All dispenser printed flexible 3D structured thermoelectric generators

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Abstract. This work presents a vertically fabricated 3D thermoelectric generator (TEG) by dispenser printing on flexible polyimide substrate. This direct-write technology only involves printing of electrodes, thermoelectric active materials and structure material, which needs no masks to transfer the patterns onto the substrate. The dimension for single thermoelectric element is 2 mm × 2 mm × 0.5 mm while the distance between adjacent cubes is 1.2 mm. The polymer structure layer was used to support the electrodes which are printed to connect the top ends of the thermoelectric material and ensure the flexibility as well. The advantages and the limitations of the dispenser printed 3D TEGs will also be evaluated in this paper. The proposed method is potential to be a low-cost and scalable fabrication solution for TEGs.

1. Introduction
Flexible thermoelectric generators (TEGs) have the potential for use in generating electricity from heat flux to power small devices in wearable systems [1][2]. Flexible TEGs are becoming more attractive for wearable health and environmental monitoring because of the combination of comfort, silent operation ability to supply power over a long time period [3].

The basic module of a TEG is a thermocouple, which consists of two thermolegs, one thermoleg being n-type and the other p-type material. When a heat flux passes through a thermocouple from one p/n junction to another, a voltage and current will be generated with the electrical power dissipated in a load resistor $R_L$. This arises from the Seebeck effect [4]. In order to fabricate the TEGs onto flexible substrates, dispenser and inkjet printing technologies have been introduced to realise thermocouples on Kapton [5][6]. However, only planar structured thermocouples have been printed with the final TEG being coiled up to form a cylinder that harvests the temperature gradient along its length. These planar structures are less efficient than vertically fabricated thermocouples [7], such as those found in conventional rigid thermoelectric devices.

This work shows the use of the dispenser printing process to fabricate 3D thermoelectric structures on Kapton substrate. Both n and p types of thermocouples have been dispenser printed layer by layer to form the cube structure. A polymer based structure layer was also been printed with the same height to physically support the top electrodes, therefore enabling a fully 3D dispenser printed, vertical TEG to be realised.

2. Experiment
The setup for dispenser printing includes a 3 axis stage (Sigma Koki SGSP26-50), a stage controller (Sigma Koki SHOT-204MS), a dispenser (Musashi ML-808 FX COM-CE) and an air pump (JUN-AIR
OF302). The dispenser printer used in this experiment was a pneumatic type dispenser printer. This dispenser machine can print pastes with a wide range of viscosity (100 − 10000 cP) by varying the nozzle size, air pressure and dispensing time.

For a working TEG the thermocouples should be connected electrically in series, which requires both the top and the bottom of the thermoelectric material cubes to be connected to electrodes. This 3D structure is illustrated in figure 1.

![Figure 1. Illustration of a 3D-structured dispenser printed BiTe/SbTe thermocouple.](image)

Figure 1. Illustration of a 3D-structured dispenser printed BiTe/SbTe thermocouple.

The thermoelectric materials used here were bismuth telluride (BiTe) and antimony telluride (SbTe) for n-type and p-type thermoelectric legs, respectively. The compositions of the dispenser printable pastes were the same as the screen printable pastes from previous work [8]. The thinner ratios in both pastes were modified to meet the required viscosity level. The bottom silver (Ag) electrodes can be printed onto the
substrate, while a structure layer is required in order to support the top electrode layer. The dispensable silver used here was Johnson Matthy s-020 silver polymer conductive ink. Kapton was used as the substrate. The ultraviolet (UV) curable epoxy OG675 from EPO-TEC was used as the structure layer material. This UV curable single component epoxy has a pot life over 3 hours and fast curing time of 2 seconds, which makes it suitable for dispenser printing. Also, a non-thermally cured structure layer minimises the oxidation of the thermoelectric materials.

Firstly, the Ag paste was dispenser printed onto the Kapton substrate and cured. Then, the SbTe and BiTe pastes were dispenser printed onto the Ag electrodes in the required patterns. The stage was heated up to 60° C using a Peltier plate. The printed patterns were dried using the heated stage in order to build up the thickness of the cubes. The dimensions of individual cubes was $2 \times 2 \times 0.5$ mm. The distance between adjacent cubes was 1.2 mm. The thickness of the bottom silver electrodes was 10 μm. The stage controller has a resolution of 1 μm, which meets the requirements of these dimensions. The fabrication processes are illustrated in figure 2-(a). The curing of thermoelectric materials were processed in nitrogen to prevent oxidation. The images of a dispenser printed TEG sample at different stages of the process are shown in figure 2-(b).

