

Summary for publication

Summary of the context and overall objectives of the project

More than 60% of the global power is lost as waste heat. Thermoelectric (TE) materials can convert vast amounts of this waste heat into electricity and significantly contribute to the current energy challenge. Despite large efforts to identify better TE materials, still, the TE technology is limited by low efficiency. One of the two performance improvement routes, thermal conductivity reduction, has already reached its limit, which makes the other route, power factor (PF) improvements, crucial.

Current strategies targeting PF enhancements have only reached modest improvements, mainly due to the adverse interdependence of the Seebeck coefficient (S) and the electrical conductivity (σ), which produces a decrease in one of these properties if the other is increased. This is a serious obstacle to achieve the widespread application of the TE technology, since $PF = \sigma S^2$.

UncorrelaTEd will realize the dream of breaking the S - σ correlation by introducing a new paradigm in thermoelectricity that comes from the connection of TEs and electrochemistry, using a properly designed hybrid system, formed by a porous TE solid permeated by a liquid electrolyte (ions in a liquid), as shown in Fig. 1. The porous solid provides a low thermal conductivity, whereas the electrolyte tactically interacts with the solid to enlarge the PF. Unprecedented PF improvements (above 35 times) have already been observed by UncorrelaTEd members in this system using a material with modest TE properties (Sb-doped tin oxide, ATO). UncorrelaTEd aims at extending these improvements to different materials (bismuth telluride alloys, oxides, and polymers) with state-of-the-art TE properties, potentially leading to an extraordinarily powerful technology able to provide more than 4 times larger PF than state-of-the-art low-mid temperature ($<150\text{ }^\circ\text{C}$) materials and $ZTs > 3$. This will enable the TE technology to be implemented in many areas, such as self-powered sensors, empowering the elimination of batteries, textiles, factories, power plants, and combustion engines.

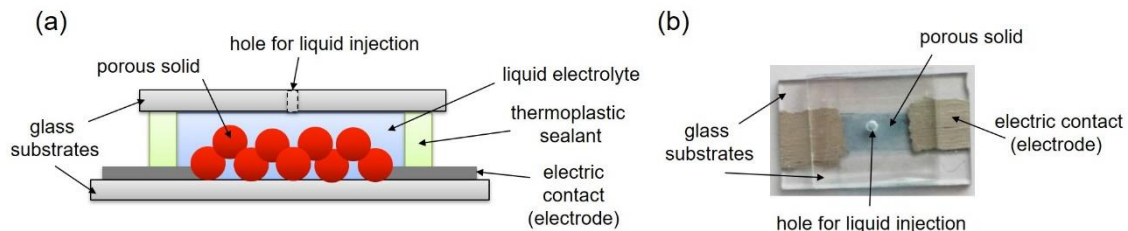


Fig. 1. (a) Schematic of the hybrid solid-liquid UncorrelaTEd device and (b) a picture of the same.

Work performed from the beginning of the project to the end of the period covered by the report and main results achieved so far

During the first year of the project, the UncorrelaTEd consortium has worked on four main aspects: (1) to understand the phenomena that produced the observed PF improvements in our preliminary results, which were obtained using Sb-doped tin oxide as TE solid material, (2) to fabricate Sb-doped tin oxide films with different porosity levels in order to investigate how porosity affects the PF improvements, (3) to synthesize bismuth telluride based materials and fabricate films of different porosity and doping levels with TE properties close to the state of the art, and (4) to construct a simulator able to simulate the hybrid solid-liquid systems of the project.

1. To understand the phenomena that produced the observed PF improvements obtained using Sb-doped tin oxide (ATO): In our preliminary results, we observed that using nanostructured and porous ATO as the TE solid and HI dissolved in water as electrolyte, the Seebeck coefficient of

ATO increased from $-38 \mu\text{V/K}$ (without electrolyte) to $-213 \mu\text{V/K}$ (with electrolyte). On the other hand, the electrical resistance of the device varied from $19 \text{ k}\Omega$ (without electrolyte) to $17 \text{ k}\Omega$ (with electrolyte). That led to an unprecedented PF improvement of 35.8 times.

