Marine Engine Testing and Emissions Laboratory (METEL)

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Thermoelectric Exhaust Heat Recovery Generator (TEG) Project

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1. Introduction

Thermoelectric waste heat recovery is an enabling technology that can be used to increase the overall plant efficiency of marine and industrial power plants by recovering heat from the exhaust that would otherwise be wasted. Using a thermoelectric generator (TEG), this energy can be recovered and converted to usable electricity using a solid state material. These types of materials could potentially be used in a myriad devices onboard marine vessels, which use heat exchanger technology extensively in the majority of its systems, in order to increase the overall plant efficiency. In order to understand and predict the outputs of TEGs when implemented in these heat exchange systems, a predictive model is required. Wallace et al. and Jin et al [1-3] developed modeling techniques to predict the output of thermoelectric materials when differing temperature profiles are applied across the material. The experimental work described in this report shows the effort towards the production of data to validate this predictive model so that it can be used to develop TEGs to be used in the marine industry.

2. Experimental Description

METEL and UMaine researchers were awarded $98,776 from the universities’ Research Reinvestment Program to support a grant entitled “Layer-by-layer Fabrication of Thermoelectric Films Using Polymerized Bismuth-Telluride Nanoparticles to Yield High-Efficiency Thermoelectric Generators for Marine Applications.” The first objective of the project is to develop a methodology for inexpensively producing nanoscale thermoelectric materials.

To that end bulk p-type, bismuth antimony telluride from Sigma Aldrich (99.99% trace metal basis) was combined with 40% by mass Polyallyltrimethylammonium chloride (PADAMAc) and ball milled with 0.1 mm zirconium oxide shot for 30 minutes. The PADAMAc is necessary to modify the surface properties of the newly generated particles and keep them from agglomerating. Average particle diameter is measured using X-ray diffraction, dynamic light scattering and scanning electron microscopy (Figure 1). The powder is then poured into a 13mm diameter pellet press and compressed at 24,000 psi for 3 minutes.

The electrical conductivity of the resulting pellets is low ostensibly because of the presence of the polymer, which is nonconducting. Thermogravimetric studies under flowing nitrogen gas show that the polymer desorbs from the sample at temperature between 200-300°C. In keeping with this observation Figure 2 shows that the conductivity of macroscopic pellets increases significantly over this temperature range and that those increases are permanent.
A procedure for rapid, controllable and repeatable production of nanoscale thermoelectric material was developed at the Laboratory for Surface Science and Technology (LASST) at UMaine using only bulk thermoelectric materials, surfactant polymers and ball milling. The resultant powders were then pressed into 5mm diameter cylindrical pellets (~4 mm thick) using a hydraulic press for materials testing. To initiate particle sintering and remove polymers, pellets were heated either during the press using a barrel heater or post pressing using an inert atmosphere quartz tube furnace. The cold pressed pellets resulted in good thermal and electrical properties, but poor mechanical properties (frequent macroscopic cracking). Simultaneous pressing and heating resolved this issue.

Pellets were pressed at 200, 250 and 300°C and then tested for thermal and electrical conductivity and Seebeck coefficient at the Cornell Center for Materials Research (CCMR,
Ithaca, NY). The data shows that samples pressed at 200˚C have similar Seebeck coefficients and thermal conductivities to samples pressed at higher temperatures, but significantly lower electrical conductivities. This is consistent with thermal gravimetric data (Figure 3), which shows that polymer removal only begins to occur at 254˚C. Seebeck coefficient and thermal conductivity data is less straightforward, with better/lower thermal conductivities in pellets pressed at 250˚C and better/higher Seebeck coefficients from pellets pressed at 300˚C (Figure 3).

![Graph 1](image1.png)  ![Graph 2](image2.png)

**Figure 3:** (left) Room temperature thermal conductivity and (right) Seebeck coefficient data from pellets made with 40 nm particle, p-type BiTe powder

The effect of average particle size on thermoelectric materials properties was also investigated. Electrical conductivity changed nominally with particle size, but fairly significant changes in Seebeck coefficient and thermal conductivity were observed (Figure 4).

