Search for Energetic-Charged-Particle Emission from Deuterated Ti and Pd Foils

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Searching for evidence of "cold" nuclear fusion in deuterium-loaded Ti and Pd foils with plastic track detectors, we detected the emission of α particles from trace-heavy-element decay, but found no evidence of dd fusion. Cycling TiD_2 and $PdD_{>0.4}$, in high-pressure D_2 cells between 1 and 15 bars and 77 and 300 K, gave an upper bound of 0.7 $cm^{-3}s^{-1}$ for the mean rate of $dd \rightarrow {}^3He+n$ fusion. For electrolytically deuterated $PdD_{0.8}$ our upper bound is 0.0018 $cm^{-3}s^{-1}$ for the mean rate of $dd \rightarrow p+t$. This is $\sim 1.5\times 10^6$ and 180 times lower than "cold"-fusion rates reported by Fleischmann, Pons, and Hawkins and Jones *et al.*, respectively.

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Our work was motivated by recent reports[1-6] of neutron emission from deuterated palladium and titanium. Those results have been interpreted as positive evidence for "cold" fusion of deuterons in these materials. To complement those experiments, we have searched for the recoiling charged particles which would also be produced by "cold" dd-fusion reactions.

Two types of experiments have yielded positive evidence of excess neutrons in nearby detectors. In the first, electrolysis of heavy-water electrolyte solutions is used to load Pd or Ti with deuterium by diffusion. From the neutron flux (BF_3 detector) reported by Fleischmann, Pons, and Hawkins,[1] we calculate a specific rate for the neutron-producing dd-fusion channel in their PdD_x of 2700 $cm^{-3}s^{-1}$. From the results of Jones *et al.*,[2] we calculate 0.33 $cm^{-3}s^{-1}$ for the neutron channel based upon their observations of 2.5-MeV neutrons in scintillation detectors near their PdD_x and TiD_2 cathodes. Wolf *et al.*[3] report neutron-source strengths of 0.8 s^{-1} for PdD_x cathodes of unspecified volume.

In the second type of experiment, high-pressure D_2 gas is used to drive deuterons into Ti and Pd samples, which are then subjected to thermal and/or pressure cycling. De Ninno *et al.*[4] detected bursts of neutrons using a BF_3 counter during such sample cycling. Average source strengths during two separate episodes of activity were 20 and 260 neutrons/cm^3s. Ricci[5] reported a source strength of 10^6 neutrons/cm^3s for one 10-min episode. Menlove *et al.*,[6] using ^3He neutron detectors, reported infrequent, low-level (~ 100) neutron bursts and random emission levels between 0.001 and 0.04 neutrons/cm^3s for sample mixtures containing Ti, Pd, V, and Sn.

In our experiments, we used CR-39 plastic film (Track Analysis Systems Inc., Bristol, United Kingdom) to detect energetic charged particles. CR-39 detects products arising from both conventional fusion channels: $d+d \rightarrow p(3.02\ \text{MeV})+t(1.01\ \text{MeV})$, and $d+d \rightarrow {}^3He(0.82\ \text{MeV})+n(2.45\ \text{MeV})$. Damage tracks produced in CR-39 by ionizing particles are chemically etched (6.25 mol NaOH, 70°C) at a rate $v_T > v_G$, where v_G is the etch rate of the undamaged plastic. The resulting conical etchpits of cone angle $\Theta = \arccsc(s)$, where $s = v_T/v_G$, are identified and counted using optical-scanning methods. A particle's velocity βc and charge Z can be determined from its range R and from s, which is a function of the ratio (Z/β) (Ref. 7). Detection efficiency is 100% for charged particles, including protons,[8] of energy ≥ 0.2 MeV under ambient laboratory conditions.

