

Fig. 15 Correlation of creep buckling theory and secant modulus approach with experimental creep crippling times for long, flat plates of aluminum alloy 2024-0 at 500°F under axial compression with $b/h = 23$, expressed in normalized form.

are necessary in order to establish a base point for the use of normalized theories of creep buckling and creep crippling.

References

- ¹ Gerard, G., "Theory of creep buckling of perfect plates and shells," *J. Aerospace Sci.* 29, 1087-1090 (1962).
- ² Mathauser, E. E. and Deveikis, W. D., "Investigation of the compressive strength and creep lifetime of 2024-T3 aluminum alloy plates at elevated temperatures," NACA TN 3552 (January 1956).
- ³ Deveikis, W. D., "Investigation of the compressive strength and creep of 7075-T6 aluminum-alloy plates at elevated temperatures," NACA TN 4111 (November 1957).
- ⁴ Stein, B. A., "Compressive strength and creep of 17-7 PH stainless-steel plates at elevated temperatures," NACA TN 4296 (July 1958).
- ⁵ Gerard, G. and Papirno, R., "Classical columns and creep," *J. Aerospace Sci.* 29, 680-688 (1962).
- ⁶ Gerard, G. and Papirno, R., "Correlation of plate creep buckling theory with experiments on long plates of aluminum alloy 2024-0 at 500°F," *Aeronaut. Systems Div. TDR 62-865* (September 1962).
- ⁷ Papirno, R. and Gerard, G., "Investigation of creep buckling of columns and plates, Part II: Creep buckling experiments with columns of Ti-7Al-4Mo titanium alloy," *Wright Air Dev. Center TR 59-416* (July 1960).
- ⁸ Papirno, R. and Gerard, G., "Compression testing of sheet materials at elevated temperatures," *Am. Soc. Testing Materials Special Tech. Publ.* 303, pp. 12-13 (1962).
- ⁹ Becker, H., "Handbook of structural stability, Part II: Buckling of composite elements," NACA TN 3782 (July 1957).
- ¹⁰ Gerard, G. and Becker, H., "Handbook of structural stability, Part I: Buckling of flat plates," NACA TN 3781 (July 1957).
- ¹¹ Gerard, G., "A creep buckling hypothesis," *J. Aeronaut. Sci.* 23, 879-882 (1956).
- ¹² Bijlaard, P. P., Wong, R. E., Goldberg, M. A., and Dukes, W. H., "Strength analysis of high-speed-structures," *Wright Air Dev. Center TR 55-305, Part 2, Sec. 7* (October 1955).

Thermogalvanic Energy Conversion

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Conversion from thermal energy to electrical energy has become an increasingly important area for investigation in recent years. A means for obtaining electrical power from thermal energy sources will be described here. The principle upon which this device is based is the change in chemical potential with temperature of a reversible cell. Some electrical and thermodynamic data are given for an elementary examination of device performance. Efficiencies and operating characteristics appear to be interesting for at least limited future application. However, greater understanding of the microscopic behavior is necessary in order to develop and improve materials handling, fabrication techniques, and cell construction.

Introduction

DEVICES that convert heat energy to electricity generally are referred to as thermoelectric generators. These devices almost invariably do not involve mechanical motion of any kind for their operation such as is necessitated in conventional rotating machinery. A well-known example of such static thermoelectric generators uses the Seebeck voltages produced at the junctions of dissimilar metal conductors and semiconductors when suitable temperature differentials are established between junctions.

Many aspects of the performance of thermoelectric devices must be considered in determining the extent of their utility. Among the more desirable and important parameters to be examined, the following may be listed: 1) high power-to-

weight ratio (specific energy drain rate); 2) long operating and shelf life; 3) usable temperature range, both for high Carnot efficiency and in terms of conveniently available temperatures; 4) minimum complexity and moving parts; 5) ease of assembly and repair; 6) compatible materials combinations; 7) in cases of industrial or commercial application, low materials and fabrication costs; 8) capability of withstanding damage due to mechanical vibration, nuclear radiation, thermal shock, etc.; 9) high energy conversion efficiencies; and 10) convenient electrical output characteristics.

This paper will be concerned primarily with presenting the application of the thermogalvanic effect to the problem of thermoelectric power generation. This relatively unexplored approach, also referred to as ionic-thermoelectric conversion, appears promising. However, electrical conduction processes and thermoelectric phenomena in ionically conducting media such as ionic crystals have not received nearly the attention that pure metals and semiconducting materials have.

