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(54) IMPROVED ELECTRICALLY CONDUCTIVE AND CORROSION  
RESISTANT CURRENT COLLECTOR AND/OR CONTAINER

- (71) We, FORD MOTOR COMPANY a Corporation organized and existing under the laws of the State of Delaware, United States of America, of The American Road, Dearborn, State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:- 5
- This invention relates to an improved electrically conductive current collector suitable for use in high temperature applications in the presence of corrosive environments.
- More particularly this invention relates to an electronically conductive current collector or current collector/container for use in energy conversion devices such as the sodium-sulfur battery, 10
- Still more particularly this invention relates to two methods for preparing electronically conductive rutile titanium dioxide which is ideally suited for use in the current collector of the invention.
- There are a number of electrical applications involving various energy conversion devices in which the environment to which the current collector of the device is exposed is extremely corrosive. For example in energy conversion devices of the type comprising a molten cathodic reactant such as sodium polysulfide the selection of a suitable current collector as well as a suitable container has been a source of considerable concern. 15
- One of the prime candidates to date for use as a current collector or current collector/container for such devices have been certain metals. However, metal systems, both pure and alloyed, often exhibit the phenomenon of severe plastic deformation under stresses (external and from their own weight). For this reason and because of severe corrosion problems, many metals are not practical for use in such high temperature or corrosive (oxidative) environments. 20
- Since the thermodynamic stability of ceramic materials such as oxides and sulfides in the presence of corrosive environments is well established and since it is also known that the thermodynamic stability of such materials is maintained to temperatures much higher than is compatible for metal systems, it has been suggested to employ a ceramic coating on a metal which is used as the load bearing element of the current collector or container. Where a metal system operates as the load bearing element and includes a protective covering separating the metal from the corrosive substance, the selection of a suitable covering must be made from materials which (1) are noncorrosive and impermeable to the corrosive substance, (2) adhere well under conditions of thermal cycling and (3) have sufficient electronic conductivity. Often times a thermal expansion mismatch between the attached metal and ceramic covering results in fractures, microcracks and eventual spalling of the coating from the metal surface. In addition to mechanical incompatibility, conventional methods of applying the ceramic coating such as by anodizing often result in an insulative rather than a conductive coating. In summary, the concurrent development of the requisite noncorrosive character, good adherence, and adequate conductivity in a coating which will be mechanically compatible under recurring cycles of thermal expansion has long presented a difficult challenge in this field of art. 25 30 35 40
- In view of the above discussed inherent limitations of current collecting systems comprising a metal load bearing element with a corrosion resistant ceramic coating, the use of corrosion resistant ceramic per se has been suggested. However, the vast majority of useful ceramics are electrical insulators, thus making them unsuitable for current collection 45

purposes. Of course, some ceramics are known to be conductive in the metallic sense, but are not economically attractive.

A large class of ceramics can be made moderately conductive, but with conductivities which are much less than metals. Consequently, a current collector constructed of an electronically conductive ceramic will exhibit a much higher resistance than that of a similarly shaped metal current collector.

It is therefore an object of this invention to overcome the above deficiencies by combining the aforementioned best characteristics of both conductive ceramics and metals.

The above object is accomplished by the invention disclosed and claimed herein, which invention is an electrically conductive current collector suitable for use in high temperature applications in the presence of corrosive environments, comprising:

(A). A high strength, noncorrosive electronically conductive polycrystalline ceramic member of rutile which is doped with ionic metal species having a stable valence in said polycrystalline ceramic of at least +5 which serves as the primary load bearing member of said current collector, said ceramic being substantially impervious to materials constituting said corrosive environment; and

(B). A highly electronically conductive metal cladding intimately attached to a substantial portion of one surface of said ceramic member, said metal cladding having a thickness sufficiently thin to be plastically deformable in relation to said ceramic which preserves the function of said ceramic member as the primary load bearing element of said current collector and being based on the relative elastic modulus of the metal of said metal compared to that of the ceramic member, said metal cladding being arranged to direct current flow through said ceramic member and to shunt said current between said member and external contact.

