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Published in:
Energy Science & Engineering

Link to article, DOI:
10.1002/ese3.8

Publication date:
2013

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):
Practical evaluation of organic polymer thermoelectrics by large-area R2R processing on flexible substrates

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Keywords
Device architecture, large scale, life-cycle assessment, polymer, roll-to-roll, serial connection, thermoelectric.

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Funding Information
This work was supported by the Danish Ministry of Science, Innovation, and Higher Education through the EliteForsk initiative and the 2011 Grundfos award.

Received: 23 February 2013; Revised: 22 April 2013; Accepted: 22 April 2013
doi: 10.1002/ese3.8

Abstract
Here, we present a process based on roll-to-roll (R2R) technology which allows for very fast processing of polymer thermoelectric (TE) devices and we furthermore demonstrate a simplified but more efficient way of serially connecting these devices by means of R2R thin-film processing. The new device architecture makes it possible to use only one TE material (opposed to two materials which are employed in well-known Peltier elements), and a total of 18,000 serially connected junctions were prepared by flexoprinting of silver electrodes and by rotary screen printing of poly(3,4-ethylenedioxythiophene) (PEDOT):poly-styrene sulfonate (PSS) as the TE material. Testing of devices revealed that the new architecture clearly showed to be functioning as expected, but also pointed toward challenges for thin-film TE development which is the influence of the substrate thickness on the thermal gradient over a device and the currently low performance available. A life-cycle assessment (LCA) was carried out in order to evaluate the sustainability of the new architecture and to estimate the requirements for development of a successful technology.

Introduction
The possibility of exploiting waste heat to generate electricity via thermoelectric (TE) materials has fascinated scientists for decades as such “free” energy can potentially be harvested from a multitude of sources. The use of polymers as thermoelectric materials offers in addition the possibility of fast solution processing of large volumes at a very low cost, but so far the polymeric thermoelectric research has primarily been based on materials properties and only very little effort has been put into actual preparation of devices and the challenges that are associated with demonstrating practical use as a technology.

One of the major challenges for a number of organic electronic technologies has proven to be the actual transfer from the small-scale laboratory device into a process that is scalable for manufacture of large volumes. These technologies have evolved around the conditions of the laboratory and optimization has been performed using processing techniques well suited for these surroundings. Unfortunately, most of these techniques, such as spin coating and vacuum deposition of electrodes, do not correlate well with fast processing using roll-to-roll (R2R) systems and flexible substrates which in most cases has been/is the final goal. The reason for this lies in the possibility of high throughput production through solution processing of devices at very low cost. As a result it is often found that the careful optimization of the small-scale device cannot be directly transferred and scaled as new processing methods often rely on different optimization parameters.

Another important issue which is generally not prioritized in the lab is the critical evaluation of the materials and energy consumptions related to device preparation. Especially within technologies related to energy such as organic solar cells, organic fuel cells, and organic thermoelectric devices it is extremely important to be aware of the process energy flow and the energy embodied in the materials used in order to be able to assess the technology’s future potential. Life-cycle assessment (LCA) is an important tool which can be used to direct research toward a more optimized process, by pinpoints procedures or materials which are simply too energetically demanding to be considered suitable for the technology.
Basically it is simple accountancy: How much energy is put into the preparation of each material used in the process, how much energy is used during the process, what is the expected power output from the final device, how much energy will be used in assembling the final device as well as in its installation, and what is the expected lifetime of the device. This calculation should preferably show that the energy payback time of the device (the time it will take a device to produce the same amount of energy that was put into its manufacture and installation) is considerably lower than the lifetime of the device.

Thermoelectric polymers have recently received increasing attention, and several reviews and perspective studies have been published on the subject [1–6]. Thermoelectric materials can be used in devices with no moving parts either as Peltier coolers (directional transport of heat by application of electrical energy) or as thermoelectric power generators (generation of electrical energy by exposure to a temperature gradient). Unfortunately, most of the known high-performance thermoelectric materials available today (such as bismuth telluride) are related to either rare elements, toxicity, or a combination of both in complicated and highly costly manufacturing processes. Polymeric materials on the other hand can generally be processed as solutions, which open up a variety of processing methods which can be carried out using R2R technology on flexible substrates, and the optimization of the polymeric properties can be carried out fairly easily though chemical modification.

