



Improvement in Power Output for CNT Polymer Hybrid Film and Accompanying Thermoelectric Generator

Cooperative Research and Development Final Report

CRADA Number: CRD-15-596

NREL Technical Contact: Jeffrey Blackburn

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Technical Report
NREL/TP-5900-76255
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Cooperative Research and Development Final Report

Report Date: 11/9/2019

In accordance with requirements set forth in the terms of the CRADA agreement, this document is the final CRADA report, including a list of subject inventions, to be forwarded to the DOE Office of Science and Technical Information as part of the commitment to the public to demonstrate results of federally funded research.

Parties to the Agreement: International ThermoDyne, Inc.

CRADA number: CRD-15-596

CRADA Title: Improvement in Power Output for CNT Polymer Hybrid Film and Accompanying Thermoelectric Generator

Joint Work Statement Funding Table showing DOE commitment: No NREL Shared Resources

Estimated Costs	NREL Shared Resources a/k/a Government In-Kind
Year 1	\$0.00
TOTALS	\$0.00

Abstract of CRADA Work:

NREL personnel will enhance International ThermoDyne’s (ITD) understanding of the controlling factors for power output within a process for the manufacturing of high-performance carbon nanotube (CNT) thermoelectric generator (TEG) structure (alternative areas of p and n type semiconductor) and provide ITD with samples (“Deliverables”) demonstrating these advances in power output that can be used. The Deliverables will have performance characteristics outlined in Table 1, for use in ITD’s PowerFelt product. The initial goals of this project are to achieve thermoelectric p and n films with power factors of at least 600 μ W/mK² made through NREL’s process for TEG paper manufacture with high conductivity and low thermal conductivity and eventually achieving higher performance of > 900 μ W/mK².

Summary of Research Results:

The full details and outcomes of these results can be found in the paper that we published jointly with ITD (also included in this final report below):

MacLeod, Bradley A., Noah J. Stanton, Isaac E. Gould, Devin Wesenberg, Rachelle Ihly, Zbyslaw R. Owczarczyk, Katherine E. Hurst, Christopher S. Fewox, Christopher N. Folmar, Katherine Holman Hughes, Barry L. Zink, Jeffrey L. Blackburn and Andrew J. Ferguson, “Large n- and p-type thermoelectric power factors from doped semiconducting single-walled carbon nanotube thin films.” *Energy &*

Phase 1: Understand the Role and Ratio of polymer and dopant choice in electrical conductivity and Seebeck of hybrid films

Task 1.1: Vary polyethylene oxide PEO:SWCNT ratio away from current 1:1 up to 10:1

- Proposed equipment needed: sonicator, centrifuge
- Proposed output: report

Task 1.2: Vary p-type and n-type doping choice and level to search for maximum Power Factor for various polymer levels for each polymer

- Proposed equipment needed: sonicator, centrifuge
- Proposed output: report

Task 1.3: Explore the role of the particular polymer used in the hybrid film

- PEO
- Others, TBD
- Proposed equipment needed; sonicator, centrifuge
- Proposed output: report

Task 1.4: Manufacture of film with best power output from the findings of above

- Proposed equipment needed; sonicator, centrifuge
- Proposed output: Pieces of film; report

Phase 1 Results: We initially began Task 1.1 of the project by using an aqueous two-phase enrichment (ATPE) process to separate the semiconducting SWCNTs that were most desired for the thermoelectric (TE) thin films. This ATPE process was easily integrated with the PEO polymer originally used by the ITD team to fabricate their TE thin films, so the initial goal was to vary the PEO:SWCNT ratios to track the TE performance. We found that increasing the PEO ratio simply deteriorated the TE performance of the thin film, since the PEO is entirely insulating and the SWCNTs are the primary conducting material. We also found that the ATPE process was relatively low throughput and was not amenable to creating the amounts of SWCNTs needed to produce multiple samples and/or thick samples for testing reproducibility. As a result, we switched our primary separation process to the polyfluorene extraction process that is performed with toluene as the solvent. Moving on to tasks 1.2 and 1.3, we first compared multiple polyfluorene polymers for the extraction of high purity semiconducting SWCNTs (task 1.3):

- Poly[(9,9-dioctylfluorenyl-2,7-diyl)-alt-co-(6,60-{2,20-bipyridine})] (PFO-BPy) American Dye Source, Inc., Quebec, Canada
- poly[(9,9-dihexylfluorenyl-2,7-diyl)-co-(9,10-anthracene)] (PFH-A) American Dye Source, Inc., Quebec, Canada.
- 1,10-(((1E,10E)-(9,9-didodecyl-9H-fluorene-2,7-diyl)bis(ethene-2,1-diyl))bis(6-methyl-4-oxo-1,4-dihydropyrimidine-5,2-diyl))bis(3-dodecylurea) (SMP) Synthesized at NREL

- poly[(9,9-di-n-dodecyl-2,7-fluorendiyl-dimethine)-(1,4-phenylene-dinitrilomethine)] (PF-PD) Synthesized at NREL and by ITD

The first two of these polymers remain in the film following film formation, whereas the second two polymers are ‘cleavable polymers’, where the polymer can be removed completely from the film following film formation. We found that the cleavable polymers always produced more conductive films and higher TE power factors than films utilizing non-cleavable polymers. We found that this was a result of the better charge carrier mobility in films made with cleavable polymers, since the s-SWCNTs in these films were better coupled electronically. (Task 1.4) We found that the PF-PD polymer produced the most conductive films with the highest TE power factors, reaching over $700 \mu\text{W m}^{-1} \text{K}^{-2}$, which is at least a factor of 20 higher than previous power factors achieved with ITD’s original process. We also found that two dopants in particular (Task 1.2) produced the large TE power factors. The dopant triethyloxonium hexachloroantimonate (OA) produced good p-type films, while the dopant benzyl viologen (BV) produced good n-type films. Due to the equivalent effective masses of electrons and holes in s-SWCNTs, the resulting TE power factor was equivalent for the n- and p-type thin films. Although the as-prepared n-type films are unstable in air, we found that the application of a thin (~50 nm) coating of Al_2O_3 to the n-type s-SWCNTs made their TE power factor stable indefinitely.

