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TRITIUM AND NEUTRON MEASUREMENTS OF A SOLID STATE CELL

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TRITIUM AND NEUTRON MEASUREMENTS OF A SOLID-STATE CELL

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ABSTRACT

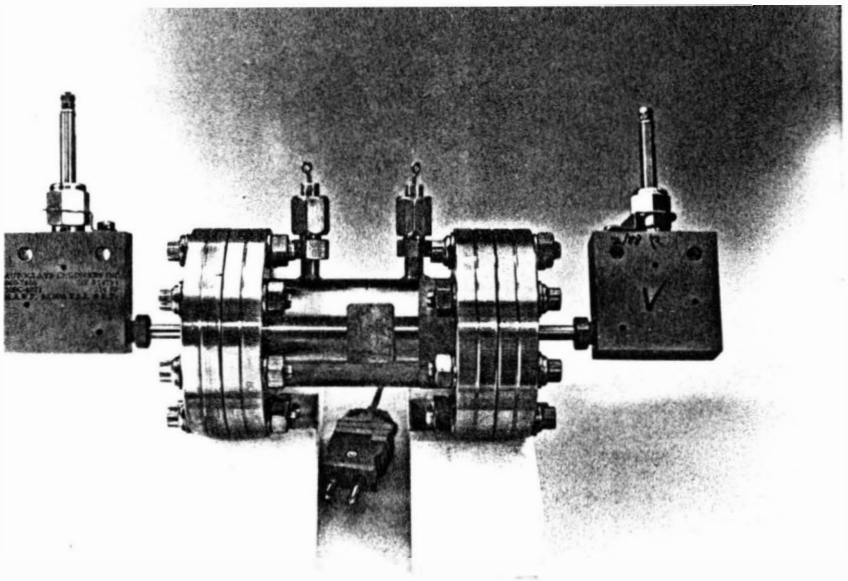
A solid state "cold fusion" cell was constructed to test for nonequilibrium D-D fusion in a solid. The stimulus for the design was the hypothesis that the electrochemical surface layer in the Pons-Fleischmann cell could be replaced with a metal-insulator-semiconductor (MIS) barrier. Cells were constructed of alternating layers of palladium and silicon powders pressed into a ceramic form and exposed to deuterium gas at 110 psia, resulting in a D/Pd ratio of 0.7. Pulses of current were passed through the cells to populate nonequilibrium states at the MIS barriers. One cell showed neutron activity and had a large amount of tritium. Other cells have produced tritium at a low rate consistent with neutron emission at or below the threshold of observability. The branching ratio for n/p was about 3×10^{-9} in all the experiments where a substantial amount of tritium has been found.

Introduction

Recent experiments[1–4] have indicated that Pons-Fleischmann electrochemical cells produce neutrons, tritium, and perhaps heat by means of an unknown new "cold fusion" process. These cells seem to be remarkably sensitive to palladium surface preparation, electrolyte impurities, and exact cell configuration. It is reasonable to assume that the fusion mechanism is a near-surface phenomenon dominated by the high concentration of deuterium electrically driven into the material. Electrochemical surface barriers are similar (electrically) to the barrier at metal-semiconductor or metal-insulator-semiconductor contacts.[5] Therefore, a MIS (metal-insulator-semiconductor) device was fabricated from slightly oxidized palladium and silicon powders.

Apparatus

Figure 1 shows the cell schematically. Layers of powder were pressed into the ceramic form at 11.2 MPa, resulting in densities of 26% and 75% of theoretical density for the palladium and silicon, respectively. The belleville washers at each end maintained a constant pressure of 3.3 MPa as the palladium swelled during deuteriding. Samples were deuterided at 0.76 MPa, resulting in a D/Pd ratio of 0.72. Table I lists the gas analysis of the three bottles used to fill the cells as well as the analysis of the major impurities in the silicon and palladium. The silicon and palladium powders used in these experiments were analyzed for intrinsic tritium. None was found in the silicon, and an upper limit of 0.2 nCi/g may be set for the palladium powder. Both the silicon and palladium powders were coated with an oxide layer that is thought to be important. Auger analysis indicated



