

1. Chemicals and Materials

1.1 The following chemicals were obtained from Sigma-Aldrich: palladium chloride, copper chloride, lithium chloride, sodium hydroxide, deuterated water, 0.25 mm diameter silver wire, and 0.25 mm diameter platinum wire. These chemicals and metal wires are readily available at any university.

1.2 Prepare plating solutions that is 0.03 M PdCl₂ (or 0.03 M CuCl₂ for the control experiment) and 0.3 M LiCl. In a 50 mL volumetric flask, weigh out 0.27 g PdCl₂ (0.2017 g CuCl₂) and 0.636 g LiCl. Add about 20 mL D₂O to the volumetric flask. The PdCl₂ will slowly go into solution (it forms a complex with the Cl⁻ ions from the LiCl, PdCl₄²⁻). Once in solution, add the rest of the D₂O (solution will be red-brown in color).

1.3 Acrylic boxes (1.125 in L x 1.125 in W x 2.5 in H). These boxes can be found at hobby stores or any stores that sell acrylic products (tubes, sheets, rods, etc.). They are used because they are inexpensive and can be easily modified.

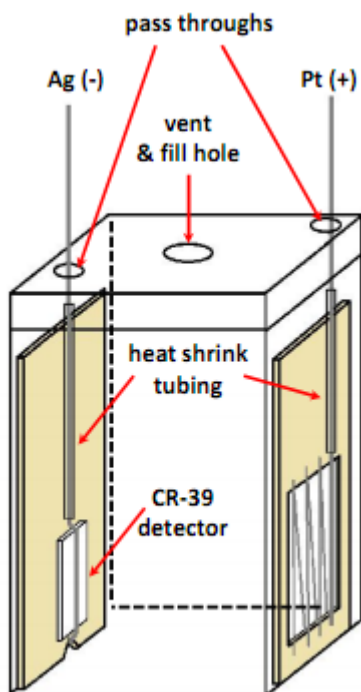
1.4 High density polyethylene sheet (at least 0.031 in in diameter) is used to support the CR-39 and wires used to make the anode and cathode.

1.5 Fukuvi CR-39 chips (1 cm x 2 cm x ~1 mm) were purchased from Landauer. 1.6 Clear polyethylene heat shrink tubing can be obtained from an electronics store.

1.7 Monofilament fishing line can be obtained at any store that sells sporting goods.

2. Cell and Electrode Assembly

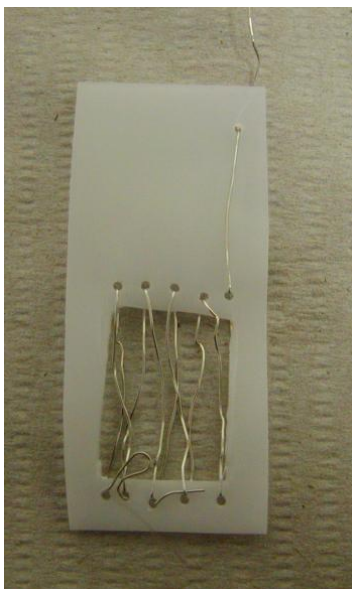
2.1 Schematic of the cell used in the experiments (the spring that holds the electrodes in place is not shown):



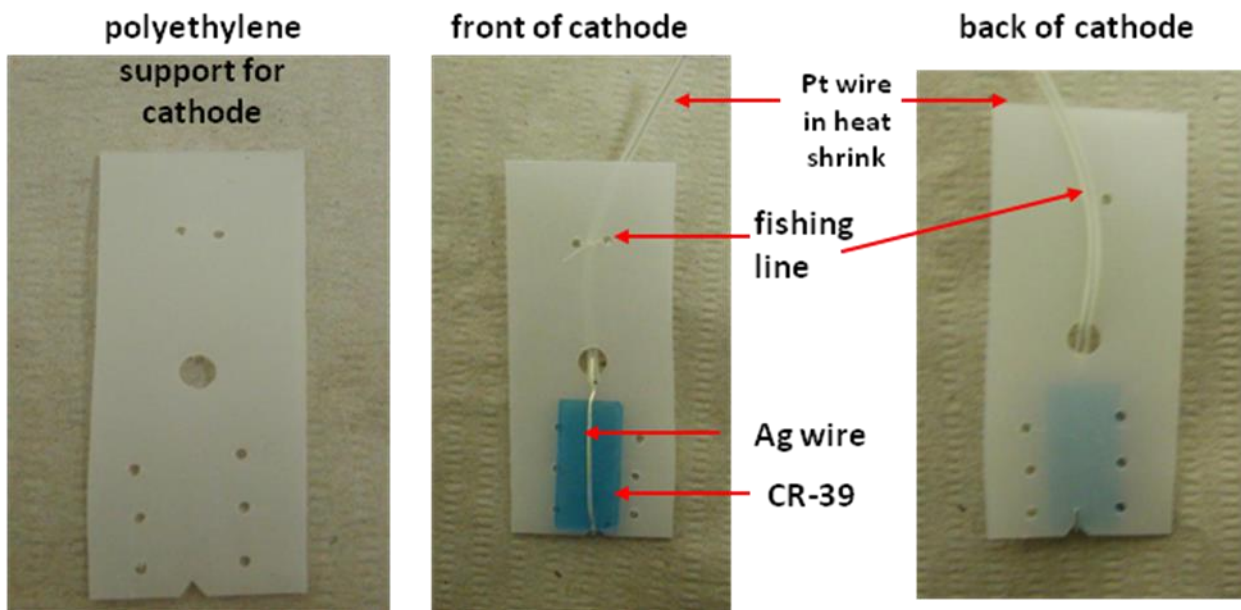
2.2 Drill three holes in the lid as shown in the schematic. One hole is used to fill the cell with plating solution and deuterated water. Two holes are pass throughs for the wires of the anode and cathode.

2.3 Wear gloves when assembling the anode and cathode.

2.4 The anode is Pt wire (0.25 mm in diameter). Polyethylene heat shrink is used to insulate the lead. Photograph of the assembled anode is shown:



2.5 Ag cathode onto which the Pd/D co-deposition occurs:

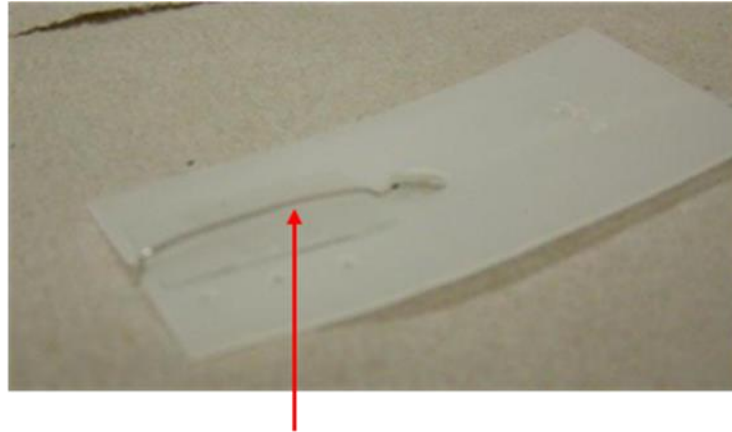


Polyethylene heat shrink is used to establish Ohmic contact between the Pt wire and Ag wire onto which the Pd/D co-deposition takes place. The Pt wire needs to be insulated from the solution or else Pd will electrochemically plate on it. Use polyethylene heat shrink for this.

