Investigation of Track Formation in CR-39 for Various Hydrated Environments

Micah Karahadian, Austin Smith, and Emma Vahle

2019 PHY4072/Senior Lab

Physics and Engineering Department, Point Loma Nazarene University

Dr. Michelle Chen

Abstract

CR-39, a thermoset resin, is a well characterized integrative detector that, when etched, shows tracks created by energetic charged particles produced in nuclear reactions. It has been questioned whether this detection method can be used in paladium and deuterium (Pd/D) electrolytic cell environments. Of concern is whether the pyrophoric nature of hydrogen's interaction with palladium and its recombination with oxygen within the cell can create similar tracks. The validity of this detection method in an electrolytic cell environment is investigated. Additionally, track comparisons from detectors used in a Pd/D co-deposition experiments utilizing ⁴⁰K or ⁶Li electrolytes were done to determine if ⁶Li contributes to the observed tracks.

Introduction

There has been much debate on whether energetic charged particles are produced during a Pd/D co-deposition process. This process was first introduced in 1991 by Szpak et al. [1]. Yet, sixteen years later the first observations of energetic charged particle emission using this method were reported by Mosier-Boss et al. in 2007 [2], who has also summarized the advantages and disadvantages of CR-39 in the context of Pd/D co-deposition [3]. By April of 2020, there have been 86 published refereed papers: 15 discussing modeling and theory, 17 on thermal effects, 40 discussing nuclear emissions, and 14 co-deposition replications. These replications include a group at SRI International and a group at UCSD as described by Krivit Marwin [4], and a group at the Institute of Physics NAS of Ukraine [5]. Even with all these repeatable results, some have suggested that these observations are spurious results [6] [7]. A question that arises in the discussion of results is the detection method. A solid-state nuclear track detector (SSNTD), Columbia Resin 39 (CR-39) is integrative over time. This is the common method used for detecting energetic charged particles.

Cartwright et. al. [8] were the first to demonstrate in 1978 that CR-39 (composition C12H18O7) could be utilized to detect particles of nuclear origin. CR-39 is synthesized through the polymerization of diethyleneglycol bis allycarbonate in the presence of an isopropyl peroxydicarbonate catalyst [9]. It is insensitive to electromagnetic fields and has been

well characterized for protons, deuterons, tritons, alpha particles, and neutrons [10]. This detector is optically clear, amorphous, and has been manufactured in such a way that when heated, pressurized, or exposed to radiation the curing process allows the allyl functional groups to cross-link which creates a chemical bond that prevents the material from changing phase; making it a thermoset resin.

CR-39 has many practical applications including its ability to detect charged particles from inertial confinement fusion (ICF) plasmas [10], as well as proton spectrometers at the National Ignition Facility. Aboard the International Space Station it is used to characterize cosmic particle reactions [11]. In 2014 CERN developed a passive neutron dosimeter based on CR-39 nuclear track detectors, which has been successfully tested at the CERF facility at CERN [14].

When energetic charged particles traverse through the SSNTD they leave a trail of broken bonds and free radicals. CR-39 can be used to distinguish particle energies between energies from 0.144 MeV to 19.0 MeV. [15] due to the Linear Energy Transfer (LET) function of the SSNTD. This LET function is an intrinsic property of the detector that governs the amount of energy that a charged energetic particle transfers to the material per distance. Slower particles spend more time in a given location, hence depositing more of their energy there. Faster, more energetic particles deposit less energy in a localized area they are traversing. The impacted area is more sensitive to chemical etching than the bulk substance [9]. After exposure to an etching reagent, tracks created by energetic particles in the detector can be observed with an optical microscope. The size, depth of penetration, shape, and surface luminosity provide information regarding the mass, energy and direction of motion of the incident particle just before striking the detector. It has been suggested that the Pd/D co-deposition electrochemical cell has a highly loaded Pd lattice with deuterium, which may lead to conditions for the following fusion reactions to occur:

$${}_{1}^{2}H + {}_{1}^{2}H \rightarrow {}_{2}^{3}He(0.82MeV) + {}_{0}^{1}n(2.5MeV)$$
(1)

$${}^{2}_{1}H + {}^{2}_{1}H \to {}^{3}_{1}H(1.01MeV) + {}^{1}_{1}H(3.02MeV)$$
(2)

$${}^{2}_{1}H + {}^{3}_{1}H \rightarrow {}^{4}_{2}He(3.54MeV) + {}^{1}_{0}n(14.05MeV)$$
(3)

$${}^{2}_{1}H + {}^{3}_{2}He \rightarrow {}^{4}_{2}He(3.68MeV) + {}^{1}_{1}H(14.62MeV)$$
(4)

