

Characterization of the Magnetoresistance of Polypyrrole

by

Nathaniel Stein Sharpe

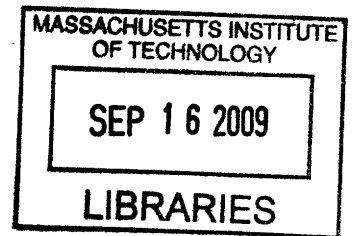
SUBMITTED TO THE DEPARTMENT OF MECHANICAL ENGINEERING IN  
PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

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MASSACHUSETTS INSTITUTE OF TECHNOLOGY


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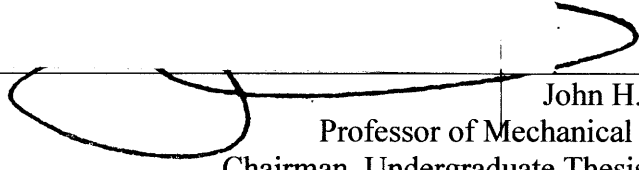
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# **Characterization of the Magnetoresistance of Polypyrrole**

by

Nathaniel Stein Sharpe

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requirements for the Degree of Bachelor of Science in  
Mechanical Engineering

## **ABSTRACT**

Conducting polymers such as polypyrrole have been the subject of intensive study due to their light weight and useful electrical properties. Many applications of such polymers, such as for use as motor windings or as magnetic field sensors, require a precise knowledge of the electrical properties of the polymers being used. This thesis presents a study of the magnetoresistance of the conducting polymer polypyrrole. It was found that the electrical resistance of polypyrrole wires is not correlated to the strength of a perpendicular magnetic field, but exhibits a large dependence on the operating temperature of the wire.

Thesis Supervisor: Ian W. Hunter

Title: Hatsopoulos Professor of Mechanical Engineering



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## 1. Introduction

In the year 2000, Alan J. Heeger, Alan MacDiarmid and Hideki Shirakawa were awarded the Nobel Prize in chemistry for their work on conducting polymers [1], which were first discovered in 1963 by a group of Australian scientists [2]. Interest has grown rapidly since then as the possible applications of such lightweight, high conductivity materials have become clear. Their light weight has become very important in today's increasingly energy conscious society. As the price of fuel and the distance that people travel increase, it has become more and more crucial to reduce the amount of fuel consumed by transportation vehicles. One option is to reduce the weight of the motor used to power the vehicle. Of all the components that make up a motor, the only ones that have not been manufactured out of lightweight plastics are the motor windings and the magnetic core. Research at Brigham Young University has shown that replacing these elements with polymers could reduce the weight of such components by as much as 1/6 [3]. Polymers in such an application would undergo changing magnetic fields of significant strength, yet no data exists concerning the magnetoresistive properties of such conducting polymers.

Three main types of magnetoresistance are known to exist: Normal Magnetoresistance, Giant Magnetoresistance, and Colossal Magnetoresistance. The latter two are exclusively found in superconducting materials and materials specifically engineered to exploit the effects of large magnetoresistance. Such materials are used to increase hard disk memory storage and as highly sensitive magnetic field sensors. For materials being used in environments like the inside

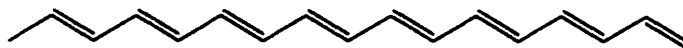
of an electric motor, it is important to understand how the resistive properties will change during the use of the motor. The aim of this research is to determine the level of magnetoresistance exhibited by the conducting polymer polypyrrole.

## 2. Background

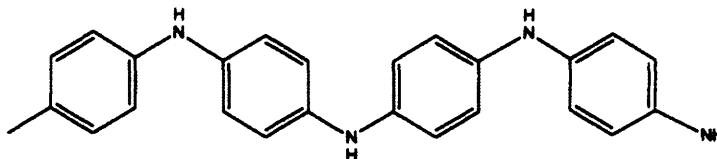
### 2.1 Conducting Polymers

All conducting polymers have a few common characteristics, the most prominent being the means of electron transport resulting in conductivity. Some of the more commonly used conducting polymers are shown in Figure 1.

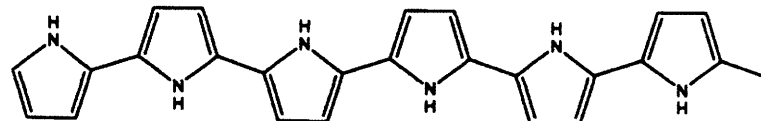
**Polyacetylene**



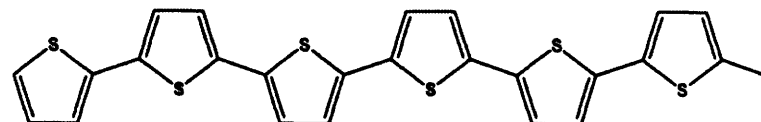
**Polyaniline**



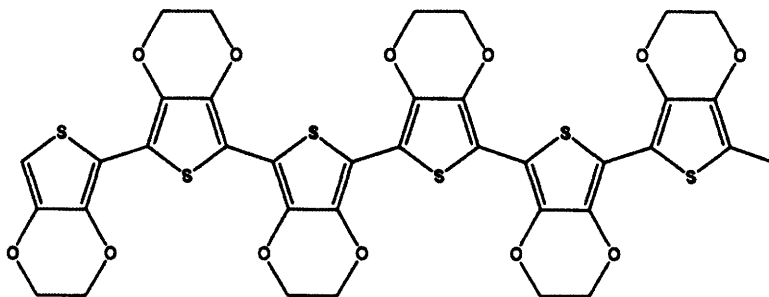
**Polypyrrole**



**Polythiophene**



**PolyEDOT**  
(Polyethylene dioxythiophene)



**Figure 1** Common conducting polymers, including polypyrrole, the subject of this research. Taken from [4].

It is important to note the alternating single and double bonds along the polymer backbone that is common to all of the above conducting polymers. Such polymers are not intrinsically conductive, however, and a dopant must be added in order to alter the band structure of the polymer backbone. The addition of the dopant allows the displacement of the weakly bonded electrons in between the stronger double bonds as shown in Figure 2, resulting in the conductive properties exhibited by these materials.



**Figure 2** Polyacetylene during the charge transport process. Taken from [5].

## **2.2 Polypyrrole**

The polymer under consideration in this research is polypyrrole, which has been chosen for its ease of manufacture and high environmental stability. While some other conducting polymers, such as polyacetylene, have higher conductivities, they are frequently unstable in open environments and thus are unsuited for the applications being studied. This instability has led to the development of more mechanically stable polymers based on five and six-member conjugated heterocycles [5]. Polypyrrole is one such polymer; it exhibits quite stable electrical properties over long exposures to air, and has been shown to be a promising electromechanical actuator [5] and sensor [6].

