

The logo features a stylized starburst shape on the left, composed of a blue upper half and a green lower half. To the right of this graphic, the word "CROSSLINK" is written in a bold, black, sans-serif font, followed by a trademark symbol (TM).

**CROSSLINK™**

## **Supercapacitors Using n and p-Type Conductive Polymers Exhibiting Metallic Conductivity**

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*Crosslink, Missouri, USA*

20<sup>th</sup> International Seminar on Double Layer Capacitors  
& Hybrid Energy Storage Devices  
Deerfield Beach, Florida

December 6 - 8, 2010

A decorative horizontal bar at the bottom of the slide, consisting of a green section on the left and a blue section on the right, separated by a diagonal line.

# Crosslink

- Crosslink is a technology company focused on developing and commercializing products using advanced organic materials
- Headquartered in St. Louis Missouri with R&D laboratories in Springfield Missouri (the Jordan Valley Innovation Center) and Hattiesburg Mississippi (The Accelerator)
- Deep experience in electrochemistry, polymer synthesis and device manufacturing
- Funding from private equity and government development contracts



# Focus on Electroactive and Conductive Polymer Systems

- R&D
  - Advanced Materials for high power and high energy density supercapacitors
  - Self-Detoxifying Polymer Systems
  - Smart Composites for state of health monitoring
  - Controlled Delivery of Therapeutic Agents for trauma induced wounds and burns
- Commercial Products
  - Flexible EL Lighting Systems
  - Transparent ESD coatings
  - “Smart” anti-corrosion coatings for aerospace aluminum alloys

## Illumination Systems:

- Polymer Light Emission
- Super-flexible
- VIS and NIR

## Performance Coatings:

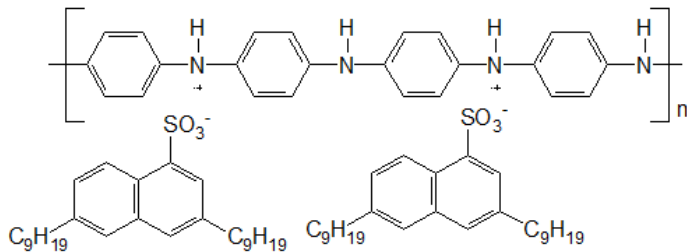
- Anti-Corrosion
- Anti-Static/ESD
- Actives Release

## Research & Development:

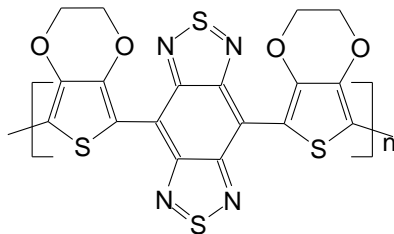
- Self-decontamination
- Supercapacitors
- High voltage capacitors
- Smart composites

# Presentation Outline

- Supercapacitor Background
- Electroactive and Conductive Polymers

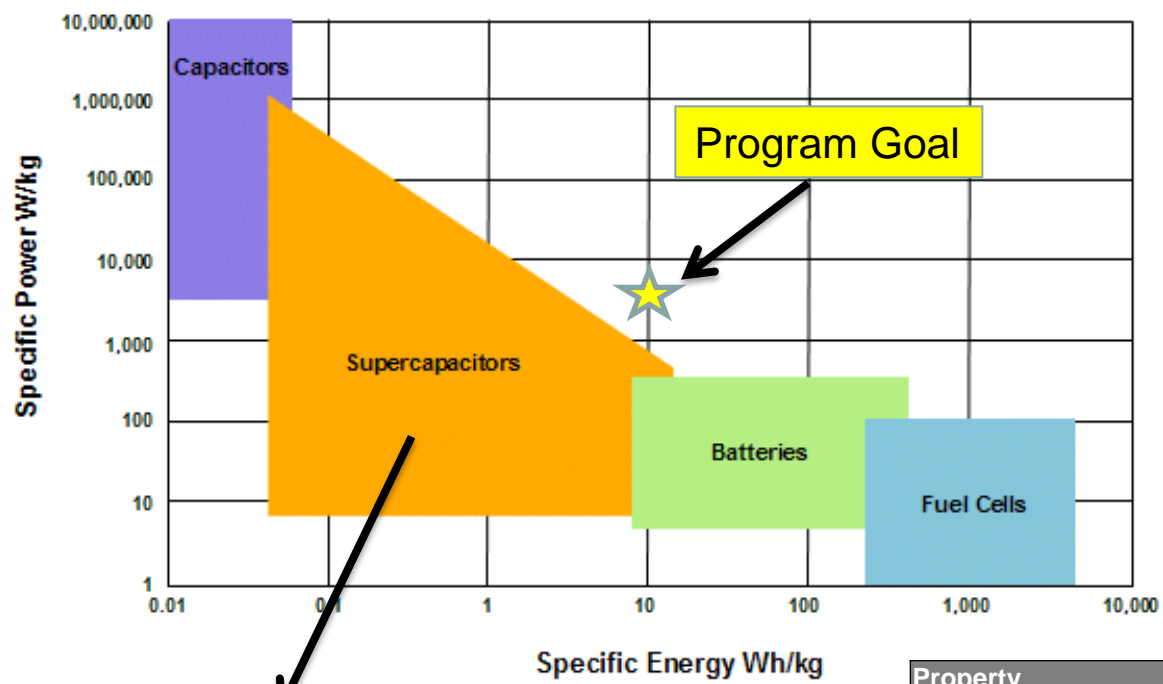


Polyaniline (PANI) (p-type)



Poly(BEDOT-BBT) (n-type & p-type)

- Redox Active Supercapacitors
  - Types I, III and IV
  - Liquid and gel electrolytes
  - Bipolar architecture
- Prototype Construction
  - Prismatic
  - Cylindrical roll design
- Performance
  - Energy and Power densities
  - Cycle Life



# Comparison of Energy Storage Technologies

## Applications

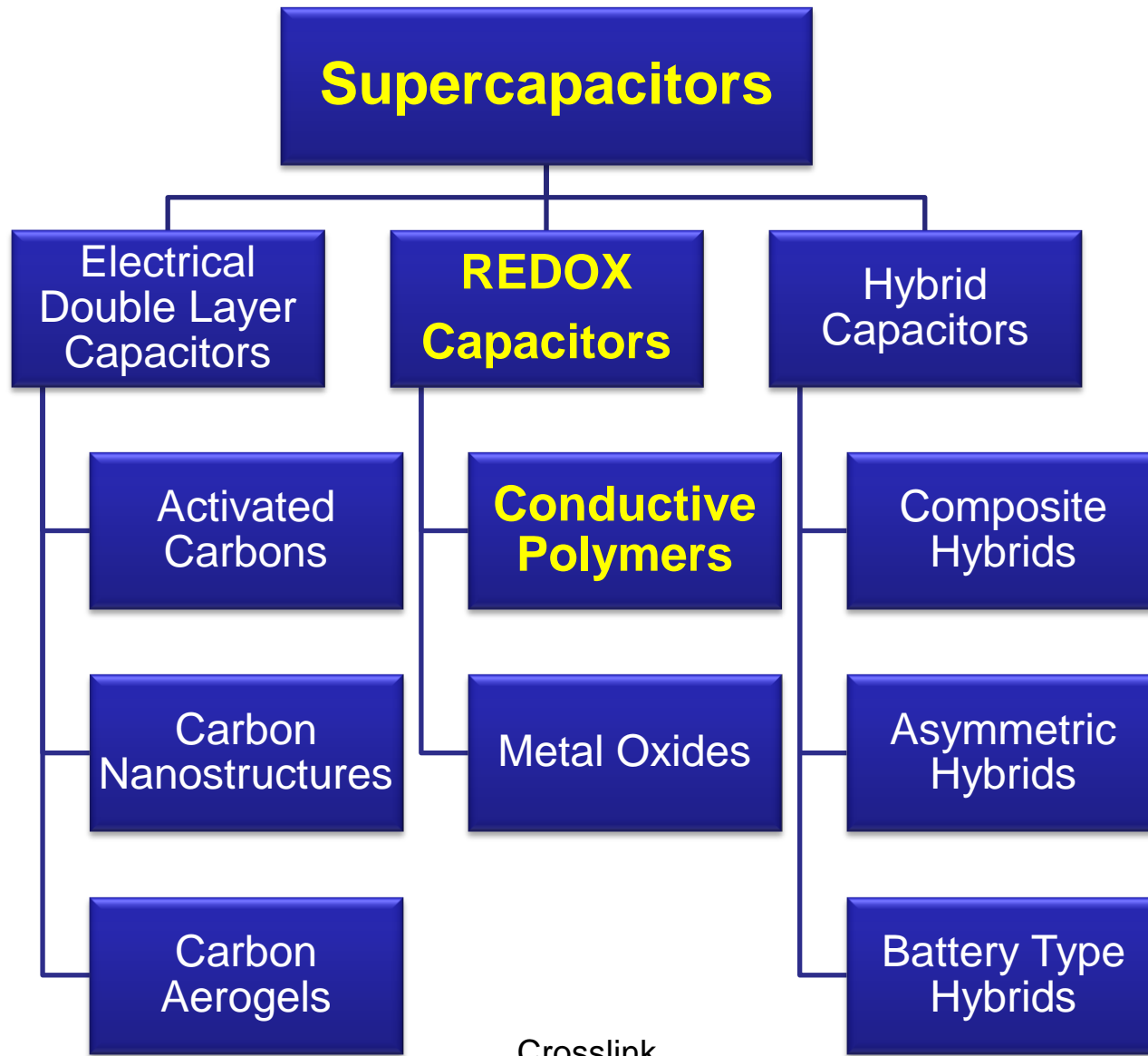
- **Pulse Power**
  - Medical Devices, Military
- **Load Leveling**
  - Wind, Solar → Micro grid power quality
- **Transportation**
  - Regenerative braking for automotive, mass transport (subways, buses, trains)
  - Elevators
- **Power Sources**
  - Digital Cameras, Automated Meter Readers
  - Laptops, Cell phones

Property	Supercapacitors	Capacitors	Batteries
<b>Charge/Discharge Time</b>	Milliseconds to Seconds	Picoseconds to Milliseconds	1 to 10 hrs
<b>Operating Temperature</b>	-40 to +85 °C	-20 to +100 °C	-20 to +65 °C
<b>Operating Voltage</b>	1.2V - 2.75V/cell	6 to 800 V	1.25 to 4.2 V / cell
<b>Capacitance</b>	100 mF to > 2F	10 pF to 2.2 mF	N/A
<b>Life</b>	30,000+ hrs average	>100,000 cycles	150 to 1500 cycles
<b>Power Density</b>	10 to 100 kW/kg	0.25 to 10,000 kW/kg	0.005 to 0.4 kW/kg
<b>Energy Density</b>	1 to 5 Wh/kg	0.01 to 0.05 Wh/kg	8 to 600 Wh/kg
<b>Pulse Load</b>	Up to 100 A	Up to 1000 A	Up to 5 A

# Project Goals

- Light weight, compact, polymer based system that outperforms standard carbon-based systems
  - Energy density (target 10 Wh/Kg)
  - Power density (target 5000 W/Kg)
  - Fast charge/discharge cycling
  - Stability to >30,000 charge/discharge cycles
  - Operational temperature -60 to +165F
- Path forward requires ICPs that possess:
  - Solution processibility
  - Near metallic conductivity
  - Fast and reversible charge transfer
  - Mechanical and thermal stability
  - Extended lifetime