In the present application, plastic-track detectors such as CR-39 offer several advantages over solid-state silicon-surface-barrier (SSB) detectors like those used by Ziegler *et al.*:[9] (a) Electronic noise in SSB's limits particle detection to energies > 1 MeV at low count rates. (b) SSB background counts between 1 and 3 MeV, ~ 2.5 $cm^{-2}d^{-1}$, are $> 25\times$ the integral background rate in CR-39. (c) Burst emissions of particles may not be detected by SSB's because of their finite response time (> 5 μs) and limited energy window (1–8 MeV). (d) CR-39 determines particle charge, energy, *location, and propagation direction,* whereas single-element SSB's simply measure the integral energy deposited in the active volume of the detector within its response time. (The ranges of the protons are long enough that a two-element silicon-particle telescope could be used to identify both charge and energy.)

There are three types of charged-particle backgrounds in CR-39 which are relevant to the present experiments. Between the time it is made and the time it is used, CR-39 accumulates cosmic-ray spallation tracks and α-decay tracks due to airborne radon. In our laboratory, the rate of production of detectable spallation recoil tracks is ~ 1 $cm^{-2}yr^{-1}$, and radon α tracks accumulate at a rate ~ 1 $cm^{-2}d^{-1}$ while the film is exposed to open air. We were able to reduce these two sources of background to an accumulation rate of < 0.1 $cm^{-2}d^{-1}$ by preetching the CR-39 for 8 h and locating existing tracks before starting the present experiments, and by protecting the CR-39 from airborne radon during the experiments.

The third source of background tracks is α-emitting

nuclides, predominantly the ^{238}U and ^{232}Th series, present as impurities in the Pd and Ti at ppm levels. α particles emerge from the surfaces of the Pd and Ti foils with a continuous distribution of energies, from 0 to 8.8 MeV in this case, because their ranges are less than the thickness of the foils. In a control experiment, we determined the α-track production rate of our Pd and Ti foils due to this source by exposing them to CR-39 for 41 d. Etching and analysis above yielded a production rate for ≥ 0.2-MeV α tracks of ~ 5 cm^{-2}d^{-1} for the Pd foil and ~ 1 cm^{-2}d^{-1} for the Ti foil. Note that α tracks do not interfere with a search for recoiling protons or tritons in CR-39, but those with lowest energy do place constraints on the determination of ^{3}He production rates.

Figure 1 shows the results of a calibration of the CR-39 film as well as the data for the two experiments discussed below. The dashed curve through the points labeled "alphas" was obtained by irradiating CR-39 with α particles, slowed to various energies, from a ^{252}Cf source. The curves labeled "tritons" and "protons" were scaled from the α-particle curve using a restricted-energy-loss model of track formation.[7] The proton curve is quantitatively similar to that obtained for CR-39 neutron spectrometers whose basis of operation is the detection of recoiling protons.[8]

Assuming that particles are emitted isotropically and uniformly throughout the samples, then the product of detection efficiency and effective source thickness, $\langle \eta H \rangle$, can be calculated by integrating over emission zenith angle Θ and depth z measured from the CR-39 into the source:

$$\langle \eta H \rangle = \tfrac{1}{2} \int_0^{z_{\max}} \int_0^{\Theta_{\max}} \sin\Theta \, d\Theta \, dz \,, \qquad (1)$$

where $\Theta_{\max}$ is the smaller of $\Theta_{\max} = \arccos(z/z_{\max})$ or $\Theta_{\max} = \arccos(v_G/v_T)$ and $z_{\max}$ is the smaller of $z_{\max} = d_s$, where d_s is the sample thickness, or $z_{\max} = (R - \delta R) - \sum d_i$. R is the particle's range in the material, δR is the minimum range needed for detection in the CR-39, and $\sum d_i$ is the sum of density-corrected thicknesses of all materials between the sample and CR-39. The *dd*-fusion products are calculated to have the following ranges: in $PdD_{0.8}$, $R(p) = 33$ μm, $R(t) = 4.6$ μm, and $R(^3\text{He}) = 1.3$ μm; in TiD_2, $R(p) = 65$ μm, $R(t) = 6.5$ μm, and $R(^3\text{He}) = 2.2$ μm. As an example, for 0.82-MeV ^{3}He produced from *dd* fusion and detected in CR-39, $\arccos(v_G/v_T) \sim 80°$, $\langle \eta H \rangle \sim 0.5$ μm in $PdD_{0.4}$ and $\langle \eta H \rangle \sim 0.8$ μm in TiD_2.

