Enhancement of power generation of thermoelectric generator using phase change material

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Abstract. This paper demonstrates a thermoelectric generator (TEG) that embeds phase change material (PCM) for waste heat energy harvesting. In this TEG module, a volume of molten carbonate salt is encapsulated in a cuboid polydimethylsiloxane (PDMS) body. In order to study the effect of embedded PCM on the TEG performance, we compared the performance of TEGs with and without PCM. The results show that a higher output voltage and a longer energy harvesting time can be reached in TEG with PCM in compared with the corresponding values in the TEG without PCM once the heat source stops supplying heat. Especially, the relative increase of the total electricity by adopting the PCM is as large as 25%. Our work proposes an effective and feasible way to enhance the performance of the TEG system by application of the PCM.

1. Introduction

With the rapid development of industrialization, energy crisis and environmental pollution become increasingly worse. Energy saving and the development of new green energy sources have become the important national policy for many countries. There are a lot of low-grade energy sources in the existing energy system, such as extremely rich solar energy and waste heat of huge potential for recovery. It is very important to use these low-grade energy sources effectively for relieving energy crisis and environmental pollution. Thermoelectric generator technology is a new type of green conversion technology that can convert heat directly into electricity [1], which has the advantages of no noise, compact structure, light in weight, high reliability, low operating costs and long life. Therefore the TEGs have attracted more and more attention in scientific community [2-4]. So far, many kinds of TEGs have been used in recycling these low-grade energy sources [5-8]. But the relatively low efficiency of the TEGs still limits the widely use in commercial applications.

The material properties [9-12] and the device structure of thermoelectric modules [13-15] are primary factors that determine the energy conversion efficiency. Hsu et al. designed a system for the recovery of waste heat that comprises 24 TEG modules to convert heat from the exhaust pipe of an automobile to electrical power [16]. Yee et al. showed that even very expensive thermoelectric materials have the potential to be the most cost effective at the system level, if incorporated with sufficiently short legs and small fill factor [17]. The design of the geometry of the TEGs is useful for the TEGs, but the energy conversion efficiency of TEGs is still limited. The reason may come from the fluctuation of the heat sources. For example, the low-grade energy sources, such as solar energy and waste heat are intermittent, periodic and would vary over time and space. The fluctuation of the
heat sources decreases the expected performance of the TEGs and this issue demand detailed investigation.

Adopting PCM is one possible way for storing the heat dissipation of TEGs. PCM can store a large amount of heat energy through the latent heat of melting when the phase change occurs. As a result, the TEG can continue to work without the heat source when the PCM are encapsulated near to the hot junction of a TEG. Jo et al. proposed a TEG that embeds PCM for recycling wasted heat and found that the TEG continued to produce electricity as heat source by using the heat stored in the PCM [18]. Zhang et al. proposed a TEG for solar and ambient energy harvesting [19-21]. The PCM is used as heat sink at day and as heat source at night. So the system can work continuously day and night. Yoon et al. demonstrated an impact-triggered thermoelectric generator that uses latent heat liberated from the crystallization of supersaturated sodium acetate trihydrate (SSAT). With SSAT as the phase change liquid, a single IT-TEG can generate a maximum instantaneous power of 2.08 mW [22]. Tan et al. proposed a thermoelectric cooling system integrated with PCM for space cooling purpose, in which PCM stores cold thermal energy at night and functions as a heat sink to reduce hot side temperature of thermoelectric modules during daytime cooling period and thus improve the performance efficiency of the system [23]. Jaworskia et al. presented a TEG with PCM module. The solar radiation is used as a heat source. PCM absorbs heat during its melting as heat sink to stabilize temperature of the cool side. Thus, electrical properties of the TEG are stable and clearly greater than in the phase of solid/liquid heating [24].

These literatures investigated an analogous TEG device structure using PCM as heat sink. The PCM is embedded in the cold side of a TEG and the efficiency of the TEG decreases because of the dropping of the temperature gradient when the PCM absorbs the dissipated heat from heat source. In this work, we propose a TEG system, in which the PCM is close to the top face of the TEG. In this system, two pairs of \( p \)-type and \( n \)-type semiconductor columns connected in series by metal electrodes in a cuboid polydimethylsiloxane body and PCM acts as heat source to generate electricity uninterruptedl when the heat source is removed. The proposed TEG can generate electrical energy uninterruptedl with the stored heat in the PCM when the heat source stops supplying heat energy, without any break in the output voltage and any change in the voltage direction.

2. Design and methods

Among various PCM, molten carbonate salt, a kind of high temperature phase change material, is widely applied in solar energy heat storage and waste exhaust gas recycling and reusing for its advantages, such as large latent heat, small sub cooling, high thermal capacity, good thermal stability, low cost etc. A kind of mixture molten carbonate salt mixed with \( \text{Li}_2\text{CO}_3\), \( \text{Na}_2\text{CO}_3 \) and \( \text{K}_2\text{CO}_3 \) (named \( \text{M}_2\text{CO}_3 \)), prepared by static melting method is used in this study. It has a large phase change enthalpy about 162 kJ/kg and a high phase change temperature between 363.9 to 399.5 °C. In addition, it has very low volume changes during melting.

Figure 1(a) shows a cross-sectional view of the experimental system. The apparatus includes the fabricated TEG, a vacuum chamber, a thermostatic water bath and a data acquisition unit. In order to form a thermoelectric couple, \( p \)-type and \( n \)-type semiconductor columns are connected in series by some copper electrodes. As showed in Figure 1(a) and (b), the TEG is assemble by the following several parts. Two pairs of thermoelectric couples with the diameter of 0.6 cm and the length of 2 cm are employed. A cuboid PDMS body with the side length of 4 cm and the height of 1.7 cm is used to support the TEG. It has an inner annular space for loading PCM. A papery square PDMS cover matched the size of PDMS body about 0.1cm thickness is covered to form an enclosure space.
As showed in Figure 1, the position of PCM is asymmetric about the z-axial direction and close to the top face of the TEG. Two pairs of p-type n-type semiconductor columns run through the PDMS body. The electrical connections for the semiconductor columns on the top face of the TEG are in thermal contact with a heating copper block source. The temperature of heat source ($T_h$) and PCM ($T_p$) is separately measured for comparison. The bottom face of the TEG with circulating cold water in another square copper block is defined as the cold junction (heat sink). Cold junction temperature can be derived from three thermoelectric couples’ temperature ($T_{c1}$, $T_{c2}$, $T_{c3}$). Two copper electrodes are welded on the ends of two semiconductors for voltage output. There is an AlN substrate between the copper electrodes and the cold square copper block for thermal insulation. The entire equipment is in a vacuum chamber for suppressing interference by air convection.

**Table 1.** A list of equipment uncertainty and experiment uncertainty.

| Equipment uncertainty | Operating or measuring range | Resolution | Relative uncertainty |
|-----------------------|----------------------------|------------|----------------------|
| Heater                | 470-530 °C                 | 0.3 °C     | 0.1%                 |
| Low temperature chiller | 10-25 °C                  | 0.2 °C     | 1.0%                 |
| Agilent 34970A        | 1-5 mV                     | 3 μV       | 0.3%                 |

| Variable | Measure value @500°C | Mean value | Sample standard deviation | Uncertainty |
|----------|----------------------|------------|--------------------------|------------|
| $T_h$ (°C) | 503.2 504.3 503.8 | 503.8     | 0.6                     | 0.1%       |
| $T_c$ (°C) | 14.4 15.4 14.8       | 14.9       | 0.5                     | 3.4%       |
| $U$ (mV)   | 118.712 119.232 118.946 | 118.963   | 0.260                   | 0.2%       |

