Electrical Characterization of Nanomaterials

By

Chase Martin

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ABSTRACT

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ADVISORS: Rebecca Cortez, Michael Hagerman

Our dependence on energy sources and depleting fossil fuel reserves are forcing the world to look for efficient and renewable sources of energy. Current renewable technology lacks the efficiency and storage capability necessary to continue our heavy reliance on energy. This project focuses on understanding the physical and electrical properties of nanomaterials for their use as supercapacitors and as photovoltaic cells. Using multiple microscopy techniques on the Cascade Probe Station and Veeco Dimension V Atomic Force Microscope, local and bulk conductivity measurements were performed on Laponite RD infused polyaniline (PANI) samples synthesized by Union College Chemistry Department Students. Four different polyaniline and four control samples were examined throughout this project. My work focused on understanding and developing protocols for the previously mentioned microscopy techniques to ensure accurate and repeatable measurements. With complete comprehension of the tools and techniques available, future measurements can be conducted with complete reliability. The developed protocols will be instrumental in the examination and understanding of these PANI materials and others, and will assist in the publication of scientific papers.

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1. Purpose

The drive for my senior research project is based on my interest in understanding the potential use of nanomaterials in photovoltaic cells and supercapacitors. My project will expand upon research performed by Jared Mondschein, Isaac Ramphal and Suan Quah, three of Professor Hagerman's research students, by using a variety of microscopy techniques to further understand their prepared samples. I will aid in their research by providing a greater knowledge about the morphologies and conductive properties of their materials and help with the publications of scientific papers. This project will allow me to expand my knowledge of nanomaterials, their uses and develop a greater understanding of microscopy techniques through hands-on experience.

2. Introduction

Jared Mondshein's thesis work focuses on the synthesis times and the addition of Laponite RD to polyaniline (PANI) films in order to improve their electrical properties. This material is particularly interesting for use as a heterojuction layer in photovoltaic cells. During these short time syntheses, the PANI precipitates severely decreased in size to roughly 500 nm in diameter. This green precipitate is the conductive part of the polymer and the primary interest in this material making it an important property to control. Jared's work also focused on the addition of Laponite RD during synthesis to act as a template for the PANI precipitate to grow from. This addition of Laponite was shown to influence the morphology of the film[1].

Isaac Ramphal's thesis work focuses on the inclusion of Laponite in polyaniline/Graphene Oxide nanocomposites to improve water processability. The material is particularly interesting for its use as a supercapacitor. His work includes a brief finding of his conductivity measurements with a scanning probe microscope[2]. In order to receive publication it may be necessary to include both localized and bulk conductivity measurements.

3. Accomplishments

Veeco Atomic Force Microscope

My work on the Veeco AFM was performed on Jared Mondshein's polyaniline samples. The purpose of this work was to improve my microscopy skills by replicating AFM images found in Jared's thesis work[1]. Before any imaging, I read and discussed Jared's thesis[1] so that I could develop a better understanding of the researched material and the images I planned to replicate.

The first sample I imaged was JM2-86a, a short time synthesis with no added Laponite. I initially imaged the sample under the optical microscope to identify an ideal sample area to perform the atomic force microscopy. I performed over ten scans in multiple locations starting with 5 μm x 5 μm scan areas at 512 samples per line. Once a clear image of the desired morphology was obtained, I decreased the scan area to 2 μm x 2 μm for an enhanced image. Figure 1 shows the comparison of Jared's AFM images (a) compared to my AFM image; both images are at the same scale. The images show the green PANI precipitate as 100 nm spheroids that are spread evenly across the sample area. Note that these images were taken using different microscopes.