2.6 Once the anode and cathode (without the CR-39 detector) are assembled, rinse them in a dilute nitric acid solution (~10%) and then DI or distilled water. The nitric acid rinse removes any contaminants (organics and oxides) on the wires. Removal of these

contaminants improves adherence of the Pd/Cu deposit on the surface of the cathode. Allow the cathode and anode to dry overnight before placing them inside the cell (do not want to contaminate the heavy water with light water).

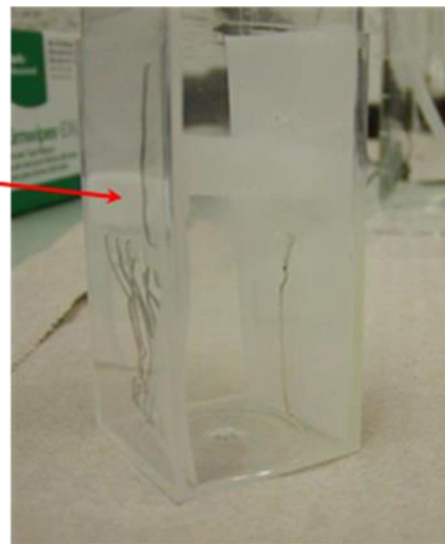
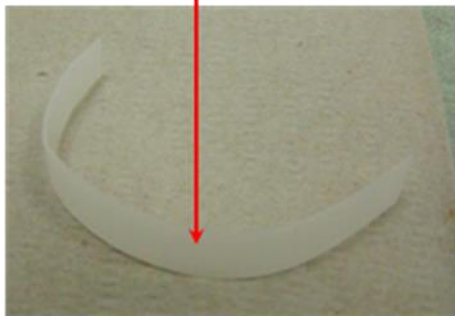
2.7 Before assembling the cell, remove the blue plastic covers on the CR-39 detector as shown:



CR-39 in direct contact with Ag wire

2.8 Prepare a polyethylene ‘spring’ that is used to hold the electrodes in place. Assemble the cell as shown in the diagram. The photographs show the spring and the assembled cell:

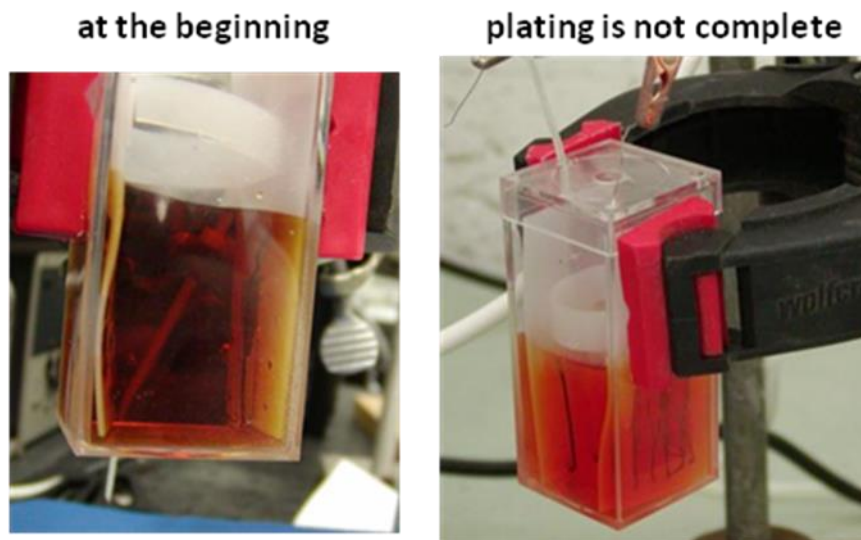
spring used to hold anode and cathode in place



3. Metal Electroplating Experiment

3.1 Once the cell is assembled, place a known volume of the plating solution (PdCl_2 or CuCl_2). For PdCl_2 , the solution is red-brown in color. The electrodes need to be

completely immersed in the solution. This typically requires 20 mL of solution. To determine the Faradaic efficiency, the students need to know exactly how much metal they have present in solution and they will have to keep track of the time kept at each current level. Below is a photograph showing the cell just before the current is turned on. No Pd is present on the Ag electrode and the solution is red-brown in color. The second photograph was taken before the plating is complete. The solution is orangish in color and a black Pd deposit can be seen on the surface of the Ag electrode.



3.2. Place the cell in a well ventilated area such as a fume hood as D_2 , O_2 , and Cl_2 gases are evolved during electrolysis. The potentiostat should be grounded.

3.3 Charging procedure using a potentiostat: Any cathodic (negative) current can be used to electrochemically reduce the Pd and electrolyze the D_2O . The key is to do a slow plating at first to get good adherence between the electrode substrate and the Pd. The students need to record the time when the experiment is started and whenever the current is changed. In this way the students will know the time intervals spent at each current and will be able to calculate the Faradaic efficiency. Below is a typical charging protocol that exhibits good adherence to the Ag substrate:

$I = -0.1$ mA for 1 day or more (this provides a good base coat of Pd on the electrode substrate). The Pd will appear as a black deposit on the electrode substrate. As the plating progresses, the plating solution will get lighter in color. The students may also notice a chlorine-like smell due to oxidation of chloride ions occurring at the anode. Chlorine gas evolution ceases once the Pd has completely plated out.

$I = -0.2$ mA for 1 day or more.

$I = -0.5$ mA until completely plate out Pd (solution will be clear, may see a red-brown precipitate, this is $Pd(OD)_2$ As higher currents are applied, this precipitate will re-dissolve).

$I = -1$ mA for 1 day

$I = -5$ mA for 1 day

$I = -10$ mA for 1 day

I = -25 mA for 1 day

I = -50 mA for 1 day

I = -100 mA for 1 day

During the course of the experiment the students may have to add more D₂O.

Terminate experiment and etch CR-39 chips.

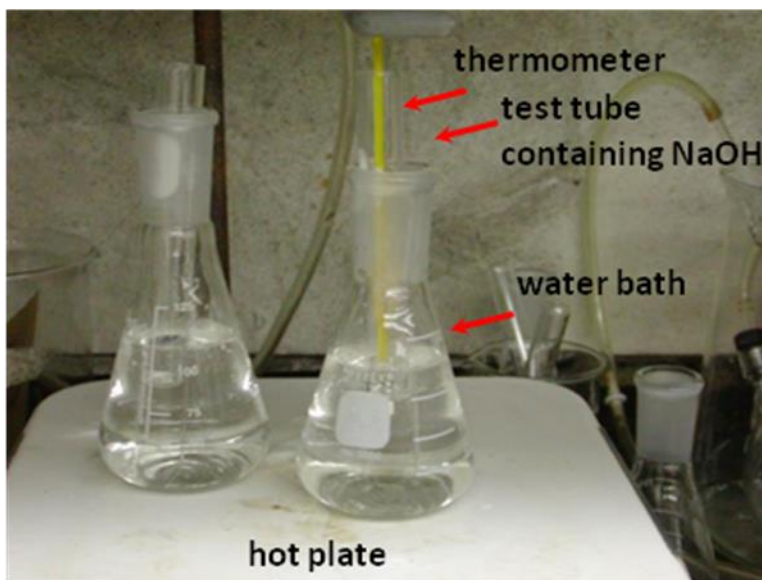
4. CR-39 Etching Procedure

4.1 Disassemble cell. Remove CR-39 detector. Rinse with water and wipe off Pd metal on CR-39 detector with a Kimwipe. Properly dispose of the remaining electrolyte and Pd deposit.