When the heat energy is supplied to the hot side, since the PCM are located close to the hot side, the heat conducts from the heat source to the embedded PCM. A large amount of heat energy is absorbed along with the temperature of PCM rising until occurs phase change. Because the thermal resistance between the PCM and the TEG is much larger than that between the heat source and the
TEG, the junction temperature of the TEG is dominated by the heat source. Once heat source stops supplying energy, the PCM plays the role of heat source to generate electrical energy uninterrupted because of phase change. The temperature on the hot side of the TEG is mainly determined by the melting point and the latent heat of the PCM. The asymmetric displacement of the PCM leads to this temperature difference between the pairs of junction. Therefore, such a device structure is expected to maintain its energy conversion efficiency and to produce electricity continuously.

Before experiments were carried out, the heater and low temperature chiller as well as thermocouples were calibrated to ascertain their accuracies. All the experimental data are obtained from the average of multiple measurements. The relative uncertainties of the adopted equipments are listed in Table 1. It can be seen that the relative uncertainty due to the equipments is no larger than 1.0%. To provide an error analysis of experiments, Table 1 also lists the data of temperatures and voltage in the experiments where the hot junction temperature ($T_h$) and cold junction temperature at 500 °C and 15 °C, respectively. It can be seen that the uncertainty is controlled to be below 3.4%.

3. Results and discussion

To discuss the influence of the PCM embedded on the performance of the TEG, the performance of the TEGs with and without PCM were compared in this work. The temperatures of the heat source, heat sink and the PCM were measured by exact Omega K-thermocouples. The power supply system was controlled by a PID temperature controller. An Agilent data collector 34970A was used for collecting the output voltages and temperature signals.

![Figure 2](image.png)

**Figure 2.** Output voltages of each TEG as a function of $\Delta T$.

The heating copper block was attached to the hot side of the TEG for half an hour at a setting temperature and then stopped working. Figure 2 shows the output voltages of each TEG as a function of the temperature difference ($\Delta T$) between the hot and cold junctions. The output voltages of the TEGs increases linearly with the increasing $\Delta T$ and the output voltages of the TEGs with and without PCM show a similar average output voltage of 270 µV K$^{-1}$ for all thermoelectric couples.

The heat source is in contact with the TEGs with the heat source temperature set at 500 °C for proper time and then stops supplying. The measured junction temperature and output voltage are shown in Figure 3. The temperature of the cold-end ($T_c$) is obtained by the average of three thermocouples. $T_c$ curves show stable regular wavy due to the PID temperature controller. When the heat source is in contact with the TEGs (switch closed), the temperatures of the hot junctions ($T_{Cu}$ and $T_{PCM}$) and output voltages ($U_V$) show similar behavior for each type TEGs (with R$_2$CO$_3$ named type R and empty named type E). Temperatures of hot junctions rise rapidly when the heating copper block sources supply heat to the TEGs. However, once the heat source is removed (i.e., the switch is open), variation in the change of the temperatures are observed for each type. In the case of type E (Figure
3a), the hot junction temperature decreases rapidly after heat source removals. In the case of type R (Figure 3b), the temperature holds for a period of time about 100s because the stored heat in the PCM releases into the thermal circuit. Therefore, the temperature of hot junction of type R does not decrease rapidly. Consequently, the temperature difference across the thermopile junctions of type R is maintained longer than that of type E.

Figure 3. Temperature and output voltages variations in the whole working process. (a) TEG without PCMs, (b) TEG with PCMs.

The output voltages for each type of TEG as functions of time with different heating temperatures (470, 500, 510, 530 °C, respectively) are shown in Figure 4. As addressed above, in the case of type E, the hot junction temperature decreases rapidly once the heat source removals. However, in the case of type R, the temperature holds for several period of time about 50-250 s due to the stored heat in the PCM. The initial output voltages (with the contacted heat source) of type R are higher than those of the type E. After the removal of the heat source, the output voltages of type R decrease slowly due to the holding temperature. It is about 5-10 mV lower than that of the type R under the same conditions. Figure 4(b) shows the results of the output voltages and temperature when the heat source temperature is set at 500 °C. When the heat source is removed from the TEGs, the temperature of the hot junction for type E decreases faster than that for type R. The temperature for type E is about 10 °C lower than type R under the same conditions. It is also found that in the process of the hot junctions’ temperature from the top (heating temperature) to the environment temperature (30 °C), the energy harvesting time for type E is much shorter than that for type R. And in the case of the junction temperatures lower than phase change temperature, type E and type R show similar behavior.

Figure 5 shows the energy harvesting time of each TEG. It can be seen that the energy harvesting time could last 4-5 hours at least in a vacuum environment. Type R last 40-50 min longer than that of the type E during the total harvested energy period. This comes from that type R uses the stored heat in the PCM and consequently the total extended energy harvesting time is increased by about 10%-19%. The energy harvesting time of each TEG becomes longer with increasing heating temperature. But when the heating temperature is above 510 °C, the energy harvesting time would no longer extend. These results indicate that type R can work longer and generate more electricity than type E.

Figure 6 shows the maximum output voltages of each TEG. The TEG produces higher output voltages with the increasing heating temperature. The output voltage of the type R almost equals to that of the type E when the heating temperature is 470 °C, whereas the output voltage of type R is about 6mV higher than that of the type E when the heating temperature is increased above 500 °C. When the TEG is embedded with PCM, the active lengths of p-type and n-type thermoelectric material of type R are shorter than that of type E at the same conditions. It may lead to a higher output voltage [25].
Figure 4. Temperature and output voltages variations under different heating temperature when stop supplying heat.

Figure 5. Energy harvesting time of each TEG.

Figure 6. Maximal output voltages of each TEG for different heating temperature.

Figure 7 shows the total electrical energy produced for each TEG with different heating energy when a constant 1.0 Ω resistor (optimized value with impedance matching) is connected to the output of the TEG. With the energy harvesting time shown in Figure 5, the average power (ratio of the total
power versus time) measured in type R is 821μW while the type E indicates a value of 802 μW. The average power is increased by 23.7%. The TEGs produce 12.3 J energy at least and 17.8 J at most due to the different temperature thermoelectric effect. Types R also produces about 2-3 J larger magnitude of electrical energy than type E during the total energy harvesting period. Each TEG could produce much more energy with increasing heating temperature. When the heating temperature reaches 530 °C, type R even produces 3.3 J energy more than type E in the same progress. The total electrical energy is increased by 18.1% in average. The maximum increase is 23.3% when the heating temperature is 530 °C. That is, the adoption of the PCM enhances the total output energy of the TEG effectively. The dissipated heat was stored in the PCM during the heat source contact and type R TEG used the stored heat more efficiently than type E.

According to these results, it can be known that the effect of the embedded PCM on the electrical power generation of the TEG is small when the heat source is in contact with the TEG. The effect of the latent heat of the PCM manifested when the heat source was removed from the TEGs: type R (with PCM), maintained a higher output voltage, a longer working time and produced much more energy than type E (without PCM).

**4. Conclusion**

In this study, TEG embedded PCM for wasted heat energy harvesting has been proposed. The fabricated TEG can generate electrical energy uninterruptedly with the stored heat in the PCM when a heat source stops supplying heat energy, without any break in the generated current and any change in the current direction. The experimental results for the thermoelectric generator fabricated indicate that the TEG with PCM adopted has a higher output voltage and a longer energy harvesting time than that without PCM when the heat source stopped supplying heat energy to the TEG. The total extended energy harvesting time could last 4-5 hours at least in a vacuum environment and is increased by about 10%-19%. Especially, the relative increases of the total electrical energy can reach 25% in average.

**Acknowledgment**

This work was supported by the Major Program of the National Natural Science Foundation of China (51590902), the National Natural Science Foundation of China (51676117, 51876111), “Shu Guang” project supported by Shanghai Municipal Education Commission and Shanghai Education Development Foundation (18SG54).
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