Content of Research Report

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Electrospun Nanofibers for Energy Storage and Conversion

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ABSTRACT

In this work, we explore composite nanofibers that are manufactured through electrospinning for energy storage and conversion. The fibers will either be composed of a conductive composite or a ceramic composite, depending on application. For the ceramic nanofibers, their response to an external electromagnetic field is characterized to observe the heat generation in the fiber. In addition, we will also measure the current passing through the fiber under the polarization of DC potential. For the conductive nanofibers, the electrical resistance and thermal conductivity of the material will be measured under the polarization of DC potential. Based on previous research, for the ceramic nanofibers, it is found that the fiber has intensive heating behavior when it is exposed to the electromagnetic field. The temperature increases more than 5 degrees in Celsius scale, only after 5 seconds of exposure. The current–potential curve of the ceramic nanofibers confirms the hypothesized dielectric behavior. Based on previous research, for the conductive nanofibers, it is found that the electrical resistance is increased as thermal conductivity is reduced; therefore there must be a compromise between those two. It is concluded that the conductive nanofiber’s thermoelectric property is increased significantly compared to the bulk reference material. It is also concluded that the ceramic nanofiber has the potential to be used for hyperthermia-treatment in biomedical engineering or for energy conversions. Further research is currently being conducted to improve the efficiency of both, conductive and ceramic, nanofibers.
OBJECTIVES

The objective of our research is to create composite nanofibers through electrospinning, in order to use them for energy conversion and storage. Our goal is to create ceramic nanofibers for energy storage, as well as conductive nanofibers for energy conversion; however, the objective does not stop there, these nanofibers can serve a great application in the Biomedical Engineering field.

BACKGROUND

Dr. Yong X. Gan has successfully achieved the goals of this research in the past. Through electrospinning, along-side his students Arturo Bautista and Juan Aguado, he created Sodium-Cobalt Oxide ceramic nanofibers. In addition, also through electrospinning, along-side his students Bruce Y. Decker and Sinclair Calderon, he created Bismuth Telluride Filled Silicone conductive nanofibers. We will be recreating these experiments, using different infused nanoparticles, base materials, and solvents, searching for an increase in the nanofiber’s efficiency. Using the results from these past experiments, allows us to set a base for our research.

Electrospinning is one of multiple techniques, used for the fabrication of one-dimensional nanostructures. In 1934, a man named Anton Formhals, produced cellulose filaments with a device which used electrostatic repulsions between surface charges, which further developed electrospinning towards commercialization. The electrospinning process is a production method that uses electric force to draw charged threads of polymer solutions up to Nano-sized fiber diameters. Electrospinning is one of the most versatile methods capable of producing a controllable chemical and structural composition. In addition, this process is also cost effective and can be produced in large quantities. The electrospinning machine in our lab is set up, such that the electrospinning generates the nanofibers by the use of electrostatic repulsions between surface charges as found by Formhals. The system contains a syringe, which has a desired diameter, used to extrude the nanofiber fluid. The syringe has a metal tip, which is positively charged. There is a collector plate on the opposite end of the syringe, which is negatively charged. The opposing charges cause the nanofiber to be extruded.
towards the collector plate. Keep in mind that the collector does not necessarily have to be a plate, in fact, some electrospinning machines use rollers to collect the nanofibers. The system is powered by an electrical circuit, which runs on a required high power supply, due to the high resistance of the ambient air between the syringe tip and the collector tip. The voltage supplied is determined, based on the distance between the syringe tip and the collector. When setting up the electrospinning machine, there are a couple of additional things which should be considered, such as the room temperature and humidity in the room. The syringe's feed rate is also important, because this determines if the nanofiber solution is fully developed by the time that it exits the syringe.

FIGURE 1: ELECTROSPINNING MACHINE SCHEMATIC

Electrospun nanofibers for energy conversion and storage is desired due to their large surface area to volume ratio, as opposed to a single crystal.

The objective of creating ceramic nanofibers is for them to behave just as a dielectric would behave. A dielectric material is an insulating material, which is a poor conductor of current. This nanofiber shall behave opposite to the behavior of a metal, where there should be no current flow, in other words, no loosely bond or free electrons are allowed to travel though the material. In Dr. Gan’s previous research, when he created ceramic nanofibers, he used NaCo2O4. Analysis was performed on Sodium-Cobalt Oxide and it showed that enhancements were for the material’s conductivity and thermoelectric power. These results pointed toward the application of the material in high temperature thermoelectric
applications. The NaCo2O4 nanofibers were composed, by processing sodium acetate, cobalt acetate, and polynvinylpyrrolidone powder (PVP).

