Do We Really Need High Thermoelectric Figures of Merit? A Critical Appraisal to the Power Conversion Efficiency of Thermoelectric Materials

Supplementary Information

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1 Exact analysis of the thermal power dissipated in a secondary energy conversion scenario

Eq. (5) of the main manuscript computes heat fluxes disregarding the amount of heat actually converted into electric power. In the following the exact computation of the heat fluxes is reported, actually showing that the correction is actually of order a few percents of the input power.

An exact computation must also account for the heat converted into electrical energy. Heat equation in one dimension for thermoelectric materials reads as

$$\kappa \frac{\mathrm{d}^2 T(z)}{\mathrm{d}z^2} + \Phi(z) = -\frac{j^2}{\sigma} \tag{1}$$

where j is the TE current, $\Phi(z)$ is the heat rate (per unit volume) generated within the hot bath. All other symbols are defined in the main manuscript. Setting $\Phi(z) = q\delta(z)$ (where $\delta(z)$ is the Dirac function and $q \equiv \dot{Q}/A_\mathrm{c}$) and integrating over z one gets

$$\kappa \frac{\mathrm{d}T(z)}{\mathrm{d}z} + q = -\frac{j^2}{\sigma} z \tag{2}$$

For a system like the one described in the manuscript, the heat problem implies the simultaneous solution of two ordinary differential equations, namely

$$\left\{ \begin{array}{lcl} \kappa_\mathrm{A} \frac{\mathrm{d}T_\mathrm{A}(z)}{\mathrm{d}z} + q & = & -\frac{j_\mathrm{A}^2}{\sigma_\mathrm{A}} z \\ \kappa_\mathrm{B} \frac{\mathrm{d}T_\mathrm{B}(z)}{\mathrm{d}z} + q & = & 0 \end{array} \right. \tag{3}$$

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where $q_{\rm A}+q_{\rm B}=\dot{Q}/A_{\rm c}$ and $j_{\rm A}$ is the TE current flowing through the TE material A. We impose $T_{\rm A}(0)=T_{\rm B}(0)=T_{\rm H}$. Direct integration of Eq. (3) between 0 and z leads therefore to

$$\begin{cases} \kappa_{\rm A}\left(T_{\rm A}(z)-T_{\rm H}\right) &= -q_{\rm A}z-\dfrac{j_{\rm A}^2}{\sigma_{\rm A}}\dfrac{z^2}{2} \\ \kappa_{\rm B}\left(T_{\rm A}(z)-T_{\rm H}\right) &= -q_{\rm B}z \end{cases} \tag{4}$$

In addition, we also impose $T_{\rm A}(d)=T_{\rm B}(d)=T_{\rm C}$, treating the thermal conductivities as adjustable parameters to be chosen in such a way to guarantee that all the thermal power generated within the hot sink is spilled out. This leads to

$$\begin{cases} q_{\rm A} &= \dfrac{\kappa_{\rm A}}{d}\Delta T\left(1-\dfrac{j_{\rm A}^2}{2\kappa_{\rm A}\sigma_{\rm A}\Delta T}d^2\right) \\ q_{\rm B} &= \dfrac{\kappa_{\rm B}}{d}\Delta T \end{cases} \tag{5}$$

If we refer to the alternative situation of a single TE material with an optimal thermal conductivity $\kappa_{\rm opt}$, dissipation of the thermal power $\dot{Q}$ through the entire surface (of area S) may be obtained provided that [cf. Eq. (2)]

$$\dot{Q}=S\frac{\kappa_{\rm opt}}{d}\Delta T\left(1-\frac{j_{\rm opt}^2}{2\kappa_{\rm opt}\sigma_{\rm opt}\Delta T}d^2\right) \tag{6}$$

where $j_{\rm opt}$ is the TE current flowing through the optimal TE material and $\sigma_{\rm opt}$ is its electrical conductivity. In view of the definition of $q_{\rm A}$ and $q_{\rm B}$ we can therefore write

$$\kappa_{\rm opt}\left(1-\frac{j_{\rm opt}^2}{2\kappa_{\rm opt}\sigma_{\rm opt}\Delta T}d^2\right)=x\kappa_{\rm A}\left(1-\frac{j_{\rm A}^2}{2\kappa_{\rm A}\sigma_{\rm A}\Delta T}d^2\right)+(1-x)\kappa_{\rm B} \tag{7}$$

that reduces to Eq. 7 of the manuscript if we set $j_{\rm opt}=j_{\rm A}=0$.