After investigating the reasons behind these improvements, it was found that the anion I^- from the HI electrolyte can react with oxygen in the solution to produce I_3^- , leading to an electrolyte that contains both I^- and I_3^- . These two anions form what is called a redox couple, which is the combination of two compounds that can exchange electrons with the metallic contacts (electrodes) of the device. These metallic contacts are attached to each side of the ATO film and are also in contact with the electrolyte (see Fig. 1).

To understand clearer the role of the electrolyte with I^- and I_3^- , a new hybrid device was prepared with these two anions in the electrolyte (solution of LiI and I_2 in water). Note that I_3^- is formed in this case by this reaction: $\text{LiI} + \text{I}_2 \rightarrow \text{I}_3^- + \text{Li}^+$. In this device, it was observed a variation of the Seebeck coefficient from $-65 \mu\text{V/K}$ (without electrolyte) to $-365 \mu\text{V/K}$ (with electrolyte), and the device resistance dropped from $6.0 \text{ k}\Omega$ (without electrolyte) to $0.12 \text{ k}\Omega$ (with electrolyte). This again led to a huge PF improvement. However, we fabricated a device with the same configuration, but now without the presence of ATO, that is, two metallic contacts (Pt) separated by the same electrolyte. When the Seebeck coefficient and electrical resistance was measured in this device, $-370 \mu\text{V/K}$ and $0.11 \text{ k}\Omega$ were obtained, respectively, which are basically the same values found in the device with ATO when the electrolyte was added. These observations led to the conclusion that ATO was doing nothing in the device and all the TE properties come from the electrode/electrolyte/electrode configuration, which is known as the configuration of a thermocell [1].

After realising that the unprecedented preliminary results found came from a configuration which was already known (thermocells), rather than being an effect of the interaction between the ATO and the electrolyte, a new approach was investigated in the project. In this new approach it was proven that a metallic material, such as Pt, could exhibit a large Seebeck coefficient (above 1 mV/K) without a significant variation of its electrical conductivity. This is remarkably interesting since metals show good electrical conduction, but their Seebeck coefficients are very small ($1\text{-}10 \mu\text{V/K}$ usually), hence, the fact of being able to reach Seebeck coefficient values above 1 mV/K without impacting the electrical conducting leads to extremely large PFs never achieved before. This strategy is currently under further development.

2. To fabricate ATO films with different porosity levels in order to investigate how porosity affects the PF improvements: In order to prepare these films, a controlled nanoparticle aggregation approach was followed. ATO nanoparticles were purchased from a commercial supplier and after different optimisation procedures, a suspension of the nanoparticles in a solvent (mixture of water and ethanol) was formed that led to an interconnected network of these particles (gel) in the solvent after employing a destabilizer agent. Once the gel is formed, the solvent was removed (drying) under controlled conditions, leading to the network of interconnected nanoparticles which form porous films. The level of porosity was controlled by modifying the deposition and drying conditions. Film porosities, estimated from SEM images, covered a wide range, from 8% to 58% (see Fig. 2). The porosity level was not determined by a unique parameter, but it strongly depended on several factors including the stability of the initial dispersion, its concentration, the amount of destabilizer introduced and the drying temperature. Final film porosity also strongly depends on ambient parameters that determine the drying process, such as the atmosphere humidity.

To produce films with a wider range of thicknesses (from 1 to 3 μm) and higher homogeneity, and to remove cracks that appeared, multiple assembly processes, mediating an annealing step (heat treatment at 550 $^{\circ}\text{C}$ for 45 min) between them, were carried out. The samples produced will be tested in different hybrid devices to investigate the effect of porosity in the PF improvements in the next period of the project.