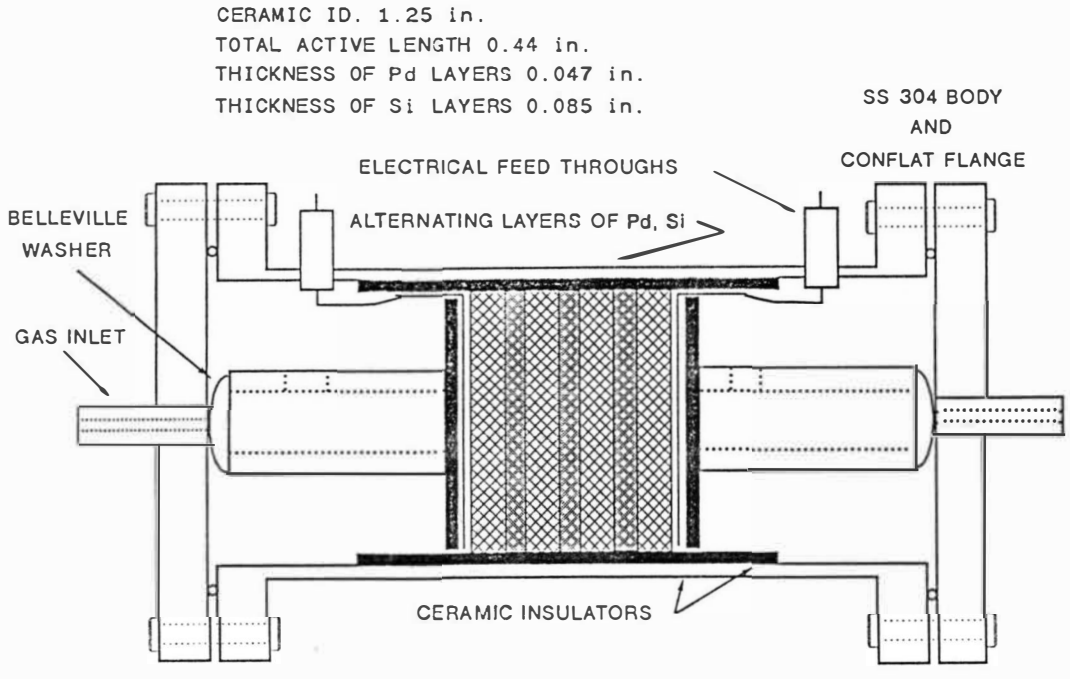


Figure 1. The experimental cell showing the layers and the electrical connections.

that the silicon oxide layer is approximately 10 to 20 Å thick. Figure 2 shows the unusual morphology of the palladium powder (formed during precipitation) and the size and shape of the silicon powder. Figure 3 shows the powder after pressing.

Voltage-current plots indicate that the cell resistance is controlled primarily by the silicon oxide layer. Typically, the curves are highly nonlinear, suggesting that the current results from tunnelling or a variety of other conduction mechanisms[6] previously observed in MIS devices. The voltage-current data were taken under pulsed conditions to keep the cell from heating by more than a few degrees.

Gas Bottle No.	Deuterium	Hydrogen	Tritium	Helium 4	Other (all bottles)
Deuterium Bottle 1:	99.3	0.6	110	15 ppm	H_2O, O_2, CO, CO_2, N_2 < 0.1%
Deuterium Bottle 2.	99.34	0.66	28	15±5	
Deuterium Bottle 3:	99.33	0.67	20	15±5	
Hydrogen Bottle 1:	<0.1%	99.9	<1	15±5	
Palladium Analysis	(μg/g)	(Engelhard)			
Oxygen	928				
Nitrogen	65				
Carbon	47				
Chlorine	80				
Ag=35, Fe=20, Pt=35, Zn=10, Au=30, Si=15, B=15, Pb=2,				all others <10 ppm wt	
Tritium <0.2 nCi/g					
Silicon Analysis major impurities	(μg/g)	(Union Carbide)			
Chromium	3000				
Iron	800				
Tantalum	300–3000				
Tritium <0.1 nCi/g					

Note: Deuterium and hydrogen in terms of mole %, tritium in terms of micro curies per meter cubed.

Table I. Material analysis of the deuterium, hydrogen, palladium and silicon used in the experiments. The gas analysis was done with a mass spectrometer and a tritium ionization gauge. The palladium and silicon were analyzed by wet chemistry.

To enhance the detection of the neutrons and to obtain the highest current densities possible, we used a pulsed excitation source in all experiments. The voltage and current pulse was 1 μs to 1 ms in width at up to 3000 V at currents as high as 0.5 A with a low duty cycle (such as 10 ms). Usually, the pulse width and duty cycle were adjusted so that 1 W was dissipated in the cell. However, the peak power was often 100 W or more, limiting the joule heating to a few degrees and resulting in little change in the average D/Pd ratio. Initial neutron data were collected with a detector consisting of a bank of 15 ^{3}He proportional counters moderated by polyethylene. The efficiency of this system as measured with a ^{252}Cf source was 1.3%. Time correlation was used instead of energy discrimination. The pulse to the cell triggered the time-of-flight electronics of the Low-Q diffractometer at LANSCE (Los Alamos Neutron Scattering Center). The time correlation was intended to give a concurrent background measurement by recording counts well after the current pulses. Figure 4 is a schematic of the experimental apparatus.

To test for tritium, we constructed a gas line using an ionization gauge as the measurement device. The system rejects radon and other radioactive ions that do not produce ionization characteristic of 18.6-keV endpoint electrons. Figure 5 shows a schematic of the system. The system is used to pump down and fill the cell as well as measure the tritium in the deuterium gas before and after cell operation.