We are now in the position of computing the efficiency. The efficiency is defined as the ratio between the electric power output $P_{\rm el}$ and the (total) thermal power input $\dot{Q}$. Since only material A can generate an electric power output, we can write $\eta_{\rm eff}$ as

$$\eta_{\rm eff}=\frac{P_{\rm el}}{\dot{Q}}=\frac{P_{\rm el}}{\dot{Q}_{\rm A}}\frac{\dot{Q}_{\rm A}}{\dot{Q}} \tag{8}$$

Manifestly enough, $P_{\rm el}/\dot{Q}_{\rm A}$ is the TE efficiency of material A while we can compute $\dot{Q}_{\rm A}/\dot{Q}$ based on Eq. (5):

$$\frac{\dot{Q}_{\rm A}}{\dot{Q}}=\frac{q_{\rm A}xS}{q_{\rm A}xS+q_{\rm B}(1-x)S}=\frac{x\kappa_{\rm A}\left(1-\dfrac{j_{\rm A}^2}{2\kappa_{\rm A}\sigma_{\rm A}\Delta T}d^2\right)}{xA\left(1-\dfrac{j_{\rm A}^2}{2\kappa_{\rm A}\sigma_{\rm A}\Delta T}d^2\right)+(1-x)\kappa_{\rm B}} \tag{9}$$

so that Eq. (8) can be finally written as

$$\eta_{\rm eff} = \eta_{\rm C} \frac{x\kappa_{\rm A}\left(1 - \dfrac{j_{\rm A}^2}{2\kappa_{\rm A}\sigma_{\rm A}\Delta T}d^2\right)}{xA\left(1 - \dfrac{j_{\rm A}^2}{2\kappa_{\rm A}\sigma_{\rm A}\Delta T}d^2\right) + (1-x)\kappa_{\rm B}} \frac{\sqrt{1+Z_{\rm A}\bar{\bar{T}}}-1}{\sqrt{1+Z_{\rm A}\bar{\bar{T}}}+T_{\rm C}/T_{\rm H}} \tag{10}$$

that clearly collapses to Eq. (8) of the manuscript for $j_{\rm opt} = j_{\rm A} = 0$.

Eq. (10) can be easily rearranged to lead to the equivalent of Eq. (9) of the manuscript. Actually, one gets the very same equation but a different definition of χ, namely

$$\chi = (1-x)\frac{\kappa_{\rm B}}{\kappa_{\rm opt}\left(1 - \dfrac{j_{\rm opt}^2}{2\kappa_{\rm opt}\sigma_{\rm opt}\Delta T}d^2\right)} \tag{11}$$

The final issue to be worked out is verifying the relevance of the correction term $(j^2d^2)/(2\kappa\sigma\Delta T)$. Taking p-type PbTe as the reference material, it is immediate to compute that $(j^2d^2)/(2\kappa\sigma\Delta T) = 3.9\times10^{-2}$. As expected, the correction is of order the efficiency of TE materials, namely of a few percent.

