

Sept. 17, 1968

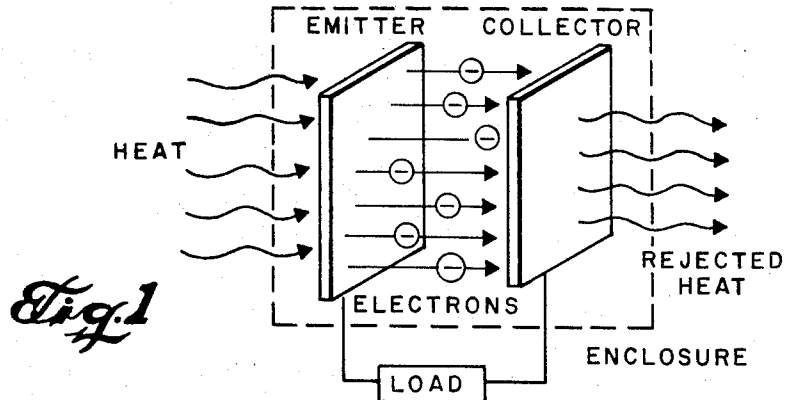
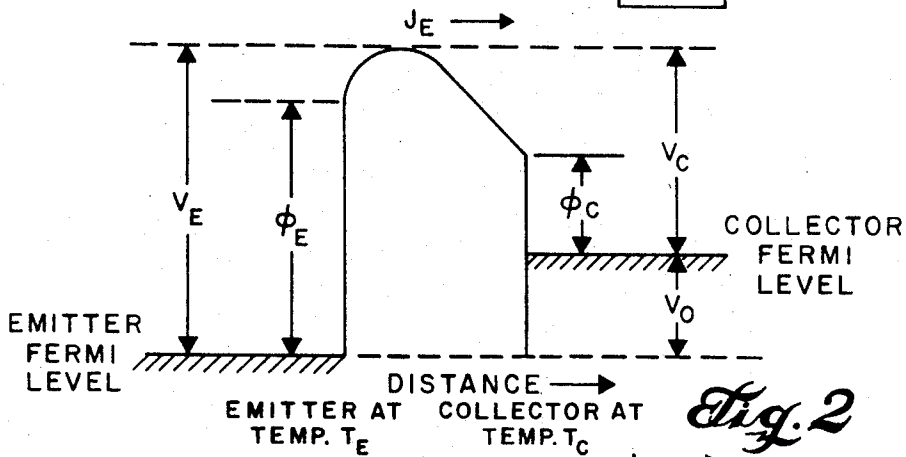
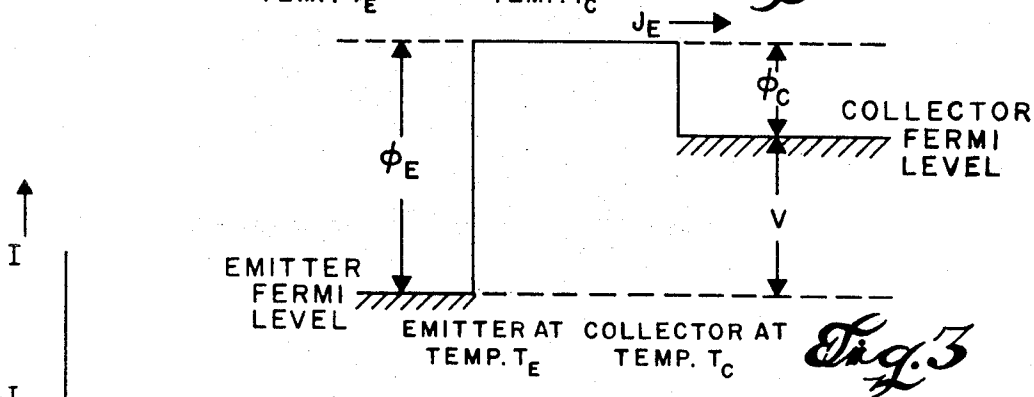
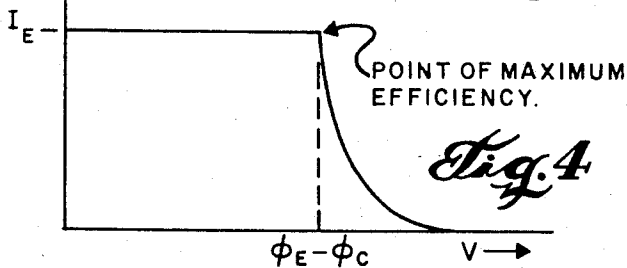
R. A. CHAPMAN ET AL