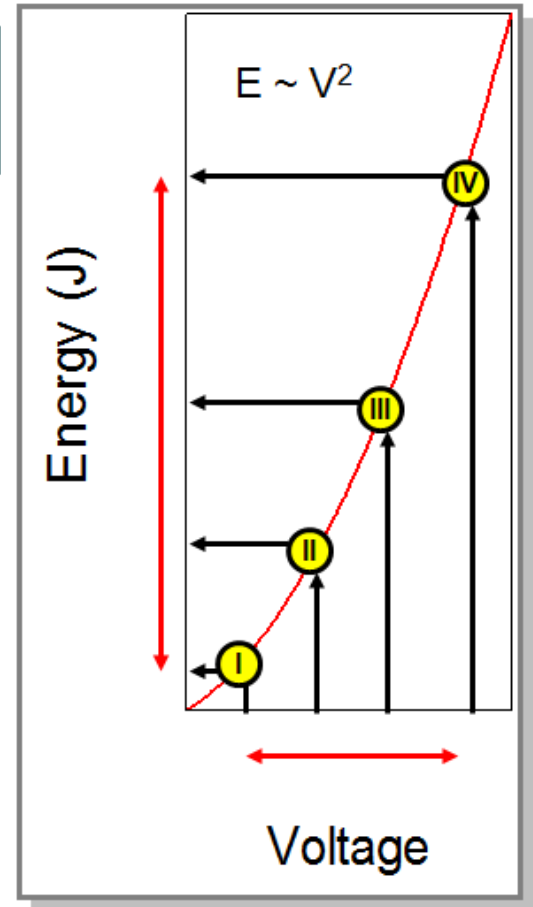
# Classification of Supercapacitors



Crosslink

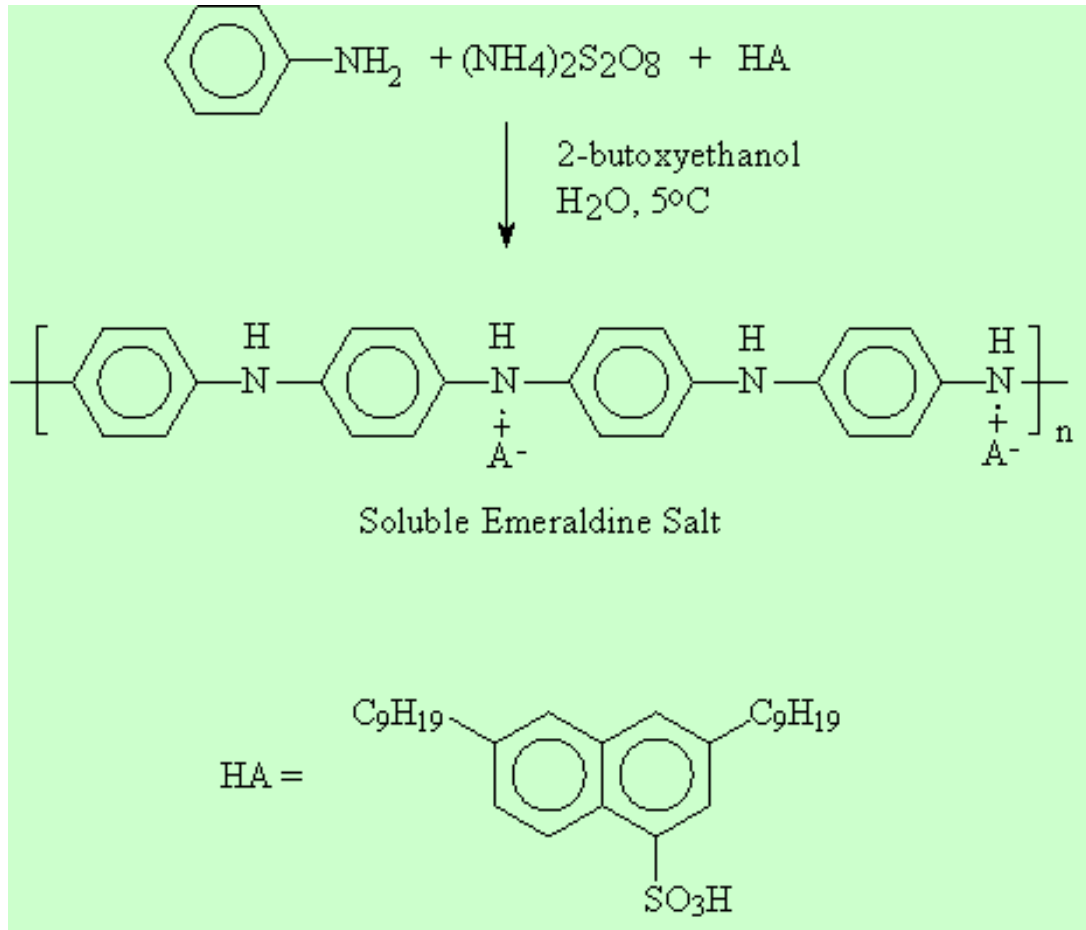
# Classification of Electroactive Polymer Supercapacitors

- Type I: same p-doping polymer for both electrodes (symmetric)- PANI
- Type II: different p-doping polymers on each electrode (asymmetric)
- Type III: uses the same material for both electrodes that may be n-doped or p-doped (symmetric)- Poly(BEDOT-BBT)
- Type IV: uses different polymers for the n-doping and p-doping electrodes (asymmetric)- PANI/Poly(BEDOT-BBT)



# Soluble Polyaniline

United States Patent 5,567,356; *Macromolecules*, 31, 1735 (1998).

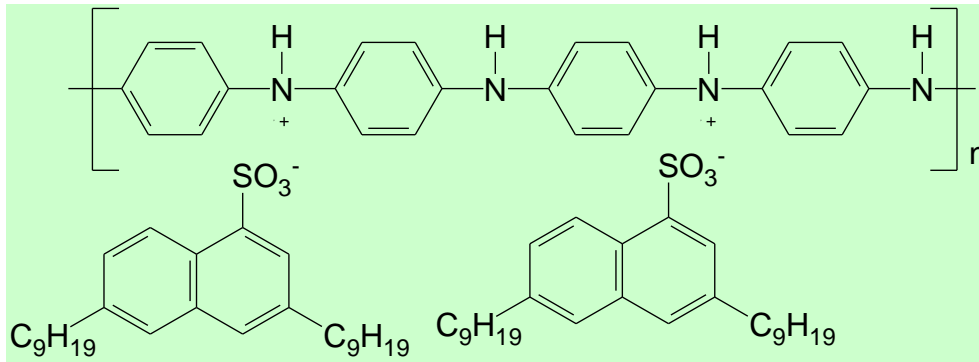


## PANI-DNNSA

- Emulsion Polymerization
- Soluble Conductive Polymer
- Solution Processibility

Crosslink

# PANI Conductivity Enhancement



(Denoted PAC1003)

- As cast film slightly conductive
- Solvent or thermal treatment enhances conductivity 5 orders of magnitude
- To meet performance specifications for supercapacitors need 2-3 orders of magnitude higher conductivity

