Thermoelectric Power Generation: Efficiency and Compatibility

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1. Introduction

In a thermoelectric material, heat can be transported or used to generate electricity based on the Peltier and Seebeck effects. The efficiency of a thermoelectric device is traditionally described in terms of the extensive[a] or system parameters such as hot and cold side temperature, length and area of thermoelectric element, and applied voltage or load resistance. In only the most simplified cases (*e.g.* temperature independent thermoelectric properties) can this efficiency be computed analytically, where it can be shown that the thermoelectric figure of

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[a] Extensive refers to properties that depend on material sample size

merit z is the intensive[b] material property of prime importance [1][or earlier chapters in this book][2, 3]. At the optimal electric current, z alone determines the efficiency.

Although very instructive, such simplifications ignore the effect of thermoelectric compatibility in real thermoelectric devices. The thermoelectric compatibility factor is the reduced electric current which is necessary to achieve the highest efficiency determined by z. Because the compatibility factor changes with temperature while the electric current is constrained, the efficiency of a real device will be less than that calculated from z. The effect of thermoelectric compatibility is most important for segmented thermoelectric generators, but it also affects the exact calculation of performance for all thermoelectric devices.

To calculate the exact performance of a thermoelectric generator analytically, it is simplest to use a reduced variables approach which will separate the intensive properties and variables (such as temperature gradient, Seebeck coefficient, current density, heat flux density) from the extensive ones (*e.g.* voltage, temperature difference, power output, area, length, resistance, load resistance) [4, 5]. This approach allows a definition of a local, intensive efficiency in addition to the traditional system efficiency [6-9] as well as the derivation of the compatibility factor [5].

1.1. Definitions

Consider the one dimensional ($\nabla = \dfrac{d}{dx}$), steady-state, thermoelectric power generation problem, where (for now) only a single (*n*- or *p*-type) leg is considered. The thermoelectric material properties all vary with (absolute) temperature, T: the Seebeck coefficient α, the thermal conductivity κ, and electric resistivity ρ. In the following discussion, we will assume isotropic materials properties. For anisotropic materials, the tensor representations of the materials properties and equations are required [7]. Positive electric current density, $J > 0$ and heat flux (heat current density) $Q > 0$ (with units of Watt/cm^2) flows from T_h to T_c (Figure 1). Positive electric field E and temperature gradient ∇T is in the opposite direction of J and Q. The subscripts h and c (lower case) denote the value at a particular (hot or cold side) temperature ($\kappa_h = \kappa(T_h)$, $\nabla T_h = \nabla T(T_h)$).
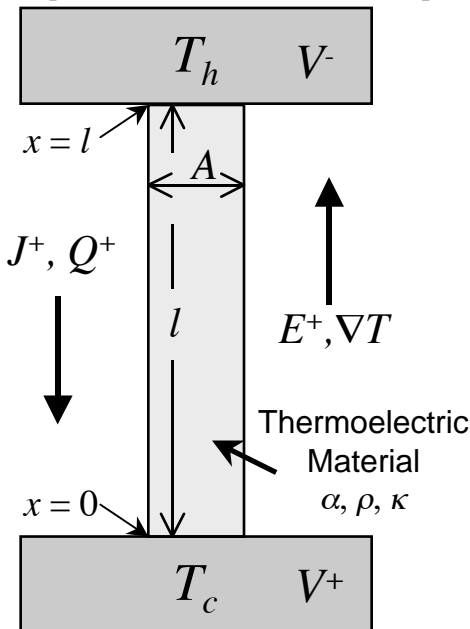
Figure 1. Diagram of a single element thermoelectric generator. The direction of positive variables is shown relative to the hot and cold side. For positive Seebeck coefficient (α), all of the variables are positive for a generator operating efficiently. For negative Seebeck coefficient ($\alpha < 0$), the electric current, field and potential (J, E, V) will be negative, or opposite to the direction shown.

The electric current density is for a simple generator, given by

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[b] Intensive refers to properties independent of material sample size

$$(1) \qquad\qquad J = \frac{I}{A}$$

where *I* is the electric current (Amps) and *A* is the cross sectional area of the thermoelectric element.

The electric field is given by a combination of the reversible Seebeck effect and the irreversible effect of Ohm's law. Using the sign convention described above the electric field from a purely resistive element using Ohms law is $E = -\rho J$. The electric field produced by the Seebeck effect is $E = \alpha \nabla T$. Combining the Seebeck and Ohm effects, gives the electric field at any position.

$$(2) \qquad\qquad E = \alpha \nabla T - \rho J$$

Similarly, heat is transported reversibly by the Peltier effect, $Q = \alpha T J$ (where αT is the Peltier coefficient, related to α by the Onsager reciprocal relations [3]) and irreversibly by Fourier's law $Q = \kappa \nabla T$ (using sign convention of Figure 1).

$$(3) \qquad\qquad Q = \alpha T J + \kappa \nabla T$$

The Peltier effect is often considered a surface effect between two materials but the heat transported is a property of a single material [10].

In both cases (equations (2) and (3)) the irreversible and reversible effects are treated independently, and can simply be summed. This treatment is related to Kelvin's assumption [2]. The irreversible heat flow is further constrained by the steady-state heat equation

$$(4) \qquad\qquad \nabla(\kappa \nabla T) = -T\frac{d\alpha}{dT}J\nabla T - \rho J^2$$

where $T\dfrac{d\alpha}{dT}$ is the Thomson coefficient. From equation (4), we see that the heat produced (or consumed) by the Thomson effect is transported away from (or toward) that location by the irreversible part of equation (3) as a part of $\kappa \nabla T$.

The electric power density *P* (power produced per volume) is the product of the electric field *E* and current density *J*.

$$(5) \qquad\qquad P = E \bullet J$$

Using the sign convention in Figure 1, a purely resistive element ($\alpha = 0$) would require a negative electric field $E = -\rho J$ to make a positive current ($+J$) so that the power density $P = -\rho J^2$ is negative (electric energy consumed).

The heat equation (equation (4)), which includes the Thompson effect can be derived by invoking the conservation of energy. The divergence of the heat flow should be compensated by the sources (or sinks) from the electric power generation (work).

$$(6) \qquad\qquad \nabla Q = P$$

Substituting equations (3), (2), and (5) into (6) and evaluating ∇J and $\nabla(\alpha T)$ will derive the steady state heat equation (4). For the one dimensional problem,

$$(7) \qquad\qquad \nabla J = 0$$

because there is no build up of electric current in the steady-state. To evaluate $\nabla(\alpha T)$, it is first noted that, in the power generation problem, there is a temperature drop at every point ($\nabla T > 0$, for thermoelectric material and electric and thermal contacts); thus, the temperature profile *T(x)* is invertible to a well defined *x(T)*. In this way, $\alpha(T) \equiv \alpha(x(T),T)$ is defined and then the gradient of α is simply $\nabla \alpha = \dfrac{d\alpha}{dT}\nabla T$ (note the use of total not partial derivatives). This gives:

$$(8) \qquad\qquad \nabla(\alpha T) = T\frac{d\alpha}{dT}\nabla T + \alpha \nabla T$$

2. Reduced Variables

2.1. Relative current density

For calculating and comparing generator properties it is most convenient to use a reduced variable in place of the actual current density J. This is because the most efficient current density scales with the length of the thermoelectric element in the same way that ∇T does. By dividing the two, a simplified expression for reduced efficiency is derived.

Here we use is the relative (reduced) current density u, which is the ratio of the electric current density (J) to the heat flux by conduction ($\kappa \nabla T$) given by

$$(9) \qquad\qquad u = \frac{J}{\kappa \nabla T}$$

(again, $\nabla T > 0$, for power generation). The electric power density (from equations (2) and (5)) in terms of u is given by:

$$(10) \qquad\qquad P = \kappa (\nabla T)^2 \times u(\alpha - u\rho\kappa)$$

The heat flux density (from equation (3)) in reduced variables is:

$$(11) \qquad\qquad Q = \kappa \nabla T (\alpha u T + 1)$$

The variation of u is governed by the heat equation (4). For the one dimensional problem with cross sectional area A a constant, equation (4) combined with (7) gives $\nabla(1/u) = -T\dfrac{d\alpha}{dT}\nabla T - \rho J$. For this one dimensional problem we can substitute $\nabla(1/u) = \dfrac{-1}{u^2}\dfrac{du}{dx}$, $\dfrac{du}{dx} = \dfrac{du}{dT}\nabla T$, and $J = u\kappa\nabla T$ to give

$$(12) \qquad\qquad \frac{du}{dT} = u^2 T \frac{d\alpha}{dT} + u^3 \rho\kappa$$

Again, the material properties α, κ, ρ can be functions of temperature. Notice that here we have removed all reference to the spatial coordinate x, so that u can be considered a function of temperature T only.

2.1.1. Other representations of the reduced current

The relative current density $u = \dfrac{J}{\kappa \nabla T}$ is the most instructive form of the reduced current. Sherman [4] uses $y = 1/u$ which simplifies the thermoelectric potential (equation (21)) but becomes ill defined for an open circuit generator, when $J = u = 0$. For power generation, small u is of most interest, specifically $0 \leq u \leq z/\alpha$ (Figure 2). Other multiplicative factors of $\dfrac{J}{\nabla T}$ are less instructive because u has the least variation in a thermoelectric generator and therefore allows the comparison of compatibility factors (equation (18)). For example, the relative change ($\dfrac{du}{udT}$) of u is vanishingly small for small u ($J \approx 0$, $u \approx 0$): from equation (12) $\dfrac{du}{udT} = u\left(T\dfrac{d\alpha}{dT} + u\rho\kappa\right)$ vanishes as u approaches zero. Other forms of the reduced current such as $u\dfrac{\alpha}{z}$ or $i = \dfrac{\pi J}{\kappa\nabla T} = \alpha T u$ [9] have non vanishing relative derivatives, *e.g.* $\dfrac{di}{idT} = \dfrac{d\alpha}{\alpha dT} + \dfrac{1}{T} + i\left(\dfrac{d\alpha}{\alpha dT} + \dfrac{i}{zT^2}\right)$ does not vanish as i approaches zero.

