THERMOELECTRIC PROPERTIES OF LEAD TELLURIDE FILLED SILICONE

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ABSTRACT

Lead telluride filled silicone composite was processed into wires under high-voltage electric field using an electrospinningfacility. It has been found that the electric field helped to mix the PbTe power with the silicone rubber matrix in liquid form and the final composite product is aligned into millimeter sized wires. The length of the manufactured wire was about 50 mm in length and 1 mm in diameter. Electrical resistance and Seebeck coefficient of the lead telluride filled silicon matrix composite wires were tested. The electrical property of the thermoelectric lead telluride/silicone composite wire follows the Ohm's laws. Its resistivity, at the order of 10^{-6}ohm*m,is determined by the intrinsic electron conductive behavior. The material exhibits a relatively high Seebeck coefficient. The figure of merit of the composite wire is estimated as 2.8×10^{-6}. Further improvement on the energy conversion efficiency is needed for the material to be used for alternative energy harvesting.

INTRODUCTION

About two-thirds of energy input of electricity generation in the U.S is lost as useless thermal energy during the conversion process [1]. Thermoelectric materials can offer promising breakthroughs due to their ability to recover thermal energy and convert it into electricity.The scientific discoveries of thermoelectricity were mainly found during two periods of history. From 1821 to 1851, fundamentals of thermoelectric properties were understood. Intensive experiments were done to understand thermoelectric materials microscopically since 1930s [2]. The properties of thermoelectric materials depend on the Seebeck, Peltier and Thomson coefficients αor S, Π, and τ. Thomas Johann Seebeck discovered the Seebeck effect in 1823. In a circuit with two dissimilar conductors, a and b, each has different temperatures at junction W and X. If those two conductors are p-type and n-type materials, voltage difference can be induced in the circuit. This effect is called Seebeckeffect [3]. The equation for Seebeck coefficient is $\alpha_{ab}=dV/dT$ under open circuit condition[2]. If the temperature at junction W is higher than junction X, α takes a positive valuebecause a thermocouple ab would produce a clockwise current. The electric potential that is induced depends on the material and the temperature gradient. Hence the equation to calculate the induced electromotive force is $E_{AB}= S_{AB}\Delta T$. S_{AB} is defined as the relative Seebeck coefficient between the conductors, A and B. If more than one pair of conductors are present, then the equation becomes $E_{AC}= E_{AB} + E_{BC} = (S_{AB}+S_{BC})\,\Delta T$. S_{AB} is calculated by subtracting S_B from S_A [3].

The efficiency of thermoelectric materials is determined by the figure of merit. A figure of merit is a quantity that describes performance of the device. A large dimensionless figure of merit value, ZT, indicates a good thermoelectric property. The equation is$ZT= (S^2 *\sigma*T)/k$. S is the Seebeck coefficient. σ is the electrical conductivity. k is the total thermal conductivity [4]. The equation above shows that the figure of merit should increase proportionally to the square of Seebeck coefficient. To ensure that the thermoelectric figure of merit is maximized, a large thermopower which is an absolute value of the Seebeck coefficient S, high electrical conductivity σ, and low thermal conductivity k are required [5]. The electrical conductivity can be increased by adding conductive fillers to form interconnected networks [6]. To confirm that the Seebeck coefficient is large, only a single type carrier should be present. Both charged carriers would move to the cold end and cancel out the induced

Seebeck voltage if mixed n-type or p-type conduction is present [5]. The thermoelectric power factor PF = $S^2\sigma$ (with the unit of $Wm^{-1}K^{-2}$) is another wayof determining thermoelectric property other than Seebeck coefficient. The thermoelectric power factor is used for application on energy generation because it indicates the quantities of electric power [7].

