Electrical Characterization of Organic Conducting Polymers

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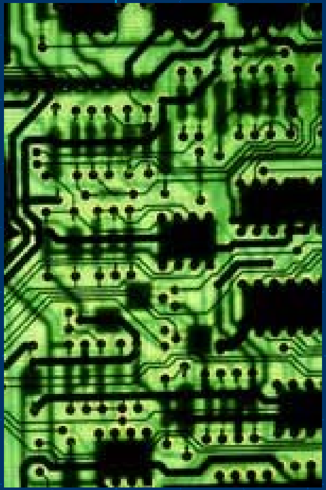
Molecular Devices:

Semiconductors of the near future



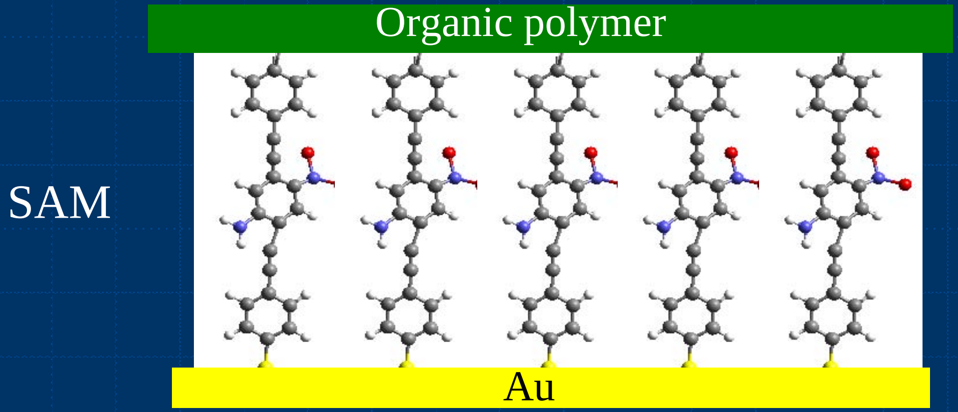
- Semiconductor technology continues to increase in complexity and decrease in size

- Soon silicon will be unable to meet market demands for small devices

- Molecular devices could promote technological advance by creating smaller, more complex devices than are possible with silicon

Electrical Characterization of Self-Assembled Monolayers (SAM)

- Individual molecules as conductors, switches, and memory devices
- Self-assembly technique used for determining behavior of single layer of molecules or even single molecules

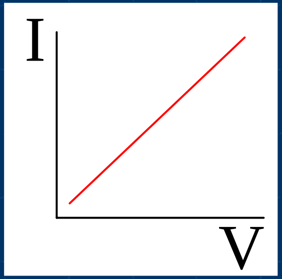


- Organic top contact optimal for integrity of device measurements

Previous work

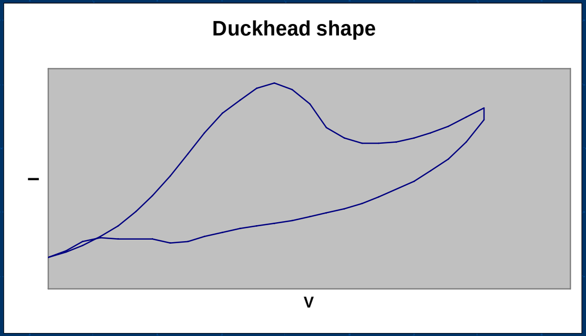
Electrical characterization of other organic polymers

- generally linear I-V curve on large scale
- some switching behavior for low-temperature measurements
- believed to be good, consistent conductors in thin films