2.2. Reduced Efficiency

Efficiency η is defined as the power produced divided by the power supplied to the system. The (infinitesimal) efficiency along the infinitesimal distance dx is the power produced (per cross sectional area) Pdx divided by the heat flux through, Q, or

$$(13) \qquad \eta = \frac{Pdx}{Q}$$

In equation (13) dx is in the direction of the temperature gradient so $dx = \frac{dT}{\nabla T}$. Substituting this with equations (10) and (11) into (13) gives

$$(14) \qquad \eta = \frac{dT}{T} \frac{u(\alpha - u\rho\kappa)}{u\alpha + \frac{1}{T}}$$

The first term is recognizable as the infinitesimal Carnot efficiency, $\eta_C = \frac{\Delta T}{T_h}$. The reduced efficiency, η_r, defined by $\eta = \eta_C \eta_r$, is not an infinitesimal quantity.

$$(15) \qquad \eta_r = \frac{u(\alpha - u\rho\kappa)}{u\alpha + \frac{1}{T}}$$

The reduced efficiency can be succinctly written in terms of $u\frac{\alpha}{z}$ [5] when $z \neq 0$, where z is the thermoelectric figure of merit

$$(16) \qquad z = \frac{\alpha^2}{\rho\kappa}$$

If the current is non zero, $u \neq 0$ ($J \neq 0$) and $\alpha \neq 0$, the reduced efficiency is simply written as

$$(17) \qquad \eta_r = \frac{1 - u\frac{\alpha}{z}}{1 + \frac{1}{u\alpha T}}$$

Similar to u, the reduced efficiency $\eta_r(u(T),T)$ is simply a one dimensional function of temperature once an initial u is applied. This allows the exact calculation of efficiency using a simple spreadsheet calculation (described below, section number?).

2.3. Efficiency dependence on Current

Whether in power generation or Peltier cooling mode, the reversible, useful thermoelectric effects compete with the irreversible Joule heating. Because the linear effects are directly proportional to the electric current while the irreversible Joule heating is proportional to the square of the current, there is necessarily an optimum operating current to achieve the optimum efficiency. The variation of reduced efficiency with u current (Figure 2, equation (15)) is analogous to the variation of the power output to the electric current: At zero u current, there is voltage produced but neither power nor efficiency. As u increases, the efficiency increases to a maximum value and then decreases through zero. Past this zero-efficiency crossing where $u = \frac{z}{\alpha}$, the Ohmic voltage drop is greater than the Seebeck voltage produced, and thus the power output and efficiency are negative.
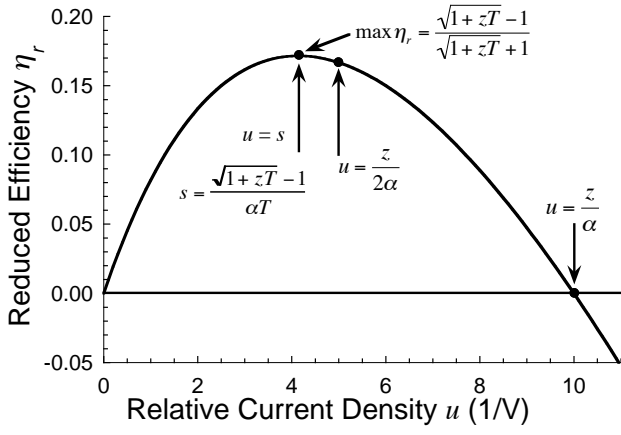
Figure 2. Variation of reduced efficiency (equation (15) with relative current density, u. The maximum efficiency is achieved at the compatibility factor, $u = s$. For the plot, $zT = 1$, $\alpha T = 0.1V$ similar to the values for $(Bi,Sb)_2Te_3$.

The value of u which gives the largest reduced efficiency (equation (15)) is thermoelectric (power generation) compatibility factor s.

$$(18) \qquad s = \frac{\sqrt{1 + zT} - 1}{\alpha T}$$

For small zT, this can be approximated by

$$(19) \qquad s \approx \frac{z}{2\alpha}$$

This largest reduced efficiency $\eta_r(u = s)$ is given by

$$(20) \qquad \max \eta_r = \frac{\sqrt{1 + zT} - 1}{\sqrt{1 + zT} + 1}$$

Thus, in the most general case (α, κ, ρ, temperature dependent), the thermoelectric figure of merit z, is the material property that determines the maximum local efficiency. This can be used to derive the definition of z as the local thermoelectric figure of merit.

From equation (18) it is clear that the compatibility factor s is, like z, a temperature dependent materials property derived from the temperature dependent materials properties α, κ, ρ. Thus s can not be changed with device geometry or the alteration of electric or thermal currents.

If $u \neq s$ then the efficiency is less than the maximum efficiency of equation (20). Since $u = \dfrac{J}{\kappa \nabla T}$, there is some control over u from the applied current density J (traditionally regulated by a load resistance). However, once u is selected at one point, it can not be adjusted in a thermoelectric element to follow the temperature variation of s (Figure 3), because the variation of u is fixed by the heat equation (equation (12)).

Conveniently, the variation of u within a thermoelectric leg is typically small. Since all segments in a thermoelectric element are electrically and thermally in series, the same current $I = AJ$ and similar conduction heat $A\kappa \nabla T$ flow through each segment. When the electric current is near zero ($J \approx 0$) the heat flow is very uniform ($\nabla(\kappa \nabla T) \approx 0$) so u is nearly constant. For $I \neq 0$, the conduction heat is only slightly modified by the change in temperature gradient due to the Thompson and Joule sources of heat (equation (4)). Thermoelectric generators operating at peak efficiency typically have u that varies less than 20 % within all thermoelectric materials in the entire element (Figure 3).
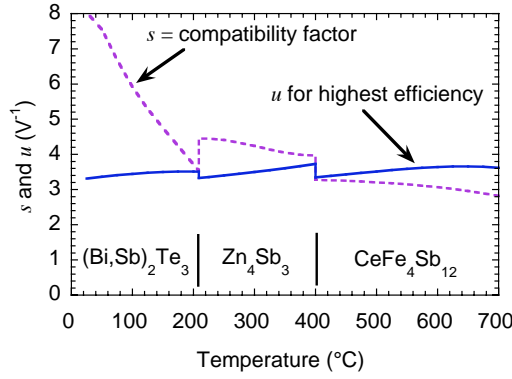
Figure 3. Variation of relative current density, *u* with temperature for a typical thermoelectric generator. The total variation of *u* within a material and the change at the segment interfaces is less than 20%. The *u* shown is that which gives the highest overall efficiency. For $(Bi,Sb)_2Te_3$ and Zn_4Sb_3, *u* is less than the compatibility factor *s*, while for the $CeFe_4Sb_{12}$ segment *u* is greater than *s*.
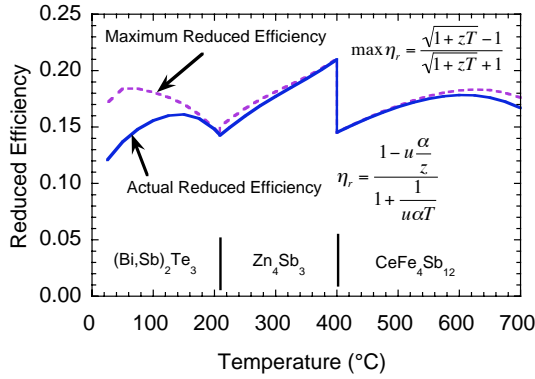

Figure 4. Local, reduced efficiency (using optimized *u* from Figure 3) compared to the maximum reduced efficiency (if *u* = *s* for all temperatures, equation (20)). The difference is most substantial in the regions where *u* is most distant from *s* (Figure 3).

To a reasonable approximation, *u*, once established, remains constant throughout the thermoelectric element [11]. Thermoelectric coolers, on the other hand, are typically driven with much higher *u*, up to $u = \infty$ ($\nabla T = 0$) at the end being actively cooled.

The actual reduced efficiency of a material depends not only on the maximum reduced efficiency (equation (20)) determined by *z*, but also on how close *u* is to *s* (Figure 2). The actual reduced efficiency (equation (15)) is always less than the maximum reduced efficiency (equation (20)), because *u*, as determined by the heat equation (equation (12)) varies differently from the material property *s*, so they can not be equal at more than a few isolated points. The difference between the maximum and actual reduced efficiency is largest for large differences between *u* and *s*. This can be seen graphically in Figure 3 and Figure 4.

2.4. Thermoelectric Potential

For many expressions and calculations, it is convenient to use the thermoelectric potential Φ, (with units of Volts) [5], which is related to the electrochemical potential μ ($\mu = q\Phi$ with q the charge/particle). The thermoelectric potential is given by

$$(21) \qquad \Phi = \alpha T + \frac{1}{u} = \alpha T + \frac{\kappa \nabla T}{J}$$

The heat flux Q containing both the Peltier and Fourier heat (equation (3)) is simply

$$(22) \qquad Q = J\Phi$$

Multiplying by *A* gives the heat flow $U = AQ$ in terms of current.

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$$(23) \qquad\qquad U = I\Phi$$

The electric field E containing both the Seebeck and Ohm effects (equation (2)) is given by

$$(24) \qquad\qquad E = \nabla\Phi$$

where equation (4) and (8) are used. Thus the electric power density (equation (5)) produced is

$$(25) \qquad\qquad P = J \bullet \nabla\Phi$$

3. Generator Efficiency and Performance

3.1. *Efficiency of a thermoelectric device*

Once the intensive (local) reduced efficiency is known at every point, the total system efficiency can be calculated. Because efficiency is strictly a fractional quantity less than one, care must be taken to use the appropriate summation metric when calculating combined efficiencies.

For a general energy conversion process, let U be the heat energy into the system and W be the work removed. By conservation of energy the heat energy out of the system is $U - W$. The efficiency of such a system is.

$$(26) \qquad\qquad \eta = \frac{W}{U}$$

3.1.1. Parallel efficiency

For two thermoelectric elements thermally in parallel (such as a thermocouple of *n*- and *p*-type elements), the combined efficiency is a (weighted) average of the efficiency of both generators, weighted by the heat flowing through each generator.

$$(27) \qquad\qquad \eta_{1\&2,parallel} = \frac{W_1 + W_2}{U_1 + U_2} = \frac{\eta_1 U_1 + \eta_2 U_2}{U_1 + U_2}$$

3.1.2. Series efficiency

For two processes in series the heat out of system one is the heat into system two: $U_2 = U_1 - W_1$. The efficiency of the combined system is the work from both systems divided by the energy supplied to the first system in the series $\eta_{1\&2,series} = \frac{W_1 + W_2}{U_1}$. Combining these relations gives the summation rule for efficiencies in series.

$$(28) \qquad\qquad 1 - \eta_{1\&2,series} = (1 - \eta_1)(1 - \eta_2)$$

For many processes in series this becomes

$$(29) \qquad\qquad 1 - \eta_{series} = \prod_i 1 - \eta_i$$

By taking the logarithm of both sides, the product series can be changed to a summation, which in the limit of infinitesimally small steps becomes an integral. For infinitesimally small η_i, we have $\ln(1 - \eta_i) \approx -\eta_i$ [3, 12].

$$(30) \qquad\qquad \ln(1 - \eta_{series}) = \int_i \ln(1 - \eta_i) = -\int_i \eta_i$$

Note that since $\eta_{series} \neq \int_i \eta_i$, it is best to refrain from identifying infinitesimally small η_i with $d\eta$; instead, it is simply a local efficiency.

$$(31) \qquad\qquad \eta_{series} = 1 - \exp\left[-\int \eta_{local}\right]$$

Using the expression for the local efficiency in terms of the reduced efficiency (equation (14)), the overall efficiency of a finite segment can be derived using temperature T to define the integration path.

$$（32） \quad \eta = 1 - \exp\left[-\int_{T_c}^{T_h} \frac{\eta_r}{T} dT\right]$$

3.2. Single Thermoelectric Element

A thermoelectric generator consists of a n-type element and p-type element connected thermally in parallel but electrically in series. Often, it is simpler to compare the efficiency and performance of individual elements rather than n-p couples, for example, when one is selecting materials.

3.2.1. Thermoelectric element efficiency

The thermoelectric potential becomes a convenient integration variable for evaluating equation (31). Integrating the local efficiency (equation (13)) by substituting equations (22) and (25) becomes simply a function of the thermoelectric potential at the two ends of the process.

$$（33） \quad \int_{T_c}^{T_h} \frac{P}{Q} dx = \int_{T_c}^{T_h} \frac{\nabla\Phi}{\Phi} dx = \int_{T_c}^{T_h} \frac{d\Phi}{\Phi} = \int_{T_c}^{T_h} d\ln(\Phi) = \left(\ln\Phi\right)\Big|_{T_c}^{T_h} = \ln\left(\frac{\Phi_h}{\Phi_c}\right)$$

Here the thermoelectric potential is a parametric function of T, because u is also a function of T (*e.g.* $\Phi_c = \Phi(u(T_c), T_c)$). This provides a simple expression for the efficiency (equation (31)) of a single thermoelectric element.

$$（34） \quad \eta = 1 - \frac{\Phi_c}{\Phi_h} = \frac{\Delta\Phi}{\Phi_h}$$

In terms of u and T this is

$$（35） \quad \eta = 1 - \frac{\alpha_c T_c + \dfrac{1}{u_c}}{\alpha_h T_h + \dfrac{1}{u_h}}$$

The maximum efficiency of a thermoelectric element is computed by finding the initial u that maximizes equation (35) for a given temperature range (T_h and T_c). Once an initial u (for example u_h) is established, all the other $u(T)$ (for example u_c) are defined by equation (12).

3.2.2. Thermoelectric element performance

With $E = \nabla\Phi = \dfrac{d\Phi}{dx}$ (equation (24)), the output voltage $V = \int E dx = \int d\Phi = \Phi_h - \Phi_c = \Delta\Phi$ is

$$（36） \quad V = \Delta\Phi$$

Because $u = \dfrac{J}{\kappa\nabla T}$, any current density J can lead to any u provided the appropriate temperature gradient is supplied. The absolute magnitudes of J and $\kappa\nabla T$, for a given u, will depend on the length of the thermoelectric element $l = x(T_h) - x(T_c)$ (Figure 1). Integrating $u = \dfrac{J}{\kappa\nabla T}$, gives $\int \kappa u dT = \int J dx$. Assuming a uniform element with constant cross sectional area ($J(x) = $ constant) gives:

$$（37） \quad \int_{T_c}^{T_h} \kappa u dT = Jl$$

Thus the heat flux Q (at any point) (equation (22)) can be rewritten

(38)
$$Q = \frac{1}{l} \times \Phi \int_{T_c}^{T_h} \kappa u \, dT$$

Similarly, the power output (work) per unit area ($\frac{W}{A} = \int P \, dx$) is the product of Q_h (equation (38)) and efficiency (equation (34)) can be written

(39)
$$\frac{W}{A} = \frac{1}{l} \times \Delta\Phi \int_{T_c}^{T_h} \kappa u \, dT$$

The design condition of maximum thermoelectric efficiency, sets the value of $u(T)$ and therefore also Φ and $\Delta\Phi$. Thus the heat flux and power output at maximum efficiency conditions are directly proportional to $1/l$, and can be computed from equations (38) and (39) once l is selected. Typically, l is a design variable set to work with a desired heat flux (see example below, section number?).

The temperature variation along the length $l(T)$ can be calculated from equation (37):

(40)
$$l(T) = \frac{1}{J} \int_{T_c}^{T} u \kappa \, dT$$

3.3. Thermoelectric Couple

The performance and output of the entire generator scales in a simple way with that of the thermoelectric couple. The performance of the couple, however is not simply the average or sum of the corresponding n and p elements.

3.3.1. Thermoelectric couple efficiency

For an n- and p- element in parallel (equation (27)) the efficiency of each segment (equation (34)) can be combined using the heat flow equation (23). Since is the electric current I flows in the opposite direction in the n-element compared to the p-element (Figure 6), we have $I_n = -I_p$.

(41)
$$\eta_{n \& p} = \frac{\Delta\Phi_p - \Delta\Phi_n}{\Phi_p - \Phi_n}$$

In terms of u and T this is

(42)
$$\eta = 1 - \frac{\alpha_{p,c} T_c + \dfrac{1}{u_{p,c}} - \alpha_{n,c} T_c - \dfrac{1}{u_{n,c}}}{\alpha_{p,h} T_h + \dfrac{1}{u_{p,h}} - \alpha_{n,h} T_h - \dfrac{1}{u_{n,h}}}$$

For an n-type material operating efficiently, α_n, u_n, Φ_n, and $\Delta\Phi_n$ are all negative. Finding the maximum efficiency of equation (42) requires optimizing the initial conditions for both n- and p-type elements (for example $u_{p,h}$ and $u_{n,h}$).

3.3.2. Thermoelectric couple performance

The output voltage is the sum of the voltage from the two elements (equation (36))

(43)
$$V = \Delta\Phi_p - \Delta\Phi_n$$

For a typical n, p thermocouple, the electric current through both elements is the same, but the relative contribution of heat flux is regulated by having different cross sectional areas A_p and A_n. The maximum efficiency condition, which defines $u_p(T)$ and $u_n(T)$, requires a specific ratio of A_p/A_n.

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Assuming the *n*-element and *p*-element have the same total length, the ratio of the cross sectional areas can be calculated by equating the currents ($\pm I = JA$).

$$（44）\qquad I = J_p A_p = -J_n A_n$$

combining this equation with equation (37) gives

$$（45）\qquad \frac{A_p}{A_n} = \frac{-J_n}{J_p} = \frac{-\int_{T_c}^{T_h} u_n \kappa_n dT}{\int_{T_c}^{T_h} u_p \kappa_p dT}$$

Incidentally, the most efficient area ratio is found from the most efficient $u_p(T)$ and $u_n(T)$.

The above two equations ((44) and (45)) with equation (37) can be solved for *I*, in terms of the total area

$$（46）\qquad A_{total} = A_p + A_n$$

to length ratio (regardless of whether the most efficient *u* are used).

$$（47）\qquad I = \frac{A_{total}}{l} \times \frac{-\int_{T_c}^{T_h} u_p \kappa_p dT \times \int_{T_c}^{T_h} u_n \kappa_n dT}{\int_{T_c}^{T_h} u_p \kappa_p dT - \int_{T_c}^{T_h} u_n \kappa_n dT}$$

Notice that once a *u* is selected the current is directly proportional to the A_{total}/l ratio.

The load resistance R_{Load} is traditionally used to adjust the current. For given *u* , the load resistance can be calculated using the current from (47), combined with Ohm's law and (43) to give:

$$（48）\qquad R_{Load} = \frac{\Delta\Phi_p - \Delta\Phi_n}{I}$$

The current can be used to find the total heat flux and power produced by the thermocouple. The combined, total heat flowing $U_{total} = Q_{total} A_{total}$ is the sum of the heat flowing through each (*n*- and *p*- type) element ($U_p + U_n = I\Phi_p - I\Phi_n$), giving.

$$（49）\qquad U_{total} = I(\Phi_p - \Phi_n)$$

Using equations (26), (41), and (49) (or $W = IV$ and (43)) the total electric power (work/time) is simply

$$（50）\qquad W = I(\Delta\Phi_p - \Delta\Phi_n)$$

The temperature variation along the length $l(T)$, which will have different variation for *n* and *p* elements, can be calculated from equation (40).

4. Computation of Generator Performance

4.1. Analytic Example using Constant Coefficients

When α, κ, ρ, and therefore *z*, are constant with respect to temperature the performance of a generator operating at maximum efficiency can be calculated analytically. The solution to equation (12) for $u(T)$ in this case is

$$（51）\qquad \frac{1}{u^2} = \frac{1}{u_c^2} - 2(T - T_c)\kappa\rho$$

where $u(T_c) = u_c$ is used as the (not necessarily most efficient) initial condition.

With $T = T_h$ in (51), the efficiency (equation (35)) can be maximized with respect to the initial *u* condition (*e.g.* u_h) to find the most efficient $u(T)$:

$$(52) \qquad \frac{1}{u^2} = \frac{1}{s(\bar{T})^2} + (\bar{\bar{T}} - T)2\kappa\rho + \left(\frac{\Delta T}{2}\kappa\rho s(\bar{T})\right)^2$$

where $\bar{\bar{T}} = \dfrac{T_h + T_c}{2}$. Note that when ($\alpha$, ρ, κ) are constant with respect to temperature, z is also a constant but s is not.
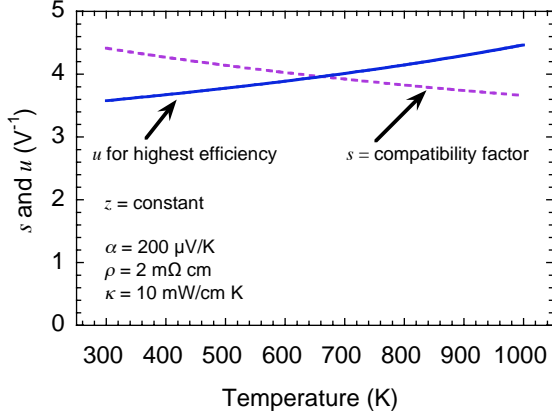

Figure 5. Variation of relative current density, *u* compared to the compatibility factor *s* with temperature for a thermoelectric generator with α, κ, ρ, and therefore *z*, constant.

For u_h and u_c this gives : $\dfrac{1}{u_h} = \dfrac{1}{s(\bar{T})} - \dfrac{\Delta T}{2}\kappa\rho s(\bar{T})$, $\dfrac{1}{u_c} = \dfrac{1}{s(\bar{T})} + \dfrac{\Delta T}{2}\kappa\rho s(\bar{T})$ The resulting efficiency is given by

$$(53) \qquad \eta = \frac{\Delta T}{T_h} \cdot \frac{\sqrt{1 + z\bar{\bar{T}}} - 1}{\sqrt{1 + z\bar{\bar{T}}} + T_c/T_h}$$

This equation is normally derived starting with the extensive expression for efficiency [2]. For comparison, if the maximum reduced efficiency could be used (equation (20)), known as an infinitely staged or cascaded system, where $u = s$, the efficiency is given by [13]:

$$(54) \qquad \eta = 1 - \frac{\left(\sqrt{1 + zT_c} + 1\right)^2}{\left(\sqrt{1 + zT_h} + 1\right)^2} \cdot \exp\left(\frac{2\left(\sqrt{1 + zT_h} - \sqrt{1 + zT_c}\right)}{\left(\sqrt{1 + zT_h} + 1\right)\left(\sqrt{1 + zT_c} + 1\right)}\right)$$

Equation (53) demonstrates the importance of the figure of merit when the compatibility factor is nearly temperature independent. For real materials where α, κ, ρ, vary with temperature, it commonly desired to find an averaged Z (upper-case) [10, 14] to calculate the efficiency in place of z (lower-case) defined by equation (16). It is the effect of the compatibility factor that explains why averaging works well in some cases (when *s* does not vary significantly) and not in others (when *s* varies by more than a factor of 2).

4.2. Calculation of exact solution

The methods typically used for the computation of efficiency are complex, requiring finite element methods that include both volume and surface terms using averaged material parameters [4, 6, 15-18]. By using the reduced variables, however, computation and optimization of segmented thermoelectric generator performance (including even contact resistances) can be performed with a simple spreadsheet type calculation. Because *u*, once

established, can be represented by a 1-dimensional function of T, the generator efficiency can be calculated with a 1-dimensional function.

The thermoelectric properties (α, ρ, κ) are tabulated as a function of temperature. For now, we need only the temperature drop desired across a material, not the physical length. The length will be calculated later and the temperature drop allocated can be adjusted to coincide with a desired length if necessary. In Tables I and II the properties are tabulated at a minimum of every 25K.

For computation, the differential equation (12) can be approximated by combining the zero Thomson effect ($d\alpha/dT = 0$) solution with the zero resistance ($\rho\kappa = 0$) solution [19, 20].

$$(55) \qquad \frac{1}{u_n} = \frac{1}{u_{n-1}}\sqrt{1 - 2u_{n-1}^2 \overline{\rho\kappa}\Delta T} - \overline{T}\Delta\alpha$$

where $\Delta\alpha = \alpha(T_n) - \alpha(T_{n-1})$ and $\overline{\rho\kappa}$ denotes the average of $\rho\kappa$ between T_n and T_{n-1}.

At the interface between two materials, where α may be discontinuous, the properties of both materials are tabulated at the same interface temperature ($\Delta T = 0$, $\Delta\alpha \neq 0$). This allows the discontinuous change in u to be correctly calculated from equation (12) ($\Delta u \cong u^2 T\Delta\alpha$).

Using equation (55), $u(T)$ can be calculated given an initial condition (u_h is used in example of Table I). The maximum single element efficiency is found by varying these initial u conditions and calculating the efficiency from equation (35) (or couple efficiency from equation (42)). In Table I, the highest generator efficiency was found when $u_h = 3.62$ V^{-1}.

Tables I and II demonstrate the process both with and without interface resistances. Table I demonstrates the calculation of a segmented p-type element without contacts, while Table II demonstrates a n-type element with metal interconnects and interface resistances. For simplicity, the metal contact and contact resistances were given a 1K budget (each) for the temperature drop. Such contacts have little effect on the value for u within the thermoelectric materials. The value for u in the metals, however, is temporarily reduced due to the Peltier effect at the interfaces ($\Delta u \cong u^2 T\Delta\alpha$).

Table I. Spreadsheet calculation of *p*-type element performance. α, ρ, κ are the measured material properties. zT, the maximum reduced efficiency , and s are calculated from equations (16), (20), (18). The calculation uses $u_h = 3.6179$ V^{-1} as a starting value for u. The subsequent values of u use

$$\frac{1}{u_n} = \frac{1}{u_{n-1}}\sqrt{1 - 2u_{n-1}^2\left(\frac{\rho_n \kappa_n + \rho_{n-1}\kappa_{n-1}}{2}\right)(T_n - T_{n-1})} - \left(\frac{T_n + T_{n-1}}{2}\right)(\alpha_n - \alpha_{n-1})$$

following equation (55). The reduced efficiency is given by equation (15), the maximum reduced efficiency ($u = s$, infinitely staged), by equation (20). The column "*uk dT*" is used to find the physical length of each interval. Specifically,

$$(u\kappa dT)_n = \frac{u_n\kappa_n + u_{n-1}\kappa_{n-1}}{2}(T_{n-1} - T_n)$$

following equation (40). Jl is the running sum of $(u\kappa dT)_n$ and is proportional to the distance to the hot end. The thermoelectric potential (voltage), Φ is given by equation (21). 'efficiency' is the single element efficiency, including Carnot, (equation (35)) from the hot end (700 C) to the point in question.

T (C)	Material	T (K)	α (μV/K)	ρ (10-3 Ω cm)	κ (mW/cm K)	zT	max Red eff	s (1/V)	u (1/V)	Red eff	u κ dT (A/cm)	Jl (x) (A/cm)	Φ (V)	efficiency
700	CeFe4Sb12	973	156	0.849	26.89	1.04	17.62%	2.82	3.6179	16.70%		0.00	0.42833	
675	CeFe4Sb12	948	160	0.842	26.98	1.07	18.04%	2.89	3.6457	17.26%	2.4457	2.45	0.42643	0.44%
650	CeFe4Sb12	923	164	0.834	27.06	1.09	18.27%	2.96	3.6573	17.62%	2.4668	4.91	0.42443	0.91%
625	CeFe4Sb12	898	166	0.826	27.12	1.10	18.34%	3.02	3.6551	17.81%	2.4763	7.39	0.42237	1.39%
600	CeFe4Sb12	873	167	0.818	27.17	1.09	18.26%	3.07	3.6413	17.84%	2.4757	9.86	0.42024	1.89%
575	CeFe4Sb12	848	167	0.809	27.20	1.08	18.06%	3.11	3.6184	17.74%	2.4668	12.33	0.41807	2.39%
550	CeFe4Sb12	823	167	0.800	27.22	1.05	17.75%	3.15	3.5884	17.52%	2.4512	14.78	0.41588	2.91%
525	CeFe4Sb12	798	166	0.791	27.23	1.02	17.36%	3.18	3.5533	17.19%	2.4303	17.21	0.41366	3.43%
500	CeFe4Sb12	773	164	0.782	27.23	0.98	16.89%	3.20	3.5146	16.78%	2.4056	19.62	0.41143	3.95%
475	CeFe4Sb12	748	162	0.772	27.22	0.94	16.37%	3.23	3.4737	16.30%	2.3781	22.00	0.40921	4.46%
450	CeFe4Sb12	723	160	0.762	27.21	0.89	15.79%	3.25	3.4317	15.76%	2.3490	24.35	0.40699	4.98%
425	CeFe4Sb12	698	157	0.752	27.19	0.84	15.18%	3.26	3.3893	15.16%	2.3189	26.66	0.40479	5.50%
400	CeFe4Sb12	673	154	0.741	27.16	0.80	14.54%	3.28	3.3474	14.53%	2.2885	28.95	0.40261	6.01%
400	Zn4Sb3	673	200	3.118	6.37	1.35	21.04%	3.97	3.7279	20.99%	0	28.95	0.40261	6.01%
375	Zn4Sb3	648	195	3.064	6.37	1.27	20.18%	3.99	3.6651	20.09%	0.5889	29.54	0.39950	6.73%
350	Zn4Sb3	623	191	3.008	6.32	1.20	19.45%	4.05	3.6063	19.28%	0.5768	30.12	0.39643	7.45%
325	Zn4Sb3	598	187	2.949	6.22	1.14	18.78%	4.14	3.5512	18.51%	0.5607	30.68	0.39338	8.16%
300	Zn4Sb3	573	182	2.889	6.10	1.08	18.13%	4.24	3.4991	17.73%	0.5430	31.22	0.39035	8.87%
275	Zn4Sb3	548	178	2.825	6.00	1.02	17.43%	4.33	3.4498	16.89%	0.5257	31.75	0.38736	9.57%
250	Zn4Sb3	523	173	2.760	5.93	0.96	16.64%	4.41	3.4028	15.98%	0.5107	32.26	0.38441	10.25%
225	Zn4Sb3	498	168	2.691	5.91	0.88	15.71%	4.45	3.3576	14.96%	0.4999	32.76	0.38151	10.93%
209	Zn4Sb3	482	165	2.645	5.93	0.83	15.02%	4.45	3.3295	14.26%	0.3167	33.08	0.37970	11.35%
209	p-Bi2Te3	482	196	2.225	10.71	0.78	14.31%	3.53	3.5079	14.31%	0	33.08	0.37970	11.35%
200	p-Bi2Te3	473	198	2.174	10.43	0.82	14.86%	3.72	3.5107	14.83%	0.3339	33.41	0.37866	11.60%
175	p-Bi2Te3	448	202	2.016	9.92	0.92	16.14%	4.24	3.5109	15.77%	0.8932	34.30	0.37551	12.33%
150	p-Bi2Te3	423	204	1.834	9.71	0.99	17.03%	4.75	3.4999	16.12%	0.8603	35.16	0.37209	13.13%
125	p-Bi2Te3	398	203	1.632	9.70	1.04	17.64%	5.29	3.4783	16.02%	0.8466	36.01	0.36846	13.98%
100	p-Bi2Te3	373	200	1.415	9.79	1.08	18.08%	5.92	3.4474	15.58%	0.8435	36.85	0.36471	14.85%
75	p-Bi2Te3	348	194	1.198	9.87	1.11	18.41%	6.69	3.4085	14.81%	0.8424	37.70	0.36089	15.75%
50	p-Bi2Te3	323	185	1.015	9.85	1.11	18.40%	7.55	3.3633	13.69%	0.8350	38.53	0.35708	16.63%
25	p-Bi2Te3	298	173	0.927	9.63	1.00	17.14%	8.02	3.3128	12.09%	0.8132	39.34	0.35341	17.49%

Table II. Spreadsheet calculation of *n*-type element performance including contacts and contact resistances. The procedure is the same as for Table I.

Material	T (K)	α (µV/K)	ρ (10-3 Ω cm)	κ (mW/cm K)	zT	max Red eff	s (1/V)	u (1/V)	Red eff	u κ dT (A/cm)	Jl (x) (A/cm)	Φ (V)	efficiency
metal	975	0	0.0200	1190	0.00	0.00%	0.00	-1.8558	-7.99%		0.00	-0.53886	
metal	974	0	0.0200	1188	0.00	0.00%	0.00	-1.8556	-7.97%	-2.2062	-2.21	-0.53891	-0.01%
contact	974	0	10000	0.00238	0.00	0.00%	0.00	-1.8556	-7.97%	0	-2.21	-0.53891	-0.01%
contact	973	0	10000	0.00237	0.00	0.00%	0.00	-1.8555	-7.95%	-4.41E-06	-2.21	-0.53895	-0.02%
n-CoSb3	973	-186	0.981	42.74	0.80	14.62%	-1.89	-2.7929	12.43%	0	-2.21	-0.53895	-0.02%
n-CoSb3	948	-188	0.985	41.86	0.82	14.80%	-1.95	-2.7886	12.95%	-2.9512	-5.16	-0.53716	0.32%
n-CoSb3	923	-191	0.988	41.02	0.83	14.95%	-2.00	-2.7828	13.41%	-2.8861	-8.04	-0.53526	0.67%
n-CoSb3	898	-193	0.991	40.24	0.84	15.07%	-2.05	-2.7754	13.80%	-2.8229	-10.87	-0.53326	1.04%
n-CoSb3	873	-194	0.992	39.50	0.84	15.14%	-2.10	-2.7666	14.12%	-2.7621	-13.63	-0.53116	1.43%
n-CoSb3	848	-196	0.993	38.83	0.84	15.17%	-2.15	-2.7560	14.36%	-2.7040	-16.33	-0.52896	1.84%
n-CoSb3	823	-197	0.993	38.23	0.84	15.15%	-2.20	-2.7437	14.52%	-2.6491	-18.98	-0.52667	2.26%
n-CoSb3	798	-198	0.992	37.71	0.84	15.08%	-2.25	-2.7296	14.59%	-2.5979	-21.58	-0.52431	2.70%
n-CoSb3	773	-198	0.989	37.27	0.83	14.94%	-2.29	-2.7137	14.57%	-2.5509	-24.13	-0.52188	3.15%
n-CoSb3	748	-198	0.985	36.93	0.81	14.73%	-2.33	-2.6959	14.46%	-2.5086	-26.64	-0.51940	3.61%
n-CoSb3	723	-198	0.979	36.68	0.79	14.45%	-2.36	-2.6762	14.26%	-2.4715	-29.11	-0.51687	4.08%
n-CoSb3	698	-197	0.972	36.55	0.76	14.09%	-2.38	-2.6546	13.95%	-2.4401	-31.55	-0.51431	4.56%
n-CoSb3	673	-196	0.963	36.54	0.73	13.65%	-2.40	-2.6312	13.56%	-2.4147	-33.97	-0.51174	5.03%
n-CoSb3	648	-194	0.952	36.65	0.70	13.13%	-2.41	-2.6061	13.07%	-2.3956	-36.36	-0.50918	5.51%
n-CoSb3	623	-191	0.939	36.89	0.66	12.54%	-2.41	-2.5794	12.49%	-2.3832	-38.74	-0.50663	5.98%
n-CoSb3	598	-188	0.924	37.25	0.61	11.87%	-2.40	-2.5514	11.83%	-2.3774	-41.12	-0.50412	6.45%
n-CoSb3	573	-184	0.907	37.75	0.56	11.13%	-2.38	-2.5222	11.10%	-2.3783	-43.50	-0.50166	6.90%
n-CoSb3	548	-179	0.888	38.37	0.51	10.34%	-2.35	-2.4921	10.31%	-2.3855	-45.89	-0.49928	7.34%
n-CoSb3	523	-174	0.867	39.10	0.46	9.51%	-2.32	-2.4617	9.48%	-2.3984	-48.28	-0.49699	7.77%
n-CoSb3	498	-168	0.845	39.92	0.41	8.65%	-2.27	-2.4313	8.62%	-2.4164	-50.70	-0.49480	8.18%
n-CoSb3	473	-161	0.822	40.82	0.37	7.80%	-2.22	-2.4014	7.75%	-2.4387	-53.14	-0.49273	8.56%
n-CoSb3	448	-155	0.799	41.79	0.32	6.95%	-2.16	-2.3726	6.89%	-2.4649	-55.60	-0.49079	8.92%
n-CoSb3	440	-153	0.791	42.12	0.31	6.69%	-2.13	-2.3637	6.62%	-0.7948	-56.40	-0.49019	9.03%
metal	440	0	0.0200	537	0.00	0.00%	0.00	-2.0400	-1.97%	0	-56.40	-0.49019	9.03%
metal	439	0	0.0200	536	0.00	0.00%	0.00	-2.0399	-1.96%	-1.0938	-57.49	-0.49021	9.03%
contact	439	0	10000	0.00107	0.00	0.00%	0.00	-2.0399	-1.96%	0	-57.49	-0.49021	9.03%
contact	438	0	10000	0.00107	0.00	0.00%	0.00	-2.0398	-1.95%	-2.18E-06	-57.49	-0.49024	9.02%
n-Bi2Te3	438	-161	2.88	12.78	0.31	6.68%	-2.03	-2.3816	6.51%	0	-57.49	-0.49024	9.02%
n-Bi2Te3	423	-171	2.92	12.07	0.35	7.52%	-2.25	-2.3999	7.49%	-0.4454	-57.94	-0.48903	9.25%
n-Bi2Te3	398	-187	2.94	10.92	0.44	9.02%	-2.66	-2.4272	8.96%	-0.6933	-58.63	-0.48657	9.70%
n-Bi2Te3	373	-201	2.90	9.80	0.53	10.59%	-3.16	-2.4474	10.13%	-0.6312	-59.26	-0.48355	10.27%
n-Bi2Te3	348	-210	2.79	8.72	0.63	12.17%	-3.79	-2.4577	10.89%	-0.5679	-59.83	-0.48002	10.92%
n-Bi2Te3	323	-213	2.61	8.23	0.68	12.96%	-4.32	-2.4556	10.89%	-0.5206	-60.35	-0.47614	11.64%
n-Bi2Te3	298	-209	2.38	8.00	0.68	12.91%	-4.76	-2.4397	10.24%	-0.4966	-60.85	-0.47210	12.39%
contact	298	0	10000	0.00073	0.00	0.00%	0.00	-2.1182	-0.97%	0	-60.85	-0.47210	12.39%
contact	297	0	10000	0.00072	0.00	0.00%	0.00	-2.1181	-0.97%	-1.54E-06	-60.85	-0.47212	12.39%
metal	297	0	0.0200	362	0.00	0.00%	0.00	-2.1181	-0.97%	0	-60.85	-0.47212	12.39%
metal	296	0	0.0200	361	0.00	0.00%	0.00	-2.1180	-0.96%	-7.66E-01	-61.61	-0.47214	12.38%

In order to calculate l and further operating conditions, the total heat flux $U_{total,h}/A_{total}$ or power/area desired W/A_{total} must be given.

The current density J_p is calculated from (46), (44) and (49), giving

$$(56) \qquad J_p = \frac{U_{total,h}}{A_{total}} \times \frac{1 + \dfrac{A_n}{A_p}}{\Phi_{p,h} - \Phi_{n,h}}$$

The *n*-element current density, J_n, and l can then be calculated from equations (45) and (37).

For example, assume we desire to make a thermoelectric couple out of the *p*-type element of Table I with the *n*-element of Table II. The area ratio which ensures that the desired u current flows in each element using the same electric current I, is from equation (45): $\dfrac{A_p}{A_n} = \dfrac{61.63}{39.34} = 1.57$. If the desired total heat flux into the hot side is 20

W/cm^2, then from equation (56), $J_p = 20 \dfrac{W}{cm^2} \times \dfrac{1 + \dfrac{1}{1.57}}{0.4283 + 0.5388} = 34 \dfrac{A}{cm^2}$. Similarly, $J_n = -53 \dfrac{A}{cm^2}$. The

desired length (from equation (37)) is $l = \dfrac{\int_{T_c}^{T_h} u\kappa dT}{J} = \dfrac{39.34\ \dfrac{A}{cm}}{34\ \dfrac{A}{cm^2}} = 1.16$ cm. For a total thermoelectric couple

area of 1 cm^2, $A_p + A_n = 1.0$ cm^2, the individual areas are $A_n = 0.39$ cm^2, $A_p = 0.61$ cm^2 and finally the current in the couple is $I = 20$ A (from $I = JA$). The output voltage for each couple is 0.142 V using equation (43).

5. Thermoelectric Compatibility

   If the compatibility factor s (most efficient u current, equation (18)) of one part of the thermoelectric is significantly different from the s of another part, there will be no suitable current where both parts are operating close to maximum efficiency. This is the physical basis for thermoelectric compatibility, and is most apparent for segmented generators.

   To achieve high efficiency, segmented generators use large temperature differences to increase the Carnot efficiency $\eta_C = \dfrac{\Delta T}{T_h}$. Since the material thermoelectric properties (α, κ, ρ) vary with temperature it is not desirable or even possible (most have maximum operating temperature where they may melt or otherwise decompose) to use the same material throughout an entire, large temperature drop. Ideally, different materials can be combined such that a material with high efficiency at high temperature is *segmented* (Figure 6) with a different material with high efficiency at low temperature [21]. In this way both materials are operating only in their most efficient temperature range.
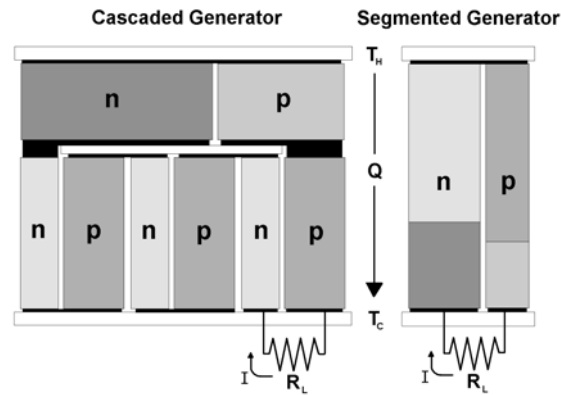

Figure 6. Schematic diagram comparing segmented and cascaded thermoelectric generators. The cascaded generator has a cascading ratio of 3.

   If u could be constrained to be always equal to s, then the most efficient material to choose for a segment would be that with the highest thermoelectric figure of merit z. In this case known as *infinite staging* [2] (or upper limit of efficiency [3]) the interface temperature between segments would ideally be the temperature where the z of both materials cross. For example, according to Figure 8, the best infinitely staged p-leg (0 °C to 1000 °C) would contain (Bi,Sb)$_2$Te$_3$, Zn$_4$Sb$_3$, TAGS, CeFe$_4$Sb$_{12}$, and SiGe with interfaces of about 200 °C, 400°C, 550°C and 700°C.

   Unfortunately, in a real generator, $u = s$ is not possible, so a compromise value for u must be selected. If the compatibility factors s of the segmented materials differ substantially, all segments can not be simultaneously operating efficiently, and the overall efficiency may actually decrease as compared to a single segment alone. Figure 7 shows graphically that a suitable average value for u can be found for the three materials (Bi,Sb)$_2$Te$_3$, Zn$_4$Sb$_3$, and CeFe$_4$Sb$_{12}$, which have compatibility factors within about a factor of two. The reduced efficiency at this average u is not far from the maximum reduced efficiency. SiGe on the other hand, has a much lower value for s, such that if the u shown in Figure 7 is used, a large negative efficiency will result for the SiGe segment and the overall efficiency will decrease. If a smaller u is used, so that positive efficiency will result from the SiGe segment,

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the efficiency of the other segments will have deteriorated more than the efficiency increase from the SiGe segment. Thus, despite having a reasonably high value of z for good efficiency, SiGe can not be segmented with the other materials in Figure 7 because of different compatibility factors.

As a rule of thumb, the compatibility factors of segmented materials should be within about a factor of two. Within this range, a suitable average u can be used which will allow an efficiency close to that determined by z. Outside this range of s, are materials that are incompatible where the efficiency will be substantially less than that expected from z. The compatibility factor is therefore, like z, a thermoelectric property essential for designing an efficient segmented thermoelectric device.
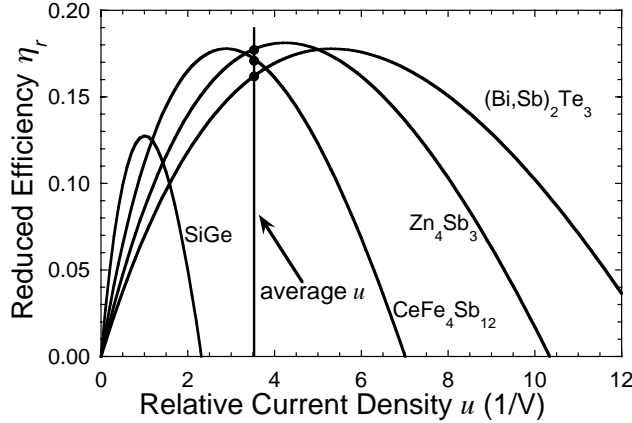

Figure 7. Comparison of reduced efficiency as relative current density, u, varies for different p-type thermoelectric materials. An average value for u can be found for $(Bi,Sb)_2Te_3$ ($125°$ C), Zn_4Sb_3 ($300°$ C), and $CeFe_4Sb_{12}$ ($550°$ C), that gives a reduced efficiency (indicated with a "•") near the maximum efficiency. SiGe ($800°$ C), on the other hand, has such a low compatibility factor s, that using a u appropriate for the other materials would result in a negative reduced efficiency for SiGe. This makes SiGe incompatible for segmentation with the other thermoelectric materials.

5.1. Materials selection

For segmented generators high z materials need to be selected that have similar compatibility factors, s. Other factors (not considered here) may also affect the selection such as: thermal and chemical stability, heat losses, coefficient of thermal expansion, processing requirements, availability and cost [22].

The compatibility factor (Figure 8) can be used to explain why segmentation of $(AgSbTe_2)_{0.15}(GeTe)_{0.85}$ (TAGS) with SnTe or PbTe has produced little extra power [23], but using filled skutterudite would increase the efficiency from 10.5% to 13.6% [24].

Very high efficiency segmented generators to $1000°$ C could be designed with skutterudites or PbTe/TAGS as long as compatible, high temperature materials are used [24]. The compatible, high zT n-type material La_2Te_3 [25] would be ideal as long as a compatible p-type material is found.

For the high temperature p-type element, a high zT material that is also compatible with PbTe, TAGS or Skutterudite has not been identified. Even if the material has low zT, *e.g.* $zT \approx 0.5$, it will produce some power, *as long as it is compatible*. For a material with a low zT to be compatible with PbTe, TAGS or Skutterudite it must have $s > 1.5$ V^{-1}, ideally $s \approx 3$ V^{-1}. Since $s \approx z/2\alpha$, the $zT \approx 0.5$ material can not be a high Seebeck coefficient band or polaron semiconductor. Materials with high z and s have thermoelectric properties typical of high α metals. In a metal, the thermal conductivity is dominated by the electronic contribution given by the Wiedemann-Franz law $\kappa_\varepsilon = LT/\rho$ where $L \approx 2.4 \times 10^{-8}$ V^2/K^2. The compatibility factor $s \approx \alpha/(2\kappa\rho) \approx \alpha/(2LT)$ would then be appropriate if α is greater than 100 μV/K at 1000 K [24]. For example, a candidate for such a refractory p-type metal is $Cu_4Mo_6Se_8$ [26].
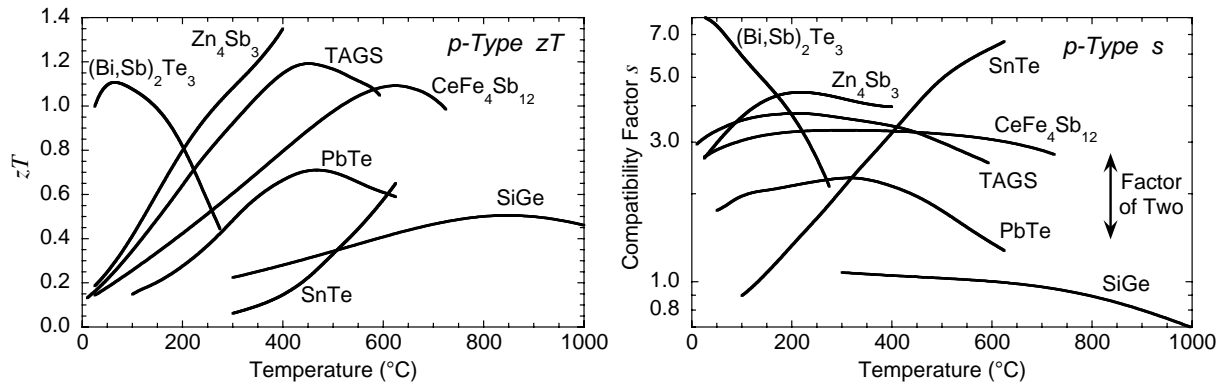
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Figure 8. Figure of merit (*zT*) and compatibility factor (*s*) for *p*-type materials.
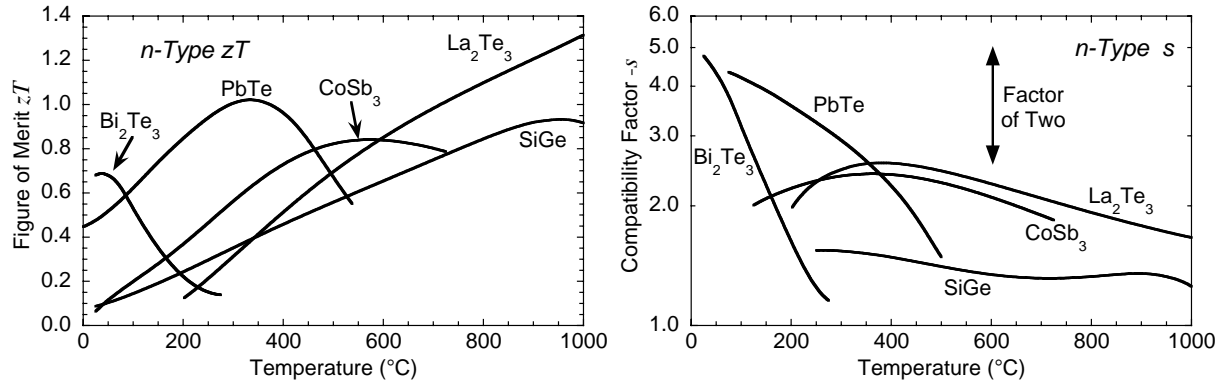

Figure 9. Figure of merit (*zT*) and compatibility factor (*s*) for *n*-type materials.

5.2. Cascaded Generators

Cascaded generators (Figure 6) can avoid the compatibility problem between segments [5]. In a segmented element all segments are thermally and electrically in series so that a single u_h defines $u(T)$ throughout the element. However a cascaded device contains an independent electric circuit for each stage, allowing an independent J and therefore u in each stage. In this way, different, optimal values of u can be used for each stage. It is because of the compatibility difference between materials that makes cascading always more efficient than segmenting [2, 3]. However, cascading is much more difficult to implement than segmentation.

Truly independent circuits will require an electric connector between a stage at high temperature and the load at ambient temperature. In practice, it is best not to connect the high temperature stages directly to the load. Such connectors must have some loss because they can neither have very low electric resistance (or they will conduct heat away from the hot side - due to Wiedemann Franz law), nor have high electric resistance (large Joule losses). It can be shown that the loss from such connectors is proportional to $1/N$ where N is the number of couples for each connector. Thus to minimize these losses, the ratio of the number of thermoelectric couples to the number of connectors should be large.

To avoid such losses entirely the electric current should pass from the high temperature stage to the load by going through the thermoelectric elements of the low temperature stage (Figure 6). The differing values of u is provided by having a different number of couples in each stage. The ratio of the number of couples (N_2/N_1) in the cooler stage (Stage 2, N_2 couples) to that of the hotter stage (Stage 1, N_1 couples), called the *cascading ratio* [27], is derived by equating the heat flux out of the hot stage to the heat input to the cold stage (thus T in the following formulas is the interface temperature between the two stages). This can be expressed succinctly (including both the Peltier and conduction terms) using the thermoelectric potential [24] (equation (49)).

Equating the heat from N_1 stage 1 couples with N_2 stage 2 couples operating with the same electric current I, gives:

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$$(57) \qquad \frac{N_2}{N_1} = \frac{\Phi_{p,1} - \Phi_{n,1}}{\Phi_{p,2} - \Phi_{n,2}} \approx \frac{\alpha_{1,p}T + \dfrac{1}{s_{1,p}} - \alpha_{1,n}T - \dfrac{1}{s_{1,n}}}{\alpha_{2,p}T + \dfrac{1}{s_{2,p}} - \alpha_{2,n}T - \dfrac{1}{s_{2,n}}}$$

where, for maximum efficiency, u is approximately equal to an averaged s.

The simplification where the thermoelectric properties (α, ρ, κ) are constant with respect to temperature is given by Harman [27]. For SiGe cascaded with TAGS/PbTe the optimum cascading ratio is 2.21, so that there should be about twice as many TAGS/PbTe couples as SiGe couples. With this cascading ratio the efficiency of the generator can achieve the sum of the two stages, 10.39% + 4.39% = 14.78% [24].

5.3. Functionally graded

The importance of compatibility has been made apparent for a segmented thermoelectric generator, but compatibility is also a consideration for all thermoelectric devices whether the materials are homogeneous or inhomogeneous from segmentation or being functionally graded. Since the compatibility factor of even a homogeneous material is temperature dependent, the change in s from one end of the leg to the other will, in general, adversely effect device performance. The consideration of compatibility within the same material has been called *self-compatibility* [11]. Due to the explicit temperature dependence of s (equation (18)) in conjunction with the typical temperature dependence of z and α, the problems with self-compatibility are generally more apparent at low temperatures [11].

For inhomogeneous materials, the compatibility factor must be considered when optimizing the compositional variation. The thermoelectric properties of most materials can be altered with small changes in doping, that allows a tuning of both z and s [Ref Gascoin?]. The most efficient material will not only have high zT, but will also be compatible with the other materials. For example, $(Bi,Sb)_2Te_3$ with the highest zT also has a large compatibility factor compared to TAGS. By lowering the carrier concentration from the highest zT composition, a more compatible material can be used that is more efficient when segmented with TAGS despite having a slightly lower zT.

True functionally graded materials can have a continuum of different compositions along the length of the material, which can enhance efficiency [28, 29]. Ideally, it would be best to have a local criterion for maximizing efficiency [8]. By examining the reduced efficiency (equation (15)) at every location, it can be rationally determined if alterations in materials properties that change z and s will further increase efficiency. This also avoids the complex numerical methods used to predict the performance gains of functionally graded designs.

6. Design Optimization

The performance of a thermoelectric generator is dependent on many variables which could be optimized globally to find the optimum design. However, by using a reduced variable approach to the design problem, many interdependencies of the design variables are eliminated which allows a better understanding of the effect of each variable.

The following discussion is intended primarily for ideal thermoelectric generators. In "ideal" systems [30] there are no thermal losses, no contact (thermal or electric) resistances and only 1-dimentional heat flow. Many non-idealities can be considered part of the system design, allowing the thermoelectric portion of the generator to be considered ideal. In addition, the effect of some non-idealities scale with length the same way as the thermoelectric material (such as interconnect metals with a fixed ΔT budget), which allows them to be incorporated without significant modification of the design algorithm. Finally, non-idealities which scale with length differently, (such as contact resistances) should lead only to small corrections that will give a quick convergence if calculated iteratively.

6.1. Efficiency Matrix

The first goal of the design process is to evaluate the highest possible thermoelectric efficiency for all hot and cold side temperatures (of the thermoelectric generator, not the heat sinks) that may be viable. This will produce an optimized efficiency that is only a function of the thermoelectric hot and cold side temperatures.

(58) $$\eta = \eta_{\max}(T_h, T_c)$$

The presumption is that any other variables (such as materials chosen, interface temperatures, geometry, current, *etc.*) that may be required for the calculation of efficiency can be optimized given a T_h and T_c. This is true for the thermoelectric material interface temperatures, but less true for size of metal interconnect and contact resistance.

6.1.1. Interface Temperatures

Once the materials are selected based on z and s, the interface temperature between thermoelectric segments must be optimized. The interface temperature can be estimated by where the value of z crosses or by using the approximation that u remains constant within a thermoelectric leg [11]. Calculating the efficiency (as described above section number?) for different initial conditions u_h for both the *n*- and *p*- element, will allow a quick convergence to the most efficient (equation (42)) $u_{p,h}$. and $u_{n,h}$.

The ideal optimum interface temperature is the one which has equal reduced efficiency for either material at that temperature (see 209° C rows in Table I). By estimating the change in reduced efficiency with temperature (using an optimized u), the optimum interface temperature can be found with an iterative process. Often the interface temperature is simply the maximum operating temperature of a material (see 400° C rows in Table I).

6.2. Thermoelectric Element Length

Once the optimized efficiency (equation (58)) is found given a T_h and T_c, the values of $u(T)$ and $\Phi(T)$ for both the *n*- and *p*- element are defined. Most of the remaining performance parameters also require the thermoelectric element length. This is usually determined by the desired total heat flux $U_{total,h}/A_{total}$ (or power/area W/A_{total}). As shown in the discussion of equation (56), l can be calculated from $U_{total,h}/A_{total}$ with $u(T)$ defined by optimizing the efficiency between T_h and T_c. Thus l is a function only of T_h, T_c. and $U_{total,h}/A_{total}$.

(59) $$l = l(T_h, T_c, U_{total}/A_{total})$$

Once functions (58) and (59) are evaluated for a variety of T_h, T_c. and $U_{total,h}/A_{total}$, they can be incorporated into the system model to find the optimal system operation condition.

For example, often in a thermoelectric generator the power/mass is the primary concern. In this case, the power/mass can be increased by reducing the mass of the heat exchangers at the cost of reducing the temperature difference which lowers the efficiency. By knowing how the optimum efficiency and length vary with input temperature and heat flux, the exact system solution is found without requiring the systems analysis to be capable of thermoelectric calculations. The system power and voltage are directly proportional to the size of the generator (through A_{total}) and number of couples. Once the system trades are complete, the final configuration of the thermoelectric generator can be established.

6.3. Voltage

The voltage produced V_{system} is the number of couples connected in series N_{series} times the couple voltage V_{couple} (equation (43)).

(60) $$V_{system} = V_{couple}N_{series}$$

Thus the number of couples in series is determined by the voltage requirement. Often redundancy is desired by including additional parallel circuits $N_{parallel}$.

(61) $$N_{system} = N_{series}N_{parallel}$$

Once the thermoelectric length is fixed, the total power desired W will define the total cross sectional area A_{total}. The relationship between the area of a couple and the number of couples N_{system}, is given by.

$$(62) \qquad A_{couple} = \frac{W}{\dfrac{U_{total}}{A_{total}} \eta N_{system}}$$

6.4.Maximum power density/matched load

For many power generation applications, the power output is of greater concern than efficiency. In solid state thermal to electric conversion, an important characteristic of the system is the aerial power density (power provided per cross sectional area W/A_{total}). Equations (47), (50), show that the aerial power density is inversely proportional to the thermo-element length l. At a local level, this can be seen using the approximations $\nabla T \approx \dfrac{\Delta T}{l}$ and $\dfrac{W}{A} \approx Pl$. Equation (10) then becomes

$$(63) \qquad \frac{W}{A} \approx \frac{\Delta T^2}{l} \times \kappa u(\alpha - u\rho\kappa)$$

Thus any aerial power density can be achieved by adjusting l, allowing the reduced current u which provides the maximum efficiency to always be used.

In real generation systems it is the characteristics of the heat source and sink, heat exchangers and heat concentrators that are needed to find the conditions for maximum aerial power density. Such passive heat transport systems require significant temperature drops to achieve high heat fluxes needed for high aerial power densities. The temperature drop used in the thermal transport system reduces the temperature drop in the thermoelectric generator, and therefore the Carnot efficiency. Thus aerial power density of the system can be increased at the cost of reduced *system* efficiency. As a rule of thumb, the maximum power is generally found when only 1/2 of the heat source – heat sink temperature difference is used across the thermoelectric (by thermal resistance load matching [31]) with the other half used in the heat transport system. Nevertheless, the thermoelectric generator itself should be designed to operate as efficiently as possible with the heat flux and temperature difference it is allotted. In the discussions of this article, (ΔT) refers to the temperature difference across the thermoelectric only, not the entire system [ref Gao Min next chapter?].

Maximum power density in thermoelectric generators has been frequently analyzed [2, 32, 33] by distinguishing the different operation condition which in a given thermoelectric generator provides more power (at lower efficiency) than the maximum efficiency condition ($u = s$). For a given generator (l is fixed) and constant temperature difference (ΔT), (equation (63)) the maximum aerial power density is found when $u = \dfrac{z}{2\alpha}$ which is slightly larger than $u = s$ (Figure 2). However, the larger u will require additional heat (from Peltier effect) to be supplied and the overall process is at a lower efficiency (because of Joule losses).

This analysis is traditionally performed using load resistance R_{Load} as the current adjusting variable as opposed to u or even electric current I. In addition, the approximation α, κ, ρ, and therefore z are constant is also commonly made. By approximating $\nabla T \approx \dfrac{\Delta T}{l}$, and combining with $I(R_{Load} + R) = \alpha \Delta T$ and equation (9) gives

$$(64) \qquad u \approx \frac{z}{\alpha} \frac{R}{R_{Load} + R}$$

Thus the $u = \dfrac{z}{2\alpha}$ condition is given by $R_{Load} = R$ (matched load) while the $u = s$ condition corresponds to $R_{Load} = R\sqrt{1 + ZT}$ (with $Z = z$), the load resistance for maximum efficiency [2].

However, when designing a system (with length, l, is a design parameter), the matched load condition ($R_{Load} = R$, $u = \dfrac{z}{2\alpha}$) is a poor choice not only when considering efficiency, but also when optimizing aerial power density, size, weight or even voltage. For example, consider a design where the matched load condition was selected for the thermoelectric generator. This generator has Q heat flux supplied to it, at some T_h and T_c, and generates $\dfrac{W}{A} = \eta_{\frac{z}{2\alpha}} Q$ aerial power density ($\eta_{\frac{z}{2\alpha}}$ is the efficiency when $u = \dfrac{z}{2\alpha}$), with a length $l_{\frac{z}{2\alpha}}$. Now, replace this $u = \dfrac{z}{2\alpha}$ generator with a $u = s$ ($R_{Load} = R\sqrt{1+ZT}$) generator having the same T_h and T_c, and heat flux Q. For a small ΔT generator equation (38) can be approximated

$$(65) \qquad\qquad Q \approx \frac{\kappa \Delta T}{l}\left(\alpha T u + 1\right)$$

To utilize the same heat flux Q, the $u = s$ generator will need to have a smaller length l_s, than a $u = \dfrac{z}{2\alpha}$ generator because $s < \dfrac{z}{2\alpha}$. From equation (65) the ratio of the two lengths is approximately given by

$$(66) \qquad\qquad \frac{l_s}{l_{\frac{z}{2\alpha}}} \approx \frac{\sqrt{zT+1}}{zT\big/2 + 1}$$

Operating at the same temperatures but different currents, the longer, matched load generator will always have lower efficiency than that of the shorter $u = s$ generator, because $\eta_{\frac{z}{2\alpha}} < \eta_s$. For comparison, a generator operating with $u = \dfrac{z}{2\alpha}$ will have a reduced efficiency of $\eta_r = \dfrac{zT}{2zT+4}$, which is always less than that of the $u = s$ generator given by equation (20). Since the heat entering both generators is the same, the $u = s$ generator will provide more power ($\dfrac{W}{A} = \eta Q$, Q is the same) as well as greater efficiency (and higher voltage). Also because $l_s < l_{\frac{z}{2\alpha}}$ the $u = s$ generator will be smaller and therefore lighter.

It is worth emphasizing again that for a system which includes heat exchangers, the temperatures chosen for the thermoelectric will be different for the maximum power density, and the maximum efficiency problem. But in both cases, the generator should be designed such that the current used corresponds to the maximum efficiency and not the matched load condition.

When losses are introduced in the thermoelectric portion of the generator which do not scale with length in the same way as the thermoelectric materials, the optimal current may deviate toward the matched load condition. An example is electric contact resistance which is independent of length. For systems with small l, the contact resistance becomes more important and so designing a longer generator by increasing the current toward the matched load condition increases both thermoelectric generator efficiency as well as power density. Such losses also lower the effective Z for the generator (an average of the $z(T)$ of each material [10]) including contact resistances, which also brings the load for maximum efficiency closer to the matched load condition.

6.5. Non Optimal Operating conditions

Once the optimal configuration is established, the performance at non-optimal conditions, such as the full I-V curve can be calculated. In general, the heat flow, the temperatures, and the current can all vary from the optimal but the geometry remains fixed. The heat flow and temperatures will change in a correlated way determined by the thermal impedance of the components external to the thermoelectric converter, just as the electric current will change due to a change in the external electric impedance. Given the electric current in the generator and two out

of three of the heat flux, hot and cold side temperatures (or equivalent relationships), the relative current density u, and therefore the generator characteristics can be determined.

For example, if the hot and cold side temperatures are known (*e.g.* remain constant for low external thermal impedance) the relative current density $u(T)$ of each element can be calculated (and estimated with $\approx$) from

$$(67) \qquad I\frac{l}{A} = \int_{T_c}^{T_h} u\kappa dT \approx \overline{u}\,\overline{\kappa}\Delta T$$

The approximation in equation (67) is good when $u(T)$ remains approximately constant. This is typically true for electric currents up to those required for maximum efficiency. For very large currents, u no longer remains constant and diverges at the hot side. A is the current for a thermoelectric cooler operating at maximum ΔT ($\nabla T = 0$ at T_h). The corresponding u_c does not diverge, so it is more stable to compute using u_h rather than u_c as initial conditions.

If the effective external thermal impedance is high, an *I-V* curve can be calculated assuming the heat supplied remains constant (and the hot or cold side temperature or a relationship is given). In this case, the three unknowns (the unknown temperature, and an initial value for u_n and u_p) are solved from three equations: two of the form (67), for *n*-type and *p*-type, and the heat flow (49) for the couple.

For low current operation, the Peltier cooling at the hot end of the thermoelectric will decrease, requiring an increase in the hot side temperature and the interface temperatures. Such high temperature operation may advance the degradation of the thermoelectric materials. If such degradation is detrimental to system performance, lower optimal operation temperatures should be selected.

Because the geometry of the elements (in particular the length and area of each segment) remains the same when changing the current, the interface temperatures between the segments will drift from their optimal values. The interface temperatures can be found by finding the interface temperatures that keep the lengths of each segment constant, using equation (67) as a guide. Even for low external thermal impedance, where the hot and cold side temperatures remain constant, the interface temperatures between the segments will change somewhat with varying electric current.

7. Acknowledgements

8. References

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