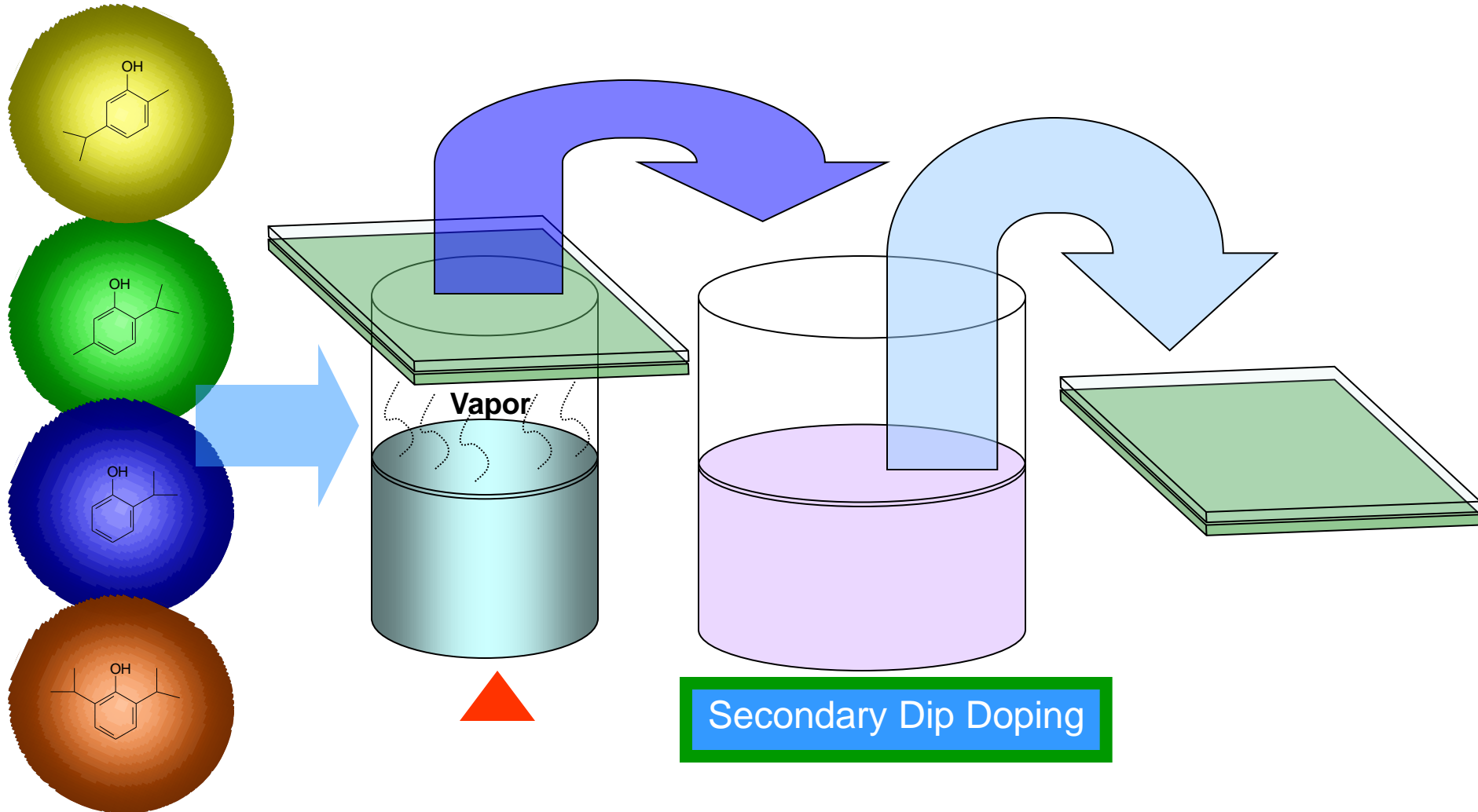
Cast Film

10<sup>-5</sup> S/cm

Methanol, isopropanol or thermal treatment  
United States Patent 5,780,572

0.1-2 S/cm

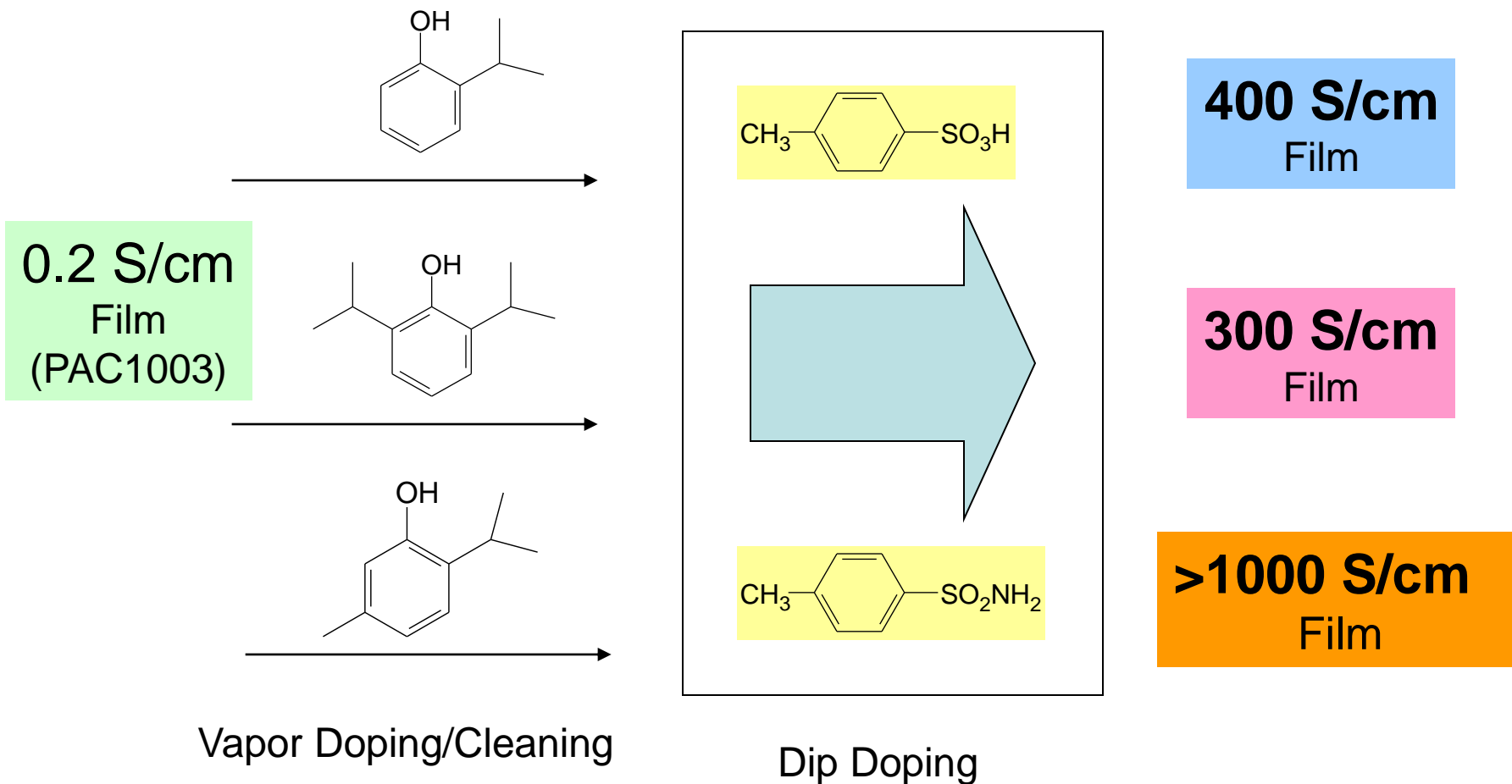
# Vapor/Dip Doping Process



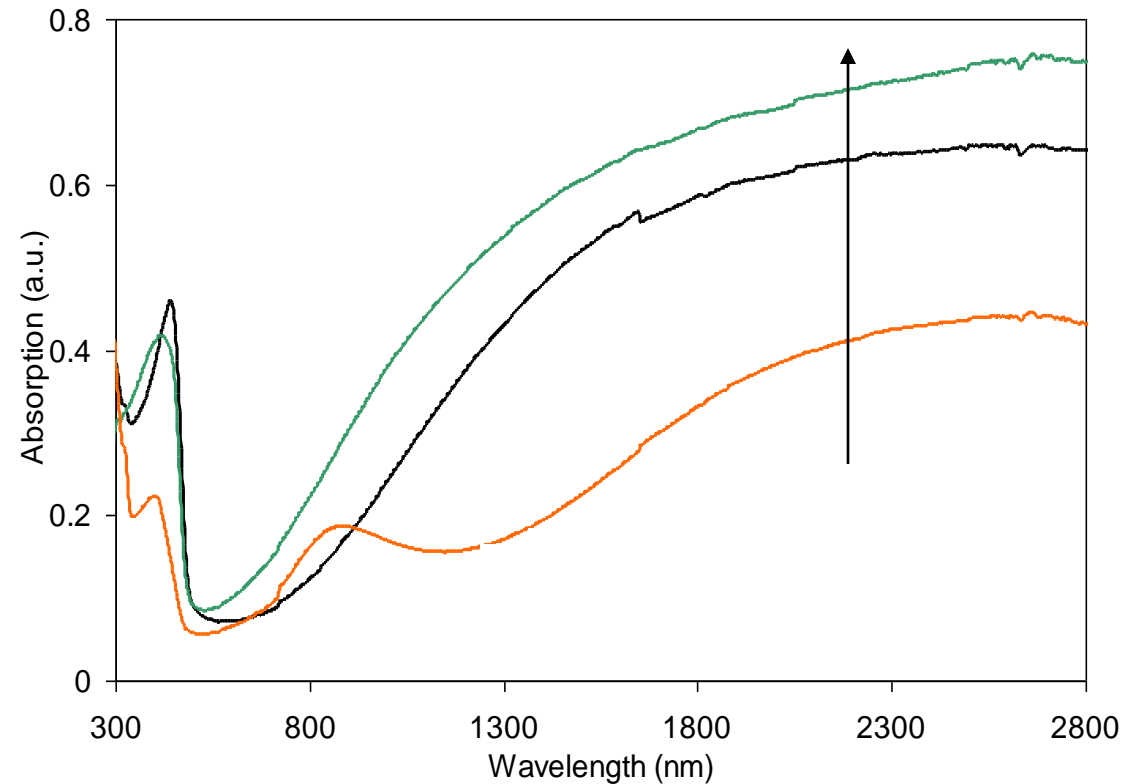
Crosslink

# PANI Vapor Phase Secondary Doping/Dip Doping

Non-provisional Patent # WO/2010/065859



# Free-Carrier Enhancement



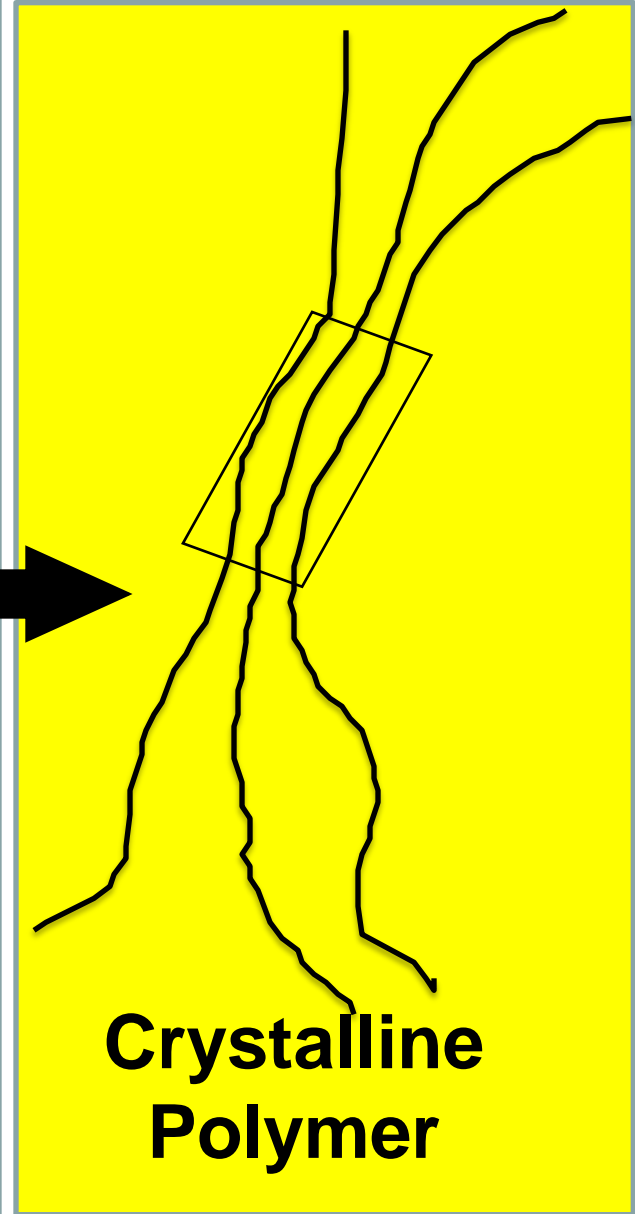
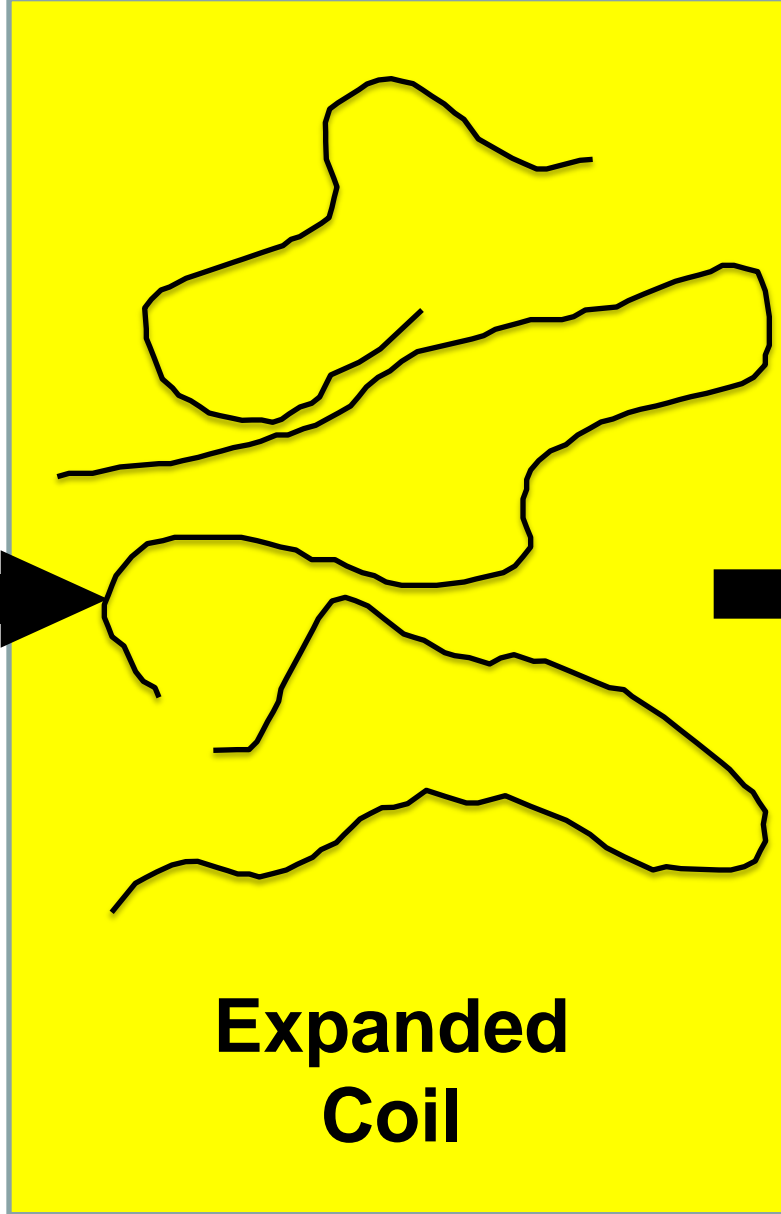
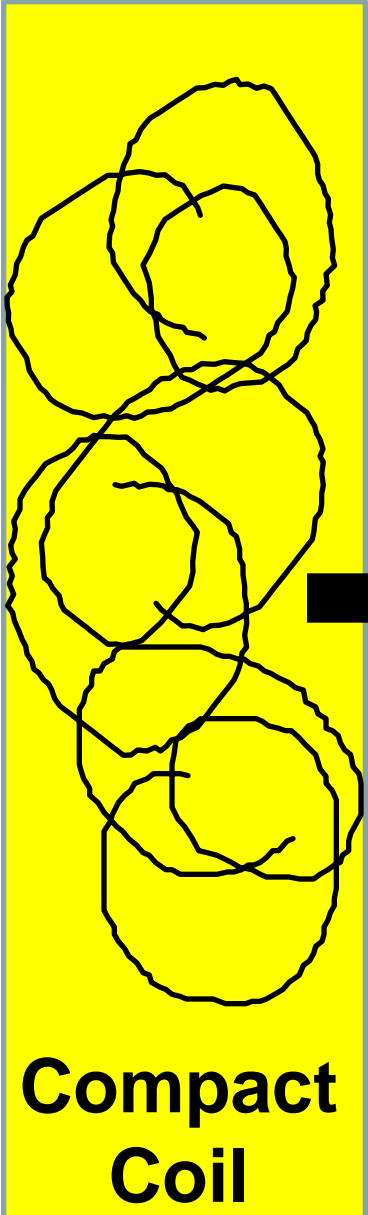
Dopants	Film Thickness (nm)	Conductivity (S/cm)
<b>ROH/PTSA-PTSAM</b>	<b>207.39</b>	<b>825.67</b>
ROH	232.2	25.2
PAC1003	438.0	0.16

Crosslink

# Proposed PANI Doping Mechanism

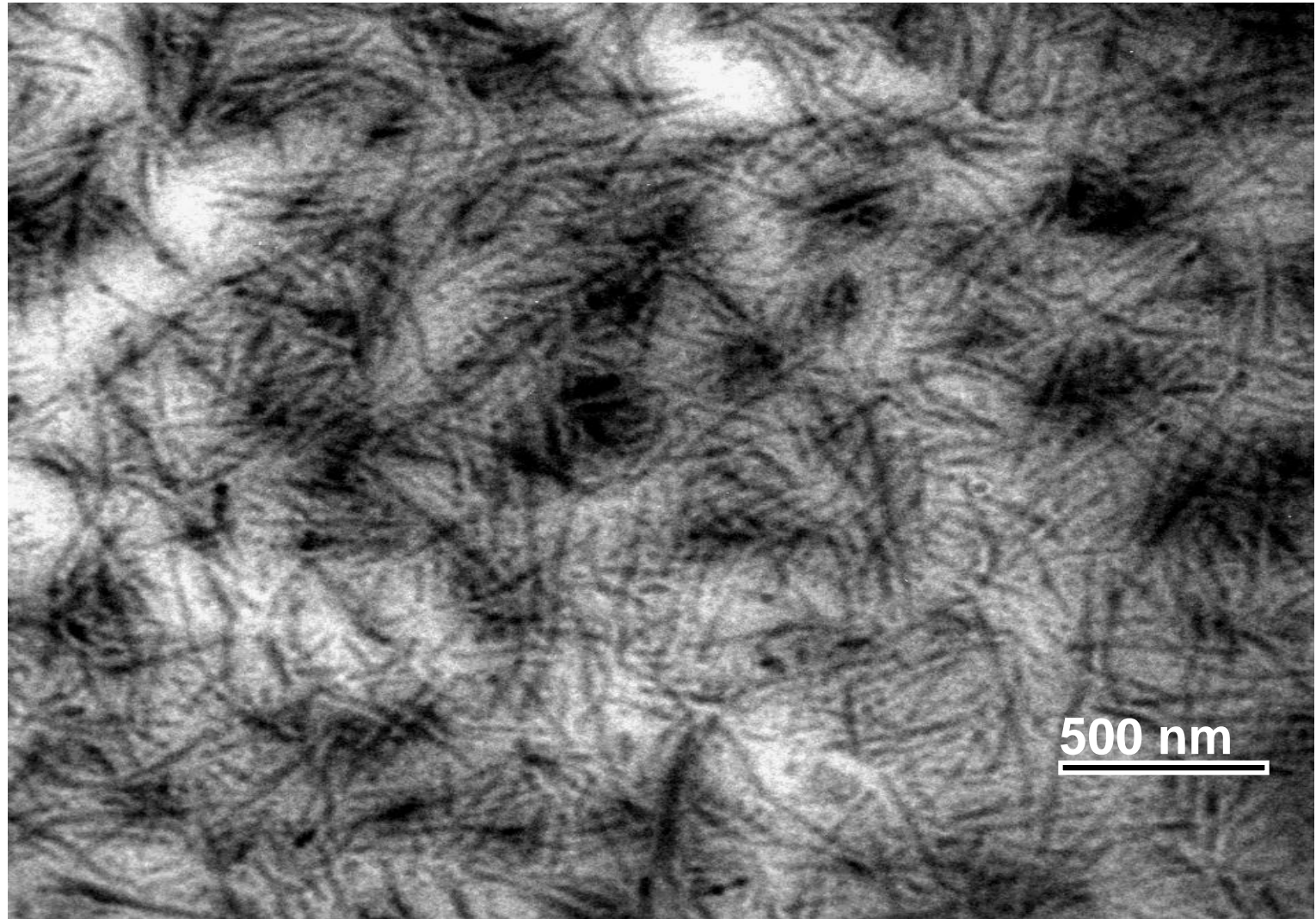
- Vapor Exposure
  - Phenol vapor removes un-bound DNNSA and residual solvent
  - Porous voids created that accommodate incorporation of secondary dopants
- PTSA/PTSAM Dip Doping
  - DNNSA dopant supplemented with PTSA
  - Conformational rearrangement of compact coil-like polymer structure to extended structure
  - Enhancement of chain-to-chain hole hopping

