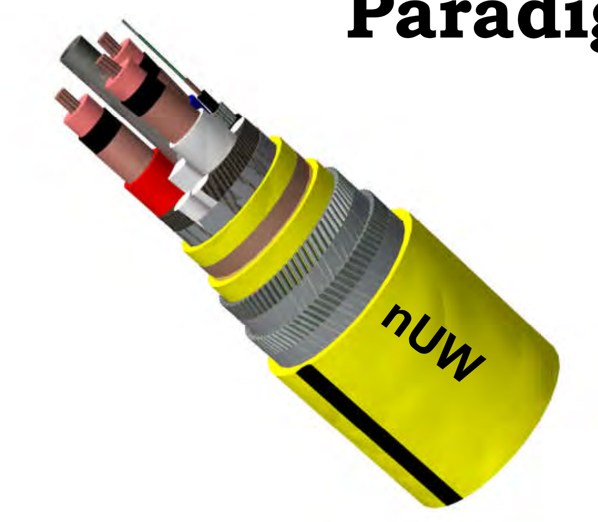
Paradigm Change in Electrical Conductors



nanoUmbilical Workshop

Participants:
NanoRidge Materials: Dean Hulsey, Lori Jacob
Rice University: Enrique V. Barrera, Pulickel Ajayan, Padraig Maloney, Yao Zhao, Divya Chakravarthi
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Duco, Inc.: David Madden

Acknowledgements: DOE RPSEA, Chevron

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Outline

1. Nanocomposites, Approaches and Applications
2. Polymer Nanotube Umbilical: A High Current Density Conductor
3. Motivation and Concerns for a Nanotube Based Conductor
4. Approach to Producing a PNU
5. Test Methods and Parallel Characterization
6. Current Outcomes

Opportunities for Augmenting Composites with Nanotubes

• Low concentrations of nanotubes for matrix enhancement in fiber reinforced laminate composites. (Improvements have been demonstrated)

Z-axis enhancement, high temperature use, improved toughness.

• Nanotube dispersion in resins and the study of viscosity changes with degree of dispersion for nanotube only composites. (Viscosity Modification)

Must overcome viscosity increases and dispersion problems.

• Interpenetrating nanotube networks. (Demonstrated)

Low cost approach that does not require nanotubes to get unentangled.

• Resin formulation for hybrid polymer formation at both low and high nanotube concentrations. (Demonstrated and high conc. underway)

Fully integrated nanotube composites. (Demonstrated)

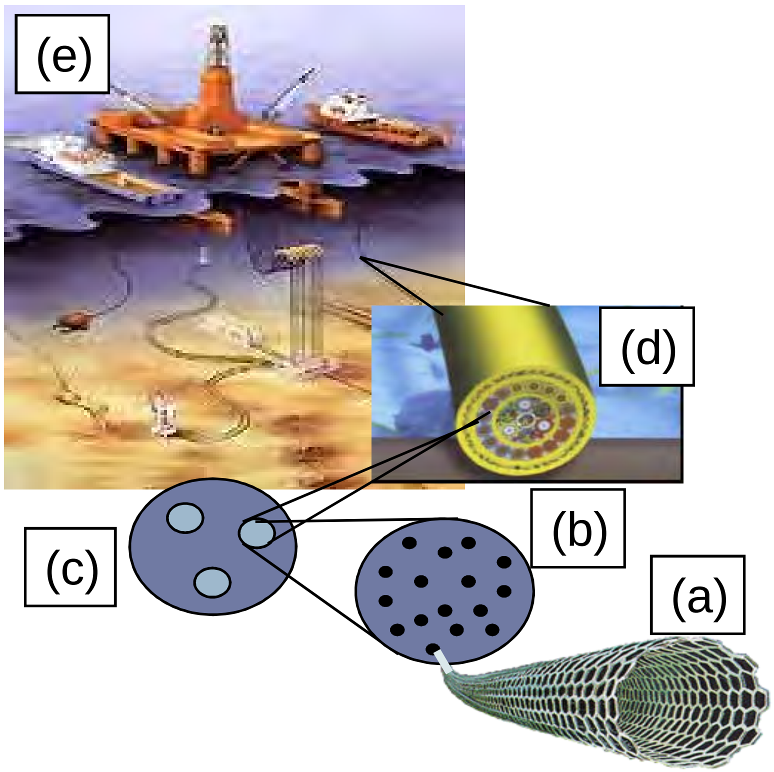
• Cold formable composites that deform like thermoplastics or aluminum.

A paradigm change in the way we make composites. (Demonstrated)

Polymeric Applications and Drop-off Technologie

1. Electrostatic Discharge Materials (ESD)
2. Lightning Strike Protection
3. Conducting Wires, etc.
4. Multifunctional Composites
5. Reinforced commodity plastics

Polymer Nanotube Umbilical



The PNU is a polymer-nanotube wire that can carry high power to the sea floor.

(a) A SWCNT as the conducting species for the conductor wiring,

(b) Cross-section of a Polymer-nanotube Umbilical (PNU) where nanotubes are dispersed in a polymer,

(c) Cross-section for a three phase power cable,

(d) The umbilical cable that provides power lines to the seafloor, and

(e) The offshore Platform and subsea system.

Team: Rice University, NanoRidge Materials, Inc., Technip, USA and DUCO, Inc. (all are Houston based institutions)

Producing a Conducting Wire or Fiber

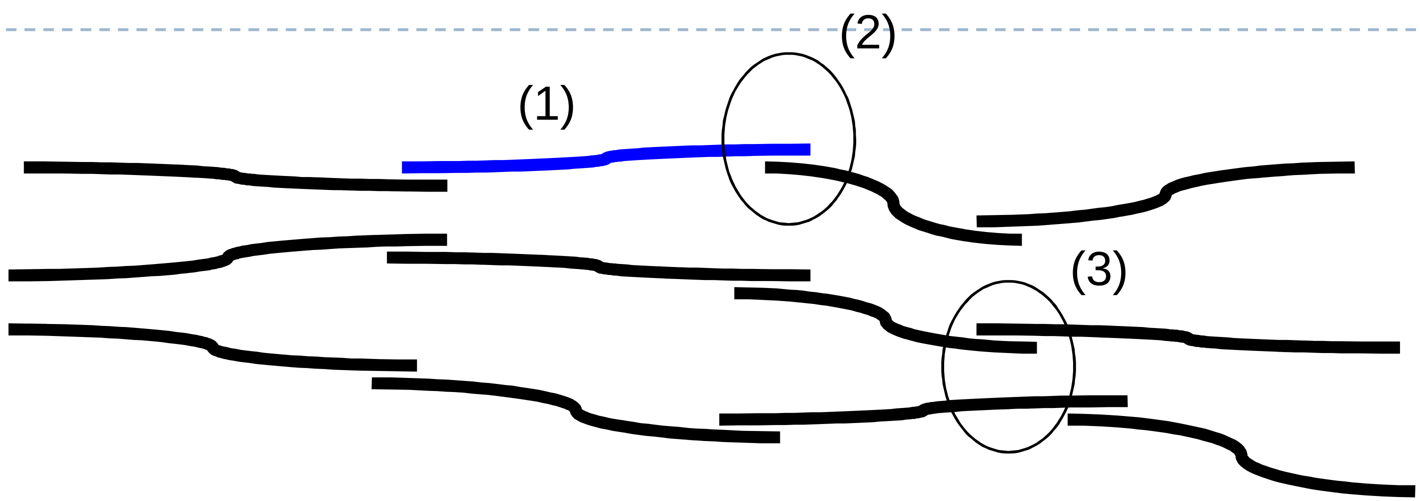
Think about a 50K Tow of fibers and how impressive it is to bring together 50,000 individual fibers.

Consider a 10 wt.% SWNT loading in a polymer which would corresponds to about 300,000,000 individual nanotubes brought together in the polymer

-a 300,000K or 300M Tow product.

A large number of nanotubes produces numerous pathways for electrical conduction.

Directed Nanotube Network (DNN)



A schematic depicting a network of (1) m-SWCNTs that are arranged to promote maximum electrical conduction. The network is made up of (2) connected nanotubes that provide for *ballistic transport* along the nanotube length and *resonant quantum tunneling* from one nanotube to the other. Gap distances between the various chains prevent electron hopping from one pathway to the next. m-SWCNTs may vary in length but the (3) connections will be optimized for low contact resistance.