One of the inherent challenges, when developing thermoelectric materials, lies in the requirement that they should be very good conductors of current while simultaneously being poor conductors of heat. This allows for one side of the device to be significantly colder than the other without equalizing the temperature and it is this temperature gradient over the material that is the driving force for power generation. The thermoelectric properties of a material are generally expressed by the dimensionless figure-of-merit $ZT$ given by the equation $ZT = (S^2\sigma)T/k$, where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $T$ is the absolute temperature, and $k$ is the thermal conductivity. Sometimes the thermoelectric performance is assessed by the power factor $P = S^2\sigma$ when thermal conductivity data are not available.

Several polymers have so far been tested, including polyacetylene [7, 8], polyanilines [9–11], polypyrroles [12–14], polycarbazoles [15–17], polythiophenes [18–20], and mixtures of poly(3,4-ethylenedioxythiophene) (PEDOT) and polystyrene sulfonate (PSS), or tosylate [21–25]. The different polymers vary in Seebeck coefficient, electrical conductivity, and to some extent also in thermal conductivity, but common for almost all reports is that the figure-of-merit $ZT$ lacks at least two orders of magnitude to become interesting for commercialization, which requires a $ZT$ of $\sim 1$. A few exceptions exist though showing that it is actually possible to obtain good results with organic polymers [21, 26, 27]. Among the best results are the report by Bubnova et al. [21] where $ZT = 0.25$ (at room temperature) was obtained by tuning the degree of PEDOT oxidation by exposure to tetrakis(dimethylamino) ethylene (TDAE) vapors in inert atmosphere using tosylate as counter anion. However, the tuned PEDOT cannot be processed directly and the requirement of a postprocessing chemical reaction steps is a drawback seen from a production point of view.

It is a general trend within the existing reports on polymer thermoelectrics that very little effort has been made toward how these compounds could actually be processed when going to a larger scale and generally characterization of new materials has been carried out on a microscopic level (very small single devices). In the few reports where attempts have been made to approach the challenge of preparing serially connected devices (which is required to build up voltages that are practically useful), focus has mostly been on reproducing the traditional architecture of inorganic thermoelectric devices rather than how the thin-film device properties can be used with advantage, that is, in a R2R processed architecture [21, 27, 28]. In the inorganic thermoelectric geometry, which typically operates best at elevated temperatures ($T > 400^\circ\text{C}$), relatively thick layers of thermoelectric material are used, and for practical reasons, alternating n-type and p-type materials are employed in order to be able to connect the devices top-to-top and bottom-to-bottom as indicated in Figure 1A.

As most conjugated polymers are generally p-type this poses a problem when using them as thermoelectric materials as they should preferably have very similar properties, but with opposite Seebeck coefficients, and from a processing point of view it will furthermore always be more economical to process a single layer than two.

We here present the fabrication of 18,000 thermoelectric junctions in series, processed as a silver|PEDOT:PSS|silver stack entirely by R2R methods on flexible polyethylene terephthalate (PET) foil (60 $\mu$m) at processing speeds of 2–10 m/min for each layer, resulting in a final processing speed of 1.3 m/min (300 junctions/min, 6 cm$^2$ per junction) for the complete stack. The processing is carried out in a manner where only one thermoelectric material is needed. This is achieved by use of an intricate topology taking advantage of the relative ease with which bottom and top electrodes of adjacent junctions can be connected when using R2R thin-film processing of the electrodes as shown in Figure 1B. Devices of serially connected junctions have been tested and LCA has furthermore been carried out in
order to evaluate the different processing steps and materials.