Lead telluride is a semiconductor that has one of the best thermoelectric properties [9]. It has a high melting point, good chemical stability [8] [11]. PbTe is one of the best solid-state thermoelectric materials, and its temperature range is 323-900 K in energy generators [9]. It has a narrow band gap of 0.31 eV at 300K, face centered cubic structure (FCC), and large exciton Bohr radius of 46 nm which makes an ideal material to observe its properties and behaviors under quantum confinement conditions [9,10]. By utilizing this material, thermal energy can be converted into electric energy. PbTe is used for thermoelectric power thermo-generation for temperature range 500-900 Kelvin [11]. But PbTe is poisonous due to the heavy metal of Pb. In order to encapsulate it, filling it into polymer matrix may be a way to reduce its danger.For the first time, the Seebeck effect of PbTe filled silicone composite is tested in this work. Our experiment generatescorrelation between the electrical potential difference andthe test temperatures.The lead telluride filled composite may have a wide arrange of uses. It can be used to reuse waste heat from refrigeration, power generation and electronics cooling.

The silicone/PbTecomposite is produced by mixing lead telluride with silicone rubber matrixin liquid form. Silicone is selected for its low thermal conductivity, low chemical reactivity and non-toxicity. Silicones are also very good water repellent. Due to its flexibility and impermeability, lead telluridefilled into thesilicone matrix withthe flexibilitymay be applied on industrial heat pipes to recover waste thermal energy. Silicone's hydrophobicity is caused by low weight molecules in the bulk of the material that skim up to the surface because of difference in diffusion density [12]. Under normal steam pressure, silicone rubber shows no signs of deterioration. In solid form, it is able to retain water repellency, dielectric properties and thermal degradation resistance [12]. $-[Si\text{-}O]_x$- chain segments provide flexibility and Si-O bonds have high strength. Silicones have low heat release rate, and this property allows PbTe to absorb heat more efficiently.

It is expected that lead telluridemixed with silicone matrix can be manufactured into wire form using electrospinning. As thePbTe powder-silicone liquid was extruded out, the electric field continuously bends and stretches the ejected fluid into very thin shape. An electrical field influences the liquid droplet until it reaches a critical voltage Φ_0 [13]. As results of electrospinning,theproductcouldhave high surface to volume ratio and enhanced strength [13]. Electrospinning is the ideal method to produce continuous rods, wires orfibers due to its versatility. Electrospinning is easy to set up, and fiber diameter is controllable. This process is used widely in various fields. For the development of electronics, catalytic and hydrogen storage systems, nanofibers are manufactured by such process [14]. Nanofibers generated by electrospinningare very fine with the sizes ranging from less than 3 nm to over 1μm [15]. The process of electrospinning was first dated back to the 17th century. William Gilbert first discovered this technology in 1600 [16]. In 1745, Bose created aerosol by using high electric potential to a liquid at the end of a glass capillary tube[17]. Lord Rayleigh predicted the minimum charge thata liquid could carry to overcome its surface tension. If the charge is unstably large, fission takes places and stabilizing effect of surface tension is minimized [18]. John Francis filed the first electrospinning patent in 1900 [19]. In this paper, for the first time, we generated fairly thick wires containing the PbTe powder and the silicone matrix. The composite wire was tested in view of the thermoelectric behavior.

MATERIALS AND EXPERIMENTAL METHODS

0.8 g of silicone was weighed prior to mixing. 0.2 g lead telluride powder with the diameter of 50 micronas supplied by Alfa Aesarwas mixed with the liquid form silicone and transferred to a plastic syringe. The volume of the syringe was 10 mL. As illustrated in Figure 1, a syringe pump was installed to push the liquid at a constant speed of 0.05 mL/min. A DC power supply was adjusted to deliver 10 kV of voltage to the syringe tip. The voltage applied in the electrospinning process is usually ranged from 10 kV to 30 kV [20]. The metal plate was used as a grounded collector for the lead telluride-containing composite material. Due to theelectrostatic attraction, a continuous uniform small rod was extruded towards the grounded collector as the syringe pump pushing liquid from the syringe. In this experiment, the grounded collector was a flat rectangular metal plate. The grounded collector is also known as the counter electrode. In addition, other types of possible counter electrode are rotating cylinders, disks, two parallel bars, etc. [20]. The Seebeck coefficient of lead telluride filled in silicone was measured with a self-designed instrument.

To implement the experiments, a Talboys (trade mark)electrical heating plate was used to generate temperature gradient. An infrared thermometer was used to measure the temperature. The two ends of the PbTe/silicone composite rod/wire specimens were wrapped by aluminum conducting foils to make sure the heat conducting is good. The aluminum foil at each end serves as the electrical conducting path for the electrical resistance and the Seebeck coefficient measurements. For the Seebeck experiment, one end was put on the Talboys hot plate, and the other end was exposed at the ambient temperature of 25 ^{o}C. For both resistivity and Seebeck coefficient measurement, a CHI 600E Electrochemical Analyzer was used to record the current, electrical potential data. The recorded data were used to calculate the resistivity and the Seebeck coefficient of the composite material. When measuring the electrical resistance of the sample, scan rate was set at 0.01 volt/second. Initial voltage was set at 0 V, and final voltage was 0.1 V. For measuring Seebeck coefficient, the electrical potential range was adjusted between 0-1 V and the runtime was set as 50 seconds to prevent any overflow of data.

RESULTS AND DISCUSSION

In this section, the results related to the resistivity measurement will be presented first. Then, the Seebeck coefficient measurement data will be illustrated. Finally, the estimation of the figure of merit will be given. Figure 2 and 3 showed the relationship between voltage and current. The CHI 600E Electrochemical Analyzer was used to supply an increment voltage of 0.001 from 0 to 0.1 V When current is zero, the voltage is relatively high. Hence, the material behaves like a circuit with high impedance. As current increases, the electrical potential decreases as shown in Figure 3. In this case, the material behaves like a circuit with decreasing impedance.

Since silicone matrix has the potential to be used as an insulator for the thermoelectric material. Adequate measurements of electrical properties of such material are indispensable. The other reason for testing electrical resistance was that electrical resistivity was one of the factors that determine the figure of merit. The equation of electrical resistivity is $R = \rho*L/A$. The length of the manufactured rod using electrospinning was measured as 50 mm and the diameter was measured as 1 mm. Due to the fact that the highest electrical resistance of the thermoelectric Lead Telluride measured was $5.93*10^{10}$ ohms, the electrical resistivity was calculated to be $9.31*10^{5}$ ohm*m. One of the reasons for selecting silicone rubber is because of its hydrophobicity. Hydrophobicity is related directly with current leakage [24]. Thus, silicone rubber functions as an insulator for the Seebeck coefficient experiment. In addition, insulators generally have high seebeck coefficients.

Lead telluride doped with silicone exhibits enhanced Seebeck coefficient and significant increase in resistance. This is due to Silicone's low thermal conductivity and low chemical reactivity. Electrons cannot pass through the lattice structure as easier as other types of materials.

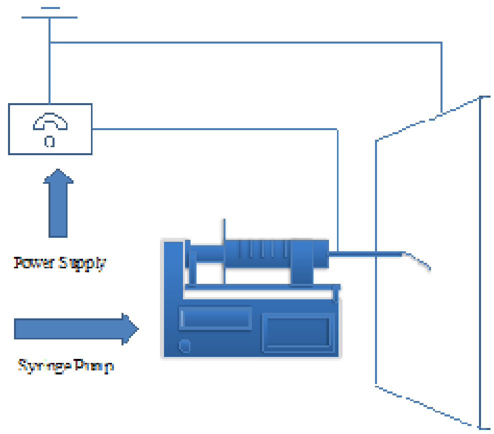

Figure 1: Experimental setup diagram. The syringe tip was connected to the power supply which delivered 10 kV DC voltage. Due to electrostatic attraction, a PbTe/silicone composite rod was extruded.

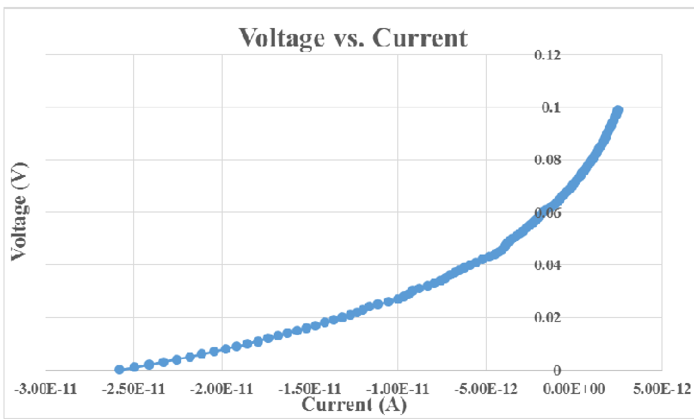

Figure 2: CHI 600E Electrochemical Analyzer supplied an increment voltage of 0.001 Vfrom 0 to 0.1 V.

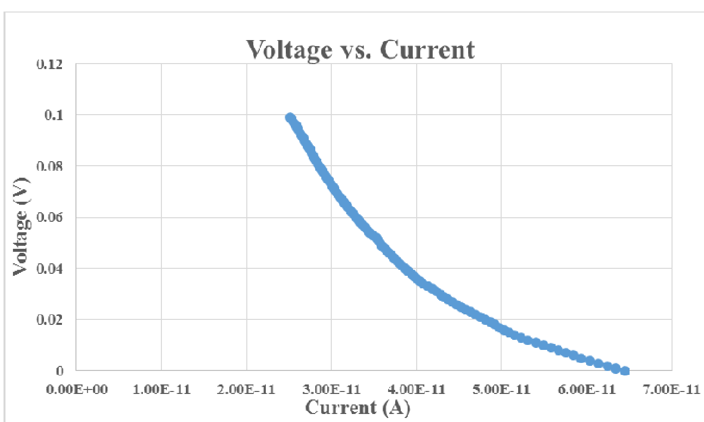

Figure 3: CHI 600E Electrochemical Analyzer supplied a decrement voltage of 0.001 V from 0.1 to 0 V.

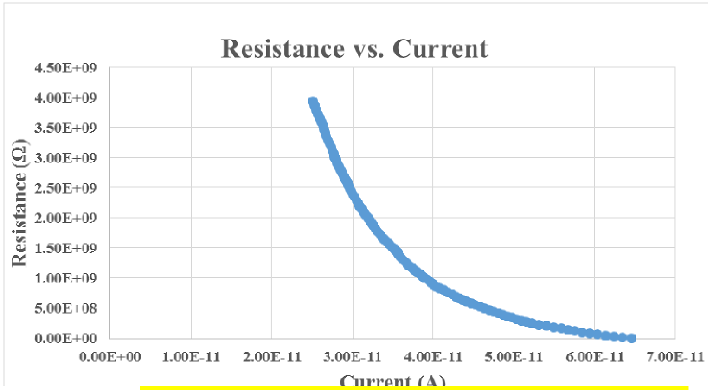

Figure 4: The relationship between resistance and current

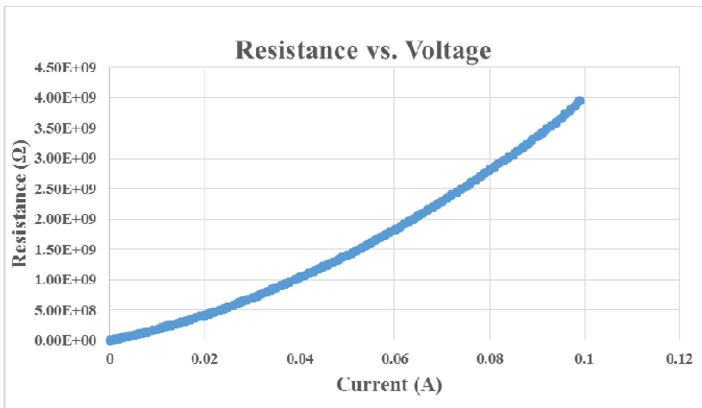

Figure 5: The relationship between resistance and current

In order to calculate the resistance of the composite material wire/rod, the I~V data generated from the potential scan tests are used in calculations using Ohm's law. Figure 4 represents the results of resistance as obtained from Figure 2. The trend of change shows a monotonically decreasing in the resistance. Similarly, the I~V data as shown in Figure 3 were used into resistance change. The resulted trend is given in Figure 5. Obviously, the general trends are like the intrinsic electron conducting behaviors.

From Figure 6-9, the temperature dependentSeebeckcoefficients of the lead telluride/silicone composite show negative Seebeck coefficients, which means electrons are the dominant charge carriers [21]. If electrons are diffused from the hot side to the cold side, then the material is n-type. In contrast, electrons tend to diffuse from the cold side to the hot for p-type materials [22]. A large Seebeck coefficient requires the material to be only a single type of carrier. Mixing n-type and p-type will cause both charge carriers to be moved to the cold end and cancel out the induced voltage [23]. Seebeck coefficient is calculated by the ratio between the voltage different induced by the material and temperature gradient, i.e. $S = \Delta V/\Delta T$. Since Seebeck coefficient is temperature dependent, several runs of measurements were performed. Figure 6-9 illustrated the Seebeck coefficient of the thermoelectric material was measured when the hot end temperature was set at 319K, 321K, 325K and 331K, respectively. The material in this experiment exhibits high absolute Seebeck coefficient valuesbecause it is about three times higher than that of the bulk PbTe. The Seekbeck effect may also be related with the concentration of lead telluride in the silicone rubber matrix. IN the currently made composite wire, the ratio of PbTe to silicone is about 2:8. However, if we increase the addition of PbTe too much,the flexibility of silicone will decrease. There is a trade-off for increasing the lead telluride content. Proper concentration of lead telluride was considered prior to the experiment.

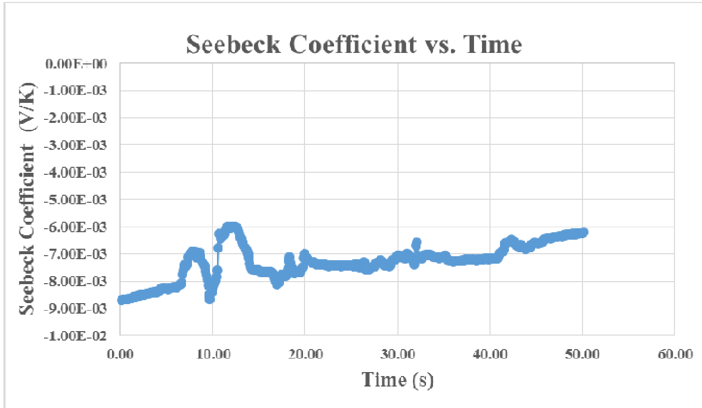

Figure 6: Seebeckcoefficient measured at the hot end temperature of 319 K

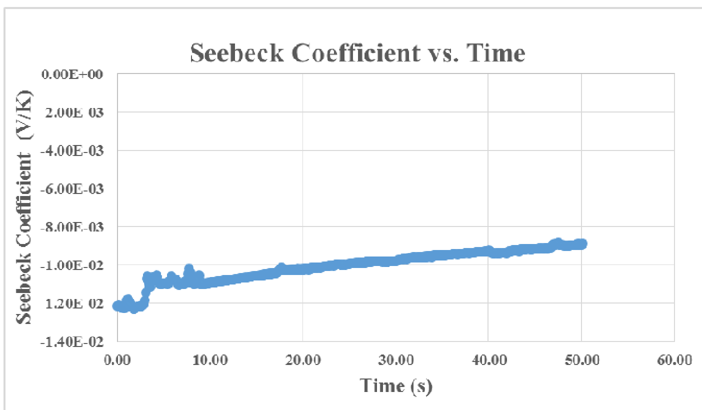

Figure 7: Seebeckcoefficient measured at the hot end temperature of 321 K

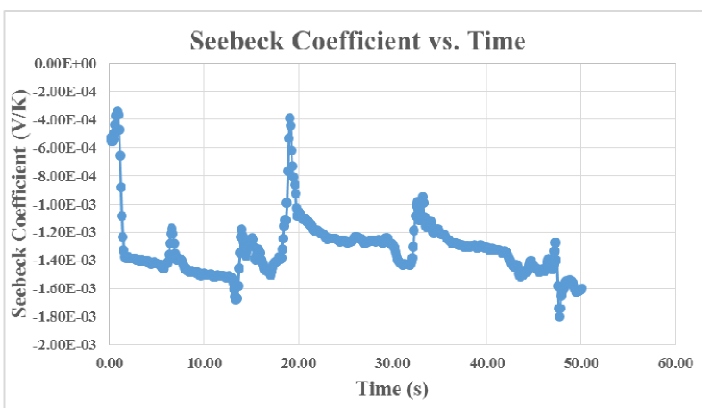

Figure 8: Seebeckcoefficient measured at the hot end temperature of 325 K

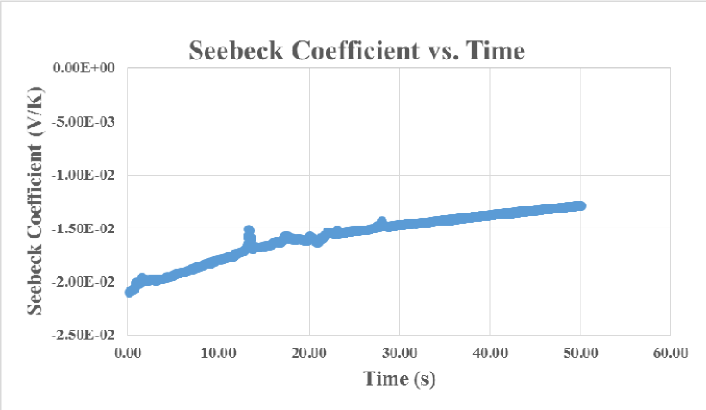

Figure 9: Seebeckcoefficient measured at the hot end temperature of 331 K

In order to examine the energy conversion efficiency, the figure of merit of the composite materials is estimated. Earlier study showed that the thermal conductivity of the PbTe is about 0.7 $W/m^{-1}K^{-1}$ [25]. The silicone rubber has a lower band of thermal conductivity of 0.2$W/m^{-1}K^{-1}$[26]. By Rule of Mixture for composite materials, the thermal conductivity of the PbTe/silicone composite material with 20 wt% (or 0.04 vol %) PbTe made in this work is about 0.22 $W/m^{-1}K^{-1}$. The electrical resistivity as determine from Figure 4 and 5 is about the $9.31*10^{5}$ ohm*m. The electrical conductivity should be $1/(9.31*10^{5}$ ohm*m)=$1.07*10^{-5}$ S/m. The Seebeck coefficient as determined from Figure 6 to 9 is around $-07*10^{-3}$V/K. Thus the ZT value is about $2.87*10^{-6}$ at the temperature range of 320 K. This value is considerably low which is compared to the values of oxide ceramics and some conducting polymers. Therefore continued improvement on the thermoelectric property of this composite material is needed before the consideration for real world energy conversion applications.

CONCLUSIONS

In summary, this preliminary study investigates the thermoelectric property of lead telluride filled silicone matrixcomposite material viaelectrospinning. The material exhibits relatively highSeebeck coefficient, but shows large electrical resistance. This is due to the fact that silicone rubber functions as an insulator. The mixture showed high Seebeck coefficient value because of the strong thermoelectric behavior of the filler, PbTe powder. The results showed significant increase in Seebeck coefficient because of silicone rubber's hydrophobic ability to inhibit current leakage. The loss of hydrophobicity of silicone rubber will result in a conductive film being formed on the surface. Leakage current is the inevitable loss of the current under high voltage. The experiment tested the electrical properties of this mixture. The highest electrical resistance measured was $5.93*10^{10}$ ohms. Hence, the highest electrical resistivity was calculated to be $9.31*10^{5}$ ohm*m. Since majority of the energy in industries are lost as waste, lead telluride has intrinsic properties which can offer promising potentials in the development of thermoelectric devices. But for the PbTe filled composite material, the figure of merit is only at the order of 10^{-6}. A significant improvement of the thermoelectric property is needed before its application for waste energy harvesting.

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