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4B Nanotechnology Engineering
Group 7

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Lab 4 Production of a SWNT/PDMS Nanocomposite

Introduction and Objective

The objective of this laboratory experiment is to produce dog bones of a composite material made of PDMS homogenously interspersed with SWNTs. The electrical conductivity of these dog bones will be determined using 2-point and 4-point probes. With these conductivity values, we will be able to determine the relationship between the nanocomposite's electrical conductivity and the SWNT loading percentage. Homogenous dispersion of the SWNTs in the PDMS matrix will be achieved using an ultrasonic disperser and high shear mixing using an electrical homogenizer.

Experimental Procedure

The procedure for this laboratory was obtained from the NE 455L/491L Nanomaterials Laboratory 4 part of the Nanotechnology Engineering Program 4B Lab Manuals, 2010. No deviations were observed.

Discussion and Analysis of Data

We were **Group B**. We had a CNT percentage weight loading of 1.5%. We therefore added 0.1675g of SWCNT to form our polymer composite matrix.

In the following table, we calculated the 4-probe conductivity using the equation $\sigma = \left(4.53 \times \dfrac{\Delta V}{I} \times t \right)^{-1}$. The average and deviation were calculated using the AVERAGE() and STDEV() functions in Excel. In computing the average conductivity, we choose to ignore the conductivity of Sample 4 since Sample 4 was an outlier.

Table 1 Four-Probe Conductivity and Deviation

	Thickness (cm)	I (A)	ΔV (V)	σ (S/cm)
Sample 1	0.192	26.0E-6	1.05	2.85E-05
Sample 2	0.196	13.1E-6	1.60	9.22E-06
Sample 3	0.193	8.40E-6	2.05	4.69E-06
Sample 4	0.186	0.36E-6	3.72	1.15E-07

∑σ/4 (S/cm)	Deviation
1.41E-05	1.26E-05

In the following table, we calculated the 2-probe conductivity of the 4 samples prepared using the equation $\sigma = \left(\dfrac{\Delta V}{I} \times \dfrac{w \times t}{L} \right)^{-1}$. Again, in computing the average conductivity, we choose to ignore the conductivity of Sample 4 since Sample 4 was an outlier.

Table 2 Two-Probe Conductivity and Deviation

|	ΔV (V)	I (A)	L (cm)	W (cm)	Thickness (cm)	σ (S/cm)
Sample 1	1.05	2.60E-05	2.066	0.505	0.192	5.28E-04
Sample 2	1.60	1.31E-05	2.066	0.505	0.196	1.71E-04
Sample 3	2.05	8.40E-06	2.066	0.505	0.193	8.69E-05
Sample 4	3.72	3.60E-07	2.066	0.505	0.186	2.13E-06

∑σ/4 (S/cm)	Deviation
2.16E-05	2.31E-07

Putting together results from all the other groups, we get the following table:

Table 3 Aggregated Results from All Groups

| Group #		A	B	C	D	E
Concentration wt %	0.0%	1.0%	1.5%	2.0%	2.25%	2.5%
4- probe conductivity S/cm	2.5E-11	2.75 E-6	1.41E-5	1.2E-4	2E-4	7.87e-4
2- probe conductivity S/cm	2.1E-11	1.41E-7	2.16E-5	4.7E-5	4.5E-7	2.41e-4