The above object is still further accomplished by the two methods for producing a high strength, noncorrosive, electronically conductive polycrystalline titanium dioxide ceramic members exhibiting high resistance to thermal shock and uniform grain size with an average grain size of less than about 25 micrometers and consisting of titanium dioxide in the rutile crystallographic form doped with a homogeneously distributed ionic metal species selected from tantalum and niobium. The first of these methods generally comprises:

(A) Dissolving in a solvent selected from water and aliphatic alcohols the pentafluoride salt of said metal species in an amount adapted to provide from about .01 to about 8 atomic percent of said metal species in said ceramic member;

(B) adding titanium dioxide powder in either the rutile or anatase form to the solution of (A) to produce a mixed slurry;

(C) Drying said slurry to powder form at a temperature adapted to avoid evaporation of said metal species;

(D) green forming said powder to the desired shape;

(E) Heating the shaped green body to about 350°C at a rate of at least about 10°C per minute;

(F) Sintering said shaped green body at a temperature of at least about 1330°C; and

(G) Annealing said sintered shaped body in a reducing atmosphere having an oxygen partial pressure of about  $10^{-5}$  to about  $10^{-25}$  atmospheres at a temperature of from about 850°C to about 1400°C to increase the conductivity of said ceramic member.

The second such method comprises:

(A) Disposing a mixture of a pentachloride-diethyletherate complex of said metal species and titanium dioxide powder in either the rutile or anatase form to form a slurry, said slurry components being included in amounts adapted to provide from about .01 to about 8 atomic percent of said metal species in said ceramic member;

(B) Drying of said slurry to powder form at a temperature adapted to avoid evaporation of said metal species;

(C) green forming said powder to the desired shape;

(D) Heating the shaped green body to about 500°C at a rate of at least about 40°C per minute;

(E) Sintering said shaped green body at a temperature of at least about 1330°C; and

(F) Annealing said sintered shaped body in a reducing atmosphere having an oxygen partial pressure of about  $10^{-5}$  to about  $10^{-25}$  atmospheres at a temperature of from about 850°C to about 1400°C to increase the conductivity of said ceramic member.

The invention will be more fully understood from the following detailed description of the invention taken in conjunction with the drawings in which:

Figure 1 shows one embodiment of the current collector in accordance with the invention;

Figure 2 shows an energy conversion device incorporating the current collector of the invention;

Figure 3 shows another energy conversion device incorporating a current collector in accordance with the invention;

Figure 4 shows the current collector employed in the device of Figure 3; and Figure 5 shows a graph depicting the reduction in resistivity achieved in rutile titanium dioxide by annealing.

5 As discussed briefly above the current collector of this invention comprises the combination of an electronically conducting ceramic oxide, which forms the load bearing element of the current collector and which is corrosion resistant to the substances to which the current collector is to be exposed at elevated temperatures, with a metal conductor intimately attached to the ceramic with negligible electrical resistance at the ceramic metal interface.

10 Extreme importance must be attached to the concept of using the ceramic as the load bearing element in this construction. By maintaining a relatively thin metallic coating which normally is plastically deformable compared to the ceramic, deformation of the ceramic as for instance through thermal expansion, causes the metal to flow. The inverse design where the metal is thick compared to the conducting ceramic will require plastic flow of the ceramic in order to maintain mechanical and electrical integrity at their interface, a condition difficult to achieve with the normally brittle ceramic.

15 The usefulness of the design is predicted on the existence of available materials which can be processed in strict accordance with the aforementioned design requirements and which are compatible with one another in the sense of metal adherence to the electronic ceramic and small or negligible contact resistance between the metal and electronic ceramic. Suitable highly conductive ceramics may be prepared in accordance with known prior art techniques.

20 Preparation of highly corrosive oxide ceramics is accomplished in the art by four commonly accepted methods: (1) intrinsic high conductivity, (2) reduction of the oxide ceramic causing a deficiency in oxygen ions and subsequent electrical compensation by the addition of conducting electrons, (3) controlled addition of an ionic species differing from the solute cationic species in both constitution and electric charge, the added species occupying an interstitial crystal site, charge neutrality considerations creating conducting electrons and higher conductivity, and (4) controlled addition of an ionic species differing from the solute cationic species in both constitution and electric charge, the added species occupying by substitution the sites of the parent cationic species with charge neutrality considerations producing conducting electrons.

