Thermoelectric “Fabrics” based on carbon nanotube composites

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A “macro-electronics’ approach to Thermoelectrics

Focus of Research
Increasing the figure of merit of thermoelectric materials drives the majority of the research on thermoelectrics.

Benchmarks
Bismuth Telluride (Bi$_2$Te$_3$) is the most common commercially used TEP material, and has a ZT~1. However, it is speculated that a ZT $\geq 3$ is required before TEP materials can become competitive with current sources of electricity. Although there have been reports of ZT values around 2, these values have not been verified.

Manufacturing and Commercialization
Importantly, their use of exotic nanostructured crystalline materials makes them both expensive and difficult to reproduce on a large scale. Therefore, it is useful to explore more economical sources of thermoelectric power.
Composite Thermoelectrics are not very good

Figure 2: SEM images of a) 25 b) 50 c) 75 d) 100 wt% SWNT/PVDF films. All four images show film surface (bottom/right of image) and a cross section of the film (top/left of image).
Our Thermoelectrics Measurement

Figure 3: Experimental setup for measuring thin film (S) resistivity and TEP. Resistivity is measured by a 4-probe method using electrodes V+, V-, I+, I-. TEP is measured by heating copper block Cu₁ via heater H to create ΔT, and measuring ΔV across V+, V-. ΔT is measured by Si diode thermometers Tₐ and Tₑ. The whole assembly is inserted into a vacuum chamber via transfer rod R where T can be controlled from 20K to 290K.
Resistivity of Composites

Figure 4: Film resistivity vs Absolute T for varying SWNT wt%.

Figure 5: Film resistivity vs SWNT wt% for T = 290K.
Seeback Coeff. vs. Loading
Seeback Coeff. vs. Loading

SwNT/PVDF Film Seebeck Coefficient vs NT Concentration

Figure 7: Film TEP vs SWNT wt% at 290K.
Figure 8: Power factor vs SWNT wt% at 290K.
SWNT vs. MWNTs

Figure 9: TEP vs Absolute T for MWNT and SWNT films.
Dispersion

Figure 10: TEP vs Absolute T for raw and clean SWNT films.
Module Design

Fig. 1. TE heat engines. (A) When current is run across a TE junction, it heats or cools through the Peltier effect, depending on the direction of the current flow. (B) When heat flows across the junction, electrical current is generated through the Seebeck effect. (C) Practical TE generators connect large numbers of junctions in series to increase operating voltage and spread heat flow.
Fig. 3. Alternative TE junction geometries. (A) A traditional junction. Current and heat flow in the same general vertical direction, and there is a long current path through shunts and tall narrow TE elements. (B) A stack junction. The current flow is perpendicular to the heat flow, the current path is minimized through shunts, and the TE elements are short and wide.
Nanotube Modules

Thermally/electrically insulating layers

Electrical connection points

assembly
A two-probe measurement of the temperature dependence of $R$, normalized to 320 K, after degassing in vacuum at 320 K for three days, is shown. All three mats exhibited non-metallic behavior over the entire temperature range ($dR/dT < 0$).

Activation energy from Arrhenius plot:

$$\rho = \rho_0 \exp\left(\frac{E_a}{kT}\right)$$

B-doped $\sim$ 12 meV  
N-doped $\sim$ 2 meV
Module Design

- Undoped MWNT Mat
- B-doped MWNT Mat
- N-doped MWNT Mat
Figure 11: SEM image of multilayer CNT/polymer stack with 3 layers. The temperature gradient ($T_{\text{hot}} - T_{\text{cold}}$) creates $+V$ in the p-type films (1), and $-V$ in the n-type film (2) as measured from left to right. The alternating connection between films (4) adds the potentials in series. The rest of the films are kept electrically isolated by insulation (3).
Nanotube Modules

Figure 12: TEP vs T for layered films
Demonstration
Summary

We have demonstrated:

1) Composites of Carbon Nanotubes within polymers can approach thermoelectric response of Carbon Nanotubes mats which is advantageous for products.

2) A novel and simple module design that allows for these very thin materials to be integrated into a basic device. These devices can be made in large areas and are about as thick as a fabric. The thermoelectric fabrics can be applied in a wide range of applications not currently accessible to BiTe.