## **2.3 Magnetoresistance**

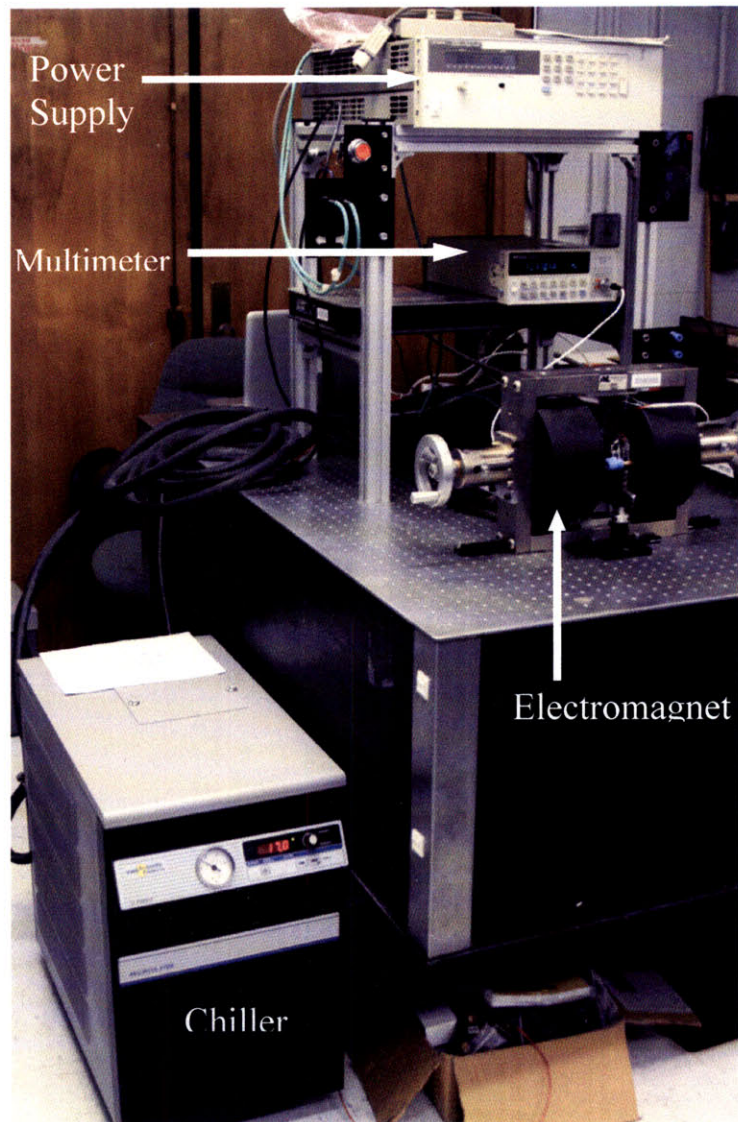
Magnetoresistance was first discovered in 1856 by William Thomson (Lord Kelvin), who observed that the conductivity of iron decreased by roughly 5% when subjected to a magnetic field perpendicular to the direction of current flow [7]. This effect, known as anisotropic magnetoresistance (AMR), has since been used in a wide array of applications such as measuring the earth's magnetic field and traffic detection [8].

Recently, new types of magnetoresistance known as giant magnetoresistance (GMR) and colossal magnetoresistance (CMR) have been discovered. GMR arises in engineered magnetic multilayers and granular alloys and is attributed to the modulation of electron transport due to the magnetic field response of interfacial spins. GMR is used extensively in the read heads of hard drives as well as a means of memory storage [9]. Von Helmholt et al. first discovered CMR in 1993 and the physical mechanism behind it is still not fully understood. Where GMR causes changes in resistance of as much as 40%, materials exhibiting CMR (mostly manganese-based perovskite oxides [9]) can experience changes of up to 100%. The magnetoresistance expected for polypyrrole would be very small, since it falls into none of the above categories of materials exhibiting large magnetoresistance. Small variations over each cycle in the rotation of a motor can have serious long-term effects, however, necessitating a detailed study of the effect of magnetic field strength on the electrical resistance of polypyrrole wires.

### 3. Experimental Methods

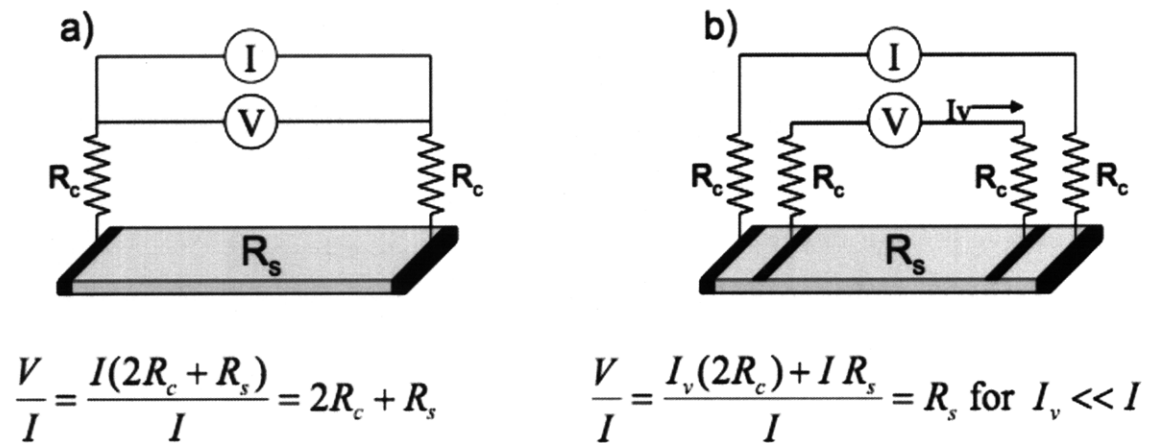
#### 3.1 Experimental Setup

The experimental setup used to measure the resistance of samples of polypyrrole wire in variable magnetic fields is shown in Figure 3.



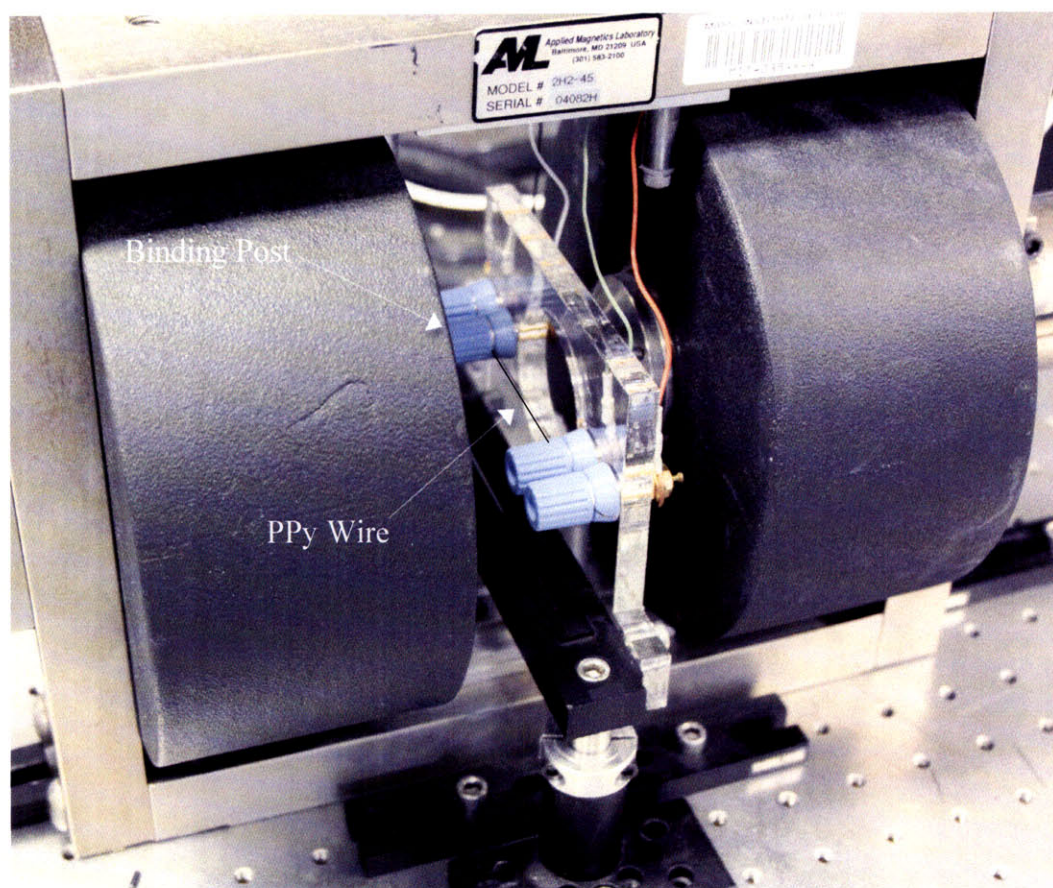
**Figure 3** The experimental setup used for this research.

An Applied Magnetics Laboratory 2H2-45 electromagnet [10] used was water-cooled using a VWR International 1171P recirculating chiller [11]. The magnet was powered using an Agilent E4356A 80V/30A power supply [12] and resistance measurements were taken using an Agilent 34420A nanoVolt/micro-Ohm meter [13] in four-wire resistance mode. Due to the small resistance changes expected, the error induced by a two-wire resistance measurement was removed by using the four-wire measurement scheme shown in **Figure 4**.