Results and Discussion

Thermoelectric junctions were fabricated on PET foil (60 μm) in three steps: (1) Flexoprinting of a nanoparticle silver ink for the bottom electrode (PChem PFI-722, 10 m/min), (2) rotary screen printing of PEDOT:PSS (AGFA 5010:2-propanol (10:2), 2 m/min, ~1.2 μm dry thickness), and (3) flexoprinting of a silver paste as the back electrode (DuPont PV410, 10 m/min). The prints were aligned in a manner where each junction is serially connected to the two adjacent ones, creating an infinite connection along the web as illustrated in Figure 2. A video of the manufacturing can be found in the supporting information.

Drying was performed at 140°C using a total of 4 m of oven for the printing of the electrodes and 2 m of oven for the thermoelectric PEDOT:PSS. The polymer is thus exposed to 140°C for 1 min and 24 sec in total. For the first nanoparticle silver and for the PEDOT:PSS, three IR lamps (900 W each) were used in addition. In this study a total of 18,000 serially connected junctions were produced, but the number of connected junctions is in principle only limited by the length of the foil and the size of the junction. The active area of each individual junction is 1 × 6 cm².

After finishing the printing process the complete stretch of thermoelectric junctions was subsequently divided into smaller stretches which were each rolled up on an aluminum cylinder, as shown in Figure 3, and the cylinder was then filled with hot water after which the whole device was immersed into ice water to ensure good heat sink capacity on the outside. The temperature on the outside and the inside of the device was continuously monitored using two thermocouples to give the temperature difference ∆T.

Two types of rolled-up devices were prepared: (a) a pressure sensitive adhesive (60 μm) was applied to the back side of the entire stretch of foil ensuring that everything is tightly glued together when wound onto the cylinder (good thermal contact between the layers); and (b) the foil was wound directly onto the cylinder without any adhesive. In order to assess the importance of the number of windings in a rolled-up structure, serial devices with 10 windings (576 junctions, ~1 m²) and 106 windings (7000 junctions) were prepared. The outcome is presented in Figure 4. Note that the Seebeck coefficients presented are estimates calculated as the average for a single junction assuming an evenly distributed thermal gradient through the complete wound structure and then using the average thermal gradient over each winding (S = U/ (ΔT* number of junctions/number of windings), where U is the voltage).

The data clearly show that R2R methods can efficiently be employed for the successful fabrication of devices and that they work in a serially connected setup, but it also clearly reflects a potentially large challenge for thin-film thermoelectric devices which is the relative thicknesses of the thermoelectric material and the substrate. The results shown are for a temperature gradient applied to the whole device, including the substrate and the adhesive (when used) and although very thin substrates are used, this still constitutes the majority of the material over which the thermal gradient is applied. Figure 5 illustrates the relative thicknesses of the different organic layers in the stack, and it is reasonable to assume that the thermal

Figure 1. Schematic illustrations of (A) a traditional thermoelectric design employing complementary p- and n-type materials in order to avoid charge build up in the series connected system. (B) New thin-film-based design employing only one thermoelectric material for series connection. When printing the top electrode of a junction this is simultaneously connected with the adjacent bottom electrode, thus allowing for directional charge transport without charge build up (the arrow tracing through the stacks show the flow of electrons).
conductivities through these polymeric materials are roughly of the same order of magnitude, whereas the silver electrodes (very good heat conductors) can be assumed to have a negligible contribution to the thermal gradient through a device.

Using an adhesive thus might ensure a good thermal contact between each layer of foil, but it simultaneously increases the amount of nonthermoelectric material in the stack. These consequences can be observed quite clearly by comparing the slopes of the voltage data points of the devices with and without adhesive in Figure 4. The device without adhesive clearly shows a higher increase in voltage per Kelvin correlating well with the fact that the effective increase in thermal gradient over the TE material is roughly twice as big because of the thinner stack. In the middle-to-lower temperature range the heat transfer between the foils without adhesive is limited. The better heat transfer at higher temperatures could be explained by the fact that most polymers soften when heated, thus creating a better contact between the layers.

Similar voltages are as expected observed for the same temperature gradient when going from 10 to 106 windings with adhesive, but the current drops with increasing number of windings as a consequence of the bigger internal resistance of the final device.