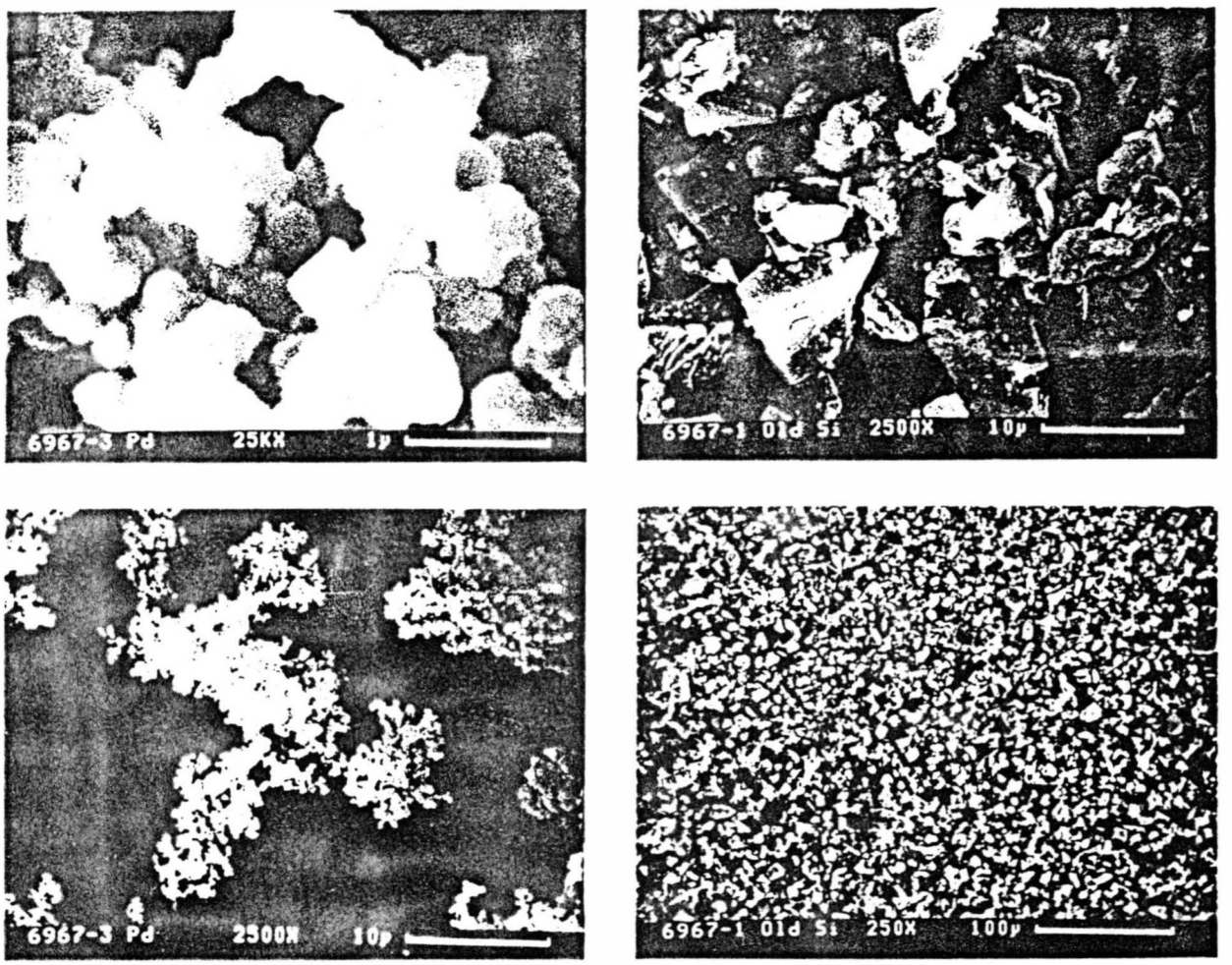


Figure 2. SEM photographs of the palladium and silicon powders used in the cells. The palladium is produced from a precipitation process that leaves the surface coated with an oxide layer. The silicon is ball-milled from ingots.

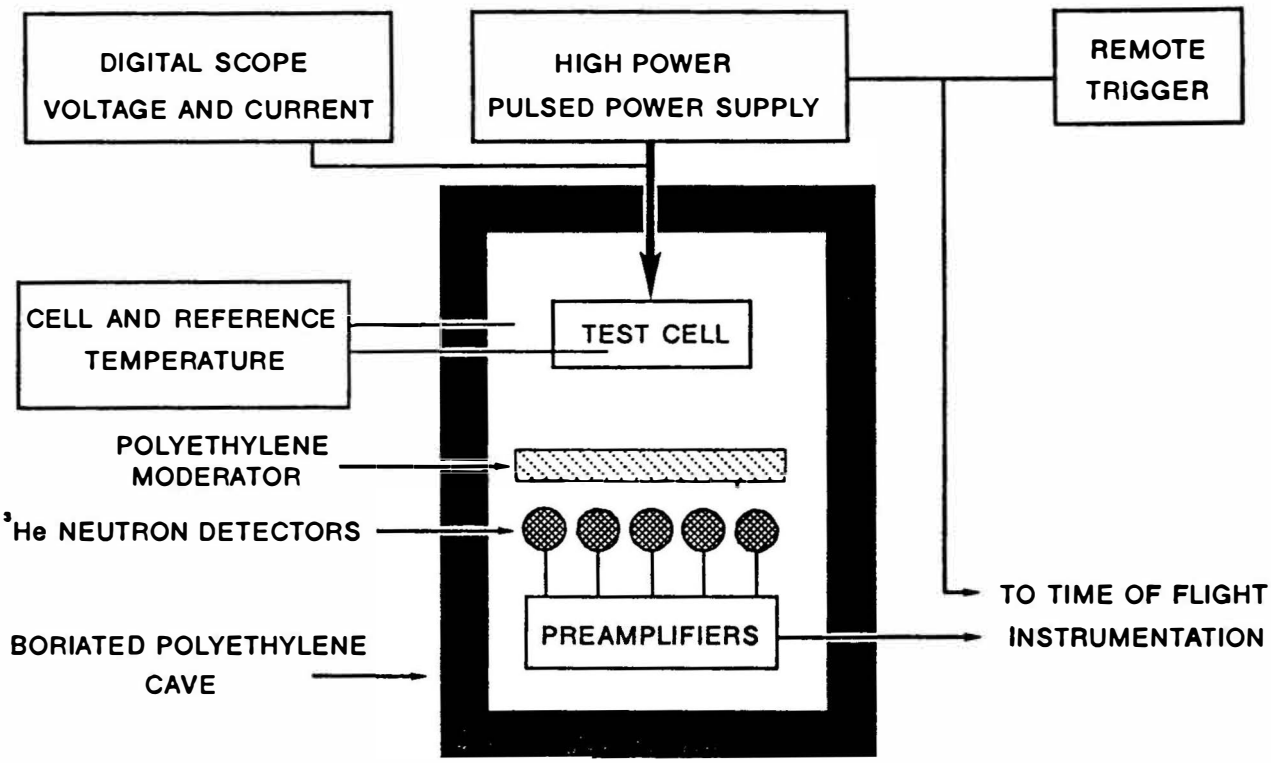


Figure 4. A schematic of the neutron measurement system at LANSCE.