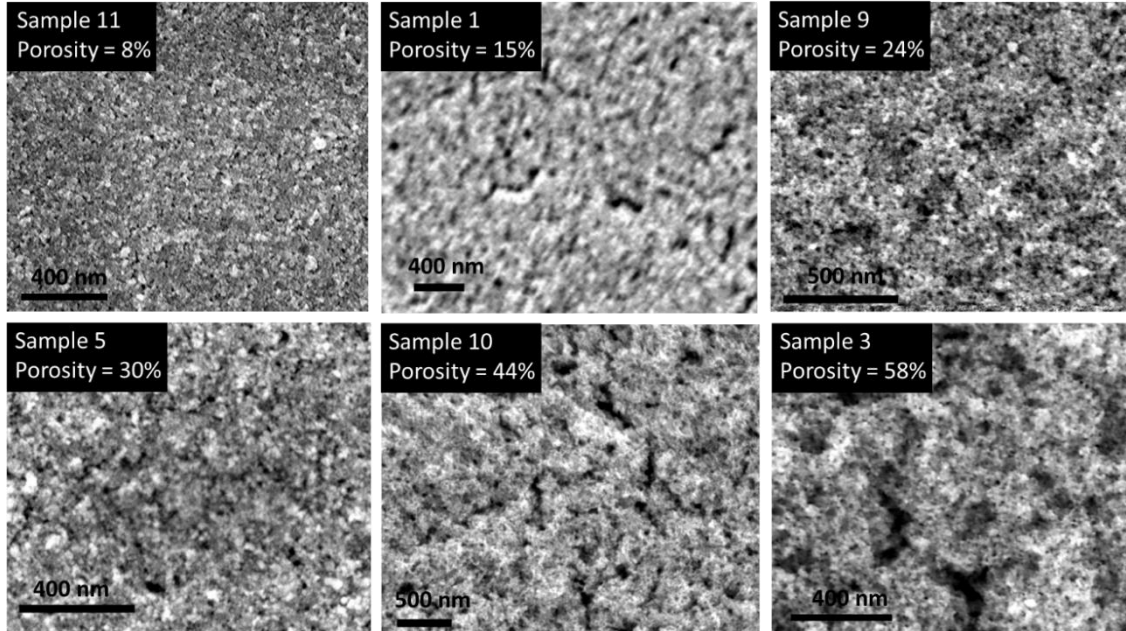


Fig. 2. SEM images of selected Sb:SnO₂ porous films covering the porosity range from 8% to 58%.

3. To fabricate bismuth telluride films of different porosity and doping levels with TE properties close to the state of the art: In order to fabricate these films, nanoparticles of different compositions based on Bi_{2-x}Sb_xTe₃ were prepared first using three different solution synthesis methods (polyol method, aqueous synthesis using a reducing agent, and thermolysis in oleic acid) assisted by microwave heating.

The aggregation of the prepared nanoparticles in order to obtain porous films was performed by electrophoretic deposition (EPD) process. EPD is a process in which charged colloidal particles, dispersed or suspended in a liquid medium, are migrated by an applied electric field in order to be adsorbed on a substrate. There are two main steps in this process: electrophoresis and deposition. Electrophoresis is the migration of the charged particles towards an oppositely charged metal (electrode) under the influence of an electric field. The second step of EPD is the deposition, which consists of the coagulation of particles to a dense matter. In the EPD process there are several parameters that influence the amount of the deposited material, which relate to the characteristics of the solvent and the dispersed nanoparticles, as well as the electric field and the electrodes.

A thorough systematic testing of different parameters allowed to obtain various solvent options for n-type TE material. One of the best results for n-type TE material was obtained using Bi₂Te₃ nanoparticles synthesized in water (hydrothermal synthesis), using an organic mixture as solvent. Under these conditions, a homogenous and porous film was obtained. In addition, using polyol synthesized Bi₂Te₃ nanoparticles, the substrate coverage density was rather high, having a capability to reach thickness of 10 μm and above by merely tuning the time of the EPD process (see Fig. 3).

