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 heat into electricity and significantly contribute to the current energy challenge. Despite large efforts to identify better TE materials, 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=σS^2.

UncorrelaTEd will realise the dream of breaking the S-σ correlation by introducing a new paradigm 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 have already been observed by UncorrelaTEd members in this system using a material with modest TE properties (Sb-doped SnO_2). 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 powerful technology able to provide more than 4 times larger PF than state-of-the-art low-mid temperature (<150 ºC) materials and ZTs>3.

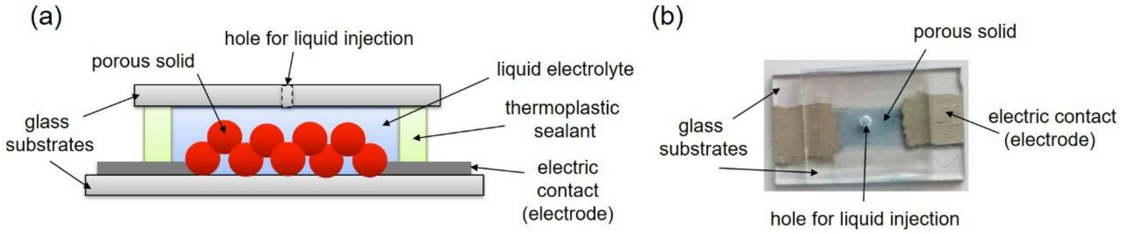

Fig. 1. (a) Schematic of the hybrid solid-liquid UncorrelaTEd device and (b) a picture of the same.

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

The main tasks developed have been: (1) to create a new device concept combining a porous solid with an electrolyte leading to a remarkably high Seebeck coefficient (>1 mV/K) with no degradation of the electrical conduction, (2) to fabricate bismuth telluride porous films by means of electrophoretic deposition (EPD), (3) to create an advanced simulator.

1. New device concept: This new concept consists of an electrically conductive material (in the form of a very thin film or a porous solid with low particle size) in contact with a redox electrolyte, with the additional requirement that the external electrical contacts should not be in touch with the electrolyte. Under this configuration, it is expected that the S of the redox electrolyte (usually >1 mV/K) be transferred to the electrical conductor without affecting the electrical conduction (or even decreasing it) in the system. When a redox electrolyte is in contact with a metallic material at each end, it is formed a thermocell, which are systems usually exhibiting very large S values.

Fig. 2a shows 3 different materials deposited on glass substrates that were placed in contact with a 0.4 M ferro/ferricyanide aqueous electrolyte (most common electrolyte in thermocells with S≈1.4 mV/K) in the configuration shown in Fig. 2b. The 3 samples of Fig. 2a are (i) two separated very thin (<8 nm) Pt films (thermocell configuration), (ii) a continuous very thin (<8 nm) Pt layer, and (iii) an Sb-doped SnO_2 film with 4-10 nm particle size contacted by Pt contacts. In the figure it is also indicated the area that will be in contact with the electrolyte by the red dashed lines.

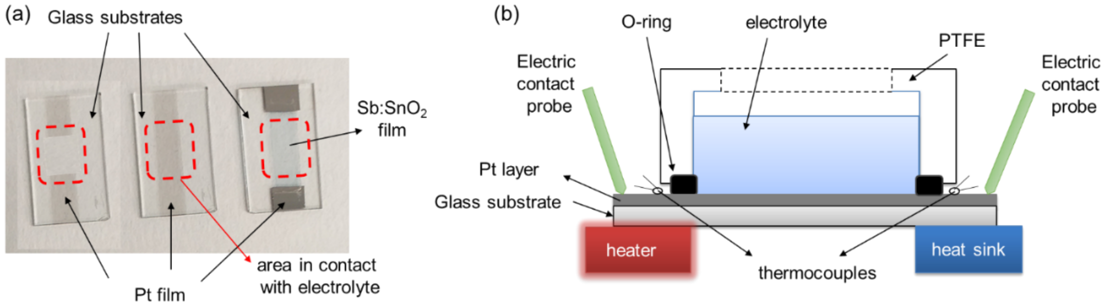

Fig. 2. (a) Pictures of different samples prepared and (b) the schematic of the measuring system for the case of a continuous Pt film.

The TE properties of the 3 systems are shown in Table 1, before and after the contact with the electrolyte. The sample with the thermocell configuration (separated Pt contacts) showed the expected S value (1.848 mV/K) and a similar value (1.473 mV/K) was found for the continuous film sample, hugely different from the value of the film without the electrolyte (1.71 µV/K). In addition, the resistance remained similar to the value without electrolyte, even slightly reduced. This remarkable result demonstrates that the S of a redox electrolyte can be transferred to Pt without affecting its electrical conductivity.

The sample with Sb-doped SnO_2 showed a similar result to that found in the continuous Pt film, and S in the presence of electrolyte achieved a value of 2.349 mV/K, even higher than the value of the thermocell configuration (Table 1). Moreover, the electric resistance of the device significantly dropped. This proves that the approach also works in an oxide (semiconductor), so it could probably be applied generally.

Table 1. Thermoelectric properties identified in different devices of the ferro/ferricyanide system.