In this experiment, 3 samples with the same thermoelectric material cubic size but different number of thermocouples were dispenser printed. The matrix of the cubes were 1×2, 2×2 and 4×4 for sample (a), sample (b) and sample (c) respectively. The flexibility of the samples are shown in figure 3.

![Image](image_url)

**Figure 3.** Flexibility demonstration of 3 fully dispenser printed TEGs, sample (a): 1 thermocouple with 1×2 cubes, sample (b): 2 thermocouples with 2×2 cubes, sample (c): 8 thermocouples with 4×4 cubes.

### 3. Measurement and results

For dispenser printed 3D TEGs, the heat flux must be perpendicular to the substrate. The temperatures on each side of the vertical sample was measured from the hot and cold source it is attached to. In figure 4-(a), aluminium (Al) blocks were used as heat conductors to allow the temperature to be measured, while also supplying a temperature gradient.

The 3D TEGs were placed between two Al blocks. The thermal conductivity of the Al is 205 W/(m·K), which is 5 times higher than the ceramic plates used on the Peltier. The high thermal conductivity ensures a uniform temperature distribution over the surface of the TEGs. Figure 4-(b) and (c) show the temperature distribution over these 2 Al blocks, which were measured by the Testo 875 thermal imaging camera. The probes of the thermometer were put in the middle of the Al blocks by drilling a hole into the centre, and sealing with thermal grease.
From the above figure, it can be seen that the output voltage increased linearly with an increase in the temperature gradient. A temperature gradient of 60°C, a single thermocouple can generate a voltage of 4.5 mV, 3.6 mV and 3.2 mV calculated from sample (a), sample (b) and sample (c) respectively, which are all lower than the 16.6 mV generated by a single planar BiTe/SbTe thermocouple [8]. The actual temperature gradient is difficult to maintain in the experiment setup due to the close proximity of the two Al blocks. In addition, the vertically fabricated device is on a polyimide substrate, which has a low heat conductivity. This will limit the accuracy of the Seebeck voltage and power test.

The calculated α value from both the Seebeck voltage and power measurement along with the resistance of the single thermocouple for these three samples are shown in table 1. The voltage measurement over the load resistor shows the maximum power per single thermocouple among sample a, b and c is 1.5 nW at a temperature difference of 20 °C, which is much lower than the 48 nW for the planar thermocouple [8]. The resistance of a single dispenser printed thermocouple is much higher than the screen-printed planar one (160 Ω in reference [8]).

An experiment was carried out to find which part in the TEG contribute the highest resistance. 8 printed thermocouples with bottom silver electrodes are shown in figure 5, the whole resistance was 480 kΩ. The same BiTe and SbTe pastes, same silver paste and same curing condition were applied in this experiment.

The resistance measured using a multimeter is shown in table 2. The resistance of the junctions contributed 85% of the entire resistance. The resistance was measured using a Wayner Kerr 4300 LCR Meter. The applied AC voltage had a frequency of 1 kHz.
4. Discussion
In this paper, using dispenser printing technology to print vertical TEGs was investigated. The dispenser printer demonstrated the ability to build up 3D-structured thermocouples. However, the time spent on printing the cubes increased with the number of the cubes. With the desired resolution in this work, printing two cubes in sample (a) took nearly 100 minutes while printing the 16 cubes in sample (c) took over 700 minutes. The printing time can be decreased by applying a dispenser printer with multiple nozzles to build up the thickness of the repeated pattern [9].

The reason behind the dispenser printed samples having a higher resistance than screen-printed samples, comes from the contact resistance of the junction between silver electrodes and the thermoelectric materials. In addition, from figure 5, the overlap areas of the silver patterns and the thermoelectric materials patterns show a different colour from the other parts. A potential reason is that there was a chemical reaction between the silver electrode patterns and the uncured thermoelectric materials during the curing process.

In conclusion, dispenser printing is able to fabricate TEGs with 3D structures. However, the mechanism behind the high contact resistance needs to be further investigated. Evaporating and sputtering could be alternative solutions to deposit the conductive electrodes.

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