Nanotubes are nanometers (1.4nm) in diameter and microns in length.
Electrical conduction is as high to better than copper.
Mechanical properties include: UTS: ~50-150GPa/Elastic Modulus: 1 TPa

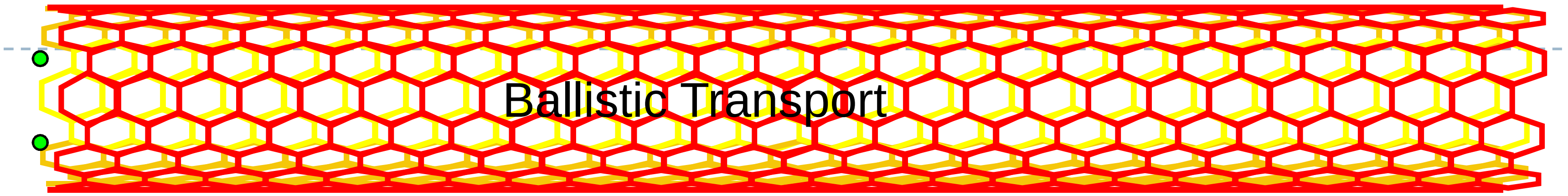
Nanotube Conductivity

http://www.nano.gov/html/news/SpecialPapers/Nanotubes%20For%20Power%20Transmission%20Line%20MaterialsA.htm.
This reference cites the following:

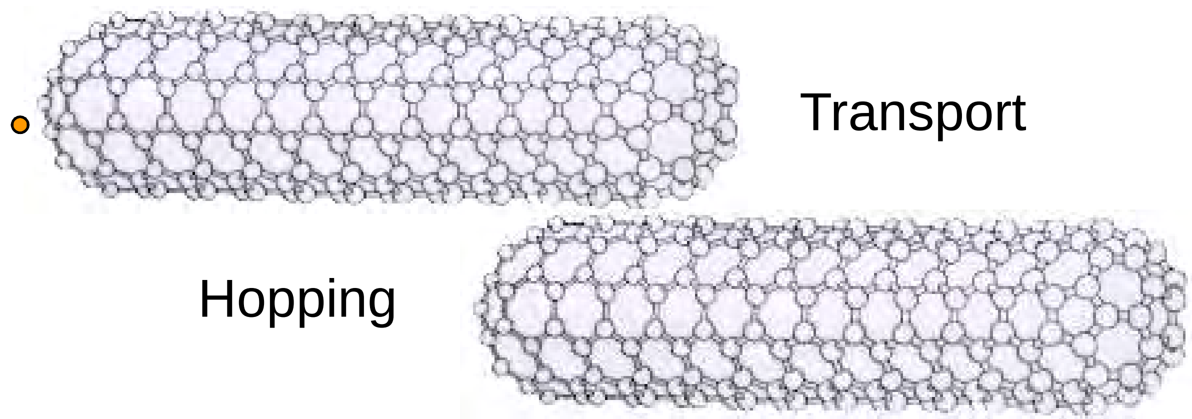
"This high conductivity derives from the highly efficient transmission of electrons down the individual tubes acting as quantum wave guides in one direction, and the efficient resonant quantum tunneling of the electrons from tube to tube as the current passes down the fiber."

Several researchers have demonstrated that one single wall carbon nanotube can carry currents up to **20 microamperes**.

Electron Transport Mechanisms



Ballistic conduction allows electrons to flow through the material without collisions. The collisions cause the electrons to slow down, and cause the material to heat, effectively creating resistance in the material.

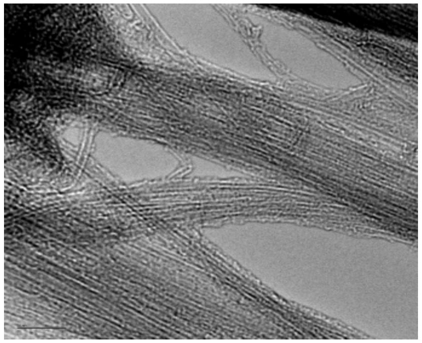


Hopping conduction allows electrons to jump from one nanotube to another. Short contact lengths limit electrons from jumping back and forth.

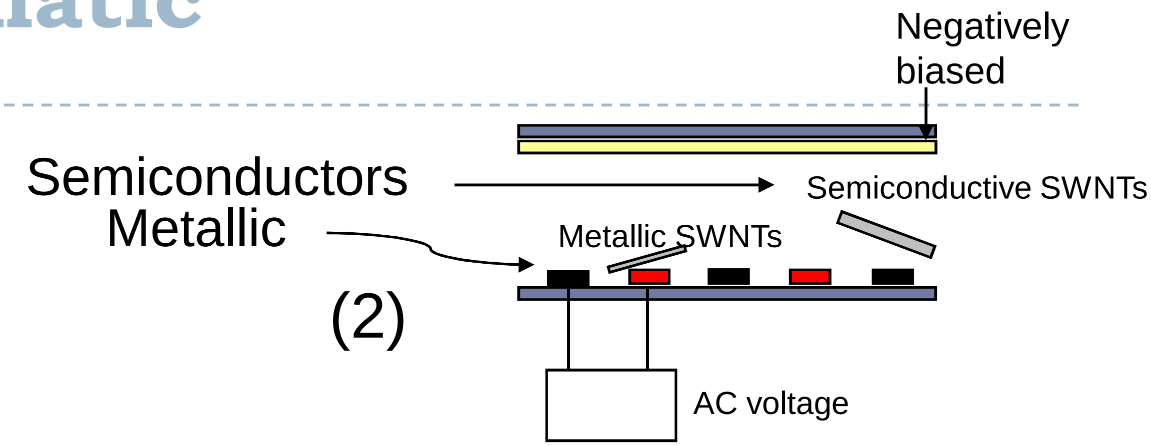
To maximize conduction, Metallic Nanotubes are needed.

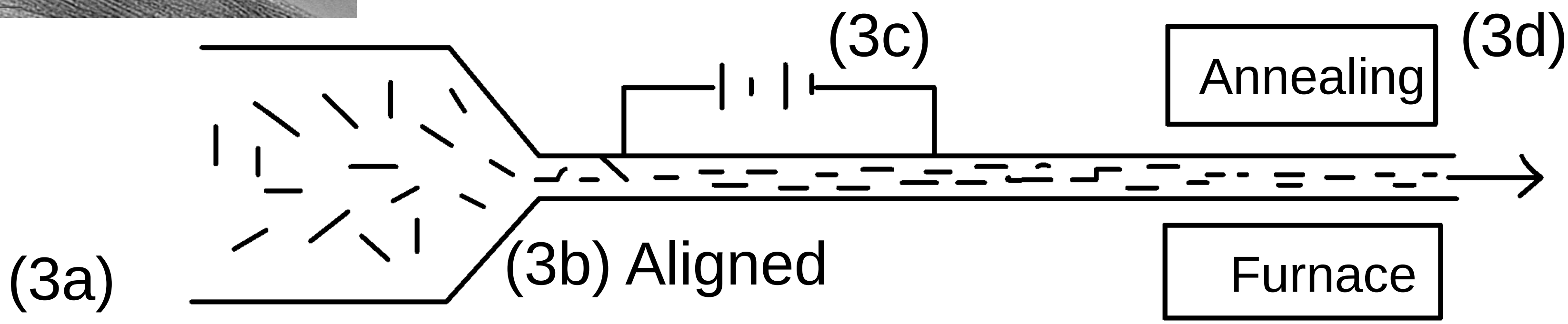
Alper Buldum and Jian Ping Lu, Phys. Rev. B 63, 161403 R (2001).