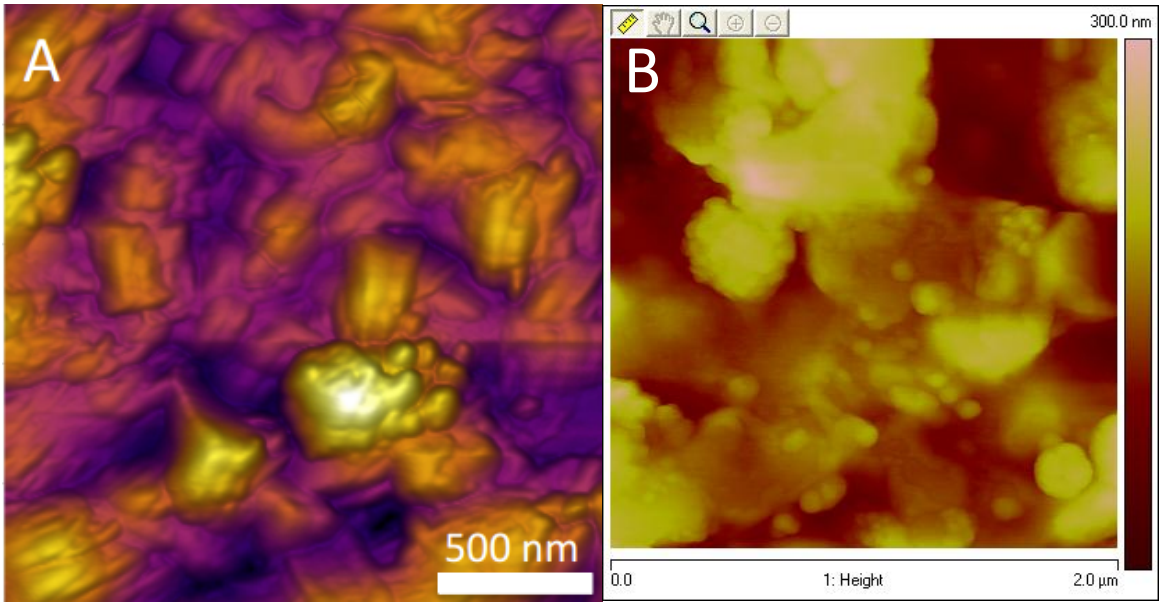

Figure 1. AFM tapping mode images of (a) thesis image[1] (b) my image. (JM-86a)

The second sample I imaged was JM2-86c, a short time synthesis with 15 mg of Laponite RD added. Figure 2 shows a comparison of Jared's thesis image compared to my AFM image of the same sample. The images show the growth of 100 nm green precipitate spheroids off of the Laponite nanoparticles. Both images are at the same scale.

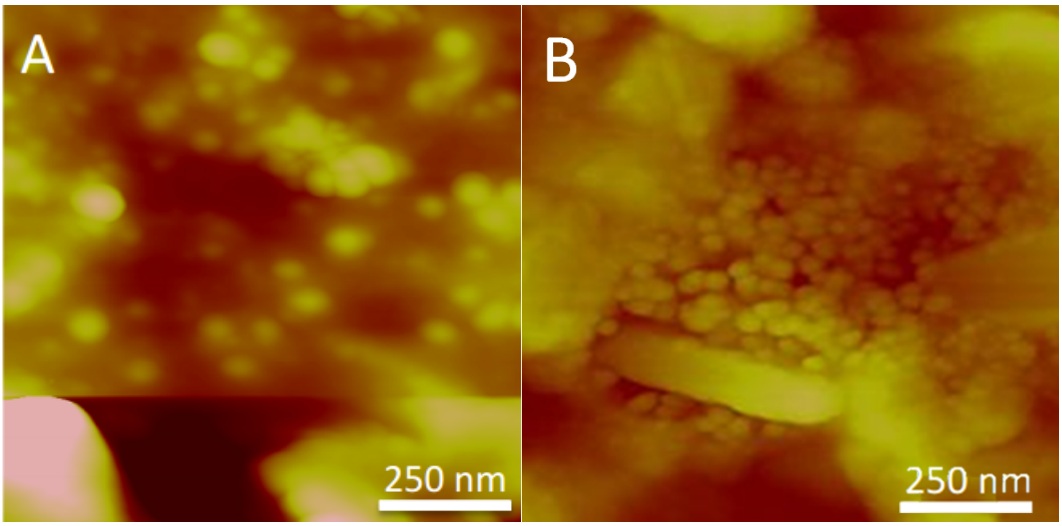

Figure 2. AFM tapping mode images of (a) thesis image[1] (b) my image. (JM-86c)

Conductive Atomic Force Micrsocopy

Conductive AFM measurements are important for understanding local electrical characteristics of materials. I learned and performed some work with conductivity measurements but was relativley unsuccessful. One of Isaac Ramphal's samples was examined with the AFM but showed no signs of conductivity. However, this does not mean that the sample he synthesized was not conductive. There are many issues that occur when examining a sample on the micron level. One issue that occurred frequently was completing a full circuit. The sample that he developed was rather homogeneous leaving many gaps between the sampled area and the attached copper tape. Without a complete circuit, conductivity is impossible to measure.

In order to verify that conductivity measurements were possible and working correctly, a voltage sweep was performed on the copper tape. Figure 3 shows a -10V to 10V sweep performed on a 2μm area of copper tape. The current readings show that the AFM is working as expected. With better understanding of the AFM parameters and sample preperation, conductive atomic force microscopy will aid in the knowledge of specific nanofeatures.

