

Thin-Foil Electrochemical Cells: High-Sensitivity Fusion Tests and *in-Situ* Ion Beam Measurements of Deuterium Loading

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Electrochemical cells constructed with a thin Pd or Ti foil electrode mounted at one wall of the cell have been used both to test for the existence of "cold fusion" and to measure directly D:Pd loading ratios in an operating cell. The first type of experiment used a surface-barrier particle detector positioned a few millimeters from the foil to provide a very sensitive monitor for possible fusion-generated protons at 3.02 MeV. The detection limit for this arrangement is estimated to be 10^{-24} fusions/deuterium/s, assuming a bulk fusion effect. These experiments included cells with 5- and 25- μm -thick Pd foils, 10- μm Ti foils, parallel experiments with 0.1 M LiOD (heavy water) in one cell and LiOH (light water) in another, current densities up to 0.5 A/cm², and run times as long as 22 days. No evidence for fusion products was seen. The second type of experiment using these cells, both as an adjunct to the fusion tests and to provide new information, was the use of external beam nuclear reaction analysis to monitor directly the loading and unloading of deuterium in the foil of an operating cell. Using a 1.5-MeV ³He ion beam in air, the deuterium in the outer 2 μm of the exposed Pd foil was measured for the first time using the D(³He,p) nuclear reaction. The maximum D:Pd ratios observed using this technique were 0.8–0.9.

1. INTRODUCTION

A sensitive test of recent claims of fusion in electrochemical cells operating with Pd or Ti cathodes^{1–4} would be the detection of fusion-generated protons using a suitable arrangement of detector and thin-foil electrode. The sensitivity of such an experiment can be better than that of the more commonly used detection of neutrons because the solid-state surface barrier detectors used for charged particle detection are essentially 100% efficient, and more important, there is almost no MeV-energy charged particle background with which to contend. We and a number of other laboratories^{5–8} began

using this approach to search for evidence of cold fusion within days of the initial reports.

An additional advantage of the thin-foil electrode cell is that the deuterium content of the foil can be directly measured using a suitable external ion beam arrangement. A key claim in the University of Utah reports² is that the D:Pd loading ratio in the operating cell is greater than 1. Measurement of the deuterium loading for such bulk electrodes is difficult and indirect. By using external ion beam analysis at the exposed surface of our thin-foil electrodes, we have been able to measure the D:Pd ratio *in situ* while the cell is in operation, providing a direct and unique test of the claims of unusually high deuterium loadings. To our knowledge, no other laboratory has combined ion beam analysis for *in situ* measurements of deuterium loading with a search for the

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presence of fusion products using a thin-foil electrode. This paper presents results from both aspects of our experiments.

2. TESTS FOR COLD FUSION

Figure 1 shows a diagram of the electrochemical cell configuration. The cell is constructed with an O-ring-sealed Pd foil electrode mounted at one wall of the cell, which is exposed to air on the back side. The counter electrode is a Pt wire mesh. The exposed foil area is ~ 4 cm² and the solid angle for particle detection is ~ 4 sr. An important concern is possible loss of deuterium from the foil where it is exposed to air, which would limit the loading which could be achieved. Two steps were taken in the design to prevent this. First, the exposed side of the Pd foils were coated with 100–200 nm of Au prior to cell assembly. Au is expected to block deuterium recombination and prevent loss of deuterium from the foil. Second, the outside edge of the foil is surrounded by another O-ring and several holes are drilled through to the space between the two O-rings, allowing electrolyte

to contact the foil around its edges. Electrical contact to the foil is also made through one of the holes, using a Pt wire. Through these arrangements, only Au-covered foil is exposed to air.

The first type of experiment used a surface-barrier particle detector positioned a few millimeters from the foil to provide a very sensitive monitor for fusion-generated protons at 3.02 MeV. Figure 1 shows a detector mounted behind the foil. We used detectors with a 200-mm² active area, "ruggedized" and passivated for exposure to hydrogen gas.⁹ The latter treatment is an important consideration in these experiments, since there is typically a substantial partial pressure of hydrogen or deuterium gas in the vicinity of the cell. We found that a nonpassivated detector would start to degrade within a few hours when operated near these cells.