The objective of creating conductive nanofibers is to produce a flexible thermoelectric material for alternative energy applications. This composite material shall exhibit the Seebeck effect and reduce electrical resistance. The Seebeck effect is a phenomenon in which a temperature difference between two dissimilar electrical conductors or semiconductors produces a voltage difference between the two substances. In other words, this is the direct conversion of temperature differences to electric voltage. In Dr. Gan's previous research, when he created conductive nanofibers, he used Bismuth Telluride as the additive nanoparticle and silicone rubber as the base material. Polymers such as silicone rubber, provide flexibility to the composite; however, due to its insulating behavior, it does hinder the Seebeck effect. In order to increase the conductivity of this material, the rubber matrix is filled with semiconductor bismuth telluride. The silicone rubber matrix can increase phonon scatters, which will reduce the thermal conductivity. Since silicone rubber possesses high heat resistance and thermal stability, it can be implemented in a large temperature gradient environment for thermoelectric applications. There is a drawback when adding fillers in the silicone rubber. The strength and flexibility of the composite will be sacrificed if fillers are added in large quantity. In order to further increase the conductivity of the silicone rubber composite, we can also heat treat the material. Heat treating this silicone rubber base material will increase the electrical conductivity, which is the opposite behavior of heat treating a conductive material, such as Aluminum. In a metal, such as Aluminum, when heat treated, the atoms are quenched or rapidly cooled in order to freeze. This distorts and stresses the structure, making the electron movement more difficult, thereby decreasing the electrical conductivity. This behavior is opposite, when dealing with a silicone rubber matrix.
Recall that the objective of our research is to create composite nanofibers through electrospinning, in order to use them for energy conversion and storage. Regardless of the application of the final application of these nanofibers, the overall set-up and process is relatively similar. The primary difference between creating a ceramic nanofiber and a conductive nanofiber is the infused nanoparticles that are implemented in the base material, which give the resulting nanofibers their unique properties.

In Dr. Gan's previous research, when making the sodium cobalt oxide nanofibers, the following steps were taken. First, the Polyvinylpyrrolidone powder (PVP) was mixed with ethanol in a glass beaker. 0.375 grams of PVP and 5 milliliters of ethanol alcohol were used for the solution. After mixing the solution, 0.0683 grams of sodium acetate trihydrate was added. Finally, 0.0625 grams of cobalt (II) acetate tetrahydrate was added. The final solution was thoroughly mixed until the homogeneous solution was generated. The mixture was performed at room temperature, making sure that all solids were dissolved. After several minutes, the mixture was ready to be transferred into the syringe. The syringe was then mounted onto the electrospinning machine, where the syringe was controlled by a pump. As
explained earlier, the tip of the syringe was connected directly with a positive electrode. The pump extruded the nanofiber solution onto the negative electrode, which was connected to an aluminum plate, directly in front of the needle. A clean white paper towel was mounted on the plate to catch the nanofiber. This experiment was performed at room temperature for several hours. Here are some pictures of the sodium-cobalt oxide nanofibers:

![FIGURE 3: SODIUM-COBALT OXIDE NANOFIBERS](image1)

![FIGURE 4: SODIUM-COBALT OXIDE NANOFIBER DISTRIBUTION](image2)

The hypothesis for the sodium cobalt oxide nanofibers was that the fibers would behave as a dielectric material does, meaning that there would minimal current running through it, with increasing voltage. The material would experience net polarization of permanent dielectric dipoles which are already in the material; in other words, no loosely bond, free electrons, are allowed to drift through the material. After the nanofibers were Electrospun, they were tested to verify the hypothesis through tests that measured the temperature of the material, as it was
exposed to a 900Watt electromagnetic field over different time intervals. The following figure shows the temperature versus time of the sodium cobalt oxide nanofibers:

FIGURE 5: AVERAGE TEMPERATURE VS. TIME

This figure proves that the nanofibers have the ability to absorb heat almost instantly when exposed to an external electromagnetic field. The temperature increases more than 5 degrees in Celsius scale, only after 5 seconds of exposure. In order to test the nanofibers for their dielectric properties, a linear sweep voltammetry analysis was performed. Three trials were performed for this analysis. The following figures show the nanofiber's conductive response to an increasing applied voltage:

FIGURE 6: CURRENT VS. VOLTAGE TRIAL 1
The figures above show how the current in the nanofiber maintains relatively constant, as the voltage is increased across the material. Following Ohm’s Law, as the voltage increased, the resistance increase, maintaining the current relatively constant. The voltage was increased from 0 to 0.1 volts, in 0.001 intervals. In research conducted by Maensiri et al, it was shown that the CoO$_2$ component is responsible for the electrical conduction of the nanofiber, and the Na provides a charge reservoir to stabilize the structure. Research performed by K. Parker, shows that the thermoelectric properties could be enhanced effectively if the CoO$_2$ is
partially substituted for Cu. The following images are some of the compounds used by Dr. Gan in his previous research:

![Several compounds used in previous research](image)

**FIGURE 9: SEVERAL COMPOUNDS USED IN PREVIOUS RESEARCH**

In Dr. Gan's previous research, when making the conductive bismuth-telluride filled silicone nanofibers, the following steps were taken. First, 0.2 grams of bismuth telluride was mixed with 1.0 grams of silicone rubber. Thereafter, the solution was thoroughly mixed at room temperature and 0.12 grams of the solution was transported to the syringe. The syringe was set up onto the electrospinning machine, just as it was set up for the ceramic nanofibers, using the syringe pump and collector plate. The syringe pump operated at a rate of 0.1 mL per minute. The DC voltage that was connected to the syringe tip, delivered up 30 kV of voltage. Due to the high-voltage electric field, the bismuth telluride and silicone rubber solution was stretched and extruded under electrostatic and surface tension.

In order to test the conductive bismuth-telluride filled silicone nanofibers, two separate sets of experiments were performed to test for electrical resistivity and Seebeck coefficient. It was expected that the presence of the silicone rubber matrix would increase phonon scatters and hence reduce thermal conductivity. Although thermal conductivity of bismuth-telluride filled...
silicone nanofibers was not tested, the Wiedemann-Law can be used to relate the electrical conductivity to the electrical component of the thermal conductivity $\chi^e/\sigma T = \text{constant} = \text{Lorenz number}$, where $\chi^e$ is electron thermal, and $\sigma$ stands for electrical conductivity. Two composites of the bismuth-telluride filled silicone nanofibers were tested for resistivity and Seebeck coefficient. The following figures shows two trials for each of the two samples that were tested, as well as the Seebeck Coefficient varying with time, under two different temperatures:

FIGURE 10: VOLTAGE VS CURRENT OF SAMPLE 1
FIGURE 11: VOLTAGE VS CURRENT OF SAMPLE 2

FIGURE 12: SEEBECK COEFFICIENT AT TWO DIFFERENT END-TEMPERATURES
The test results showed no significant differences in the two consecutive experiment trials. The silicone rubber exhibits high electrical resistance in the nanofiber. By Ohm's Law, as the voltage increases and the current decreases, the resistance increases. Although electrical resistance is increased by using silicone rubber matrix, thermal conductivity is reduced as a result of an increase in phonon scatters. Therefore, there is a compromise between the electrical resistance and the thermal conductivity when choosing silicone rubber as the matrix. The figure above presented the Seebeck coefficient of the material with varying hot end temperatures. After reviewing the analysis, at 313 K, an average Seebeck Coefficient of 0.029 V/K is exhibited in the material. It is apparent that the presence of bismuth telluride in the silicone rubber matrix can effectively enhance the thermoelectric property. The average Seebeck Coefficient in pure bismuth telluride is 250E-06 V/K. This increases the Seebeck Coefficient by a factor of 116. As a result, the thermoelectric property of the composite material is increased significantly compared with the bulk reference material. In further improvement on the energy conversion efficiency, it is possible for making a flexible thermoelectric material for alternative energy applications. Generally, a good thermoelectric material should have a high Seebeck Coefficient. An excellent thermoelectric material should have a low thermal conductivity value.
PROGRESS

Currently, we have tested the hyperthermia effect of non-infused Electrospun nanofibers, under normal conditions where the nanofiber has not been exposed to any post-processes, as well as under a heat treatment post-process. We heat treated the nanofibers for 2 hours at 500 degrees Celsius and then tempered down to room temperature. We test both of these scenarios, prior to infusing the base with a nanoparticle, in order to see if the heat treatment of the base material will have an effect on the final product. Unfortunately, we have not been able to infuse our base materials with nanoparticles at the moment; however, that is the next step in our research.

In our current research, we have successfully Electrospun polyacrylonitrile (PAN) fibers, which were initially dissolved in N-Dimethylformamide solvent, resulting in a liquid nanofiber substance. First, we obtained 0.375 grams of the polyacrylonitrile (PAN) and dissolved in in 15 ml of the N-Dimethylformamide solvent. This substance was then capped off from ambient air, or else the solvent will evaporate. The solution was later placed in the syringe pump and put through the Electrospinning process. The syringe pump operated at a rate of 0.05 ml per minute. We used 10 ml of the nanofiber solution. Our results were successful, the following temperature vs. time data and figures show the nanofiber’s response to hyperthermia. The data tables show the different trials, average temperature, and natural log value for each time interval. The figures below, plot the relationship between the temperature and time. The natural log plot, shows the behavior of the data as an exponential function:
TABLE 1: HYPERTERMIA TEMPERATURE DATA

<table>
<thead>
<tr>
<th>Time (seconds)</th>
<th>Temperature (°C)</th>
<th>Avg.</th>
<th>ln(Temp)</th>
</tr>
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<td>29.600</td>
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<td>36.600</td>
<td>3.581</td>
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<tr>
<td>30</td>
<td>41.400</td>
<td>41.400</td>
<td>3.701</td>
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</tbody>
</table>

FIGURE 13: TEMPERATURE VS. TIME
FIGURE 14: Ln (TEMPERATURE) VS. TIME

TABLE 2: HYPERTERMIA TEMPERATURE DATA AFTER HEAT TREATMENT

<table>
<thead>
<tr>
<th>Time (seconds)</th>
<th>Trial 1 (°C)</th>
<th>Trial 2 (°C)</th>
<th>Trial 3 (°C)</th>
<th>Trial 4 (°C)</th>
<th>Trial 5 (°C)</th>
<th>Trial 6 (°C)</th>
<th>Avg. (°C)</th>
<th>ln(Temp)</th>
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<td>46.600</td>
<td>46.000</td>
<td>46.133</td>
<td>3.832</td>
</tr>
</tbody>
</table>
Polymer & Solvent - Heat Treated

FIGURE 15: TEMPERATURE VS. TIME AFTER HEAT TREATMENT

\[ y = 0.8322x + 18.082 \]

Ln Plot

FIGURE 16: LN (TEMPERATURE) VS. TIME AFTER HEAT TREATMENT

\[ y = 0.0265x + 2.9825 \]
\[ R^2 = 0.9604 \]
CONCLUSION

After evaluating our produced nanofibers and reviewing our data, part of our hypothesis thus far proves to be correct. The heat treatment of the nanofibers has increased the heat generation of the material, when exposed to an external electromagnetic field. After testing both of the samples, heat-treated and non-heat-treated, it is clear that the heat-treated sample has a faster exponential increase in temperature. When looking at the temperature vs. time data plots above, when observing the natural log plots, the exponential curve of the heat treated nanofiber is greater, judging by the $R^2$ value of the plot. When plotting data as a natural log value we assume that the data is exponential and the accuracy of this assumption is dictated by the $R^2$ value of the data plot. The non-heat-treated data yields an $R^2$ value of 0.9564, while the heat-treated data yields an $R^2$ value of 0.9604. An $R^2$ value equal to 1.0 would mean that the function is truly exponential. Although the $R^2$ values between the two data sets is not significantly different, it does show that the heat-treatment has an effect on the heat generation of the material. The heat-treated nanofiber has the potential to be used as the base of a ceramic nanofiber, which exhibits a dielectric behavior. Moreover, this nanofiber has the potential to be used as a form of energy storage in the biomedical engineering field. After heat treatment, this nanofiber would not be a wise choice as the base material of a conductive nanofiber, due to its high thermal conductivity. In a conductive nanofiber, we want a low thermal-conductivity and low electrical resistivity. The goal of a conductive nanofiber is to achieve a high Seebeck Coefficient, and that is achieved by having a high temperature difference, meaning that we do not want the material to store any of the heat. On the other hand, the goal of a ceramic nanofiber is to have high electrical resistivity and high thermal conductivity in order not to generate a current in the material. We want all of the heat to be captured in the material and maintained stored.

The next steps in our research are to infuse the solution with nanoparticles to either produce a ceramic nanofiber or a conductive nanofiber; depending on heat-treatment. We will also be using alternative solvents and polymer base materials. Our goal is to achieve a ceramic nanofiber that with higher dielectric and hyperthermia properties than the
previously created NaCo2O4 nanofibers. We also aim to create a conductive nanofiber that has higher Seebeck Coefficient and lower electrical resistance than the previously created bismuth-telluride filled silicone nanofibers. The following figures are images of our current lab and research progress:

FIGURE 17: THE POLYMER BASE MATERIAL & SOLVENT –
polyacrylonitrile (PAN) & N-Dimethylformamide solvent

FIGURE 18: NANOFIBER SOLUTION & ELECTROSPINNING POWER SUPPLY
FIGURE 19: SYRINGE PUMP SET-UP

FIGURE 20: NANOFIBER COLLECTOR PLATE & NANOSCALE MICROSCOPE

FIGURE 21: 900W MICROWAVE FOR HYPERTERMIA TESTING & TEMPERATURE READING
FIGURE 22: PRODUCED NANOFIBERS

FIGURE 23: HEAT TREATING FURNACE & HEAT TREATED NANOFIBER
BIBLIOGRAPHY