3,402,074

ENERGY CONVERTER

Filed March 23, 1964

2 Sheets-Sheet 1



INVENTOR
Richard A. Chapman
John J. Connolly Jr.
BY
Harold Levine
ATTORNEY

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2 Sheets-Sheet 2

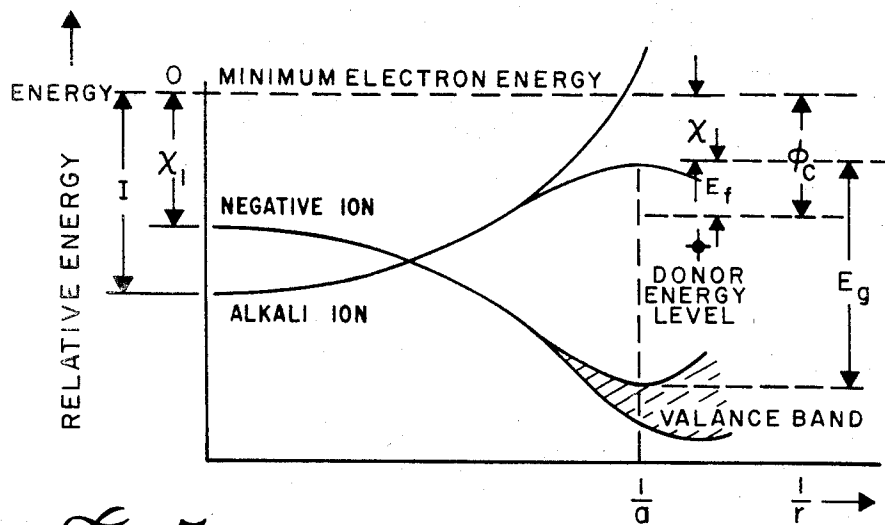


Fig. 5

RECIPROCAL OF INTERATOMIC SPACING

Fig. 6

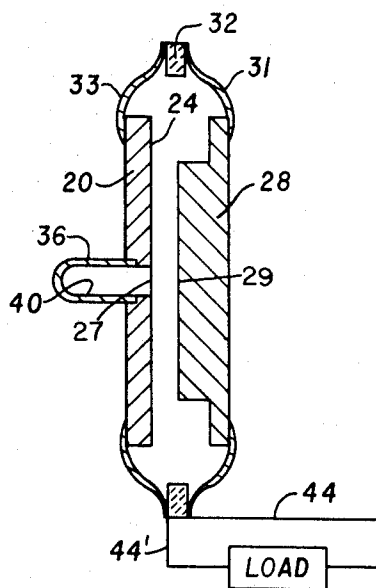
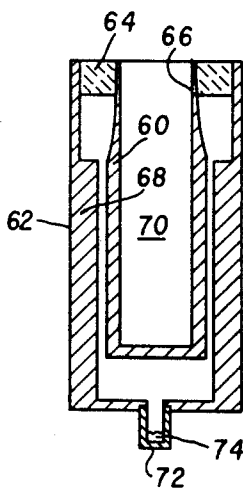


Fig. 7

INVENTOR
Richard A. Chapman
John J. Connelly Jr.
Hazel Levine
ATTORNEY

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3,402,074

ENERGY CONVERTER

Richard A. Chapman, Richardson, Tex., and John J. Connelly, Jr., Chevy Chase, Md., assignors to Texas Instruments Incorporated, Dallas, Tex., a corporation of Delaware

Original application Mar. 22, 1963, Ser. No. 267,179.