The determined average Seebeck coefficients in Figure 4 are all quite low, but it should be stated that they represent a Seebeck coefficient of the entire device including substrate, adhesive, and all printed layers. If the ratio between thermoelectric material and substrate/adhesive thickness is taken into account (1:50 without adhesive and 1:100 with adhesive) and it is assumed that the thermal gradient is distributed evenly with the same ratio, then the estimated average Seebeck coefficients, considering just the thermoelectric material, all lie within 0.7–3.5 μV/K which is quite close to the coefficients determined for the PEDOT:PSS ink itself after drying and pressing it into a pellet (all are around 12 μV/K for temperature differences of 30–100°C between two copper blocks). This clearly shows that the relative thickness of the TE material and the substrate are extremely important factors in the processing of organic thermoelectric devices. Polymeric (organic) substrates such as PET are generally considered the best candidates for R2R processing because of

Figure 2. Illustration of the printing process showing the pattern of each printed layer and the final device architecture.

Figure 3. Top: Illustration of and picture of the rolled-up final device. Bottom: Illustration of the heat transport in the final setup.
their relatively low cost and easy handling, but because organic materials have thermal conductivities of approximately the same order, the substrate becomes a very important factor for the thermal gradient over a junction as this reduces the gradient over the thermoelectric material. In this study, a 60-μm substrate, a 60-μm adhesive, and a 1.2-μm-thick PEDOT:PSS layer were used, reducing the actual thermal gradient over the TE material to ~1% of the thermal gradient over the device. With respect to R2R processing on thinner substrates, a thickness of around 10–20 μm is probably approaching the limit of what can be practically handled and although quite thick wet layers can be printed or coated using R2R technologies, such thick layers put demands on the ink to be very viscous and simultaneously increases the drying time (energy input) of the layer significantly. It is furthermore doubtful that dry layer thicknesses above much more than
20 μm can be handled as a flexible device without risking damaging the printed layer (delamination, cracking formation during drying). Even in such a best case scenario the substrate will still constitute 50% of the material that the device is composed of and it is worth considering whether new expressions such as “device Seebeck coefficient” and “device thermal gradient” including the complete thin-film stack are more suited for the assessment of thin-film thermoelectric devices.

As mentioned in the introduction, the energy payback time is extremely important when assessing an energy producing technology, and in order to do so it is not only necessary to take into account the energy used in the processing of the device but also the embedded energy of the materials used must be considered. Figure 6 illustrates the total embedded energy in a 10 winding device with adhesive considering both the processing and the materials used. The major part of the energy originates from the materials and both substrate and adhesive are substantial parts of this. Making the substrate thinner would thus both improve the thermal gradient over the active material and reduce the embedded energy in the device. The question is whether it is possible to tune all the possible factors of both minimizing the embedded energy and improving device performance to a level where the energy payback time is realistic. The device discussed here (10 windings + adhesive) would be required to produce 0.204 W in order to have an energy payback time of 1 year. As it stands the device is significantly removed from this goal as the energy payback time calculated with the results from this study is presently at 3.7 billion years. There are of course several parameters that can be tuned in order to improve this, increasing the coverage of the substrate (at present at around 40%) and increasing the thermal gradient over the TE material by using thinner substrates, thicker TE material layers, decreasing the number of windings, or simply by increasing the temperature gradient. With respect to the latter, such an increase is limited as organic materials generally cannot sustain elevated temperatures for a very long time. Adding to this, cheap substrates such as PET are generally also temperature sensitive, and polymer-based thermoelectric devices should therefore be operated at temperatures below 140–150°C. If the thermoelectric device is to reflect the idea of exploiting “waste energy,” this upper temperature should be set in context to the ambient temperature, leaving a relatively restricted temperature span to navigate within. A last and an extremely important parameter is the improvement of the thermoelectric properties of the materials. As of now the power factor/thermal conductivity relationship of printable polymer thermoelectric materials is still too low to attract interest for commercialization. New and improved materials are required for the technology to be relevant for energy production, whereas it is likely that niche applications are possible with a suitably refined version of the device presented here.