The foil thicknesses used were 5- and 25- μ m Pd and, for a few experiments, 10- μ m Ti. A calculation using the TRIM¹⁰ implantation code shows that even the 25- μ m foils are thin enough that 3-MeV protons produced at the far side of the foil can escape through the foil with about 1 MeV of energy remaining. Further energy losses in the thin Au layer and the air gap are

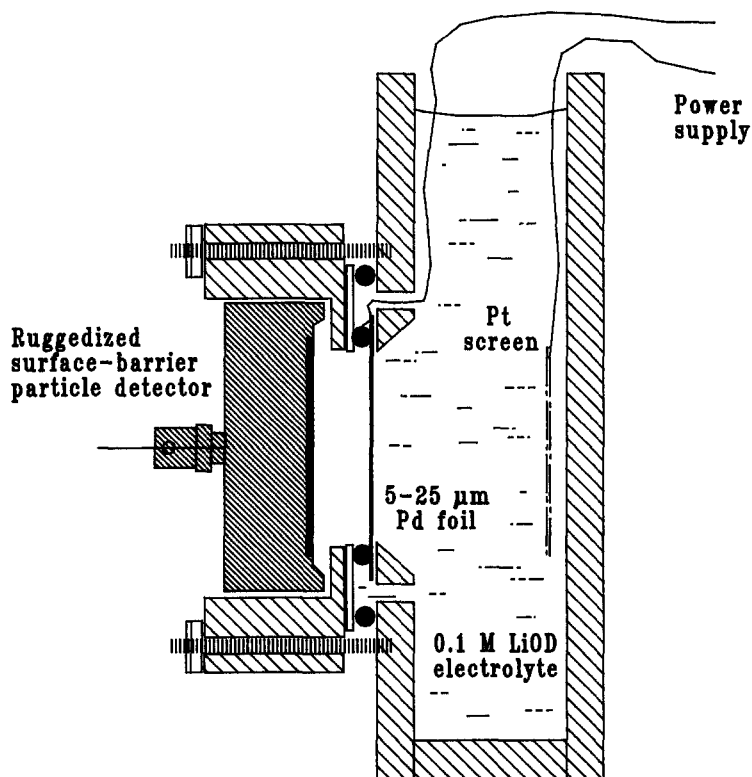
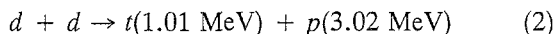
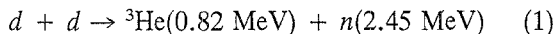


Fig. 1. Schematic diagram of the thin-foil electrochemical cell.

not significant. The nuclear reactions between deuterium pairs are



Reaction (2) is the branch that we are testing, and it also produces a 1.01-MeV tritium particle. If fusion were occurring throughout the foil and not just at the interface with the electrolyte, our experiment would also detect tritium at 1 MeV and below. If an interface reaction is involved, only protons would be detected. A further possibility which has been proposed is a $d-d$ reaction to form ${}^4\text{He}$ and a γ , with a Q -value of 23.8 MeV. It is not clear what energy might be imparted to the ${}^4\text{He}$ product in this reaction, but if it received as much as 1 MeV, we would detect such particles from the outer few microns of the foil.