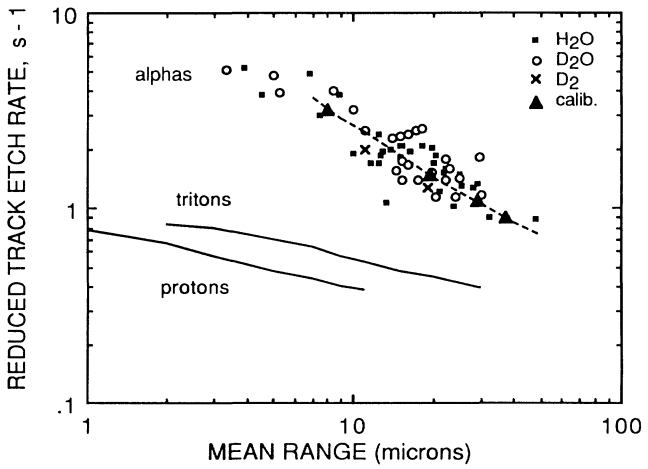

FIG. 1. Energetic particles detected by CR-39 film next to Pd foils: ■, electrolysis cell, H_2O, 1 mol LiOH; ○, electrolysis cell, D_2O, 1 mol LiOD; ×, high-pressure D_2 gas cell; ▲, calibration with ^{4}He particles from ^{252}Cf.

For our first experiment we cleaned a 0.1-mm-thick Ti foil (purity $> 99.6\%$) and a 0.23-mm-thick Pd foil (unknown purity) using *aqua regia*. After heating the foils to 550 °C for 3 h in D_2 gas at 1 bar they were allowed to cool in D_2 to room temperature overnight. The diffusion coefficient for D in Pd at room temperature is 5×10^{-7} cm^{2}s^{-1} (Ref. 10), high enough to fill the foil in a few hours, but temperatures ~ 500 °C are required to achieve the same diffusion coefficient in Ti (Ref. 11). Final stoichiometries of the deuterated foils were determined by weight gain to be TiD_2 and $PdD_{>0.4}$, the value for Pd being a lower bound because of possible loss of deuterium during handling.

The deuterated foils were then clamped against CR-39 sheets (contact area 2 cm^2 for each sample) and put inside a stainless-steel pressure cell attached to a source of D_2 gas. After evacuating the cell using a roughing pump, we loaded D_2 gas to a pressure of 15 bars and immersed the cell in liquid nitrogen for 1 h to allow sufficient time to cool the chamber, and then removed it from the liquid nitrogen, allowing it to warm to 20 °C in about 2 h. The cooling and warming cycle was repeated two more times. Prior to the last warming we removed the D_2 gas from the chamber with a roughing pump. The entire experiment lasted about 9 h, after which we etched the CR-39 films for 1.7 h and searched the regions that had been in contact with the Pd and Ti foils for tracks produced since the preexisting ones were located.

Two tracks of particles with $Z = 2$ came from the Pd (labeled × in Fig. 1), and no tracks came from the Ti. We calibrated the response of CR-39 in the high-pressure cell at 15 bars and 77 K using α particles from ^{238}U decay. We found that the sensitivity to an isotropic flux of particles with $Z = 2$ inside the cell at 77 K was $\sim 80\%$ of that at 20 °C and 1 bar. The energies of both $Z = 2$ particles from the deuterated Pd foil were too high to be due to 0.82-MeV ^{3}He. The track production rate is consistent with the α-particle emission rate for the Pd foil determined in the control experiment. This null result was converted into an upper limit for the rate of the $dd \rightarrow {}^3\text{He} + n$ channel using Eq. (1), and is compared in Table I with the *dd*-fusion rates inferred from the neutron fluxes reported by De Ninno *et al.*, Ricci, and Menlove *et al.* Lacking a source of particles with $Z = 1$ for a

TABLE I. "Cold"-fusion rates inferred from measurements of energetic particles.

