Screen printed thermoelectric devices based on PEDOT:PSS/CNT composites

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INTRODUCTION

Organic thermoelectric generators (TEGs) are devices that convert heat into electricity using organic materials. These materials typically have good electrical conductivity and low thermal conductivity, allowing them to efficiently convert temperature gradients into electrical power. Organic TEGs have potential applications in wearable devices, IoT sensors, and other low-power electronics. They are also lightweight and flexible, making them suitable for a variety of portable and flexible electronics [1,2].

For the fabrication of organic TEGs, thick-film technologies such as screen printing [3] and spray coating [4] are most used. Although the thermoelectric properties of conductive polymers are usually poor, they can be easily improved by combining them with other materials such as carbon nanotubes (CNTs) [5]. Carbon nanotubes, due to their electrical and mechanical properties, are excellent as a functional phase of thermoelectric nanocomposites. Composites based on carbon nanomaterials and conducting polymers feature a much simpler fabrication process than conventional semiconducting inorganic thermoelectric materials. The fabrication of composites is most suitable for thick-film technology. They require fewer resources than thin-film technologies or the fabrication of inorganic solid TEGs (such as a high vacuum).

In this work, we propose active p-type poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)/carbon nanotube (SWCNT, DWCNT e MWCNT) films based on screen-printing technique and investigate the effect of CNT on thermoelectric properties. In particular, the performance of PEDOT:PSS/CNT composites have been optimized by changing the formulation inks to make them suitable for screen printing, by varying the CNT concentrations and by treating the printed polymeric films in Ethylene Glycol (EG). The best and optimized films have been used as p-material in TEG devices with horizontal planar structure using printed silver as n-type material, realizing a fully screen-printed TEG.

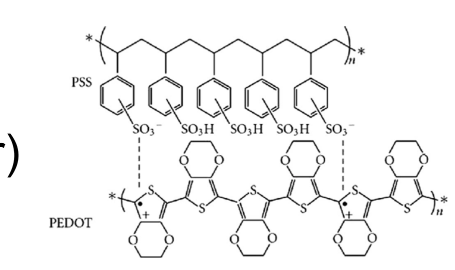
MATERIALS AND METHODS

Active material:

PEDOT:PSS/Carbon Nanotubes (CNTs) Composites

- PEDOT:PSS (Clevios PH 1000)
- Carbon Nanotubes: - SWCNT (single walls) (≥80 %, carbon basis, 1.2-2.0 nm diameter)
  - DWCNT (double walls) (>95% carbon basis, <2 nm diameter)
  - MWCNT (multi-walls) (>95% carbon basis, 50-90 nm diameter)

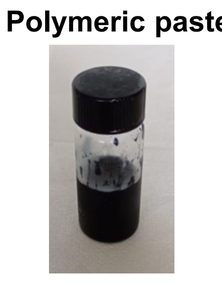
PEDOT:PSS



Ink formulation:

Aqueous dispersions of PEDOT:PSS with different CNT concentrations (5-50 wt%)

Polymeric paste



Ink preparation:

Pastes with viscosity values of 150-180 mPa·s were obtained by drying the dispersions at 60° C for 6 hours in oil bath

Deposition and processing:

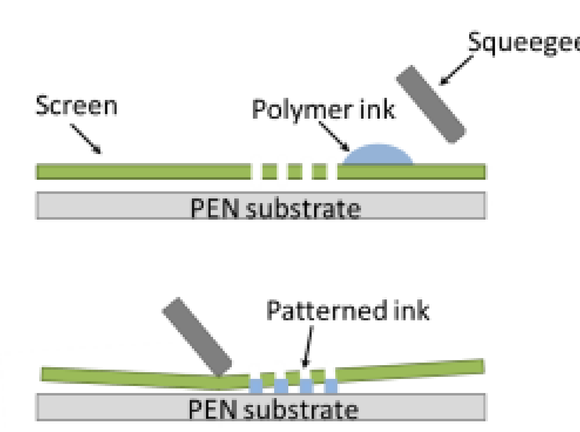
- Screen printing by AUREL
- Process parameters:

Print velocity (mm/sec)	Snap-off * (mm)	Pressure Racla (kg)
50	0.3-0.9	2-3

* The distance between squeegee and substrate

AUREL mod. VS1520A HIC

Screen-printing process

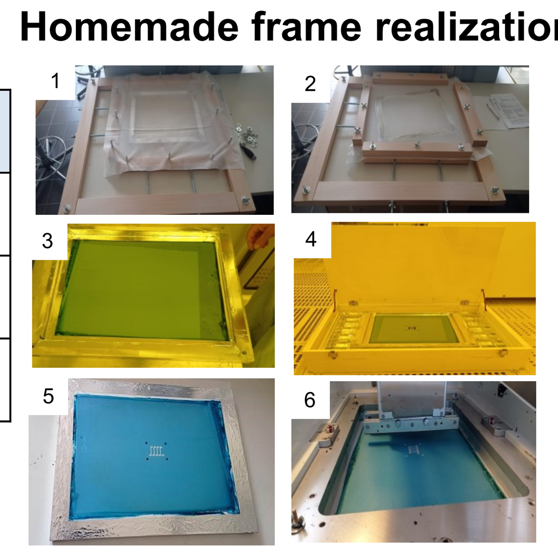


TEGs Device preparation

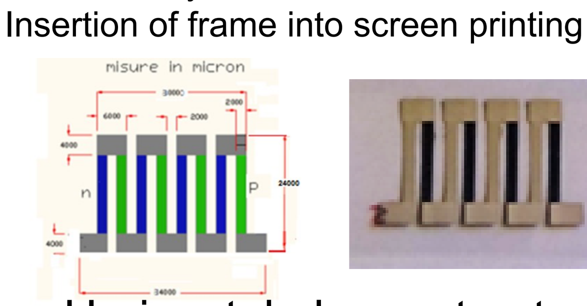
Printing material	Mesh*	Wire diameter (mm)	Opening width (mm)
PEDOT:PSS/CNT (p-type)	77	65	67
Silver (n-type)	120	36	47
Silver (electrical contacts)	120	36	47

* Mesh count in Screen Printing refers to the number of polyester threads crossing each other per square inch on a screen

Homemade frame realization



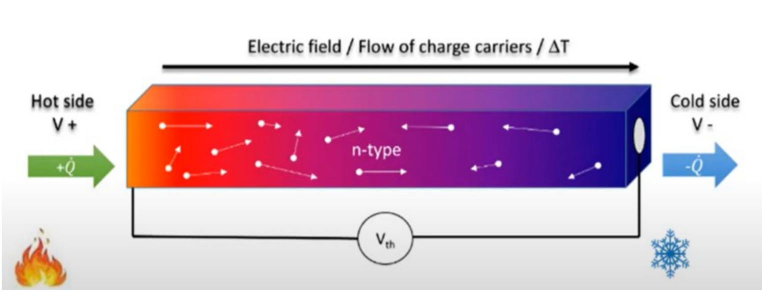
1.2. Canvas application on frame
3. Photoemulsion deposition
4. A stencil with the design to print is then placed on the emulsified screen and UV exposed
5. Frame ready
6. Insertion of frame into screen printing machine



Horizontal planar structure

RESULTS

Thermoelectric Effect



Voltage ΔV induced by temperature gradient ΔT

Criteria for estimating TE properties

Seebeck coefficient

$$S = -\frac{\Delta V}{\Delta T}$$

Power factor

$$PF = \sigma S^2 [W/m/K^2]$$

Electrical properties of PEDOT:PSS/CNT printed-films

	Before EG treatment					Post EG treatment				
SWCNT [%]	Sheet res [Ω]	Thickness nm	Conductivity [S/cm]	Seebeck [μV/°K]	Power Factor [μW/m°K²]	Sheet res [Ω]	Thickness nm	Conductivity [S/cm]	Seebeck [μV/°K]	Power Factor [μW/m°K²]
5	7100	412	3.42	16.8	0.09	39.8	412	609	15.5	14.65
10	8000	650	1.92	14.04	0.04	40	650	384	10.48	4.22
20	16000	460	1.36	18.51	0.06	28.5	460	763	16.47	20.69
40	3600	850	3.27	17.37	0.09	27.6	850	426	16.54	11.66

