Characterization of polymer and silver printed thermoelectric generators

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Abstract

This work presents current results regarding environmental friendly and cost effective thermoelectric generators (TEG) produced by different printing techniques. Thermoelectric devices convert wasted heat into electricity. It is shown that a polymer-based printed thermoelectric generator provides a cost effective alternative to standard thermoelectric devices. TEG were printed by different printing techniques and realized with commercially available Poly(3,4-ethylenedioxythiophene) Poly(styrenesulfonate) (PEDOT:PSS) in combination with silver (Ag) legs on flexible foils (Polyethylene terephthalate (PET), Polyimide (PI)). For a thermoelectric generator of three thermal legs an open circuit voltage of 1 mV can be achieved with a temperature difference of 30 K. The output voltage can be multiplied by a serial connection of thermocouples or higher temperature differences. Moreover the power factor PF and the Seebeck coefficient α, which are suitable parameters for the evaluation of efficiency of thermoelectric material, are determined and will be presented.

Introduction

For the reduction of energy costs it is necessary to develop new devices and applications of energy harvesting systems. Printed thermoelectric generators can be an opportunity for converting thermal waste heat into electrical energy by using the Seebeck effect. Here, an electrical potential and subsequently a current is generated by a temperature gradient in two different thermoelectric materials [1].

Standard thermoelectric materials are composed of non-environmentally compatible inorganic semiconducting materials (e.g. bismuth telluride or lead telluride). Consequently, in order to ensure the environmental compatibility it is necessary to use environmental friendly and low-cost thermoelectric materials. One promising material is poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) which is a conducting polymer. This polymer has high potential due to its low thermal conductivity, high electrical conductivity, the flexibility and the environmental friendliness [2], [3]. In addition to the material cost minimization the reduction of production costs is a key requirement. This can be realized by flexible printing techniques [4] because standard thermoelectric generators processing techniques are not cost and time effective. Thermal legs of standard thermoelectric devices are cut out of polycrystalline material and mostly hand-assembled into a module. Furthermore, flexible thermoelectric generators are attractive for applications in microelectronic devices, sensors or for wearable electronics.

In this study we present early samples of thermoelectric generators with one, two and three leg configuration, which were produced by different printing techniques like screen printing, inkjet printing and aero jetting procedure and a combination of these technologies on flexible foils (PET and PI). For the realization commercially available PEDOT:PSS and silver (Ag) inks and pastes were used.

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Theoretical Background

Thermoelectric generators can produce electricity by converting thermal energy of waste heat into electric energy by use of Seebeck effect.

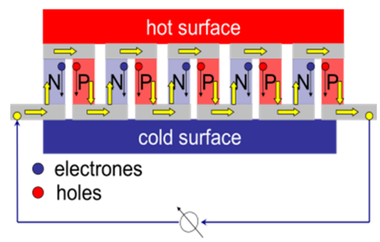

***Figure 1**. Schematic structure of thermoelectric generators*

Within an electric circuit of two different (semiconducting) materials results a charge carrier concentration gradient due to a temperature gradient. Therefore a potential difference (Φ) is generated, which is called thermoelectric voltage (ΔU_T) and defined as:

$$\Delta U_T = \Phi_B - \Phi_A = \int_{T_1}^{T_2} \underbrace{(\alpha_B - \alpha_A)}_{\Delta\alpha} \, dT = \Delta\alpha \Delta T \qquad (1)$$

with the Seebeck coefficient of material A α_A, the Seebeck coefficient of material B α_B and the temperature difference ΔT. Due to the potential difference majority charge carriers are flowing from the hot to the cold end, which generates an electric current [5].

The performance of thermoelectric material is described with the dimensionless figure of merit:

$$zT = \frac{\overbrace{\Delta\alpha^2 \sigma}^{P}}{\kappa} T \qquad (2)$$

where σ is the electrical conductivity, P is the power factor, κ is the thermal conductivity and T is the absolute temperature [1]. For good thermoelectric material a high power factor and low thermal conductivity are needed. In this publication we only determined the power factor.