Evidence of these reactions would result in tracks created within the SSNTD that display energetic alpha particles and proton tracks. Neutrons are also produced but are absent of charge, so they do not directly cause tracks as they pass through the detector. Instead, the neutrons can cause secondary reactions through interactions with detector nuclei; resulting in the production of charged particles [14]. For detection, a neutron must either scatter off of detector nuclei producing a recoil of charged particles, or undergo a neutron capture and subsequently decay into transient charged particles. These radioactive decay products can be measured.

Of the neutron interactions that may occur within the CR-39 the reaction easiest to identify is the ${}^{12}C(n, n')3\alpha$ carbon break-up reaction.

$${}^{12}_{6}C + {}^{1}_{0}n (\ge 9.6 MeV) \to 3{}^{4}_{2}He + {}^{1}_{0}n \tag{5}$$

This reaction results in three tracks stemming from one origin. Appropriately named 'triple tracks,' these trails are a key piece of evidence that suggest DT nuclear reactions. It is important to note that LiCl is also present in the electrochemical cell. LiCl serves as a complexing agent to form PdCl4, which aids in aquation, and it serves as a background electrolyte during electrolysis. Li can also co-deposit onto the cathode with D and Pd, and if the energetic reactions listed in Eqn. 1-4 occur, then it is plausible to expect a lithium interaction. Li has the propensity to undergo the following reactions:

$${}_{3}^{6}Li + {}_{0}^{1}n \rightarrow {}_{2}^{4}He(2.05MeV) + {}_{1}^{3}H(2.72MeV)$$
(6)

$${}^{1}_{0}n(fast) + {}^{7}_{3}Li \rightarrow {}^{3}_{1}H + {}^{4}_{2}He + {}^{1}_{0}n(slow)$$
(7)

Where in the context of these nuclear reactions, fast neutrons hold energy values ranging from 1 - 20 MeV, while slow neutrons have energy of 1 - 10 eV.

The alpha particles produced through this process unfortunately have adverse effects when the CR-39 is etched and analyzed. The alphas produced from lithium breeding are indistinguishable from those from Pd/D energetic particle emission. In an attempt to mitigate this issue and therefore identify what the role of lithium is in the Pd/D system, a KCl electrolyte is substituted and analyzed in contrast.

The question has been proposed whether the use of CR-39 is an acceptable detection method in the context of this hydrated environment. The proposal entails oxygen bubbles resulting from electrolysis in the Pd/D system interacting with the palladium deposit to produce an energetically favorable, extremely exothermic reaction. This reaction could theoretically carry enough energy to cause shock waves resulting in pits of a non-nuclear origin, that would similarly be unidentifiable. In order to test this, pulverized Pd is exposed to the oxyhydrogen gas resultant from the dissociation of deionized water. The results of which [ref] confirm that shock waves produced from this exothermic reaction do not contribute to overall track formation.

Materials and Methods

Electrochemical Cell

The butyrate electrochemical cells (1.12" 1.125" 2.5") were purchased from Rideout Plastics. Within the cell a polyethylene mesh (often used for cross stitch and available at craft stores) supported the cathode (99.99% Au 0.25 mm wire, Sigma-Aldrich) and anode (99.99% Pt 0.25 mm wire, Sigma Aldrich). The wires were cleaned in a 10% nitric acid solution. The upper portion of the electrodes were shrink wrapped in clear polyethylene to assure that no deposit forms on the wire above the cathode. If any deposit forms on the wire above the detector and makes contact with air-solution.