Figure 2 shows a pulse-height spectrum obtained from a typical run using the above configuration, collected over a period of 23.2 h. The electrolyte was 0.1 M LiOD and the foil was 25- μm Pd, which had been annealed at 1075°C for 15 h at 10^{-6} Torr prior to Au deposition. A charging current of 0.5 A/cm² was used, after a short anodic/cathodic cycling step to clean the immersed surface of the foil. The detector was calibrated for each run with 5-MeV ${}^4\text{He}$ particles from a ${}^{241}\text{Am}$ source and the resulting energy scale is shown at the top of Fig. 2. There are 17 counts in the region from 1 to 3 MeV: this is statistically equal to the background for this same detector, obtained with the detector separated from the cell. Background counts were found to vary some-

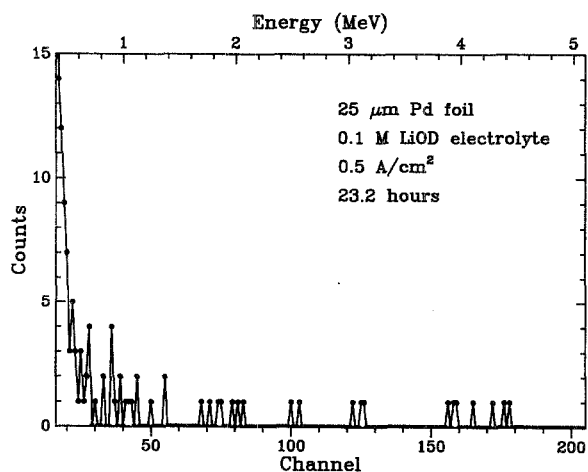


Fig. 2. Charged particle pulse-height spectrum obtained during a 23.2-h run using 0.1 M LiOD and a charging current density of 0.5 A/cm². Fusion products would be detected at 3 MeV and below.

what with the detector/electronics combination used and with the time of day but, in all cases, were less than 5/h in this energy range. The dependence on time of day suggests that power line noise is a contributor to the background, in addition to the expected, occasional cosmic ray events. Many experiments were run with one detector on the cell and another detector sitting several centimeters away on the bench, with spectra being collected from both. The detectors and amplifiers were switched for different runs to check for detector-dependent effects. We also did experiments with two cells running simultaneously, one with heavy water electrolyte and the other with light water, each with its own detector. Most experiments were performed with 0.1 M LiOD electrolyte, with a few runs made with a Ti foil and a Pd(NO₃)₂/Li(NO₃) electrolyte similar to that used by Jones *et al.*;⁴ loading times were as long as 22 days, and charging currents up to 0.5 A/cm² were used. No statistically significant counts above background were seen in any run.

The sensitivity limit for this experimental arrangement is calculated by assuming a fusion count rate equal to the background (which would be 4× the standard deviation of the background counts for a 24-h run), a Pd volume of 4 cm² × 25 μm , and a D:Pd loading of 1:1. Dividing counts by solid angle, number of available deuterium atoms, and collection time gives a limit of 1×10^{-24} fusions/deuterium/s. This approach assumes fusion throughout the volume of the foil; if fusion were occurring in a monolayer of deuterium at the electrolyte interface, the limit would be 5×10^{-20} fusions/deuterium/s at the interface. We have also assumed an equal branching ratio between reaction (1) and reaction (2). Since we do not see significant counts, these numbers represent the upper limit for fusion rates in our cells.

3. ION BEAM MEASUREMENTS OF DEUTERIUM LOADING

The second type of experiment using these cells was carried out to check the claims of D:Pd loading ratios of 1:1 or higher.² An external beam nuclear reaction analysis was performed to monitor directly the loading and unloading of deuterium in the foil as the cell was operated. Using a ${}^3\text{He}$ ion beam in air, the deuterium in the outer part of the exposed Pd foil is measured using the D(${}^3\text{He}$,p) nuclear reaction.¹¹ Figure 3 shows a diagram of the beam line and cell configuration. A 3.0-MeV ${}^3\text{He}$ beam passes through a thin window consisting of 3.0- μm Al covered with 0.5 μm of Au, crosses 5 mm of air gap, and enters the exposed side of the foil. The Au on the window backscatters a small part of the

