July 8, 1969 B. DEVIN ETAL 3,454,797

THERMIONIC CONVERTER

Filed Aug. 20, 1965

Fig. 1.

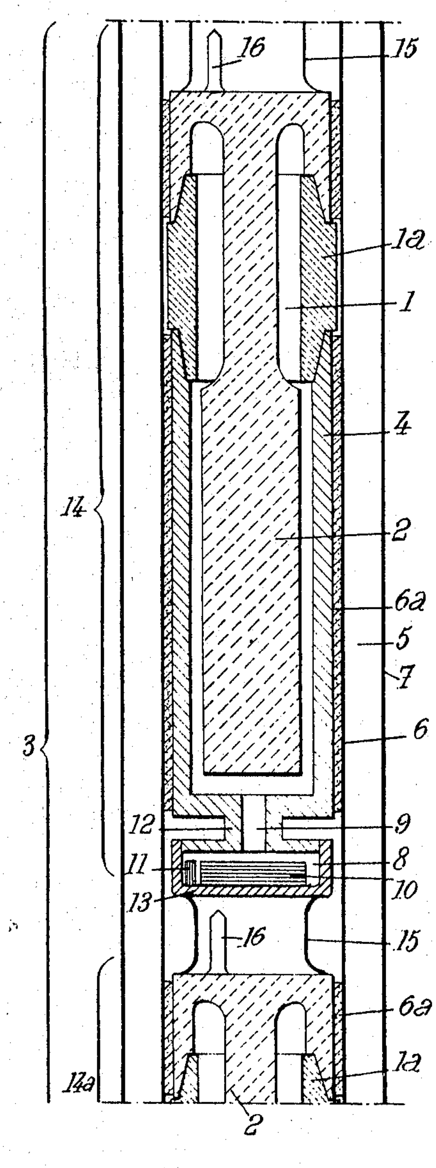
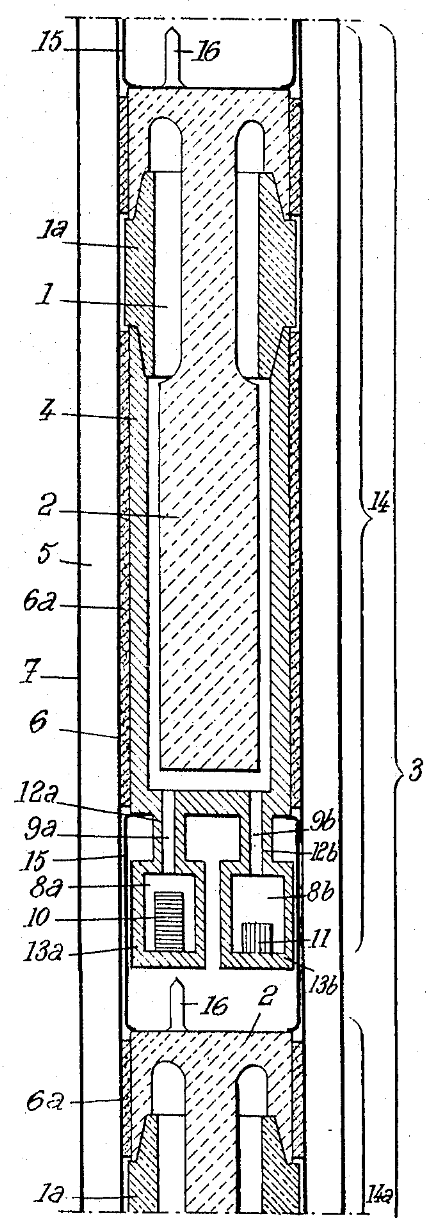


Fig. 2.



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THERMIONIC CONVERTER

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U.S. Cl. 310—4 11 Claims

ABSTRACT OF THE DISCLOSURE

The diode comprises an evacuated envelope in which are disposed a heated cathode and an anode kept at a temperature lower than that of said cathode. Reservoir means are provided, in free communication with the inside of this envelope, containing: (1) a compound of insertion in graphite of an alkali metal selected from the group of rubidium, potassium and especially cesium, and (2) a metal having a low work function and not forming a compound of insertion in graphite. This last-mentioned metal, which can advantageously be an alkaline-earth metal, is volatile or incorporated in a volatile compound, so as to be able, during operation of the diode, to be volatilized and a cover, at least partly, the surface of the cathode and/or anode, thus lowering the work function thereof.