**Figure 4** The measured resistance using the two-wire method (a) includes the contact resistance between the probes and the sample. By using the four-wire method (b) this error is removed since the current in the voltage channel is so low. Taken from [5].

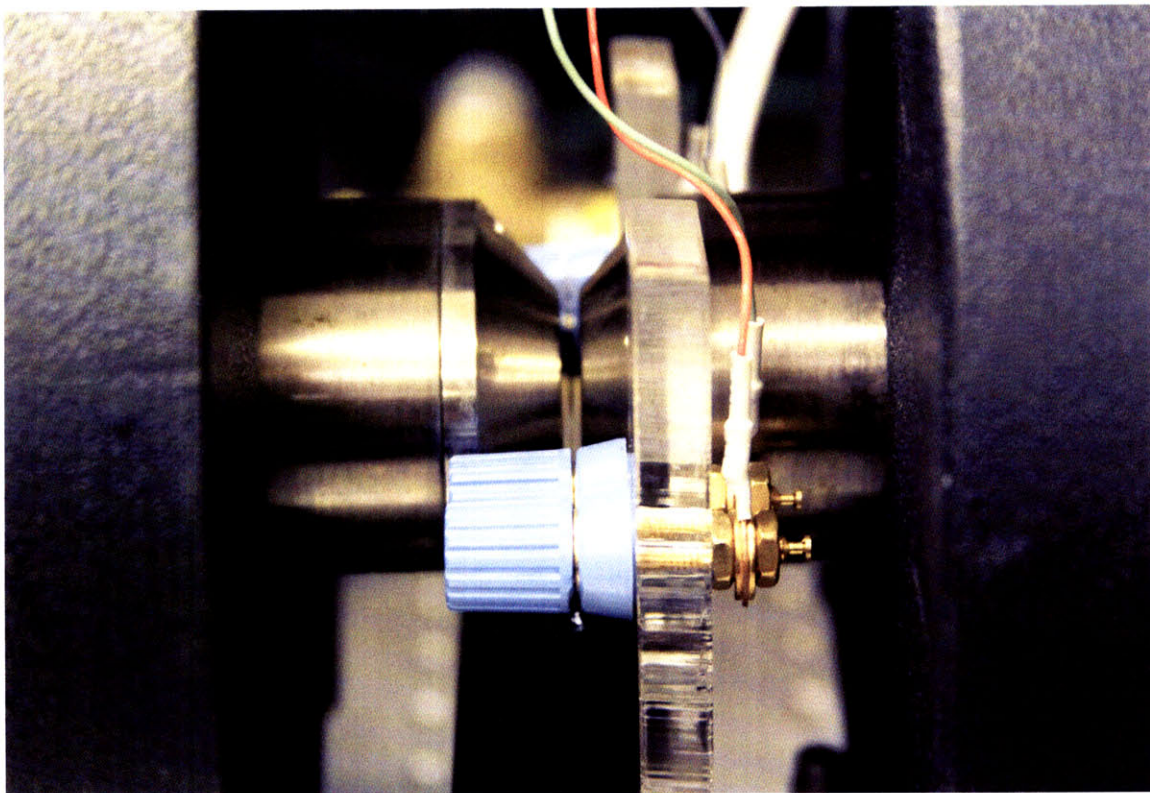
In order to hold the polypyrrole wires perpendicular to the magnetic field produced by the electromagnets, the clamp shown in Figure 5 was used to constrain the wire relative to the magnets as well as to provide the electrical contacts for the four-wire resistance measurements.



**Figure 5** The wire clamp used to constrain the polypyrrole wires used in this experiment. The voltage measurement wires can be seen in green and white, with the current measurement wires in red and black.

The polypyrrole wires were fed through the holes drilled through the binding posts, which were then screwed down to provide the contact force with

the wire. The spade lug connectors on the end of the voltage and current wires were clamped down between two washers using the nuts on the back of the binding posts as shown in Figure 6. All electrical contacts were gold plated to ensure good connectivity.



**Figure 6** The attachment mechanism for the measurement wires and polypyrrole samples.

The magnet poles were adjustable in order to change the maximum field strength generated by the magnets. Tests were conducted with the poles 50 mm apart (Figure 5) and with the poles 1.5 mm apart (Figure 6) in order to achieve maximum field strengths of 0.4 T and 2.8 T respectively.

### **3.2 Data Collection Program**

In order to semi-automate the data collection process, a series of virtual instruments were created using National Instrument's LabView program [14] (see Appendix A). The virtual instruments allow the experimenter to choose the maximum current with which to drive the magnets, how much to increment the current between measurements, and how many times to cycle the current up to the maximum value and back down to zero. After the data was collected it was written to a spreadsheet file for ease of analysis.

### **3.3 Procedure**

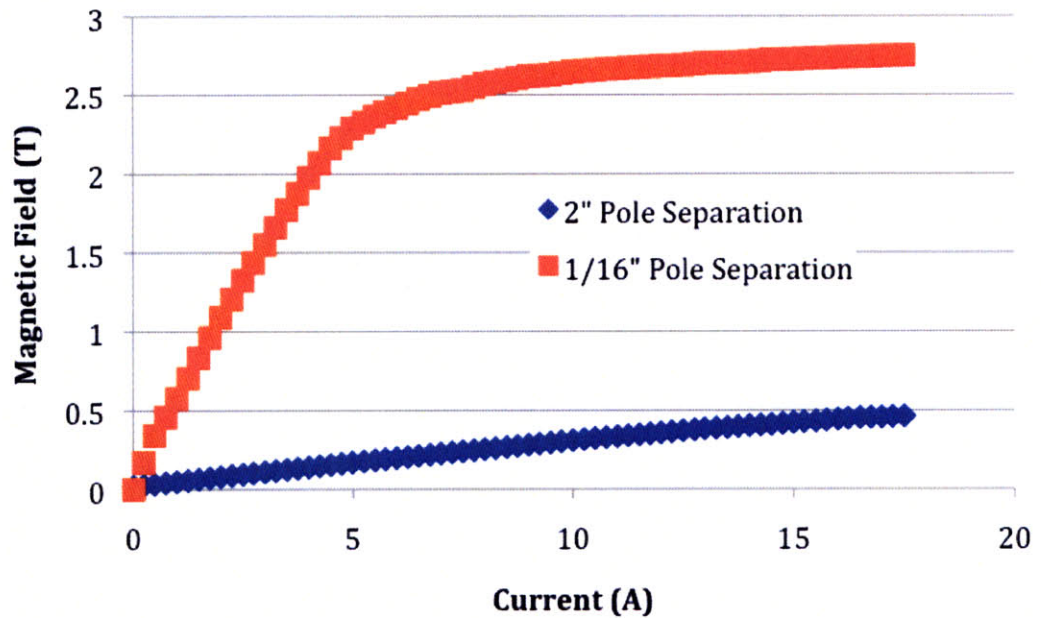
Data was taken on 3 different types of wires: 0.381 mm (0.015") diameter Flexinol wire, 1 mm wide gold backed polypyrrole wire, and 1 mm wide polypyrrole wire. The polypyrrole wire was prepared using a 10 hour long deposition at -40 °C propylene carbonate and 0.05M tetraethylammonium hexafluorophosphate (TEAP) solution plus 1mL of pyrrole. Before the deposition for the gold backed wire, the crucible was electroplated with gold using a neutral non-cyanide gold plating solution called Techni Gold 25 ES RTU [15]. The deposition was run at a constant current density of 10.75 A/m<sup>2</sup> for 5 minutes and yielded a thin layer of gold approximately 100 nm.

For each test, the chiller was set to 17 °C in order to properly cool the magnets, the multimeter was set to four-wire resistance mode, and the power supply was set to 0V/0A. The maximum current and value by which to increment the current between measurements were then chosen. Finally, the number of cycles from 0 A to the max current and back down was chosen in order to assess

the repeatability of the experiment. The current was cycled up and down in order to detect any hysteresis present in the measurements.