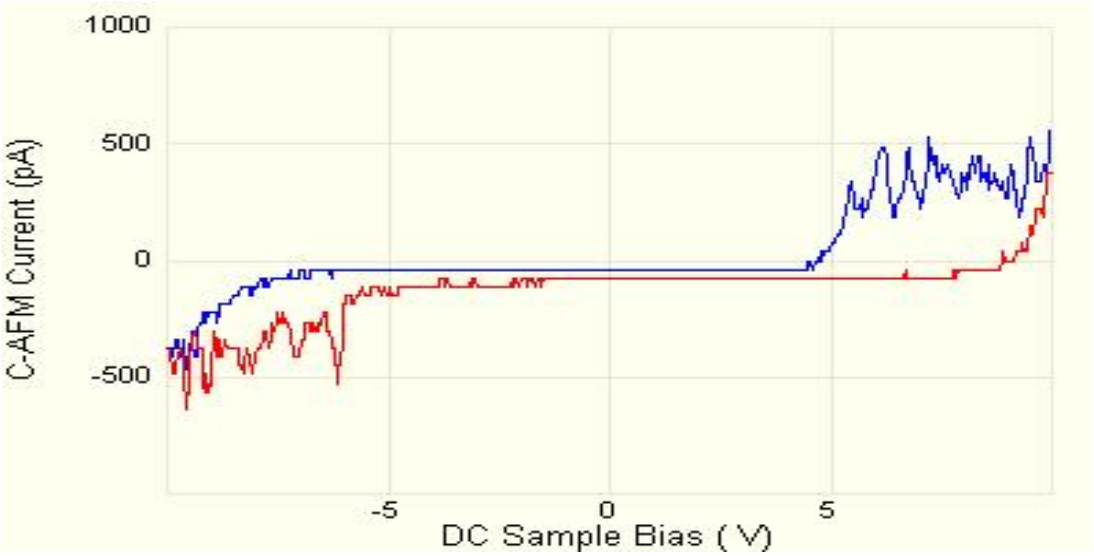

Figure 3. IV curve of copper tape. -10 to 10V sweep.

Cascade Microtech Probe Station

The Cascade Microtech Probe Station is a relatively new microscope acquired by Union College. Its purpose is to measure the conductivity of small samples by applying voltage across two probes. In order to ensure accurate and repeatable measurements with the use of this system, it is important to develop a protocol. My work on the probe station involved gaining familiarity with the interface and developing the protocol to be used for future measurements. The protocol I developed is found in the Appendix.

Parameter Testing

In order to come to the conclusions laid out in the protocol, it was extremely important to first gain familiarity with the system. I began my work by experimenting and learning the different parameters within the TPS software. For our purposes, we were only interested in generating sweep functions and therefore disregarded the bias function. For sweep functions it is necessary to set the voltage sweep, source current range, measure range, number of data points and time per point.

The first parameter I experimented with was the measure range. When experimenting with this parameter I learned that it controlled the range of current measurements that were taken. The smallest measure range available was 1 pA ranging all the way up to 1A in increments of magnitude ten (i.e. 1pA, 10 pA, 100 pA, 1 nA …). The maximum measure range of 1.5A however, does not follow this pattern. Within the software I noticed an auto-ranging feature that I also experimented with. In order to determine which measure range was appropriate for the sample in question, I ran experiments on multiple material samples. One material that I experimented with was indium tin oxide (ITO). For this test I ran a -500mV to

500mV sweep with the source range set to 1.5A, only varying the measure range between each sweep. Fifty points were measured at 10 ms/point. Figure 4 shows the results of the sweeps at each measure range, the conductivity for each measure range is displayed next to the legend. The graph and conductivities show that there is only a small difference in conductivity between each measure range. Due to their similarities, it is reasonable to conclude that the measure range does not alter the data as long as it is greater than the highest current measurement. However, this was not the case when a PANI sample was tested under similar conditions.