The plot below plots the standard data provided by the instructor instead of aggregated results from the above table. This plot helps us see the relationship between conductivity vs. weight loading of the SWCNTs.
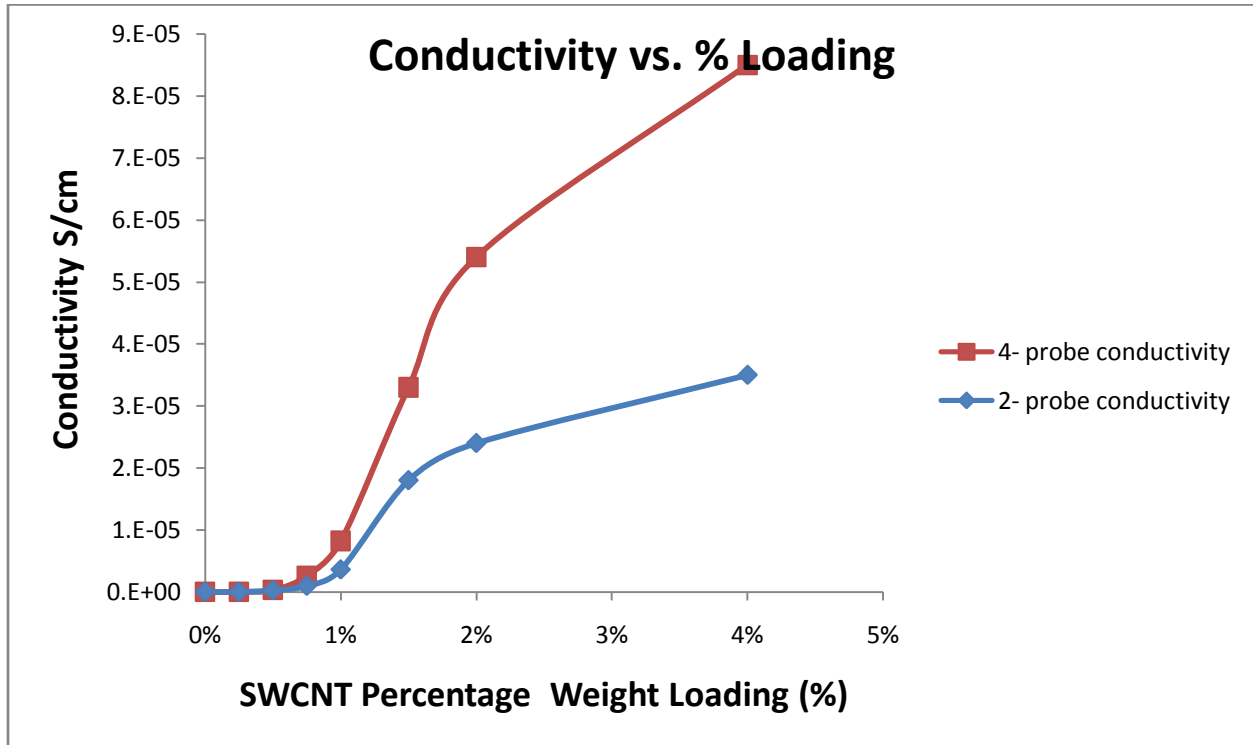
The percolation threshold can be determined directly from big jump of several orders of magnitude in conductivity in the figure above. The conductivity of the system will increase dramatically near the critical concentration. Examining the graph above, it seems that the percolation threshold occurs at roughly **1%** (or 0.01) of CNT loading. To save cost and maintain the best reinforcement performance, *low* percolation threshold is highly desired while engineering good composites.

The plot below plots the log of the conductivity vs. the log of the % loading. The slope of the curve produces the conductivity critical exponent *b*.