The present invention relates to plasma diodes and it is more especially concerned with diodes intended to transform into electrical energy the thermal energy generated in a nuclear reactor.

The chief object of the present invention is to provide an improved diode of this type which makes it possible, on the one hand, independently to adjust both the ionized atmosphere or plasma, to neutralize the space charge inside the diode, and the work function of the electrodes, and, on the other hand, to locate the plasma source in a zone at predetermined high temperature (ranging for instance from 500 to 1000° C.).

The diode according to the present invention comprises an evacuated envelope in which are disposed at least one heated cathode and at least one anode kept at a temperature lower than that of the cathode and this diode is characterized by the fact that it comprises at least one reservoir in free communication with the inside of said envelope and containing, on the one hand, at least one compound containing an alkali metal, this compound advantageously consisting of a compound of insertion of an alkali metal, such in particular as cesium, in graphite and, on the other hand, at least one metal, either volatile or belonging to a volatile product, having a low work function value (in particular an alkaline-earth metal) capable, during the operation of the diode, of volatilizing and of covering at least partly the surface of said cathode and/or of said anode, in order to reduce the work function value thereof.

The invention is more especially intended for systems including several plasma diodes incorporated in nuclear reactors and working at anode temperatures higher than approximately 500° C.

Preferred embodiments of the present invention will be hereinafter described with reference to the appended drawings, given merely by way of example, and in which:

FIG. 1 is a sectional view of a plasma diode according to the present invention and belonging to a system of several plasma diodes housed in the core of a nuclear reactor, said diode including a single reservoir for the alkali metal compound and for the metal of low work function; and

FIG. 2 is a view similar to FIG. 1 but corresponding to the case where are two distinct reservoirs, for the alkali metal compound and for the low work function metal, respectively.

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It will first be reminded that several types of plasma diodes have been suggested, in particular for transforming into electrical energy the thermal energy created by fissions taking place in a nuclear reactor.

Said prior plasma diodes comprised, in an evacuated gastight envelope, at least one cathode and at least one anode located at a distance from each other of some millimeters or of a fraction of a millimeter. The cathode was heated to a temperature corresponding to an abundant electron emission (through thermionic effect) and the anode was kept at a temperature substantially lower than that of the cathode for collecting the electrons emitted by the cathode without in turn emitting a substantial number of electrodes. A reservoir containing an alkali metal having a low ionization potential, for instance cesium, was in communication with said envelope, this reservoir constituting the coldest point of the system constituted by the envelope and the reservoir but being however at a temperature sufficient to have a partial evaporation in the reservoir, the alkali vapor being in equilibrium with the liquid at the temperature of the reservoir and having no chance of substantially condensing on the cathode and on the anode, both at a temperature higher than that of the reservoir. The temperature of the reservoir was generally chosen such that the alkali metal pressure (in particular the cesium vapor pressure in the envelope and reservoir system) was of the order of 2 mm. of mercury (a higher pressure producing too high a electrical resistivity between the cathode and the anode) which required a relatively low reservoir temperature, 300° C. in the case of cesium.

Such a conventional arrangement of a plasma diode involved drawbacks well known to those skilled in the art, and in particular the following ones:

(a) The alkali metal (cesium for instance) served two purposes, to wit, on the one hand, to lower the work function value of the electrodes, partly coated with cesium during the operation, due to the fact that the work function valve of the alkali metal is lower than that of the electrode itself (that of cesium is of 1.8 electron volts), and, on the other hand, to produce positive ions which neutralize the (negative) space charge resulting from the emission of electrons by the cathode, this production of positive ions taking place according to the Langmuir effect, the alkali metal of low ionization potential (3.9 volts in the case of cesium) getting ionized by contact with electrodes made of a material having a work function value higher than this ionizing potential. Due to the fact that this alkaline metal (cesium) served both of these two purposes, the relative importance of which depended upon the temperature of the electrodes (immediate re-evaporation of the alkali metal on one electrode and complete ionization of this metal taking place when the temperature of the electrode exceeds a critical value proportional to the temperature of the cesium reservoir), it was not possible to adjust the two functions of the alkali metal separately;

(b) The necessity of ensuring a satisfactory degree of ionization of cesium (or other alkali metal) made it necessary to keep the cesium (or other alkali metal) reservoir at a temperature not very high, averaging 300° C., whereby the efficiency of the diode was low, especially when it was intended to convert thermal energy of nuclear origin into electrical energy;