2 A numerical evaluation of the effective efficiency of a construction based on paired TE–non TE wall sections

In this numerical example reference will be made to p-type PbTe (doped with 0.1 % at. Na) as the TE material (A) and to stainless steel as the non-TE material (B). The wall, macroscopically sectioned in TE and non-TE section (cf. the inset of Fig. 1 in the manuscript), will be considered as the heat exchanger of a chemical reactor needing to dissipate 10^4 kcal/min (6.97×10^5 W) of heat with a cold bath at 300 K while keeping its temperature at 350 K. This leads to an optimal thermal conductivity $\kappa_{\rm opt}$ [Eq. (6) of the main manuscript] of 13.9 W m^{-1} K^{-1}. As of the material properties, p-type PbTe is reported [1] to have a value of Z at 300 K of 1.3×10^{-3} K^{-1} and a thermal conductivity of 2.2 W m^{-1} K^{-1}. For stainless steel we will take a thermal conductivity of 30 W m^{-1} K^{-1}.

The optimal ratio x of Te/non-TE wall areas can be obtained from Eq. (7) of the main manuscript setting wall thicknesses $d_{\rm A}$ and $d_{\rm B}$ to be the same:

$$x = \frac{\kappa_{\rm B}-\kappa_{\rm opt}}{\kappa_{\rm B}-\kappa_{\rm A}} = 0.579$$

Thus, using Eq. (8) of the main manuscript, one can easily compute the effective efficiency:

$$\eta_{\rm eff} = \eta_{\rm C}\frac{2.2\ {\rm Wm^{-1}K^{-1}}}{13.9\ {\rm Wm^{-1}K^{-1}}}x\times0.574$$

i.e. $\eta_{\rm eff} = 7.52\times10^{-3}$, almost a factor two smaller than the thermoelectric efficiency of p-type PbTe ($\eta_{\rm TE} = 1.43\times10^{-2}$).

This shows how the choice a non-κ matched material in heat exchangers may severely lower the TE conversion efficiency of a Seebeck generators.

3 Evaluation of cost effectiveness

In order to evaluate the competitiveness of thermoelectric generators (TEGs) for bulk electric power production, several economic parameters have to be considered. An actual estimate of all factors affecting costs is extremely speculative for any technology that has not entered the market yet. Thus, the criterion that will be used in the forthcoming analysis will be only that of estimating the lifetime required for a device to pay back its manufacturing cost.

The requested lifetime of a *deployed* device to pay back correlates to both its production cost C_{m} (including its installation) and to the electrical power it can generate. Let C_{W} be the energy unit price, and let $\langle\dot{Q}\rangle$ be the average thermal power the device can convert into electrical energy. Thus, for the device to be economically feasible its lifetime τ_{dev} must exceed

$$\tau_{\mathrm{dev}} = \frac{C_{\mathrm{m}}}{\eta_{\mathrm{TE}}(T_{\mathrm{C}}, T_{\mathrm{H}})\langle\dot{Q}\rangle C_{\mathrm{W}}} \tag{12}$$

where $\eta_{\mathrm{TE}}(T_{\mathrm{C}}, T_{\mathrm{H}})$ is the conversion efficiency when the device operates between a cold sink at T_{C} and a hot sink at T_{H}. Needless to say it is difficult (when not impossible) to make a realistic estimate of C_{m}, manufacturing costs varying by orders of magnitude for new technologies from their first appearance on the market to their maturity. Nonetheless, Eq. (12) may serve the scope of ruling out applicative scenarios where the device lifetime is limited by its embodier lifetime — and that of estimating a case–to–case efficiency threshold for thermoelectric (TE) devices to be of industrial interest.

A TEG will be therefore considered as *economically sustainable* if it pays for its manufacturing cost within a time not exceeding that of the source of the heat it converts. It should be possibly stressed that for TEGs, differently from any other electricity source, no other generation cost exists, as the heat to be converted is anyway available — and eventually TE conversion may lower the current costs that have to be faced to dissipate heat (through heat exchangers or likely devices). This makes the economic analysis of TEGs much simpler than for Peltier devices (coolers). A complementary analysis of the economic sustainability of Peltier coolers was proposed by Xuan [2] and Min [3] where accounts had to be been given also for the actual electric power cost.

Note that since no competing technologies are either available or currently thinkable to convert low-temperature heat into electricity, it makes no sense to analyze the electric power production cost in itself.

In this Supplemental Information three different types of secondary generation scenarios will be considered. The conservative (and, alas, quite optimistic) assumption will also be made of a fixed energy cost, its value being kept fixed to that reported by the U.S. Department of Energy in December 2010 [4], namely

9.56 \$/kWh (2.7×10^{-6} \$/J) [5]. In all case studies, σ (the electrical conductivity), α (the Seebeck coefficient) and κ (the thermal conductivity) will be assumed to be constant so that Ioffe's model [7, 8] can be used. As mentioned in the main paper, this is not surely appropriate for large temperature differences between hot and cold endpoints [9]. However, as this estimate aims at a rough evaluation of TEG feasibility, the use of an 'ideal' TE model is anyway consistent with the level of approximation of this economic analysis, its target being that of depicting scenarios where bulk energy production by TEGs might be considered. Account for transport coefficient variability with the temperature would make the whole evaluation dependent upon single material properties, thus disabling the possibility of reaching general conclusions. On the other side, the possibility of tailoring the temperature dependency of transport coefficients so as to improve conversion efficiency is a challenging and highly motivating (and rewarding) field of research. More general and accurate discussions about the behavior of TEGs under large temperature differences are available in the literature [9].

3.1 Conversion of heat released by a car radiator

To make this line of reasoning clearer, let us consider the possible use of a TE device to generate electrical power in a car from its radiator. Typically, a car radiator has a cooling capability of 3 W K^{-1} m^{-2}. Operating over a temperature difference of 150 K, a radiator exchanging heat over a surface of 0.2 m^2 has a cooling power of about 90 W. Thus, the generator breaks even after being used for a time

$$\tau_{\mathrm{dev}} = \frac{C_{\mathrm{m}}}{\eta_{\mathrm{TE}}(300\,\mathrm{K}, 450\,\mathrm{K}) \times (90\,\mathrm{W}) \times (2.7 \times 10^{-6}\,\$/\mathrm{J})}$$

Since the average running lifetime of a car is about 25,000 hours (9×10^7 s) one can conclude that the installation is economically convenient if

$$C_{\mathrm{m}}/\eta_{\mathrm{TE}}(300\,\mathrm{K}, 450\,\mathrm{K}) \leq (90\,\mathrm{W}) \times (2.7 \times 10^{-6}\,\$/\mathrm{J}) \times (9 \times 10^7\,\mathrm{s}) \approx 22,000\,\$$$

At the current TE efficiencies (5 %) this sets a threshold for the manufacturing cost $C_{\mathrm{m}} \leq$ 1,100 \$, i.e. less than 0.55 \$/cm^2 of TE active surface. Considering that Bi_2Te_3 generators today sell around $2 \div 3$ \$/cm^2, the application would require a rather unrealistically low cost/high efficiency for today's technology.

3.2 Conversion of heat in a tandem solar plant

Likely considerations hold for a TEG converting solar power from heat into electrical energy, operating in tandem with a standard photovoltaic panel. Consider a standard solar panel, extending over an area of 2 m^2. Let us take the irradiance Φ_{rad} to be 10^3 W/m^2 with a solar spectrum of AM 1.5, and assume that 50% of the solar power is converted into electricity by the photovoltaic module. Thus, an effective irradiance Φ_{eff} of 5×10^2 W/m^2 is left available to be converted by the TEG. It is sensible to immagine TE conversion to be implemented by focusing the solar radiation onto a gray body with a TE-active area $\mathcal{A}$. Textbooks equations [10] lead to an estimate of the gray body temperature $T_{\rm eq}$ at equilibrium:

$$a(T_{\rm eq}, \lambda)\Phi_{\rm eff}(\lambda) = \varepsilon(T_{\rm eq}, \lambda)\sigma_{\rm SB}T_{\rm eq}^4 \tag{13}$$

where ε and a are the emissivity and the absorptivity of the gray body, both functions of the temperature and of the wavelength of the emitted and absorbed radiation, and $\sigma_{\rm SB}$ is the Stefan–Boltzmann constant. Averaging ε and a over λ for the solar spectrum and taking $a/\varepsilon \approx 6$ (a realistic value for solar thermal converters) one computes $T_{\rm eq} \approx 480$ K, i.e. about 200 °C. Thus the TEG is cost–effective when

$$\tau_{\rm dev} = \frac{C_{\rm m}}{\eta_{\rm TE}(300\,{\rm K}, 480\,{\rm K}) \times (500\,{\rm W/m^2}) \times (2.7 \times 10^{-6}\,\$/{\rm J})}$$

Taking the lifetime of a solar module to be of about ten years, and assuming it operates at AM 1.5 for 30% of its duty cycle, $\tau_{\rm dev} = 9.5 \times 10^7$ s and the threshold for $C_{\rm m}$ accounts to 0.64 $/cm^2 – still a too small value to be realistic. However, if the heat flow can be spilled through a reduced section, say 1/10 of the exposed surface, the figure we obtain (6.4 $/cm^2) gets into the real world, also in view of the fact that no actual alternative to convert such a large fraction of the solar power spectrum into electrical power looks at reach.

3.3 Conversion of heat generated by a chemical plant

As a final example, let us consider a TEG operating at constant heat flow. For the industrial chemical reactor considered in the previous calculation (dissipating 10^4 kcal/min $= 7.0 \times 10^5$ W over an area of 10 m^2 at 350 K), taking a lifetime of 5 years of continual operation we get

$$\begin{aligned} C_{\rm m} &\leq (1.6 \times 10^8\,{\rm s}) \times \eta_{\rm TE}(300\,{\rm K}, 350\,{\rm K}) \times (10^4\,{\rm W/m^2}) \times (2.7 \times 10^{-6}\,\$/{\rm J}) \\ &= 21.6\,\$/{\rm cm^2} \end{aligned}$$

well above the current *price* of TEGs. It is interesting to note that TE conversion would be here cost–effective even for a much lower $\eta_{\rm TE}$, actually down to about 0.5 %. This is not a marginal consideration, since it quite well illuminates the perspective of using TE materials with relatively low ZT — namely materials that are optimized by their $\mathscr{P}$ but are κ–matched to guarantee the needed thermal dissipation. Note that this possibly surprising result is correct if the low efficiency of the TEG is compensated by the fact that the device is able to accept a large thermal power input — what actually happens if the TE κ is large enough to admit the whole heat current from the chemical reactor. Were κ minimized to raise $\eta_{\rm TE}$, a reduction of the electric power output of more than one order of magnitude would occur [cf. Fig. 2 in the main paper], making the whole generation process economically inconvenient.

4 Engineering aspects

In the whole economic analysis a number of technological aspects affecting deployed TEGs have been disregarded. The most important one is surely related to the role that TEG–to–heat sink contacts play. As shown in great details by Min [3], thermal contacts may significantly lower the efficiency of a TE converter by increasing the thermal impedance of the overall system. Although in principle the thermal contact resistance may be kept low at will, exactly as for electrical contact resistances in integrated circuits poor contacts may make deployed TEGs extremely inefficient, downgrading their power output by up to a factor ten. Furthermore, whenever one considers the use of TEGs as integral parts of heat exchangers in industrial plants, reliability of thermal contacts becomes critical not just from the viewpoint of energy production but also from that of plant integrity. Thus, the search for efficient TE materials is only one part of the effort on the avenue toward TE bulk production, the other being the optimization of materials (polymers and composites, mostly) able to guarantee efficient and reliable heat transmission from/to the TEG and the heat sinks. Such materials are required to sustain relatively high temperatures without detaching or anyway deteriorating their thermal conductivity over time. In addition, contact metallurgies enabling low electrical resistances between TE materials and the metallic leads connecting p- and n-type TEG legs need to be optimized. Also in this case, they are supposed to hold the relatively high temperatures of the hot sink not degrading over time. To the best of my knowledge, much less has been done on this topic until today, sensibly because of the current scenarios wherein TEGs are deployed, where current densities are small enough not to make Joule heating a real concern. However, the situation might change significantly, should TEGs be considered for bulk power generation. In this respect, the possibility of reverting toward technologically mature materials such as silicon, where such issues have been already faced and solved for e.g. power transistor manufacturing [11], would be an advantage.