	Sample	Duration (h)	Particle (detector)	Fusion rate ($cm^{-3}s^{-1}$) [a]
		Electrolysis experiments		
Fleischmann, Pons, and Hawkins (Ref. 1)	PdD_x	50	Neutrons (FB_3)	2700
Jones *et al.* (Ref. 2)	TiD_2 (#6)	8	Neutrons (scint.)	0.33
Wolf *et al.* (Ref. 3)	PdD_x	1–2	Neutrons (NE213)	$(0.8/V_{Pd})$
Ziegler *et al.* (Ref. 9)	$PdD_{>0.6}$	250	Protons (SSB)	<0.028
This work	$PdD_{0.8}$	307	Protons (CR-39)	<0.0018
	$PdD_{0.8}$	307	Tritons (CR-39)	<0.011
		High-pressure D_2 gas experiments		
Menlove *et al.* (Ref. 6)	"Ti-1"	18	Neutrons (^{3}He)	0.001–0.04
De Ninno *et al.* (Ref. 4)	TiD_x	13 [b]	Neutrons (BF_3)	~20
	TiD_x	40 [b]	Neutrons (BF_3)	~260
Ricci (Ref. 5)	PdD_x	0.17 [b]	Neutrons	Up to 10^6
This work	TiD_2	9	^{3}He (CR-39)	<0.73
	$PdD_{>0.4}$	9	^{3}He (Cr-39)	<2.6

[a] To convert to fusions per *dd* pair per second: For TiD_2, 1 $cm^{-3}s^{-1} = 4.72\times10^{22}$ $(dd)^{-1}s^{-1}$. For PdD_x, 1 $cm^{-3}s^{-1} = [2x/(0.3925+0.0165x)^3]\times10^{21}$ $(dd)^{-1}s^{-1}$.

[b] Period during which excess neutrons were detected.

calibration inside the high-pressure cell, we report results only for the $n+{}^3$He product channel.

Figure 2 shows an "exploded" view of the symmetric electrochemical cells used in our second experiment. Both cathodes were cut from the same piece of 25-μm-thick Pd sheet (99.9%), and had a 100-nm Au diffusion barrier evaporated on the side which faced the CR-39. The cells were operated in electrical series using a single-current source (Keithley 220). Viton O rings defined 1.26-cm^2 active electrode areas. Solutions were prepared by reacting degreased, isopropanol-etched Li under nitrogen with either 18-M Ω cm H_2O [Milli-Q Plus purified, Anal. 0.014% D, <2 tritium decays/(min ml)] to form 1.00 mol LiOH, or with D_2O [Cambridge Isotopes Laboratories, Lot No. F7962, Anal. 0.13% H, 17.9 tritium decays/(min ml)] to form 1.00 mol LiOD.

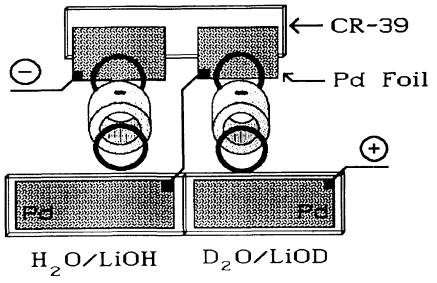

FIG. 2. "Exploded" schematic of the identical twin electrochemical cells. Cell bodies were 1.00-cm lengths of Plexiglas tubing with a 2-mm-fill/vent hole and grooves machined for the Viton O rings. Anodes were 2-μm *e*-beam evaporated Pd on 100-nm Au on microscope slides.