(c) In particular, when the diode or diodes were disposed inside a slug of fissionable material of the nuclear reactor, in particular for use on a space vehicle, it was necessary to place the alkali metal reservoir on the outside of the nuclear reactor, the temperature of which averages, during operation, 700° C. (that of the cooling fluid, such as a liquid alloy of sodium and potassium), because if the reservoir were at a temperature of 700° C., the pressure of the alkali metal vapor in the diode envelope would have been too high; and

(d) When several diodes were disposed in a fissionable slug, with the alkali metal reservoir disposed, for the above stated reasons, on the outside of the reactor, in a zone where the temperature in operation average 300° C., an alkali vapor pressure (fixed by this temperature) was produced common to all the diodes, which is prejudicial to a good operation of the diodes, because the respective diodes, which receive different neutron fluxes according to their positions in the reactor, require different alkali metal vapor pressures for the best possible operation.

The object of the present invention is to obviate the above mentioned drawbacks by permitting on the one hand, an independent adjustment of the lowering of the work function value and of the production of positive ions neutralizing the space charge and, on the other hand, of bringing the alkali metal reservoir at a relatively high temperature ranging from 500° to 1000° C.

For this purpose, we provide (FIGS. 1 and 2):

In a diode **14** comprising an evacuated envelope **1** (closed by packing members **1***a*) wherein are provided at least one cathode **2** (advantageously charged with fissionable material, in which case system **3** constitutes a nuclear reactor slug) heated to be brought to a temperature of abundant electron emission (advantageously through nuclear fissions) and at least one anode **4** kept at a temperature lower than that of the cathode (advantageously by circulation of a cooling fluid in the channel **5** provided between a tube **6** in thermal contact with anode **4** through a weld **6***a*, and an external tube **7**), packing members **1***a* being made of a material ensuring thermal insulation;

At least one reservoir (for instance a single reservoir **8** in the embodiment of FIG. 1 or two reservoirs **8***a*, **8***b* in the embodiment of FIG. 2) in free communication with said enevlope **1** (through channels **9** in the case of FIG. 1 or **9***a*, **9***b* in the case of FIG. 2) and containing:

On the one hand, at least one compound **10** containing an alkali metal in the bound or combined state (housed in reservoir **8** in the case of FIG. 1 and in reservoir **8a** in the case of FIG. 2), this compound advantageously being a compound of insertion of cesium in graphite, and

On the other hand, at least one metal **11**, either volatile or belonging to a volatile compound, having a low work function value, in particular an alkaline-earth metal housed in reservoir **8** in the case of FIG. 1 or in reservoir **8***b* in the case of FIG. 2, this metal **11** being capable, during the operation of diode **14**, of volatilizing and coming to coat, at least partly, the surface of said cathode and/or anode in order to reduce the work function value thereof.

In these conditions there exists in envelope **1** a saturated vapor pressure of the alkali metal of compound **10** and of metal **11**.

In this case, the reservoir **8** or **8***a* containing cesium or another alkali metal, may be housed, as illustrated, inside a slug **3**, hence at relatively high temperature, to with substantially that of anode **4**, a little higher than that of the cooling fluid circulating in channel **5**. In particular, the temperature of reservoir **8** or **8***a* may be adjusted to the desired value by suitably choosing the cross section of the connecting conducting pieces constituted by the walls **12** and **13** of channel **9** and reservoir **8**, respectively.

Furthermore, we may provide several diodes **14** disposed end to end, as illustrated, in the same slug **3** (limited by a tube **6**), the connection between two successive diodes **14** and **14***a* being ensured by connectors **15** the cross section and the thermal conductivity of which are chosen in such manner as to adjust, in combination with the cross sections of walls **12** and **13** (which may be different for every diode **14**, **14***a*), the desired reservoir temperature which is a function of the neutron flux received by every diode. It will be noted that the reservoir is no longer, as in the prior plasma diodes above referred to, necessarily the coldest point of the system.

It is further possible, in the case of the construction of FIG. 2, independently to adjust the respective temperatures of reservoir **8***a*, which contains the alkali metal, and **8***b*, which contains the metal of low work function value, by providing different thicknesses for walls **12***a*, **12***b*, on the one hand, and **13***a*, **13***b* on the other hand.