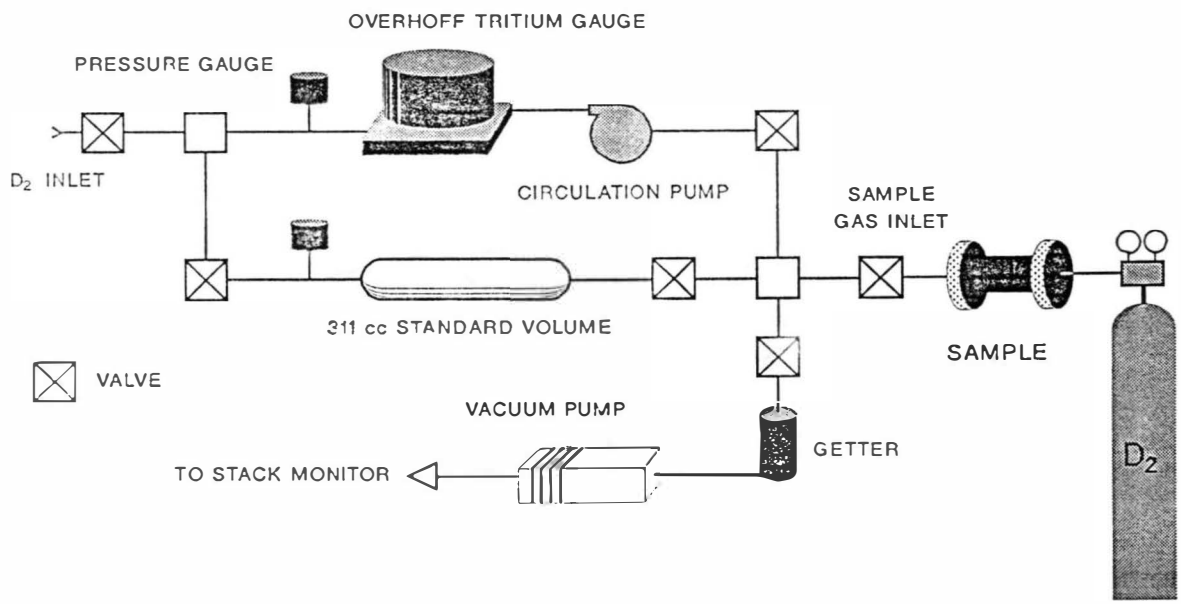
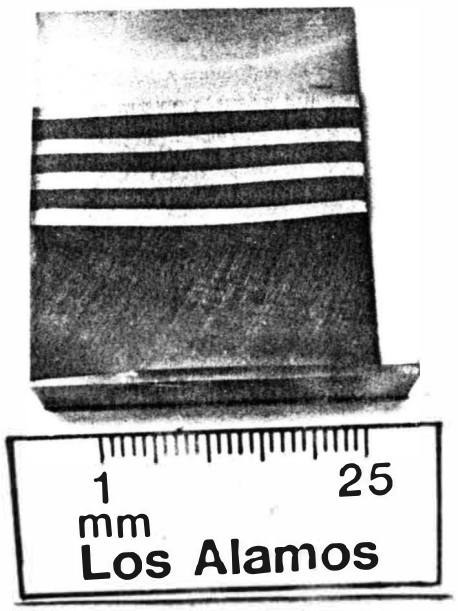


Figure 5. A schematic of the deuterium fill and analysis system. The sample is evacuated and then filled with deuterium from a bottle. The evacuated analysis system is then filled with the deuterium from the cell. This procedure permits analysis of the initial trace amounts of tritium present in the gas, cell, or palladium.



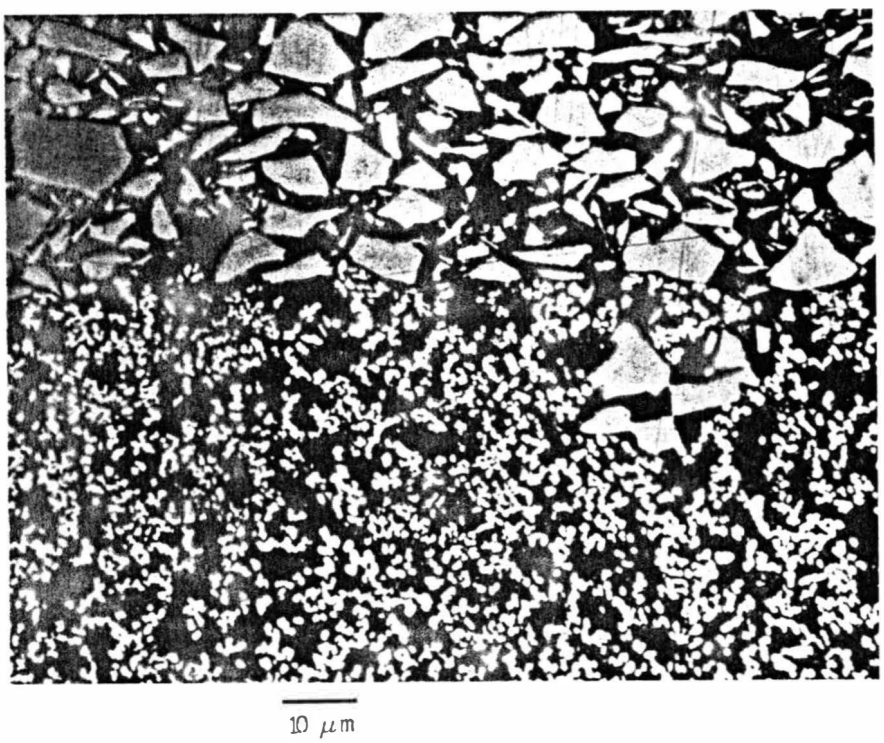


Figure 3. Cross section of a pressing showing the layered structure of the compact. The photomicrograph shows the boundary between the palladium (lower) and the sil icon (upper) layers.