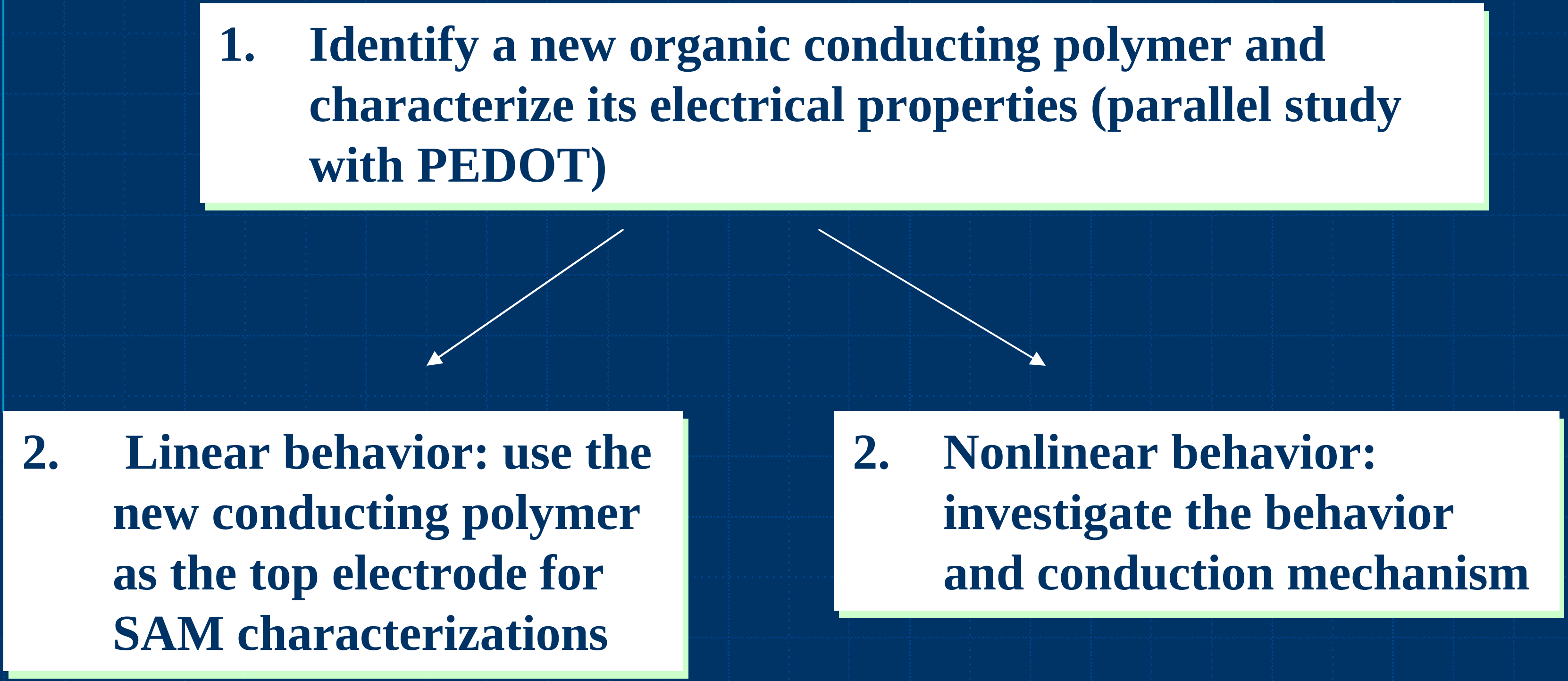


Electrical characterization of PEDOT

- John Suehle’s group found switching behavior between two conductive states
- Nonlinear hysteresis loop called “duckhead”$^{\text{TM}}$



Summer Objectives



1. Identify a new organic conducting polymer and characterize its electrical properties (parallel study with PEDOT)

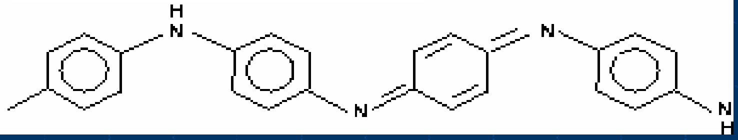
2. Linear behavior: use the new conducting polymer as the top electrode for SAM characterizations

2. Nonlinear behavior: investigate the behavior and conduction mechanism

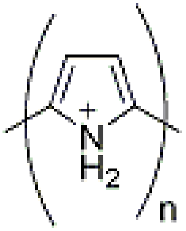
Two Polymer Candidates

Polyaniline (PANI)

Chemical structure:



Polypyrrole (PPy)