Experimental Details

All thermoelectric generators were printed by different technologies onto 50 µm thick Polyimid (PI) (Kapton HN FI 16010) as well as Polyethylene terephthalate (PET) (Mylar A) foil. These substrates are cost effective and flexible. In addition they have a good surface quality and low thermal conductivity [6],[7]. All substrates were cleaned by the following procedure prior to processing:

- 15 minutes ultrasonic bath cleaned with isopropyl alcohol
- 15 minutes ultrasonic bath cleaned with deionized water
- 15 minutes dried with convection oven at 115°C

The structures were realized by PEDOT:PSS and silver legs, printed in meander structure, shown in figure 2.

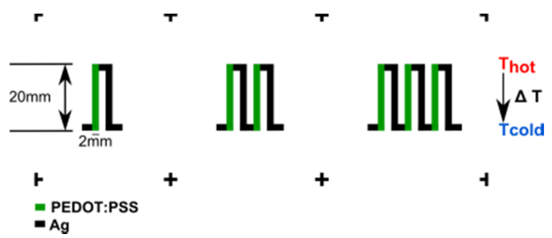

Figure 2*. Meander structure of 2D printed thermoelectric generators in one, two and three leg configuration; green leg: PEDOT:PSS and black leg: Ag*

For printing commercially available PEDOT:PSS and silver paste and inks are used, which are summarized in the following table 1.

Table 1: Characteristic of printed thermoelectric materials

Manu-facturer	**Heraeus**	**DuPont**	**Advanced Nano Products (ANP)**
Material	PEDOT:PSS	Ag	Ag
Name	Clevios SV3	DuPont 5000	DGP 40TE-20C
Viscosity	3.9 Pas	3.5 - 16 Pas	10 – 17 mPas
Solid content (%)	-	58 - 62	30 - 35
Kind of material	paste	paste	Nano particle ink

The PEDOT:PSS and Ag paste are used in a screen printer EKRA (Type: Mat S 30) and a Musashi Aero Jet M Jet-A, while the Ag silver nano ink was processed by an OmniJet 100 inkjet printer from UniJet equipped with a Fujifilm Dimatix DMC-11610 printing heads (900dpi). The drying temperatures are listed in the following table for each printing technology:

Table 2: Drying temperatures and times

	Screen Printing	**Aero Jetting**	**Inkjet Printing**
PEDOT:PSS			
PI	120°C for 10 min.		n.a.
PET	120°C for 10 min.		n.a.
Silver paste (DuPont5000)			
PI	120°C for 10 min.		n.a.
PET	120°C for 10 min.		n.a.
Silver nano ink (ANP)			
PI	n.a.	n.a.	Dried: 80°C on a hot plate, Annealed: 160°C for 1 h
PET	n.a.	n.a.	Dried: 80°C on a hot plate; Annealed: 250°C for 1 h

All printed structures were dried respectively- in case of silver nano ink - annealed in a convection oven.

Electrical characterization of PEDOT:PSS was done by standard four point probe measurement technique for aero jetted structures and by Van der Pauw measurement technique for screen printed structures. This techniques were described elsewhere [8],[9]. For Van der Pauw measurement a prober station (Signatone H150) was used with micro-positioners. For thickness determination which is important for evaluation of the resistivity a non-contact laser profilometer (NanoFocus µscan) with confocal sensor CF4 was used. The Seebeck coefficient was measured at the meander structure which was shown before. For Seebeck coefficient measurement a temperature difference is needed. This was realized by two Peltier elements which are embedded into an aluminum block, shown in figure 3.

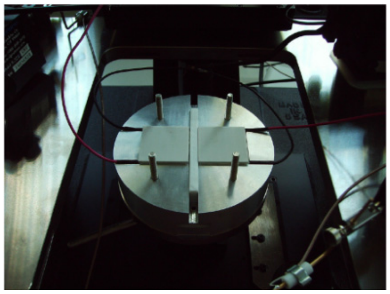

Figure 3. Measuring station for Seebeck coefficient measuring

For contact two spring contact nips were used and the open circuit voltage subsequently the thermoelectric voltage was provided. The Seebeck coefficient is the slope of the open circuit voltage depending on the temperature difference, which can be derive from equation (1).

Results and Discussion

For thermoelectric materials the efficiency is essential. In this publication we determined the power factor P for printed structures for each used printing technology (see equation (2)). For the evaluation of the Power factor the specific resistivity respectively the electrical conductivity is needed and was measured for 8 Van der Pauw structures, which were screen printed on PI and PET. For jet dispensed structures 18 PEDOT:PSS lines were measured by Four Point probe method on PI and PET. All PEDOT:PSS lines have a length of 20mm. The four point measurement probe had a distance l of 5mm. In the following table the layer thickness d and the calculated electrical conductivities are summarized.