Results

Of the 18 cells that have been built to date, cell 2 provided the most positive results. It was pulsed with 500 to 2000 V at 900- to 25-μs pulse widths with pulse rates of 80 Hz or less. The input power from joule heating was usually held at 500 to 2000 mW so that the D/Pd ratio would not change significantly. At 1 W, the cell heated to about 6°C above ambient temperature in the neutron counter cave.

The neutron counting results showed no definite time correlation on times shorter than the pulse repetition rate. Instead, when the sample was pulsed, the overall count rate was higher than the background with or without the cell. In a test for noise immunity, a resistor was pulsed with no effect in the count rate after the initial pulse. Measurements taken early in the life of the cell gave higher neutron counts than those taken 5 days later. This situation is shown most clearly in Figure 6, where the neutron count has been roughly correlated with the total energy dissipation in the sample. Later, the cell was instrumented for temperature and a long measurement was started. The results are as shown in Figure 7. We measured the temperature of the cell, ambient temperature, and power input as well as the neutron count.

The neutron count rate, delta temperature, and input power seem to correlate somewhat, but only the delta temperature and input power are even approximately consistent. Although the neutron data may look suggestive, and many precautions were taken to exclude noise, the possibility cannot be completely discounted that electrical noise from the pulser was causing spurious counts in a stochastic manner.

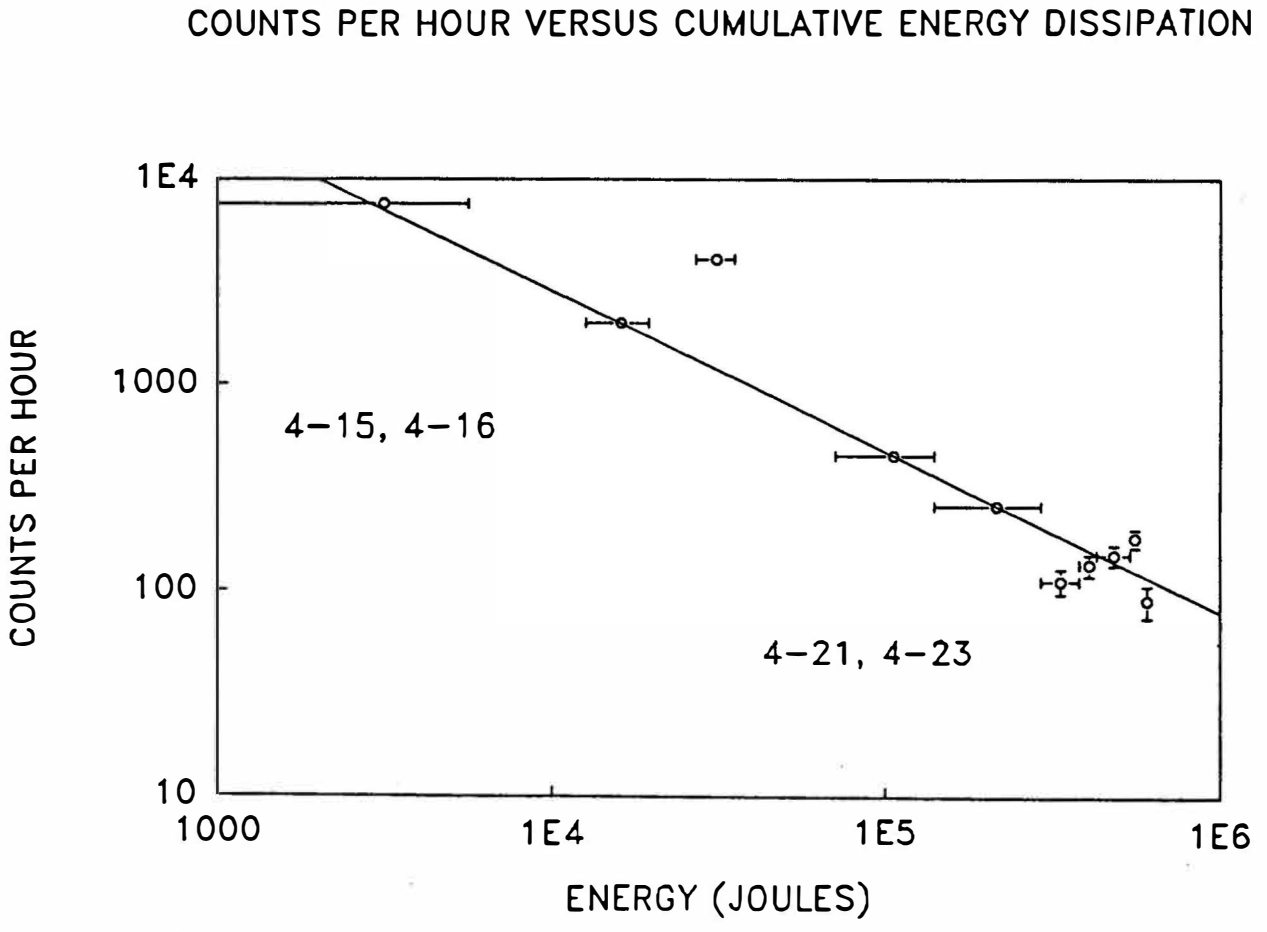


Figure 6. Cell 2 showed a decreasing neutron output as the cell was operated.

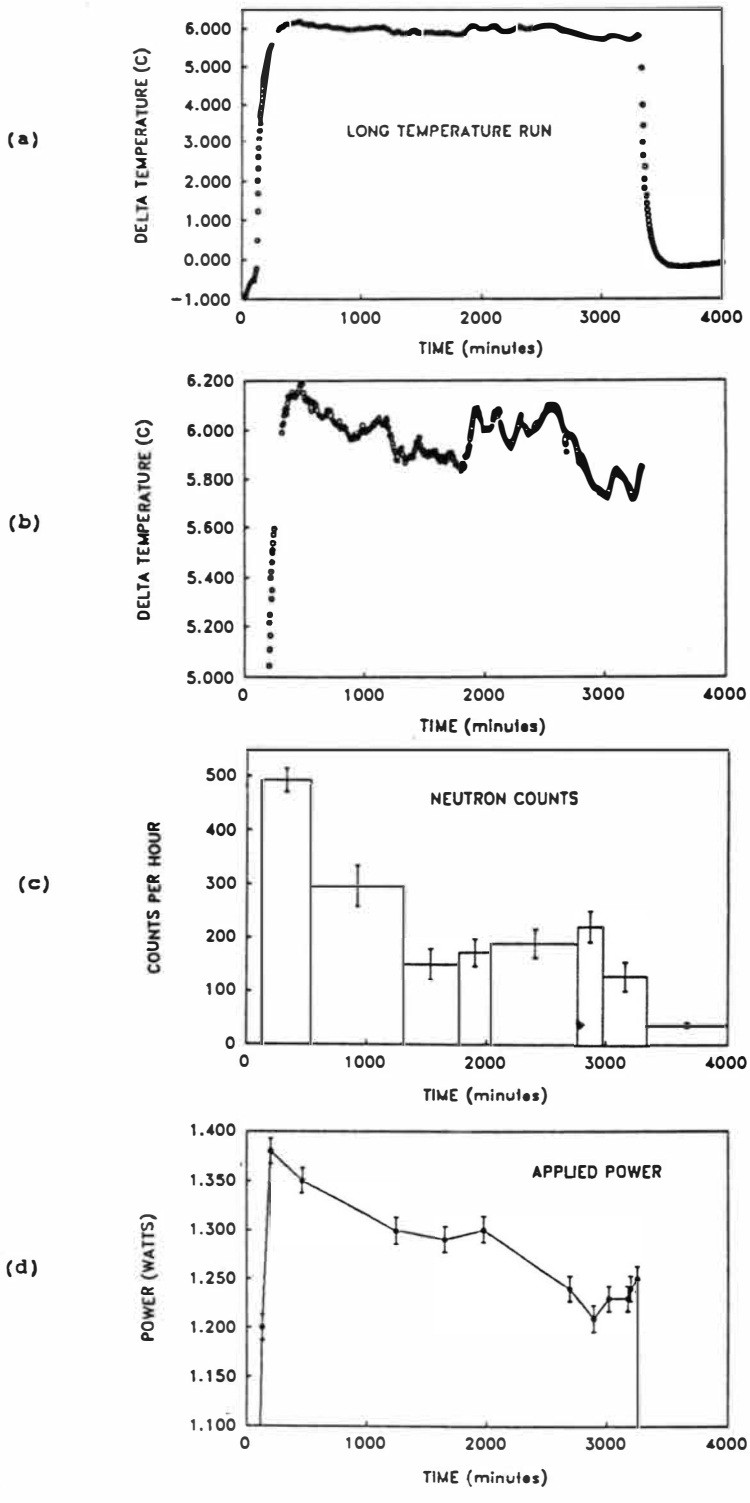


Figure 7. Results from sample 3 during the 55-h heating and neutron measurement taken over the weekend of April 21–23, 1989. Curves (a) and (b) show the difference between the ambient and cell temperature. The curves roughly correlate with the applied electrical power shown in (c). The neutron count rate decreased during the measurement period but was always considerably above the background count, shown as the last bin in (d).

Cells 1,3,4, and 5, which were controls or had mechanical faults, showed no neutron activity and were not analyzed for tritium. Cell 2 was kept in storage because it showed definite neutron activity. The subsequent tritium analysis showed that cell 2 had 1300 times the fill gas concentration of tritium, amounting to 3.5×10^{15} atoms of tritium. This level, although substantially above background, is equivalent to only 65 ppb.

Since both neutrons and tritium were produced and measured, the branching ratio (n/p) may be estimated. An upper limit of 2.7×10^{-9} may be set for this ratio. This limit is surprisingly close to other data[7,8] (1×10^{-8} to 1×10^{-9}) on electrochemical cells or deuterided titanium experiments.

A total of 6×10^5 J were dissipated by joule heating in the cell. The production of 3.5×10^{15} tritium atoms would have yielded an additional 2200 J, so the efficiency was only 0.3%. However, most of the voltage drop occurs at Si-SiO_2-Si interfaces and only a fraction of the applied voltage is at the Si-SiO_2-Pd interface. Therefore, the efficiency of the surface layers may have been closer to 20% to 64%. At this level of efficiency, the cell would be highly economic.

