 x 10 ¹¹	45
Pd Rod ^c (2mm x 1.2cm)	2/D (5/30/93)	6.7 ± 1.1	0.060	7.0 x 10 ¹⁰	89
Pd Rod ^d (4mm x 2.3cm)	1/A (7/7/93)	5.4 ± 1.5	0.030	7.5 x 10 ¹⁰	83

^a Helium analysis by U.S. Bureau of Mines, Amarillo, Texas.

^b Corrected for background helium level of 5.1 x 10¹³ ⁴He/500 mL.

^c D₂O + LiOD (I = 400 mA).

^d D₂O + LiOD (I = 500 mA).