#### 4. Results

The direct output of the programs shown in Appendix A was the four wire resistance of the wire sample and the current used to drive the electromagnet. Since the values of interest were the resistance and the magnetic field strength, the electromagnet was calibrated to determine the relationship between driving current and output magnetic field shown in Figure 7. All magnetic field data presented below are derived from the original current data using the curves below.



**Figure 7** The calibration curves for the electromagnet.

The four-wire resistance measurements for the sample of flexinol wire (known to exhibit a small amount of magnetoresistance) are shown in

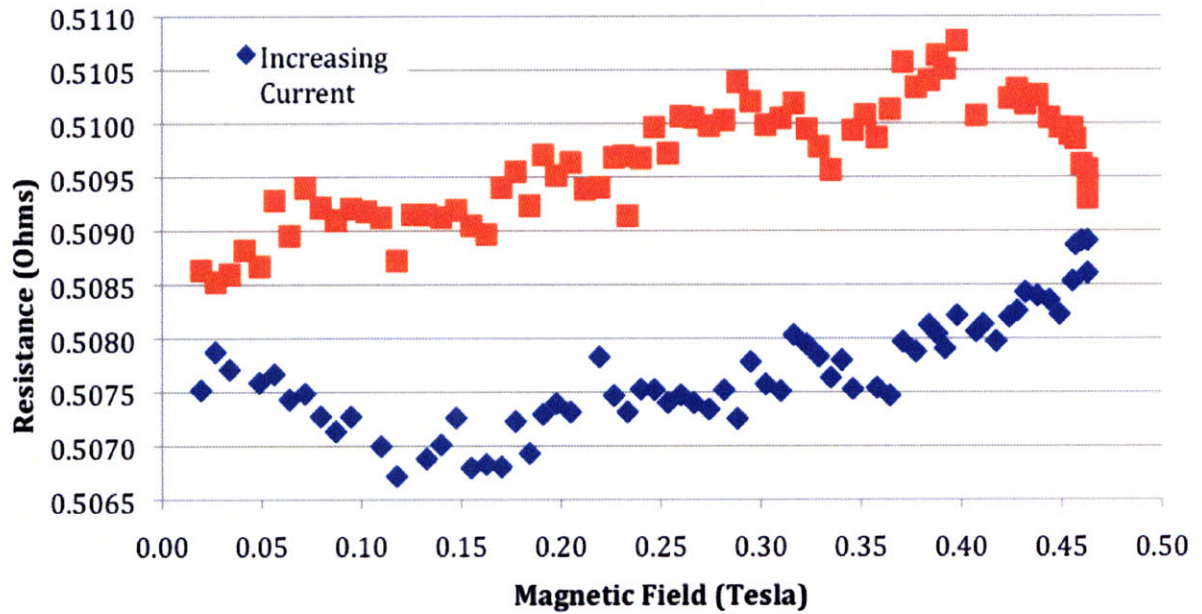
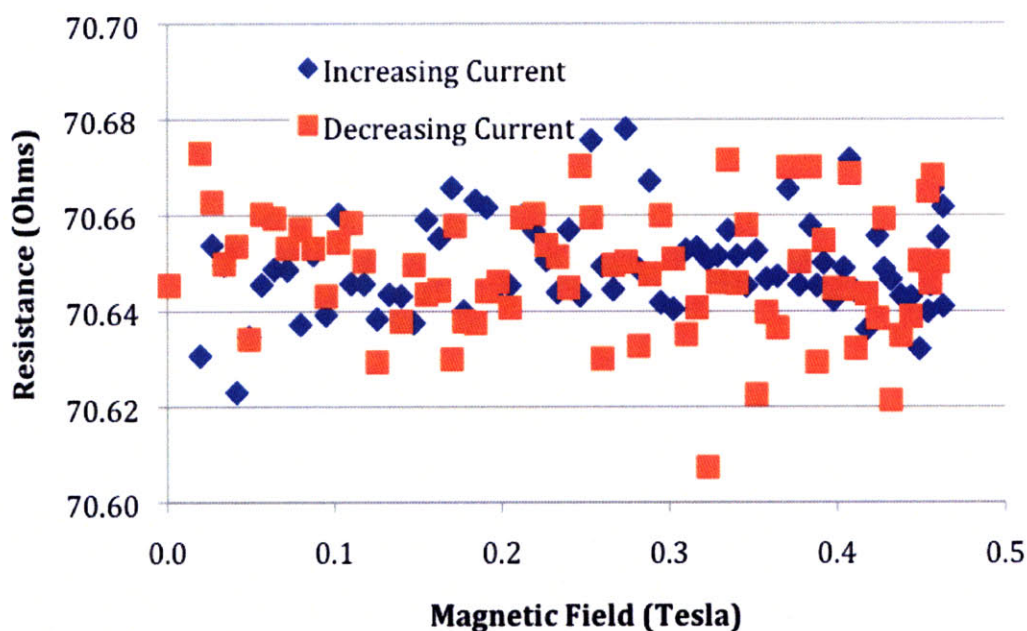


Figure 8.

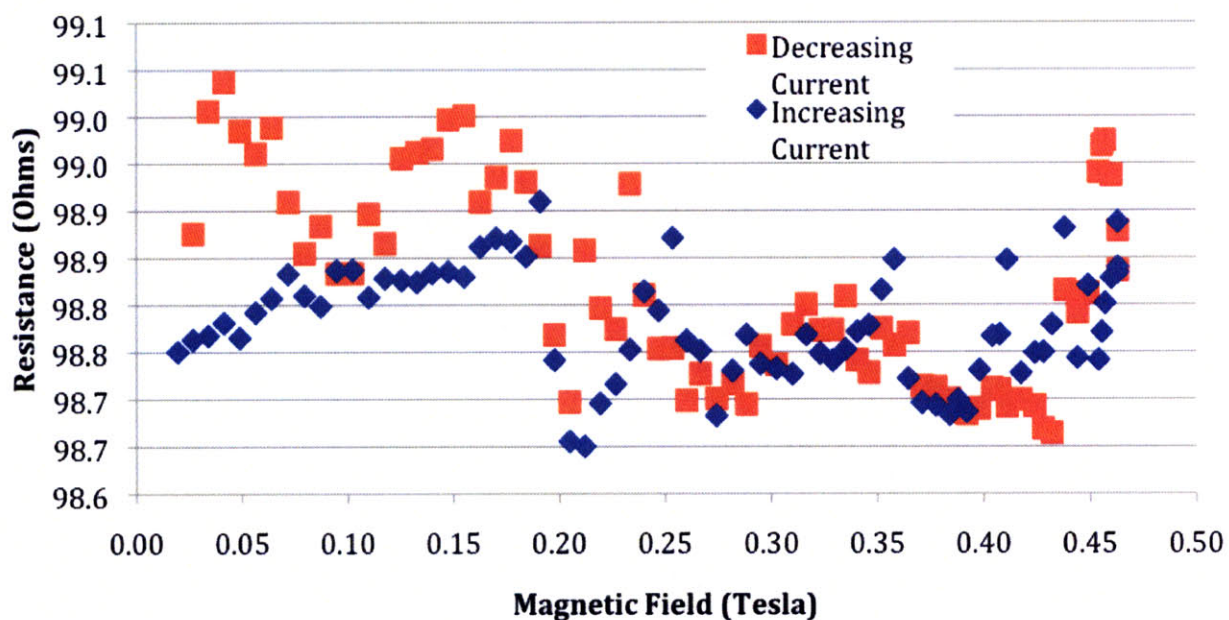
**Figure 8** Resistance of a 0.381 mm (0.015") thick flexinol wire between 0 and 0.463 T.

A clear magnetoresistance can be seen, as expected, with a magnetoresistance of 0.22% at the maximum current of 15 A, corresponding to a magnetic field of 0.463 T. The flexinol resistance also exhibits a clear hysteresis as the current and magnetic field decrease back to 0. The same data was taken for a sample of gold backed polypyrrole wire (Figure 9).