log(Conductivity) vs log(% Loading)
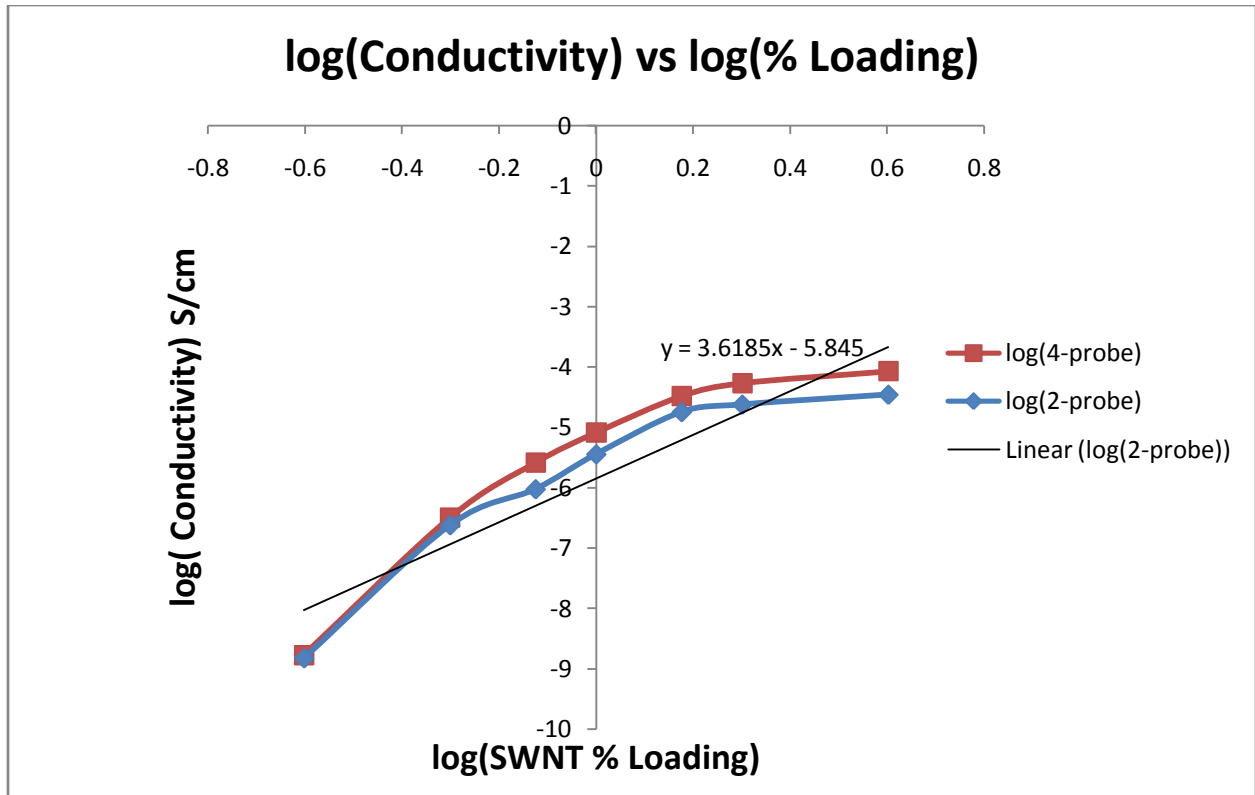
The critical conductivity exponent is the slope of the linear portion in the above plot. This gives us a *b* value of **3.62**.

Looking at the above results, we see that the percentage difference in conductivities between 2-probe and 4-probe testing is roughly 35%. This difference is considerably sufficient to warrant a need to also conduct 4-probe testing in addition to 2-probe testing.

Lab 5 Ionic Polymer Actuator

Introduction and Objective

An actuator is a device that converts electrical energy to mechanical energy. The objective of this lab is to fabricate a specific kind of actuator, known as an ionic polymer actuator (IPA) that uses material response to achieve actuation under a time-varying electric field. The electrical and mechanical properties of this IPA actuator will then be characterized and analyzed for the use of biomimetic actuators. At the end of the laboratory experiment, all the fundamental laws behind electrical actuation of IPAs will be understood.

 Ionic polymer actuators operate under low voltages and can be used in prosthetic devices and microscopic pumps. The ionic polymer used in this lab will be Nafion in a composite matrix with carbon nanotubes. Sudden migration of ions causes deformation in the structure, and this uneven deformation leads to bending of the sheet.

Experimental Procedure

The procedure for this laboratory was obtained from the NE 455L/491L Nanomaterials Laboratory 5 part of the Nanotechnology Engineering Program 4B Lab Manuals, 2010. No deviations were observed.

Discussion and Analysis of Data

The first set of testing done was to use a fixed frequency of 0.2 Hz, and to then vary the peak-to-peak voltage amplitude of the sine wave input from 1V to 8V. The tip displacement is recorded in Table 4.

The second testing done was to use the AC voltage above that gave us the maximum displacement (6V) and to then vary the frequency. Tip displacement was recorded in Table 5.

Table 4 Voltage vs. Displacement (Fixed Frequency = 0.2 Hz)

Voltage (V)	Displacement (mm)
1	0.3
2	0.5
4	4
6	5
7.8	4

Table 5 Frequency vs. Displacement (Fixed Voltage = 6V)

Frequency (Hz)	Displacement (mm)
0.2	5
0.5	2
1	1.2
1.5	0.8
2	0.5

From Table 4, it is clear that higher voltages result in larger displacements, but only to a certain extent. Above a certain threshold voltage, 6V in our case, the displacements starts to drop again. This can be explained as follows. Initially, the increasing voltage provides more electromotive force to push the ions to one side of the actuator to generate a stronger electric field and produce sheet bending. However, at higher voltages, the maximum displacement will

have been achieved since all ions will have already migrated to one side of the actuator. Any excess voltage applied will not help the ions move any further and will only lead to reduced displacement.