Divided and this application Mar. 23, 1964, Ser. No. 353,887

3 Claims. (Cl. 117-224)

This application is a division of application Ser. No. 267,179, filed Mar. 22, 1963, in the name of Richard A. Chapman and entitled, "Energy Converter."

The present invention relates to a thermionic converter for converting heat energy to electrical energy. More particularly, it relates to a thermionic converter containing cesium vapor in the interelectrode spacing and having an improved, low thermionic work function electron collector that is stable in the cesium vapor.

A thermionic converter consists of a hot electron emitter and a cooler electron collector in spaced opposing relation to the emitter, and the two are sealed in a vacuum or a gas-filled enclosure. An electron in the emitter material can escape if it has a velocity component normal to the emitting surface with a thermal energy relative to the Fermi level greater than the thermionic work function of the particular emitter material. As the emitter temperature is increased, the number of electrons which can escape the emitter is increased according to the well-known Richardson equation. When the electrons are collected by the collector electrode, they lose an amount of energy as heat which is equal to the work function of the collector material. If the work function of the emitter is greater than that of the collector, there will be an excess potential energy available which, at maximum power, is equal to the difference in work functions. This excess potential energy can be used to provide an electrical output voltage to a load across the collector and emitter.

The maximum power output of the converter is equal to the difference in the work functions times the Richardson electron current from the emitter. Thus two ways are suggested for increasing the maximum power output, which are to increase the difference between the emitter and collector work functions or to increase the Richardson current. One way in which the former can be accomplished is by increasing the emitter work function, but at the same time, the disadvantage of a decrease in the Richardson current may result. One way in which the latter can be accomplished is by decreasing the emitter work function to increase the Richardson current, although the disadvantage of reducing the magnitude of the difference between the emitter and collector work functions results. Other consequences of choosing the former is that the selection of an emitter material of very high work function necessitates a correspondingly high emitter operating temperature. At least two disadvantages result from this approach; one is that some materials of high work function decompose at the temperature required to cause substantial electron emission, and the other is that such an elevated operating temperature is undesirable in that a thermal source at this temperature may not be available, special fabrication of the device is required to withstand the temperature involved, etc.

On the other hand, a suitable electron collector material that has a very low work function makes possible the

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use of an emitter material of intermediate work function, yet at the same time a reasonable emitter temperature can be used to produce a high power output. Up until the time of this invention however, no material had been found suitable for use as an electron collector that was characterized by a work function less than that of cesium-coated metals, which have a work function of about 1.6 electron-volts, with the exception of silver-oxide which had been reacted with cesium. The latter material is characterized by cesium reacting with the silver-oxide to form cesium-oxide doped with silver, and this material possesses a work function of about 1.0 electron-volt (e.v.) at a temperature of about 400° K. However, it also decomposes rapidly and has a short operating lifetime in the continued presence of cesium vapor.

As will be explained hereinafter, thermionic converters are often provided with cesium vapor in the interelectrode spacing to neutralize the space charge barrier caused by the electron flow, and the emitter current is thus increased. The present invention has as its primary object the provision of compositions for use as the collector of a thermionic converter containing cesium in the interelectrode spacing, where the collector is stable in the cesium vapor and the work function of which is lower than heretofore obtainable. Each of the compositions of this invention contains cesium as a major constituent thereof to contribute to its stability in cesium vapor. Thus the converter can be operated at a much lower temperature than previous devices and yet provide as much or more useful power output.

Another object is to provide a thermionic diode having a stable, low work function collector composition where cesium gas is used in the interelectrode spacing of the diode and one of the major constituents of the anode composition is cesium.

A feature of this invention is the use of cesium in conjunction with a semiconductor element to provide the improved collector hereinbefore referred to.