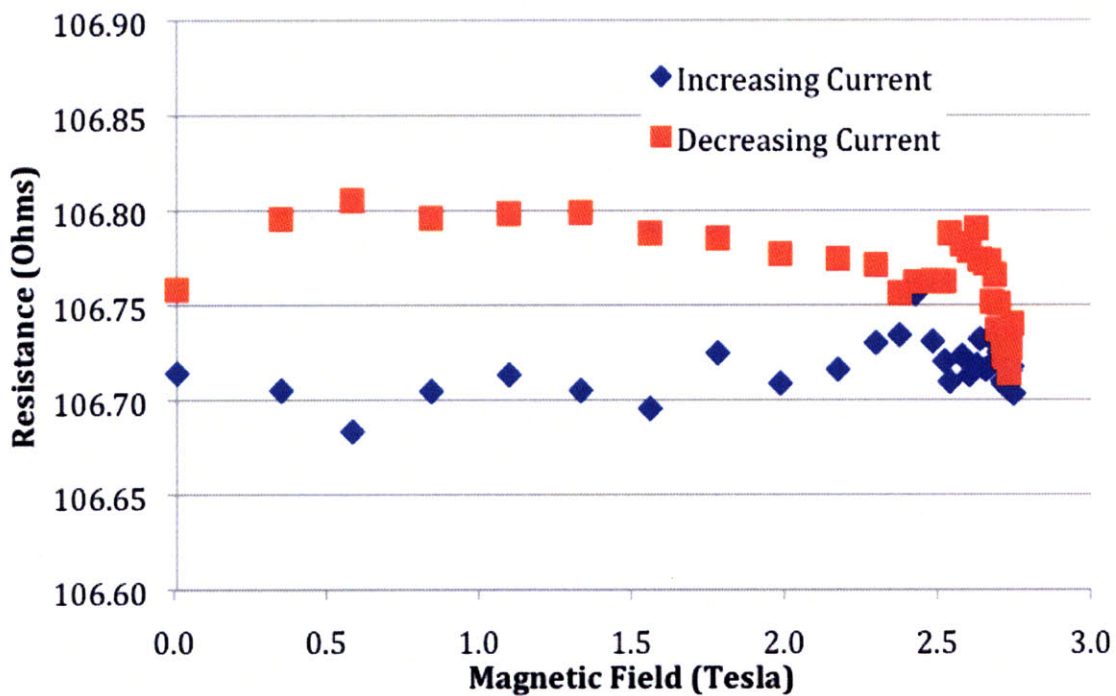


**Figure 9** Resistance of a 1 mm wide gold-backed polypyrrole wire up to 0.463 T.

No significant change in resistance is observed for the gold-backed polypyrrole, nor is there any hysteresis in the resistance data. Similar results were obtained for a 1mm wide polypyrrole wire for maximum magnetic fields of 0.4 T (Figure 10) of 2.875 T (Figure 11).

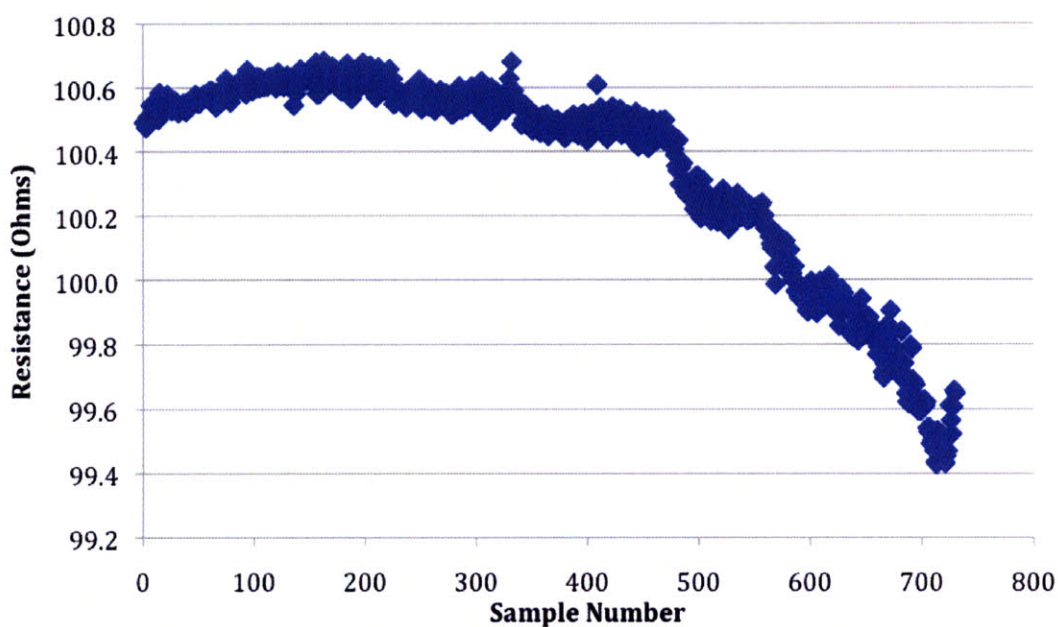


**Figure 10** Resistance measurements for a 1 mm wide polypyrrole wire up to a maximum magnetic field of 0.4 T.



**Figure 11** Resistance measurements for a 1 mm wide polypyrrole wire up to a maximum magnetic field strength of 2.875 T.

It is interesting to note that some hysteresis is observed when the polypyrrole wire is subjected to very high magnetic fields. It is possible that this hysteresis is in fact simply a shift in the resistance caused by the changing temperature of the test environment. If data were taken over a long enough time period, a significant shift in the resistance was observed, as shown in Figure 12.



**Figure 12** The resistance of a 1 mm wide polypyrrole wire over 3 hours.

The wire was cycled 10 times from 0 T to 2.85 T and back to 0 T over the period shown above. It is clear that the dominant change in resistance is a shift, most likely due to daily temperature fluctuations in the laboratory.

## 5. Conclusions and Future Work

It has been shown that the conducting polymer polypyrrole exhibits no appreciable magnetoresistance. Given the possible applications of this conducting polymer for power transmission and actuation, this is actually an advantageous property. An apparatus was manufactured to constrain a sample of wire between two poles of an electromagnet. Four-wire resistance measurements were taken on a number of different wire samples across a large range of magnetic field strengths. The resistance characteristics of polypyrrole were compared to the characteristics of flexinol, a material known to exhibit magnetoresistance. It was found that the resistance of the polypyrrole wires does not depend on the strength of the magnetic field acting on the wire, thus polypyrrole exhibits no magnetoresistance. It was also found that presence of a gold backing on the polypyrrole wire did not change its magnetoresistance. The 1 mm wide polypyrrole wires exhibited a small amount of hysteresis at large magnetic fields, and more data would have to be taken in order to fully quantify this phenomenon. Finally, it was found that the resistance of the polypyrrole wires has a strong dependence on the temperature of the film, as seen in Figure 12. While the lack of magnetoresistance is promising for the potential use of polypyrrole wires as the windings in a motor, the large temperature dependence could prohibit this specific application.

Given that the resistance of the polypyrrole wires is strongly correlated to the temperature of the environment, more study needs to be done in

order to quantify this relationship. A temperature controlled experimental environment would be useful for isolating the effects of magnetoresistance from changes in the ambient temperature. It may also be beneficial to determine whether the orientation of the magnetic field with respect to current flow affects the magnetoresistance of polypyrrole wires. The experimental setup used for this research did not allow for the testing of such a relationship, but a new setup could be constructed that would allow the angle of the wire with respect to the magnetic field to be varied.