25 Intrinsic high conductivity is exhibited by ruthenium oxide, a compound normally considered uneconomical because of the rare occurrence of ruthenium in nature. Methods (2) and (3) normally result in the creation of charged, mobile atomic entities which can move easily under the force due to an electric field. Method (4) offers the greatest promise for applicability in the current collector described in that the addition of impurity ions in a substitutional manner usually produces a nearly immobile impurity except at very high temperatures.

30 Three economically viable metal oxides which may be made conducting and which are economically viable because of natural abundance are calcium titanate ( $\text{CaTiO}_3$ ), strontium titanate ( $\text{SrTiO}_3$ ) and one of the derivatives of both titanates, titanium dioxide ( $\text{TiO}_2$ ) in the rutile crystallographic form. Common substitutional additive ions for all of these oxides include iron in the +3 oxidation state and aluminum in the +3 oxidation state. Greater electronic conductivity increase may be accomplished by the addition of an ionic metallic species having a stable valence in said ceramic of at least +5. Tantalum in the +5 oxidation state or niobium in the +5 oxidation state are preferred because of the solubility of these elements and because the charge carriers created from the niobium or tantalum impurity additions remain nearly free for electronic current flow.

35 By far the most common prior art method of adding niobium or tantalum to these metal oxides, when the resulting ceramic is to be polycrystalline, is the simple mixture of the fine powders of niobium pentoxide ( $\text{Nb}_2\text{O}_5$ ) or tantalum pentoxide ( $\text{Ta}_2\text{O}_5$ ) with fine powders of the solute substance  $\text{CaTiO}_3$ ,  $\text{SrTiO}_3$  or  $\text{TiO}_2$ . Subsequent processing by commonly known arts of pressing the mixed powders into green ceramic form and sintering at a suitable temperature yields a black, dense ceramic with conductivity drastically enhanced over the pure ceramic.

40 Grain size is generally very nonuniform coincident with the inhomogeneous distribution of the impurity in the solute. That is, the tantalum or niobium is not distributed in a homogeneous fashion, the large ceramic grains contain smaller amounts, the smaller grains existing as such because tantalum and niobium tend to serve as grain growth inhibitors. Excessive heating at very high temperatures may be employed to further homogenization but at the expense of further grain growth and excessive processing costs.

45 Barium titanate, homologous to calcium titanate and strontium titanate, may be formed as a powder and intimately mixed with tantalum oxide or niobium oxide by a gel process described in U.S. patent 3,330,697. Even if this method is extendable to  $\text{CaTiO}_3$ ,  $\text{SrTiO}_3$

and  $\text{TiO}_2$ , a need exists to simplify the powder preparation process for economic reasons when large quantities of conducting ceramic are required.

Relative abundance of  $\text{CaTiO}_3$ ,  $\text{SrTiO}_3$  and  $\text{TiO}_2$  makes these materials attractive for use in corrosion resistance, electronically conducting current collectors provided these materials may be processed at low cost and exhibit electronic conductivities adequate for the planned use of the current collector. Of special interest is the use of electronically conducting  $\text{CaTiO}_3$ ,  $\text{SrTiO}_3$  and  $\text{TiO}_2$  as materials for a current collector or current collector/container for the sodium-sulfur battery, such as is disclosed in the U.S. patents 3,404,035 and 3,468,709.

The above ceramic oxides not only may be made electronically conducting in the sense that resistivities at room temperature are less than 50 ohm-centimeters but also are known to be resistant to corrosive attack by commercial and/or electrolytic grade sodium polysulfides at 400°C or below.

Disc shaped samples of about one and one fourth inch diameter and one eighth inch thickness have been formed and sintered for the following chemical compositions and tested for corrosion resistance.