Other objects, features, and advantages will become apparent from the following detailed description of the invention, including preferred embodiments thereof, when taken in conjunction with the appended claims and the attached drawing wherein like reference numerals refer to like parts throughout the several figures, and in which:

FIGURE 1 is a simplified schematic view of a thermionic converter illustrating the principle of operation involved;

FIGURE 2 is a graphical illustration of the potential distribution between the emitter and collector of the converter of FIGURE 1 and shows the relative magnitudes of the work functions of the emitter and collector;

FIGURE 3 is a graphical illustration of the potential distribution between the emitter and collector of the converter of FIGURE 1 when the electron-space charge potential barrier has been completely neutralized by positive cesium ions interjected in the region between the emitter and collector;

FIGURE 4 is a graphical illustration of the volt-ampere characteristics of a converter having a potential distribution as shown in FIGURE 3;

FIGURE 5 is a graphical illustration of the electron energy levels of the positive and negative ions of an alkali-halide compound as a function of interionic spacing, used for the purpose of a model for the collector compositions of this invention;

FIGURE 6 is a side elevational view in section of one embodiment of a thermionic converter; and

FIGURE 7 is a side elevational view in section of another embodiment of a thermionic converter.

To better understand the invention, a brief discussion of a conventional thermionic converter is given where reference is had to FIGURE 1 which is a simplified schematic view of a thermionic converter. The converter comprises a first electrode or emitter, the material of which is a good electron emitter at an elevated temperature and a spaced, opposing second electrode or collector for collecting the electrons from the emitter. The emitter and collector are sealed under vacuum or a low-pressure gas by a suitable enclosure. The emitter is heated by any suitable means to a temperature sufficient to provide sufficient electrons with energies greater than the work function of the material, thus causing many electrons to "boil" off the emitter. The residual kinetic energy of the electrons causes them to travel to the surface of the collector, where they lose potential energy in an amount equal to the work function of the collector material. Since the electrons originally had potential energy in an amount equal to the work function of the emitter material, the maximum power available for useful work through a load connected externally across the emitter and collector is equal to the difference in the work functions of the emitter and collector material times the Richardson current from the emitter.

The potential distribution of the electrons between the emitter and collector of a vacuum sealed, thermionic converter is shown graphically in FIGURE 2, where the emitter is illustrated at the left. In order for the electrons to escape the emitter, they must have velocity components normal to the emitting surface which represent an energy relative to the Fermi level greater in amount than the work function ϕ_E of that material, which is the difference in energy between a zero kinetic energy electron just outside the surface of the emitter and the energy of an electron at the Fermi level energy of the material. In a vacuum diode, an "electron-cloud" or potential barrier V_E , hereinafter referred to as a space charge barrier is created between the emitter and collector when an electron flow is established. If the electron has sufficient kinetic energy, it will overcome this barrier and travel to the collector. Thus the electrons in the emitter must have sufficient energy to overcome this potential barrier in addition to the work function. In FIGURE 2 the total potential required for an electron to reach the collector is represented by V_E , which is equal to the work function ϕ_E plus the additional potential barrier due to the space charge. Thus at a given temperature, the electron current will be reduced much below the Richardson current from the emitter, and thus the maximum power is reduced. For a more complete discussion of the thermionic diode in this respect, reference is had to Kaye and Welsh, *Direct Conversion of Heat to Electricity*, John Wiley & Sons, Inc., New York, 1960, chap. 7.

It has long been known that the space charge can be reduced or completely neutralized by the addition of positive ions in the space between the emitter and collector. Reference is again had to chapter 7 of the Kaye and Welsh publication, supra, for a discussion of this topic. The best substance for neutralizing the space charge is cesium gas, in which a reservoir of cesium is included within the diode enclosure and is heated sufficiently to convert it to a vapor. The neutral cesium atoms in contact with the hot emitter become ionized and drift into the diode space as positive ions, thus neutralizing the space charge. Cesium absorbs on the cooler collector surface in the form of a film of ions, which as indicated earlier provide in effect a collector of low work function, viz, about 1.6 e.v. Thus the cesium serves to two purposes, one of which is to neutralize the space charge and the other of which is to reduce the work function of the collector. All of this is well known in the art. A graphical illustration showing the potential distribution in the diode space for a completely neutralized space charge using cesium ions is shown

in FIGURE 3, where the electrons leave the emitter surface with a potential equal to the work function ϕ_E , and travel to the collector without losing or gaining potential.

In FIGURE 4 there is illustrated in graphical form the theoretical volt-ampere characteristics of a thermionic diode, which acts as a constant current generator. The ordinate represents collector current, or current flowing in an external load, and the abscissa represents the output voltage across the external load connected across the emitter and collector. Assuming the diode to be operating under the Richardson saturation current I_E , the collector I_C flowing in the external load will equal I_E if the output voltage is less than $\phi_E - \phi_C$. This condition prevails when the load impedance is less than the internal impedance of the diode. As the load impedance is increased to where the output voltage is equal to $\phi_E - \phi_C$, maximum efficiency will have been achieved. Application of a positive external voltage in an attempt to further increase the collector current I_E results in a decrease in efficiency as shown by the curve of FIGURE 4. Thus it is seen that the maximum efficiency is achieved when the output voltage is equal to $\phi_E - \phi_C$, and by increasing the magnitude of this quantity, more power output can be gained.

According to the present invention, a stable cesium compound semiconductor material collector is provided that is suitable for use as very low work function collectors in a thermionic converter containing cesium vapor between the electrodes, thus maximizing the quantity $\phi_E - \phi_C$ without reducing the Richardson current. To illustrate the effectiveness of decreasing the collector work function, a converter, the emitter of which is to emit 5 amps/cm.² at an operating temperature of 1300° C., must have an average effective work function of 2.42 e.v. Ideally, the maximum power density that can be delivered by the converter is equal to the emitter Richardson current (5 amps/cm.²) multiplied by the quantity $\phi_E - \phi_C$. Conventional collectors in which cesium coated refractory metals are used have a work function of about 1.6 e.v. Thus the maximum power density is 5 amps/cm.² times the difference in work functions $\phi_E - \phi_C$ (2.42 e.v.—1.6 e.v.), or is equal to 4.1 watts/cm.². A collector material of work function of 1.3 e.v. (a decrease of about 18% from the higher work function of 1.6 e.v.) gives a power of 5.6 watts/cm.², or an increase in power of about 36%. A further decrease of the collector work function to 1.0 e.v. (a decrease of about 35% from the higher work function of 1.6 e.v.) gives a power of 7.1 watts/cm.², or an increase in power of about 73%. On the other hand the absolute percent increase in power due to decreasing the collector work function is not nearly as great when the emitter has a much higher work function and is operated at a correspondingly higher temperature. This follows from the fact that the ratio of the difference in work functions between 1.6 e.v. and the new lower value to the quantity $\phi_E - \phi_C$ is relatively small. Thus the very low work function collector material provided by this invention is primarily useful for obtaining a high power output from a converter whose emitter work function and its temperature of operation are relatively low.

As will be described hereinafter, the collector is comprised of a composition of cesium and a semiconductor material so that a low work function results. However, it is important to consider another requirement of the collector material, which is its stability against evaporation and decomposition. The converter of the present invention is designed to operate with a given amount of cesium vapor in the emitter-collector electrode spacing so that the above-mentioned neutralizing effect can be achieved, and because cesium constitutes one element of the low work function collector composition. The fact that thermionic converters are operated at elevated temperatures necessitates the stability requirement, and it is important that the collector composition does not decompose or evaporate readily during operation. Since a certain cesium vapor pressure is present at the surface of

the collector, this will prevent or retard the evaporation of cesium from the collector if the collector composition tends to decompose and evaporate in its elemental states. Likewise, the vapor pressure of the elemental constituents of the composition other than cesium will be lowered by the cesium pressure maintained at the collector surface, thus preventing or retarding the evaporation of these constituents. That is, due to the cesium vapor pressure, the partial pressures just off the surface of the collector of the constituent elements of the collector composition other than cesium, whether the composition be a chemical compound or a mixture, will be less than the vapor pressures of the same constituents in a vacuum at the same temperature. In essence, the cesium vapor pressure suppresses evaporation of the collector constituents. If the collector composition is considered as a chemical compound and evaporation can only take place in the compound state, it is true, in general, that the heat of vaporization of the compound is greater than that for any of its constituent elements. As a result of one or more of the foregoing reasons, the collector compositions of this invention possess the degree of stability required for use in a converter of the type described.