## References

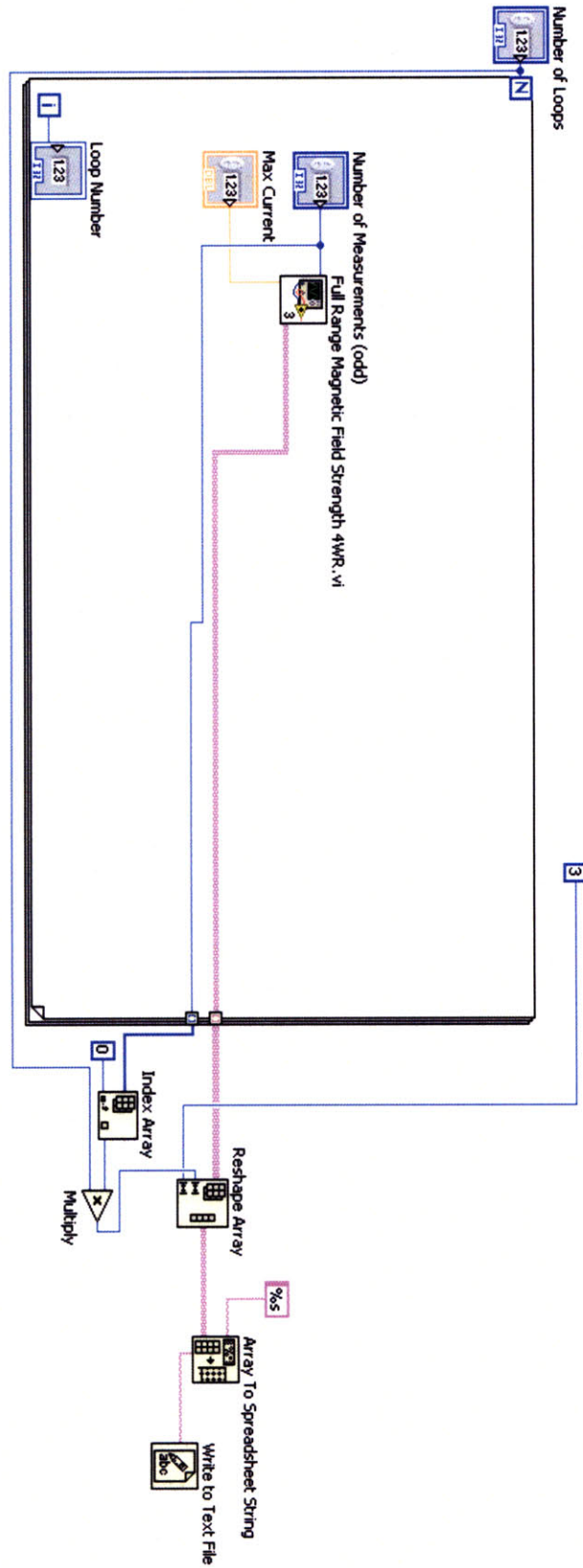
- [1] [http://nobelprize.org/nobel\\_prizes/chemistry/laureates/2000/press.html](http://nobelprize.org/nobel_prizes/chemistry/laureates/2000/press.html)
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- [12] <http://www.home.agilent.com/agilent/product.jsp?pn=E4356A&NEWCCLC=USeng>
- [13] <http://www.home.agilent.com/agilent/product.jsp?cc=US&lc=eng&ckey=1000001296:epsg:pro&nid=-536902435.536880934.00&id=1000001296:epsg:pro>
- [14] <http://www.ni.com/labview/>
- [15] [www.first.ethz.ch/infrastructure/Chemicals/Other\\_liquids/MSDS\\_TG25ES\\_RTU.pdf](http://www.first.ethz.ch/infrastructure/Chemicals/Other_liquids/MSDS_TG25ES_RTU.pdf)