Task 1.3:

We discovered that removal of the polymer uniformly improved the performance of films, so we did not pursue additional work with PEO as a polymer matrix.

Phase 2: Understand how the SWCNT diameter and diameter distribution effects performance

Probe effects of average SWCNT diameter and diameter distribution. Probe conductivity and Seebeck as a function of Fermi energy for systematically tuned diameter distributions within the laser vaporization synthesis protocol (and/or full series of commercially available SWCNTs)

- Theory suggests enhanced Seebeck for smaller diameter
- Our initial data on (7,5) suggest a higher S for similar conductivity, but these SWCNTs are prepared by CoMoCAT and purified
- Theory and some experiments suggest higher mobility/conductivity for larger diameter
- Chirality distribution exploration
- Seebeck coefficient proportional to derivative of DOS at E_f
- Would enable a jump in Seebeck at high carrier concentrations
- Success will be a jump in Seebeck coefficient at higher carrier concentrations (high conductivity)

Task 2.1: Obtain or make SWCNTs with average diameter tuned from ~0.9 nm to 1.5 nm

- Proposed equipment needed; sonicator, centrifuge
- Proposed output: Pieces of film; report

Task 2.2: Construct samples incorporating single-chirality “artificial atoms”

Either inter-mixed or layered

- Proposed equipment needed; sonicator, centrifuge
- Proposed output: Pieces of film; report

Task 2.3: Find single-diameter films and “artificial atom” films with best combo of conductivity and Seebeck by making multiple films to find relationship

- Proposed equipment needed; sonicator, centrifuge
- Proposed output: Pieces of film; report

Task 2.4: Manufacture film samples incorporating the improvements of all tasks up until this point

- Proposed equipment needed; sonicator, centrifuge
- Proposed output: Pieces of film

Phase 2 Results: Phase 2 focused solely on Task 2.1 and 2.4, as requested by ITD. We worked with a wide variety of diameters and chirality distributions of s-SWCNTs, fabricating films with both cleavable and non-cleavable polymers. We found that the original diameter dependence we observed in our first Nature Energy study, using solely non-cleavable polymers, did not necessarily hold up when we transitioned to cleavable polymers. Using non-cleavable polymers, we determined that the ideal diameter for producing high TE power factor was in the range of ca. 1.0 nm. However, for cleavable polymers, the highest TE power factor was achieved for s-SWCNTs with diameters in the range of ca. 1.3 nm. We found that the effect of diameter was convoluted with other morphological parameters of the film, in particular the size of bundles found within the films. We found that the ultimate TE power factor was correlated inversely with the bundle size, and that the 1.3 nm diameter s-SWCNTs initially wrapped with the PF-PD polymer had the smallest bundle size of all. Extrapolation of our empirical trend of TE power factor as a function of bundle size dependence also suggests that further reducing the bundle size to ca. 5 nm could more than double the TE power factor to the range of ca. $1800 \mu\text{W m}^{-1} \text{K}^{-2}$.

Phase 3 – Demonstrate the ability to produce TEG paper with a Power Factor of $600 \mu\text{W}/\text{mK}^2$

Task 3.1: Manufacture pieces of TEG paper incorporating all improvements in power outputs up until this point

- Proposed equipment needed; sonicator, centrifuge
- Proposed output: Pieces of film

Phase 3 Results: We reproducibly produced both p-type and n-type TEG papers with power factors exceeding $700 \mu\text{W m}^{-1} \text{K}^{-2}$, using the improvements discussed above. Work was performed in conjunction with ITD on applying the fabrication strategy for these types of legs to a foldable substructure with junctions between p/n sections. The full processing strategy was difficult to implement for a film that was thick enough to produce enough power, and there were some difficulties in producing narrow junctions between p/n sections.

Phase 4 – Demonstrate the ability to produce flexible TEGs with Power Factors of >900 μ W/mK² while incorporating the known improvements gained from previous Phases.

Task 4: Manufacture pieces of TEG paper incorporating all improvements in power outputs up until this point

- Proposed output: pieces of film

Phase 4 Results: We were not able to meet the goal of >900 μ W m⁻¹ K⁻² (Task 4.1), although extrapolation of our empirical trend of TE power factor as a function of bundle size dependence also suggests that further reducing the bundle size to ca. 5 nm could more than double the TE power factor to the range of ca. 1800 μ W m⁻¹ K⁻². Upon reaching the goals of Phase 3, we were asked to modify our goals towards the realization of large prototype thin-film TEG devices. As such, we were not able to focus our efforts on reaching >900 μ W m⁻¹ K⁻², therefore, discontinuing the need for Tasks 4.2-5.

Equipment Materials & Supplies:

NREL will provide all equipment and safety materials necessary to perform work.

Subject Inventions Listing:

None

ROI #:

None. We did not generate any new records of invention through this CRADA.

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