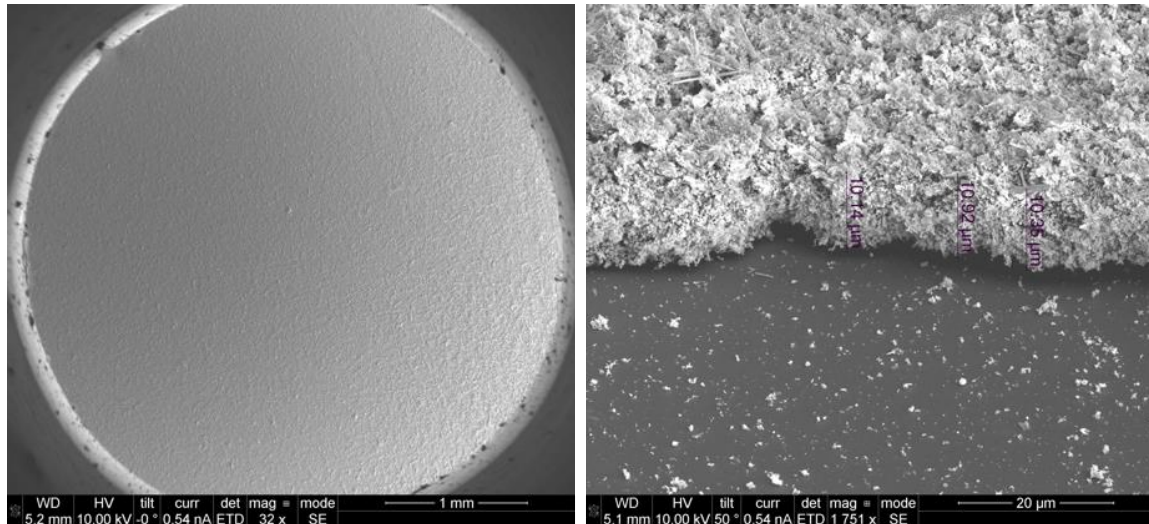


Fig. 3. SEM images of the n-type Bi_2Te_3 (polyol) film fabricated using EPD at different magnifications.

Another thorough systematic testing of EPD parameters allowed to obtain various solvent options for p-type TE material. One of the best results was from Sb_2Te_3 nanoparticles synthesized by polyol synthesis, using an organic solvent. The film coverage density was very good and homogeneous in this film (see Fig. 4), reaching a thickness of about 6 μm in one minute.