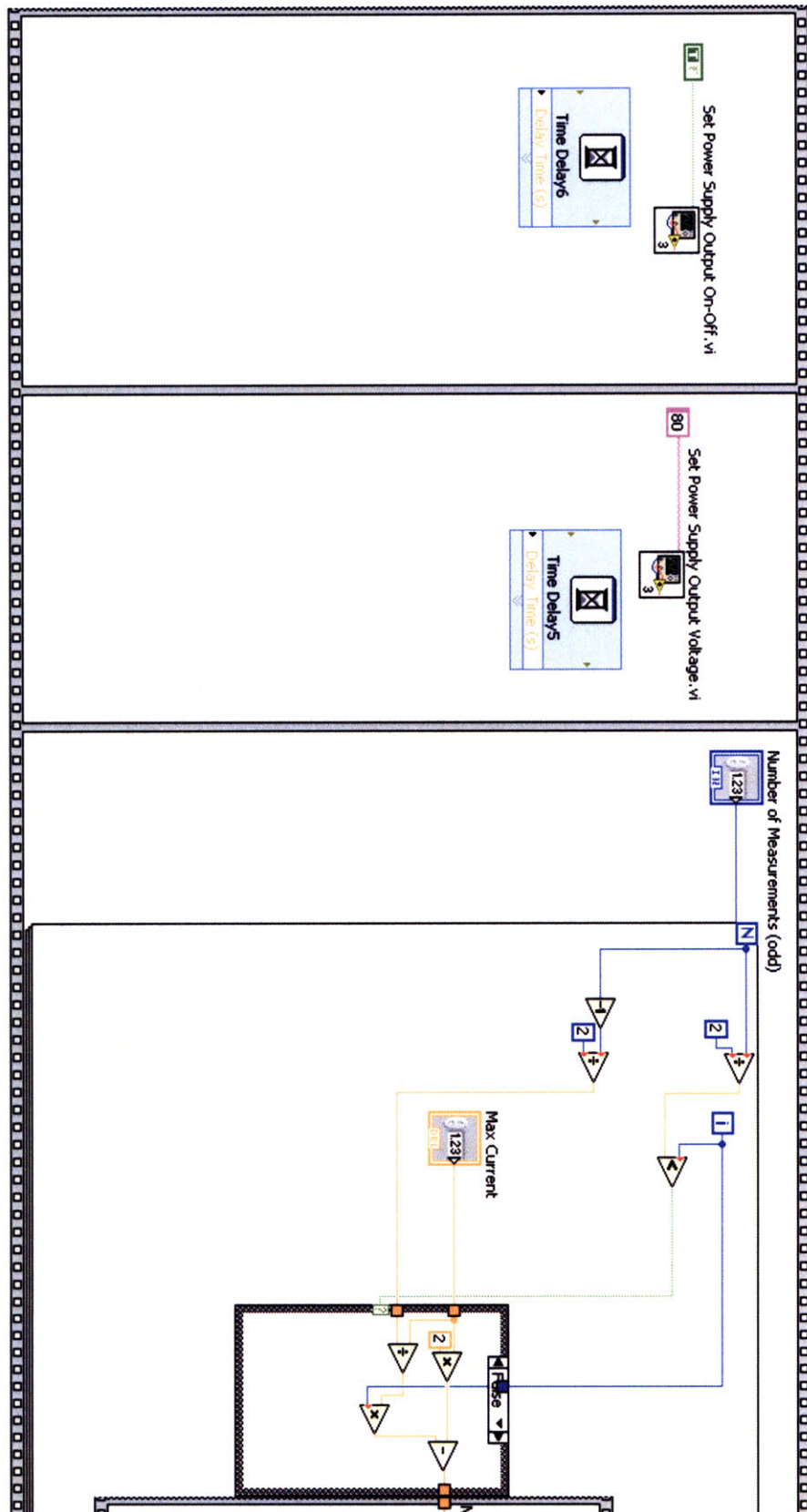
# Appendixes

## A. LabView VIs for MagnetoResistance Measurements

Full Range Magnetic Field Strength, Multiple Iterations

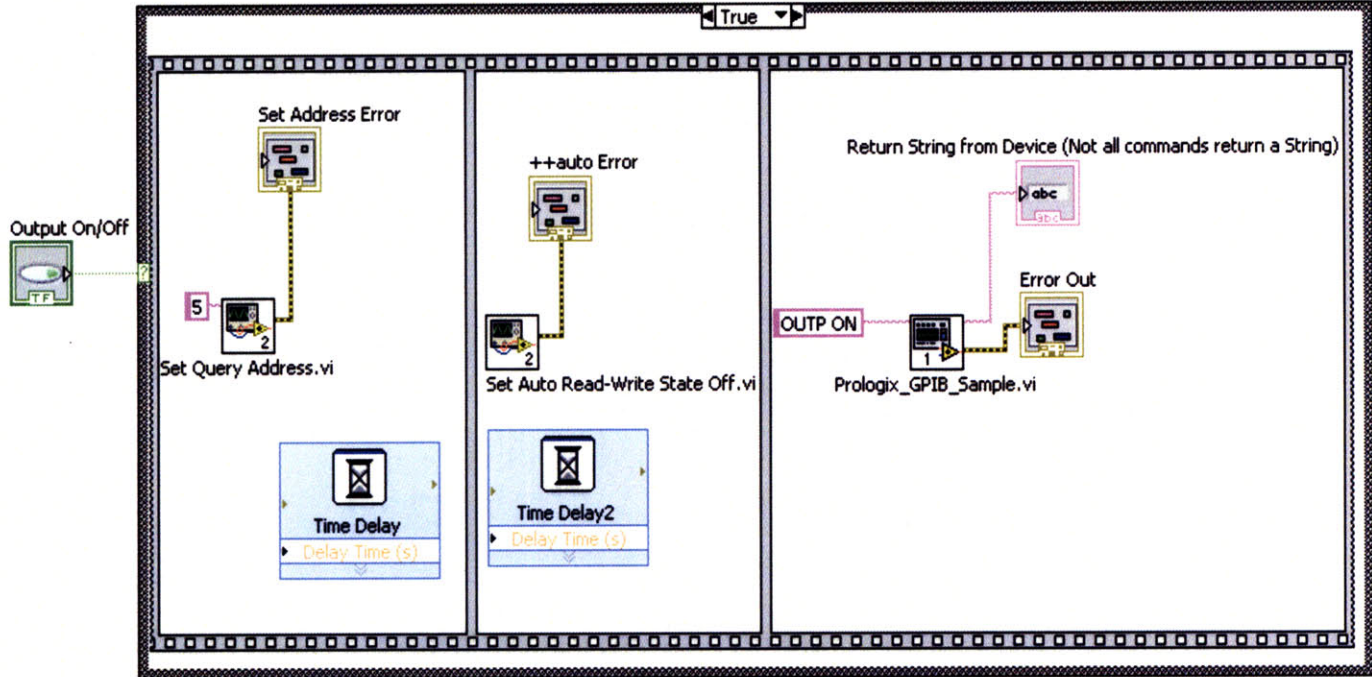


Full Range Magnetic Field Strength Four-Wire Resistance (continued on next page)

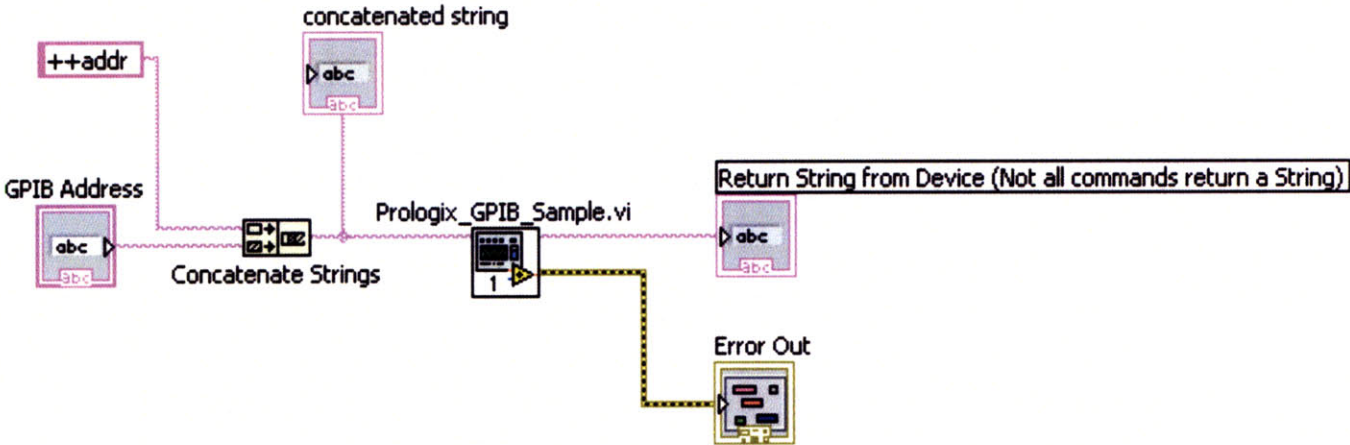




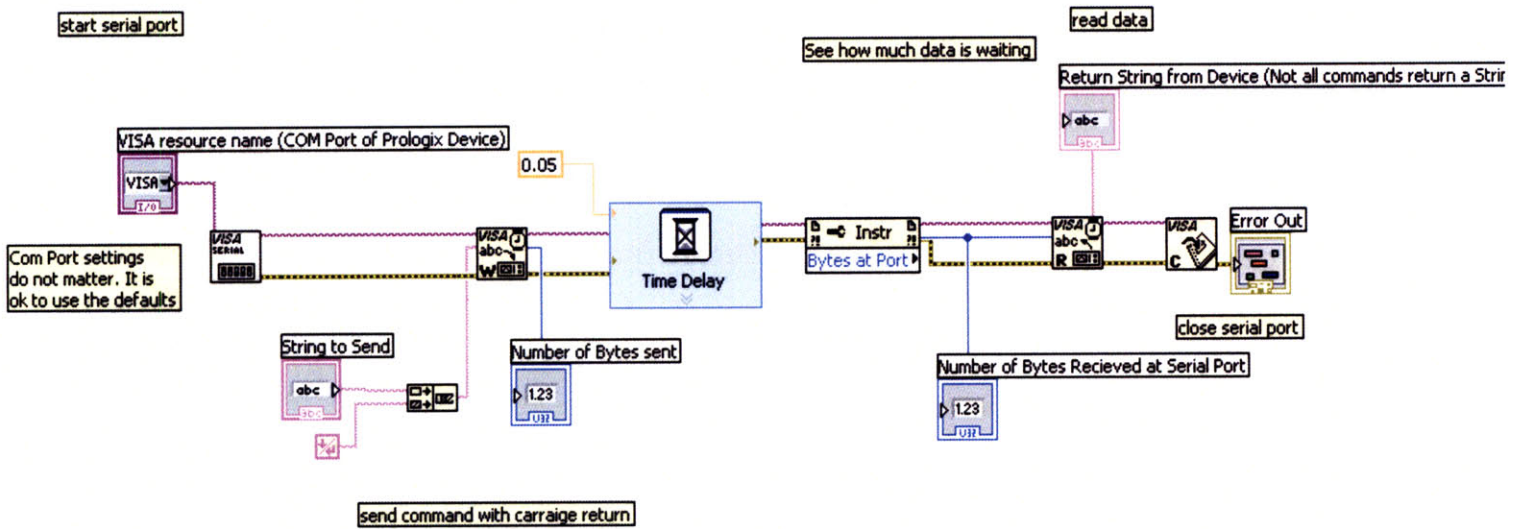
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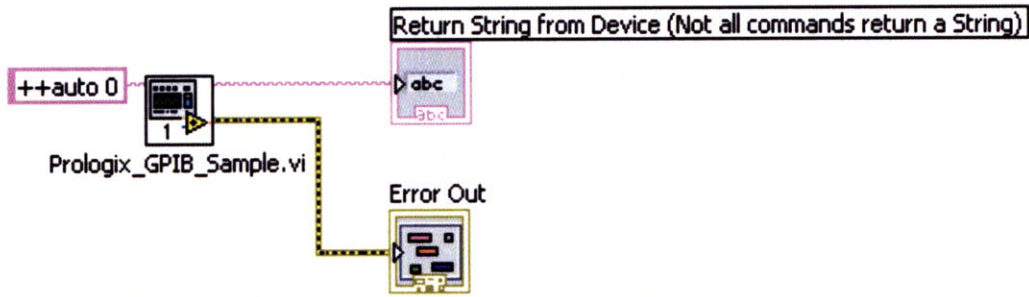
### Set Query Address