From Table 5, we see that higher voltage frequencies result in lower displacements. This is because at higher frequencies, the actuators do not have sufficient time to achieve their full mechanical response to the electrical field. The ions are therefore mostly contained within the polymer. At low frequencies however, the actuator has sufficient time to reach its full displacement at the most optimal voltage. The water and hydrated ions have more than enough time to rush out of the surface electrodes. Hence, tip displacements decreases with an increase in frequency.

3. Find the strain difference between the electrodes of the actuator for the different peak-to-peak voltages used.

The strain difference between the two electrodes of the actuator can be found using the following relationship provided to us in the lab manual:

$$\varepsilon = \frac{2d\delta}{L^2 + \delta^2}$$

where ε is the strain difference between the two electrodes, δ is the displacement of the actuator tip, d is the thickness of the actuator, and L is the length of the actuator. Using the relationship, an example calculation for the strain difference is for a displacement of 5 mm is:

$$\varepsilon = \frac{2 \times 200 \ \mu m \times 5 \ mm}{\left(150 \ mm\right)^2 + \left(5 \ mm\right)^2} = \frac{2 \times 200 \times 10^{-6} \times 5 \times 10^{-3}}{\left(150 \times 10^{-3}\right)^2 + \left(5 \times 10^{-3}\right)^2} = 8.879 \times 10^{-5}$$

The following table summarizes the strain difference for each peak-to-peak voltage used:

Voltage (V)	Strain Diff. ε
1	5.33E-06
2	8.89E-06
4	7.11E-05
6	8.88E-05
7.8	7.11E-05

4. Calculate the thermodynamic efficiency, $E_{ff,em}$

According to the lab manual, the thermodynamic efficiency, $E_{ff,em}$, can be obtained as

$$E_{ff,em}(\%) = \frac{P_{out}}{P_{in}} \times 100$$

where P_{in} is the electrical power input to the IPA. The input power P_{in} can be calculated using $\frac{V^2}{R}$. The resistance of the actuator can be calculated from the resistance using $R = \frac{\rho L}{A}$, where ρ is the resistivity of the film (1.3E7 Ω.cm for a 2.5 wt% CNT Nafion film). The cross-sectional area A of the actuator is just the width times the thickness. The output power P_{out} is $F \times \delta \times f$, where F is the force on the actuator, δ is the tip displacement and f is the input frequency. Using these formulas, the thermodynamic efficiencies of the actuator were obtained for various voltages (fixed frequency of f = 0.2 Hz) and various frequencies (fixed voltage of V = 6V):

Voltage (V)	$E_{ff,em}$ (%)		Frequency (Hz)	$E_{ff,em}$ (%)
1	5%		0.2	40%
2	4%		0.5	16%
4	58%		1	12%
6	40%		1.5	8%
7.8	15%		2	4%

5. Calculate the capacitance of the actuator

The current, capacitance, and voltage across a capacitor are related in the following way:

$i(t) = C\frac{dv(t)}{dt}$. With some simple mathematical manipulation, we find that $C = \frac{\int i(t)}{\Delta V}$. Thus the capacitance of our actuator when the applied difference is 1V is

$$C = \frac{\int i(t)}{\Delta V} = \frac{633.4 \ \mu C}{1 \ V} = 633.4 \ \mu F .$$

6. Calculate the strain ε and the stress σ of the actuator.

According to the NE 491 Lab 5 manual, the stress σ can be calculated from the applied force like so: $\sigma = \frac{6FL}{bh^2}$ where σ is the stress tensor. The force applied can be calculated from the cantilever equation $\delta = \frac{FL^3}{3EI}$ and the moment of intertia I can be calculated using $I = \frac{bh^3}{12}$, where b is the width and h is the thickness of the IPA actuator. The moment of intertia is calculated to be 1.33E-15 m⁴. Assuming linear elasticity, we can calculate *strain ε* using Hooke's law: $\sigma = E\varepsilon$. The stresses and strains for each applied voltage are summarized in the table below:

Voltage (V)	Stress σ (Pa)	Strain ε
1	200	4.00E-06
2	333	6.67E-06
4	2667	5.33E-05
6	3333	6.67E-05
7.8	2667	5.33E-05

The stresses and strains for each varying frequency are as follows:

Frequency (Hz)	Stress σ (Pa)	Strain ε
0.2	3333	6.67E-05
0.5	1333	2.67E-05
1	800	1.60E-05
1.5	533	1.07E-05
2	333	6.67E-06

Summary and Conclusions

In this laboratory experiment, we understood the fundamentals of ionic polymer actuators (IPAs). We were able to fabricate one of these IPAs and then subject it to electrical and mechanical characterization. We saw that that higher voltages across the actuator result in larger displacements, but only to a certain extent. Above a certain threshold voltage, 6V in our case, the displacements starts to drop again. We also saw that higher voltage frequencies result in lower displacements. This was attributed to insufficient time for ions to travel to the ends of the actuator to cause enough bending. The strain difference between the electrodes of the actuator was calculated to be within 7.11E-05 and 5.33E-06. The thermodynamic efficiency of the actuator varied from as low as 4% to as high as 58%. The highest thermodynamic efficiency of 58% was achieved at a voltage of 4V at a frequency of 0.2 Hz. The capacitance of the actuator was determined to be 633.3 μF. The stresses and strains experienced by the actuator were proportional to their displacements measured upon application of a voltage of a known frequency. The highest stress obtained was 3333 Pa, while the highest strain obtained was 6.67E-05.

Lab 6 Polypyrrole Nanoparticles for pH Sensor

Introduction and Objective

The objective of this laboratory is to build a pH meter by synthesis of a conducting polypyrrole (Ppy) polymer film of varied thickness via electropolymerization. We then show how the open circuit voltage of a film deposited using cyclic voltammetry (CV) varies linearly with the pH of the solution. Using this technique, we can therefore measure the pH of a solution by measuring the film's open circuit potential once the sensor has been calibrated to determine linearity characteristics.

The second objective of this laboratory is to calculate the polypyrrole's film thickness accurately using Faraday's law and show how thicker films are less sensitive to changes in pH compared to thin films.

Experimental Procedure

The procedure for this laboratory was obtained from the NE 455L/491L Nanomaterials Laboratory 6 part of the Nanotechnology Engineering Program 4B Lab Manuals, 2010. The only deviation from procedure was that instead of using 5 cycles for the first cyclic voltammetry (CV) part, we used 10 cycles.

Discussion and Analysis of Data

The following table presents the open circuit voltage of the thin and thick films.

pH	Open circuit voltage (mV) [Thin Film]	Open circuit voltage (mV) [Thick Film]
2.46	466.7	466.7
3.46	433.1	433.1
4.78	404.8	404.8
5.89	373.9	373.9
6.39	343.3	328.8
7.39	286.7	286.7
8.55	219.5	219.5
9.38	161.6	161.6