Table 3: Electrical characterization of PEDOT:PSS

	Screen printing	Jet Dispensing
Thickness d/µm		
PI	0.5±0.2	4.3±1
PET	0.5±0.2	1.6±0.5
Cross-sectional area A/µm²		
PI	not necessary	7292±1470
PET	not necessary	2291±600
Electrical conductivity σ/$\frac{S}{cm}$		
PI	27±12	143±67
PET	21±10	434±141

From table 3 it will be clear that the thickness of PEDOT:PSS layers depends on the different printing technologies although the same material was used. The layer thickness of PEDOT lines printed by jet dispensing process is less on PET than on PI and has not yet been clarified. However another measurement technique (mechanical sensing) with lower resolution was used as well, thereby it was found that the layer thickness of PI and PET are in the same range. Also the spreading of jetted lines was investigated. It results a difference of 15%, which is quite in an acceptable range. Therefore, it can be assumed that an error in the non-contact laser profilometer measurement technique is presented. Hence the same cross-sectional area is required for PET as for PI and an electrical conductivity of $(134\pm31)\frac{S}{cm}$ results. This value is assumed for the calculation of the power factor below.

However, the resistivity respectively the electrical conductivities are consistent with comparable values in literature, although the values given in [2] show a broad variety between 0.06 to 945 $\frac{S}{cm}$.

Also the Seebeck coefficient has to be determined for the calculation of the Power factor P. Therefore the thermoelectric voltage depending on the temperature difference has to be measured, which can be obtained in equation (1). Also it will be clear that the Seebeck coefficient is the slope of the resulting linear function. Figure 5 shows the measured open circuit voltage as function of the adjusted temperature difference for one leg TEG configuration, which were realized by screen printing (figure 4 (a)), jet dispensing (figure 4 (b)), combination of both whereby the silver legs were printed by screen printing and the PEDOT:PSS legs by jet dispensing were printed (figure 4 (c)). Also a combination of inkjet printed silver legs and jet dispensed PEDOT:PSS legs is shown (figure 4 (d)).

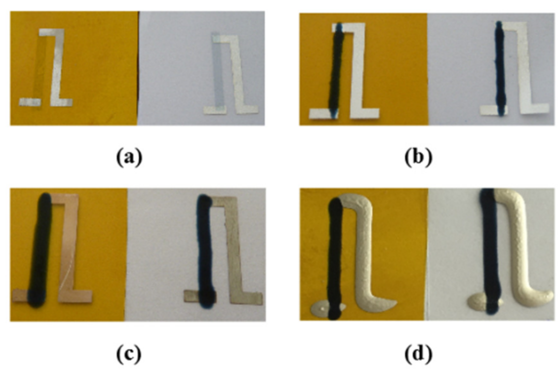

Figure 4. Thermoelectric generator in one leg configuration; manufactured by (a) screen printing, (b) combination of screen printing (silver) and jet dispensing (PEDOT:PSS), (c) combination of inkjet printing (silver) and jet dispensing (PEDOT:PSS) and (d) jet dispensing (left: PI, right: PET)

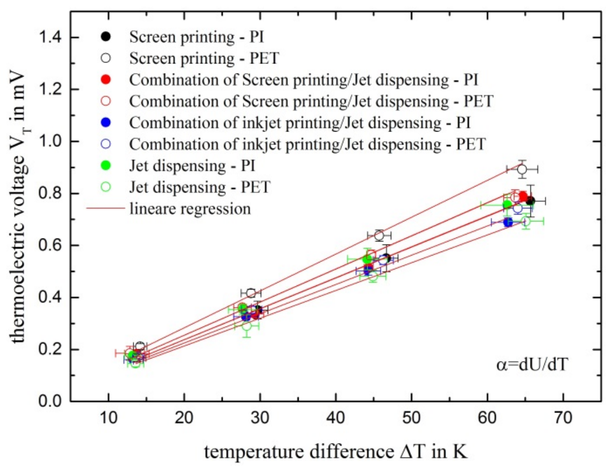

Figure 5. *Thermoelectric voltage V_T depending on the temperature difference ΔT for one thermal leg printed by different techniques for determination of the Seebeck coefficient*

The results of the Seebeck coefficient and the power factor for different printing technologies and substrates are summarized in table 4.