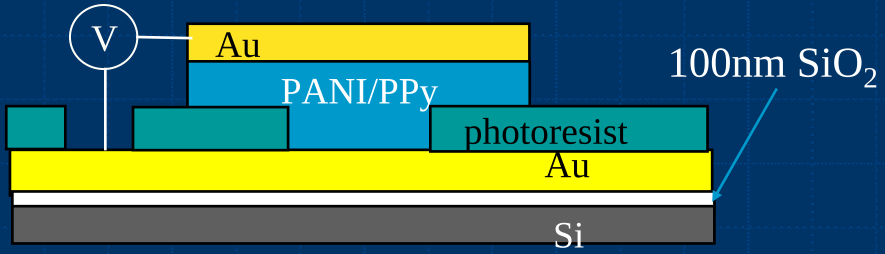


(doped with proprietary organic sulfonic acid)

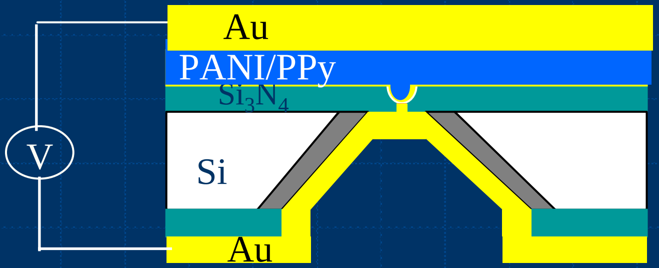
Advantages of these particular polymers:

- commercially available
- well-known as conductive polymers
- relatively environmentally stable
- some background information available in literature

Device Structure and Fabrication



Micron-size testbed



Nanopore

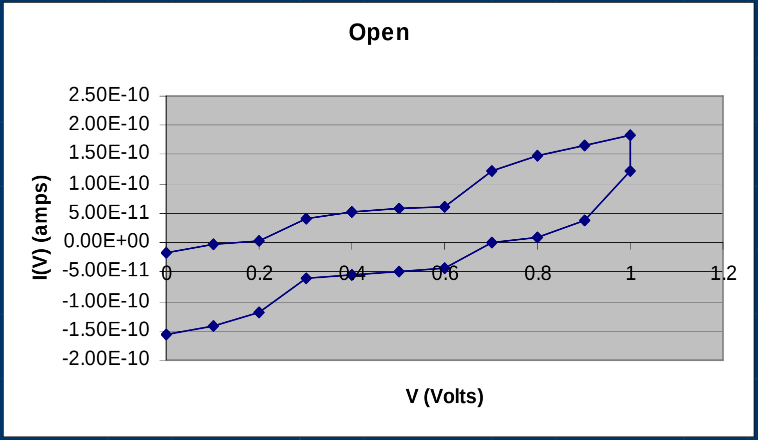
Micron-size Fabrication process:

- Use silicon wafer coated with SiO_2/Si_3N_4
- Spin-on condition: 400 rpm for 5 s; 2500 rpm for 45s

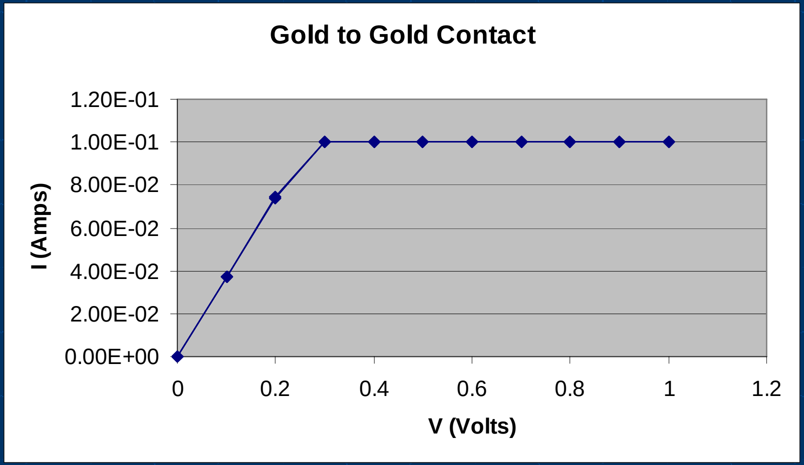
  PANI thickness: ~ 6000 Å, PPy thickness : ~ 1000 Å
- Photoresist as the insulating layer
- Baked at 50°C for 3 hours
- Top Au metalization: shadowmask, ~ 1200 Å @ 1 Å/s
- O_2 plasma to etch off the uncovered PPy/PANI