4.2 When preparing/handling the NaOH solution, students should wear goggles, gloves, and a lab coat.

4.3 Prepare etching solution (6.5 N NaOH in water).

4.4 Put ~3 mL of etching solution into a glass test tube. Put test tube in a 125 mL Erlenmeyer flask filled with water. Place the flask on a hot plate. Immerse a thermometer into the etching solution. Heat etching solution to between 62-65 °C. A photograph of the set-up to etch the detectors is shown:



4.5 Once etching solution is between 62-65 °C and holding steady, add the CR-39 detector to the solution. Etch for 6-7 hrs. After etching, properly dispose of the spent etching solution.

4.6 After etching, rinse the detector in water.

4.7 Examine the detector under a microscope

4.8 Archive the detector by placing it in a labeled, small plastic bag.

5. Control Experiments

5.1 Replace PdCl₂ with CuCl₂. Follow the same procedures as above.

5.2 For the other control experiments listed in Table 1, the students should refer to the following reference:

Mosier-Boss, P.A.; Szpak, S.; Gordon, F.E.; Forsley, L.P.G. Use of CR-39 in Pd/D Co-deposition Experiments. *Eur. Phys. J. Appl. Phys.* **2007**, *40*, 293-303.

Below is a summary of the experiments that had been done with cathodes in contact with CR-39, what was observed, and resultant conclusions:

Experiment^a	Results	Conclusions
PdCl ₂ powder placed on CR-39, no electrolysis	No tracks	No radioactive contamination; no chemical/mechanical damage
CR-39 detector placed in PdCl ₂ -LiCl-D ₂ O, no electrolysis	No tracks	No radioactive contamination; no chemical/mechanical damage
Pd, Ag, Au, or Pt wires immersed in H ₂ O; no electrolysis	No tracks	No radioactive contamination; no chemical/mechanical damage
Cu screen in LiCl-D ₂ O, electrolysis (i = -50 mA)	No tracks	No radioactive contamination; no chemical/mechanical damage
Ni screen in LiCl-D ₂ O, electrolysis (i = -50 mA)	No tracks	No radioactive contamination; no chemical/mechanical damage
Ag or Au, electrolysis in CuCl ₂ -LiCl-D ₂ O	No tracks	No radioactive contamination; no chemical/mechanical damage
Ag, electrolysis in NiCl ₂ -LiCl-D ₂ O	No tracks	No radioactive contamination; no chemical/mechanical damage
Ag, Au, or Pt wires; electrolysis in PdCl ₂ -LiCl-D ₂ O	High density of tracks coincident with Pd deposit (see Fig. 6-1a below)	Track properties similar to that of nuclear generated tracks ^b
Ag wire, electrolysis in PdCl ₂ -LiCl-H ₂ O	Tracks coincident with Pd deposit; density of tracks much less than in D ₂ O (see Fig 6-1b below)	Track properties similar to that of nuclear generated tracks ^b
Pd wire, electrolysis in LiCl-D ₂ O	Tracks coincident with Pd wire but not homogeneous (see Fig. 6-1c below)	Track properties similar to that of nuclear generated tracks ^b

a. Cathodes are in contact with CR-39 detectors

b. Properties of nuclear generated tracks: optical contrast, circular/elliptical shape, and bright spot in the center of the pit

6. Results from Other Control Experiments: Comparison of Ag/Pd/D co-deposition in D₂O, Ag/Pd/H codeposition in H₂O, and bulk Pd electrolysis in D₂O:

Figure 6-1 shows photomicrographs of CR-39 obtained at 20x and 200x magnification. Figure 6-1a was for a CR-39 detector used in a co-deposition experiment on an Ag wire conducted in D₂O. The density of tracks is high and occur homogeneously along the Ag wire. The tracks are coincident with the placement of the Pd deposit on the Ag cathodic substrate indicating that the Pd deposit is the source of the tracks. When co-deposition was done on an Ag wire in H₂O, visual examination of the detector showed sparse patches of cloudy areas along the length of the Ag wire. Figure 6-1b shows one such

patch at a magnification of 20x. At a magnification of 200x, tracks are observed in this patch, however the density of tracks is at least four orders of magnitude less than was observed for co-deposition done in D₂O. Since the natural abundance of deuterium in light water is 0.015%, it is possible that the tracks observed in the light water experiments could actually be due to Pd/D interactions.

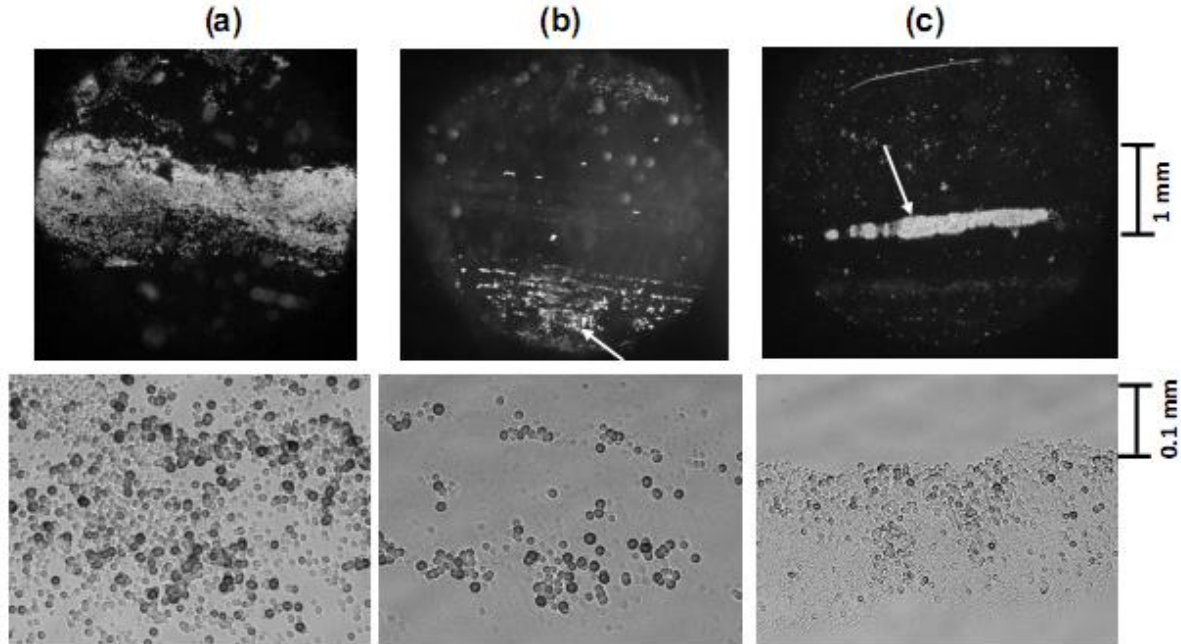


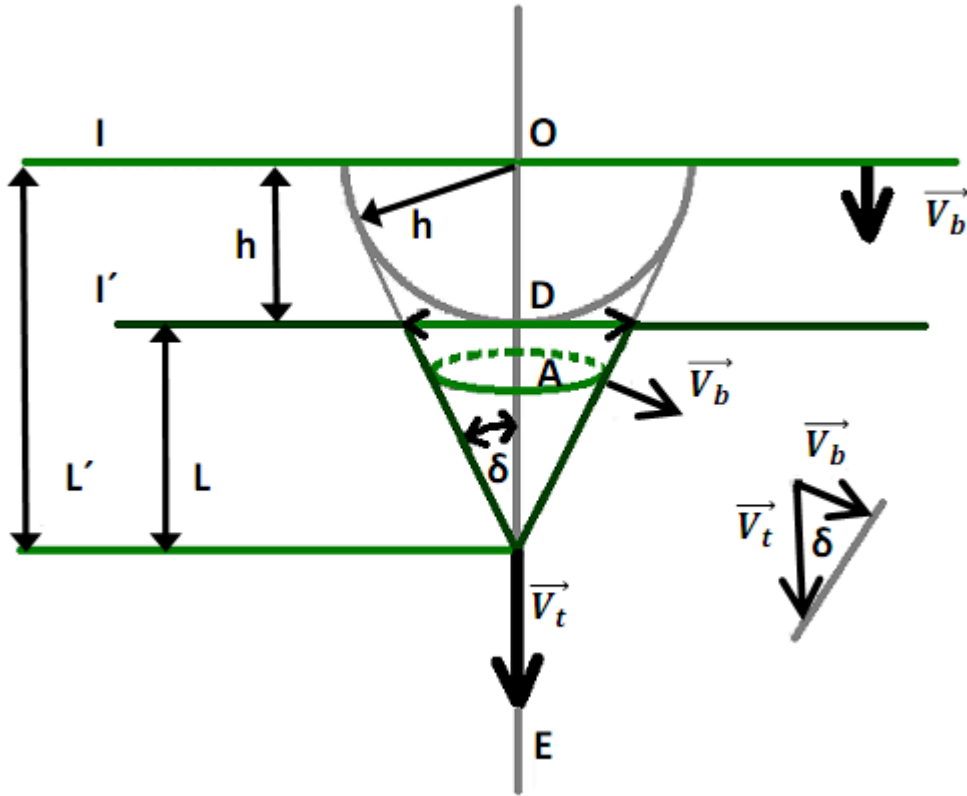
Figure 6-1. Photomicrographs obtained at 20x (top) and 200x (bottom) magnification for CR-39 used in (a) Ag/Pd/D co-deposition in D₂O, (b) Ag/Pd/H codeposition in H₂O, and (c) bulk Pd electrolysis in D₂O. The time duration of operation was the same for all three experiments. Arrows in (b) and (c) indicate the area that was imaged at 200x magnification.

Visual inspection of the CR-39 detector used in the Pd wire experiment done in D₂O showed scattered cloudy areas along the length of the Pd wire. Figure 6-1c shows photomicrographs of one such cloudy area at 20x and 200x. Tracks are observed. The density of tracks is less than that observed for co-deposition done in D₂O but more than was observed in H₂O. It has been well documented that, in the case of bulk Pd, generation of heat, tritium, and helium does not occur homogeneously throughout the Pd. This indicates that the reactions occur in localized areas within the bulk Pd. The CR-39 results show that some areas in the bulk Pd show greater activity than others. Another suggestion has been made that the pits observed in the CR-39 detectors are caused by the tips of the Pd dendrites formed during the Pd/D co-deposition either piercing the surface of the CR-39 or producing hydroxide ions that etch pits into the CR-39. Since pits are observed using a Pd wire which has no dendritic structure to it, neither of these suggested mechanisms of pit formation (piercing or localized etching) is valid.

7. Modeling of Tracks Using TRACK-TEST

When an energetic particle traverses through the plastic, it creates along its ionization trail a region that is more sensitive to chemical etching than the rest of the

bulk. After treatment with an etching agent, tracks remain as holes or pits in the plastic. The size and shape of the tracks provide information as to what type of particle created the track as well as its energy. The geometry of the track, for a particle that entered at an incident angle with respect to the detector surface, is shown below:



where I is the initial detector surface, I' is the surface after etching, V_t is the etch rate along the track (track etch rate), V_b is the etch rate of the undamaged regions of the detector (bulk etch rate), O is the entrance point and E is the end point of a particle in the detector material, h is the thickness of the layer removed by etching, L' is the total distance traveled by the etching solution along the particle, L is the track depth, δ , D is the diameter of the track opening, and the circle A represents the revolution of a point on the track wall around the particle path. During etching, the track wall moves parallel to itself.

Nikezic and Yu developed a program, called TRACK-TEST, that can be used to determine a particle's energy, and angle of incidence as well as the shape of the track formed in a CR-39 detector. The program is freeware and can be downloaded from the following site:

<http://www.cityu.edu.hk/ap/nru/test.htm>

Follow the instructions to download and install the program. When running TRACK-TEST, the following screen appears where the input parameters for the track are entered:


```
Track_test - [Graphic1]
File Edit View State Window Help
PROGRAM TRACK TEST
CALCULATES TRACK PARAMETERS, MAJOR AND MINOR AXES AND DEPTH IN micrometers
PLOT TRACK PROFILE AND TRACK OPENING CONTOUR
AUTHORS, D. NIKEZIC AND K.W.YU
CITY UNIVERSITY OF HONG KONG
E mail: nikezic@kg.ac.yu
E mail: peter.yu@cityu.edu.hk
|
FOR INPUT FROM KEYBOARD, PLEASE TYPE K
FOR INPUT FROM A FILE NAMED input.dat PLEASE TYPE I
k
INPUT DETECTOR TYPE, C FOR CR39 AND L FOR LR115
c
INPUT ALPHA PARTICLE ENERGY IN MeV
1.3
INPUT ETCHING TIME IN hours
6
INPUT BULK ETCH RATE IN micrometer/hours
1.25
INPUT INCIDENT ANGLE in degrees
35
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The input parameters are energy of the particle in MeV, time of etching in h, bulk etch rate in $\mu\text{m/h}$, and incident angle in degrees (normal incidence is 90°). For these experiments using Fukuvi CR-39, the etch rate was $1.25 \mu\text{m/h}$ and the etch time was 6 h.

The next screen of the program asks which track etch rate function to use in the calculation. In the program, there are three forms of the track etch rate function available for use. These three forms exist because the quality of the CR-39 detectors varies between different manufacturers. It is up to the user of the program to determine which etch rate function optimally describes the etching behavior of the detectors being used. This is best done by using all three track rate functions to model tracks generated by a source of known energy and determining which equation gives the best fit. By modeling ^{241}Am alpha tracks in Fukuvi CR-39 detectors, equation 2 (using the default values) was determined to be the optimum track rate function.

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Track_test - [Graphic1]
File Edit View State Window Help
ALLOWED Vt/Vb FUNCTIONS ARE AS FOLLOWS

THE FIRST ALLOWED FUNCTION IS
Vt/Vb=1+(A1*exp(-B1*Y)+A2*exp(-B2*Y))*(1-exp(-B3*Y))
DEFAULT CONSTANTS ARE: A1=11.45; B1=0.339; A2=4; B2=0.044; B3=0.58

THE SECOND ALLOWED FUNCTION IS
Vt/Vb=1+exp(-A1*Y+B1)-exp(-A2*Y+B2)+exp(B3)-exp(B1)
DEFAULT CONSTANTS ARE: A1=0.1; A2=1; B1=1; B2=1.27; B3=1.27

THE THIRD ALLOWED FUNCTION IS
Vt/Vb=1+exp(-0.06082*Y+1.119)-exp(-0.8055*Y+1.119)

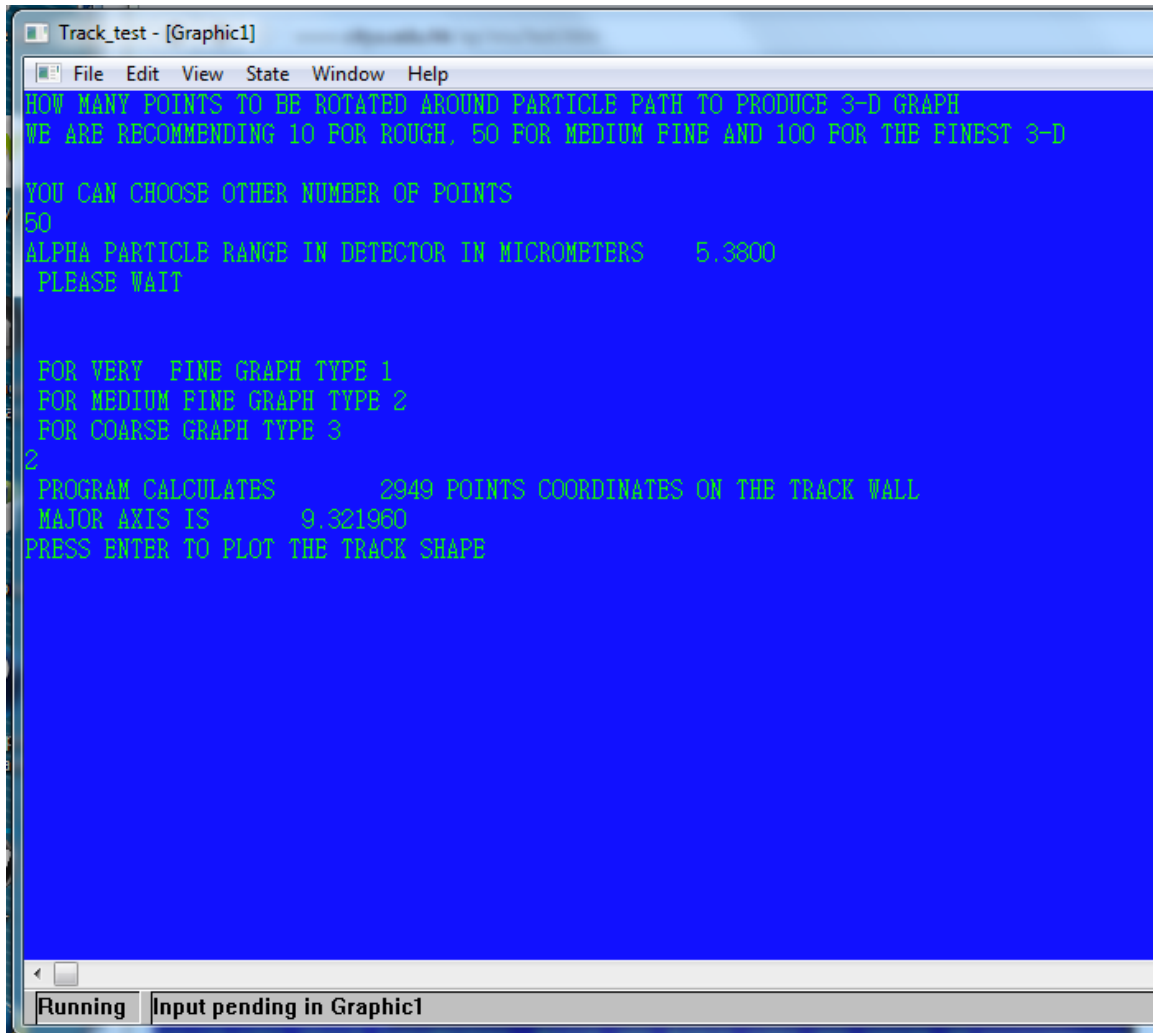
Y IS RESIDUAL RANGE OF ALPHA PARTICLE IN DETECTOR MATERIAL

TYPE 1 FOR FIRST, 2 FOR SECOND OR 3 FOR THIRD FUNCTION
2
TYPE D FOR DEFAULT CONSTANTS, OR TYPE M FOR YOUR CONSTANTS
d

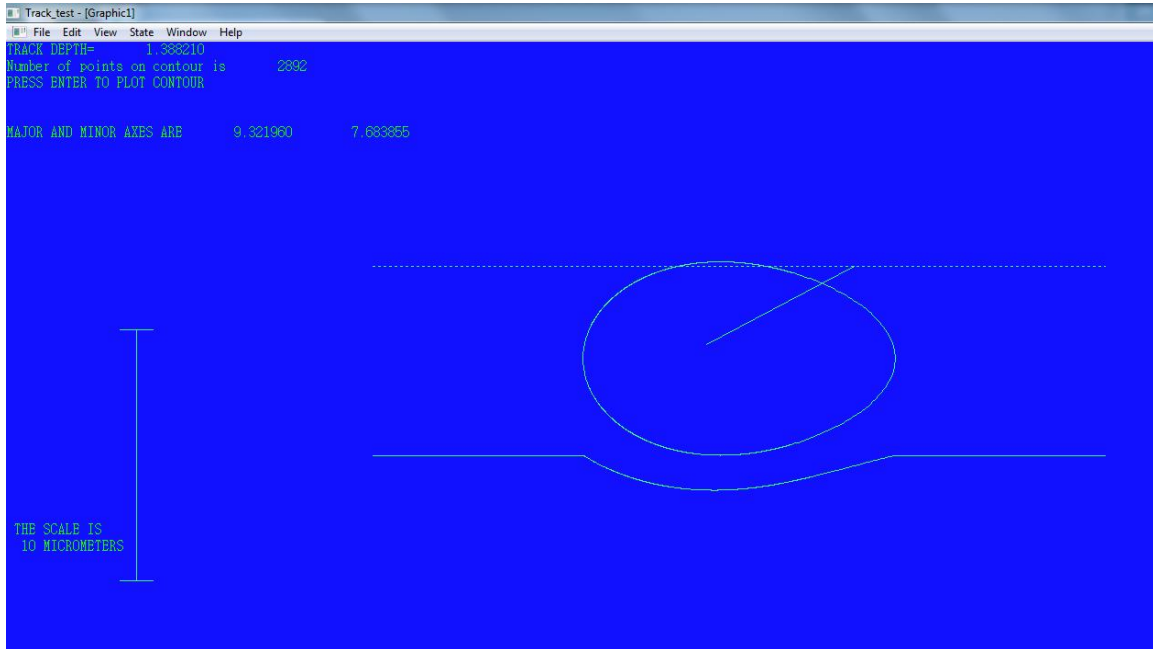
Running Input pending in Graphic1

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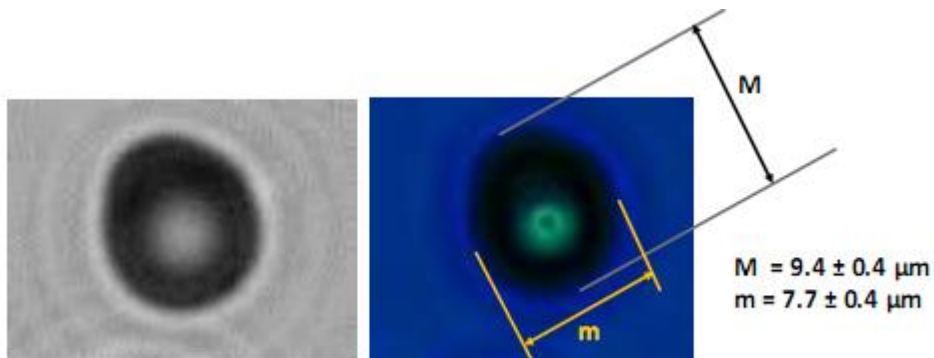
The next screen of the program defines the parameters to plot the shape of the track.



The next screen shows the shape of the track and gives the values of the minor and major axes.



To demonstrate TRACK-TEST, modeling of a Pd/D co-deposition generated track shown below was done. The photomicrograph on the left hand side was obtained by focusing the microscope optics on the surface of the detector. The photomicrograph on the right hand side was obtained by overlaying two images taken at different focal lengths (surface and the bottom of the pits). The bright spot in the right hand image is due to the bottom of the track. When backlit, the bottom of the track acts like a lens and shows up as a bright spot. Consequently, this bright spot indicates the endpoint of the particle. From the images, it is possible to measure the major axis (M) and the minor axis (m). The measurements are shown below.