The following figure plots the straight line curve between the data points to obtain the slope and linearity.
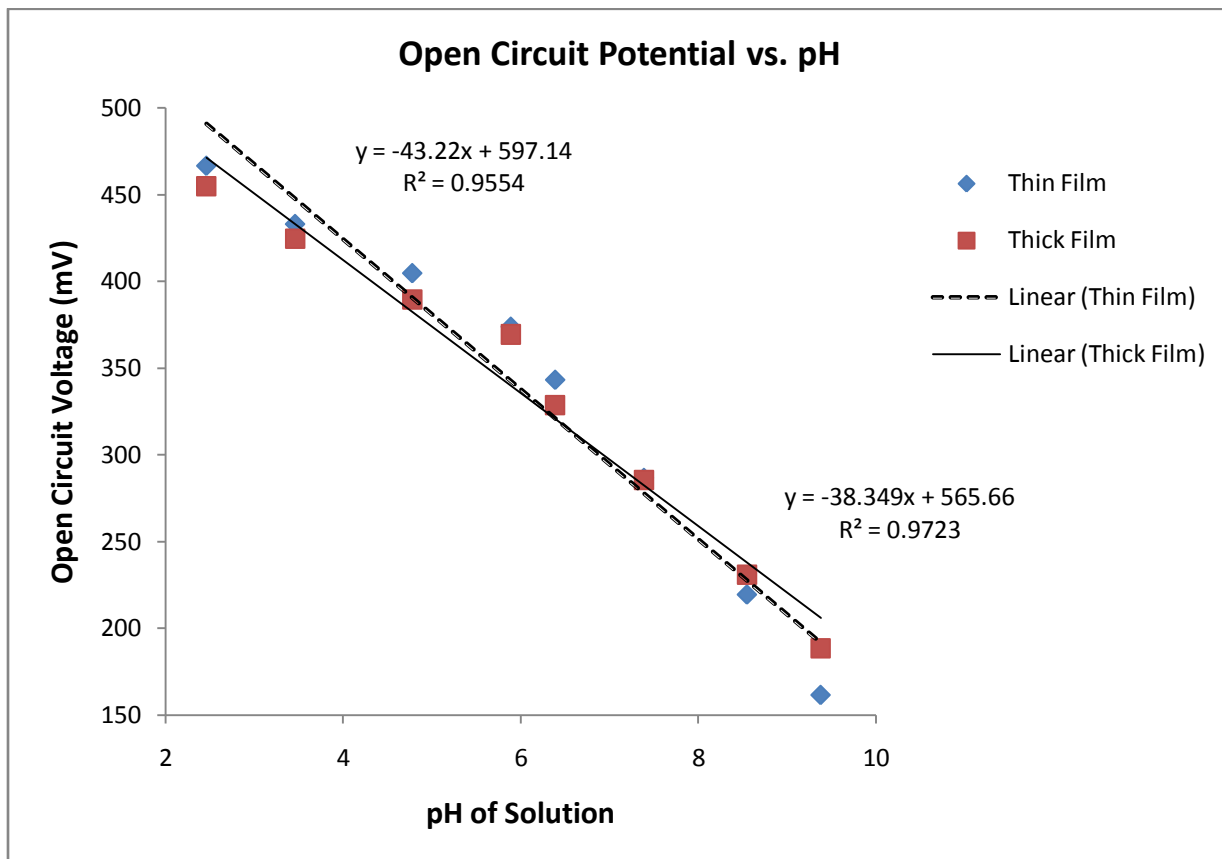
The following table summarizes the slope and linearity of the two curves.

Table 6 Slope and Linearity of the Best Fit Curves for Thin and Thick Films

Film Type	Slope (mV/pH)	Linearity (R^2 value)
Thin	-43.2	0.9554
Thick	-38.3	0.9723

The ideal value of the slope/sensitivity is -59 mV/pH-unit as predicted by the Nernst equation. However, as seen in Table 6, we obtained a sensitivity of -43.2 mV/pH for the thin film (% diff = 26.8%) and -38.3 mV/pH for the thick film (%diff = 35%). Possible reasons for this difference in sensitivity could be:

- The ideal sensitivity is obtained used the Nernst under ideal conditions such as temperature and pressure. The conditions under which our experiment was performed may not have been under the same ideal conditions. For example, the temperature inside C2-168 may have been slightly above 298 K.

- We assumed assuming 100% current efficiency for polypyrrole formation while calculating the ideal sensitivity. This efficiency, of course, is impossible to obtain in a real-life laboratory experiment.

- The glass electrode in use is very sensitive and very variable. It could have been damaged ever so slightly causing it to have different absorbancies. The glass electrode could have also been dirty and contaminated leading to uneven film development.

- The pH of the different buffer solutions provided to us may not have been exact.

- The potentiostat provided to us is an electronic hardware equipment, and as with any hardware equipment has manufacturing errors, defects and differences. Hence, calibration against the ideal sensitivity value is necessary in a commercial pH electrode.