	Before EG treatment					Post EG treatment				
DWCNT [%]	Sheet res [Ω]	Thickness nm	Conductivity [S/cm]	Seebeck [μV/°K]	Power Factor [μW/m°K²]	Sheet res [Ω]	Thickness nm	Conductivity [S/cm]	Seebeck [μV/°K]	Power Factor [μW/m°K²]
0	3100	770	4.2	19,4	0.15	23.8	770	546	16.8	15.4
5	1000	877	11.4	17.1	0.33	23.2	877	491	16.3	13.1
10	280	1234	28.9	22.6	1.48	15.2	1234	533	19.6	20.5
25	215	3059	15.2	18.3	0.51	12.0	3059	272	16.2	7.1
50	180	3758	14.8	16.2	0.39	10.5	3758	242	15.1	5.5

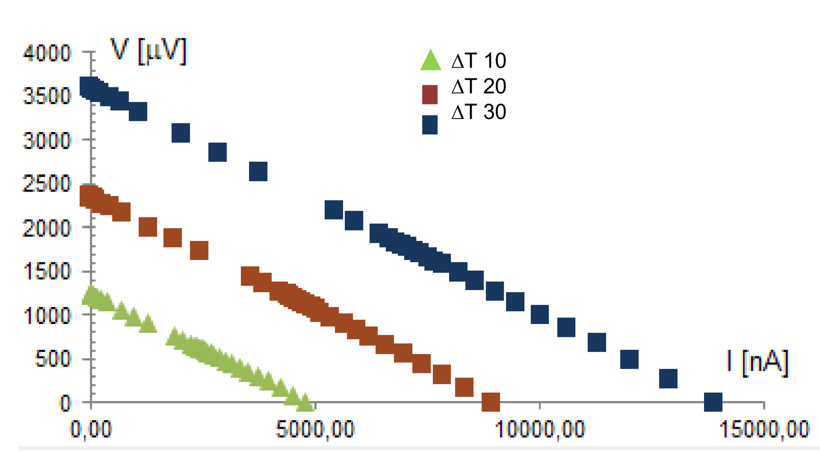
	Before EG treatment					Post EG treatment				
MWCNT [%]	Sheet res [Ω]	Thickness nm	Conductivity [S/cm]	Seebeck [μV/°K]	Power Factor [μW/m°K²]	Sheet res [Ω]	Thickness nm	Conductivity [S/cm]	Seebeck [μV/°K]	Power Factor [μW/m°K²]
5	371	920	29.30	18.88	1.04	45	371	241	17.65	7.52
10	245	1430	28.54	17.81	0.90	20	1430	349	14.22	7.07
20	900	1100	10.10	18.07	0.33	45	900	202	13.84	3.86
40	260	1800	21.36	17.65	0.66	20	1800	277	13.84	5.32

After EG treatment, the non-complexed PSS is removed and the electrical conductivity of the PEDOT:PSS films increases improving thermoelectric properties [6].