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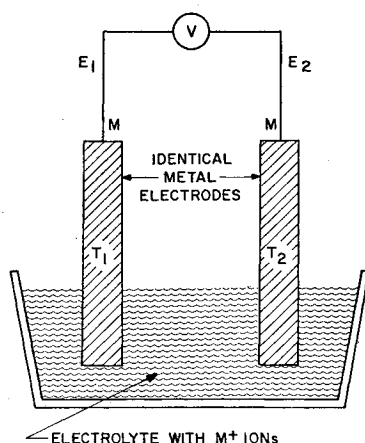


Fig. 1 Symmetrical electrode thermo-cell.

Simple Thermogalvanic Cell

The principle upon which the converters are based perhaps can be best illustrated by describing a simple aqueous solution model. This cell is dependent upon the change of chemical potential with temperature.

Consider two electrodes of the same material (metal), immersed in an electrolyte. The electrolyte in this case is an aqueous solution of a salt of the metal. There exists a potential between each electrode and the electrolyte. If the temperatures of the electrodes are the same, the net voltage across the two electrodes is zero, since they are each of the same magnitude and opposite polarity.

The temperature dependence of the electrode potential E in the electrolyte may be expressed simply as

$$dE/dT = \Delta S/zf \quad (1)$$

when other factors such as the Soret effect are neglected, where z is the charge on the ion, f Faraday number, and ΔS entropy change associated with the electrode reaction for current flow.

Figure 1 is an illustration of the basic cell; E_1 and E_2 are the electrode potentials at the temperatures T_1 and T_2 , respectively, and the net voltage becomes $E_1 - E_2$. When current flows by connecting an electrical load across the electrodes, metal will be deposited at the positive electrode and removed from the negative electrode in the normal fashion for electrolytic conduction. However, since the cell is symmetric, it is theoretically reversible, and the metal may be

restored to the depleted electrode by reversing the polarity of the temperature gradient.

Figure 2 is an illustration of a cell that may be employed in the testing of the system for voltage and current output. For systems employing two concentric copper cylinders with copper sulphate solution between them, the approximate values of the three important parameters are as follows:

$$\begin{aligned} \rho &= \text{electrical resistivity} \approx 5 \text{ ohm-cm} \\ K &= \text{thermal conductivity} \approx 0.004 \text{ w/}^\circ\text{C-cm} \\ dE/dT &= \text{thermoelectric power} \approx 1.0 \text{ mv/}^\circ\text{C} \end{aligned}$$

The spacing between the electrodes can be either very small or baffled to reduce convection.

When operating the cell over a temperature difference of 100°C , from $0^\circ \rightarrow 100^\circ\text{C}$, about 0.10-v open-circuit output is obtained. The current capacity of the device is, of course, dependent upon its internal resistance, which may be altered by designing for a given ratio of effective surface area to electrical path length. The figure of merit M for a $\text{Cu}|\text{CuSO}_4|\text{Cu}$ cell is given as

$$M = \frac{(dE/dT)^2 T_h}{4\rho K} = \frac{1 \times 10^{-6} \times 373}{4 \times 0.004 \times 5} = 0.5\% \quad (2)$$

at a hot temperature of 100°C or 373°K .

The limitation of 100° for the hot electrode temperature imposed upon the cell operation by the boiling point of water at atmospheric pressure suggests a search for other, higher temperature electrolytes. Fortunately, there are many other materials that can be investigated for thermoelectric cell electrolytes over a much wider spread in temperature. Ionic crystals and fused salts present a range of interesting materials. Ionic crystals are mostly simple salts of metals such as the alkali halides and sulfides, and the halides and oxides of various other metals, such as silver, copper, lead, cadmium, etc. Some of the fundamental physics of these structures are discussed by Jost,¹ Dekker,² and Garner.³ An excellent review of the mechanisms of ionic conduction and diffusion also has been prepared by Lidiard.⁴

Before it is possible to judge the potentialities of these materials as thermogalvanic electrolytes, more information concerning their properties must be obtained, and further studies of engineering problems must be made.

The electrolyte employed in a thermogalvanic cell, usually a halide of the electrode metal, is sandwiched between the electrodes. Ions, cations, and/or anions migrate from one electrode to the other, depending upon the temperature gradient and the polarity of the generated emf. The negative electrode accumulates the metallic component, thus growing in size at the expense of the positive electrode. The change in voltage with temperature can be broken into two parts. As in the aqueous cell, the Gibbs-Helmholtz relation may be employed to describe the parameter (dE/dT) , the heterogeneous thermoelectric power, because of the interface reaction between the electrolyte and the metal. Here the changes in entropy or free energy and their temperature dependence must be determined. In addition to this term, there is a homogeneous thermoelectric voltage generated due to the temperature gradient within the salt. Hence,

$$(dE/dT)_{\text{total}} = \alpha_{\text{total}} = \alpha_{\text{het}} + \alpha_{\text{hom}} \quad (3)$$