The low work function composition of this invention is generally classified for purposes of explanation as semiconductor compounds, although this designation is for the purpose of what is believed to be an accurate theory for predicting these compositions for the objects hereinbefore stated, and it is to be understood that the term composition is used in its broadest sense including an aggregation on mixture or elements not necessarily forming a chemical compound. Moreover, specific chemical compounds mentioned hereinafter as collector compositions may vary in their constituents from the true stoichiometric ratio expressed by the chemical formula, as where, for example, a particular compound contains an excess amount of one of the constituents as a donor impurity.

It has been found that collectors formed of compositions of cesium and a semiconductor material, particularly, for example, silicon and germanium have very low thermionic work functions and are stable in the presence of cesium vapor at the temperature of operation of the collector of the converter.

While we do not wish to be bound by any theories, it is thought that the best explanation of the low thermionic work functions of the compound cesium semiconductor collector composition of the invention is based on the theory of a compound with a strong ionic binding similar to the alkali-halide compounds, in which sodium-chloride is a good example. An ionic compound is one in which the metal atom, such as sodium, gives up an electron to the non-metal atom, such as the chlorine, and the atoms exist in the compound or molecule state as positive and negative ions. For a more complete description of ionic compounds, their theory and characteristics, see Dekker, A. J., *Solid State Physics*, Prentice-Hall, Inc., 1959, chapters 5, 7, and 15. A general rule-of-thumb that indicates whether a compound is ionic in nature is when the two components have greatly different electronegativities such as is usually the case when the two components are from two greatly different chemical groups and valences. Here, cesium has a valence of unity and silicon and germanium elements, for example, each have valences of four.

Using the ionic compound as a model, the thermionic work function can be theorized in terms of the Fermi energy and the electron affinity of the compound. Referring to FIGURE 5 there is shown a graphical illustration of the electron energy levels of an ionic compound versus the reciprocal of the interionic spacing between the positive and negative ions constituting the compound. The electronic energy levels of the alkali-halide compound sodium-chloride is generally explained on the basis of such a curve. When the ions of the compound are sep-

arated by a large distance there is no interaction between them, and the lowest unoccupied level of the metal atom is the ionization energy I , which is the amount of energy required to remove an electron from this level to the free state to ionize the alkali atom. The highest occupied level of the halide ion is the electron affinity χ_1 , which is the amount of energy required to remove the extra electron from the halide ion and thus neutralize the halide atom. As the interionic distance becomes smaller, the interaction therebetween causes the electronic levels to shift as shown in the graph, and as explained in Dekker, supra, pp. 369-371. Actually, the electronic levels broaden into bands of energy as the interionic distance becomes smaller as indicated on the graph, and at the lattice parameter a , which is the interionic separation of the ions in the compound state, the distance between the above electronic levels, now bands of energy rather than discrete energy levels, are determined. (Moreover, at the separation a , the widths of the bands can be determined.) The energy between the top of the valence band and the bottom of the conduction band is the band gap energy E_g , and the energy between the bottom of the conduction band and the energy of a free electron in a vacuum is the electron affinity of the compound. The Fermi level of the pure ionic compound is located somewhere between the conduction and valence bands. And the thermionic work function ϕ_c , which is the amount of thermal energy required to remove an electron from the compound, is equal to the sum of the Fermi energy E_f and the electron affinity of the compound.

As was mentioned earlier, one of the primary reasons that the collector composition includes cesium as a major constituent was the fact that cesium vapor is used in the interelectrode spacing of the converter to neutralize the potential barrier to current flow, and that cesium semiconductor compositions are found to be stable in a cesium vapor. Thus by providing a collector material or compound, the metal constituent of which is the same element as that which is used to perform the above-noted neutralization effect, the vapor can be used to perform yet another function, viz. excess metal is incorporated into the material to lower the thermionic work function. The amount of excess metal incorporated in the collector is governed by the temperature of the collector and the pressure of cesium vapor surrounding it.