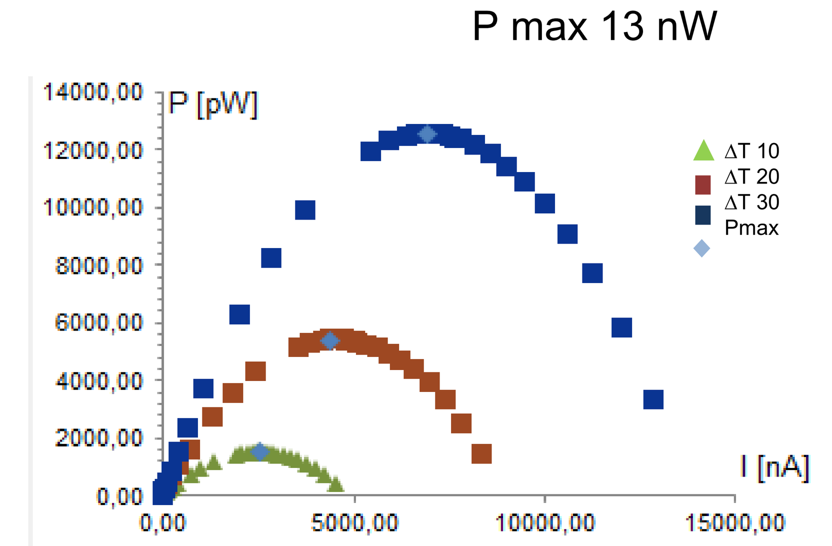
Devices Characterization

PEDOT:PSS/SWCNT 20wt%

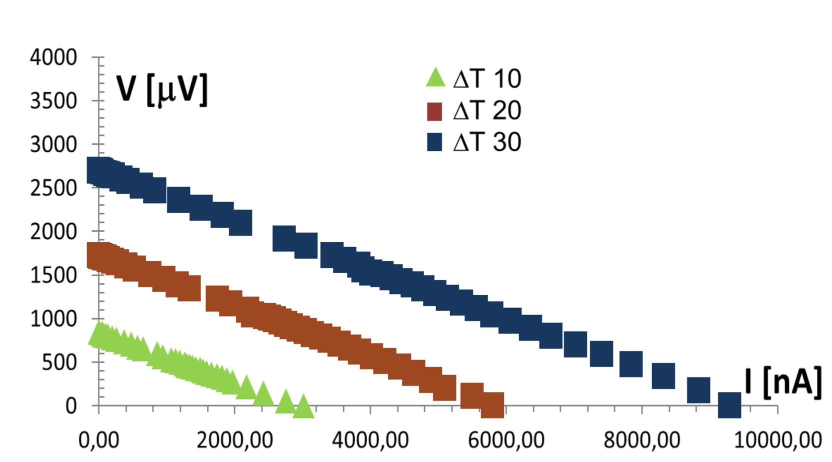
Ohmic type characteristic



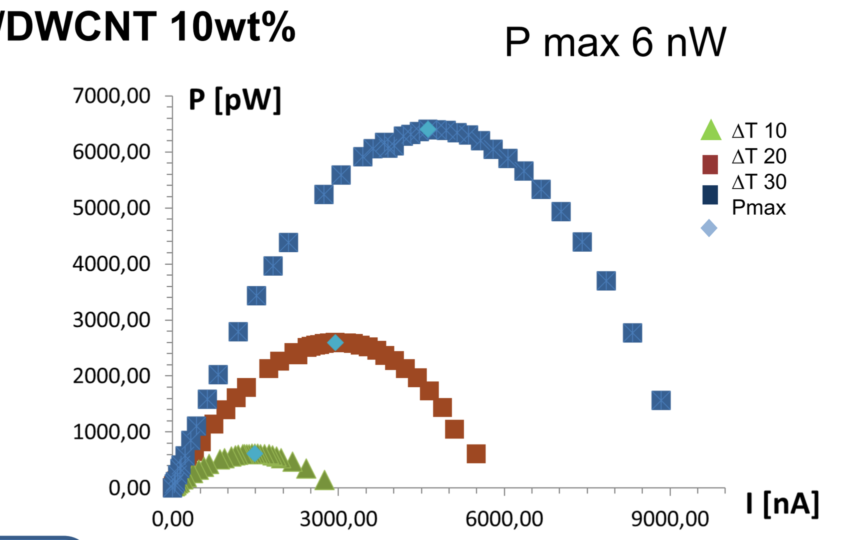
P max 13 nW



PEDOT:PSS/DWCNT 10wt%



P max 6 nW



CONCLUSIONS

Flexible TEG devices with horizontal aligned p-type PEDOT:PSS/CNT and n-type silver film thermoelements were designed, fabricated and characterized. In addition, the effect of CNT concentrations and the EG treatment on the PEDOT:PSS/CNT film were investigated. The best TE device in terms of electrical properties with a planar structure is based on PEDOT:PSS with 20wt% SWCNT with maximum power value equal to 13 nW for Δt 30° C.

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