Measurements have been made with CuBr and AgI as solid salt electrolytes.¹ In the case of the silver system, i.e., $\text{Ag}|\text{AgI}|\text{Ag}$ cell, the mean value of α_{total} between 150° and 500°C is on the order of $0.6 \text{ mv/}^\circ\text{C}$ with an overall internal resistivity¹ for the cell when operated in this fashion of 0.3 ohm-cm . Estimates of the thermal conductivity for AgI over this temperature place it at about $0.004 \text{ w/cm}^\circ\text{C}$. The figure of merit for such a cell then is

$$M = \frac{0.36 \times 10^{-6} \times 873}{4 \times 0.004 \times 0.3} = 6.5\%$$

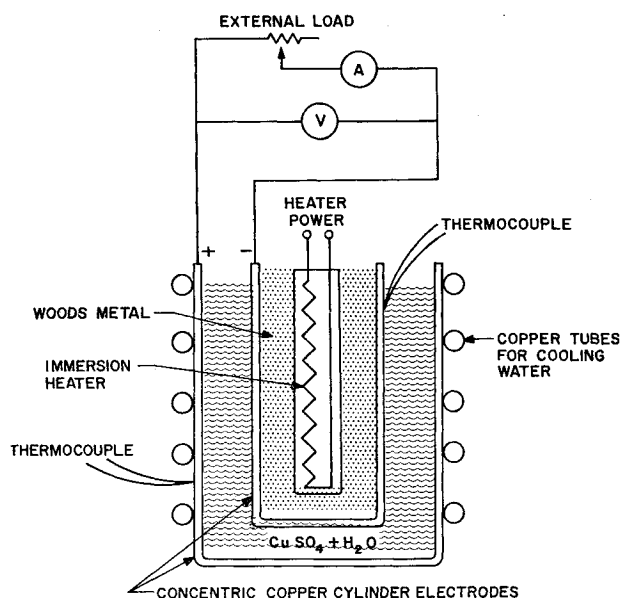


Fig. 2 Aqueous solution thermogalvanic cell.

which is considerably larger than that of the $\text{Cu}|\text{CuSO}_4(\text{H}_2\text{O})|\text{Cu}$ system.

Some of the immediately apparent attributes of thermogalvanic systems are the following:

1) Comparatively high thermoelectric powers (dE/dT) are available. Values in the range of 0.5 to 2.0 mv/°C have been observed or calculated to date as compared to values of 0.3 mv/°C or less with electronic conductors. Fewer series-connected cells therefore are needed to develop convenient current-voltage characteristics.

2) There is low thermal conduction for the various electrolyte materials. Measurements are in the range of 0.02 to 0.002 w/°C-cm.

3) The relatively large number of compounds and materials combinations available for investigation would indicate a reasonable prospect of developing high-efficiency and power-to-weight ratio generators.

4) Ionic materials properties are not particularly sensitive to nuclear radiation damage and consequently are compatible with nuclear heat sources.

There are also, however, a number of obvious disadvantages or difficulties associated with this approach to energy conversion. Among these problems, one may list the following as the most immediate:

1) Even though output voltages from such cells are quite high, most ionic materials have rather high resistivities in the low temperature ranges. This high resistivity, of course, reduces the figure of merit for these materials. Resistivities anywhere in the range of 0.01 to 10^6 ohm-cm are encountered, depending upon the compound and the temperatures.

2) Each metal electrode cell has only a finite life when operated in only one direction. This problem could be overcome partially by making provision for reversing the cells or, in some cases, by choosing appropriate materials combinations and cell construction so that there would be no need for periodic reversal.

3) Cell construction is perhaps not quite as simple as that encountered in semiconductor materials because of lack of mechanical rigidity of the electrolytes and because of the mass transport process.

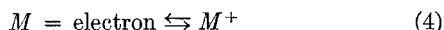
Basic Materials Parameters

A fair indication of converter operation can be obtained by considering the three basic macroscopic parameters: the electrical resistivity ρ , the thermal conductivity K , and the thermoelectric coefficient α . The third parameter, α , is perhaps deserving of the most attention from both the experimental and theoretical standpoints.

This thermoelectric coefficient α may be reduced to two major components, α_{het} and α_{hom} , as mentioned before.⁵⁻⁷

The heterogeneous, temperature-dependent voltage arises from the chemical potential of the electrode N making equilibrium contact with an electrolyte containing M^+ ions.

The energy and corresponding electrical potential associated with the process



of extracting an atom from the metal electrode surface and producing an ion varies with the temperature in the vicinity of the electrode. This reaction commonly is referred to as that of the half-cell and gives rise to a single-electrode reaction potential. From thermodynamic considerations, it can be shown that, since

$$\Delta F = -zEf \quad (5)$$

$$\Delta F = \Delta H = T\Delta S = \text{free energy change at constant pressure} \quad (6)$$

the Gibbs-Helmholtz equation may be derived in which

$$\Delta H = -zf[E - T(dE/dT)_p] \quad (7a)$$

or

$$dE/dT = \Delta S/zf = \alpha_{\text{het}} \quad (7b)$$

Another manner of expressing α_{het} is in terms of the activity coefficients for the metal and the ions in the electrolyte. The general expression is of the form

$$E = E_0 + \frac{RT}{zf} \log \left[\frac{\text{product of activities of reactants}}{\text{product of activities of resultants}} \right] \quad (8)$$

where E_0 is also temperature dependent.⁸ The activities a used in Eq. (8) are related to the activity coefficient ω as $a = \omega c$, where c is the ion or metal concentration.

The activity coefficient for solid metals is set conveniently at unity. Thus, the heterogeneous contribution to the thermoelectric potential may be regarded as being due to the difference in energy required to extract an atom from the metal at the hot electrode and to place the corresponding ion into either the aqueous solution or the ionic crystal interstitial position or vacancy, as compared to the energy required for the reverse process at the cooler electrode. Hence, for an ionic crystal MX ,

$$\alpha_{\text{het}} = (1/zf) [\Delta S(M^+ \text{ in } MX) - \Delta S(M^+ \text{ in } M)] \quad (9)$$

Investigators have performed a limited number of experiments with AgBr to determine the relative values of the thermoelectric powers and their theoretical implications. Lidiard and Howard⁶ have presented an analysis of the factors giving rise to α_{het} and α_{hom} . It has been shown that α_{het} for a solid salt electrolyte may be given as

$$\alpha_{\text{het}} = (1/zf) [(\partial u_i / \partial T) + \Delta S(M^+ \text{ in } M)] \quad (10)$$

where u_i is the chemical potential of an interstitial ion in a region of density n_i of interstitial ions.

When a temperature gradient is established across a pellet of ionically conducting material, i.e., ionic crystal, an imbalance in lattice defect concentration or interstitial and vacancy concentration is set up. Since the potential wells associated with the defect sites are functions of temperature, the ion transition probabilities are different at the cool and hot ends of the pellet. One also may consider this, in part, to constitute a change in "solubility" of defects as a function of temperature.

An expression^{5,6} arrived at by Howard and Lidiard by employing the phenomenological approach due to Onsager is as follows:

$$\alpha_{\text{hom}} = \frac{dE}{dT} \left(\frac{dx}{dT} \right) \approx \frac{2q_i + \Delta H_F}{2T} \quad (11)$$

where

$$q_i = \text{heat of transport for interstitial ions (Jost,}^1 \text{ p. 526)}$$

$$\Delta H_F = \text{enthalpy of Frenkel defect pair formation}$$

Equation (11) is applicable to the situation where Frenkel defects are the dominant type of crystal imperfections if, for the sake of simplicity, it be assumed that the conduction and α_{hom} are due to the migration of interstitial ions.

Since the temperature T appears in the denominator, one would expect α_{hom} to decrease with T . However, it is necessary also to examine the manner in which q_i and ΔH_F change with T . The term q_i , for example, may be regarded as the energy needed to move the ion out of an initial interstitial site plus the energy needed to place the ion into a final interstitial site.

Thus, changes in the height and shape of the potential wells associated with ion sites must be explored rather thoroughly before significant conclusions can be reached as to the fashion in which the thermoelectric power varies with the crystal temperatures. Both q_i and ΔH_F tend to decrease as the temperature becomes greater, tending to lower the value of α_{hom} . This general decrease in α_{hom} is substantiated by

Table 1 Homogeneous thermoelectric power for AgBr⁷

$T, ^\circ\text{K}$	$\alpha_{\text{hom}}, \text{mv}/^\circ\text{C}$
455	1.33
476	1.23
500	1.11
526	1.00
556	0.882
588	0.770
625	0.660
667	0.570

experimental evidence such as the data obtained by Patrick and Lawson.⁷ Data were obtained for both pure and doped AgBr. Table 1 is a reproduction of these data of α_{hom} for pure AgBr. The values were arrived at by measuring the total thermoelectric power α_t over 10° temperature differentials and subtracting $0.140 \text{ mv}/^\circ\text{C}$ from α as the estimated constant value of α_{het} .