Measurement Setup

Open



Short

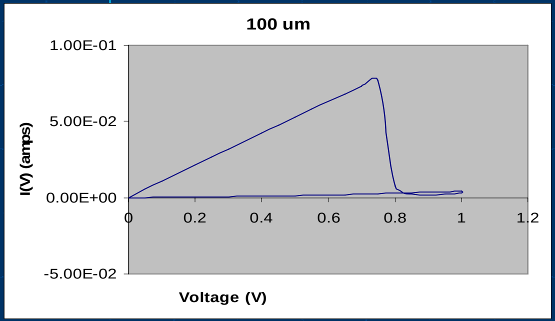


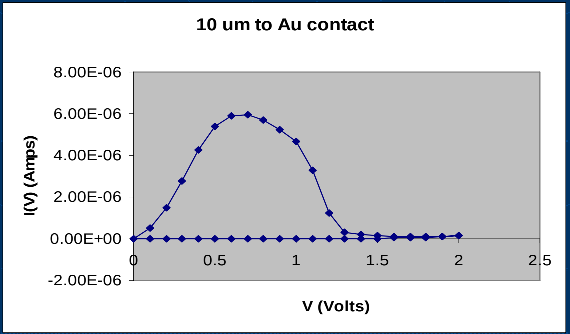
Results Summary:

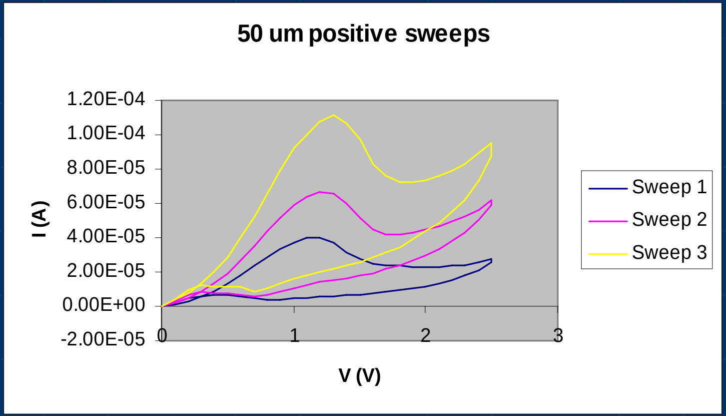
1. PPy Micron-Sized Device – nonlinear I-V curve, degradation, area-dependence
2. PPy Nanopore Device – temperature dependence and conduction mechanism
3. PANI Nanopores – nonlinear I-V curve, degradation, and higher conduction than PPy

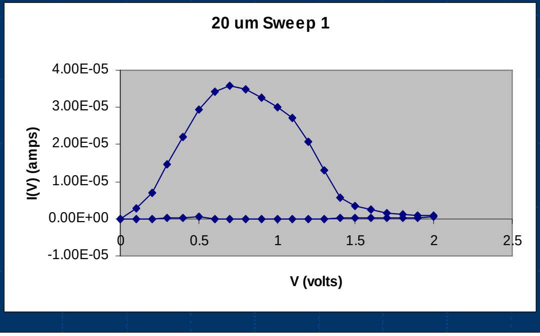
PPy Micron Device Results

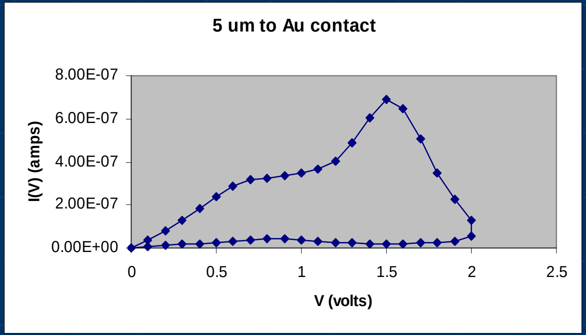
- Nonlinear hysteresis for area smaller than 100 by 100 μm device
- Device degradation for positive sweeps greater than 0.6 V
- Nonlinear behavior and degradation for negative sweeps as well


100 um


10 um to Au contact


50 um positive sweeps


20 um Sweep 1


5 um to Au contact

Similar nonlinear I-V curve for PPy nanopore devices

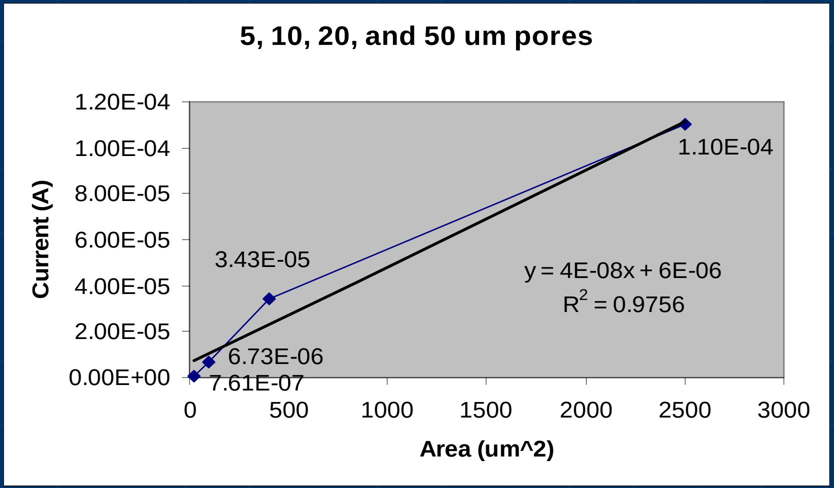
PPy Area Dependence

Constant current density of ~ 4E-8 A/um^2

Current Density (A/um^2):

Device	5 um	10 um	20 um	50 um
A	3.41E-08	6.34E-08	8.93E-08	1.61E-08
B	3.36E-08	6.26E-08	6.90E-08	7.16E-08
C	2.92E-08	5.96E-08	9.90E-08	
D	2.76E-08	7.29E-08	8.55E-08	
E	2.76E-08	7.21E-08	8.93E-08	
F		6.84E-08	8.05E-08	
G		7.20E-08	8.75E-08	
Avg	3.04E-08	6.73E-08	8.58E-08	4.40E-08

Area v. Average Highest Current

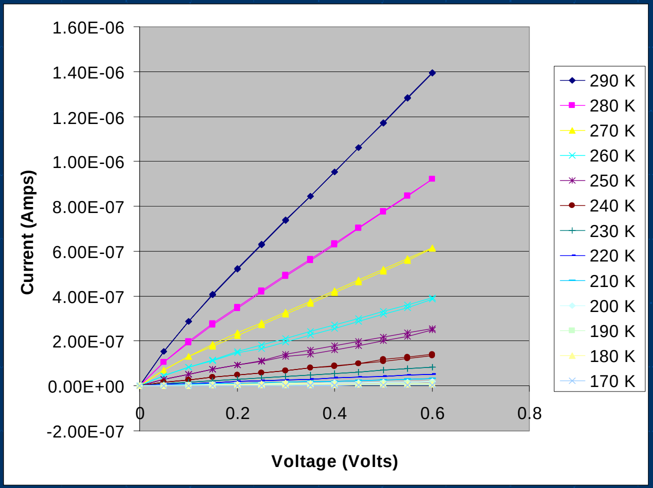


PPy Nanopore Temperature-Dependence

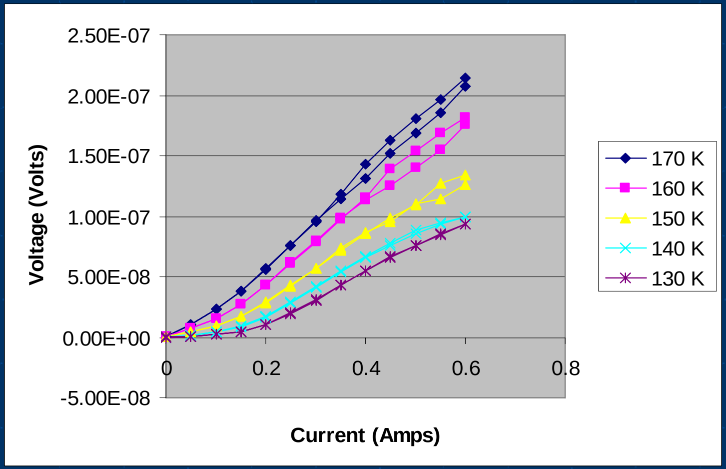
Measured four nanopore devices in cryostat, decreasing in temperature from 290 to 70 K, in order to determine the conduction mechanism

Typical Measurement Results

290 to 180 K



170 to 130 K



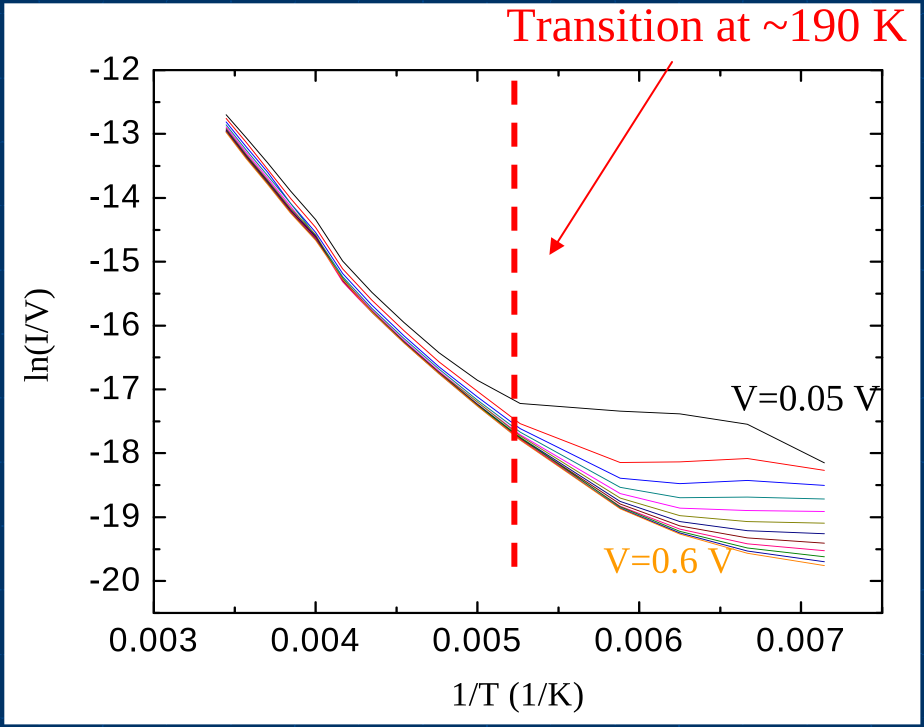
- Current decreases with decreasing temperature
- Temperature-dependent nonlinear behavior

Possible Conduction Mechanisms

	Conduction Mechanism	Characteristic Behavior	Temperature Dependence	Voltage Dependence
Tunneling no T-dependence	Direct Tunneling	$J \sim V \exp(-\frac{2d}{\hbar}\sqrt{2m\Phi})$	none	$J \sim V$
	Fowler-Nordheim Tunneling	$J \sim V^2 \exp(-\frac{4d\sqrt{2m}\,\Phi^{3/2}}{3q\hbar V})$	none	$\ln(\frac{J}{V^2}) \sim \frac{1}{V}$
Thermal activation T-dependence	Thermionic Emission	$J \sim T^2 \exp(-\frac{\Phi - q\sqrt{qV/4\pi\varepsilon d}}{kT})$	$\ln(\frac{J}{T^2}) \sim \frac{1}{T}$	$\ln(J) \sim V^{\frac{1}{2}}$
	Hopping Conduction	$J \sim V \exp(-\frac{\Phi}{kT})$	$\ln(\frac{J}{V}) \sim \frac{1}{T}$	$J \sim V$