Finally, the element **16** of FIGS. 1 and 2 constitutes the pumping nipple through which it is possible to evacuate the whole of envelope **1** and either reservoir **8** (in the case of FIG. 1) or reservoirs **8***a* and **8***b* (in the case of FIG. 2).

By way of non limitative example:

Cathode **2** may be made of uranium carbide, possibly with the addition of other carbides, partly covered with the alkali metal (cesium) during the operation;

Anode **4** may be made either of niobium or of rhenium, partly covered with the alkali metal (cesium) during the operation;

The cooling fluid may be a molten alloy of sodium and potassium;

Tubes **6** and **7** and connectors **15** may be made of stainless steel;

Packing means **1***a* may be made of alumina with an addition of yttrium oxide.

As for the alkali compound, it may be constituted by a chemical compound, an amalgam or, preferably, a compound of insertion into graphite (either natural or pyrolytic) of an alkali metal or an alloy of alkali metals (potassium and cesium, potassium and rubidium), in particular by a compound of insertion of cesium in graphite. The preparation and properties of the compounds of insertion of graphite with alkali metals are described for instance in the following publications:

A. Herold, "Recherches sur les composés d'insertion du graphite" (articles presented to the Societé Chimique, 1955, pages 999 to 1012);

Diebold and Herold, "Recherches concernant l'action des halogènes sur les composés d'insertion du graphite, avec les métaux alcalins" (articles presented to the Societé Chimique, 1963, pages 578 to 586);

Fredenhagen and Cadenbach, "Die Bindung von Kalium durch Kohlenstoff, review "Z. anorg. u. allg. Chem.," pp. 249 to 263, vol. 158;

Fredenhagen and Suck, "Uber die Binding der Alkalimetalle durch Kohlenstoff," review "Z. anorg. u. allg. Chem." pp. 353 to 365, vol. 178.

In particular, the compounds of insertion in graphite, and in particular C_8Cs, may be prepared in the following manner:

We place graphite (either pyrolitic or monocrystalline) and an alkali metal such as cesium in a bulb. The bulb is evacuated and sealed. It is heated, at 150° C. in the case where the alkali metal is cesium, for some minutes in such manner as to vaporize the alkali metal and to cause it to penetrate into the graphite, because the compound of insertion has a lower vapor pressure. The bulb is allowed to cool down, then it is broken and the compound of insertion may be placed in contact with air because oxygen does not penetrate into compounds of insertion.

The alkali compound that is brought into play constitutes a reversible association of an alkali metal maintaining in its vicinity an alkali vapor pressure in equilibrium with an alkali metal bound in the compound.

By way of example, the pressure of equilibrium of cesium with the compound of insertion C_yCs is given by the following formula (y being comprised between 8 and 24):

$$\log P = 6.3552 - \frac{5805}{T}$$

wherein P is the pressure in millimeters of mercury, or torrs, and T is the temperature in Kelvin degrees.

Thus, at a temperature of 700° C. (T=973° K.), the pressure of equilibrium P is 2 mm. of mercury, which is suitable.

In order to make diodes working at higher temperatures and at cesium pressures of the same order of magnitude (2 mm. of mercury), we will choose compounds of insertion of cesium richer in carbon, for instance $C_{24}Cs$, or $C_{36}Cs$, the pressure of equilibrium being the lower as the compound is richer in carbon.

By the use of a cesium compound ensuring a relatively low pressure of cesium (averaging 2 mm. of mercury) at relatively high temperatures (of the order of 700° C. or higher), it is possible to house the cesium reservoir **8**, *8a* inside the reactor slug **3**.

Finally, the metal or product serving to lower the work function value for the electrodes either consists of an alkali or alkaline-earth metal (beryllium, magnesium, calcium, strontium, barium, sodium, lithium) in the free state or the bound state, or consists of a volatile element or compound the work function value of which is lower than 3.5 electron volts approximately, such as polonium, lanthanum, uranium, beryllium, cerium, samarium, thorium, zinc, BaO, LaB_6.