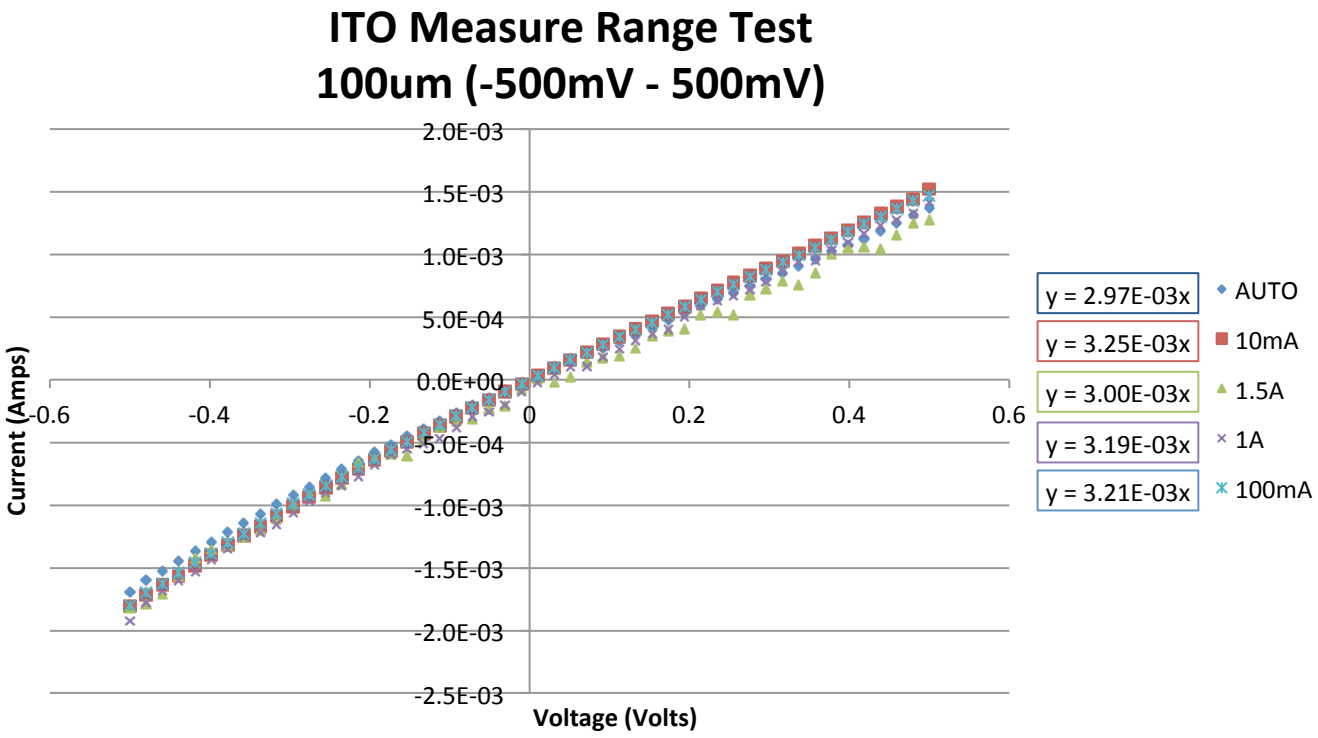

Figure 4. ITO Measure Range Test with conductivity values displayed for each measure range

In order to verify the previous conclusion that the measure range did not have a significant effect on the conductivity measurements, the experiment was performed again on a highly doped PANI sample (JM2.73). This time a -2V to 2V sweep was run (source current range of 1A, 50 points at 10ms/point). The measure range was tested at 10 mA and 1A. Figure 5

shows a comparison of IV curve generated at each measure range, note that the two tests are on separate axes. It is clear that the conductivity measured at 1A measure range is much greater than the conductivity measured at 10mA measure range. Since the measure range was the only parameter changed it is unclear why the higher measure range produces a significantly higher current. This experiment was repeated many times in other locations on the sample and similar results were concluded.

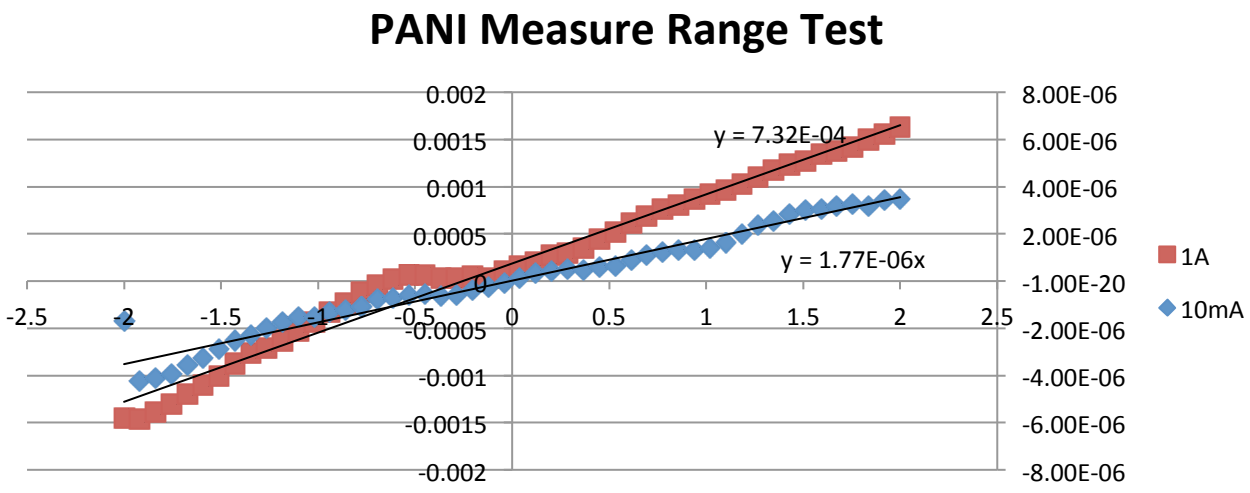

Figure 5. PANI measure range test and corresponding conductivities.The two tests are on separate axis. (JM2.73)

Probe Contact

When conducting electrical measurements it is also important to understand the thickness of the sample you are performing measurements on. Similarly it is important to understand the contact of the probes within the sample. For instance, the probes can either rest on the top layer of the sample, somewhere in the sample, or completely through the sample touching the substrate below. In order to understand the influence of probe depth on the sample's conductivity, probe depth tests were conducted on multiple materials such as copper, silver and ITO. Figure 6 below

shows a probe depth test on ITO for a 500mV sweep at a probe distance of 200um. One test (Top of material) was conducted with the probes barely touching the top of the material. A second test was conducted (Through Material) with the probes protruding through the material and touching the glass slide underneath. The test shows that the sample is more conductive when the probes contact more of the sample. In terms of a protocol, the probes should theoretically protrude through the material so that a consistent measurement can be made each time.

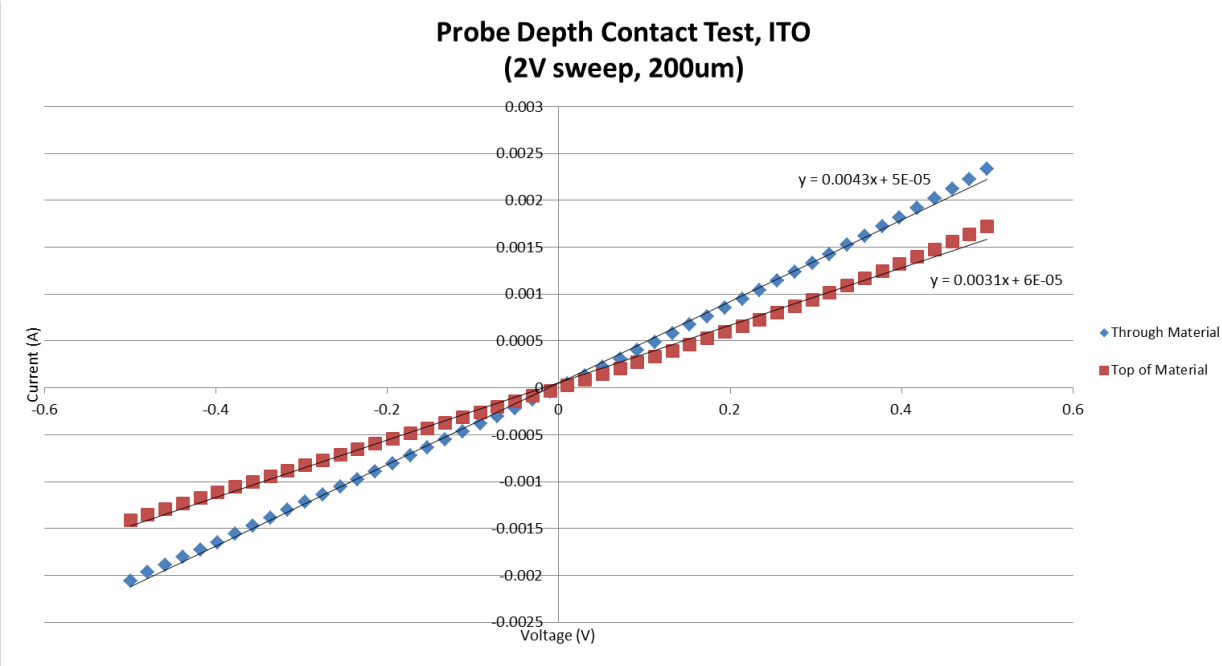

Figure 6. Probe depth contact test shows higher conductivity with more contact area.

Testing Known Resistivities

Before performing conductivity and resistivity measurements on materials with unknown electrical properties it is necessary to verify that the microscope is working properly. To do this, control tests were performed on three materials with known resistivities (copper, silver, ITO). Various voltage sweeps were applied to each material at multiple probe distances and the resulting resistances were compared with researched values.