Sample	**Seebeck coefficient (µV/K)**		**Electric resistance (kΩ)**	
	Without electrolyte	*With electrolyte*	*Without electrolyte*	*With electrolyte*
Separated Pt contacts	-	1,848	-	18.1
Continuous Pt film	1.71	1,473	9.9	7.8
Pt/ Sb:SnO$_2$ /Pt	-90.4	2,349	34.0	9.6

2. Bismuth telluride porous films: The EPD method was used to prepare porous bismuth telluride films. In this method, suspended nanoparticles in a solution migrate towards a substrate when an electric field is applied. As they accumulate on the substrate the film is created. After optimisation of many different variables, optimum results were obtained, as shown in Fig. 3 for several films of Bi_2Te_3 nanoparticles. After the EPD process, the films were spin coated with 1,6-hexanedithiol dissolved in 2-(1-methoxy)propyl acetate to exchange the surface ligands and improve the TE performance of the films. Zoomed in top-view images in Fig. 3 show the porosity of the films,

estimated in around 30% from image analysis software. The TE properties of the 3 films are shown in Table 2.

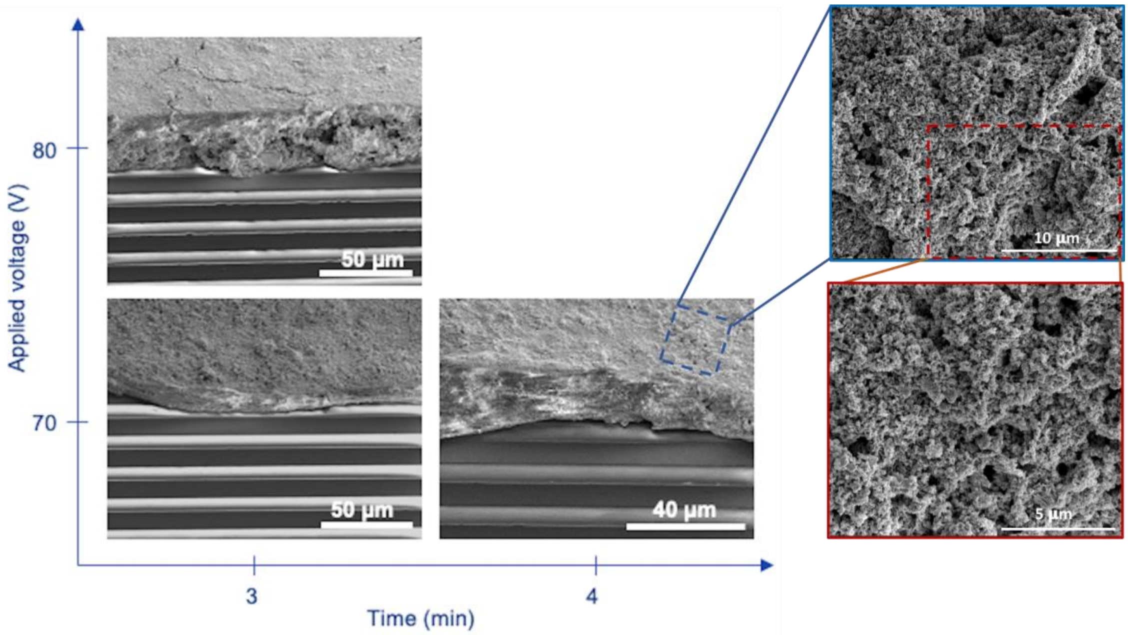

Fig. 3. SEM micrographs of EPD films of Bi_2Te_3 nanoparticles, deposited at different voltage and duration. Micrographs to the right show zoomed in top-view images of the film, revealing the porosity.

Table 2. Transport properties of several EPD films.

Sample	**Resistance (kΩ)**	**Thickness (µm)**	**Conductivity (S/m)**	**Seebeck (µV/K)**	**Power Factor (nW/K^2.m)**
EPD70V3m	16	2 - 10	7.5	-150	169
EPD80V3m	14	25 - 30	1.69	-180	60
EPD70V4m	17	15 - 45	2.16	-167	66

3. Advanced simulator: An advanced Monte Carlo (MC) electronic transport simulator, which can take into consideration in real space the complexities of the nanostructured domain was developed. The MC method solves the semi-classical Boltzmann transport equation (BTE) stochastically. It is based on the simulation of particle trajectories in real-space considering all nanostructured geometrical features. These simulations, however, tend to be overly computationally expensive and a better algorithm was developed using a hybrid approach combining the analytical BTE and the stochastic MC. Electrons are injected only from the left to the right (rather than bidirectional); they are injected uniformly in energy (rather than according to the density of states); we do not impose a voltage or temperature gradient; and we take the mean free path (mfp) approach in which the electrons get scattered at every mfp for certain. The advance simulator is available at the project website in open access.

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

The results achieved so far have demonstrated the possibility to have materials with S values above 1 mV/K without affecting their electrical conduction. This will lead to unprecedented values of the PF 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. An advanced simulator has been constructed that will be key to optimise and identify new possibilities of these new devices.

These results will be developed further in the next period and are expected to lead to extraordinarily high TE efficiencies in the conversion of heat to electricity. At the end of the project, UncorrelaTEd results will 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 ºC) heat, available e.g. in factories, the environment, biological entities, solar-thermal and geothermal energy.