**Directions for Future Work and What to Expect From Printed Thermoelectrics**

It is clear from the reduction to practice presented in this work that printing is the most rational choice for the fast preparation of thermoelectric films that can in principle

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**Figure 6.** Energy distribution diagram of the total embodied energy in a 10 winding device with adhesive (576 junctions, ~1 m²), in equivalent primary energy units (MJ\(_{EPE}\)).
be applied with ease to hot tubes whereby one can extract energy from waste heat. It is, however, also clear that the carrier substrate which is required for the R2R processing leads to a thermal gradient loss as a significant part of the volume is occupied by the carrier. This should be counteracted by employing thinner carrier substrates, but as there are limits to how efficient this would become the thermal conductivity of the carrier should also be improved. The low thermoelectric performance for organic materials does leave significant room for improvement and warrants further research into new materials. A significant improvement should also be sought through better area usage combined with a thinner substrate having a high thermal conductivity compared with the organic thermoelectric layer such that the gradient loss can be minimized while maintaining a sufficient thickness of the carrier allowing for fast R2R processing. Significant improvements by three to four orders of magnitude should thus be possible and while this would open up for niche applications, the sustainable use of organic thermoelectrics from devices with energy payback times comparable with the lifetime of devices is unlikely unless higher thermal gradients can be employed (larger than the temperature range that organic materials can generally endure). However, it is likely that the approach followed here could be employed with success by printing inorganic thermoelectrics on thermally stable substrates. Lastly, advanced lift-off techniques, where the thermoelectric devices are transferred onto its final support without the substrate, might be a solution to how to avoid the influence of the latter. Such separation of the device and substrate will be complicated, ambitious, and challenging because of the extremely thin nature of the printed device, but would be rewarding as it would make printed thermoelectrics more sustainable.

Conclusion

In this study we have demonstrated that fast large-scale R2R processing of thermoelectric junctions in series is possible through a new and simplified device architecture which is designed specifically with focus on R2R processing procedures. The architecture allows the use of one single thermoelectric material instead of the usual two complementary thermoelectric materials (a p-type and an n-type) which are typically used in a traditional series connection of thermoelectric junctions. Testing of devices with this architecture using PEDOT:PSS as the thermoelectric material revealed an important issue that has not previously been debated on thin-film thermoelectric devices, which is the relative thickness of the thermoelectric material and the substrate. In a R2R process of thin films even the thinnest possible substrates will influence the thermal gradient over the complete device significantly showing that it might make sense to introduce new concepts like “device Seebeck coefficient” and “device thermal conductivity”, when evaluating organic thermoelectric thin-film devices. Life-cycle analysis of the produced devices showed that although there are several aspects of the design that can be improved, the possibility of producing thin-film devices aimed at bulk energy production is presently very far away. In order to really assess the technology, more specific proposals toward how thin-film thermoelectric devices can be practically used must be given and in that context, more specific estimates of what kind of power per square meter of thin-film devices that can be considered good enough for energy production are also required. In this study we estimated the power required for obtaining an energy payback time of 1 year to be ~0.2 W/m², but considering the places (and the abundance of such) where such a device could be installed, the impact of a 0.2 W/m² technology will only significantly influence the world energy production for very large areas and at the moment the technology is likely to be limited to niche applications. There might be situations where on-demand electricity cannot be covered by existing technology (generator, battery, solar cell, etc.) where less efficient thermoelectric devices can have their merit, but in the context of bulk energy production such devices need to be of very low cost, high abundance, and with an efficient process having a high production throughput. We have here presented a method for fast processing of polymeric thermoelectric devices in series by use of R2R printing technologies. We believe that we have demonstrated that realistic improvements will enable manufacture of organic thermoelectrics for niche applications.

Acknowledgment

This work was supported by the Danish Ministry of Science, Innovation, and Higher Education through the EliteForsk initiative and the 2011 Grundfos award.

Conflict of Interest

None declared.

References


**Supporting Information**

Additional Supporting Information may be found in the online version of this article:

**Video S1.** Video showing the screen printing process of PEDOT:PSS, the flexo printing of the silver back electrode and the finally the assembly of a wound up device using an adhesive.