A 0.03 M solution of PdCl2 (99.9%, Pd Fisher Scientific) with 0.3M LiCl (anhydrous, freeflowing, Sigma Aldrich) in 20 mL D2O (99.99%, Sigma Aldrich) was placed in the cell after the PdCl2 dissolved. The reagents were measured using a precision weight scale (Melter, AE 240). The cells were connected in series to a constant current source (Instek, PS-6010) and a voltmeter (Keysight Technologies U3401A 41 Digital 2 Dual Display Multimeter). The current was held near 0.1 mA for 24 hours, increased to roughly 0.2 mA for the next 24 hours, and then remained at approximately 0.5 mA until the solution became nearly clear (5 to 7 days). The low initial current promotes good adherence of the Pd to the Au cathode. After the solution cleared, the current is increased to 1, 5, 10, and 25 mA over 24 hour intervals. Alongside the three cells containing LiCl electrolyte were three KCL control cells. These cells followed the same set-up and procedures above but used a 0.3M KCl electrolyte rather than LiCl. Palladium is sometimes referred to as a 'metal sponge' because it soaks up hydrogen similar to how a porous material would soak up water. At standard ambient temperature and pressure, palladium can absorb up to 900 times its own volume of hydrogen [16, 17]. This effect is poorly understood, yet we do know that a contributing factor is the lattice structure for Pd. Its face centered cubic parameters are: 389.07, 389.07, 389.07 pm, large enough to contain deuterium atoms (charge radius of 2.14 fm [18]).

The second control cell for each experimental run consisted of CR-39 with its polyethylene cover half removed (identical to the active cells), but submerged in deionized water and placed in the same hood to measure ambient radiation. The detector measuring background radiation was not vertically oriented as those in the electrolytic cell, however the vertical orientation was done in previous experiments [9]. At the end of the experiment, the CR-39 was carefully removed and rinsed with deionized water. Before the CR-39 can be etched, a thermodynamically stable environment was created to control the etch rate. A 50ml beaker was filled with deionized water, placed on a hotplate (Corning PC-420D), and insulated with aluminum foil as seen in Figure 2. The temperatures were recorded using a digital

thermometer every half hour. Once the temperature inside the beakers reached 62-65 °C, test tubes of 6.5 M NaOH were inserted. The detectors were etched for 7.5 hours and removed from the test tube. They were then rinsed in deionized water, placed in acetic acid for 5 minutes to ensure the end of the etching process, and thoroughly rinsed again with deionized water. Following this, the detectors were air dried and archived.

The CR-39 was examined using a Konus, Campus optical microscope (BM-100-FL) with 10 and 40 magnification. With IS Capture software and CCD microscope camera (Optixcam, KC110307143), dimensions of the pits were recorded. These were measured by taking the major and minor axis of elliptical tracks, or radii for normally incident particles as seen in Figure 5.

Due to variations in the CR-39 manufacturing process, it is common practice to calibrate each detector by irradiating a small corner for 5 seconds with a source where the energy is known. Each run's detector was calibrated using the known energy of the alpha particles emitted by the Am-241 source (Figure 6) and Track Test as described below. This source could not be in direct contact with the CR-39 detector, rather there was between 1 to 3 mm of air separating it from the detector depending on the run. Energy loss estimates were taken into account when calibrating each detector. These estimates were made using Stopping and Range of Ions in Matter (SRIM). After the detector was etched, measurements of the pits created by the Am-241 source were used to calibrate the Pd/D alpha particle pit measurements.

In areas of high pit density, it is almost impossible to distinguish individual tracks from one another as they overlap and display an inaccurate representation of expected singular pit dimensions. Because of this, most of the data collected were in regions of less track density. It is also difficult to differentiate particle species because of the energy losses due to the distance charged particles must traverse to interact with the detector. The Pd deposit, Au wire, thin solution separation, and polyethylene layer are all regions charge particles deposit energy before finally coming to rest within the CR-39.

The pits were distinguished from superficial blemishes in a number of ways. Charged particle tracks are clean edged pits which show brighter regions deeper within the track due to internal reflection near the end of the pit.



Figure 1: The chamber where the electrolysis of water takes place

Oxyhydrogen Generator

The oxyhydrogen generator was built using a design originally developed by Grant Thompson [11], mainly consisting of a water tight apparatus with acrylic tubing and ABS pipe fittings. The 160mm oxyhydrogen torch used was sourced from H-E (B07BFXCY4Q), and 20 gauge stainless steel plates were purchased from Industrial Metal Supply Co. and were sanded using 100 grit sandpaper to increase electrode surface area. The whole generator apparatus is then connected to a large 240W power source to induce electrolysis with the aid of a K(NO₃) electrolyte [be more specific with molarity of solution]. The catalysis experiments were

carried out in three different environments. The first being submerged in deionized water and allowing the gas to freely flow over the powdered Pd and CR-39. The second orientation had a damp detector in contact with Pd in a dry cell. Finally, a detector is completely dry and exposed to the oxyhydrogen gas mixture. Figure 2 shows the experimental set up with oxy-hydrogen generator, etching apparatus and power supply.