Hopping Conduction Analysis:

$$I \sim V \exp\left(-\frac{\Phi}{kT}\right)$$



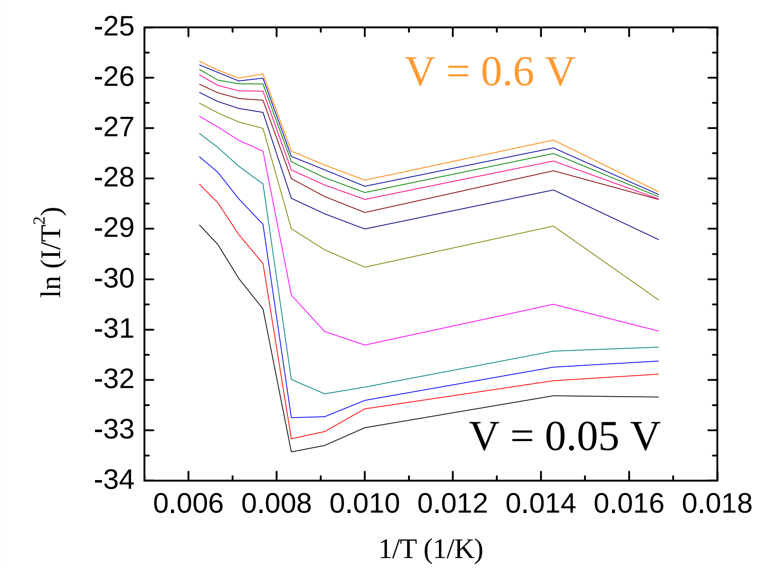
Average barrier height: $\overline{\Phi}_{hopping} = 100$ to 200 meV

Other Conduction Mechanism?