# Molecular Architecture

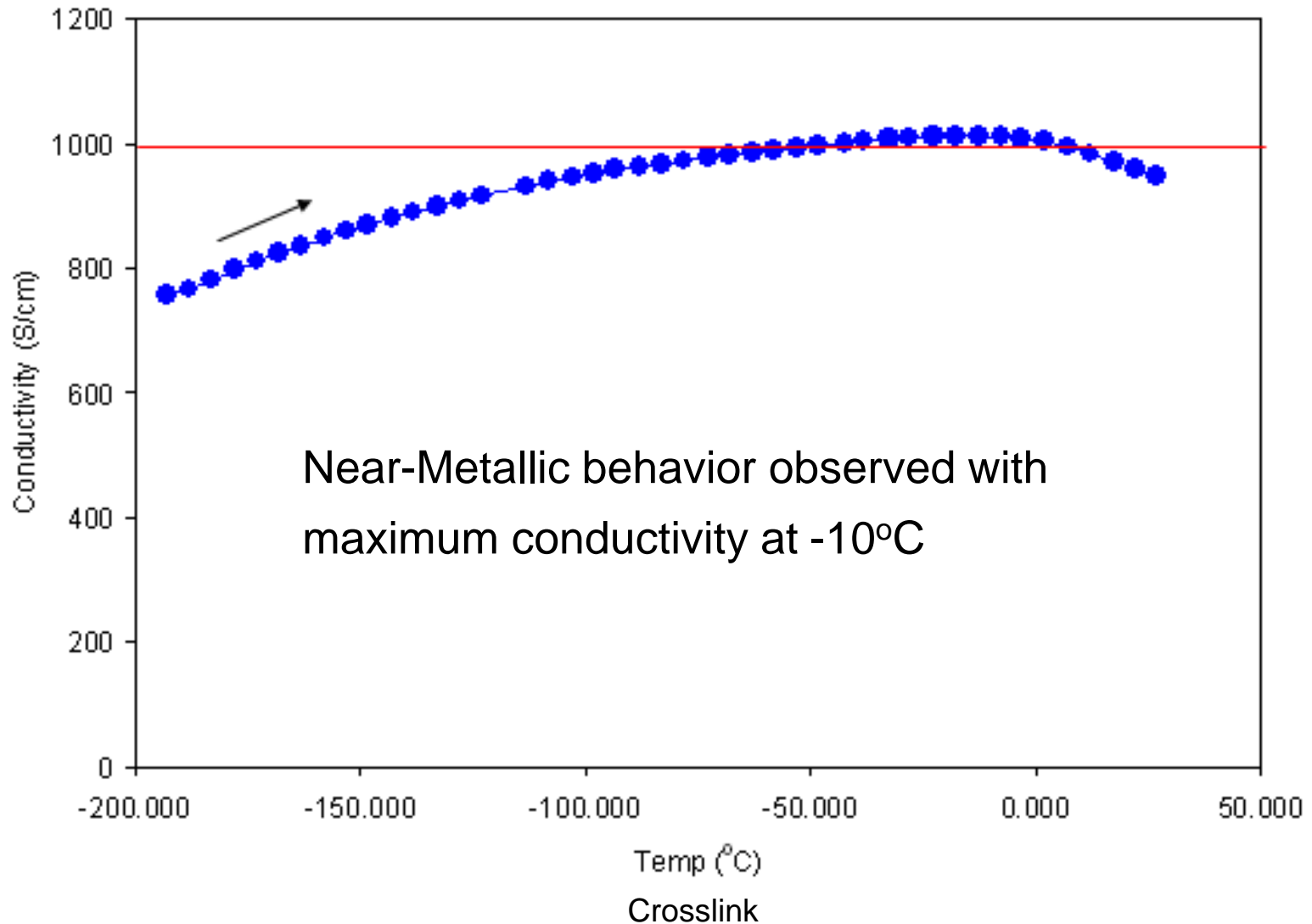


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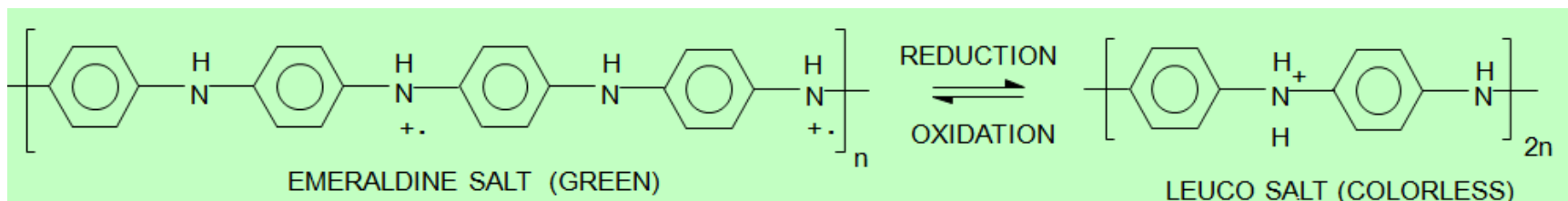
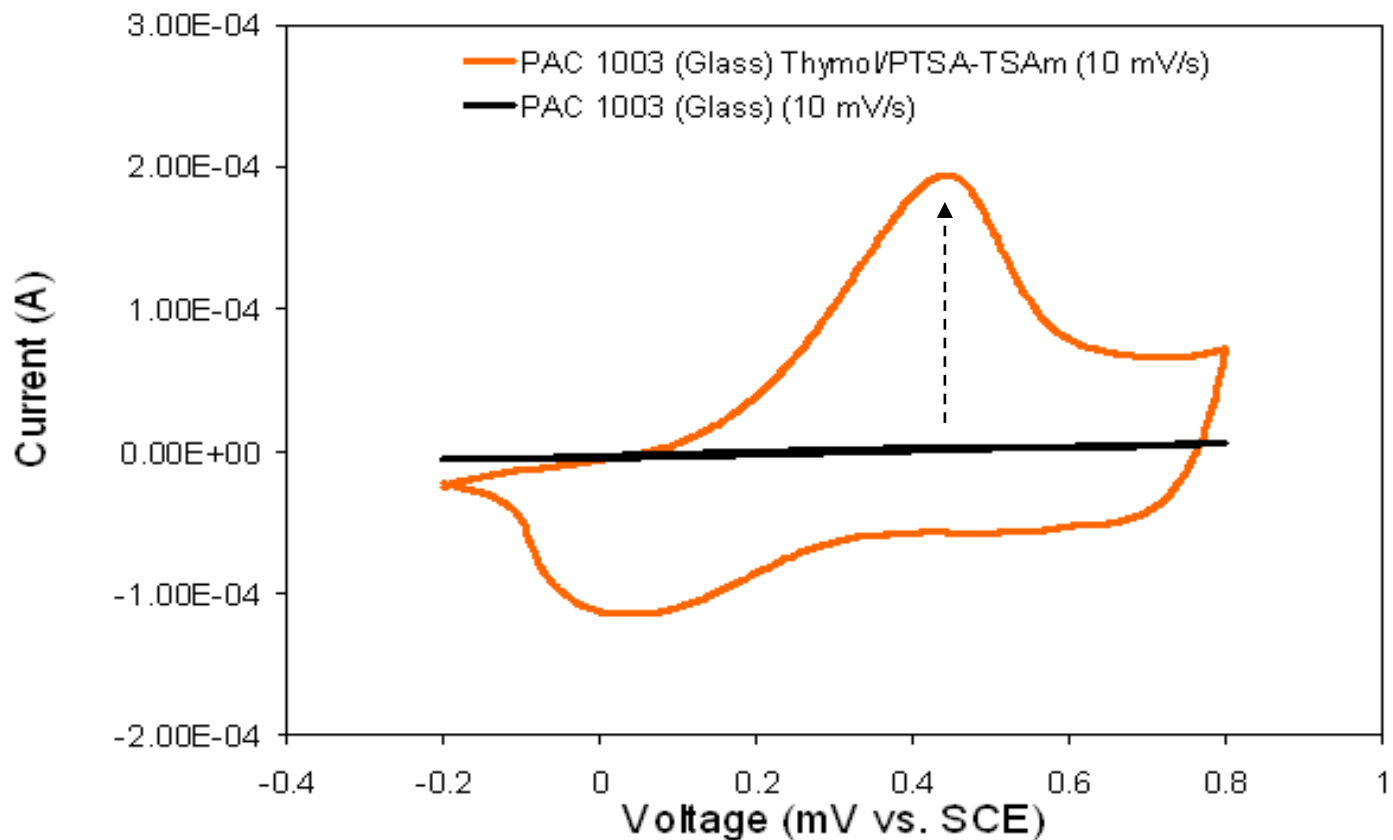
# Bright Field TEM Image of PANI-DNNSA Film



# Low Temperature Conductivity of Vapor/Dip Doped PAC1003

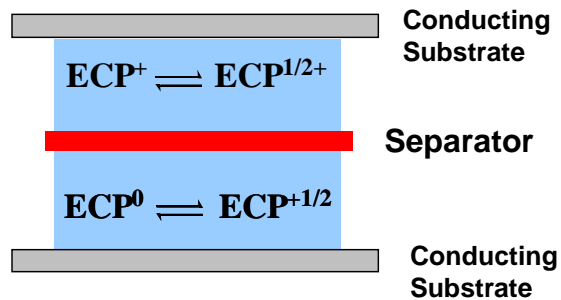
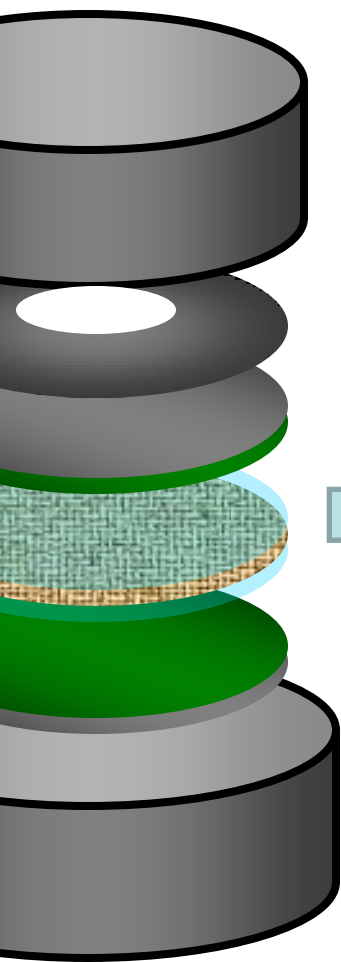


# Type I Polyaniline Supercapacitor

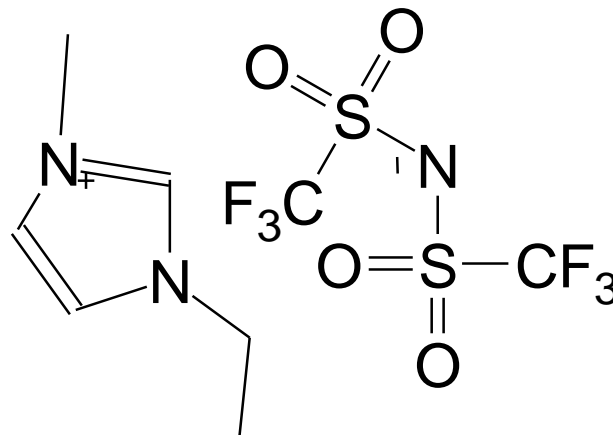


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# Type I Coin Cell Fabrication



Ionic Liquid:  
1-ethyl-3-methyl-1-H-imidazolium  
bis(trifluoromethanesulfonyl)imide  
(EMI-IM)



- Non-Flammable/Non-Corrosive
- Wide operational temperature range
- No measurable vapor pressure

# PANI Coin Cell Performance

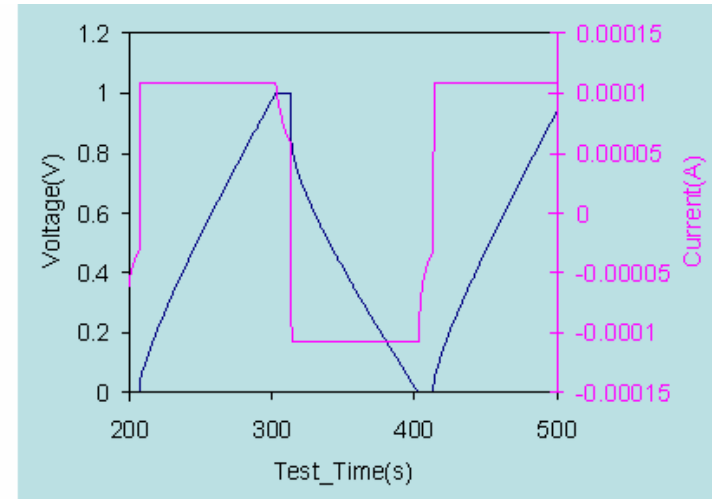
Vapor/dip doping process (Electrolyte = EMI-IM)

$$\text{Energy Density} = CV^2/2M =$$

$$it(V/2)/(3600m) \text{ [WH/Kg]}$$

$$\text{Max Power Density} = V^2/\{4(ESR)M\}$$

$$\text{[W/Kg]}$$



Film	Dopants	Polymer mass (mg)	Voltage (V)	Current	Energy Density (WH/Kg)	Power Density (W/Kg)
Spin-Coated PAC 1003 (1000rpm/30s)	PTSA-TSAm (5-0.5 w/v) in BCS	1.36	1.0	0.05 mA	0.92	36.8
	Thymol vapor /PTSA-TSAm (5-0.5 w/v) in BCS	1.22	1.0	0.05 mA	1.27	41.0
				0.10 mA	1.2	82.0
				1.0 mA	0.91	819.7
		1.5	0.10 mA	2.8	123.0	

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# Coin Cell Supercapacitor: Role of PANI Conductivity on Device Performance

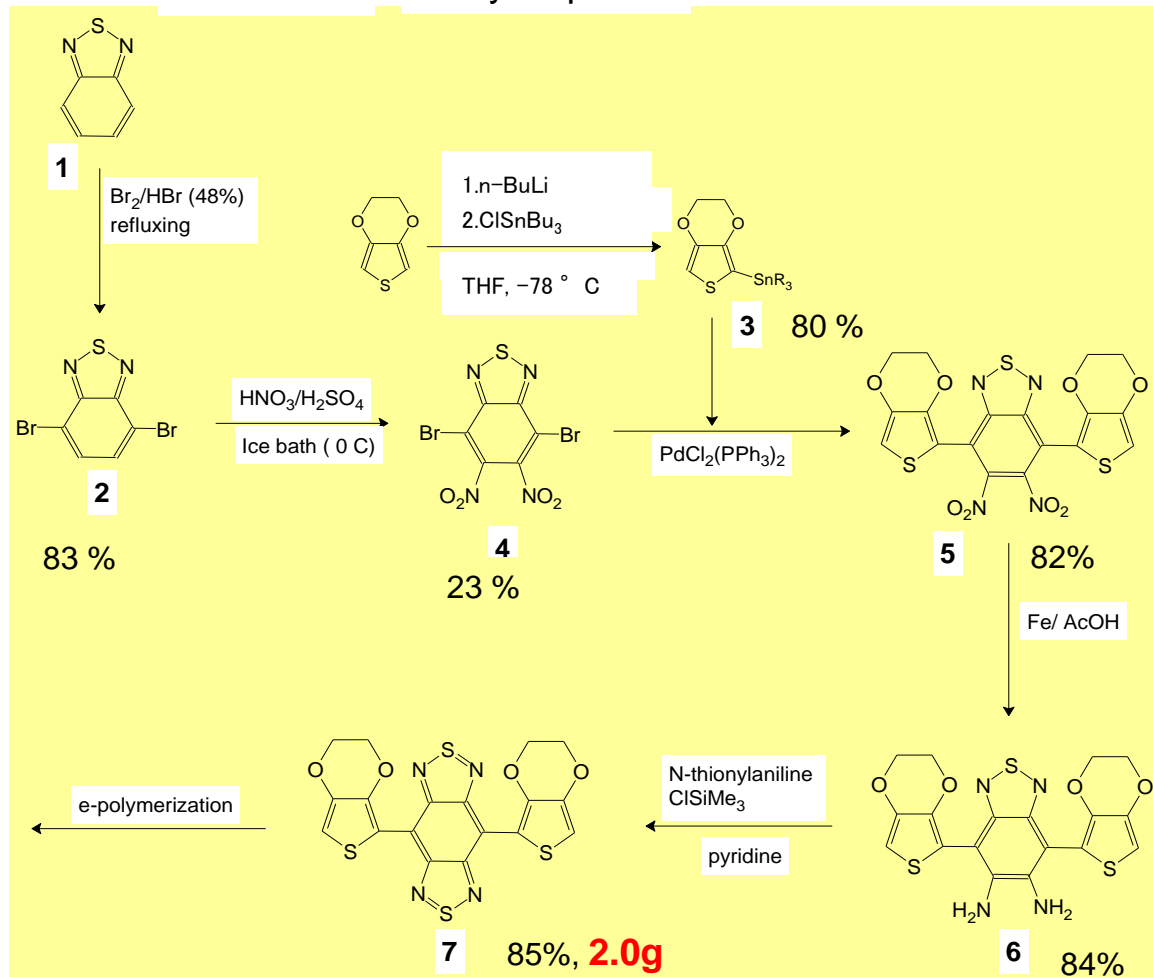
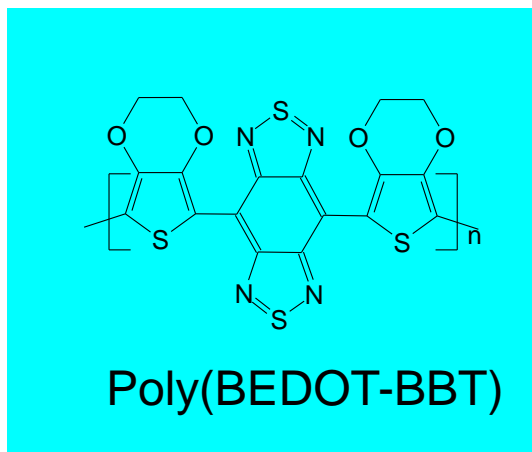
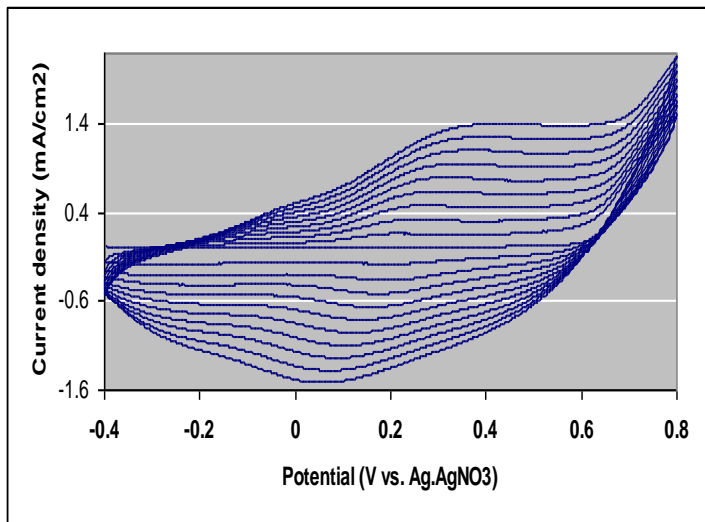
Polyaniline (PANI) Film	Electrical Conductivity (S/cm)	Specific Capacitance (F/g)	Energy Density (WH/Kg)
PAC 1003 film	0.2	1.2	0.4
Novel Secondary Doped PAC 1003 Film	250	6.1	1.9
	1000	12.5	3.4
	4000	17.2	5.4

**Electrolyte:** Ionic Liquid (EMI-Im)

# Poly(BEDOT-BBT) Synthesis

Benzo-  
thiadiazole

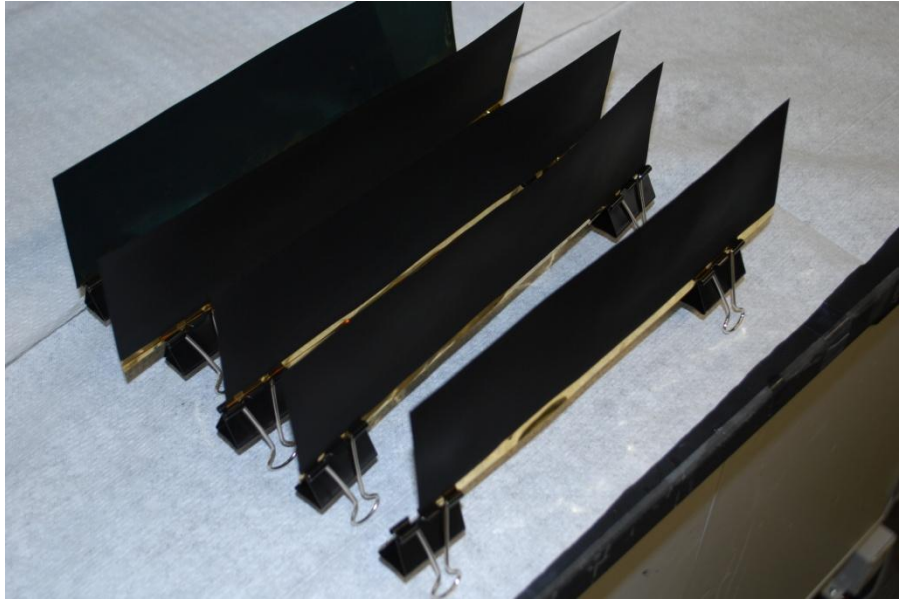
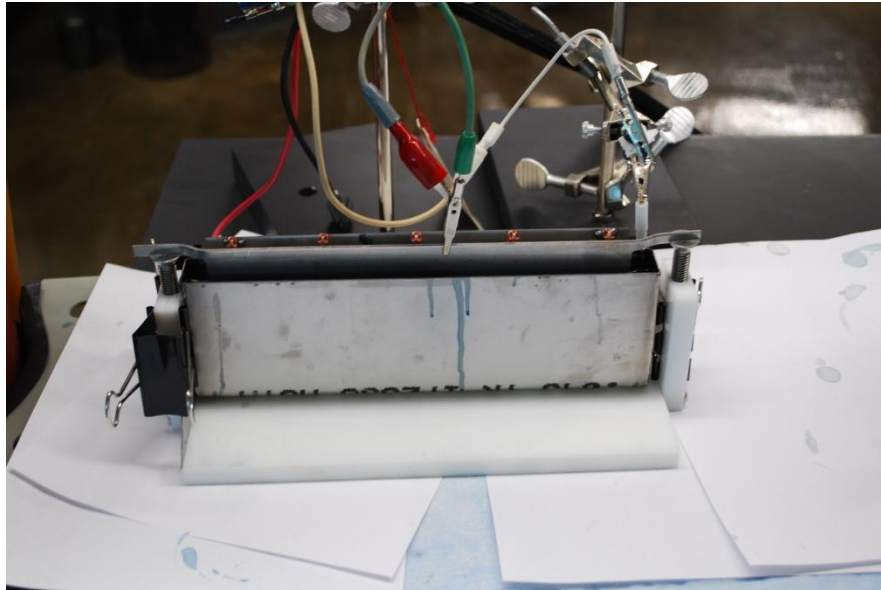
Ethylene-  
dioxythiophene



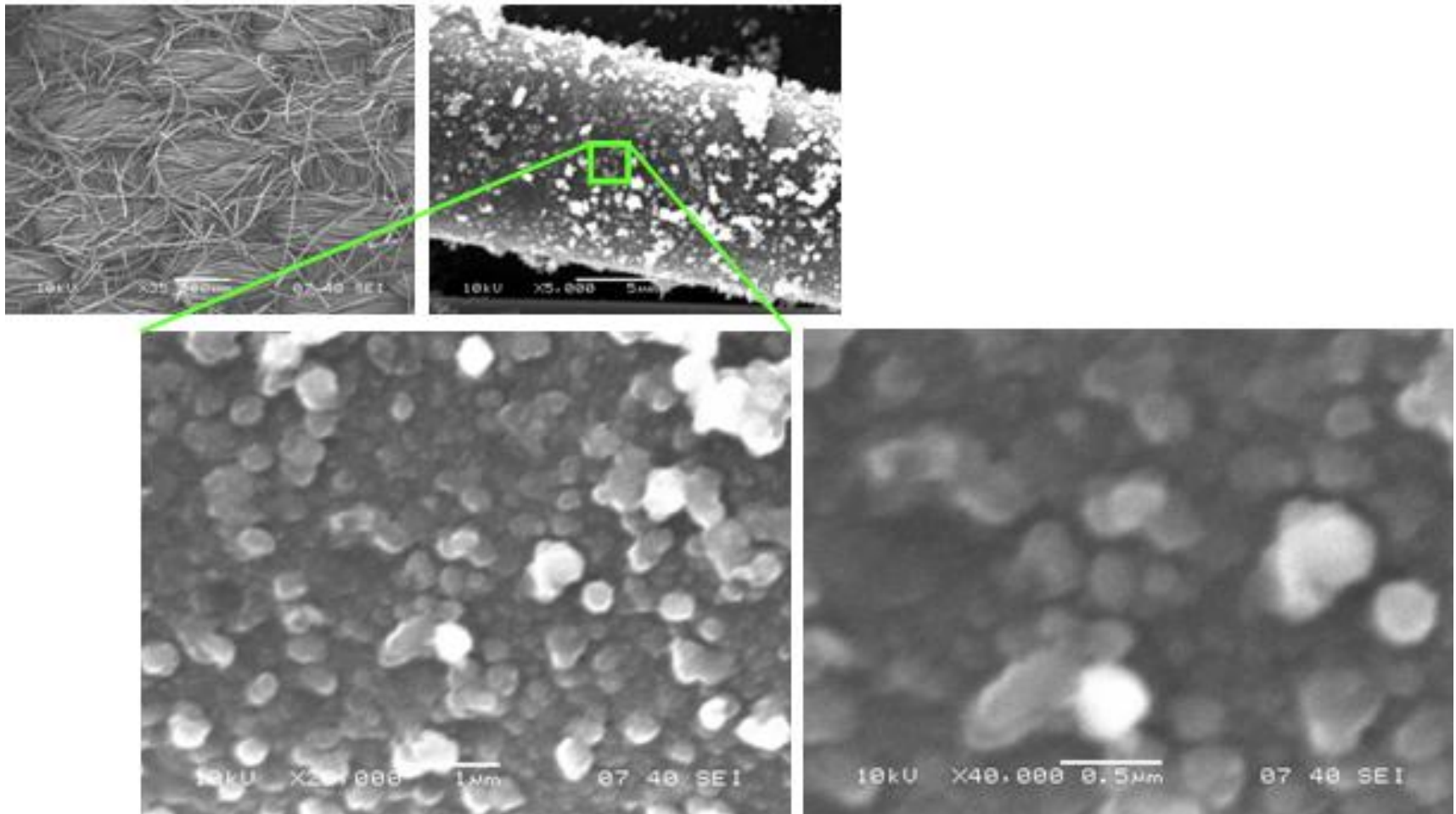
Crosslink

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# Electropolymerization Process

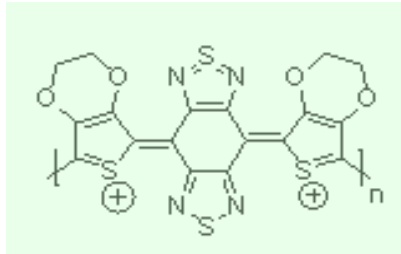


# SEM Images of Electropolymerized Poly(BEDOT-BBT) on AC Fabrics

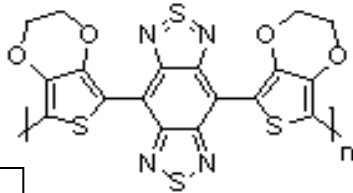
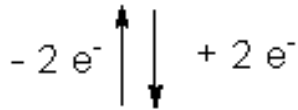


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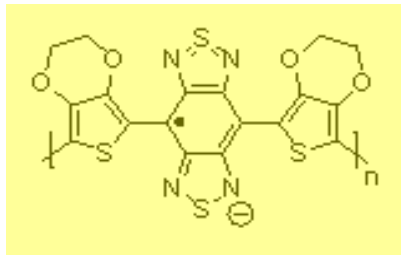
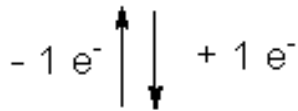
# CV of Poly(BEDOT-BBT) Derivatives



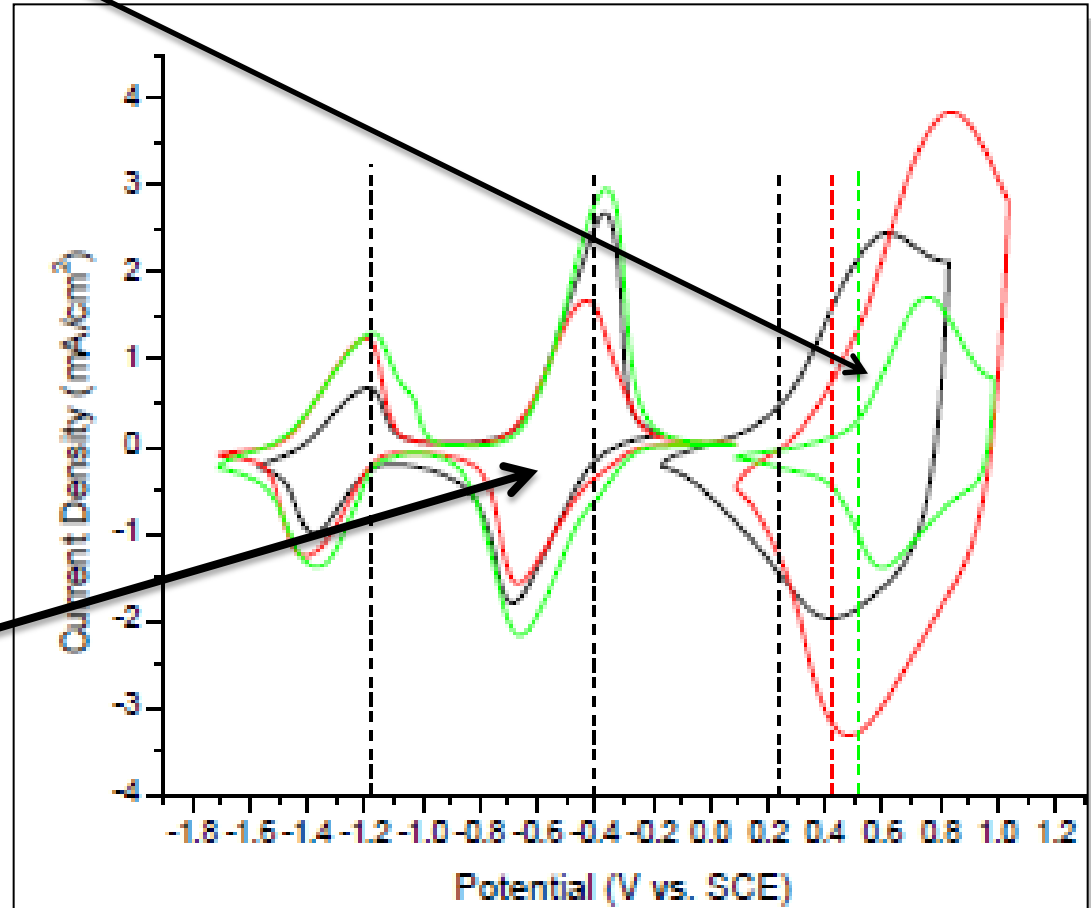
p - doping



n - doping



— P(BEDOT-BBT) ~-0.6 eV  
 — P(BProDOT-BBT) ~-0.8 eV  
 — P(BProDOTMe<sub>2</sub>-BBT) ~-0.9 eV  
 Scan Rate = 50 mV/s



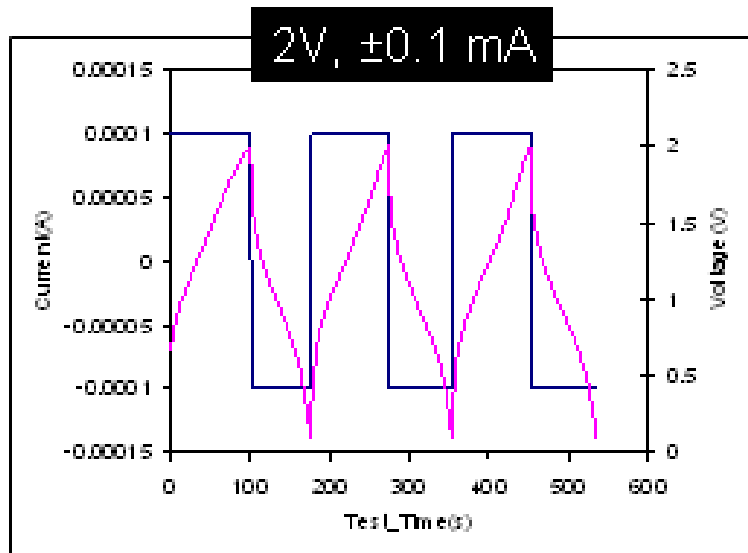
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# Type III Coin Cells

## Poly(BEDOT-BBT) Electrodes

- Both positive and negative electrodes are Poly BEDOT-BBT on Gold-SS disk
- EMI-Im electrolyte

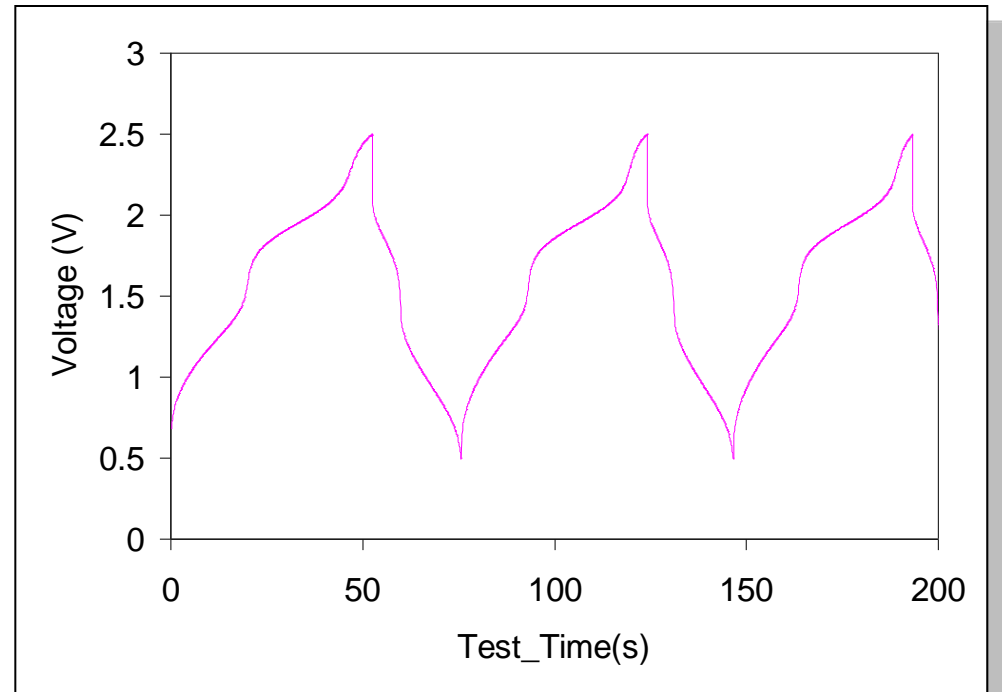
Voltage (V)	D/C Current (mA)	ED (Wh/Kg Electrode)	PD (W/Kg Electrode)
1	0.1	0.8	199.24
1.5		6.21	320.71
2		8.54	382.18
	1	6.67	3529.41



2.0 Volt Operating Window

# Type IV Devices

- Metallic PAC 1003 layer as the positive electrode and n-dopable poly(BEDOT-BBT) as the negative electrode
- PAC1003 dip coated
- poly(BEDOT-BBT) electrodeposited



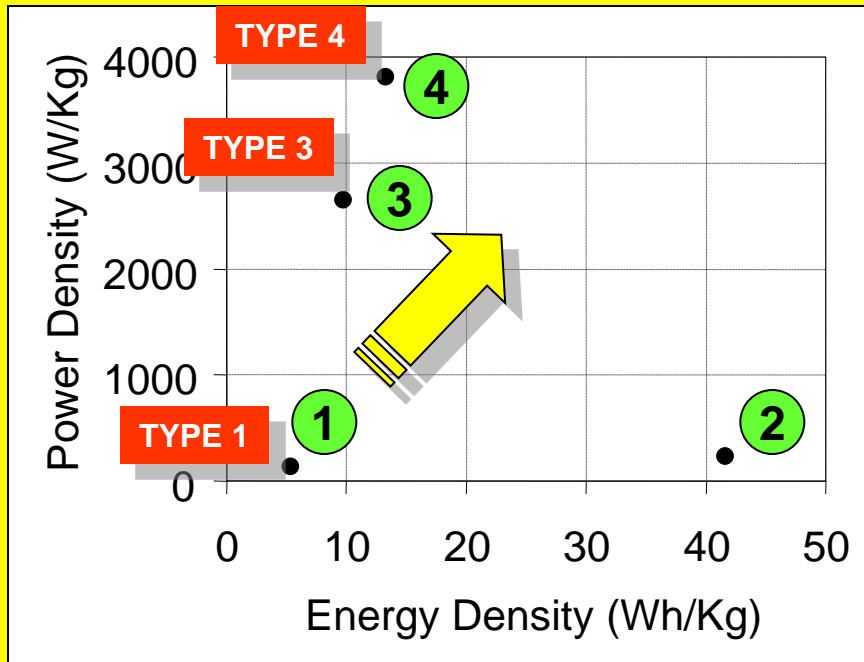
2.5 V Operating Window

# Discharge Performance of Type IV Coin Cell Using Metallic PAC 1003 and Poly(BEDOT-BBT)

Voltage (V)	D/C Current (mA)	ED (Wh/Kg Electrode)	PD (W/Kg Electrode)	Sp.Cp. (F/g Electrode)
2.0 / 0.1	1	12.69	3160	25.3
<b>2.0 / 0.5</b>	1	8.28	3440	26.5
2.5 / 0.1	1	13.78	3550	17.2
<b>2.5 / 0.5</b>	1	13.25	3800	23.8

# Ragone Plot

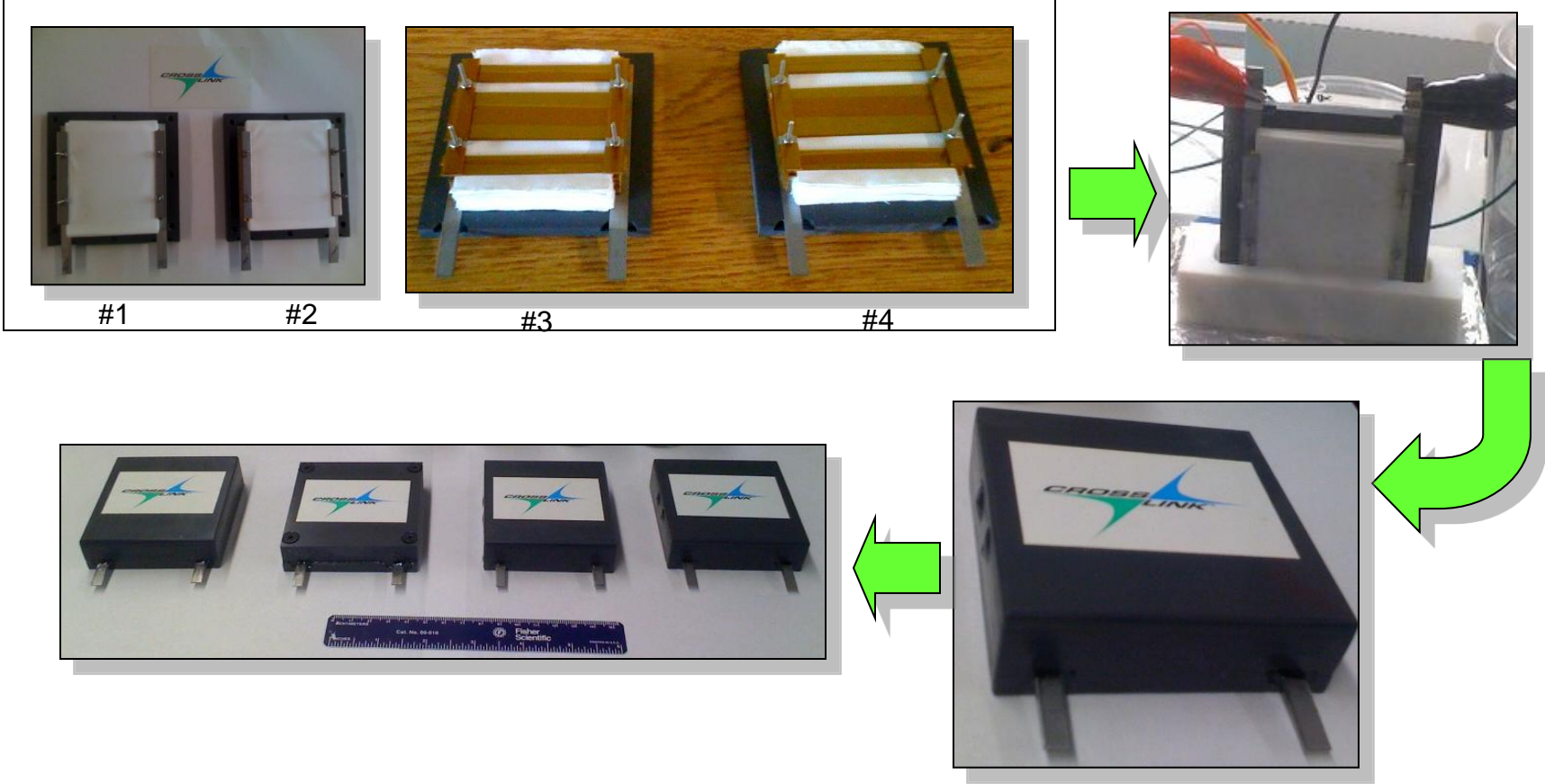
## Coin cell performance/EMI-IM



\*Energy and power densities are calculated based on polymer mass

- 1** **Metallic PAC 1003** (TYPE 1)  
5.38 Wh/Kg, 129.7 W/Kg @ 1.5 V, 0.1 mA
- 2** **Activated Carbon Fabrics** (TYPE 1)  
41.64 Wh/Kg, 230.08 W/Kg @ 3 V, 10 mA
- 3** **Poly BEDOT-BBT** (TYPE 3)  
9.7 Wh/Kg, 2650 W/Kg @ 2.5/0.5V, 1 mA
- 4** **Metallic PAC 1003/Poly BEDOT-BBT** (TYPE 4)  
13.2 Wh/Kg, 3810 W/Kg @ 2.5/0.5 V, 1 mA

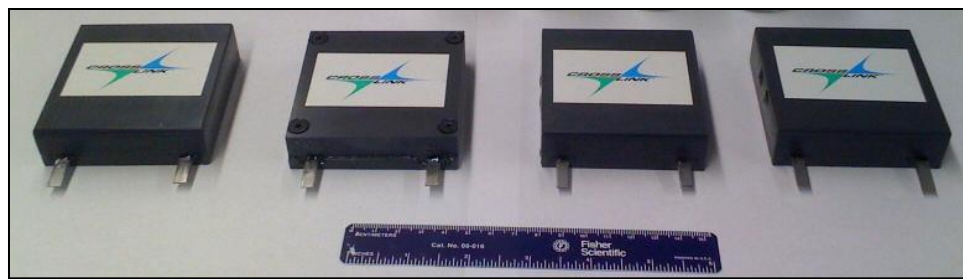
# 64 Cell-Stacks (TYPE IV) Production Procedure



# 64 Cell-Stacks (TYPE IV) Characterization

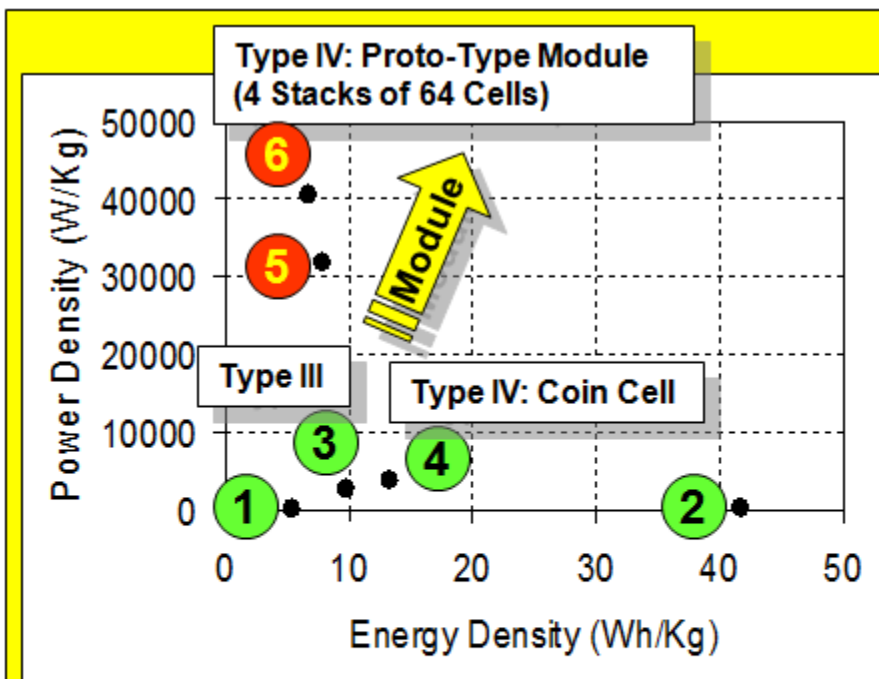
Stacks and Module	Voltage (V)	Current (A)	Capacitance (F)	DC ESR (Ohm)	Charge Time (s)
1	2.1/0.1	2	5.5	0.069	5.5
2	2.1/0.1	2	3.9	0.075	3.9
3	2.1/0.1	2	5.2	0.094	5.2
4	2.1/0.1	2	5.5	0.094	5.5
<b>Module 1</b>	<b>4.1/0.1</b>	<b>3.5</b>	<b>4.7</b>	<b>0.056</b>	<b>5.5</b>

\*Charging energy of Module:  
**44J @ 4.1V, 3.5A**



# Ragone Plot

Prototype Module, Stack and Coin Cell Performance  
Module 10 x Power Density Enhancement



\*Energy and power densities are calculated based on polymer electrode  
\*\*Fabricated in a glove box

## Coin Cells: Discharging Process

- 1 **Metallic PAC 1003**  
5.4 Wh/Kg, 129.7 W/Kg @ 1.5 V, 0.1 mA
- 2 **AC Fabrics. EMI-Im/PC**  
41.6 Wh/Kg, 230.1 W/Kg @ 3 V, 10 mA
- 3 **Poly BEDOT-BBT**  
9.7 Wh/Kg, 2653.1 W/Kg @ 2.5/0.5V, 1 mA
- 4 **Metallic PAC 1003/Poly BEDOT-BBT**  
13.2 Wh/Kg, 3806.9 W/Kg @ 2.5/0.5 V, 1 mA

TYPE 3

TYPE 4

## 64 Cells-Stack and Module: Charging Process

- 5 **Metallic PAC 1003/Poly BEDOT-BBT: 64 Cells**  
7.8 Wh/Kg, 3195.5 W/Kg @ 2.1/0.1 V, 2A
- 6 **Metallic PAC 1003/Poly BEDOT-BBT: 4 Stacks**  
6.7 Wh/Kg, 40602.6 W/Kg @ 2.1/0.1 V, 2A

TYPE 4

Stack

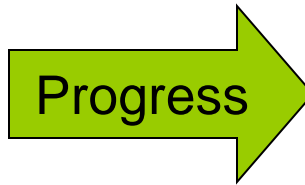
TYPE 4

Module

# Prismatic Cell Design TYPE IV EMI-IM

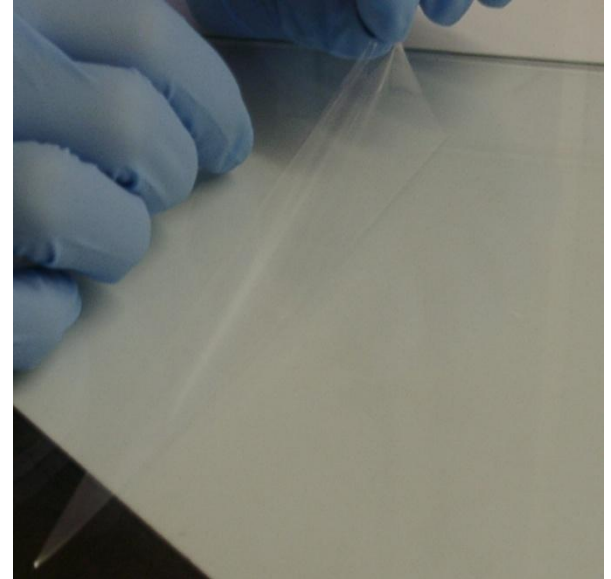


Plastic Case  
3"x3"x1" (9 cu.in.)  
200 g



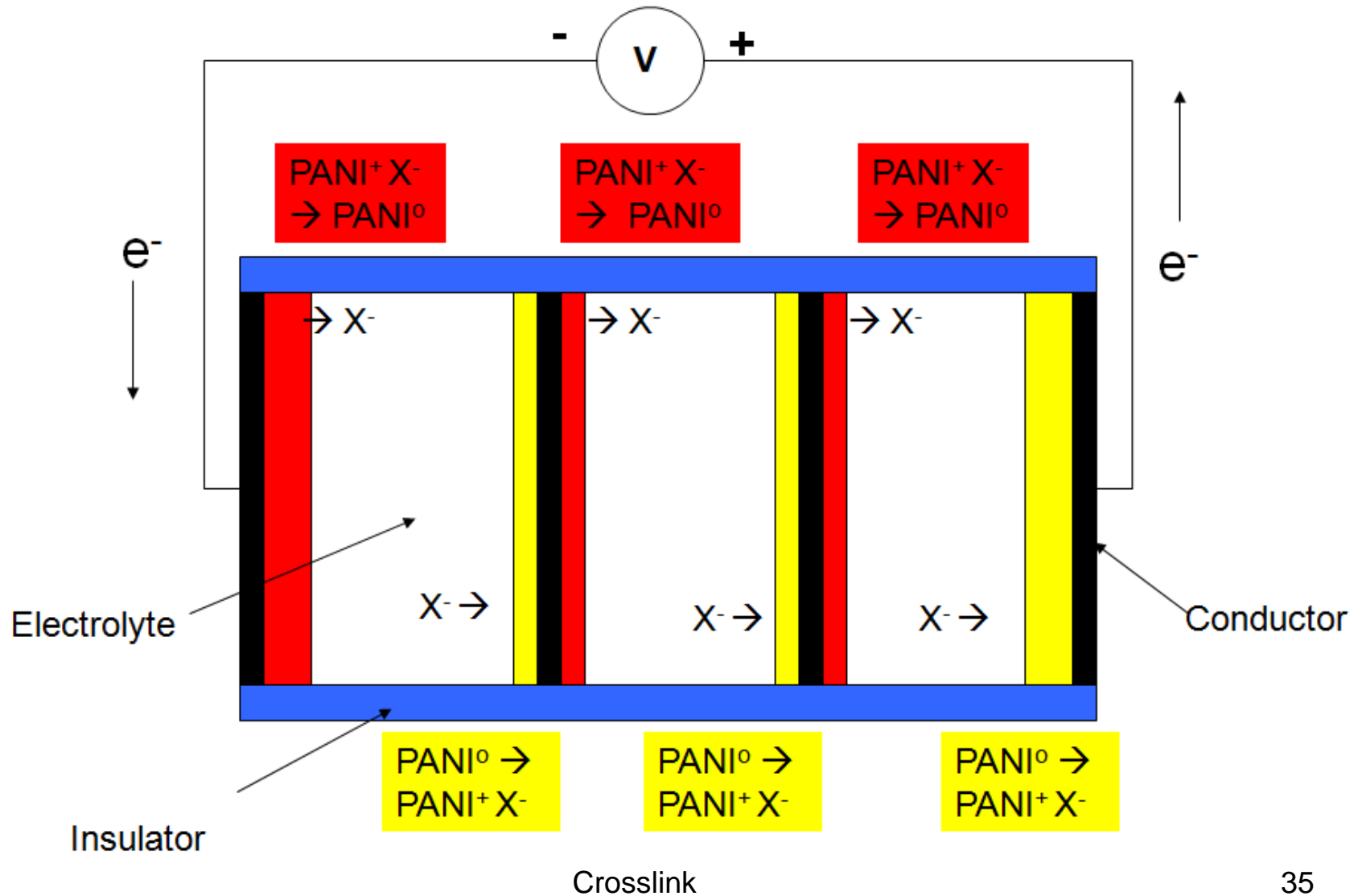
Pouch Design  
2.2"x2.3"x0.75" (3.8 cu.in.)  
89 g

# Polymer Gel Electrolyte

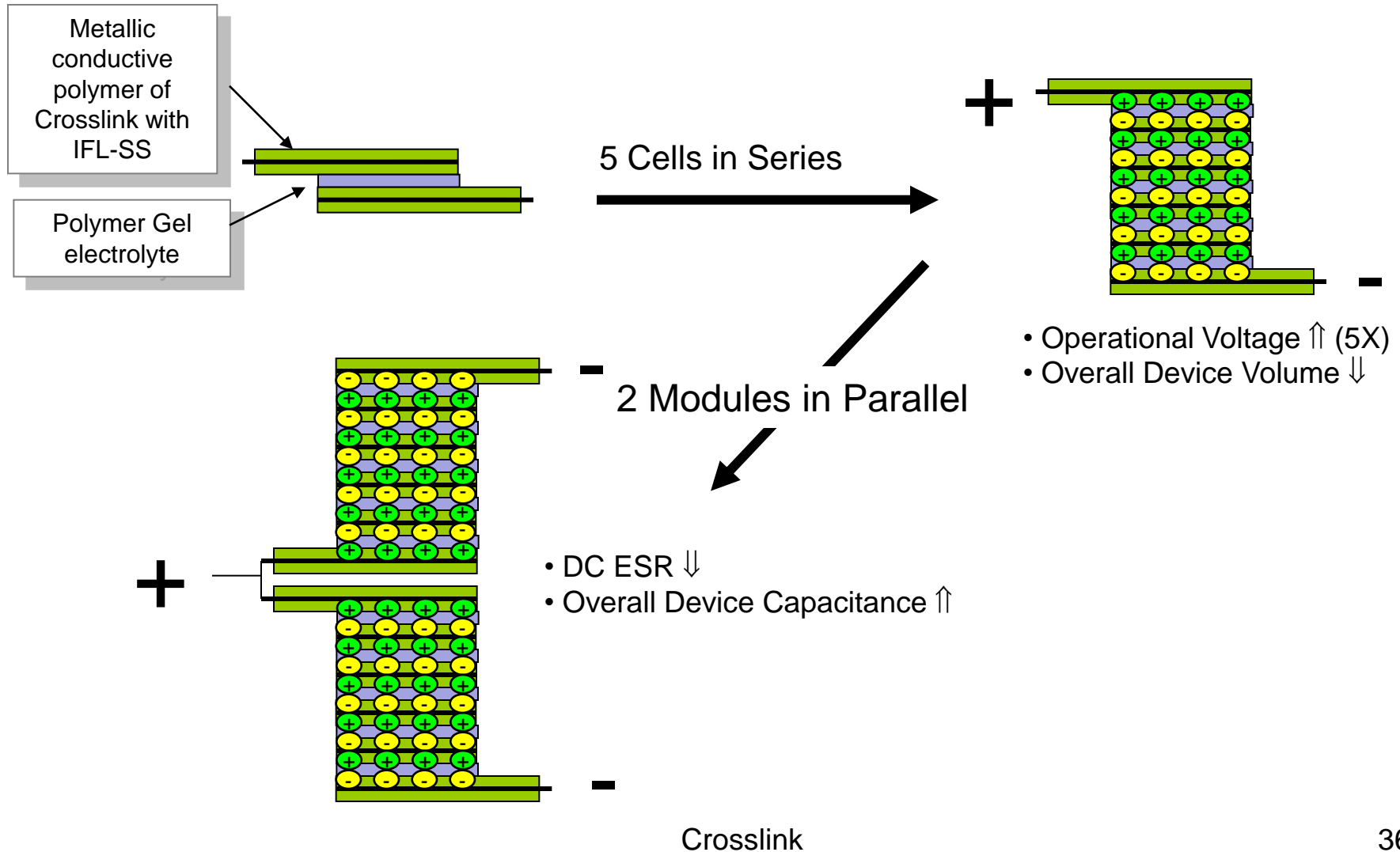


- Development of Ionogel Solid State Electrolyte
  - Ionic liquid in polymer gel matrix
    - Low Leakage Risk
    - Reasonable ESR values
    - Enables Bi-Polar Cell Configuration

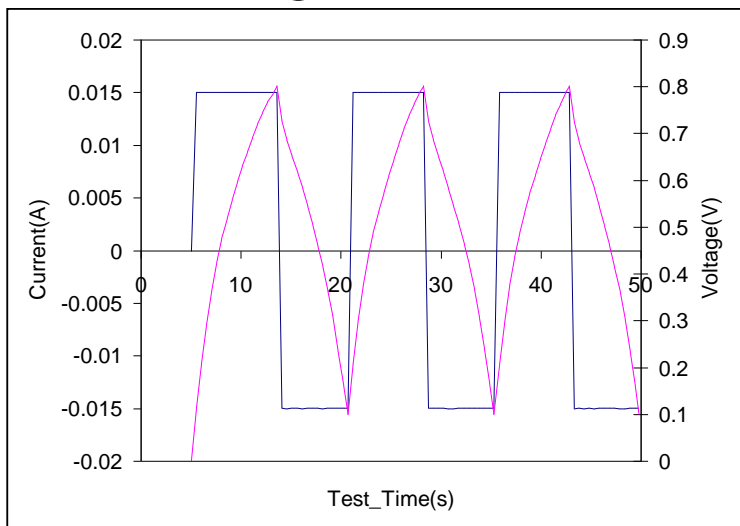
# Bipolar Type I PANI Cell



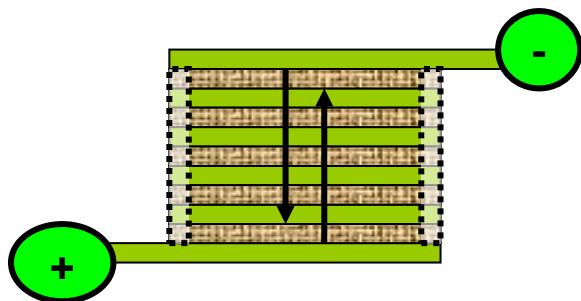
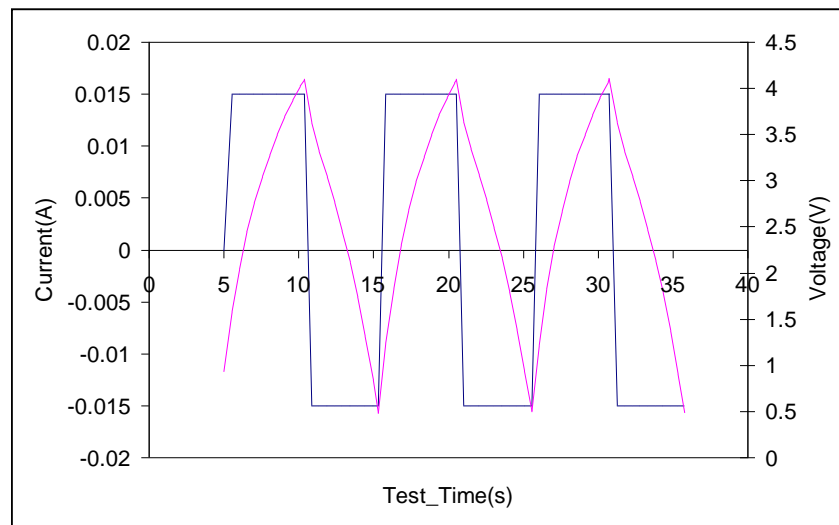
# Type I Bipolar Supercapacitor Design



## Single Cell

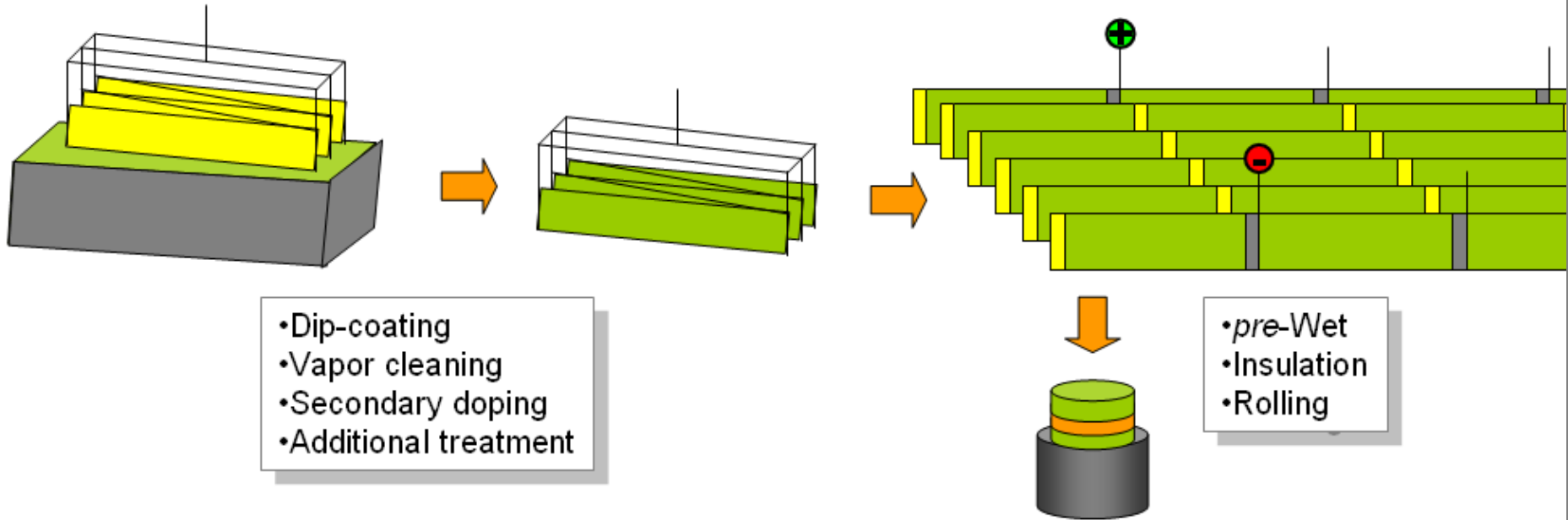


## 5 Cell Bipolar Configuration

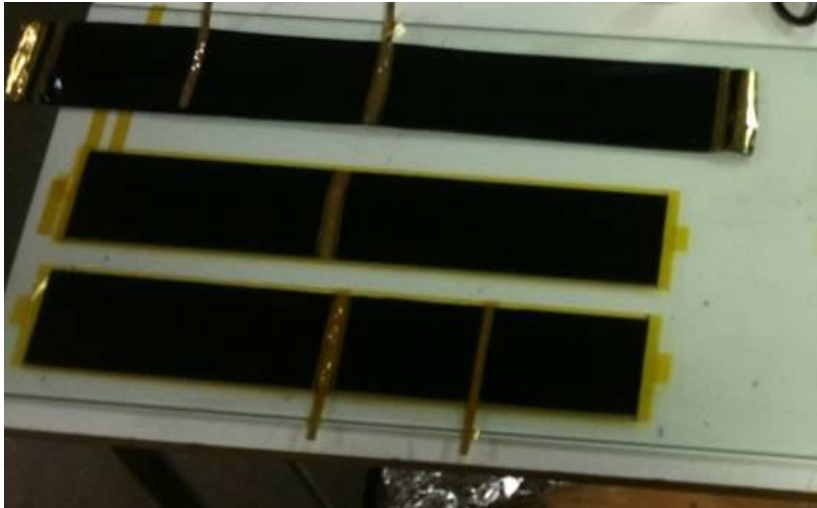


**97.78 J/Kg (80.17 J/Kg, DC)**  
**923 W/Kg**  
**4.1V, 0.97 Ohm, 5s**

# TYPE I Process Schematic



# Prototype Manufacturing



Crosslink

# Fabricated Device

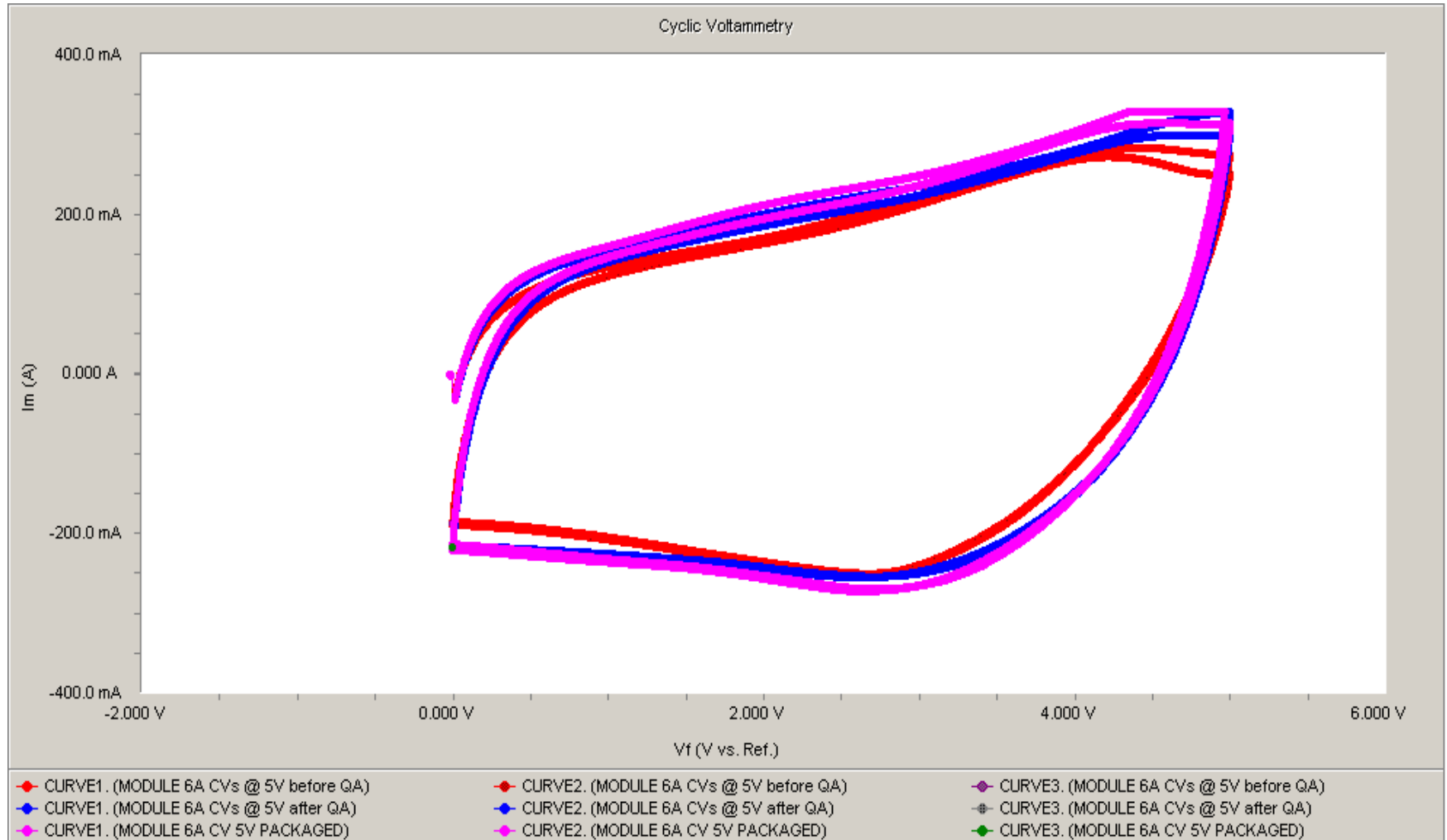
- Rolled capacitor ready for insertion into canister
- ~1.8 cu in volume



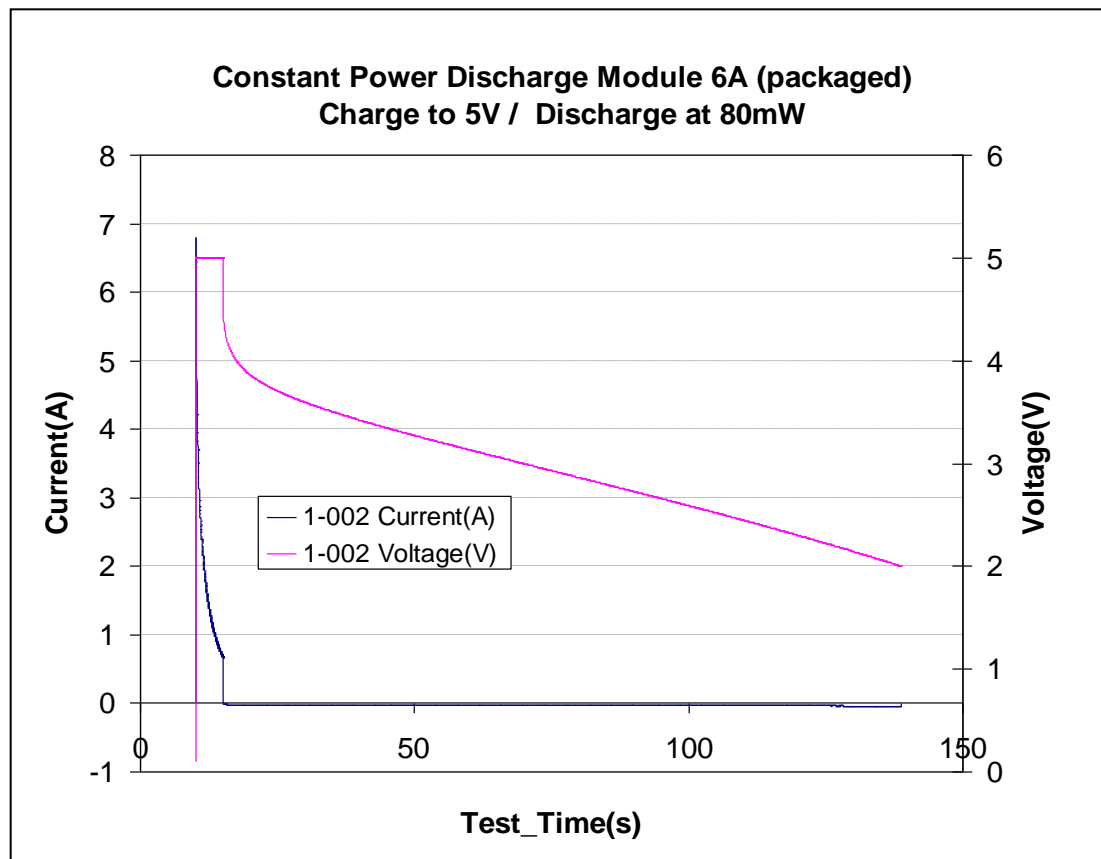
- Completed device and capacitor holder
- ~1.05 cu in volume

Crosslink

# CV of Rolled Module 6.16F; 545 mOhm



# 5 Seconds Charge to 5 Volts Constant Power Discharge



# Solid State Bipolar Module Performance

- Targets Achieved
  - Power densities 4900-5000 W/Kg
  - Charging time less than 5s
  - Volumetric capacity
  - Sufficient energy density
- Future Effort
  - Scale up
  - Manufacturing
  - Commercialization

# Acknowledgements



Electrolytic Supercapacitor Polymers for FCS  
(Future Combat Systems) Applications  
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Reynolds'  
Research Group



The Center for Applied Science and  
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