Figure 2: The full layout of the experimental apparatus in a fume hood

Reaction of Oxyhydrogen Gas with Palladium

Twelve cotton swabs were prepared in order to test the reaction of oxyhydrogen gas with palladium. The oxyhydrogen gas was introduced to dry cotton swabs, wet cotton swabs, dry cotton swabs with palladium, and when cotton swabs with palladium. There were three of each type of cotton swabs and each were tested in a separate trial.

Oxyhydrogen Reactions on CR-39 Chips

Oxyhydrogen gas and palladium were combined on the surface of three CR-39 detector chips. First, the top left corner of the numbered side of each chip was irradiated with ²⁴¹Am. The numbered side of the CR-39 detector chip was used to run dry tests in a dry weighboat. The top half of the numbered side of the chip was exposed to oxyhydrogen gas. Then, palladium was added to the bottom half of the numbered side and then it was exposed to oxyhygrogen gas. After the dry tests were completed, the chip was wiped with a kimwipe, flipped to the obverse side, and placed in a new weighboat. The obverse side of the detector chip was used to run wet tests. A drop of deionized water was placed on the top half of the chip and then this portion of the chip was exposed to the oxyhydrogen gas. Next, a drop of deionized water and some palladium were placed on the bottom half of the obverse side of the detector and then exposed to the oxyhydrogen gas. An illustration of what was tested in each portion of the CR-39 detectors see Figure 3.



Figure 3: The schematic for what each region of the CR-39 chip were exposed to

Results and Discussion

The experiments here were presented as a two-part installation of our research. The first half being able to carry out scientific protocols with the intent to validate a widely used solid-state nuclear track detector. The second installation to meticulously analyze the results unique to each hydrated environment. It was initially conjectured that the results of these various exposures would be easily distinguishable from authentic nuclear tracks. Nevertheless, the preliminary results from these experiments show that particles from nuclear origin are indistinguishable from results created from various explosions. The implications



Figure 4: A CR-39 chip used in Pd/D electrodeposition experiments with a lithium electrolyte



Figure 5: CR-39 exposed to Pd dry oxy-hydrogen catalysis.

of these results may invalidate the detector for use in Pd/D pyrophoric electrodeposition systems because of it's inability to provide objective results. Figures 4, 5, and 6 provide picture evidence to support this claim.

Figures 711 shows images of typical tracks observed for the environment listed below the image. A rough estimate of background counts was conducted, and exposed detectors all



Figure 6: CR-39 subjected to a violent Calcium Carbide acetylene explosion

had counts well above background. The electrochemical cells display a variety of pit sizes. Close to the cell cathode, track density becomes too high to accurately measure. Tracks shown are representative of regions near the edge of the dense electrodeposition site. For Pd/D with Li electrochemical experiments, radii typically range from 3 to 7 m, with a mean of 5.3 mm. For the Pd/D with K cells the overall range is about the same, with a mean of 3.7 m.

Small pits were observed with only exposure to oxyhydrogen (2 m) and larger ones for the dry Pd exposed to oxyhydrogen. Note however that one of the detectors was severely damaged when dry Pd was over exposed to oxyhydrogen gas, as oxyhydrogen does ignite in the presence of Pd powder.

Detectors submerged in water and exposed to oxyhydrogen typically show larger pits than the dry detectors subjected to oxyhydrogen gas. For detectors submerged in water and exposed to oxyhydrogen gas, observed pits are typically between 1.2 to 2.8 m. Detectors submerged in water, coated in Pd powder, and exposed to oxyhydrogen gas show a variety of pits but typical pit sizes range from about 2.3 to 4.8 m. The detector exposed to the ignition of acetylene gas showed numerous tracks with a wide variety of sizes.



Figure 7: Examples of measured pits from water, Pd, and oxyhydrogen



Figure 8: Examples of measured pits from acetylene explosion



Figure 9: Examples of measured pits from Pd/D and Li in an electrochemical cell



Figure 10: Examples of measured pits from Pd/D and K in an electrochemical cell

Track radii created from different processes were measured for processes claimed to be nuclear in nature [2] and processes with similar substances and environments that are known to be non-nuclear in nature. Typical pit radii are results are shown in Fig. 7. In previous works where tracks were claimed to be caused by nuclear processes [2], only the diameter of the radial dimensions were measured, and then compared with software that assumes the tracks are created by energetic alpha particles.