5 Comparison to other cost–effectiveness estimates

A small but significant number of estimates of the cost effectiveness of Seebeck and Peltier devices are available in the literature. Limiting to those establishing a clear technical link between cost effectiveness and technical characteristics of the material or of the device, Xuan [2] provided a detailed analysis of the cost structure of a TE cooler. Total cost is written as the sum of the material cost (per volume unit) and of a term related to the used heat exchanger area; and of the running cost per unit of supplied electricity. It is shown that, upon optimization, the cooler construction cost depends on the cooling power per unit area while its running cost is inversely proportional to the coefficient of performance, also dependent in turn on the cooling power density.

Taking a different approach, Rowe and Min [12] evaluated the role of TE contacts on the TEG efficiency accounting for the contribution of electrical contact resistances and of the thermal impedance imposed by electrically insulating layers separating the TEG from the heat sink. Actually, while the efficiency of a TEG in the 'ideal' (Ioffe) model is clearly independent of the TEG leg lengths, when contact contributions are considered the authors showed that device efficiency may be more effectively improved by enhancing thermal rather than electrical contacts, and also by reducing the insulating layer thickness more than by increasing its thermal conductivity. As of the leg length, when the thermoelement length increases, they found that the conversion efficiency increases while power output decreases (apart than for very short thermoelements). Therefore, also when contacts are properly considered, power output and conversion efficiency are found to play one against the other. Min [3] also translated these results into a stringent economical analysis, showing cost efficiency of heat pumps (Peltier coolers) and confirming that minimization of thermal contact resistance is a key issue to boost the economic feasibility of TE modules.

In all analyses, although the quantitative results critically depend upon their detail level, requirements of high conversion efficiency and high power output (cooling power for Peltier devices) are found to oppose each other, all authors agreeing however on the need of maximizing power outputs over conversion efficiency when cost–effectiveness is aimed at.

6 Concluding remarks

Before concluding this Supplemental Information, a word of caution has to be spent about the proper way to read the cost-effectiveness calculation we have just presented. Manufacturing cost is a good indicator of the real-world maturity of TEG technology — but is not the only one. TEGs compete and will compete on the market with a number of other technologies, and contend and will contend their energy niche also in other respects than current production costs only. Availability of raw materials, toxicity and safety considerations as well as device reliability are other factors to be accounted for. The simple facts that tellurium has a relative abundance in the Earth crust of 1 μg/kg (comparable to that of platinum and 500 times lower than rare earths), an average yearly production worldwide just exceeding 100 tonns, that its price increased by almost one order of magnitude from year 2000 to 2006 due to the increasing demand of tellurides (CdTe) for solar panels, and its mild toxicity when inhaled as powder should raise some concerns about the possibility of a large use of the family of currently most performing TE materials — well beyond the C_{m} factor. On the other hand, TEGs play a rather solitary game as of converting low–temperature heat into electric power, surely the most easily distributable form of energy. Thus, even when compared to other technologies able to (re)use low–temperature heat without converting it into electricity (e.g. thermodynamic solar panels to produce hot water for home usages or district heating), a fair evaluation should always weigh that the apparently high efficiency of non-TE systems (solar water heater efficiency typically ranges from 30 to 60%) is often downgraded by the need of using energy locally and immediately, as storage and distribution results in heat losses that can be estimated around 50 W per m^2 of tank or tube wall (under excellent insulation conditions). Thus, room *may* exist for TEGs made of largely available raw materials to leave the limbo of high-tech applications they are limited to nowadays — and to qualify as a complementary energy resource.

References

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