The electrodes were presaturated with either H or D by constant-current electrolysis at 10 mA cm^{-2} for 12 h. Coulometry during the presaturation period indicated initial electrode stoichiometries of $PdH_{0.65}$ and $PdD_{0.74}$ at the point of first gas bubble formation. Electrolysis was performed at 1.00 mA cm^{-2} for 13 d. Steady-state cell operating voltages (includes *IR*-drop component plus kinetic overpotential) were 2.77 V (H_2O) and 2.96 V (D_2O). Cathode stoichiometries were determined by mass change to be $Pd(H,D)_{0.8}$, a value consistent with *in situ* extended x-ray-absorption fine-structure spectroscopy measurements of Pd-foil cathodes.[12]

After the run we etched the CR-39 for 8 h and searched for new tracks in the circular areas that had been in contact with the cathodes. We found 73 tracks at the light-water location and 65 tracks in the heavy-water location; all tracks were due to particles with $Z=2$. The data are shown in Fig. 1. The track production rates agree at the 1σ level and are consistent with the α-particle emission rate for the native Pd foil discussed above. There were no tracks due to protons with 0.2 MeV $\leq E \leq$ 3 MeV or tritons with 0.2 MeV $\leq E \leq$ 1 MeV.

For 3-MeV protons from *dd* fusion, $\arccos(v_G/v_T)$ ~45° in CR-39, and Eq. (1) gives $\langle \eta H \rangle = 3.9$ μm for a 26.3-μm-thick $PdD_{0.8}$ source. Similarly, for 1-MeV tritons with $\arccos(v_G/v_T) \sim 60°$, Eq. (1) gives $\langle \eta H \rangle = 0.63$ μm for a 26.3-μm-thick $PdD_{0.8}$ source. Table I lists our two upper limits on the $dd \rightarrow p+t$ channel. We com-

pare this limit with the result of Ziegler *et al.*[9] as follows: Using Eq. (1) we get -3.1 μm for their conditions (Expt. 1) of 1–3-MeV protons, 25-μm-thick Pd cathode, 1.76-μm-thick gold diffusion barrier, and 2-mm air gap. From their observed count rate of 40 per 205 h we calculate the limiting fusion rate listed in Table I. The background rate in their experiments was consistent with the rate we found for α emission from radioactive impurities in our Pd foil. The reasons why our limit on the *dd*-fusion rate is lower than that of Ziegler *et al.* are the following: we have no detectable background for protons, we used a thinner gold diffusion barrier, there was no air gap, and CR-39 has a lower minimum detectable particle energy than SSB's.

In conclusion, the only energetic charged particles we detected in both our experiments were α particles emitted from trace radioactive impurities in Pd and Ti at rates of a few particles per cm^2 per d, independent of the deuterium content of the foils. Our upper limits on average *dd* "cold"-fusion rates are far below those inferred from neutron detection in experiments involving either electrolytic[1,2] or high-pressure[6] loading of D_2 into Pd or Ti. To rationalize our null results with claims of episodic "cold" *dd* fusion,[3–6] it would be necessary to argue that fusion at the average rate reported by Jones *et al.*[2] occurred less than $\frac{1}{180}$ of the time during which our electrolytic cell was operating and that fusion at the rate reported by De Ninno *et al.* occurred less than $\frac{1}{400}$ of the time during which we cycled TiD_2 in D_2 gas. (Although there appears to be no suitable mechanism, one might in principle observe neutrons and not short-range charged particles if deuterium were somehow depleted in a surface skin without being depleted in the interior. Such an *ad hoc* explanation of our null results could not apply to our search for protons in electrolysis.) Our limits apply to any mechanism that produces energetic charged particles in deuterated Pd or Ti, such as the neutron-initiated chain reaction proposed by Jackson.[13]

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