Engineering Consideration for Device Design

The overall efficiency of an ionic cell is defined here as the ratio of the electrical output power divided by the total thermal input power when the cell output has been terminated into its electrical image impedance. When operating a cell in this fashion, the maximum output power for a given available temperature differential is obtained. This does not, however, give the maximum efficiency of operation. These efficiencies and associated figures of merit do not account for other power losses such as ohmic losses in connecting leads or thermal losses to the outside along the length of a cell. If the cell shown in Fig. 3 is taken as a schematic representation, then the electrical power output is given as

$$P_{\text{out}} = \frac{1}{4R} \left[\int_{T_1}^{T_2} \alpha_i(T) dT \right]^2 = \frac{E_{oc}^2}{4R} \quad (12)$$

where

$$\begin{aligned} E_{oc} &= \text{open circuit voltage for a cell with } \Delta T = T_2 - T_1 \\ R &= \text{load resistance of cell} = \rho(l/a) \end{aligned}$$

If α is assumed to be constant with temperature, i.e., using the average value of $\alpha(T)$, and if the thermal loss or gain due to internal Joule heating of the pellet is ignored for the sake of simplicity, then

$$P_{\text{out}} = \frac{\alpha_{av}^2 \Delta T^2}{4\rho(l/a)} \quad (13)$$

The thermal power that must be supplied to the hot end of the pellet due to thermal conduction and Peltier cooling at the hot junction is

$$P_{\text{in}} = K\Delta T \frac{a}{l} + \frac{\alpha_{av}\Delta T \times T_2\alpha_2}{2\rho(l/a)} \quad (14)$$

The total efficiency of the cell is then

$$\text{eff} = \frac{P_{\text{out}}}{P_{\text{in}}} = \frac{\alpha_{av}^2 \Delta T}{4\rho K + 2\alpha_{av}T_2\alpha_2} \quad (15)$$

If the efficiency is low, i.e., in the order of 10% or less, a valid approximation to Eq. (15) is

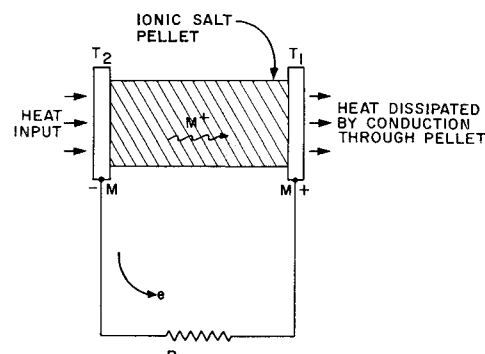
$$(\text{eff})_{\text{approx}} \approx \alpha_{av}^2 \Delta T / 4\rho K \quad (16)$$

A term that has found frequent use recently, called the figure of merit M , is defined as

$$M = (\text{eff}) \times (T_2/\Delta T) \quad (17)$$

Using the approximation for efficiency, the first estimate of figure of merit becomes

$$M_1 = (\alpha_{av}^2 / 4\rho K) \times T_2 = Z \times T_2 \quad (18)$$

**Fig. 3 Solid electrolyte thermogalvanic cell.**

and a second approximation is

$$M_2 = \frac{\alpha_{av}^2 \times T_2}{4\rho K + 2\alpha_{av}\alpha T_2} \quad (19)$$

Figure 4 illustrates the manner in which the materials factor $Z = \alpha_{av}^2 / \rho K$ varies with α and the product ρK . Obviously, Z is most sensitive to α , since α appears as a squared term. For this reason and because of the practical engineering requirements for reasonably high voltages, large values of α are desirable at the expense, perhaps, of higher ρ and K . The quantity Z affords a good comparison between various power converter materials, which is dependent only upon the materials properties. Comparison also is made in Fig. 4 between currently available semiconductor thermoelectric junctions and various galvanic cells.

Table 2 is a brief listing of thermogalvanic data for some common ionic salts. The calculated value of α_t given in the table is the thermostatic portion of the total thermogalvanic potential as termed by Holtan.⁹ This thermostatic portion is due largely to the electrode process entropy changes and is frequently calculable. In many instances the thermostatic quantity is very nearly equal to the total potential.