Table 4: Seebeck coefficient and power factor for each printing technology and substrate

	Seebeck coefficient in $\frac{\mu V}{K}$		Power factor in $P/\frac{\mu W}{mK^2}$	
	PI	PET	PI	PET
Screen printing	11.9 ±0.1	14.2 ±0.2	0.4 ±0.2	0.4 ±0.2
Combination screen printing/jet dispensing	11.7 ±0.2	12.7 ±0.1	n.a.	n.a.
Combination inkjet printing/jet dispensing	11.3 ±0.2	11.9 ±0.2	n.a.	n.a.
Jet dispensing	12.8 ±0.3	10.7 ±0.2	2.3 ±0.4	1.5 ±0.4

As a result it can be stated that the Seebeck coefficient is independent of layer thickness as well as substrate and differs minimally depending on their printing technology. In contrast the power factor of the material depends on the electrical conductivity of the material, which explains especially the difference between the screen printing and jet dispensed structures because the layer thickness is about three to eight order of magnitudes higher. Furthermore the power factors are comparable to literature, which are given between 0.04 to 4.78 $\frac{\mu W}{mK^2}$ [2].

Now the focus will be placed on the resulting thermoelectric voltage of one, two and three thermal leg based thermoelectric generators in dependence of the temperature difference. Therefore a temperature difference from 13 K to 65 K was set and the open circuit voltage was measured (figure 6).

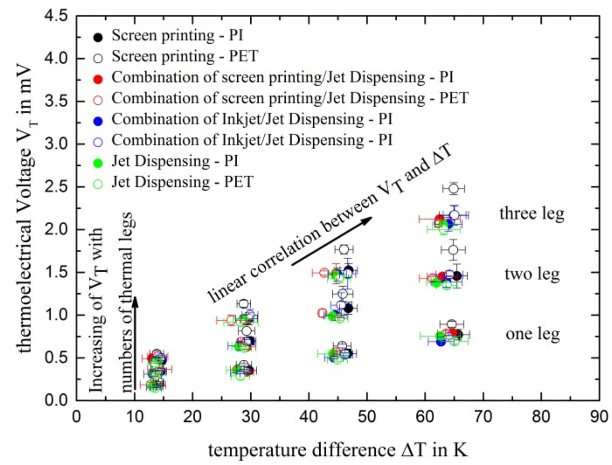

Figure 6. *Thermoelectric voltage in dependence of temperature difference for one, two and three thermal legs*

Figure 6 shows the expected context of a linear correlation between the thermoelectric voltage and the temperature difference for all thermal leg configurations and printing technologies. Also the voltage does not differ in dependence of the printing technologies if the leg configuration is considered individually. This has also been seen previously in figure 5 for one thermal leg. Furthermore it will be clear that the open circuit voltage increases with the number of thermal legs and increasing temperature difference. For example for a three thermal leg thermoelectric generator a thermoelectric voltage of 1 mV for a temperature difference of 30 K be can reached, for 60K an open circuit voltage of 2 mV is achieved.

Conclusion and Outlook

The results provide a good base for further investigation for the chosen material combination. It was seen that good electrical conductivities can be achieved and differs for each printing technology due to sample thickness. In comparison the Seebeck coefficient is independent of layer thickness and printing technologies. Values were reached from 10.7 to 14.2 $\frac{\mu V}{K}$. Consequently power factors resulted in a range of 0.4 to 1.5 $\frac{\mu W}{mK^2}$.

Also it was shown that the thermoelectric voltage can multiply by series connection of number of thermal legs.

In the future further investigations of PEDOT:PSS based thermoelectric voltage will be done and the power output will be determined which is important for an application in microelectronic devices or sensors.

Furthermore more material combinations are planned for example with Carbon nanotubes or graphene.

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Kristina Grunewald achieved her BS and MS in physics at the Carl von Ossietzky University at Oldenburg in 2013 with specialization in material science and renewable energy. Since November 2013 she works at Technische Hochschule Nürnberg (Faculty of Electrical, Precision and Information Technology) in Germany with focus on printed thermoelectric generators as research assistant within the group of Prof. Dr.-Ing. Marcus Reichenberger