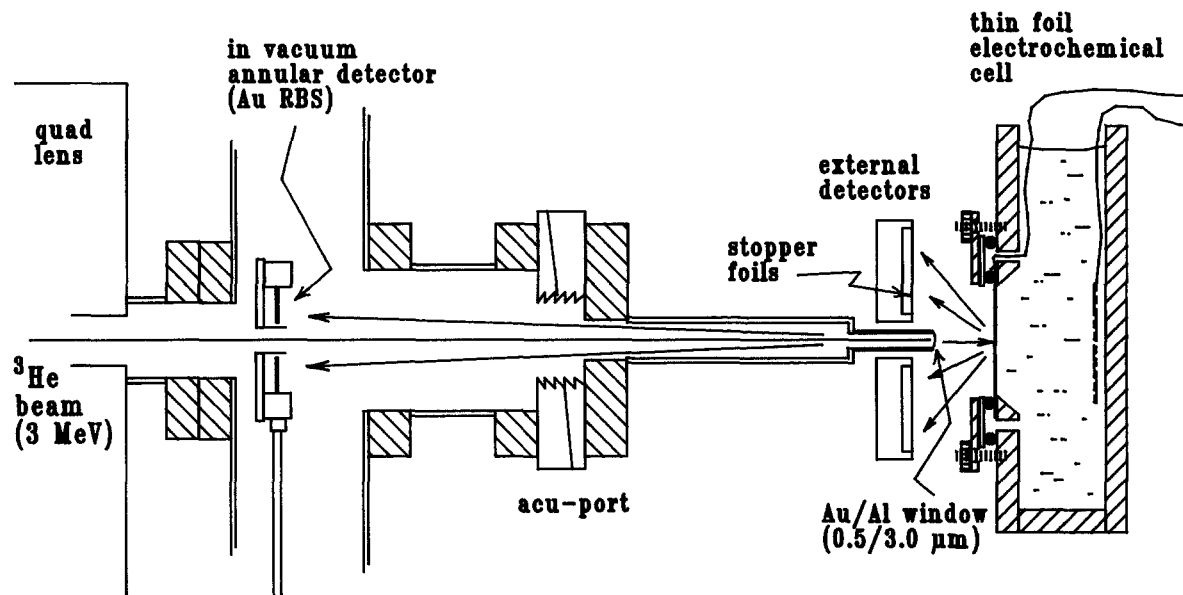


Fig. 3. Schematic diagram of the external ion beam nuclear reaction analysis configuration.

beam, which is detected with an upstream annular detector for beam intensity normalization. The ^3He beam loses energy as it crosses the air gap and enters the electrochemical cell foil at ~ 1.5 MeV. Within the foil, the beam reacts with deuterium, producing 14-MeV protons which exit the foil and are detected with Al-covered surface-barrier detectors mounted alongside the beam line. The range of the ^3He beam is such that the outer $2\ \mu\text{m}$ of the Pd foil is examined. A separately calibrated metal deuteride standard was used to correlate the yield with the amount of deuterium present in the sample.

The advantage of this approach for measuring the D:Pd ratio is that the deuterium content may be monitored continuously as the cell is turned on and off and deuterium loaded or unloaded. Figure 4 shows a history of the observed D:Pd ratio in a $25\text{-}\mu\text{m}$ Pd foil. Each point represents a collection time of either 20 or 120 s; the points from 0 to 10 min and near 55 min were obtained with 20 s/point and, thus, show more scatter than the rest of the data. The foil was cleaned with an anodic/cathodic cycle, and then charging at $0.1\ \text{A}/\text{cm}^2$ started at 5 min. The figure shows that the D:Pd ratio rose to 0.8 within 5 min, with a slight change of slope near 0.7. This latter point, corresponding to the completion of the phase change from α to β , is also the time at which bubbling from the foil surface began, indicating a slower charging rate. Clearly, diffusion of deuterium through the $25\text{-}\mu\text{m}$ foil thickness is relatively fast, as would be expected from typical diffusion rates in Pd.¹² After load-