Copper tape was the first material experimented with. Three voltage sweeps were conducted at a probe distance of 500 µm (1.5A source current range, 50 points, 10ms/point, AUTO measure range). Figure 7 shows consistent conductivities for each voltage sweep, a good indicator for future measurements. With a two probe conductivity test it is difficult to calculate the sample's resistivity since the area and thickness are unknown. However, the conductivity can be compared to that of silver. The conductivities for both metals should be very similar.

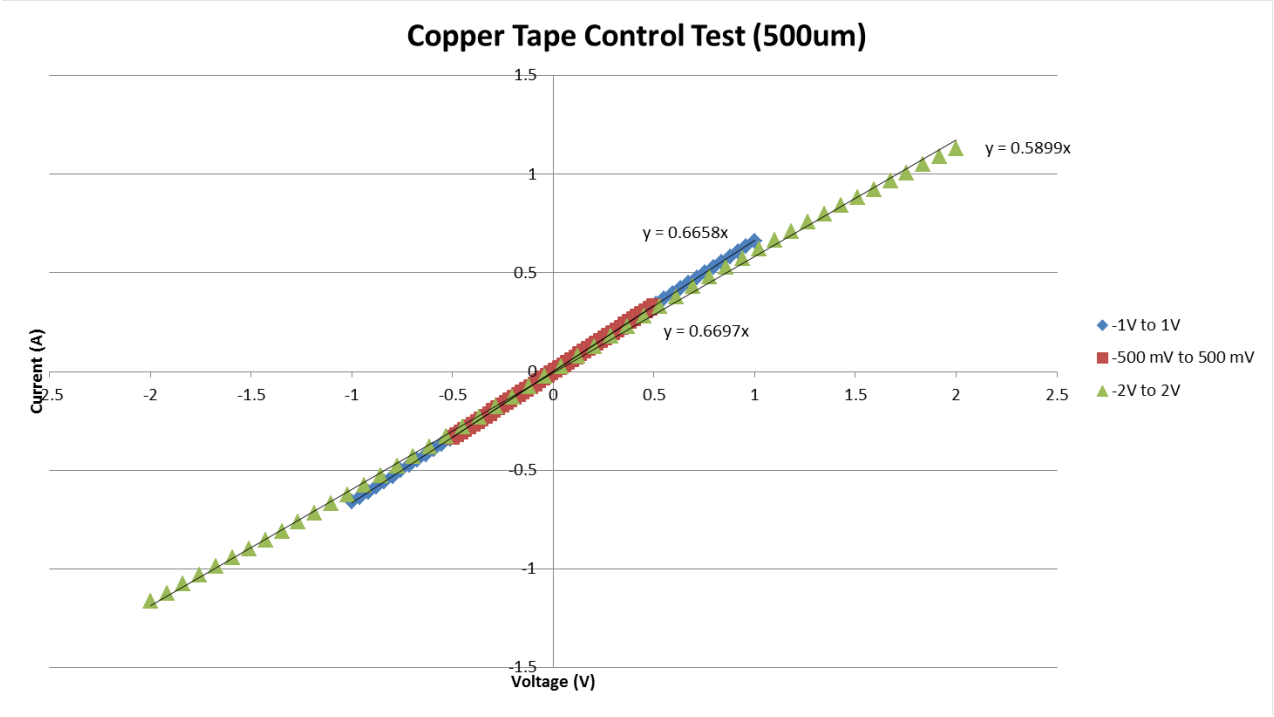

Figure 7. Multiple voltage sweeps show consistent conductivities for copper tape.

A similar experiment was performed on silver paint as was done for copper tape. The same parameters but different sweeps were used on silver. When applying the silver paint to the glass slide, the procedure found in the technical notes was used to ensure full mechanical properties. Figure 8 shows consistent conductivity measurements for both voltage sweeps. The conductivity of the silver paint is very similar to the copper tape measurements with only a 20% difference at the extremes. These results indicate a consistent and accurate conductivity testing.

