**Thermoelectrica based on organic semi-conducting polymer thin films.**

Thermoelectric materials enable the direct conversion of heat into electrical power, as applying a temperature gradient on these type of materials leads to the formation of an electric potential difference. Thus, in present times of climate change, increasing energy consumption and limitation of fossil resources, thermoelectric materials gain growing attention as they provide a potential application in waste heat recovery and therefore energy efficiency. The working principle of thermoelectric materials, the thermoelectric effect, is schematically visualized in Figure 1.

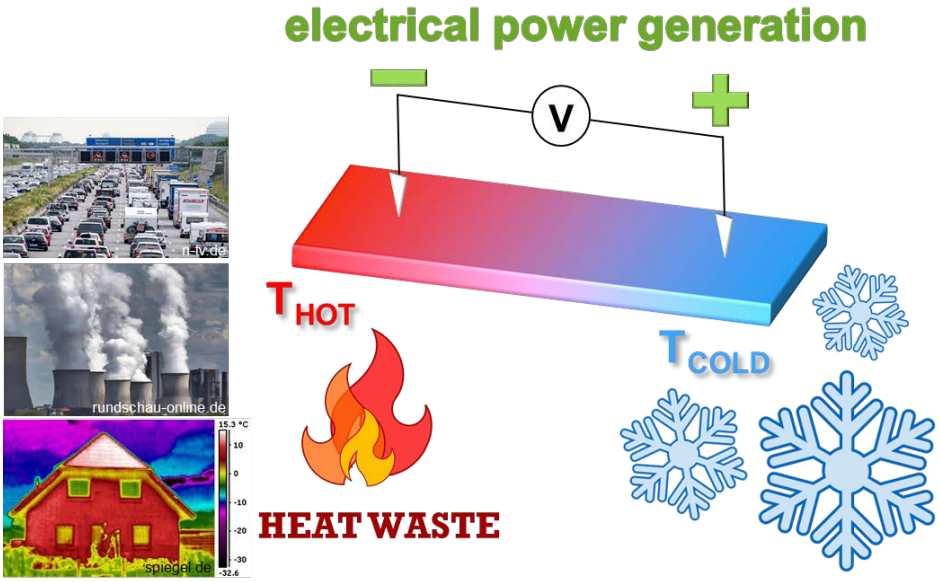


Figure 1:
The application of a temperature gradient onto a thermoelectric material (in this example p-semiconductor), leads to the generation of an electrical potential difference. Possible heat sources could be waste heat from industrial processes, power generation, electronic devices, etc.

Until now, principally inorganic semiconducting bulk alloy materials such as $Bi_2Te_3$ were used as thermoelectric materials. These inorganic materials, however, often contain rare and toxic elements like bismuth, tellurium, lead, or antimony, which are difficult and cost-intensive to process. In contrast, organic polymer-based semiconductors demonstrate significant advantages for application as thermoelectric materials, being flexible and lightweight, possessing a low- or non-toxicity and generally being soluble in common solvents allowing for a large-scale, low-cost solution-based processability like spray, spin or dip coating.

Up to now a popular and very promising candidate for the use as organic thermoelectric material is the conductive polymer blend PEDOT:PSS, consisting of poly(3,4-ethylenedioxythiophene) and poly(styrene sulfonate). Owing to its very particular structure of hole-conducting PEDOT rich domains embedded in a matrix of water-soluble non-conductive PSS, this polymer blend combines the advantages of being water-soluble while holding a potentially high hole-conductivity. In our group, the research on organic thermoelectric materials focuses on PEDOT:PSS with the aim to find treatment methods to tune and improve its thermoelectric properties. A typical parameter to evaluate the thermoelectric properties of a material is the temperature dependent figure of merit $ZT = \frac{S^2\sigma}{\kappa}T$, calculated using the Seebeck coefficient S, the electrical conductivity σ, and the thermal conductivity κ.[1]