These very positive and encouraging results prompted us to try to reproduce the data in another facility. Specifically, we wanted a corroborating measurement of the branching ratio. A noise-insensitive, high-efficiency (21%) channel counter[9] was available at Los Alamos's Safeguards Assay Group, N-1. This counter has 18 ^{3}He tubes and a background of 850 to 900 counts per hour (4050 to 4280 n/h), although about 80% of the background is due to radioactive decay intrinsic to the tube materials. The LANSCE system also had a similar background of about 62 counts per hour (4770 n/h), but the electronics had both upper and lower thresholds, which can eliminate most non-neutron background.

Very few excess neutrons have been detected at N-1. Figure 8 shows some typical plots of the backgrounds from cells 10 through 16. These neutron generation rates are far lower than those seen with sample 2, and concomitant tritium output is also less. Samples 10 and 12 gave tritium well above background and yielded branching ratios similar to that of cell 2 (see Table II). These values are only approximate because the neutron-counting statistics are so poor. As shown in Figure 8b, three large neutron events were observed with power applied to the cells. These events are indicative of a burst of 60 to 65 neutrons occurring in a 128-μs window. It is not yet clear if these are cosmic-ray spallation events (thought to give less than 10 to 20 neutrons per event) or some type of burst phenomena similar to that seen by Menlove.[10] Further tests are planned in a tunnel at Los Alamos to clarify this question.

Since sample 10 appeared to be neutron active, the excess tritium was flushed from the sample, which was then run at high voltage with very short (5-μs) pulses for 140 h. No excess tritium was found. Then the sample was flushed with fresh deuterium and run for 92 h at a pulse width of 300 μs. The background level was 1.5 times the level of the gas bottle. A subsequent run at 300 μs for 160 h gave a very slight excess over background (20%). Sample 11 was identical to sample 10, but it had leaked about two-thirds of its D_2 gas between the time it was filled and the time it was analyzed. The sample had about 4 μCi/m^3 of excess tritium, far lower than the 130 μCi/m^3 found in cell 10. Cells 12, 14, and 17 have also produced 10 nCi or more. Since parameters have been changed to determine the effect of various configurations on tritium output, it is not surprising that not all cells have produced the same amount.

Table II lists all the cells made to date and summarizes the tritium and neutron measurements. A hydrogen control cell showed no neutron production over background when used with the LANSCE counter. Although cell construction appears simple, slight variations in pressing pressure, layer thickness, the oxide layer on the silicon, and the exact fabrication details can have pronounced effects on the electrical properties and concomitant tritium production.

