THERMAL TO ELECTRIC ENERGY CONVERSION

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As research in the area of excess power production moves forward, issues associated with thermal to electric conversion become increasingly important. This paper provides a brief tutorial on basic issues, including the Carnot limit, entropy, and thermoelectric conversion. Practical thermal to electric conversion is possible well below the Carnot limit, and this leads to a high threshold for self-sustaining operation in Pons-Fleischmann type experiments. Excess power production at elevated temperatures will become increasingly important as we move toward self-sustaining devices and energy production for applications. Excess power production in heat-producing systems that do not require electrical input have an enormous advantage over electrochemical systems. Such systems should be considered seriously within our community in the coming years.

1. Introduction

Experiments over the past decade and a half have confirmed the existence of an excess heat effect in Pons-Fleischmann experiments as well as in related experiments involving metal deuterides. As the field continues to evolve, there is interest in the development of self-sustaining experiments, in which the excess power output is used to produce electricity for powering the cell. The motivation for this is that such an experiment may be required finally to convince the mainstream scientific community, as well as the public in general and potential investors, that the basic heat effect is both real and useful.

This motivates a brief discussion of the basics of thermal to electric energy conversion. The community of scientists and inventors working on the excess heat effect come from a wide range of backgrounds and disciplines, so that it seems to be of interest to try to develop a tutorial-level manuscript on this problem to help establish a common basis for discourse on the problem. For example, within the field there has been a general sense of optimism that as the power gains rise, a self-sustaining device is not far off, which is true. However, there has been less agreement on precisely what power gain is needed to achieve that goal.

There are, of course, a limit as to how efficiently thermal energy can be converted to electrical energy. Consequently, the place to begin our discussion is with the Carnot limit, and the reasons for this limit. If we could convert thermal to electrical energy with ideal efficiency as defined by the Carnot limit, then we can define a power gain requirement for self-sustaining excess heat generation. This power gain is on the order of 4.7 for normal acqueous electrochemical experiments.

Commercially available thermal to electric conversion systems do not achieve conversion efficiencies close to the Carnot limit. Consequently, the power gain required for practical self-sustaining operation are significantly higher. We consider briefly as an example thermal to electric conversion based on thermoelectrics. These arguments lead to the conclusion that we should focus on excess heat generation in metal deuteride systems that operate at elevated temperature, since the conversion efficiency improves significantly.

2. The Carnot Limit

The maximum efficiency possible for thermal to electric conversion is given by the Carnot limit[a]

$$\eta_C = \frac{T_{hot} - T_{cold}}{T_{hot}} \tag{1}$$

where T_{hot} is the absolute temperature associated with the thermal source, and T_{cold} is absolute temperature associated with the heat sink. For example, if we consider a Pons-Fleischmann cell that produces excess heat near the boiling point (100^o C), and consider the heat sink to be at room temperature (20^o C), then the associated Carnot limit on efficiency is

$$\eta_C = \frac{80K}{373K} = 21.4\% \tag{2}$$

The power gain required for self-sufficient operation in this (hypothetical) case would be

$$\frac{P_{xs}}{P_{in}} = \frac{1}{\eta_C} = 4.66 \tag{3}$$

Power gains as large as this have been discussed in connection with excess heat experiments at ICCF10 and at previous conferences. Hence, self-sustaining operation would ve possible in principle at present if only we were able to convert thermal energy to electric energy at the Carnot limit.

3. Entropy

The Carnot limit derives from arguments about entropy conservation. The notion of entropy was introduced originally in the development of classical thermodynamics as an intrinsic property of thermodynamic systems.[b] The connection between entropy

[a] There has been discussion recently in the literature about the possibility of violations of this limit under certain conditions. The eventual development of such systems into practical devices is not anticipated on a timescale relevant to the applications that we consider in this work.

[b] The discussion that follows in this section summarizes very briefly arguments given in Hagelstein, Senturia and Orlando[1].

and the microscopic states of a physical system was given in a famous paper of Planck as[2]

$$S = k_B \ln \Omega \tag{4}$$

where S is the entropy, k_B is Boltzmann's constant, and Ω is the number of accessible microstates of the physical system under consideration. Although this may seem to be a bit like estimating how many angels can dance on the head of a pin, it is possible to perform this computation for many simple microscopic physical systems explicitly, either through analytic summations or integration, or using a computer to estimate the number of accessible microstates.

The fundamental postulate of thermodynamics is that all accessible microstates are equally probable in thermodynamic equilibrium. The occupation probability of any single state is then $1/\Omega$. The determination of equilibrium conditions between different thermodynamical systems ultimately boils down to establishing conditions under which this is true for all accessible microstates of the different systems. If energy can be exchanged between two systems, then equilibrium is established when

$$\frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2} \tag{5}$$

where the number of atoms or electrons, the volume and other parameters of each system are held constant. If the system is not in thermal equilibrium and this were not true, then the total entropy of both systems could increase by exchanging energy. The requirement that all accessible microstates be equally probable is consistent mathematically with the requirement that the two systems together on average be in states where the total entropy is maximized. Since the temperature is defined in terms of the entropy through

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V} \tag{6}$$

we find that the fundamental postulate leads to conditions where the total entropy is maximized, which is equivalent to the temperatures of the two systems being the same.

4. Carnot Limit and Entropy Conservation

The Carnot limit can be interpreted as being the condition under which the flow of entropy is conserved through a thermal to electric conversion system. We consider the situation illustrated in Figure 1, in which heat flows through an idealized single-stage thermoelectric converter. The heat per unit area (heat flux) entering into the converter at the hot side is Q_{hot}, and the heat flux per unit area that leaves the cold side is Q_{cold}. The difference in the two heat flows is assumed to be the power per unit area delivered to the electrical load

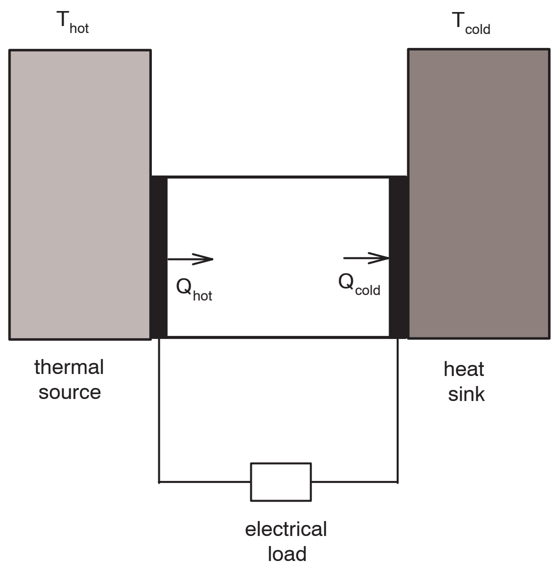

Figure 1. Schematic of thermal to electric conversion system. Heat flows through the converter, with Q_{hot} entering on the hot side at temperature T_{hot}, and Q_{cold} at temperature T_{cold} leaves on the cold side.

$$Q_{load} \;=\; Q_{hot} \;-\; Q_{cold} \tag{7}$$

In terms of these variables, the conversion efficiency is

$$\eta \;=\; \frac{Q_{load}}{Q_{hot}} \;=\; \frac{Q_{hot} - Q_{cold}}{Q_{hot}} \tag{8}$$

In association with heat flow, there is an etropy flow that is related to the heat flow according to

$$s \;=\; \frac{Q}{T} \tag{9}$$

where s is the entropy per unit time and per unit area. The relation between entropy flow and heat flow depends on the details of the quantum system, states and state occupation, but for near-thermal distributions of electrons and holes this relation holds. Phononic heat conduction also satisfies this relation between heat flux and entropy flux.

It is possible for a thermoelectric converter to add to the entropy flowing through it. For example, if no thermal to electric conversion occurs, then the input heat flow at high temperature will match the heat flow leaving at low temperature. The same heat flux at low temperature implies a higher entropy flux than at high temperature, due to the relationship between entropy flux and heat flux of Equation (9).

Consequently, in this case the thermoelectric is increasing the entropy associated with the heat flow.

Let us suppose now that we have a hypothetical perfect thermoelectric that converts as much heat to electricity as possible, subject to the requirement that the entropy flow cannot be reduced from the input value. In this case, the best that the converter can do is to maintain a constant entropy flux. In this case the heat flux is now a function of temperature in the thermoelectric

$$Q(T) \ = \ Ts \tag{10}$$

where s is assumed fixed. Under these conditions, the conversion efficiency is

$$\eta \ = \ \frac{Q_{hot} - Q_{cold}}{Q_{hot}} \ = \ \frac{T_{hot}s - T_{cold}s}{T_{hot}s} \ = \ \frac{T_{hot} - T_{cold}}{T_{hot}} \tag{11}$$

Hence, the Carnot limit in this example is a statement of entropy conservation. The only way to improve on the Carnot limit from this perspective is to work with a system in which the ratio of heat flow to entropy flow has a different dependence on absolute temperature.

5. Thermoelectric Current and Voltage Relations

The thermoelectric effect, at least as far as is relevant to thermal to electric energy conversion, shows up as an open-circuit voltage when a temperature gradient is applied across a thermoelectric material. This basic effect is accounted for in the Onsager current relation[3]

$$\mathbf{J} \ = \ \sigma \left[\nabla \frac{\epsilon_F}{q} \ - \ \Sigma \nabla T \right] \tag{12}$$

where $\mathbf{J}$ is the current density, σ is the electrical conductivity, Σ is the thermopower, and ϵ_F is the Fermi level. Under open-circuit condition (such that $\mathbf{J} = 0$), a voltage drop is induced in the presence of a small temperature difference (such that the thermopower is constant), we can write this as

$$v_{oc} \ = \ \Delta \frac{\epsilon_F}{q} \ = \ \Sigma \Delta T \tag{13}$$

The induced voltage can be used to drive an electrical load.

The current and voltage relation for the thermoelectric in this model is linear. The short circuit current density is given by the thermoelectric current density

$$J_{TE} \ = \ \sigma \Sigma \frac{\Delta T}{L} \tag{14}$$

where L is the thickness of the thermoelectric. The voltage as a function of current density is given by

$$v(J) \;=\; v_{oc}\left[1 - \frac{J}{J_{TE}}\right] \;=\; \frac{L}{\sigma}(J - J_{TE}) \tag{15}$$

The power delivered to the load per unit area is

$$Q_{load}(J) \;=\; Jv(J) \;=\; \frac{L}{\sigma}J(J_{TE} - J) \tag{16}$$

6. Efficiency of Conversion

We are interested in estimating the efficiency of the thermal to electric conversion for this device. In the simplest relevant model, we assume that the heat flow into the device is determined by the thermal conductivity

$$Q_{hot} \;=\; \kappa\frac{\Delta T}{L} \tag{17}$$

In this case, the efficiency as a function of current density is

$$\eta(J) \;=\; \frac{Q_{load}}{Q_{hot}} \;=\; \frac{L^2}{\sigma\kappa\Delta T}J(J_{TE} - J) \tag{18}$$

The maximum efficiency is obtained in this model when the current density is half of the thermoelectric current density, which leads to

$$\eta_{max} \;=\; \frac{L^2 J_{TE}^2}{4\sigma\kappa\Delta T} \;=\; \frac{\sigma\Sigma^2\Delta T}{4\kappa} \tag{19}$$

This can be rewritten in terms of the Carnot limit as

$$\eta_{max} \;=\; \frac{\sigma\Sigma^2 T_{hot}}{4\kappa}\,\frac{\Delta T}{T_{hot}} \;=\; \frac{\sigma\Sigma^2 T_{hot}}{4\kappa}\,\eta_C \tag{20}$$

The goodness of the thermoelectric for energy conversion then is proportional to the material parameters in the ratio

$$Z \;=\; \frac{\sigma\Sigma^2}{\kappa} \tag{21}$$

where Z is the Ioffe figure of merit. The product of this figure of merit and the absolute temperature produces a dimensionless figure of merit

$$ZT \;=\; \frac{\sigma\Sigma^2 T}{\kappa} \tag{22}$$

that is widely used to characterize thermoelectric materials. Within the simple model under consideration, the maximum efficiency in terms of the dimensionless figure of merit is

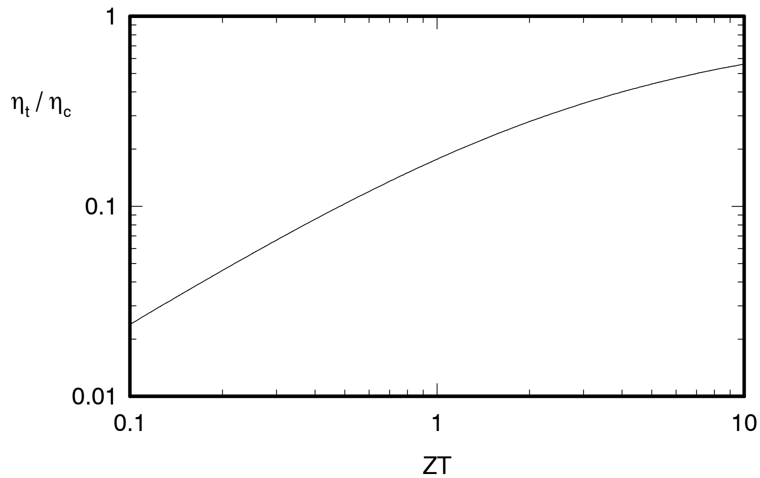

Figure 2. Optimum efficiency in terms of dimensionless figure of merit ZT.

$$\eta_{max} = \frac{1}{4} ZT \eta_C \tag{23}$$

This optimization is usually carried out with a better model for the heat flow into the hot side of the thermoelectric. The simple model that we have examined leaves out two effects that are import. There is a heat flow associated with the current, which increases the input power and reduces the efficiency. There is also an incremental heat flow out of the thermoelectric, that is often modeled as being half of the total power dissipated in the thermoelectric. Together, this leads to an improved estimate for the hot side heat flux

$$Q_{hot} = \kappa \frac{\Delta T}{L} + \Sigma T J - \frac{L}{2\sigma} J^2 \tag{24}$$

If we recalculate the optimum efficiency using this model, we obtain the results illustrated in Figure 2.

7. Real Thermoelectric Converters

From the previous section, we see that the attainable conversion efficiency of a thermoelectric depends on the material parameters. The goal of many research programs over the past 40 years has been to find thermoelectric materials with values of thermopower, electrical and thermal conductivity such that the dimensionless figure of merit ZT is maximized. The best thermoelectric materials presently available for applications have a figure of merit in the range

$$ZT \sim 2 \tag{25}$$

A thermoelectric converter with a dimensionless figure of merit of 2 would convert heat to electricity at roughly 28% of the Carnot limit.[c] The absolute conversion efficiency for such a thermoelectric converter for a Pons-Fleischmann cell operating near the boiling point is

$$\eta = 0.060 \tag{26}$$

We see that the power gain required for self-sustaining operation is now

$$\frac{P_{xs}}{P_{in}} = 16.7 \tag{27}$$

The efficiency of excess heat production in Pons-Fleischmann cells will need to improve substantially in order to achieve self-sustaining operation with this technology.

8. Discussion

There are several general directions that one can proceed in light of the considerations outlined above. On the one hand, it may be appropriate to begin focusing greater effort on excess heat conversion at higher temperature, since the Carnot limit permits higher conversion efficiencies when the temperature difference is greater. There are many different approaches to this problem that have been discussed at the ICCF conferences and described in the literature:

(1) Miles has proposed taking advantage of the increase in boiling point at ultrahigh concentration of salts in the electrolyte as a route to acqueous electrochemistry above 100^o C
(2) Nonacqueous electrochemistry in solvents with elevated boiling points
(3) Electrochemistry in molten salts
(4) Plasma discharge loading at elevated temperatures, as has been pursued at the Lutch Institute.

For example, if we assume that a high temperature discharge experiment produces excess heat at 1000^o C, then the associated Carnot efficiency is 70%, and one might expect conversion to electricity at close to 20%.

There are ongoing research efforts that have as a goal the development of new converters that have a higher conversion efficiency. New thermoelectric materials are being developed that take advantage of layered materials to hinder thermal conductivity, and reduced dimension to increase the thermopower. Solid-state

[c] A search of commercial suppliers for thermoelectric converters on the web will not show very many devices available yet with a conversion efficiency this high.

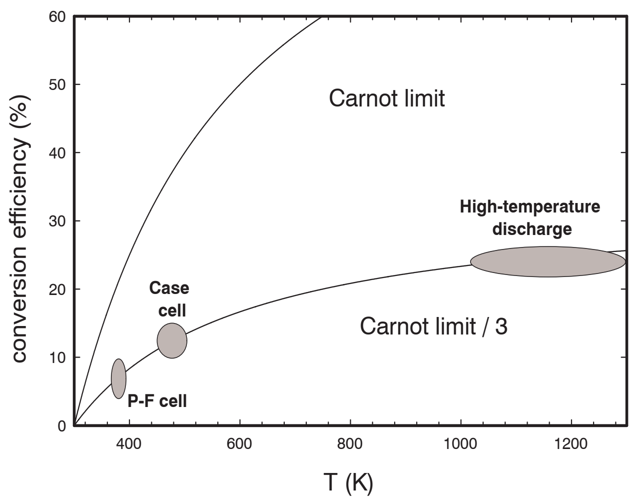

Figure 3. Carnot limit, and Carnot limit divided by 3, as a function of thermal source temperature assuming $T_{cold} = 300K$. The gray bubbles indicate approximate projected operating regimes for some of the different approaches.

thermionic conversion is being explored. Thermoelectric semiconductors with emitter layers and blocking layers have recently shown performance well beyond that of bulk semiconductors. Research in the area of thermophotovoltaics continues to show promise for achieving high conversion efficiency. Industrial electricity production at present is done primarily with gas and steam turbine technology. Absolute conversion efficiencies with these technologies are be in the range of 30%-40%, where the higher numbers correspond to systems with very high operating temperatures and regeneration.

This discussion motivates us to consider approaches to the excess heat problem that do not require electrical drives. Early observations of the "heat after death" effect by Pons and Fleischmann indicated that electrolysis is probably not a prerequisite for excess heat production. The Case cell is of interest in this discussion in that it operates without electrolysis or internal currents, and hence only requires heat to self-sustain. This is an important advantage in the effort to develop self-sustaining excess heat producing systems.

9. Summary and Conclusions

We have considered in this paper very basic issues associated with thermal to electric conversion, in a paper intended to be a tutorial on the topic. The Carnot limit is fundamental to the problem, and we view the Carnot limit as a thermodynamic limit of an ideal converter that does not generate entropy in association with the conversion process. Practical thermal to electric conversion at present achieves conversion efficiencies well below the Carnot limit in the case of small scale converters.

The poor conversion efficiency associated with the Pons-Fleischmann cell leads one to the conclusion that the development of a self-sustaining system with this approach will be very difficult, requiring a power gain of more than 15. This requirement is probably beyond the present capabilities of the most successful groups working in the area.

The basic conclusion from this discussion is that other approaches need to be focused on as candidates for self-sustaining power generation, and ultimately for commercial applications. Excess power generation at elevated temperature should be a fundamental goal, as energy conversion can be more efficient in this case. Excess power generation in systems that require either minimal or no electrical power input are clearly going to play a dominant role in efforts to make self-sustaining devices due to the tremendous advantage of avoiding the conversion cycle completely. Such systems that operate at elevated temperature will have clear advantages in the conversion of thermal to electrical energy.

References

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