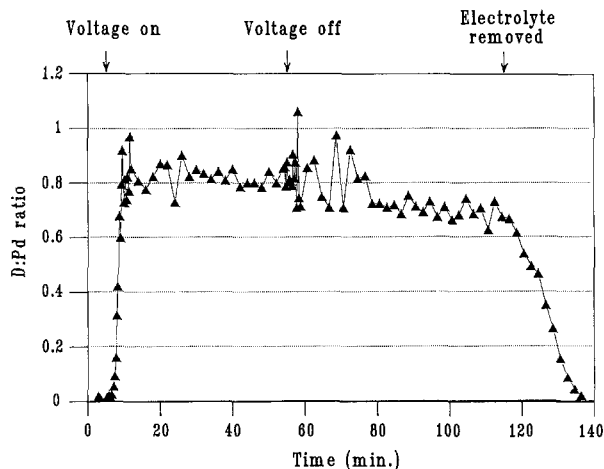


Fig. 4. D:Pd ratio vs time for a $25\text{-}\mu\text{m}$ Pd foil loaded at $0.1\ \text{A}/\text{cm}^2$, using $0.1\ \text{M}$ LiOD electrolyte.

ing for 55 min, during which time the D:Pd ratio did not rise above ~ 0.85 , the charging current was turned off. As the plot shows, the foil lost deuterium over the next several minutes, but the rate of loss slowed dramatically as it reached 0.7. At about 115 min the electrolyte was removed from the cell, exposing the clean Pd surface: the remaining deuterium left the foil within 30 min.

The results shown in Fig. 4 are typical of all the

experiments we have performed to date. Foils were observed to load to 0.8–0.9 D:Pd within 5–10 min and remain at that level; continued charging for up to 3 days did not result in a higher loading ratio, nor did charging at higher current densities. Furthermore, the thickness of the Au layer did not affect the loading ratio which could be achieved. In fact, a foil that had no Au layer at all reached the same D:Pd ratio as the Au-covered foils. We infer that the oxide and contamination on the uncleaned, exposed surface were sufficient to poison the recombination process and block loss of deuterium, even without the Au diffusion barrier. This inference is strengthened by the observation that the deuterium leaves the foil quickly once the clean inner surface of the foil is exposed to air, as above.

Another key question which has been raised¹³ is whether the presence of hydrogen in the foil or in the electrolyte would lock up trapping sites in the Pd and prevent sufficient loading of deuterium. With the external ion beam measurement, we can directly address this question. Preliminary experiments, in which heavy and light water electrolytes were exchanged back and forth while monitoring deuterium content in the foil, indicate that hydrogen does load into the foil preferentially over deuterium when both are present. Increasing the light water component of the electrolyte to ~30% reduces the D:Pd ratio to 0.3–0.4, but returning to a 99.99% heavy water electrolyte recovers a D:Pd ratio of 0.8–0.9 within a few hours as the deuterium exchanges for hydrogen. Further experiments are planned, with a sealed cell using isotopically pure heavy water electrolyte, to test whether a higher loading may be achieved. These results will be reported elsewhere,¹⁴ as well as details of experiments relating potentials of Pd cathodes (vs a reference electrode) with measured deuterium loadings. Such measurements provide a direct correlation between electrode loading and chemical potential.

4. SUMMARY

A number of experiments have been performed using thin-foil electrochemical cells, both the provide a sensitive test for fusion and to measure directly D:Pd ratios in operating cells. The detection limit for the fusion tests, assuming a bulk effect, is calculated to be 1×10^{-24} fusions/deuterium/s, which corresponds to a level of ac-

tivity similar to that now reported to be an average rate for the Brigham Young University experiments⁴ and five orders of magnitude lower than originally claimed by the University of Utah.¹ We have seen no evidence of fusion products. The second aspect of our experiments has been to measure directly deuterium loading in Pd foils in operating cells, in order to test the claims of D:Pd ratios substantially exceeding 1:1.² The maximum loading we observe under any conditions is 0.9.

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