Reasonably accurate estimates of α may be made from the phenomenological relation, Eq. (20), employed by Holtan:

$$f \frac{dE}{dT} = \alpha = \sum_{k=1}^n \frac{t_k}{z_k} S_k^* - S_{e1}^* - \Delta S + \sum_{k=1}^n \frac{t_k}{z_k} S_k + S_{e1} \quad (20)$$

where

$$\begin{aligned} f &= \text{Faraday number} \\ t_k &= k \text{ ion transport number} \\ z_k &= \text{number of equivalents of the } k \text{ ion} \\ S_k^* &= k \text{ ion transport entropy in the electrolyte} \\ S_{e1}^* &= \text{electron transport entropy in the electrolyte} \\ S_{e1} &= \text{electron transfer entropy in the metal} \\ S_k &= k \text{ component external transfer entropy} \\ \Delta S &= \text{entropy change for the electrode reaction} \end{aligned}$$

Depending upon the manner in which the electrical charge is transported through the electrolyte, Eq. (20) usually simplifies into an expression involving only thermodynamic terms of known values. If the comparatively small contributions of the transport entropies are ignored, for salts whose transport numbers k are available, calculations may be performed for evaluating α with only the entropies $S(MX)$, $S(M)$, and $S(X)$ over the temperature range of interest. Good agreement of these theoretical potentials with available empirical values was obtained by Holtan for a number of salts.

Halogen reversible electrodes generally produce higher thermogalvanic potentials than that obtained with the corresponding metal electrodes, as is indicated by the three systems AgCl, PbCl₂, and PbBr₂ in Table 2. Table 3 presents conductivity data at various temperatures for some of the same salts. Thermal conductivity values are generally

Table 2 Approximate thermogalvanic data for some salt systems

Salt system	Charge carriers	Thermogalvanic coeff. ^a α , mv/°C		Temp. range, °C	Ref.	Salt melting point, °C	Salt boiling point, °C
		Meas.	Calc.				
Ag AgI(s) Ag	cation	0.60		140 to 500	10	550	
Ag AgCl(s) Ag	cation	0.80	0.80	350 to 460	9,11,12	455	1550
Cl ₂ AgCl(s) Cl ₂	cation	1.29	1.29	300 to 410	9,11		
Ag AgCl(l) Ag	cation anion	0.40		460 to 650	9		
Pb PbCl ₂ (s) Pb	anion	0.54	0.54	200 to 470	9,11,13	501	950
Cl ₂ PbCl ₂ (s) Cl ₂	anion	1.28	1.28	260 to 400	9,11		
Pb PbBr ₂ (s) Pb	cation anion	0.40		350	9,11	373	916
Br ₂ PbBr ₂ (s) Br ₂	cation anion	1.20	1.39	320	9,11		
Ag AgBr(s) Ag	cation		0.90	230 to 400	9,11	434	700
Cu CuCl(s) Cu	cation		0.82	300 to 400	9,11	422	1366
I ₂ AgI(s) I ₂	cation		1.25	140 to 500	(theoretical)	550	
Ag AgNO ₃ Ag	cation anion	0.30 to 0.40	0.345	300 to 1000	17,18	212	

^a Positive algebraic sign of α indicates that the cold terminal is positive, e.g., electron flow in the external circuit is from the hot terminal to the cold.

low, but the electrical resistivity for most salts below their melting points is far too great. For example, the resistivity of AgCl(s) over a reasonable temperature range varies from 10 to 40 ohm-cm, whereas the molten salt AgCl(l) has a value of about 0.2 ohm-cm. Unfortunately, the thermoelectric power also has dropped significantly with the change in phase.

The Z value for the Ag|AgI(s)|Ag system is approximately 0.3×10^{-3} , which is somewhat lower than those for semiconductor materials. However, these values are truly meaningful only when further qualified as to the temperature range over which the Z value is valid. Since the thermogalvanic potential is in the vicinity of 1.0 mv/°C for the better materials, the product ρK cannot be much greater than 2×10^{-3} in order for efficiencies to be competitive with other conversion methods.

If approximate magnitudes are assigned to the fused salt systems, an estimate of the Z values may be made. Most fused salts have resistivities lying within the limits of 0.10 to 1.0 ohm-cm and thermal conductivities within the bounds of 0.001 and 0.010 w/°C-cm. Employing a mean value of about 1.0 mv/°C for α for a $X_2|MX(l)|X_2$ cell, the Z factor is then somewhere between the broad limits of 10×10^{-3} to 0.10×10^{-3} .

Besides evaluating the performance of ionic salts as thermogalvanic converters in terms of α , ρ , and K , other properties

must be investigated when considering these materials as practical power generators.

Materials merely having electrical and thermal coefficients giving high performance efficiency values are not necessarily useful for effective converter application. The properties of importance may be placed in two categories; the first pertains to the fundamental properties of the materials themselves and the second more directly to thermoelectric converter operation.

The materials properties are as follows:

- 1) Salt melting and softening effects on device design.
- 2) Metal electrode melting point limitations for $M|MX|M$ systems.
- 3) Changes in specific volume of salt with temperature, with the resultant electrode contact problems.
- 4) Chemical stability, decomposition temperatures, and pressures of the electrolyte.
- 5) Electrode corrosion by the fused salt or the oxidizing anion component.
- 6) Usable range of values for α , ρ , and K over a practical temperature range for a given materials combination.
- 7) Growth of metal filaments through the electrolyte, resulting in electrical shorting of $M|MX|M$ systems.
- 8) X_2 gas diffusion rates through porous, inert electrodes for $X_2|MX|X_2$ cells.

The second set is the converter design factors:

- 1) Encapsulation problems due to vapor pressures of constituents.

Table 3 Electrical and thermal conduction data^{10,14-17}

Salt	Electrical resistivity, ohm-cm		Thermal conductivity K , w/°C-cm		Melting point of salt, °C
	Value	Temp., °C	Value	Temp., °C	
AgI	0.30	150 to 500	0.004	200	550
	0.40	550			
	0.45	700			
AgCl	36	400	0.011	0	455
	8.3	455	0.006	100	
	0.216	700			
PbCl ₂	630	400	0.0054	15	501
	200	501	0.0033	20	
PbBr ₂	0.52	600			
	1300	300	0.0026	20	373
AgBr	330	373			
	2.3	400	0.010	0	434
CuCl	1.4	434	0.006	100	
	0.29	700			
	5.0	400			422
AgNO ₃	2.0	422			
	0.29	500			
	0.50 to 0.20	300 to 1000	0.008	(fused salt)	212

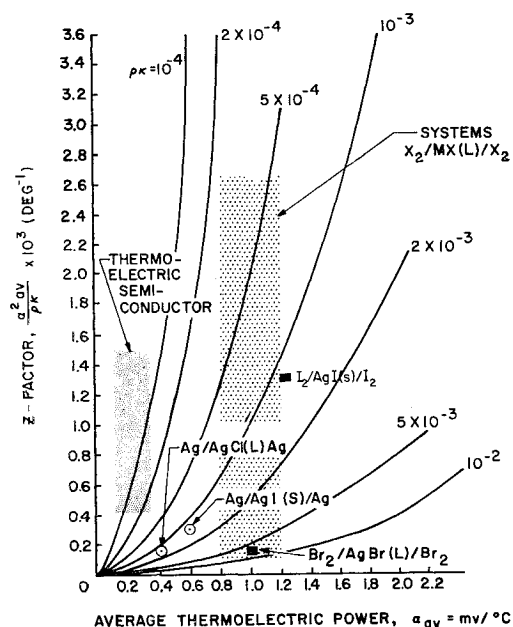


Fig. 4 Variation of figure of merit with thermoelectric potential. Comparison of various materials.

- 2) Absence of mechanical rigidity with fused salt cells.
- 3) Power/weight ratio of a converter device.
- 4) Availability and cost of materials such as electrodes and supporting structures.
- 5) Development of suitable methods of cooling and heating the electrodes.
- 6) Provision for cell reversing, if needed, or continuous operation by material recycling techniques.
- 7) Minimizing heat losses due to necessity for metallic return path for current flow from hot to cool terminals.
- 8) Use of more than one salt to cover a larger spread in temperature; multiple stage or stacked arrays.

Each of the previous items must be analyzed on the basis of fabricating a usable device for specific applications, since one design or materials combination may prove quite impractical for other applications. There are some instances where, for example, finite cell life can be tolerated. Here a simple cell design may be employed for which no involved reversing procedure need be provided. However, the device must have advantages over other more conventional power sources, such as longer shelf life, greater power/weight ratio, or greater adaptability to available thermal energy sources.

Summary

In addition to the metal halide salts, recent investigation has been made by Sundheim^{17, 18} and Schneebaum¹⁷ into the $\text{Ag}|\text{AgNO}_3|\text{Ag}$ system. An average value of $\alpha = 0.345$ $\text{mv}/^\circ\text{C}$ for the thermopotential, as cited by Sundheim, gives the rather low figure of about $5 \times 10^{-5} \text{ deg}^{-1}$ for the Z factor of the materials. Practical converter devices employing solid or fused salt electrolytes have been suggested by others in the literature.¹⁹ Weininger of the General Electric Research Laboratories in a 1959 patent²⁰ outlined a converter system using the symmetrical thermocell $\text{I}_2|\text{AgI}|\text{I}_2$ with gas diffusion electrodes for continuous operation.

Laboratory experiments conducted by Weininger^{21, 22} with silver halide galvanic cells also have provided additional material data. His recent studies with the iodine-silver iodide cell obtained thermoelectric potentials of 1.2 to 1.4 $\text{mv}/^\circ\text{C}$ over the temperature range of 150° to 500°C for the iodine electrodes. A paper²³ describing these experiments has been submitted to the Electrochemical Society for publication.