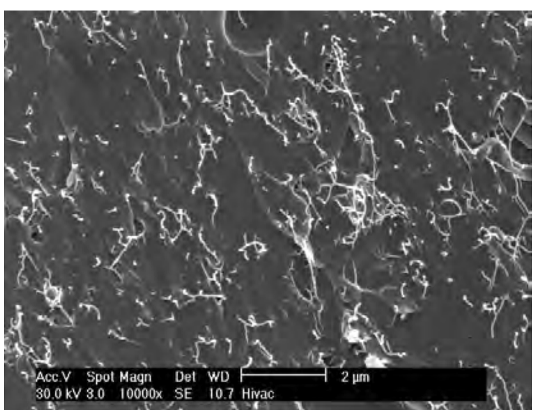
Process Schematic

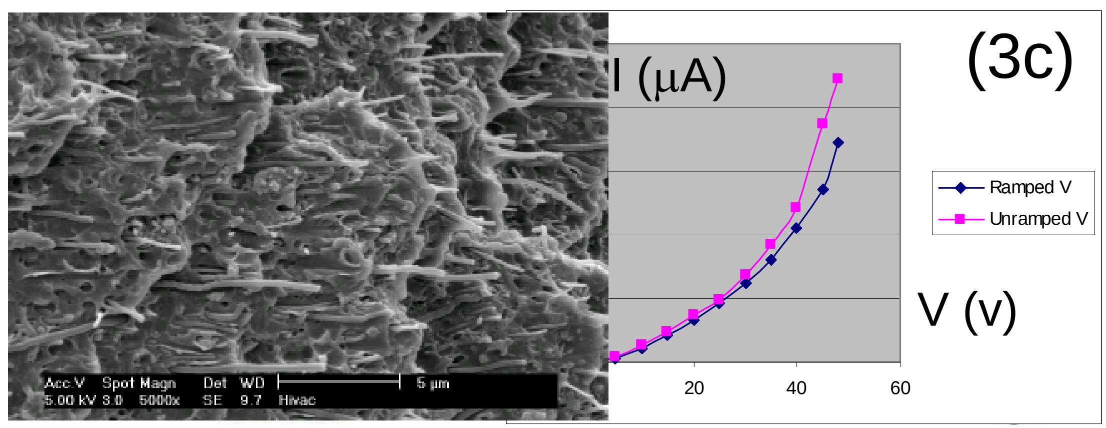


(1)









Taking a Similar Approach

Self-sorting of Metallic Carbon Nanotubes for High Performance Large Area Low Cost Transparent Electrodes

Zhenan Bao, Department of Chemical Engineering, Stanford University

“The use of carbon nanotubes (CNT) for transparent conducting electrodes in photovoltaic applications.

In order to decrease the sheet resistance, both the electronic properties of the CNTs – namely the tube conductivity and tube-to-tube contact resistance – and the sheet morphology have to be controlled.

Reach this target through the development of solution-based processes to simultaneously separate metal from semiconductor nanotubes using specific surface functional groups (such as amino- and phenyl-silanes on SiO_2 substrates) and control the alignment of the CNTs into bundles during spin-coating deposition.

CNT doping methods are also being investigated to further improve the sheet conductivity.

http://gcep.stanford.edu/research/factsheets/metallicnanotubes.html

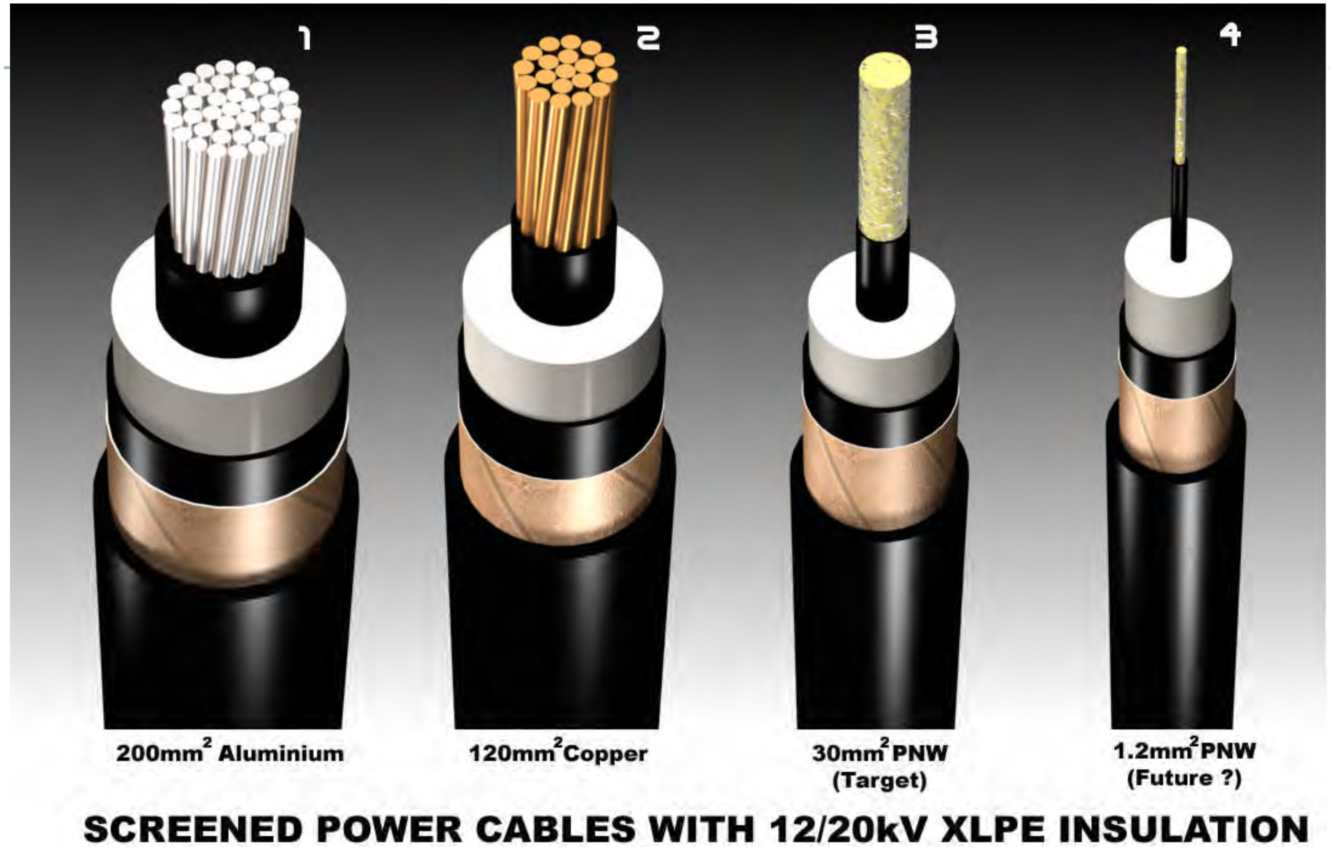
Deliverables

(1) Bridge the gap between engineering science and manufacturing technology to produce a piece of wire.
The wire conductor will be a polymer-Nanotube composite that is half the diameter of a Cu conductor that can carry 500 amps at the same voltage used for the Cu conductor.

(2) Enable engineering aspects of the wire such as crimping, terminations, splicing, and augmentation.

(3) Develop as a low cost conductor with a broad range of uses.

PNU compared to Cu Wire & Cu Stranded Wire



Overall objective is to design, build and test an engineering prototype of a working ultra-high conductivity “wire” that could in later stages be incorporated into an umbilical exceeding 100 miles in length and called upon to deliver up to 10 MW at up to 36 kV with an operating envelop ranging from -1 to 121ºC (~ 30 – 250ºF) and pressure from
0 to 31.03 MPa (0 to 4500 psi).

Picture compliments of Dave Madden

Concerns

1. Starting purity plays a role.
2. Obtaining separated nanotubes.
3. Level of disentanglement plays a role.
4. Nanotube type is important for two reasons.
   - Probabality of metallic to metallic plays a role.
   - Nanotube to Nanotube contact is important.
   - (S to M (10^0), S to S (10^1), M to M (10^3))
5. Properties produced in the laboratory are not what can be produced in manufacturing.
   - Ropes vs. single nanotubes plays a role.
   - Polymer between the nanotubes plays a role.
     - Wire diameter plays a role.

5. Conditions of the electric fields play a role.
6. Final annealing plays a role.

Improving Percentage of Metallic Nanotubes

(2) Higher percentage m-SWNTs ensures similar type NT-NT contacts. Current nanotube compositions have some metallic to semiconductor contacts (not optimal contacts).