Some successful approaches for enhancing the electrical conductivity of PEDOT:PSS have already been demonstrated, generally achieved by removing the excess of non-conductive PSS. For example, our group was able to show that by treating PEDOT:PSS thin films with

different acids and bases[2], with ethylene glycol[3], [4], or adding surfactant into the aqueous PEDOT:PSS solution[5], a change towards a more favorable PEDOT:PSS morphology can be effected, resulting in an increase of the electrical conductivity. Another effective attempt demonstrated by our group aims at improving the Seebeck coefficient by changing the electronic structure of PEDOT:PSS, meaning to induce a reduction of PEDOT by mixing inorganic redox-active or basic salts into the aqueous PEDOT:PSS solution.[6] Recently, Saxena et al. were able to achieve an increase in electrical conductivity as well as an increase of the Seebeck coefficient of PEDOT:PSS thin films by post-treating them with ionic liquids.[7] With this method it is possible to simultaneously improve the electronic and morphological features of PEDOT:PSS.

Currently, our research work focuses on further investigating the effects of ionic liquid treatment on the structure of PEDOT:PSS thin films in terms of domain sizes, inter-domain distances, as well as crystal sizes and orientations. Therefore, we use grazing incidence small/wide angle x-ray scattering (GISAXS/GIWAXS).[8] At synchrotron facilities like DESY or ELETTRA, we are able to investigate degradation processes of the ionic liquid post-treated PEDOT:PSS thin films in-situ under different ambient conditions. Furthermore, we aim to study the thermal conductivity of such treated PEDOT:PSS films[9] and investigate further promising polymer candidates for use in thermoelectric devices.


[1] O. Bubnova and X. Crispin: *Towards polymer-based organic thermoelectric generators*; Energy Environ. Sci. **5**, 9345-9362 (2012)

[2] L. Bießmann, N. Saxena, N. Hohn, M. A. Hossain, J. G. C. Veinot, and P. Müller-Buschbaum: *Highly Conducting, Transparent PEDOT:PSS Polymer Electrodes from Post-Treatment with Weak and Strong Acids*; Adv. Electron. Mater. **5**, 1800654 (2019)

[3] C. M. Palumbiny, C. Heller, C. J. Schaffer, V. Körstgens, G. Santoro, S. V. Roth, P. Müller-Buschbaum: *Molecular Reorientation and Structural Changes in Cosolvent-Treated Highly Conductive PEDOT:PSS Electrodes for Flexible Indium Tin Oxide-Free Organic Electronics*; J. Phys. Chem. C **118**, 13598-13606 (2014)

[4] C. M. Palumbiny, F. Liu, T. P. Russell, A. Hexemer, C. Wang, and P. Müller-Buschbaum: *The crystallization of PEDOT:PSS polymeric electrodes probed in situ during printing;* Adv. Mater. **27**, 3391-3397 (2015)

[5] C. M. Palumbiny, J. Schlipf, A. Hexemer, C. Wang, and P. Müller-Buschbaum: *The Morphological Power of Soap: How Surfactants Lower the Sheet Resistance of PEDOT:PSS by Strong Impact on Inner Film Structure and Molecular Interface Orientation*; Adv. Electron. Mater. **2**, 1500377 (2016)

[6] N. Saxena, J. Keilhofer, A. K. Maurya, G. Fortunato, J. Overbeck, and P. Müller-Buschbaum: *Facile Optimization of Thermoelectric Properties in PEDOT:PSS Thin Films through Acido-Base and Redox Dedoping Using Readily Available Salts*; ACS Appl. Energy Mater. **1**, 336–342 (2018)

[7] N. Saxena, B. Pretzl, X. Lamprecht, L. Bießmann, D. Yang, N. Li, C. Bilko, S. Bernstorff, P. Müller-Buschbaum: *Ionic Liquids as Post-Treatment Agents for Simultaneous Improvement of Seebeck Coefficient and Electrical Conductivity in PEDOT:PSS Films*; ACS Appl. Mater. Interfaces **11**, 8060–8071 (2019)

[8] A. Hexemer and P. Müller-Buschbaum: *Advanced grazing-incidence techniques for modern soft-matter materials analysis*; IUCrJ **2**, 106-125 (2015)

[9] A. Greppmair, B. Stoib, N. Saxena, C. Gerstberger, P. Müller-Buschbaum, M. Stutzmann, M. S. Brandt: *Measurement of the in-plane thermal conductivity by steady-state infrared thermography*; Rev. Sci. Instrum. **88**, 044903 (2017)