For further data, both experimental and theoretical, the reader may refer to various sources in the literature, such as the more recent publications by Kiukkola,²⁴ Pitzer,²⁵ and Delimarskii.²⁶ As more materials data become available in the future, the question of potential practicality of thermogalvanic systems may be answered more properly.

References

¹ Jost, W., *Diffusion in Solids, Liquids and Gases* (Academic Press, New York, 1952), Chap. IV.

² Dekker, A. J., *Solid State Physics* (Prentice-Hall Inc., Englewood Cliffs, N. J., 1957), Chap. VII.

³ Garner, W. E., *Chemistry of the Solid State* (Academic Press, New York, 1955), Chaps. I and II.

⁴ Lidiard, A. B., "Ionic conductivity," *Handbuch der Physik*, edited by S. Flugge (Springer Verlag, Berlin, 1957), Vol. XX, pp. 246-348.

⁵ deGroot, S. R., "Thermoelectricity," *Thermodynamics of Irreversible Processes* (North-Holland Publishing Co., Amsterdam, 1951), Chap. VIII.

⁶ Howard, R. E. and Lidiard, A. B., "Thermoelectric power of ionically conducting crystals," *Phil. Mag.* **2**, 1462-1467 (1957).

⁷ Patrick, L. and Lawson, A. W., "Thermoelectric power of pure and doped AgBr ," *J. Chem. Phys.* **23**, 1492-1495 (1954).

⁸ Potter, E. C., "Cell and electrode potentials," *Electrochemistry, Principles and Applications* (Macmillan Co., New York, 1956), Chap. IV.

⁹ Holtan, H., "Electric potentials in thermocouples and thermocells," M.S. Thesis, Univ. Utrecht (1953).

¹⁰ Zito, R., Jr., unpublished experimental data (September 1958)

¹¹ Reinhold, H., "Solid cells, in particular thermoelements, solid electrolytes," *Z. Anorg. Allgem. Chem.* **171**, 181-230 (1928).

¹² Reinhold, H. and Blachny, A. Z., "Thermoelectric investigations on solid electrolytes," *Electrochem.* **39**, 290-305 (1933).

¹³ Tubandt, C., *Handbook Exptl. Phys.* **XII**, 383 (1932).

¹⁴ Conway, B. E., *Electrochemical Data* (Elsevier Publishing Co., Houston, Texas, 1952), Chap. VIII.

¹⁵ Gray, D. E. (ed.), *American Institute of Physics Handbook* (McGraw-Hill Book Co. Inc., New York, 1957), pp. 5-185-5-197, 4-72-4-73.

¹⁶ Washburn, E. W. (ed.), Natl. Res. Council, *International Critical Tables* (McGraw-Hill Book Co. Inc., New York, 1929), Vol. 5, pp. 216-233.

¹⁷ Schneebaum, R. and Sundheim, B., "Thermoelectric properties of the silver nitrate and sodium nitrate system," *Discussions Faraday Soc.* **32**, 197-202 (1962).

¹⁸ Sundheim, B., "Molten salts vs. thermoelectric materials," *Thermoelectric Materials and Devices*, edited by I. B. Cadoff and E. Miller (Reinhold Publishing Corp., New York, 1960), Chap. 14.

¹⁹ Christy, R. W., "Ionic materials," *Thermoelectric Materials and Devices*, edited by I. B. Cadoff and E. Miller (Reinhold Publishing Corp., New York, 1960), Chap. 12.

²⁰ Weininger, J. L., solid electrolyte thermocell, to General Electric Co., U. S. patent 2,890,259 (June 9, 1959).

²¹ Weininger, J. L., "Halogen-activated solid electrolyte cell," *J. Electrochem. Soc.* **105**, 439-441 (1958).

²² Weininger, J. L., "Iodine-activated solid electrolyte cell for use at high temperature," *J. Electrochem. Soc.* **106**, 475-481 (1959).

²³ Weininger, J. L., "Thermogalvanic cells with silver iodide as a solid electrolyte," *J. Electrochem. Soc.* (to be published).

²⁴ Kiukkola, K. and Wagner, C., "Measurements on galvanic cells involving solid electrolytes," *J. Electrochem. Soc.* **104**, 379-387 (1957).

²⁵ Pitzer, K. S., "Thermodynamics of thermocells with fused or solid electrolytes," *J. Phys. Chem.* **65**, 147-150 (1960).

²⁶ Delimarskii, Iu. K. and Markov, B. F., "Electric conduction and ionic transfer in fused salts," *Electrochemistry of Fused Salts* (Sigma Press, Washington, D. C., 1961), Russian transl., Chap. I.