With unseparated nanotubes:

First nanotube is metallic	(1/3 chance is metallic)
Second nanotube is metallic	(1/3 chance is metallic)
Chance of metallic to metallic:	(1/9)

With current sorted nanotubes:

First nanotube is metallic	(2/3 chance is metallic)
Second nanotube is metallic	(2/3 chance is metallic)
Chance of metallic	(4/9 chance, improved by 2)

With proposed enhancement:

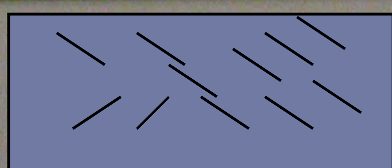
First nanotube is metallic	(8/9 chance is metallic)
Second nanotube is metallic	(8/9 chance is metallic
Chance of metallic	(64/81 chance, improved by 7)

Resulting Diameters

PE w/10 wt% SWNTs/Processed by melt spinning.

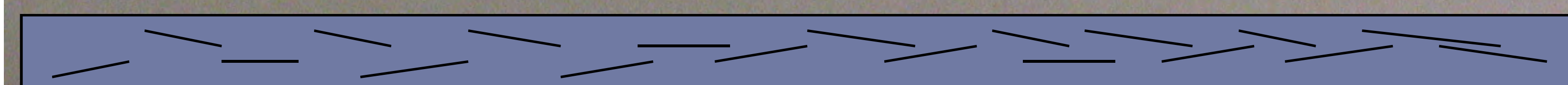
Various diameters have been produced with smaller diameters being more optimal at this time.

Smaller diameters lead to smaller distance between nanotubes.



Explanation for thinner wire, better conductivity

Keep the same volume, 1/2 diameter, ¼ cross section area, 4 x length (a cost savi



Better alignment in uniaxial direction

The Role of Concentration and Shear

High Mechanical Performance Composite Conductor: Multi-Walled Carbon Nanotube Sheet/Bismaleimide Nanocomposites By Qunfeng Cheng, Jianwen Bao, JinGyu Park, Zhiyong Liang,* Chuck Zhang, and Ben Wang, Adv. Funct. Mater. 2009, 19, 1–7.

"Applying mechanical stretching and prepregging (pre-resin impregnation) on initially randomly dispersed, commercially available sheets of millimeter-long MWNTs leads to substantial alignment enhancement, good dispersion, and high packing density of nanotubes".
"The nanocomposites demonstrate high electrical conductivity of 5 500 S cm^{-1} along the alignment direction". Concentration of nanotubes was 60 wt% MWNTs.

High concentrations and shear can enhance conduction conditions.

Electric Field Specifications

A review and analysis of electrical percolation in carbon nanotube polymer composites Wolfgang Bauhofer, Josef Z. Kovacs,
Composite Science and Technology, 69 (2009) 1486-1498.

Review of 121 papers on electrical properties.
Results from the review: (1) Dispersion is very important.
(2) Entanglements reduce conductivity (up to 50 times (MWNTs))
(3) Electric fields align nanotubes and enhance attractive forces between nanotubes.

400 x 10^{-6}m (0.4 mm) separation between electrodes for electric field use.

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Electric Field Alignment

Electric-field assisted assembly and alignment of metallic nanowires
Peter A. Smith, Christopher D. Nordquist, Thomas N. Jackson, and Theresa S. Mayera, *Benjamin R. Martin, Jeremiah Mbindyo, and Thomas E. Mallouk*

"This letter describes an electric-field assisted assembly technique used to position individual nanowires suspended in a dielectric medium between two electrodes defined lithographically on a SiO2 substrate. During the assembly process, the forces that induce alignment are a result of nanowire polarization in the applied alternating electric field. This alignment approach has facilitated rapid electrical characterization of 350- and 70-nm-diameter Au nanowires, which had room-temperature resistivities of approximately 2.9 and 4.5 x 10- 6 ohm cm".

(5 micron wide electrodes)

http://research.chem.psu.edu/mallouk/articles/APL01399.pdf

Electric Field Alignment

Aligned Single-Wall Carbon Nanotube Polymer Composites Using an Electric Field CHEOL PARK, JOHN WILKINSON, SUMANTH BANDA, ZOUBEIDA OUNAIES, KRISTOPHER E. WISE, GODFREY SAUTI, PETER T. LILLEHEI, JOYCELYN S. HARRISON, Journal of Polymer Science: Part B: Polymer Physics, 44 (2006) 1751-1762.

Use of electric fields 0.03 wt% Hipco.

Electrodes placed at a separation distance of 2.3 mm. In the electric field for 10 minutes. 10^{-6} S/cm

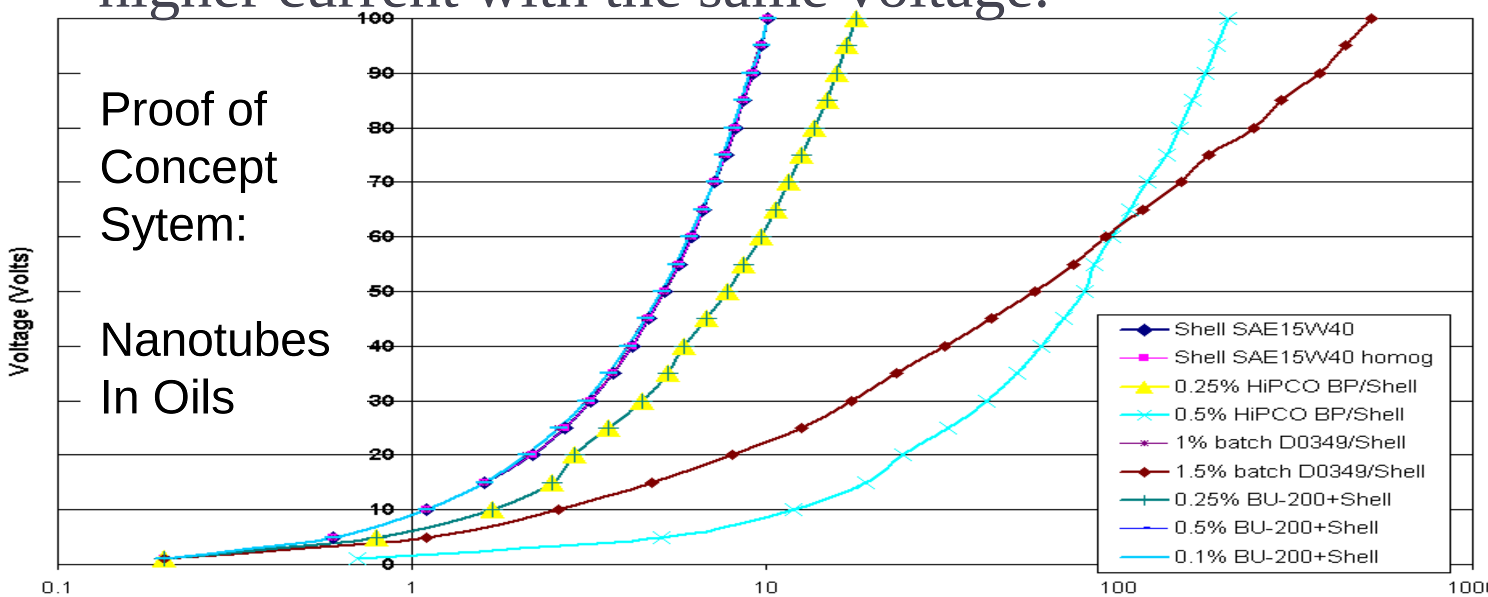
Self-Assembled Linear Bundles of Single Wall Carbon Nanotubes and Their Alignment and Deposition as a Film in a dc Field Prashant V. Kamat, K. George Thomas, Said Barazzouk, G. Girishkumar, K. Vinodgopal, and Dan Meisel†.

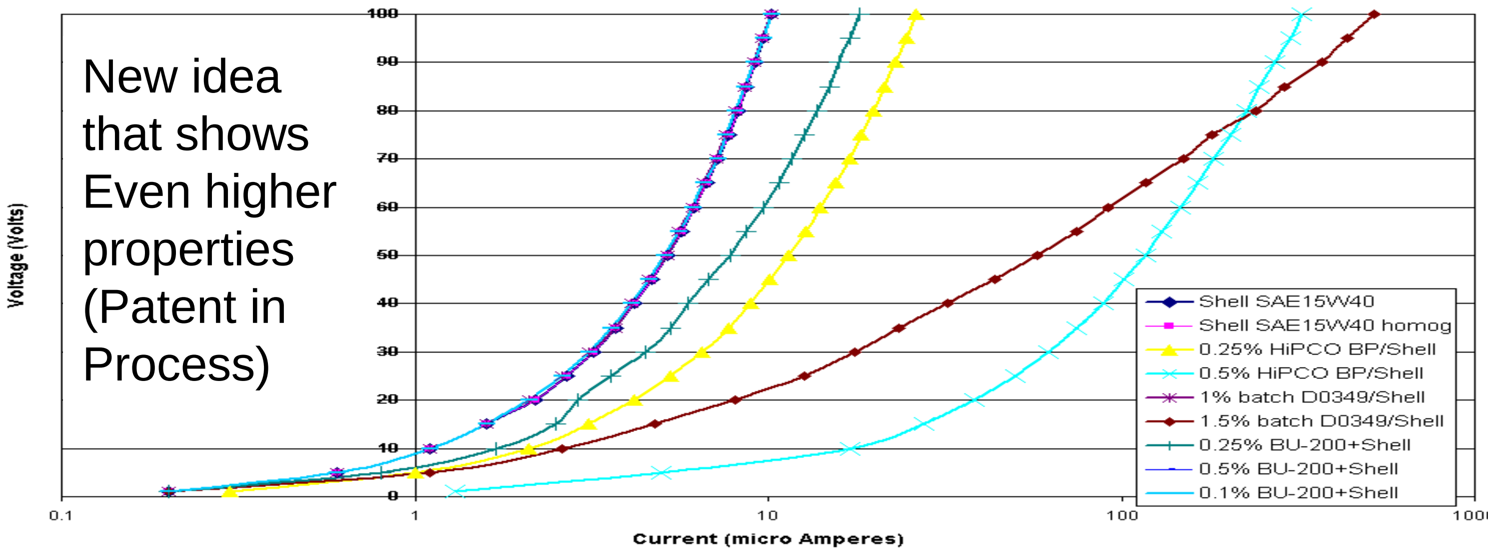
5 mm apart.

“When a dc voltage of ~40 V was applied, we observed a slow movement of carbon nanotubes from the suspension toward the positive electrode”.

Proven Increase in Electrical Conductivity

Voltage vs. Current: Curves with nanotubes achieve higher current with the same voltage.





Tunneling

Dominant role of tunneling resistance in the electrical conductivity of carbon nanotube–based composites Chunyu Li, Erik T. Thostenson, and Tsu-Wei Chou,
Applied Physics Lett. 91 (2007) 223114-1 to 223114-3.

Maximum tunneling distance is found to be 1.8 nm.

"Electrical conductivities of composites with in plane random distributions of carbon nanotubes follow the scaling law and the critical exponent depends on the level of contact resistance".

"It is also noted that the extrapolation of the EC of CNT networks without insulating layers at 100% content gives about 7.2 - 10^5 S / m, which is very close to the conductivity of 10^6 S / m of individual CNTs we used".

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Conduct NT-NT Study/Improve NT-NT Connection

Three Approaches: (1) Zyvex manipulation
(2) Ames Interdigitized Sample
(3) Use of Focused Ion Beam Equipment
(4) Doping

Use of Focused Ion Beam Equipment

IPICyT in San Luis Potoci, Mexico has equipment for conducting high sensitivity nanotube manipulation.

With this equipment we can imagine at the nanoscale, move nanotubes around, and create contact conditions for measuring electrical conductivity (NT-NT contact).

Experiments are being conducted to achieve samples of several nanotube conditions.

Nano-Manipulator Approach to Transport Measurement: Initial work

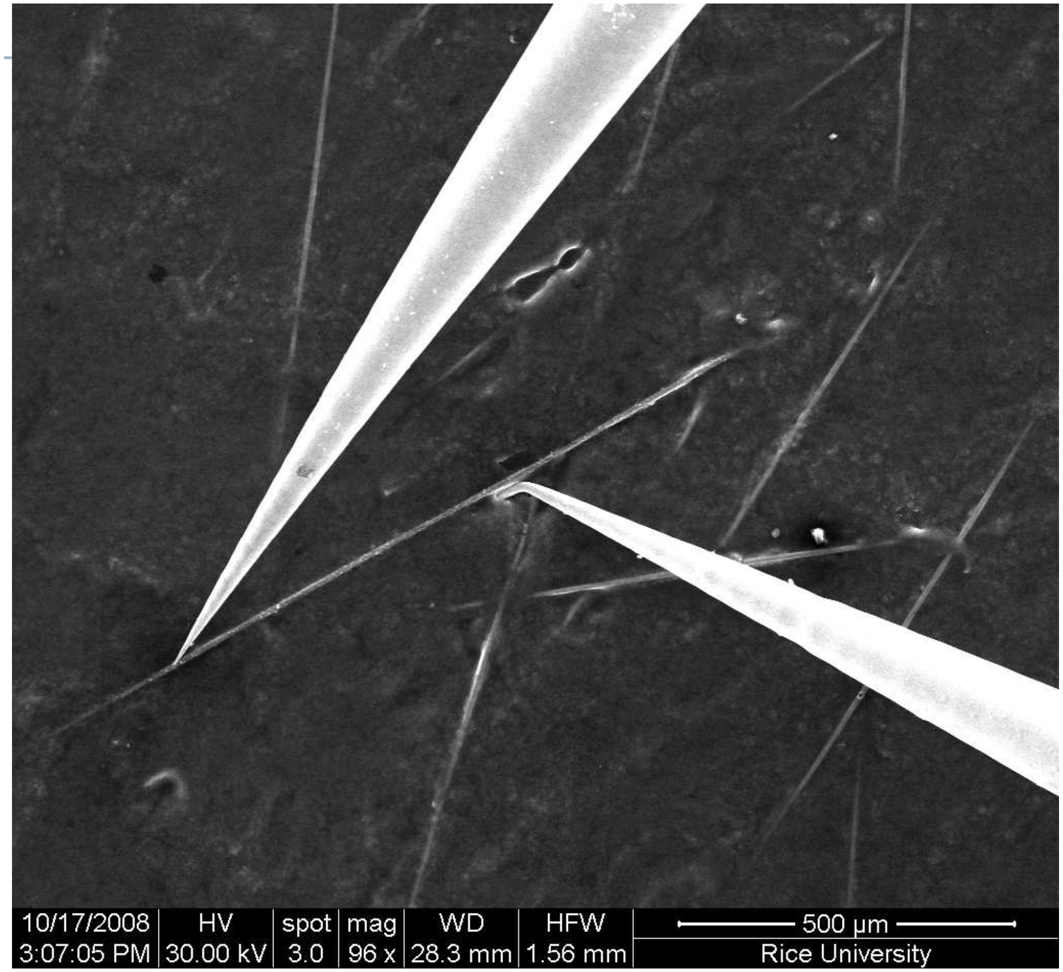
Currently a two-probe contact system is used where the nanotube is isolated from the substrate surface.

Options for a four point contact arrangement are available depending on the space around the four contacts.

Consistency of contact to the nanotube must be achieved and optimized for best contact conditions.

Properties as a function of temperature will also be measured.

Nanotube manipulation is necessary in order to manipulate the contact conditions.



- Instrument is available and inexpensive.

-(MWCNT: 105 µAmps, 9.52 kohms (clamping). Difficult to manipulate CNT in matrix.

-50 nm movement resolution. SEM resolution - large working distance.

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Nano-Manipulator Approach to Transport Measurement: Solution

GOAL: Measure Tunneling Transport b/t nanotubes In a polymer-matrix.

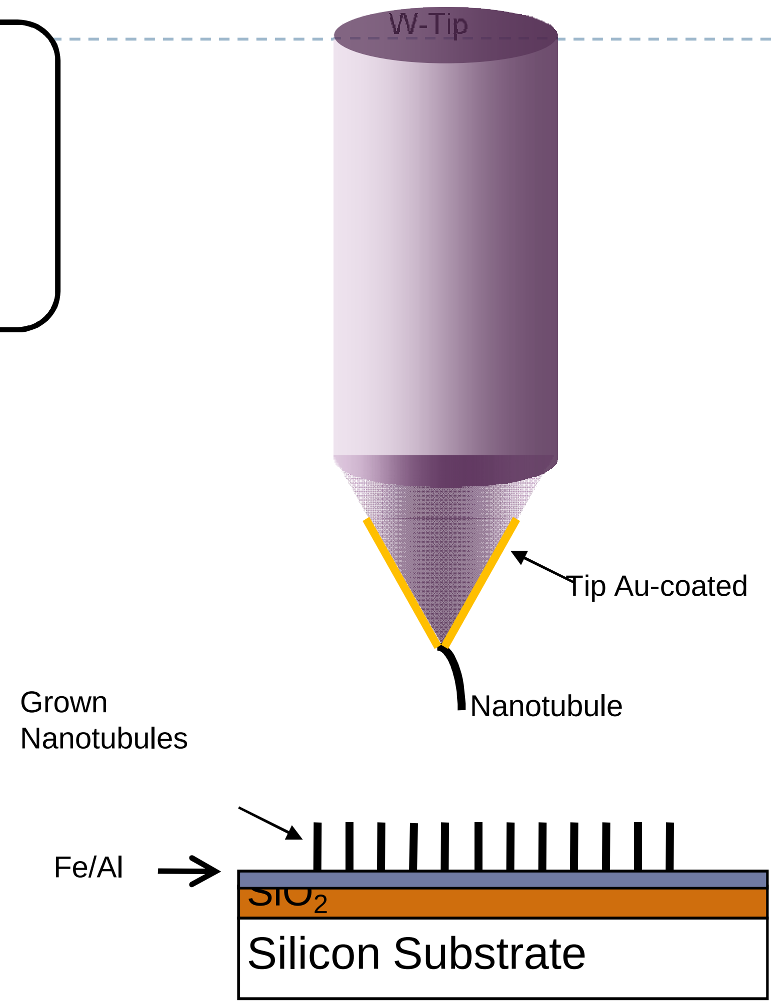
Process:

Tip

- Coat Zyvex Tips w/ Thin-Layer Au.
- Attach Nanotubule to Zyvex Tip.

Substrate

- Grow/Deposit SiO_2 on Si-subst.
- Deposit Fe/Al Film on SiO_2.
- Grow CNT (DW) on Fe-catalyst.
- Vary CNT length.
- Pattern substrate.
- Wet grown-CNTs w/ polymer matrix.



Conductivity of SWNT Networks

Electrical Conductivity of Single-Walled Carbon Nanotube Networks
P. N. Nirmalraj, P. E. Lyons, S. De, J. N. Coleman, and J. J. Boland, Nano Le
(2009) 3890-3895.

“Transport in single-walled carbon nanotube networks is shown to be dominated by resistance at network junctions which scale with the size of the interconnecting bundles”.

“Acid treatments that dope the individual nanotubes produce a dramatic reductionin junction resistance.

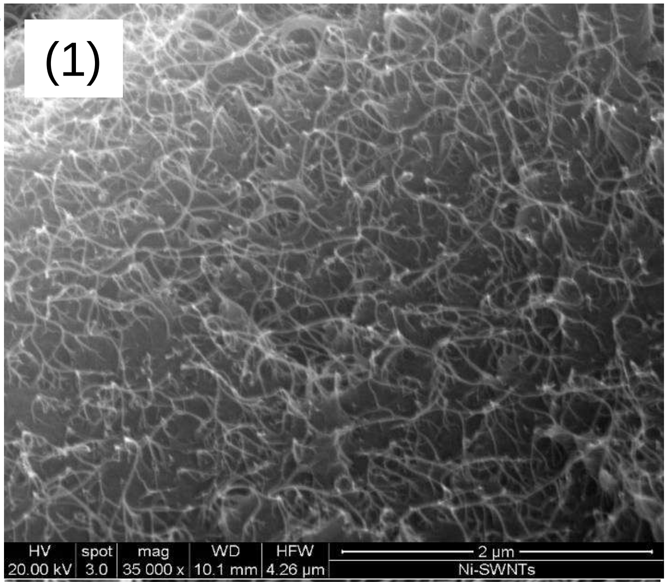
Smallest resistances occurs between individual nanotubes.

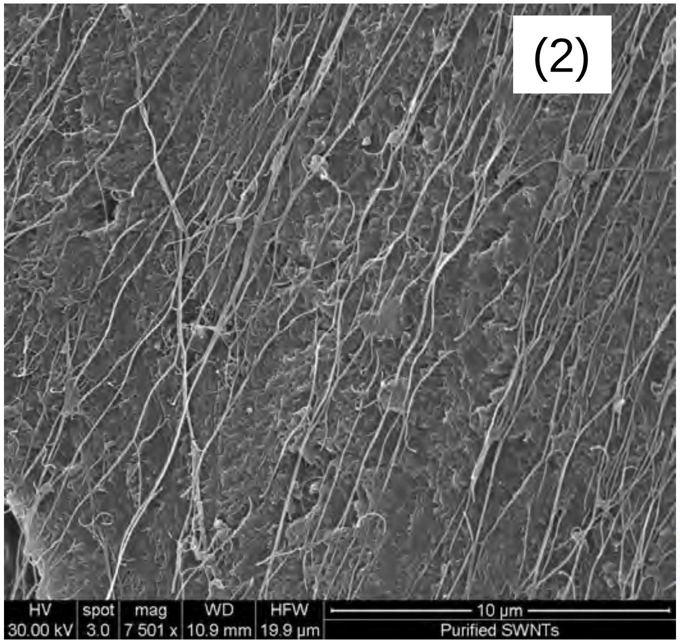
Disperse m-SWNTs

The Winey method for dispersion:

A version of the Incipient Wetting method where the following is used:

1) SWNTs are dispersed in Dichlorobenzene and sonicated. 2) After 3 hours, the temperature of the SWNT + DCB is raised to 110C. In a different beaker MDPE is dissolved in DCB at 110C. 3) The DCB + MDPE solution is added to the SWNT dispersion. 4) The mixture is placed in a ice bath and sonicated till the temperature reached below 70C. 5) The mixture is then vacuum filtered and dried.



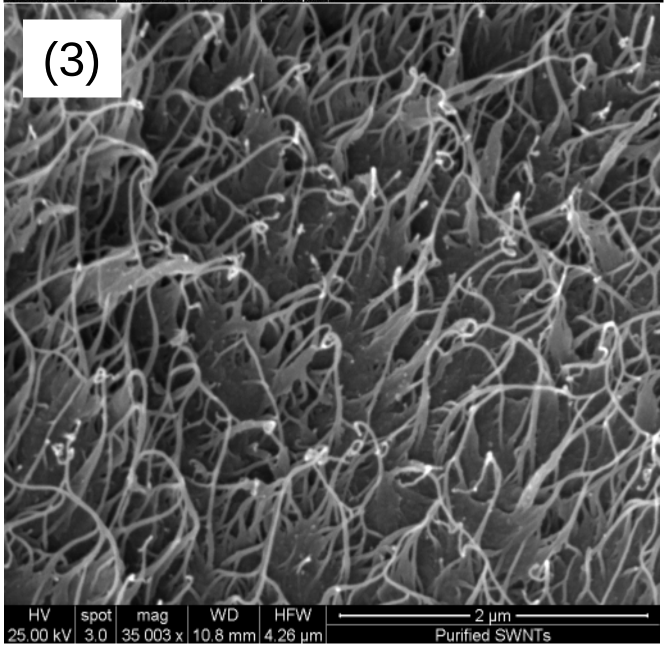


(1) After Winey Method.

(2) After electric Field applied.

(3) After electric Field applied.

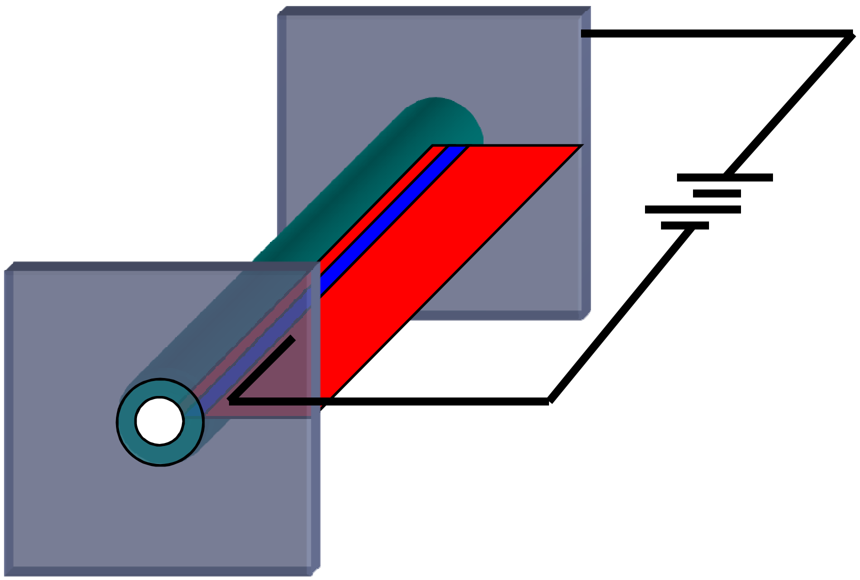
Technip



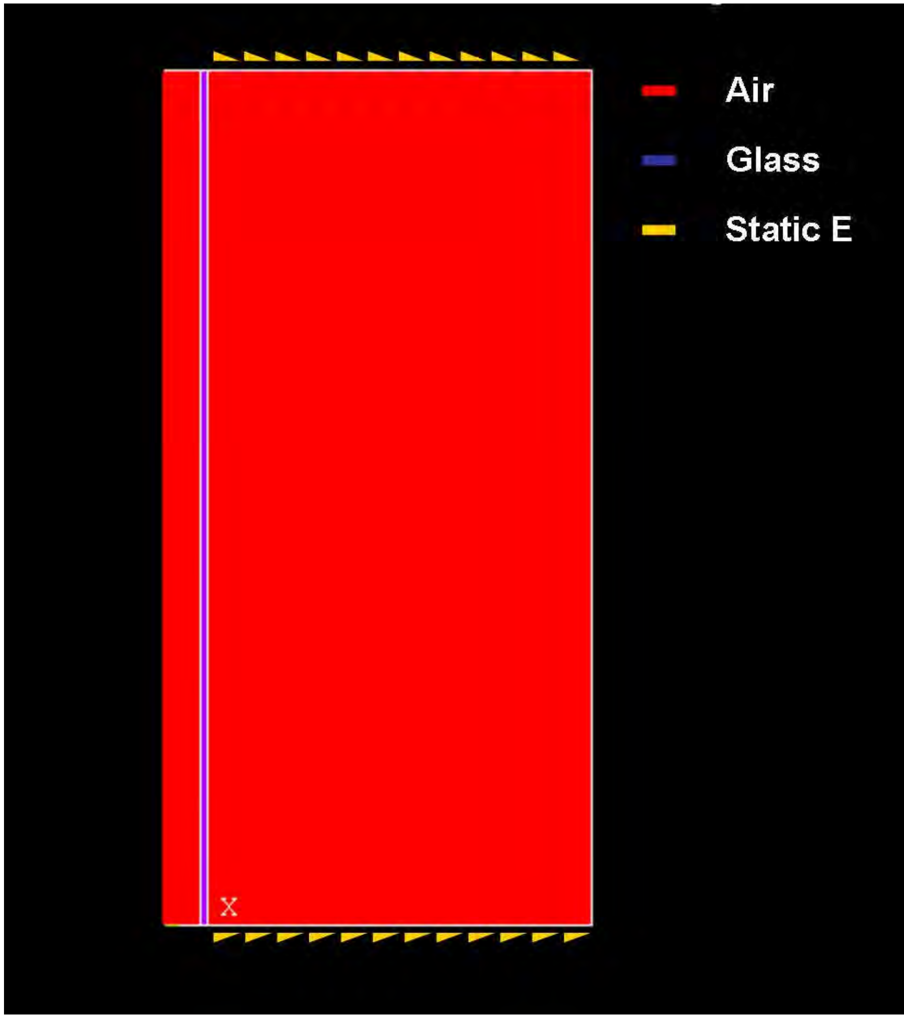
Implement Electric Fields

Design of an Electric Field Fixture:

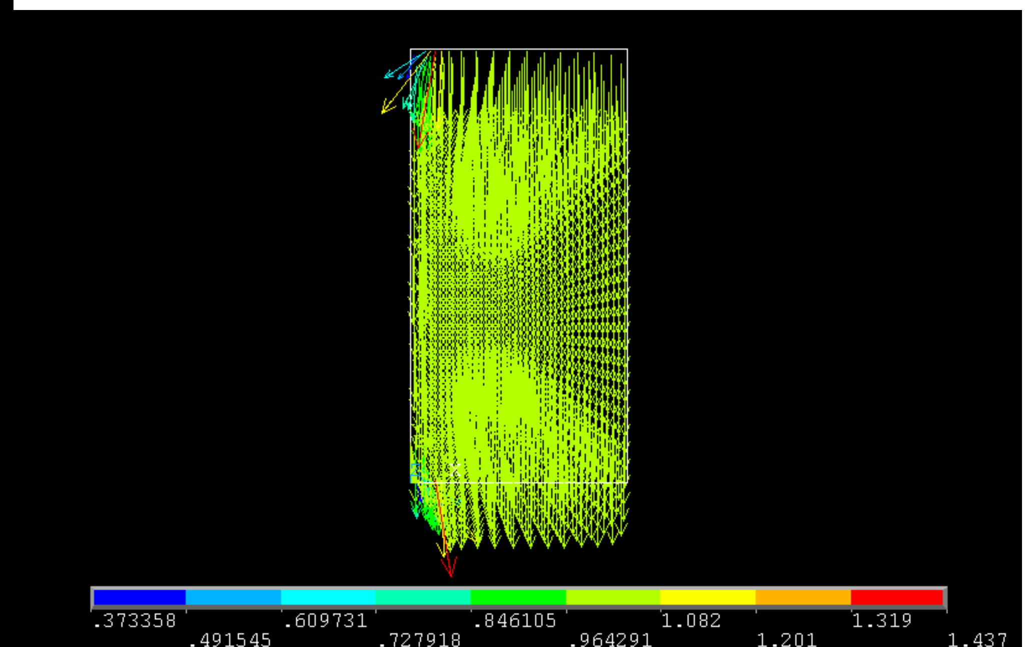
1. Separated parallel plates with a hole in the middle so the PNU can go through.
2. A tube is placed in the holes so that a heating element can be put around the wire.



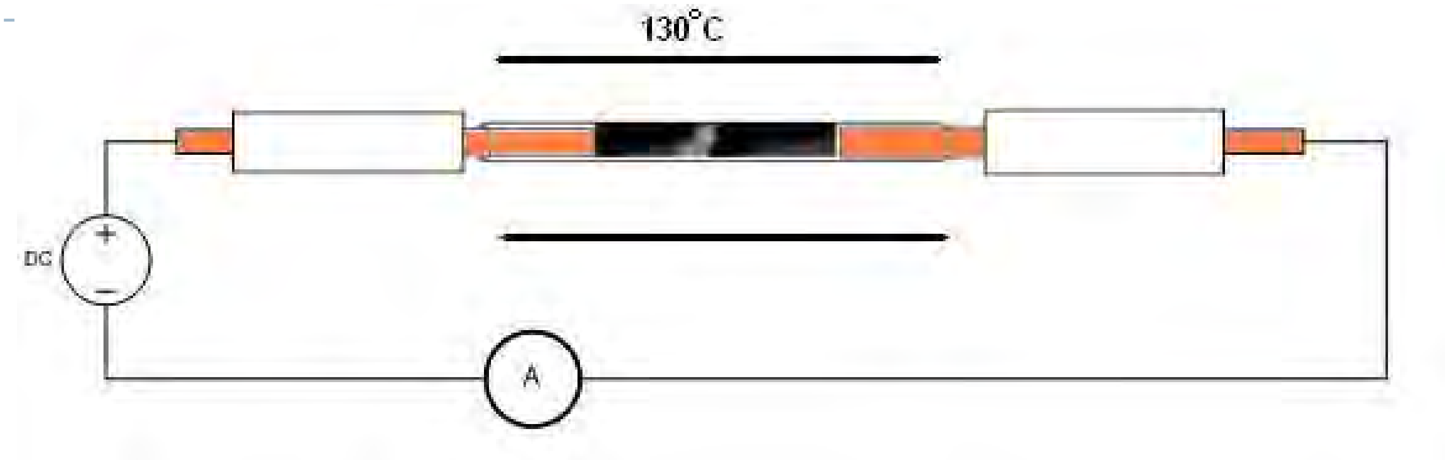
Finite element analysis



Finite Element Analysis (FEA) shows a uniform field with minor disruption at the plats around the holes.