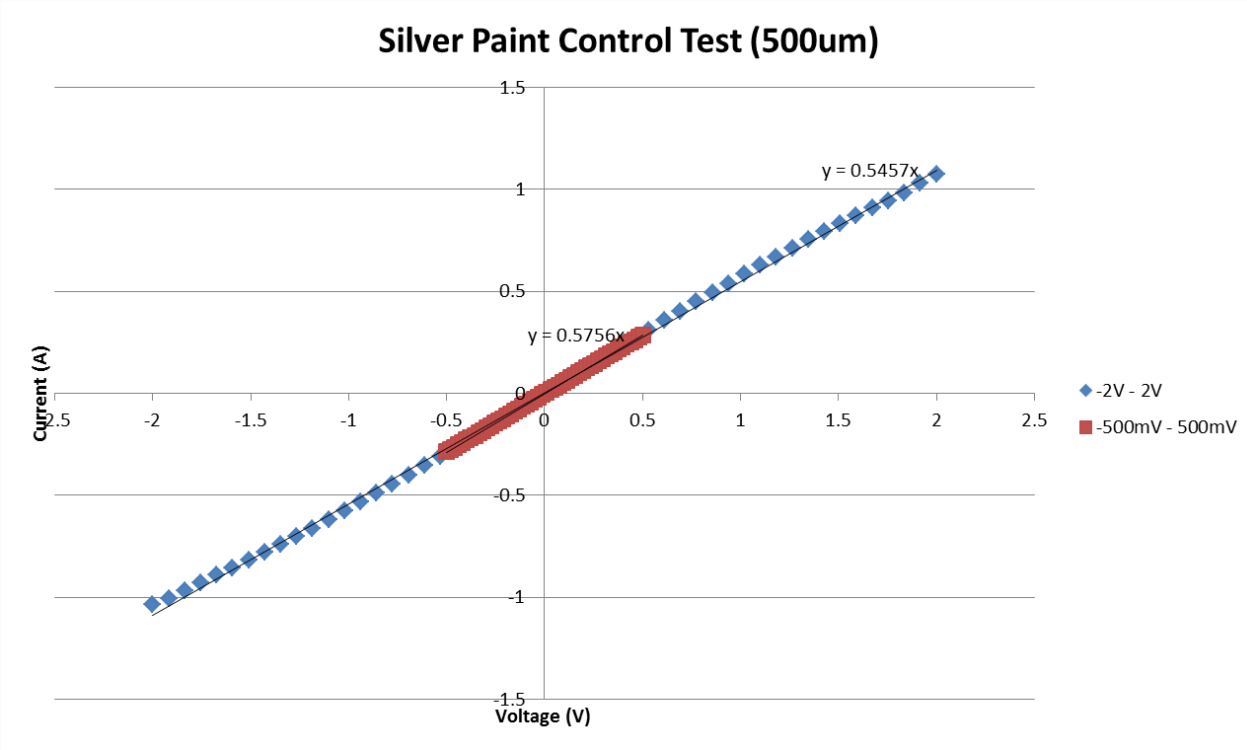

Figure 8. Silver Paint control test shows consistent conductivity measurements.

4. Lessons Learned

Developing the protocol for the Cascade Probe Station involved a multitude of tests that provided good results as well as some not so good results. However, even some of the less significant results provided further understanding of the system and its capabilities. One important lesson learned early on in my work was the condition of the probe tips and their ability to carry material. Especially when performing measurements on polymeric materials the probe tips can pick up clumps of the sample with little effort. For this reason it is important to examine the probe tips to ensure there is no contamination when moving to different locations. Even within the same material, the transporting of material between locations can cause errant measurements that can lead to false data. This is why it is important to use the provided cleaning brush to mitigate the possibility of this happening.

Another important step in the protocol that was discovered early on was the performance of a zero volt sweep before conducting measurements. Some of the material being studied is designed to hold charge at certain voltages and may not release any stored charge between measurements. This stored charge can lead to false data and unreliable conclusions. For this reason it is important, regardless of the material, to perform this zero volt sweep between measurements.

5. Future Work

With the developed protocol and proof of consistent testing, future work on supercapicitive and photovoltaic materials can be accurately and repeatably tested. The implications of this work will aid in the understanding of new materials and publication of scientific papers. Following the protocol will directly help Jared Mondschein, Isaac Ramphal and Suan Quah in the understanding of samples they have developed and are continuing to develop. With continued understanding of conductive atomic force microscopy, it will be possible to compare localized and bulk conductivity measurements. This comparison is especially important for nanomaterials as some properties vary between the macro and nanoscopic levels.

While the developed protocol lays out a solid foundation for future measurements, more tests will be necessary to fully understand this new microscopy technique. As mentioned before, some work has been conducted on understanding the measure range feature of the software however; it is still not fully understood. Therefore, more tests should be done on less conductive materials to ensure full understanding of this parameter. It is also necessary to conduct more tests on the sample's preparation. What is meant by this is the sample's synthesis on the substrate. Some samples are created on top of glass slides while others are built on ITO and other substrates. For this reason it will be necessary to continue learning how the substrate affects the sample's conductivity. More tests should also be done with probe contact on and off the sample. These tests could include placing one probe through the middle of the sample and the other probe contacting a conductive substrate below, such as ITO. Conducting this test and similar ones will help to better understand the materials electrical properties and lead to better results.