![Graph 3](image3.png)  ![Graph 4](image4.png)

**Figure 4:** (left) Room temperature thermal conductivity and (right) Seebeck coefficient data from pellets made with p-type Bi$_2$Te$_3$ powder processed to average particle diameters of 40, 100 and 300 nm.

For actual device fabrication and testing both p-type and n-type pellets were pressed at 300˚C and mounted into a traditional π shaped thermoelectric couple, shown in the figure 5 below, and tested inside a vacuum chamber at LASST, also shown in the figure 5 below, for its performance. The two graphs below in figure 6 show the results of the Peltier performance testing, where the current was increased gradually from 0A to 1A and the voltage drop, power...
input, hot side temperature, and cold side temperatures were measured and recorded. The graphs show the results as compared to a commercially available thermoelectric couple, and show that the power input is much higher due to an increased voltage drop across the couple. It is believed that joule heating at the contact interfaces is occurring and causing the higher resistances.

**Figure 5:** Thermoelectric couple Peltier testing; left, TE couple, right, vacuum chamber testing setup

![Thermoelectric couple Peltier testing](image)

**Figure 6:** Results from TE Peltier testing; left, temperature differential generated per power input, right, the voltage drop across the TE couple per amp

![Results from TE Peltier testing](image)

While performing Peltier testing of the couples, it was observed that reversing the polarity of the current flowing through the couple produced a different result for the power versus temperature profile. Upon investigating the interactions of the materials using in the initial TE couple, it was realized that there is a work function mismatch between the semi-conductor and the metal contact. The original construction of the TE couple included the use of silver paste or epoxy, which proved to be an incompatible match to the n-type thermoelectric that was causing additional joule heating when the electrons attempt to cross the boundary between the silver and n-type bismuth telluride. Figure 7 shows the differences in the TE couple temperature profile when conducting a Peltier test with forward and reverse polarity current. At these current
settings, 0-1A, the temperature difference is greatly affected by the increase in joule heating, as the cold side temperature rose, albeit at a slower rate than the hot side. To alleviate this issue, a study was conducted to find a material that was a closer match to the work function for both the p and n type bismuth telluride. Nickel and gold were both identified as available materials that were close in work function to allow the transfer of electrons more freely. Figure 8 shows the results of Peltier testing of the TE couple using nickel as a boundary contact pad between the p-type and n-type TE elements. As can be seen, using a 1mm thick nickel strip as a contact pad improved the temperature stability of the couple at the lower current setting. The development of an appropriate method of depositing a Ni layer on the ends of the TE couple is underway.

**Figure 7**: Results of forward and reverse polarity current through TE couple with epoxy and without epoxy.
**Figure 8:** Results of TE couple using nickel contacts in place of silver epoxy

Because of the limitations on testing in this apparatus, primarily due to this method utilizing the Peltier method instead of the Seebeck method, the construction of a custom load bank was required. This load bank, used in concert with a heat source and heat sink, was used to characterize the materials using a selectable load of MOSFETs and known resistor values. Utilizing this loading method, the load bank is capable of providing a complete voltage versus temperature differential and power versus temperature differential curve for the couple using a direct potential differential measurement and a hall sensor to provide a linear voltage output measurement of the current output. Once construction was completed, the load bank was validated in two ways. The first method used was to apply a known voltage and current on the input and evaluate the output, which was successful. The second method was to validate the TE couple testing method by using a known TE module and comparing the output. A HZ2 module was used in the test apparatus and its output measured using a temperature differential sweep and a matched load of 0.15Ω as compared to the module’s internal resistance. As can be seen in the figure 9 below, both the voltage and power output as measured by the load bank was consistent with the published data by the module manufacturer.

**Figure 9:** TE Load Bank validation against published output of HZ2 module [5]

Once the validation was complete, the evaluation of the TE couples proceeded. In figure 10, the test rig to evaluate the Seebeck output of various TE element is shown, with the rig in the left
picture and an example of a TE couple installed in the rig on the right. The figure shows the load bank, the hot plate providing the heat source for the rig and the circulating water system with a heat exchanger to provide the heat sink. The temperatures were measured using k-type thermocouple wire.

Figure 10: Seebeck TE output evaluation rig (left), TE couple installed in Seebeck test rig (right)

The following figures (Figures 11-16) depict some selected initial results from testing a commercially manufactured couple, a couple made of the bulk material and a couple made of the nano materials. As can be seen, there is a large gap in the data in between the open circuit voltage output of the couple and the loads on the load bank. The trends that should be observed are a negatively sloped linear trend for the voltage output and a downward parabolic trend for the power output when both outputs are plotted against current output. [5] The reason for this gap is that the discreet loads installed on the load bank (1mΩ – 30mΩ) were too small relative to the internal resistance and contact resistance of the TE couple. A 5Ω variable resistor was purchased and installed to determine the proper resistance values needed to complete the graph.
Figure 11: Commercial bismuth telluride couple voltage output versus current at differing temperature differentials

Figure 12: Bulk bismuth telluride couple voltage output versus current at differing temperature differentials
Figure 13: Nano structured bismuth telluride couple voltage output versus current at differing temperature differentials

Figure 14: Commercial bismuth telluride couple power output versus current at differing temperature differentials
Figure 15: Bulk bismuth telluride couple power output versus current at differing temperature differentials

Figure 16: Nano structured bismuth telluride couple power output versus current at differing temperature differentials
The variable resistor allowed for the evolution of the resistor values of the discreet load settings. The range of 0-5Ω was still used, but more resistors were selected in the 0.5Ω-1.5Ω range in order to show the peak of the power output versus current trend. The results of these tests are shown below in figure 17-20. Each test was performed 3 times for repeatability and error bars were generated using the standard deviation of the data points multiplied by two. The tests were all performed at a temperature differential of 150°C. The test also considered the contact resistance variable. As a semiconductor to metal contact point may introduce high contact resistance due to barrier height incompatibilities and the roughness of the material causing high electrical resistance issues, the space between each pellet and the contact pad was filled using the colloidal resin of a two part epoxy of silver (Ag) and Nickel (Ni) epoxies. These studies were compared against a baseline test using the commercially manufactured couple. This commercially manufactured couple should have lower contact resistance values, as the contact pads are already in contact with the TE materials, therefore the outputs may be higher. If the materials developed approach the baseline value, it was seen as a positive result, as similar contact resistances to the commercial couple would increase the overall output. In figure xx and xy, the bulk material test using the Ag epoxy resin seems to approach the output of the commercial couple. In figure 19 and 20, the nano material test was performed using the Ag epoxy as well, as it garnered the best result from the bulk test. As can be seen in these figures, the nano structured material seemed to outperform the commercial and bulk material couples. There are large error bars associated with this test, however. It was observed that the pellets had fractured inside the test rig during the test procedure, therefore the results had more significant variation for this test.
Figure 17: Voltage output versus current at dT=150°C for bulk bismuth telluride couple as compared to commercial material

Figure 18: Power output versus current at dT=150°C for bulk bismuth telluride couple as compared to commercial material
Figure 19: Voltage output versus current at \(dT=150^\circ C\) for nanostructured bismuth telluride couple as compared to commercial material

Figure 20: Power output versus current at \(dT=150^\circ C\) for nanostructured bismuth telluride couple as compared to commercial material

5. Conclusions and Future Work

From the results outlined above, there needs to be more characterization of the materials to verify the results, particularly using the nano structured materials. It was found that the nano materials are brittle, therefore prone to fracturing after put under thermally induced stress. An
investigation into the internal stresses in the pellet after hot pressing is underway to further study the contact resistance issue. It is clear from the data, however, that the nanostructuring the materials was able to increase the voltage and power output of the bismuth telluride couple for the case of the silver epoxy. The data developed as part of this work will aid in validating future predictive modelling code for optimizing the physical characteristics of the pellets.

References