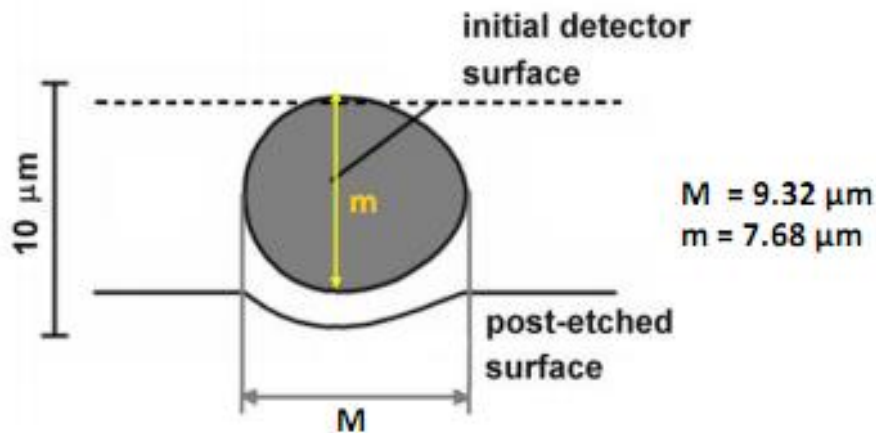


In modeling the track, the particle energy and incident angle are varied until the calculated track shape and values of M and m agree with the measured values. Etch time (6 h) and etch rate (1.25 $\mu\text{m}/\text{h}$) were kept constant. This is an iterative process to determine the particle energy and incident angle. The table below summarizes examples

of particle energies and incident angles that were entered as inputs and the resultant values of M and that were calculated by TRACK-TEST:

INPUT PARAMETERS		CALCULATED VALUES	
Particle Energy (MeV)	Incident Angle (°)	Major Axis, M (μm)	Minor Axis, m (μm)
1.1	30	7.86	6.31
1.2	30	8.28	6.52
1.3	30	8.70	6.71
1.35	30	8.91	6.80
1.4	30	9.11	6.88
1.3	32.5	9.04	7.23
1.3	35	9.32	7.68
1.3	40	9.79	8.44

The results of modeling using TRACK-TEST, and a particle energy of 1.3 MeV and an angle of incidence of 35°, is shown below. It can be seen that the shape of the calculated track is very similar to the track shown in the photomicrographs. Also the calculated values of M and m are in agreement with the measured values.



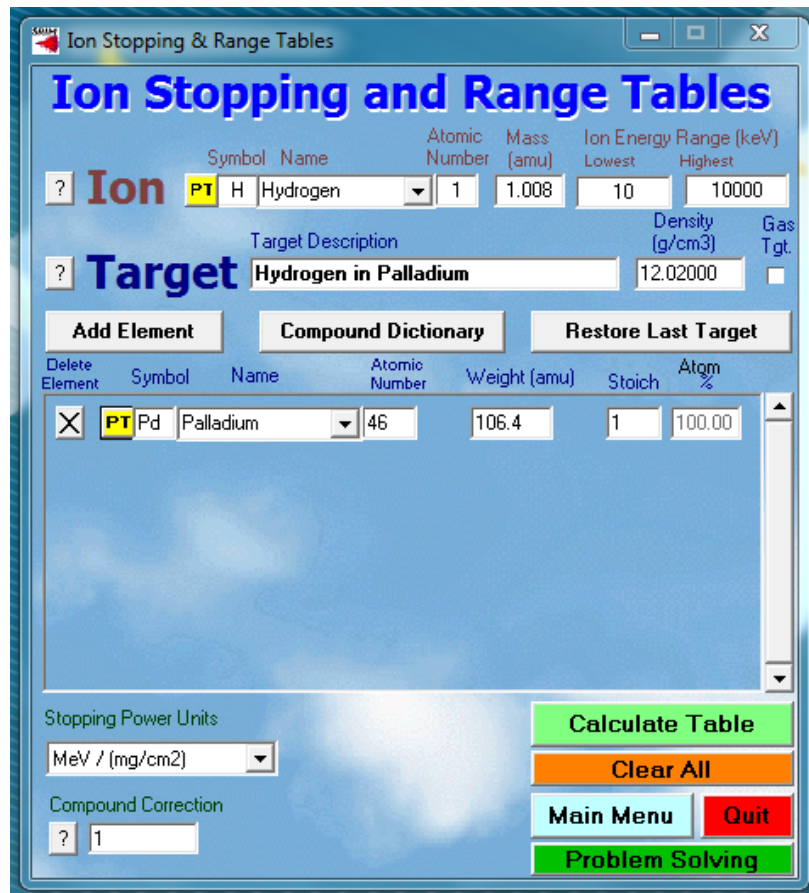
8.0 Linear Energy Transfer (LET) Analysis and Simulation of the Effect of Water on Energetic, Charged Particles

8.1 LET Analysis

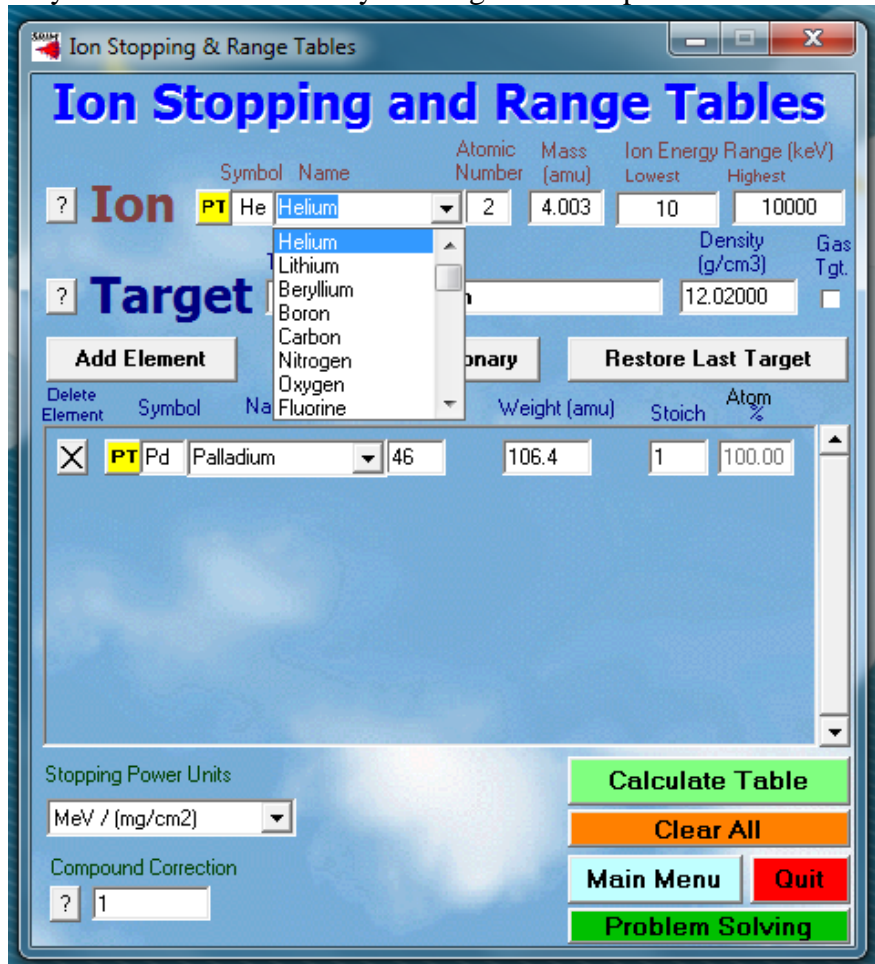
Figure 8.1-1. Schematic describing the layers a charged particle has to negotiate before it impacts the CR-39 detector.