6. Resources

This project required use and full access to the Veeco AFM and Cascade Microtech Probe Station located in Butterfield Hall. Within each microscope I needed to replace the tips as they wore. Both labs were equiped with enough tips to handle all of the measurements I made in the winter.

The project also required samples to be examined. Most of the samples that I characterized had already been made. However, some samples needed to be made for testing.

7. References

1. Mondschein, J. (2014). Morphology and Electronic Characterization of Polyaniline: A Synthetic Metal for Photovoltaics. 1-52.
2. Ramphal, I.; Hagerman, M. (2014). Water Processable Laponite/Polyaniline/Graphene Oxide Nanocomposites for Energy Applications. *Lanmuir, 1,* 1-25.

8. Acknowledgments

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Jared Mondschein

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9. Appendix

Probe Station Protocol

*Files in documents/ TSP Express Data

Set-up

1. Remove cover from source meter and probe station.
2. Plug in and turn on source meter. **Do not change settings**.
3. Turn on probe station (2 components).
4. Turn on the laptop, and open TSP Express Link located on the desktop
5. For our purposes, we are using one source meter, so choose single sweep
6. Click the SMU assignments button and assign the channels based on your set up. The default is just channel A on the Sweep Channel
7. You can modify the parameters under the sweep category. Make sure to set your source range (max voltage), current measure range (max current that the system will allow). Also under SMU Assignments tab, all the way to right is an advanced button. There, you can set the current limit (source limit x).

   When testing, only change one parameter at a time. Record all parameters.
8. When you are ready to apply a voltage, click the green arrow button on the top, which means run.
9. On the data tab on the top, select display type to be graph. The x-axis is should be sweep source voltage and y-axis is sweep measured current.
10. To save, export the graph.

Control Test

11. Examine the probe tips under the microscope and assess their condition.

    Moderate – Use the provided cleaning brush (small toolbox) to carefully clean the tips of the probes.

    Poor - Carefully remove each and replace with new tips. The angle of the probes should be very shallow with respect to horizontal.

    Caution: Do not allow the probes to contact the optics as this could cause serious damage. The tips may be bent to avoid contact with the optics.

12. Position the stage to its furthest out and lowest position. Make sure the z-stroke lever is in the down position. Place a copper grid on a glass slide and load the sample on to the stage and turn on the vacuum pump. Position under the optics and carefully raise the stage using the z-stroke lever ensuring the the sample and probe tips do not contact.
13. Position the sample into focus at the lowest magnification. The probes should be roughly 500 μm apart and centered on the grid. Each square of the copper grid is 100 um x 100 um.
14. Switch to the middle magnification and focus the grid again. The probes should be barely visible.
15. Lower the probes one at a time until they are almost in focus. The tips of the probes should be close to the sample without contact. Use the X and Y controls to move the probes to their desired distance. Carefully lower each probe slowly until it comes in contact with the copper sample. The grid will come out of focus and slightly move when contact is made.

16. Set the probe distance to 100 μm and run a 0-500 mV sweep on the grid and ensure that a current of 370 mA is measured at 500 mV.
17. Once verified, lift probes in z-direction only. Do not move X and Y, they should already be at the desired distance apart. Use the z-stroke lever to move the sample away from the tips and pull out the stage tray to remove sample.

    NOTE: The vacuum pump needs to be turned off to remove the sample. However, this will also cause the probe tip holders to become loose. Use caution so that you do not move the probe tips from their desired position.

Testing

18. Load sample onto the stage, turn on the vacuum and examine the probes for cleanliness again.
19. Slide the sample back into place and lift using z-stroke lever.
20. Bring the probes near the surface but do not contact. Carefully, contact the probe tips to the sample. Ideally the probes should be midway into the thickness of the sample. Do not let the tips touch the slide as this can cause errant measurements.
21. Once good contact is established, begin making measurements.
22. Run three sweeps at a single location (i.e. -500mV – 500mV, -1V – 1V, -2V – 2V). Record and export all data to the appropriate location. Do not move the probes during the three tests. Conduct the tests according to voltage, smallest to largest

    Run a 0-0 V sweep before each measurement to mitigate any leftover voltage the sample may have.

23. Five locations should be tested on each sample. Measurements should be made in each corner and somewhere in the middle of each sample. Clean the probe tips before moving to each location.
24. Once all five locations are completed, start again with step 15 but set the probe distance to 300 μm. Verify that a current of 140 mA is measured across the copper grid when 500 mV is applied.
25. Repeat steps 16-22.
26. Document all parameters and tests.