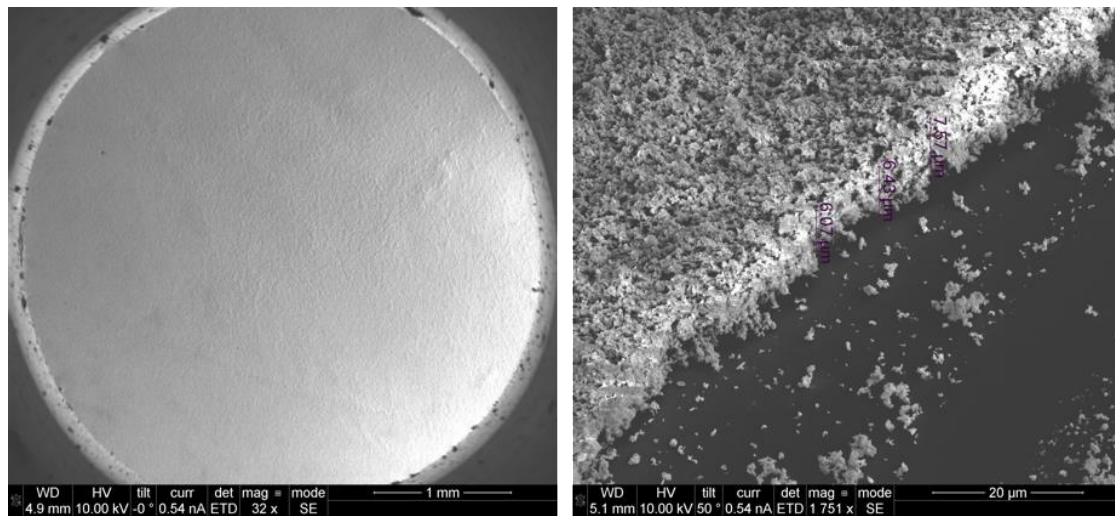


Fig. 4. SEM images of the p-type Sb_2Te_3 (polyol) film fabricated using EPD at different magnitudes.

Typically, about 40-50% porosity is expected in the films. Due to the principles of the EPD process nanoparticles are very closely attached together, which is expected to result in a high electronic conductivity of the deposited samples. A detailed evaluation of the films is under investigation, and will help to identify their transport performance, thus provide a feedback to the EPD process, allowing to study EPD parameters in relation to the eventual TE performance in the absence and presence of liquid electrolytes.

4. To construct a simulator able to simulate the hybrid solid-liquid systems of the project: This work started with the use of simple models (Boltzmann transport equation) to provide an initial

understanding of the electrical conductivity σ and the Seebeck coefficient S in highly porous materials. These porous films are formed by interconnected nanoparticles and the interfaces between each of them are considered as scattering points, which are obstacles for the electronic conduction. These obstacles were accounted for by introducing potential barriers at the nanoparticle-nanoparticle boundaries. The simulated values obtained for σ and S for this model were far from those experimentally observed for the ATO employed in the project. This is a consequence of the strong disorder (high surface area, many interphases, pores, etc.) that is present in the ATO films.

Hence, a new model was used, where the conduction of electrons is now produced by hopping events of the electrons from one localized state to another in the material. These isolated states typically appear due to the disorder and are usually located below the energy band edge, in tails of the bands extending into the bandgap. It was found using this new model that both the Seebeck coefficient and the electrical conductivity can adequately match the experimental data, so work will continue in this direction to provide more realistic simulations of UncorrelaTEd systems.

References:

- [1] Dupont MF, MacFarlane DR, Pringle JM. Thermo-electrochemical cells for waste heat harvesting-progress and perspectives. *Chem Commun* 2017;53:6288–302. <https://doi.org/10.1039/c7cc02160g>.

Progress beyond the state of the art, expected results until the end of the project and potential impacts

The results achieved so far by UncorrelaTEd have demonstrated the possibility to have metals with Seebeck coefficient values above 1 mV/K without affecting their high electrical conductivity. This will lead to unprecedented values of the power factor and the TE efficiency. In addition, it has been demonstrated the preparation of nanostructured and porous bismuth telluride films by electrophoresis deposition, a method not considered before for this common TE material, which has been shown to produce highly homogeneous films of high porosity levels.

These aforementioned results will be developed further in the next period of the project, where the prepared films will be tested with electrolytes in order to reach Seebeck coefficient values in the order of mV/K with high electrical conductivities. Moreover, low thermal conductivities originated by the porous structure of the films and the low thermal conductivity of electrolytes are also expected. This combination of properties is expected to lead to extraordinarily high TE efficiencies in the conversion of heat to electricity. Furthermore, once tested in bismuth telluride-based materials, the UncorrelaTEd approach will be evaluated in oxides and polymers.

At the end of the project, UncorrelaTEd results are expected to open a new research line connecting electrochemistry and thermoelectricity, and produce a significant number of peer-reviewed publications and several patents. The results will also allow the widespread application of TE energy conversion technologies. Thermoelectricity will become competitive for energy harvesting for μW to W applications (wearable devices, sensors, the internet of things, etc.), empowering the elimination of batteries and maintenance requirements. Moreover, it can achieve significant power generation from low grade ($<150\text{ }^\circ\text{C}$) heat, available e.g. in factories, the environment, biological entities, solar-thermal and geothermal energy.