It is believed that the thermionic work function of each of the cesium composition or semiconductor compounds of this invention is predicted in at least some degree by the model and theory alluded to above in connection with alkali-halides. Moreover, it is believed that the better explanation of these compositions is based on the theory that each is a compound, where the chemical formulae are in the silicon and germanium examples, Cs_3Si and Cs_4Ge . The use of the compound semiconductor composition as a collector in the presence of cesium vapor causes an excess amount of cesium to go into the composition. The ratio of the constituents of the compound therefore varies from the true stoichiometric ratio of the compound, and the excess cesium metal acts as a donor impurity which decreases the thermionic work function.

The preferred method of fabricating the collector which is to be doped with cesium metal is to deposit by evaporation, sputtering, electroplating, or any other suitable method, onto a chemically stable (high temperature) electrical conductor, such as nickel, a semiconductor element, for example germanium or silicon, in thickness of from several hundred to several thousand angstrom units. The deposited surface is then incorporated in a converter as the collector by forming a vacuum tight enclosure or being situated therein. The collector is then heated, say from 100°C . to 200°C ., for example, to drive off any gas as the enclosure is evacuated. Subsequently, cesium vapor is introduced in the enclosure, and the converter is then operated by heating the emitter to its operating

temperature, for example, in excess of 1200° C. During the initial period of the operation, the cesium reacts with the semiconductor element deposited on the collector surface to form the cesium compound semiconductor composition. A time of about one hour is usually sufficient to substantially complete the reaction between the semiconductor collector element and the cesium. Because of the cesium vapor present at the surface of the collector, the collector composition is essentially saturated with cesium in that an excess of cesium is essentially saturated with cesium in that an excess of cesium is incorporated in the composition or compound as a donor impurity. Representative of operating conditions for any one of the above-enumerated collector compositions are an emitter temperature in excess of 1200° C. to 1300° C., and a collector temperature of less than 300° C., the latter being controlled by its physical spacing from the emitter and/or by an independent heat source or heat sink. A cesium reservoir is incorporated in the converter, as will be seen below with references to FIGURES 5 and 6, to supply the cesium vapor in the interelectrode spacing, and the temperature of this reservoir is usually maintained at a temperature slightly less than that of the collector. In this way the cesium pressure in the converter is, to a large extent, governed by the coldest part of the converter, which is the cesium reservoir. Representative of the cesium vapor pressure for the collector compositions above-enumerated is from about 10⁻⁶ mm. of Hg to about 2.0 mm. of Hg, where the corresponding cesium reservoir temperatures are from about 25° C. to about 300° C. All of the above representative times, temperatures, pressures, etc., are not critical and are given for illustrative purposes only. Within wide limitations the work functions of the various cesium collector compositions have been found to be less than that of pure cesium and to be stable against evaporation and decomposition. Representative of the range of work functions for the compositions is from about 1.1 e.v. to about 1.7 e.v. For example, the work function of Cs₄Si ranges between about 1.5 e.v. about 1.7 e.v.

In general, the lowest thermionic work function compositions are those containing a large amount of cesium donor impurity concentration. However, it is not to be understood that no limit exists as to the amount of excess cesium dopant used. On the contrary, the amount of excess cesium should not be so great that it no longer acts as an impurity and tends to raise the work function back to that of pure cesium. Such changes and excesses can easily be detected by measuring the work function by the commonly used contact-potential method.