Figure 11: Examples of measured pits from water and oxyhydrogen gas

Figure 7 shows that similar substances as those used in electrochemical co-deposition experiments, namely Pd in the presence of water and oxyhydrogen gas, can create tracks with similar radial dimensions. Further, explosive chemical reactions producing shock waves, Fig. 8 also produce tracks with similar radial dimensions. Detectors submerged in water and exposed only to oxyhydrogen gas showed much smaller tracks, similar to former claims of proton or neutron recoil tracks in electrochemical cells [2].

Figure 7 shows that similar substances as those used in electrochemical co-deposition experiments, namely Pd in the presence of water and oxyhydrogen gas, can create tracks with similar radial dimensions. Further, explosive chemical reactions producing shock waves, Fig. 8 also produce tracks with similar radial dimensions. Detectors submerged in water and exposed only to oxyhydrogen gas showed much smaller tracks, similar to former claims of proton or neutron recoil tracks in electrochemical cells [2].

In conclusion, it cannot be claimed that tracks formed in co-deposition of Pd/D in electrochemical cells have a nuclear origin because similar tracks are observed in similar environments that have non-nuclear origins.

References

- [1] . J. J. S. J. E. Szpak, P.A. Mosier-Boss Chem, vol. 302, 1991.
- G. F. F. L. Mosier-Boss PA, Szpak S, "Use of cr-39 in pd/d co-deposition experiments," *The European Physical Journal Applied Physics*, vol. 40, pp. 293–303, 2007.
- [3] M.-B. et. al. Journal of Condensed Matter Nuclear Science, vol. 14, pp. 29–49, 2014.
- [4] S. B. K. J. Marwan J. Environ. Monit, vol. 11, 2009.
- [5] . E. A. Savrasov, V. Prokopenko J. Condensed Matter Nucl. Sci., vol. 22, 2017.
- [6] L. Kowalski Eur. Phys. J. Appl. Phys., vol. 44, 2008.
- [7] K. Shanahan J. Environ. Monit., 2010.
- [8] P. P. B.G. Cartwright, E.K. Shrik Nucl. Instrum. Meth., vol. 153, p. 457, 1978.

- [9] S. S. G. F. E. F. L. P. Mosier-Boss, P. A., "Use of cr-39 in pd/d co-deposition experiments," *The European Physical Journal Applied Physics*, 2007.
- [10] e. a. F.H. Seguin *Rev. Sci. Instrum.*, vol. 74, p. 975, 2003.
- [11] G. Thompson, "Water fuel generator," vol. 1, 2012.
- [12] J. A. F. M. G. J. A. B. Z. H. G. R. M. J. R. C. K. L. R. D. P. H. Sio, F. H. Seguin *Rev. Sci. Instrum.*, vol. 85, 2014.
- [13] L. S.-B. J. S. I. E. J.K. Palfalvi, Y. Akatov, "Cosmic particle induced reaction detection with ssntd stacks exposed on-board of the international space station in 10th international conference on nuclear reaction mechanisms," 2003.
- [14] L. S. Tata, B., "Acceptance testing of the tasl radon dosimetry system," 2016.
- [15] F. M. P. A.-. N. A. S. Caresana, M., "Dose measurements with cr-39 detectors at the cerf reference facility at cern," *Radiation Measurements*, vol. 71, 2014.
- [16] L. P. F. M. S. M. J. R. T. J. P. H. P. A. Mosier-Boss, J. Y. Dea and F. E. Gordon The European Physical Journal Applied Physics, vol. 51, 2010.
- [17] R. C. D. P. J. F. J. R. R. Ralph J. Wolf, Myung W. Lee, "Pressure-composition isotherms for palladium hydride," *Physical Review B*, vol. 48, 1993.
- [18] M. W. L. J. R. R. Ralph J. Wolf, Khalid A. Mansour, "Temperature dependence of elastic constants of embedded-atom models of palladium," *Physical Review B*, vol. 46, 1992.
- [19] T. U. A. A. A. B. H. F. A. G. T. W. H. L. J. F. K. J. J. K. L. M. A. M. R. Pohl, F. Nez and F. Biraben *Metrologia*, vol. 54, 2017.
- [20] K. Y. D. Nikezic Mater. Sci Eng. R, vol. 46, p. 51, 2004.