Current method for implementing the electric field



• 4 samples (MDPE + 10 wt% SWeNTs) were tested.

• Samples required 4 ~ 5 rounds of conditioning, before it starts conducting well.

• The best samples carried a current of close to 16 amps for 2 V.

• The distance between the leads for the best sample is close to 0.7 cm.

• Specific resistivity was 2.1 * 10^{-2} ohms / sq.cm

•Current samples require conditioning (more than one melting pass).

Example Samples Processed to Date

Composites	Wt% of NTs	Processing method
MWNTs/HDPE	5%	Dry mixing + Injection
MWNTs/HDPE	10%	Dry mixing + Injection
MWNTs/HDPE	15%	Dry mixing + Injection
MWNTs/HDPE	20%	Dry mixing + Injection
MWNTs/HDPE	5%	Dry mixing + Haake extrusion
MWNTs/HDPE	10%	Dry mixing + Haake extrusion
MWNTs/HDPE	15%	Dry mixing + Haake extrusion
MWNTs/HDPE	20%	Dry mixing + Haake extrusion
MWNTs/HDPE	5%	Incipient wetting + Dry mixing + Haake extrusion
MWNTs/HDPE	10%	Incipient wetting + Dry mixing + Haake extrusion
MWNTs/HDPE	15%	Incipient wetting + Dry mixing + Haake extrusion
MWNTs/HDPE	20%	Incipient wetting + Dry mixing + Haake extrusion
MWNTs/HDPE	5%	Dry mixing + Miniextrusion
MWNTs/HDPE	10%	Dry mixing + Miniextrusion
MWNTs/HDPE	15%	Dry mixing + Miniextrusion
MWNTs/HDPE	20%	Dry mixing + Miniextrusion
MWNTs/HDPE	30%	Dry mixing + Miniextrusion
MWNTs/HDPE	40%	Dry mixing + Miniextrusion
MWNTs/HDPE	50%	Dry mixing + Miniextrusion
MWNTs/HDPE	60%	Dry mixing + Miniextrusion
CG NTs/HDPE	10%	Winney sample + Injection
CG NTs/HDPE	10%	Winnery sample + Miniextrusion
MWNTs/MDPE	5%	Dry mixing + Haake extrusion
MWNTs/MDPE	10%	Dry mixing + Haake extrusion

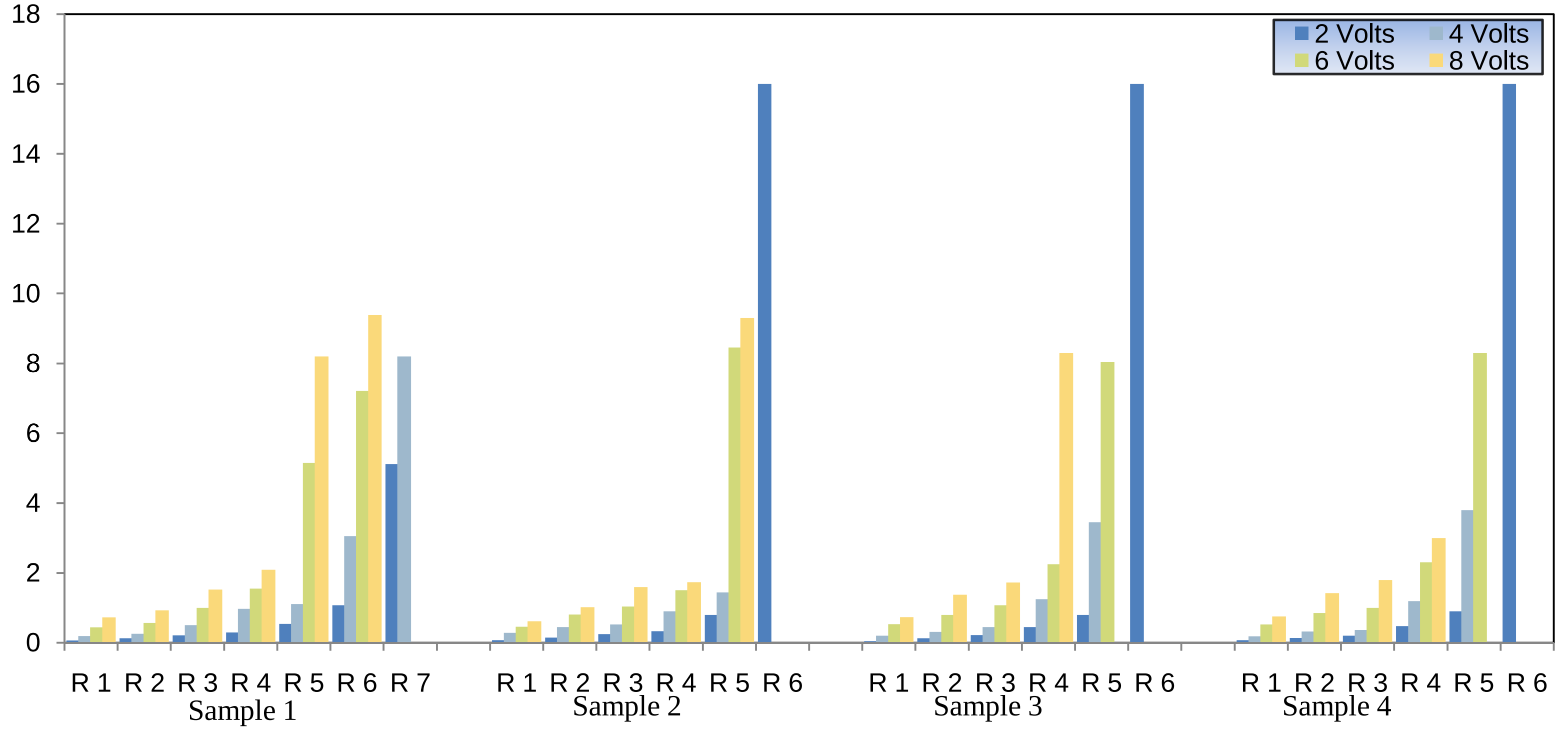
Three melt processing approaches are being used:

Injection molding (up to 6 grams)
Mini-extrusion (10 grams)
Haake extrusion (100 grams).

Wt%s from 5 to 60 are being processed. Typical concentrations are 10 wt%.

Evaluation & Optimization

Target: 500 amps at the same voltage for the copper conductor.
Proposed: (a) Stranded wire (19 strands) or (b) Solid Core wire.
For stranded wire: On average ~26 amps to be carried by each strand.
Current Design and Evaluation: Single strand of SWNTs/PE.



Recent conditions may be limited by available power supply.

Program Outcomes

1. One foot wire conductor produced.
2. High dispersion has been achieved by the “Winey” Method.
3. We have used electric fields and designed a fixture for process manufacturing.
4. We have produced a number of samples using the Dymax sample configuration. Early samples were produced with styrene. A number of samples have been processed by melt spinning.
5. A current carrying capability of 16 amps has been produced
6. where 26 A is needed..

    The sample was limited by the power supply used.

    More optimization is planned.

6. The workshop is being held on Ultra-High Conductivity Conductors.
7. The test wire is being demonstrated at the workshop.

Program Support: DOE RPSEA, Chevron