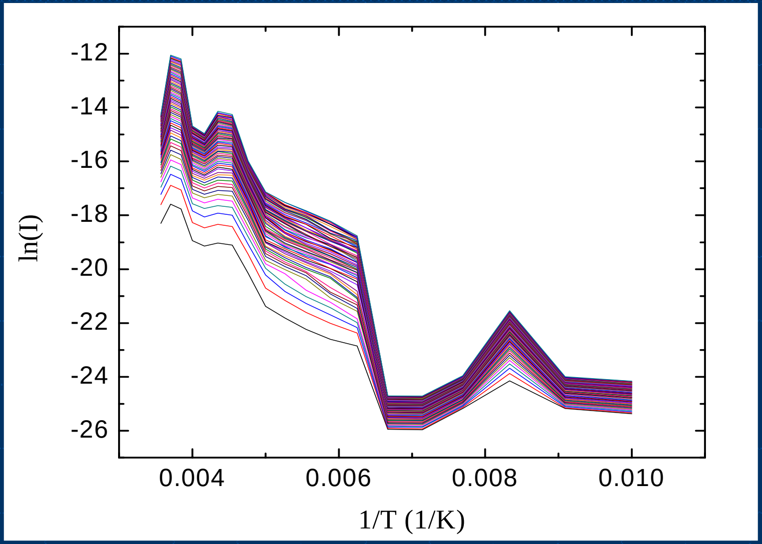
T from 170 to 60K

Thermionic Emission

$$I \sim T^2 \exp\left(-\frac{\Phi - q\sqrt{qV/4\pi\varepsilon d}}{kT}\right)$$



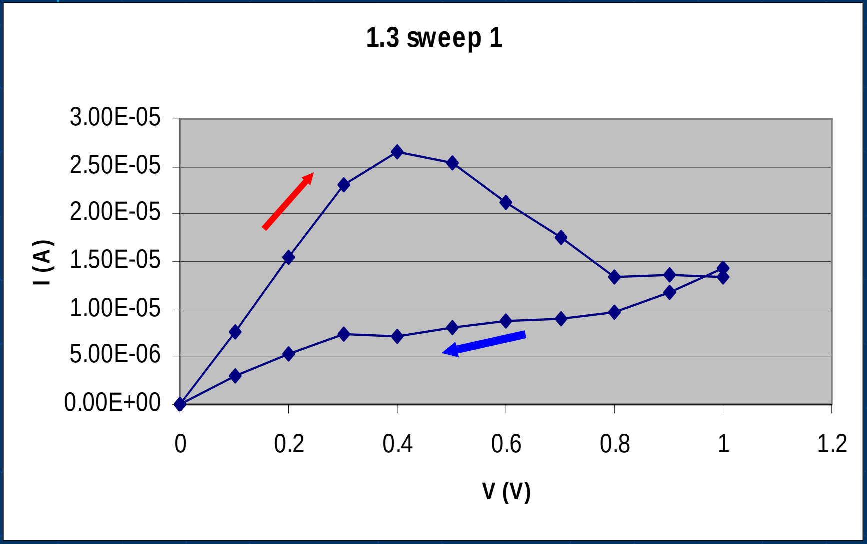
Arrhenius Analysis



Data graphed from 0.01 V to 0.6 V in increments of 0.01 V

Need further investigation to understand this transition behavior

PANI Nanopores



16 duckhead devices, 66.7%

Resistivity Measurement

Polypyrrole:	793 S/cm
Polyaniline:	526 S/cm

These values are reasonable: our results agree with published resistivity measurements to within an order of magnitude

Summary of Conclusions:

- Both PANI and PPy have *nonlinear hysteresis loops* for their I-V curves on small-scale devices
- Devices *degrade for high bias sweeps*, and degrade even more with switched direction of bias sweep
- The current of PPy exhibits *area dependence, sweep rate dependence, and temperature dependence*
- *Hopping conduction* is the conduction mechanism in PPy for T > 190 K; conduction transition at 190 K, still T-dependent but not Thermionic Emission
- PANI yields a much *higher current* than PPy

Summer Objectives

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2. **Nonlinear behavior: investigate the behavior and conduction mechanism**

With nonlinear behavior, conducting polymer makes poor top contact for SAM

Summer Objectives

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2. **Nonlinear behavior: investigate the behavior and conduction mechanism**

Future work for characterizing the electrical properties of these polymers:

- *Understand conduction mechanisms* in PPy below 190 K, PANI
- *Theoretical basis* for experimental switching results in both PANI and PPy
- Greater accuracy in resistivity value, hopping barriers, control measurement, etc.

Acknowledgements

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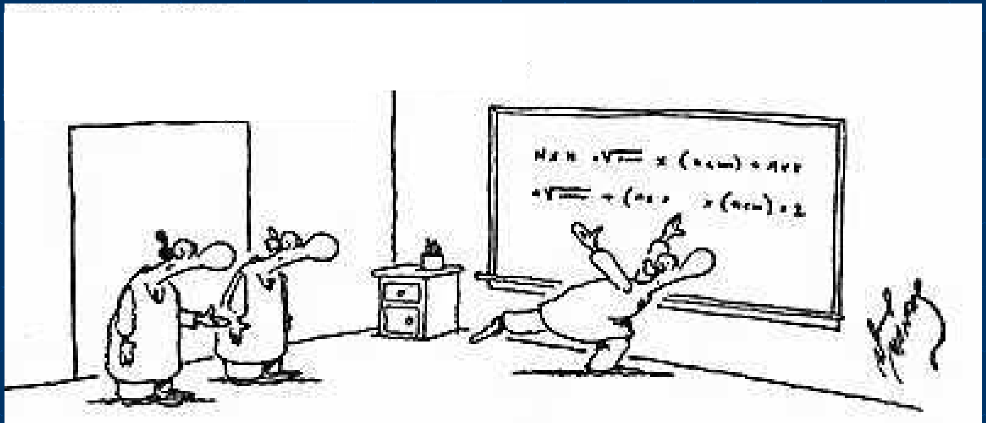

"At some point the theory becomes so abstract it can only be conveyed using interpretive dance"