Two examples of thermionic converters are shown in FIGURES 6 and 7 where the first embodiment has planar emitter and collector surfaces in parallel, opposing relation, and the second embodiment has cylindrical emitter and collector surfaces, with the collector surface surrounding the emitter. In particular, there is shown in FIGURE 6 a converter designed to operate at a relatively low emitter temperature, say 1300° C., to provide a power output of 5 watts at maximum efficiency. To obtain the necessary emitter current at the relatively low temperature, a material whose work function is from about 2.0-2.5 e.v. must be used. This intermediate work function emitter can either be a refractory metal partially covered with cesium or a "dispenser" cathode which comprises a high temperature metal, such as tungsten or tantalum, which has been impregnated by a lower work function element, such as barium or strontium. The dispenser cathode is well known and will not be elaborated on here. The converter is comprised of a first electrode 28 of one of the materials named above with a planar surface 29, and a second electrode 20 having a planar surface 24 in spaced, opposing relation to the emitter surface and onto which has been deposited one of the collector compositions of this invention. The first or emitter

electrode has the active emitter portion extended toward the collector, as shown, so that the emitter and collector surfaces are in close proximity. The second or collector electrode is made with suitable metal substrate, such as nickel, and has an aperture 27 therethrough as shown, into which is sealed a reservoir 36 for containing a small amount of cesium 40. The electrodes are supported in their respective positions by cylindrical metallic sealing flanges 31 and 33 sealed to the peripheries of the first and second electrodes, respectively, and the outer edges of the flanges are sealed to a cylindrical ceramic member 32. The flanges act as bellows in the sense that they are able to expand with thermal stresses to allow for the large temperature gradient between the emitter and collector. The flanges have small cross-sectional areas to limit the heat flow by conduction from emitter to collector to a minimum, and also serve as an enclosure for the inter-electrode spacing. A load is connected across the emitter and collector electrode by leads 44 and 44', respectively.

The converter is operated by heating the emitter by any suitable means, such as by direct thermal contact with a hot reservoir, or by a solar collector, as examples, and the collector is heated to about 100° C. to about 300° C., normally by radiation from the emitter. Since the coldest surface within the enclosure determines, to a large extent, the cesium vapor pressure in the space between the emitter and collector, the pressure can be easily regulated by controlling the temperature of the cesium reservoir. The cesium reservoir is heated to a slightly elevated temperature, say from 25° C., to about 300° C., to establish the desired amount of cesium vapor pressure within the enclosure, such as by heat conduction from the collector. Under normal operating conditions the collector is operated at a slightly higher temperature than the cesium reservoir to prevent an undue amount of cesium from condensing on the collector surface.

A cylindrical configuration of a converter is shown in FIGURE 7 that is primarily adapted to a nuclear heat source. A cylindrical ceramic member 64 supports both the emitter and collector electrodes 60 and 62, respectively. The emitter electrode is "feathered" or thinned out at its upper end 66 and sealed to the inner surface of the ceramic member, and thus when the emitter electrode is heated, the thinned portion allows flexibility in response to thermal stresses. The emitter electrode consists of a cylindrical can closed at its bottom end and into the interior 70 of which can be inserted a heat source, such as a nuclear fuel element. The collector electrode comprises a cylindrical can having an aperture through its lower end and into which is sealed a reservoir 72 for containing a small amount of cesium 74. This electrode, like that of FIGURE 6, has an extended portion onto the surface 68 of which is deposited one of the compositions of the invention. The materials comprising the electrodes and the operating conditions for the converter are essentially the same as those for the converter of FIGURE 6.

The foregoing descriptions of converters with reference to FIGURES 6 and 7 are for illustrative purposes only and are in no way to be construed in a limiting sense. Rather, the invention constitutes a new collector composition for use in combination with a thermionic converter and is to be limited only as defined in the appended claims.

What is claimed is:

1. A collector for a thermionic converter of the type having an emitter and a collector with cesium vapor disposed in the closed space between the emitter and the collector, said collector consisting essentially of an electrically conductive substrate chemically stable at high temperatures coated with a composition of cesium and an element selected from the group consisting of silicon and germanium and containing a donor impurity from Group I-A of the Periodic Table of Elements in an amount sufficient to lower the thermionic work function of said composition.

2. A collector according to claim 1 wherein said substrate is nickel.
3. A collector according to claim 1 wherein said donor impurity is cesium.

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OSCAR R. VERTIZ, *Primary Examiner.*

H. S. MILLER, *Assistant Examiner.*