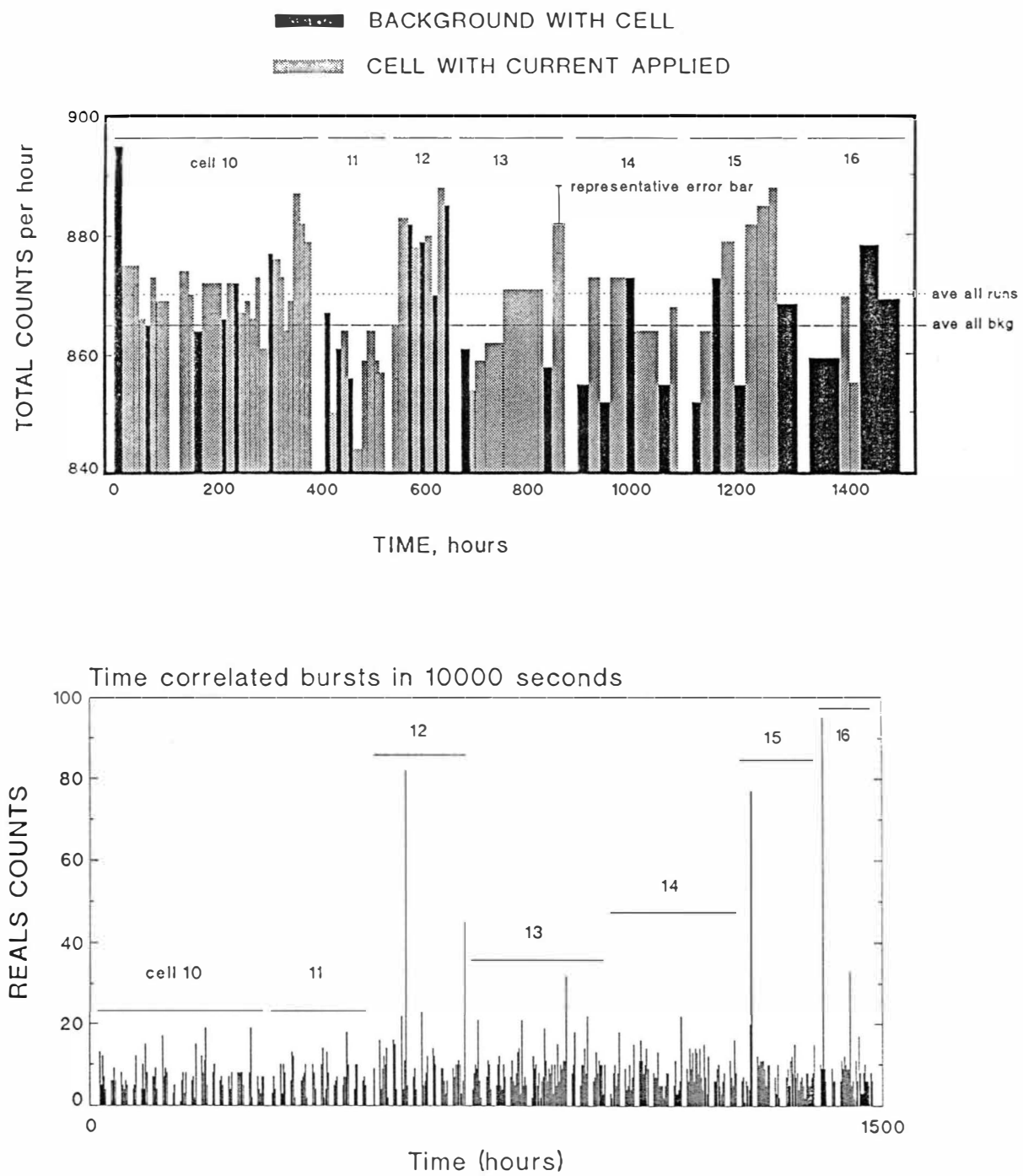


Figure 8. Recent neutron results from Menlove's counter. With the exception of the bursts recorded from cells 12,15, and 16, the neutron output has been just above the background, which has been consistent with the tritium measurements, given the branching ratio observed for cell 2.

Sample Number	Date Built	Neutron Output	Tritium Total	Hours Run	Cell Type	Fill Gas	Notes on cell
1	12-Apr	No	Not analyzed	3	O-Ring, Layered	D2, #1	Sample shorted out
2	14-Apr	Yes, >5 σ	170 μCi	96	O-Ring, Layered	D2, #1	5% Hydrogen added to cell on 4-26
3	19-Apr	No	Not analyzed	20	O-Ring, Layered	H2, #1	Hydrogen control
4	3-May	No Steady Output	Not Analyzed	<1	O-Ring, Layered	D2, #1	Leaky seal
5	8-May	No	Not Analyzed	<1	O-Ring, Layered	D2, #1	Sample shorted out
6	30-May	No, <2 σ	No	17	O-Ring, Layered-Mixed	D2, #1	Sample shorted out
7	18-Jul	Yes, >2.5 σ	68 nCi	95	O-Ring, Layered-Mixed	D2, #1	Neutron output varied with voltage
8	9-Aug	No, <1 σ	< 2 nCi	142	Flange, Mixed	D2, #2	Palladium and silicon powder mixed together
9	14-Aug	No	< 2 nCi	63	Flange, Mixed	D2, #1	Same as 8, but outgassed at 100°C
10	4-Sep	Yes?, <1 σ	320 nCi	77	Flange, Layered	D2, #2	Neutron bursts, 250 psi fill
11	11-Oct	0±35 n/h	15 nCi	162	Flange, Layered	D2, #3	Same as 10 but 70 psi fill
12	21-Nov	35±45 n/h	44 nCi	62	Flange, Layered	D2, #3	Cell shorted after 62 h
13	29-Nov	10 ± 30 n/h	< 2 nCi	169	Flange, Layered	D2, #3	no oxide on palladium
14	21-Dec	50 ± 35 n/h	10 nCi	110	Flange, Layered	D2, #3	thinner layers
15	21-Dec	50 ± 30 n/h	6 nCi	106	Flange, Layered	D2, #3	thin layers, reverse current
16	10-Jan	0 ± 45 n/h	< 1 nCi	22.2	Flange, Layered	D2, #3	Sample shorted out
17	26-Jan	0 ± 30 n/h	12 ± 3 nCi	112	Flange, Layered	D2, #3	600 psi fill pressure
18	26-Jan	35 ± 25 n/h	< 1 nCi	86	Flange, Layered	D2, #3	sulfur surface treatment
Sample 2 produced 9.5×10^{6} neutrons and 3.5×10^{15} tritium atoms							Branching ratio $n/p = 2.7 \times 10^{-9}$
Sample 10 produced 5200 ± 7500 neutrons and 6.6×10^{12} tritium atoms							Branching ratio $n/p = 0.8 \pm 1 \times 10^{-9}$
Sample 12 produced 2170 ± 2800 neutrons and 9.0×10^{11} tritium atoms							Branching ratio $n/p = 2.4 \pm 4 \times 10^{-9}$

Table II. Summary of solid-state fusion experiments to date.

Conclusion

Although the exact mechanism for fusion in the solid state is not known, our results support other measurements that find low values for the branching ratio. This work suggests an upper limit on the n/p ratio of 3×10^{-9}.

The main explanations for D-D fusion in the solid state are microcracking resulting in hot fusion, enhancement of tunnelling caused by increased electron shielding resulting from high local lattice pressures (piezofusion), nonequilibrium electron concentration (perhaps at defects), and high D/Pd concentrations. All reported measurements indicate a very low branching ratio, discrediting the cracking hypothesis. Also, since no time correlation was observed with electron injection, one can tentatively dismiss the idea of nonequilibrium, electron-aided fusion caused by injected conduction-band electrons. The possibility still exists of some site-specific fusion where the local electron concentration is high. The idea of piezofusion or locally high lattice pressures caused by phase transitions or deuterium drift cannot be discounted.

Solid-state fusion cells appear to be an alternative to the electrochemical cell approach for the investigation of anomalous effects in deuterided materials. Because of the simplicity of the cell and the possibility of creating monolithic, layered structures, efficiency can be improved considerably. Based on the power input and the amount of tritium produced in cell 2, a factor of 10 improvement in efficiency would result in economic tritium production.[11] The reduction in thickness of the silicon layers, the elimination of the hydrogen in the deuterium and palladium, and an increase in the gas pressure of the cell may improve the efficiency.

Acknowledgments

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