The ionizable alkali compound and the alkaline-earth compound or the like having a low work function value are either contained, both at the same temperature, in a common reservoir **8** (FIG. 1), or at different respective temperatures into reservoirs *8a* and *8b* (FIG. 2). But in both cases it is possible independently to adjust the saturating pressures in envelope **1**, of the ionizable gas, such as cesium and of the body used for lowering the work function value, such as barium. Thus, at 520° C., the pressure of equilibrium of barium is 0.05 mm. of mercury and that of cesium 0.1 mm. of mercury, which pressure is sufficient for producing cesium ions upon a surface covered with a thin layer of barium. This permits of separating the electronic and ionic emission functions, of lowering the pressure of alkali metal for a given temperature of the alkali metal reservoir, therefore of obtaining a high output for the diode by eliminating the losses in the plasma and the ionization by discharge (the efficiency of plasma diodes can thus be doubled).

Correlatively, the lowering of the pressure of the gases contained in the diode increases the free mean path of travel of the electrons in the diodes, which permits of providing a relatively large distance between the electrodes (averaging one half millimeter) so that the construction is made easier.

We thus obtain a plasma diode which has over prior plasma diodes the following advantages:

First it permits an independent adjustment of the emission of electrons and of the emission of ions serving to neutralize the space charge.

It is possible to dispose in a zone at relatively high temperature the reservoir of substances lowering the space charge by maintaining a low gaseous pressure in the diode; the vapor pressure of equilibrium of the alkali metal is not determined by the temperature of the cold point of the envelope but by the temperature of the graphite with which the compound of insertion is produced.

Losses in the plasma and ionization by discharge are reduced.

The distance between electrodes is easy to obtain.

The efficiency is high.

In a general manner, while we have in the above description disclosed what we deem to be practical and efficient embodiments of the present invention, it should be well understood that we do not wish to be limited thereto as there might be changes made in the arrangement, disposition and form of the parts without departing from the principle of the present invention as comprehended within the scope of the appended claims.

What we claim is:

1. A diode which comprises, in combination, an evacuated envelope,
- a first electrode in said envelope, consisting of a heated cathode,
- a second electrode in said envelope, consisting of an anode kept at a temperature lower than that of said cathode,
- reservoir means in free communication with the inside of said envelope, and
- in said reservoir means, on the one hand, at least one compound of insertion in graphite of an alkali metal selected from the group consisting of cesium, rubidium and potassium, and, on the other hand, at least one volatile product consisting, at least partly, of a metal having a low work function value and which does not form a compound of insertion in graphite, said volatile product being capable of volatilizing during the operation of the diode and of covering, at least partly, the surface of at least one said electrodes, thus lowering the work function thereof.

2. A diode according to claim **1** wherein said alkali metal is cesium.

3. A diode according to claim **1** wherein said second mentioned metal is an alkaline-earth metal.

4. A diode according to claim **1** wherein said alkali metal in cesium and said second mentioned metal is an alkaline-earth metal.

5. A diode according to claim **1** wherein said second mentioned metal is a metal of the group consisting of polonium, lanthanum, uranium, beryllium, cerium, samarium, thorium and zinc.

6. A diode according to claim **1** wherein said cathode contains a fissionable material and belongs to a nuclear reactor slug, said reservoir means being at a temperature ranging from 500 to 1000° C.

7. A diode according to claim **1** wherein said second mentioned metal is a metal of the group consisting of sodium and lithium.

8. A diode according to claim **1** wherein said reservoir means are formed by a single reservoir, both said compound of insertion and said volatile product being disposed in said single reservoir.

9. A diode according to claim **1** wherein said reservoir means are formed by two separate reservoirs, namely a first reservoir and a second reservoir, said compound of insertion being disposed in said first reservoir and said volatile product being disposed in said second reservoir, said second reservoir being located at the coldest point of the whole of said envelope and said two reservoirs.

10. A diode according to claim **1** wherein said volatile product consists of said second mentioned metal.

11. A diode according to claim **1** wherein said volatile product consists of a compound of said second mentioned metal.

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U.S. Cl. X.R.

313—229

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,454,797 July 8, 1969

Bernard Devin et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

In the heading to the printed specification, lines 1 to 7, "Bernard Devin, 47 Ave. de Seine, Rueil-Malmaison, Hauts-de-Seine, France; Robert Lesueur, 7 Square de la Porte de Vanves, Paris, France; and Ralph Setton, 703 Residence Dauphine, Rue la Mouillere, Orleans, France" should read -- Bernard Devin, Rueil-Malmaison, Robert Lesueur, Paris, and Ralph Setton, Orleans, France, assignors to Commissariat A L'Energie Atomique, Paris, France --.

Signed and sealed this 21st day of April 1970.

(SEAL)

Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents