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Thermionic Energy Conversion (TEC) Topping Thermoelectrics

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Work performed for
U.S. DEPARTMENT OF ENERGY
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Washington, D.C. 20545
Under Interagency Agreement EC-77-A-31-1062

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ABSTRACT

Long-respected international experts on thermoelectrics (Dixon, Ertl and Goldsmid supported by Ure) determine the probable maximum figure of merit ($ZT$) for fully matured thermoelectric generators as about unity from ordinary temperatures to 2000 K. Thus the maximum efficiency for fully matured thermoelectrics would be approximately $0.414 \left(1 - r_T\right) / \left(1.414 + r_T\right)$ where $r_T$ is the ratio of cold and hot junction temperatures. This limitation contrasts with the recent burst of enthusiasm for high-temperature thermoelectrics - based on calculated figures of merit and efficiencies that increase more and more rapidly with rising temperatures. Unfortunately these calculations neglect internal radiation effects which diminish thermoelectric figures of merit significantly at 1000 K and substantially at 2000 K: The effective thermal-conductivity contribution of intrathermoelectric radiative dissipation increases with the third power of temperature. Therefore the quotation from Thermoelectricity: Science and Engineering by Heikes and Ure apparently still prevails: "...thermoelectric devices appear difficult to extend in the direction of high temperature, while thermionic devices become inefficient at low temperature."

Accordingly consideration of thermoelectric power generation with high-temperature heat sources should include utilization of TEC topping thermoelectrics. However TEC alone or TEC topping more-efficient conversion systems like steam or gas turbines, combined cycles or Stirling engines would be more desirable generally.

EXECUTIVE SUMMARY

"Technologically the processes are competitive and complementary: competitive because they will tend to use the same power sources, but complementary because the thermoelectric devices appear difficult to extend in the direction of high temperature, while thermionic devices become inefficient at low temperature" (R. R. Heikes and R. W. Ure, Jr.: Thermoelectricity: Science and Engineering, Interscience, 1961: ref. 1).

"On the basis of the type of arguments given here it is impossible to predict whether small (10-20 percent) increases in $ZT$ can or cannot be expected. It is my opinion that increases of this order could be obtained if sufficient effort is devoted to it. The arguments of this report show that an increase in $ZT$ of a factor of 2 over presently available materials seems very unlikely" (R. W. Ure, Jr.: "Practical Limits to the Thermoelectric Figure of Merit," Energy Conversion, vol. 12, pp. 45 to 52, 1972: ref. 2).
"A theoretical investigation of the effect of radiative heat transfer on the performance of a high temperature thermoelectric material has been carried out.... It is difficult to see any way in which radiative heat transfer could be reduced without impairing the other properties. It is thus concluded that even at high temperatures (1000 to 2000 K) values of ZT much in excess of unity are unlikely to be attained. It is interesting to note that Ure (ref. 2) has deduced a similar limit on ZT for the types of material that are used at ordinary temperatures" (A. J. Dixon, M. E. Ertl and H. J. Goldsmid: "Radiative Heat Transfer in High Temperature Thermoelectric Materials," Energy Conversion, vol. 14, pp. 47 and 48, 1975: ref. 3).

For a thermoelectric figure of merit (ZT) of unity the maximum theoretical thermoelectric efficiency (ν) is 18.7 percent for a 0.25 ratio of cold and hot junction temperatures (rt), ν is 10.8 percent for a 0.50 rt, 4.78 percent for 0.75, and of course ν is zero for isothermal thermoelectrics. Theoretic TEC performance follows.


Note that the fully matured TEC efficiency for these electrode temperatures is about 24 percent. In contrast the maximum fully matured thermoelectric efficiency for such hot and cold junction temperatures is 8.8
percent, 6.2 percentage points below even the 15 percent cited by LASL in reference 4. Also the averaged overall efficiency for specific thermoelectric materials over the temperature range would be significantly lower than the maximum. Apparently, therefore, when thermoelectric power generation is contemplated for use with high-temperature heat sources, every effort should be made to utilize TEC topping thermoelectrics. But TEC alone would be more efficient as well as simpler. And as the preceding figures imply, TEC topping higher-performance systems like steam or gas turbines, combined cycles or Stirling engines would be far more productive.

**VIEWS OF TEC AND THERMOELECTRIC POWER GENERATION**

Traditionally TEC and thermoelectrics appear together in direct-energy-conversion texts, although their mechanistic specificities differ considerably. Both produce electricity directly from heat, have no moving parts or inherent mechanical stresses, and offer low weights with small volumes as well as modularity. In general TEC prevails at high temperatures for high power levels with high theoretic-performance potentialities. Convenient, compact thermoelectric generators offer advantages for low total power. But thermoelectrics generally carries the connotation of temperature and efficiency limitations (refs. 1 to 3).

Recently a spate of enthusiasm for predicted high-temperature, high-efficiency thermoelectric power generation has swept across the technological scene (ref. 4, for example). Characteristic of that enthusiastic wave are calculated thermoelectric figures of merit and efficiencies - rising more and more rapidly with temperatures as they pass 1000 K and approach 1800 K. Some curves in figure 1, excerpted from reference 4, exemplify this description.

Unfortunately these predictions overlook some basic limitations of the thermoelectric phenomena developed theoretically by long-recognized international experts in references 2 and 3. The present paper indicates the effects of such omissions and the advisability of TEC topping thermoelectrics. A subsequently defined figure of merit (ZT rather than Z), its theoretically determined limit and resulting efficiencies facilitate the discussion of thermoelectric performance from ordinary temperatures to 2000 K.

**A SIMPLIFIED DESCRIPTION OF TEC**

To avoid redoing the previously done, this section utilizes TEC equations and results (fig. 2) from reference 5 (also refs. 6 to 10):

TEC heat inputs can reach the order of 100 W/cm², as implied by figure 2. There TEC outputs range up to tens of W/cm² (P_{OL}) and tens of percent efficiency (n_{OL}):

\[ P_{OL} = (\phi_E - \phi_C - V_D - V_A - V_L)(j_E - j_R) \]  

(1)
\[ n_{OL} = (J_{ES} - J_{BE}) \left\{ \phi_E - \phi_C - V_D - V_A \right\} \]

\[ -2 \left[ 2.45 \times 10^{-8} \frac{n_{EC}(T^2_E - T^2_C)}{(2 - n_{EC})} \right]^{1/2} \left\{ J_{ES}(\phi_E + 2kT_E) \right\} \]

\[ -J_{BE}(\phi_E + 2kT_C) + 5.7 \times 10^{-12} \left[ 0.05 + 7.5 \times 10^{-5}(T_E - 1000) \right] (T^4_E - T^4_C) \] (2)

In these equations, \( \phi_E \) and \( \phi_C \) are emitter and collector work functions, \( V_D \) is the interelectrode voltage drop, \( V_A \) is the equivalent auxiliary input voltage for enhancement, \( V_L \) is the voltage loss required for optimum leads (equal to the expression within the square brackets in the numerator of (2)), \( n_{EC} \) is the TEC electrode efficiency (equal to (2) with \( 2V_L \) deleted from the numerator), \( T_E \) and \( T_C \) are emitter and collector temperatures, the last term in the denominator of (2) approximates non-electronic thermal transport, \( J_R \) is reverse electronic flow (including reflections, backscattering, back emission \( J_{BE} \), and other effects that diminish output current), and \( J_{ES} \) is the current density for emitter saturation:

\[ J_{ES} = A(1 - R_E)T^2_E \exp(-\phi_E/kT_E) \] (3)

where \( A \) and \( k \) are Richardson and Boltzmann constants and \( R_E \) is the emitter reflection coefficient.

Equation (2) is a simplified, yet reasonable estimate applicable for low cesium concentrations, reduced enhanced-mode pressures, close electrode spacings, and small interelectrode losses. Under such conditions the back emission \( (J_{BE}) \) approximates

\[ J_{BE} = A(1 - R_{BE})T^2_C \exp(-\phi_C + V_D/kT_C) \] (4)

where \( R_{BE} \) comprises \( R_C \) (collector reflection coefficient) and similar coefficients for all interelectrode mechanisms that return collector-emitted electrons to their source – except those for noncollisional repulsion by the emitter sheath. With negligible interelectrode losses and reflections, back emission equals that for collector saturation:

\[ J_{CS} = A(1 - R_C)T^2_C \exp(-\phi_C/kT_C) \] (5)

The preceding equations verify a previous assertion: High-temperature material effects \( (\phi_E, R_E, T_E, J_{ES}, \phi_C, R_C, T_C, J_{CS}, ...) \) determine the level of TEC performance completely. This generalization includes enhanced-mode operation also because \( V_A \) represents a small fraction of TEC output recycled to increase efficiency.

Calculated results for fully matured TEC appear in figure 2 accompanied by implied topping and process-heating temperatures.
A DISCUSSION OF THERMOELECTRICS

To introduce a theoretic description of thermoelectrics in the present context, quotations from references 1 to 3 seem apropos. Reference 1 discusses TEC in a text on thermoelectricity:

Technologically the processes are competitive and complementary: competitive because they will tend to use the same power sources, but complementary because the thermoelectric devices appear difficult to extend in the direction of high temperature, while thermionic devices become inefficient at low temperature. We may well envision two- (or more) stage devices with a thermionic high-temperature stage coupled to a thermoelectric low-temperature stage.

Reference 2 comments on "practical limits to the thermoelectric figure of merit" (ZT):

Goldsmid (ref. 11) has found a similar maximum at room temperature. There are several factors which have the effect of reducing ZT_{max} at high temperatures. Other scattering mechanisms which we have not discussed will be increasingly important as the temperature is raised.... The additional types of scattering which produce this faster decrease of mobility will reduce ZT at high temperatures.... The maximum ZT which has been found here is much lower than the maxima found for other models but is still a factor of 2 larger than the ZT of materials presently known.... However, it seems to me that it will be very difficult to find materials whose ZT is close to the maximum calculated here.... On the basis of arguments given here it is impossible to predict whether small (10-20 percent) increases in ZT can or cannot be expected. It is my opinion that increases of this order could be obtained if sufficient effort is devoted to it. The arguments of this report show that an increase in ZT of a factor of 2 over presently available materials is unlikely.

Thus Ure expects at most a 20 percent increase over the "ZT of materials presently known" because of "several factors which have the effect of reducing ZT_{max} at high temperatures."

One such factor is "radiative heat transfer in high-temperature thermoelectric materials," which reference 3 treats mechanistically:

A theoretical investigation of the effect of radiative heat transfer on the performance of high-temperature thermoelectric material has been carried out. In the temperature range 1000-2000 K liquid semiconductors are likely to be the best materials (better than solids), and the calculations based on the free-electron model show that radiative transfer has a considerable influence by reducing the figure of merit and changing the optimum carrier concentration.

Here is a factor obviously not included in the figure-of-merit and efficiency calculations of reference 4 (note the equation for Z in fig. 1 excerpted from ref. 4). Incidentally the figure-of-merit units for figure 1 are undoubtedly "x10^3/°C" as they (and the hypens) are on preceding plots in reference 4.
Understandably, effective conduction by radiation would not usually enter such computations "because thermoelectric devices appear difficult to extend in the direction of high temperature." Conversely, as revealed in the denominator of equation (2), radiative heat transfer normally appears as a dissipative effect in TEC performance calculations.

Dixon and Ertl of reference 3 used the combined conductive, radiative effect earlier to correlate thermoelectric data (ref. 12):

Detailed information of energy transport in a medium with both modes of transport operating is contained in the works of Genzel and others (Genzel 1953 (ref. 13), Czerny and Genzel 1952 (ref. 14), Walther, et al. 1953 (ref. 15)). Their results show that "in the interior of the medium" the energy flux is given by

\[ \phi = -\lambda \frac{dT}{dx} - 4\alpha n^2 \frac{dT^4}{3K} = -\left(\frac{16\alpha n^2 T^3}{3K}\right) \frac{dT}{dx} \]  

where \( \alpha \) is the Stefan-Boltzmann constant, \( n \) is the refractive index and \( K \) is the absorption constant of the material. Thus there is an apparent conductivity which has a thermal component and an optical component, the latter being strongly temperature dependent. Equation (6) was used to obtain an experimental fit to the results of Fedorov and Machuev (1969 (ref. 16)).

Obviously, effective conduction by radiation would cause large losses for thermoelectrics in the temperature ranges for TEC. And of course radiation losses occur in all semiconductor materials.

To illuminate this view reference 3 presents values of \( ZT = a^2 T/\rho K \) where \( a \) is the Seebeck coefficient; \( \rho \), electrical resistivity; and \( K \) is the effective thermal conductivity including radiative as well as charge-carrier and phonon contributions. For wide-band semiconductors, mobility \((\mu = e\ell/\sqrt{3\pi n\ell})\) is low enough to allow an interatomic-spacing approximation \((\ell = 5\times10^{-10} \text{ m})\) of the electron mean free path in this apparent lower limit for validity of the quasi-free electron mode \((m_e = \text{free electron mass, } e = \text{electron charge})\) As a result

\[ \rho = 1/\mu = \sqrt{3\pi n e^2/\mu^2} \]  

where \( \mu \) is 4.2x10^{-4} \text{ m}^2/\text{V} \cdot \text{sec} at 1000 K and 3x10^{-4} at 2000 K. The nondegenerate expression \( a = \kappa (1 - E_F)/e \), where \( E_F \) is the reduced Fermi level, estimates the Seebeck coefficient (refs. 3 and 17).

In turn calculations of thermal conductivity by electrons \( K_e = (a/e)^2 T/\rho \), by phonons \( K_{ph} = C \nu/v \) and effectively by radiation \( K_r \) (as indicated in eq. (6)) are possible (ref. 3). Here \( C \) is specific heat per unit volume (Dulong-Petit law), \( v \) is the sound velocity typically 1.25x10^3 m/sec, and \( K_{ph} \) is independent of temperature at -0.07 \text{ W/m} \cdot \text{K}. The absorption coefficient in the \( K_r \) denominator (eq. (6)) appears in references 3 and 18.

When these \( K_e, K_{ph} \) and \( K_r \) values determine \( K \) the thermoelectric figure of merit \( ZT = a^2 T/\rho K \) (maximized over \( E_F \)) becomes 0.9 at 1000 K and increases to 1.4 at 2000 K compared with 1.3 and 3.5 neglecting the effects of thermal radiation. This omission, which characterizes the calculations of reference 4, yields \( ZT \)'s 44 to 150 percent above theoretic limits for 1000 to 2000 K.
Such results led to highly significant observations by Dixon, Ertl and Goldsmid (ref. 3):

Even at 1000 K there is a noticeable reduction in the maximum value of $ZT$ which becomes a very substantial reduction by 2000 K. It is also clear that the optimum reduced Fermi energy becomes less negative as a result of radiation transport. This is because the material becomes increasingly transparent as carrier concentration falls. Calculations that we have carried out assuming higher values of mobility show very little improvement of $ZT$ when radiative transfer is included.

It is difficult to see any way in which radiative transfer could be reduced without impairing the other properties. It is thus concluded that even at high temperatures values of $ZT$ much in excess of unity are unlikely to be attained. It is interesting to note that Ure (ref. 2) had deduced a similar limit on $ZT$ for the types of material that are used at ordinary temperatures. Therefore Dixon, Ertl and Goldsmid supported by Ure estimate maximum $ZT$ values of about unity for thermoelectrics from "ordinary temperatures" to 2000 K.

Assignment of a unit $ZT$ maximum in turn allows estimations of thermoelectric-generator efficiencies for various temperatures (refs. 1, 4, 11, and 19):

$$n = (1 - r_T) \left[ (1 + Z_{TA})^{1/2} - 1 \right] / \left[ (1 + Z_{TA})^{1/2} + r_T \right] \approx 0.414(1 - r_T)/(1.414 + r_T)$$

(7)

where $r_T$ is the ratio of cold and hot junction temperatures ($T_C$ and $T_H$) and $T_{AV}$ is the average of those temperatures. Here of course $T_C$ equal to $T_H$ produces zero efficiency, and zero $T_C$ yields an ultimate efficiency $n = 1 - 1/(1 + Z_{TH}/2)^{1/2}$. The latter has a counterpart in TEC performance where zero $T_C$ eliminates back emission $(BEC)$ and allows zero $\Omega_C$ in equations (1) and (2). These are interesting limits with few practical implications - except perhaps providing performance-curve terminations on full-range plots, such as those in figure 3.

THERMOELECTRIC IMPLICATIONS AND INFERENCE

Figure 3 presents efficiency maxima for full matured thermoelectrics with unit $Z_{TA}$ (solid curve); dashed lines for $Z_{TA}$'s of 0.5, 1.5, and 2.0 allow comparisons. $Z_{TA}$ is the figure of merit in this paper as well as in references 2 and 3. But terming $Z$ alone the figure of merit as in reference 4 is also acceptable.

The previously used "maxima" is quite significant: This terminology implies that thermoelectric generators in general would have one point on each of their performance curves that would be a maximum approaching one of the values given on figure 3. The rest of the efficiencies on each performance curve would fall off from that optimum point for each set of materials and conditions. So averaged overall efficiencies for real thermoelectric generators would be substantially lower than such optimal values which would be lower in turn than figure-3 maxima.
These figure-3 performance limits \((ZT = 1)\) derive from more conventional considerations at ordinary thermoelectric temperatures (ref. 2). But at high thermoelectric temperatures \((-700 \, ^\circ C \text{ and hotter})\) internal radiative heat transfer becomes very important (ref. 3). And for radiation the effective thermal conductivity increases rapidly with temperature \((\propto T^3)\).

Dissipative effects of radiation appear in performance expressions for high-temperature generators like TEC (eq. (2)) - but not for low- and intermediate-temperature devices like thermoelectrics (ref. 4). However evaluation of high temperature thermoelectrics must include radiative heat transfer because "even at 1000 K there is a noticeable reduction in the maximum value of \(ZT\) which becomes a very substantial reduction by 2000 K" (ref. 3).

Reference 4 illustrates the criticality of the omission of radiative effects when considering thermoelectrics for high-temperature service, as compared with TEC, for example:

- The operating characteristics for thermionic converters currently under development by NASA are efficiency - 15 percent, emitter temperature - 1650 K, collector temperature - 950 K, power density - 6 W/cm\(^2\) and current density - 10 A/cm\(^2\).

Note that fully matured TEC efficiency for these electrode temperatures is about 24 percent (fig. 2). In contrast the maximum fully matured thermoelectric efficiency for such hot and cold junction temperatures is 8.8 percent, 6.2 percentage points below even the 15 percent cited as TEC "currently under development by NASA" in reference 4. And remember that the 8.8 percent is a fully matured maximum for thermoelectrics: The average overall efficiency for specific thermoelectric materials over the temperature range would be significantly lower than the maximum.

In any event high-temperature thermoelectric power generation should be advocated only after careful objective consideration of TEC topping thermoelectrics. For example, powerplant operation with a 0.25 or greater ratio of cold and hot temperatures would limit thermoelectric efficiencies to 18.7 percent or less. However topping the thermoelectric converters with fully matured TEC would raise the conversion efficiency to about 33 percent or more, an increase of over 75 percent.

But as figure 2 indicates, fully matured TEC alone would be more efficient - as well as considerably simpler. And as figure 4 shows (ref. 10), fully matured-technology combinations of TEC with high-performance conversion cycles could produce overall plant efficiencies between 45 and 55 percent. Figure 2 implies additional productive topping applications for TEC.

Thus thermoelectric applications seem to result from special requirements for convenience and compactness, where performance is a secondary consideration. Even there, however, high-temperature efficiency predictions should include effects of thermally radiative dissipation in thermoelectric materials. And compact, convenient TEC, which also converts heat directly to electricity and has no moving parts, should be considered with thermoelectrics - in combination or as a replacement.
REFERENCES


Figure 1. - Thermoelectric performance projections from reference 4.
Figure 2. The optimized load efficiency, \( \% \), and optimized load power density, \( \text{W/m}^2 \), as functions of collector temperature, \( \text{Kx10}^{-2} \), for various turbine types.

(a) Thermionic-energy-conversion efficiency.
(b) Thermionic-energy-conversion power density.

Figure 3. Projected thermoelectric-efficiency maxima (ZTE: 1.0).

<table>
<thead>
<tr>
<th>Turbine Type</th>
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<th>Power Density</th>
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</thead>
<tbody>
<tr>
<td>CCGT (ATMOSPHERIC)</td>
<td>1.0</td>
<td>1.5</td>
</tr>
<tr>
<td>CCGT (Pressurized)</td>
<td>0.5</td>
<td>1.0</td>
</tr>
<tr>
<td>CCGT (Fluidized Bed)</td>
<td>0.25</td>
<td>0.75</td>
</tr>
<tr>
<td>CCGT (Stirling Engine)</td>
<td>0.1</td>
<td>0.5</td>
</tr>
</tbody>
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Figure 4. The figure of merit, \( ZT/A \), as functions of the ratio of cold and hot junction temperatures.
Figure 4. - ECAS Phase 2 results using 30-year levelized cost in mid-1975 dollars. Fuel cost assumed constant in fixed dollars.

- **contracts**
  - GE
  - Westinghouse
  - UTC & R

- **technologies**
  - Steam with Scrubber Stack Gas
  - AFB Closed Cycle Gas Turbine/Organic
  - '78 TEC, Steam
  - SemiClean Liquid Gas Turbine/Steam
  - PFB Potassium Turbine/Steam
  - LRTU Gas Turbine/Steam
  - LRTU Molten Carbonate Fuel Cell/Steam
  - Coal Open-Cycle MHD/Steam (with TEC heat exchanger replacing water cooling in "radiant furnace" 32.7 mlls/kW-hr, 53%)

- **cost of electricity** (mlls/kW-hr)
  - 250
  - 175

- **overall efficiency** (%)
  - 30
  - 35
  - 40
  - 45
  - 50
  - 55