To reach the detector, the particles have to traverse a thin water layer. Linear energy transfer (LET) curves, calculated using the SRIM-2013 code, can be used to evaluate the impact of water on the particle energies. SRIM-2013 is freeware and can be downloaded

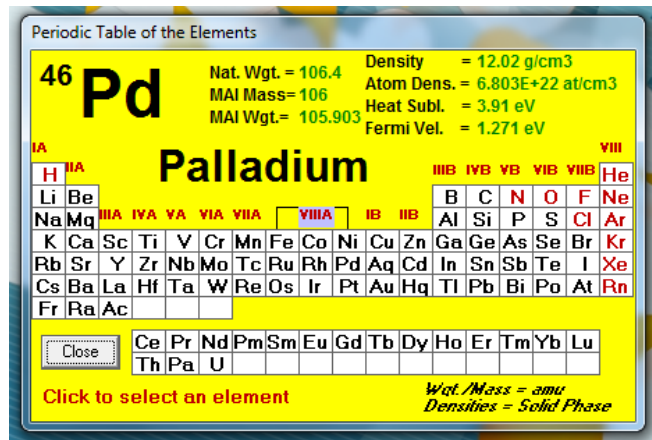
from the following site: <http://www.srim.org/> Follow instructions on the site to install and configure the program. Create a 'shortcut' and place it on the desktop. To calculate a LET curve, click on the shortcut and the following screen will appear:



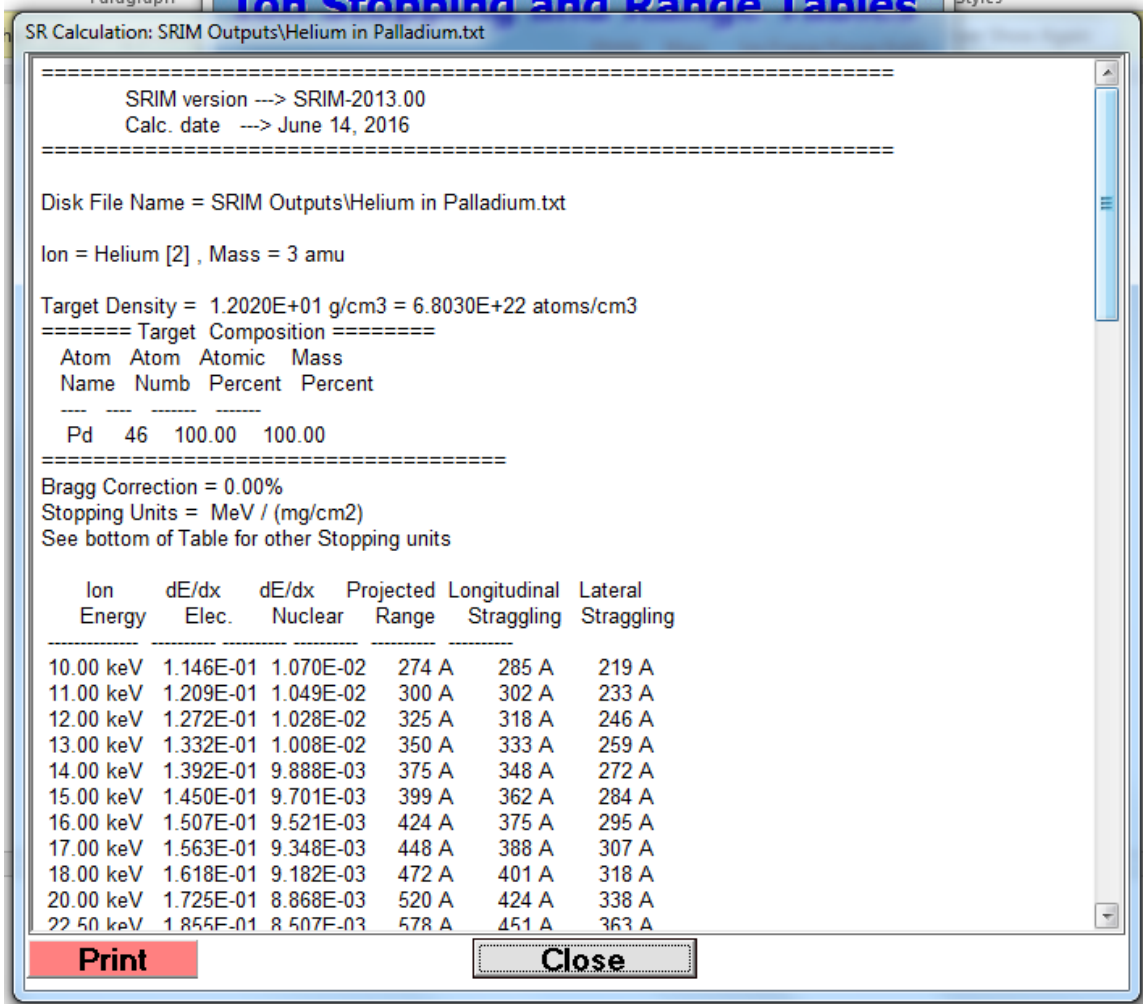
First identify the ion. This is done by clicking on the drop down tab as shown:



Once the ion has been chosen, the atomic mass of the desired isotope of the ion can be entered as well as the energy range of the ion. Once this is completed, the target needs to be specified. The target is the material that the ion will travel through. For the schematic shown in Figure 7-1, the targets are either Pd or water. To designate Pd, click on PT in the Target window and select Pd as shown:

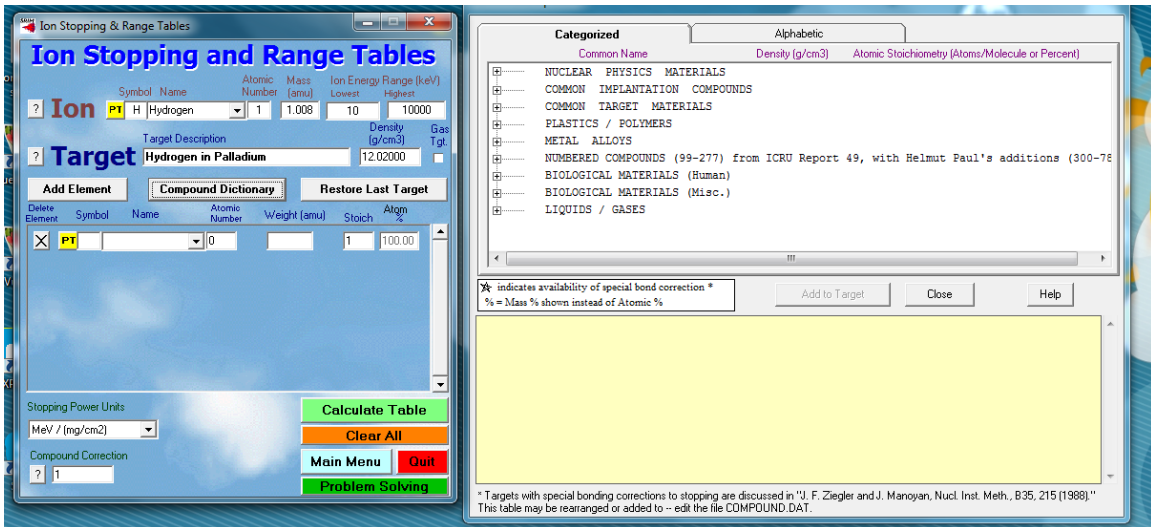


Once everything has been specified, click on ‘Calculate Table’. Below is an example of the output obtained for the calculation. The .txt file is saved in a folder called SRIM Outputs.

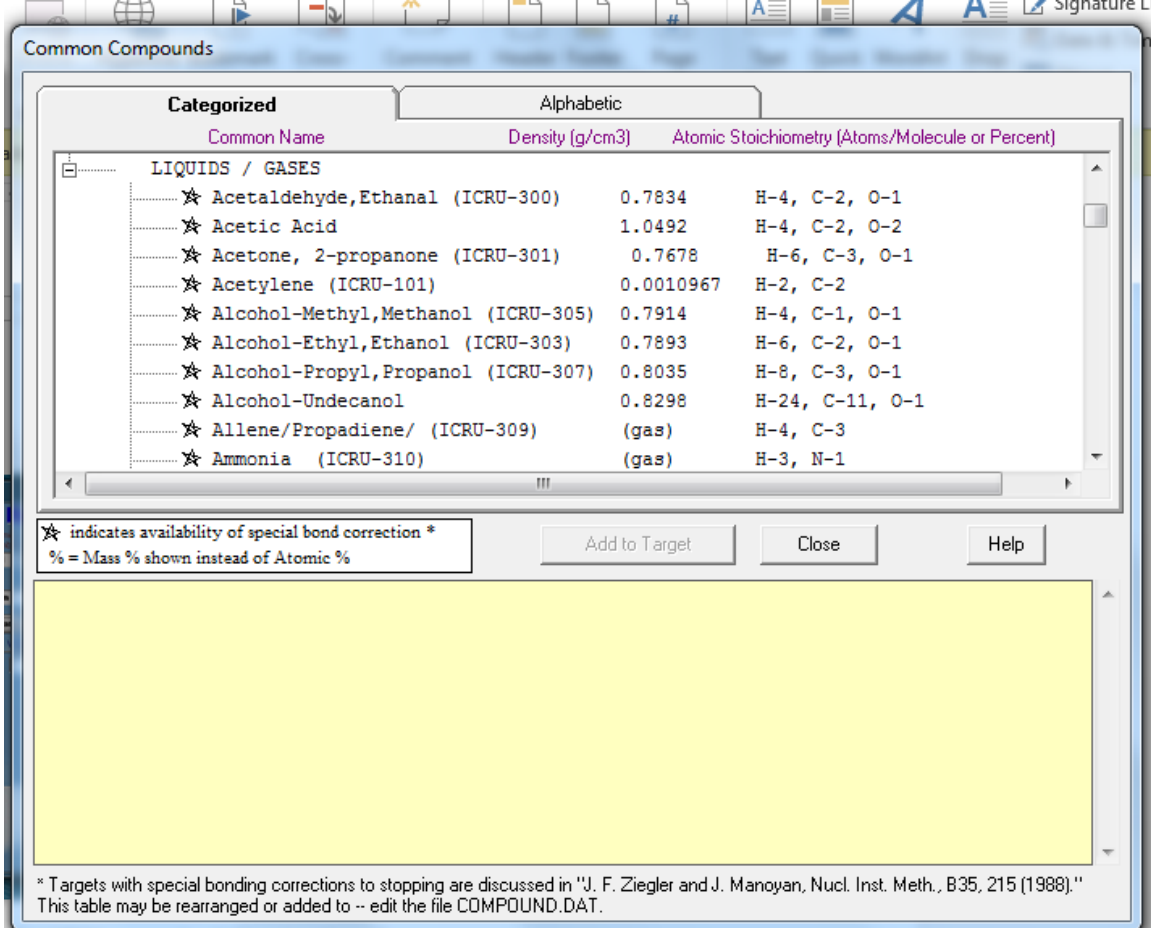


The .txt file can be opened in EXCEL. A plot of ion energy vs. projected range results in a LET curve.

To calculate the LET curve of an ion in water, delete the element and open ‘Compound Dictionary.’ The following drop down menu will appear:



Click on 'LIQUIDS/GASES' to get the following drop down menu:



Scroll down to 'Water (liquid)', click on it, then click on 'Add to Target.' The following screen will appear:



Click on 'Calculate Table' to get the .txt file that is saved in the folder called SRIM OUTPUTS.