One cycle of a typical CV of the electropolymerization for both the thin and thick film is illustrated in the following figure:
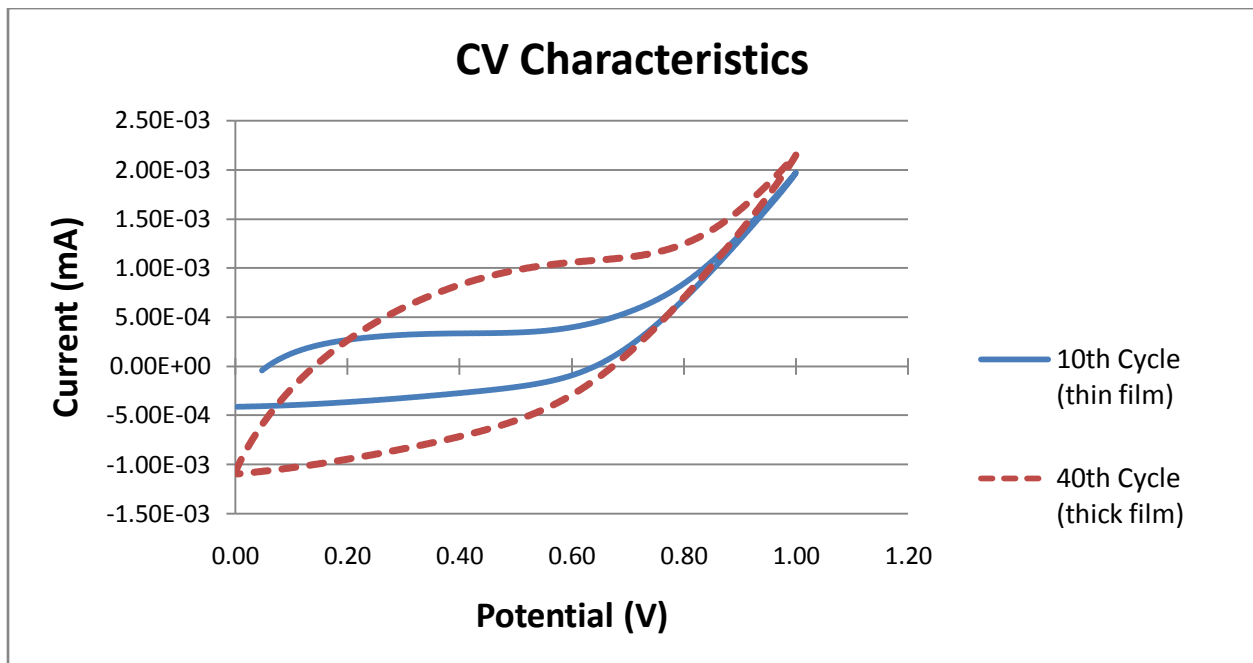

Figure 1 One cycle of a typical CV of the electropolymerization of PpY.

The mean film thickness of polypyrrole t can be estimated from the electrical charge Q ($\int idt$) associated with pyrrole oxidation by application of Faraday's Law and assuming 100% current efficiency for polypyrrole formation:

$$t_{thin} = \frac{QM}{\rho A z F} = \frac{0.01426 \text{ C} \times \left(200 \times 67.09 \frac{\text{g}}{\text{mol}}\right)}{1.5 \frac{\text{g}}{\text{cm}^3} \times 0.198 \text{ cm}^{-3} \times 2 \times 96485 \frac{\text{C}}{\text{mol}}} = 3.34 \times 10^{-3} \text{cm} = 33.4 \ \mu m$$

$$t_{thick} = \frac{QM}{\rho A z F} = \frac{0.01836 \text{ C} \times \left(200 \times 67.09 \frac{\text{g}}{\text{mol}}\right)}{1.5 \frac{\text{g}}{\text{cm}^3} \times 0.198 \text{ cm}^{-3} \times 2 \times 96485 \frac{\text{C}}{\text{mol}}} = 4.29 \times 10^{-3} \text{ cm} = 42.9 \ \mu m$$

We see that the film thickness of the *thick* film is roughly 1.28 times or 28% thicker than the *thin* film for an additional 30 cycles of CV. This change in thickness resulted in a difference in sensitivity from 43.2 mV/pH to 38.3 mV/pH, a difference of 11.3%.