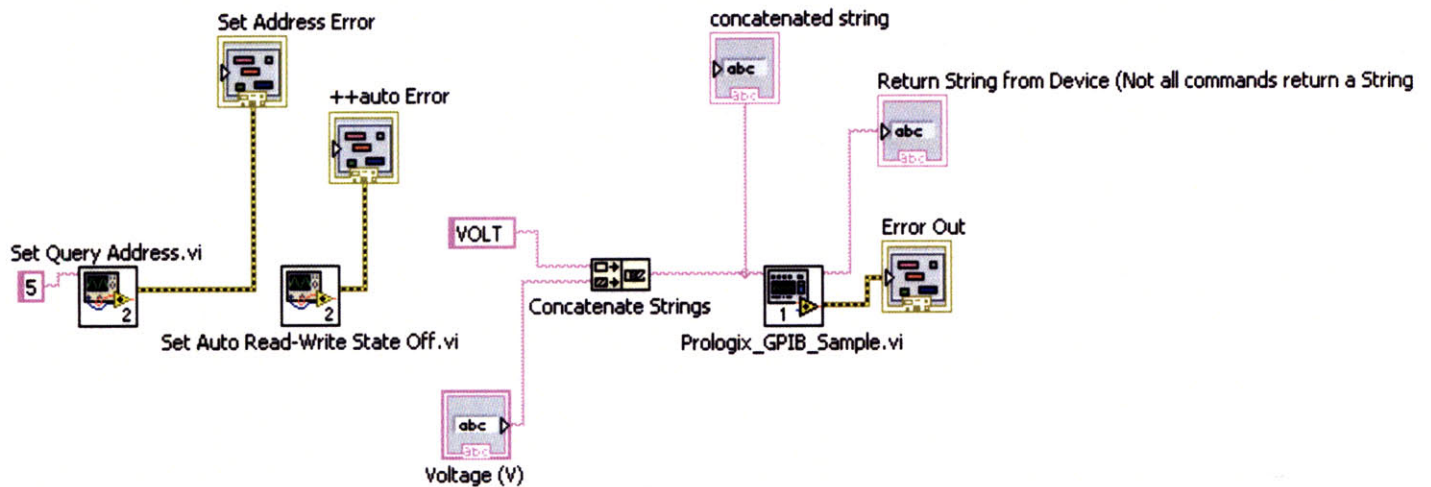
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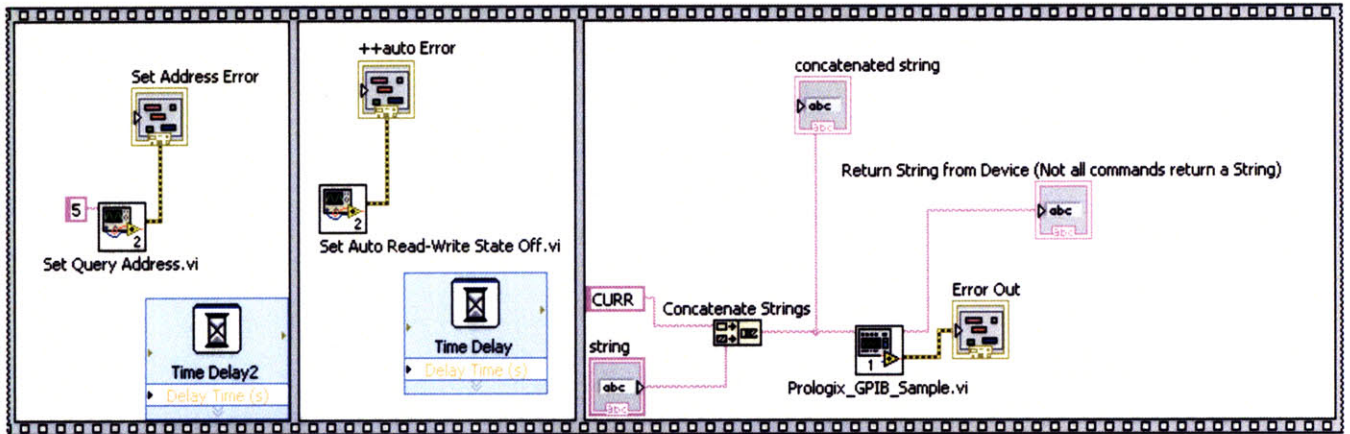
## Set Auto Read-Write State Off



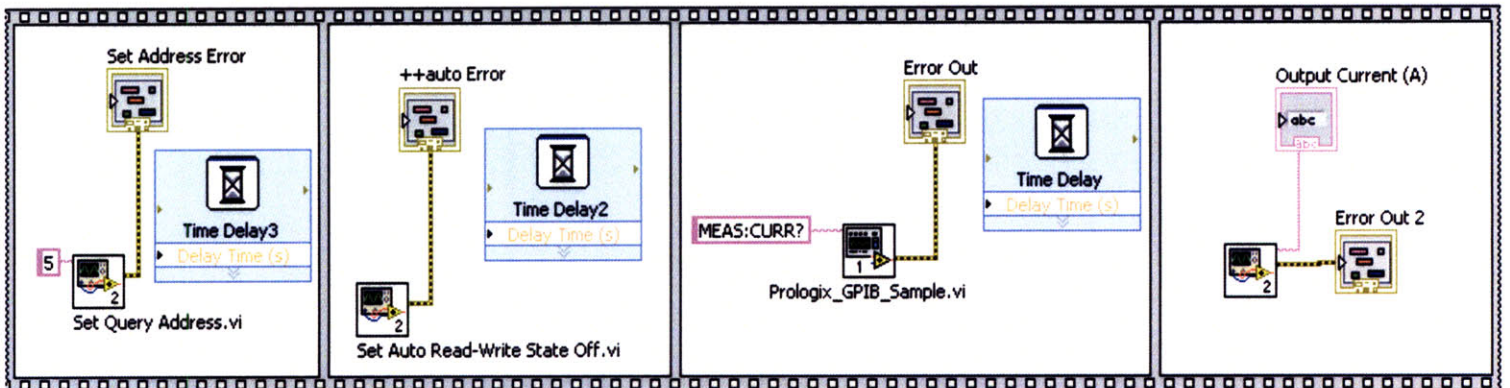
## Set Power Supply Output Voltage



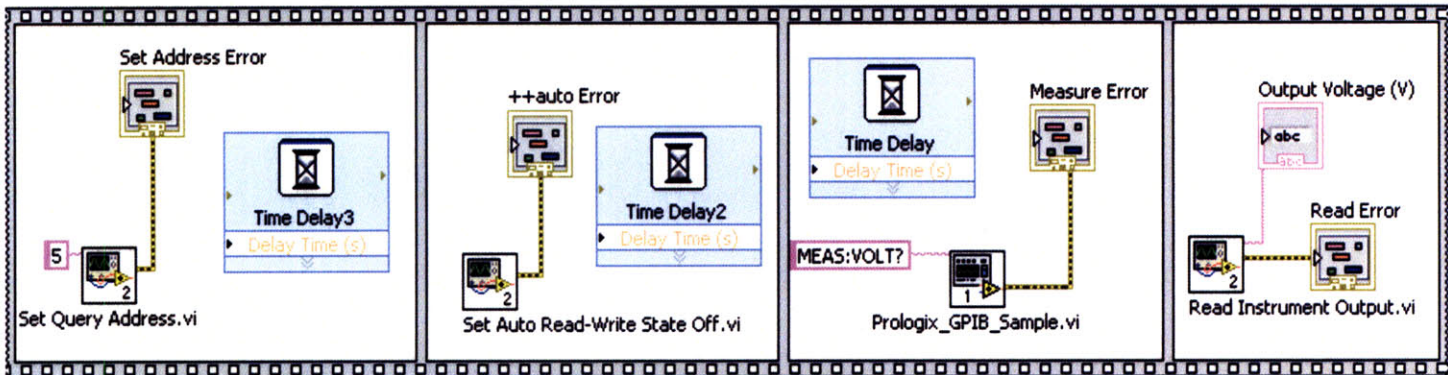
## Set Power Supply Output Current



## Read Power Supply Output Current



## Read Power Supply Output Voltage



## Measure Four-Wire Resistance