- 1)  $\text{TiO}_2$  (rutile) containing 1% tantalum
- 2)  $\text{SrTiO}_3$  reduced in water vapor atmospheres
- 3)  $\text{CaTiO}_3$  containing 3.0% iron
- 4)  $\text{La}_{0.84}\text{Sr}_{0.16}\text{CrO}_3$  with no other additives

Also, a single crystal sample of  $\text{TiO}_2$  (rutile) containing 0.05 percent tantalum has been subjected to the corrosion tests above, which are performed by the method of recording the initial sample weight, subjecting the sample to the sodium polysulfides (in either commercial grade or electrolytic grade quality) at 400°C by immersion for 14 days and subsequently weighing the cleaned samples after immersion for detection of weight loss or weight gain due to corrosive reactions with the sodium polysulfides. All of the above named samples exhibited either no weight change or a very small change after the above tests (see table below) indicating good corrosion resistance to these liquids.

Material	Form	Weight change in sodium sulfide at 400°C (PCT) after 14 days
$\text{CaTiO}_3 + 3.0\% \text{ Fe}$	Sintered	-1.45
$\text{SrTiO}_3$ - reduced	Sintered	-.141
$\text{SrTiO}_3$	Sintered	-6.0
$\text{TiO}_2 + 0.5\% \text{ Ta}$	Single crystal	0
$\text{TiO}_2 + 1.0\% \text{ Ta}$	Sintered	0

The ideal electronically conductive ceramics for use in this invention are the tantalum and niobium doped titanium dioxides prepared in accordance with the two methods of this invention which were briefly described above and will be more fully discussed hereinafter.

As noted above the construction criteria for a corrosion resistant electronically conducting, metal clad ceramic current collector requires the addition of a thin, metal cladding intimately attached to the surface of the corrosion resistant, electrically conducting ceramic. The thickness and resistivity of both ceramic and metal is adjustable to give a very wide range of total current collector electrical resistance. Broadly the ceramic may have an electrical resistivity of less than about 1000 ohm-cm, but preferably the resistivity should be less than 50 ohm-cm and most preferably less than 10 ohm-cm. Broadly, the resistivity of the metal may be as high as .001 ohm-cm, but preferably is less than about .0003 ohm-cm and most preferably less than about .0001 ohm-cm.

The geometrical sizes of the metal and ceramic composite, particularly their thickness, may be varied along with resistivities to produce a current collector of specified total resistance as measured between the inner surface and a small area contact on an outer metal surface.

In the intended uses of the current collectors of this invention the ceramic surface is the only surface to conduct corrosive substances. As a result a metal placed on one surface will not be exposed to the corrosive materials except in so far as outer ambient conditions, such as the presence of oxygen provided the use temperature does not become excessive. Such a metal place in intimate electrical and mechanical contact with the total surface of an electronically conducting, corrosion resistant ceramic can serve to shunt electrical current through a region of metallic conductivity. In essence, electronic current must then only pass perpendicular to and through the ceramic container walls to the metal shunt, rather than

pass through the ceramic parallel to the container wall. This concept (Figure 1) can serve to drastically lower the total inner area to small outer area resistance of such a containing device while maintaining the corrosion resistance of the ceramic. The metal placed in intimate contact on the outer surface of the ceramic is referred to as metal cladding.

5 For a container of length 23 centimeters, ceramic wall thickness of 0.2 centimeters, diameter of 4.0 centimeters, metal cladding thickness of 0.02, centimeters, ceramic resistivity of 0.2 ohm-centimeters and metal resistivity of  $10^{-5}$  ohm-centimeters, the total resistance of the given configuration is less than 0.6 milliohms. A container with the same dimensions which does not have the metal cladding attached will have a resistance of about 10 1 ohm, 1500 times greater than the same container with the metallic cladding.

The metal-ceramic combination must possess the characteristics of corrosion resistance, high electronic conductivity for the ceramic and the ability of the metal coating to be intimately placed onto the outside of the ceramic with negligible contact resistance between the electronic ceramic and the metal. Furthermore, the metal systems must not readily oxidize below 400°C, thereby causing the subsequent electrical degradation of the metal-ceramic interface. 15

Satisfactory materials for such cladding include but are not limited to aluminum, nickel, chromium and silicon and combinations of these substances. A primary common characteristic of such materials which tend to preserve good interface conductivity is the tendency to form thin oxides on the outer surface of the metal cladding. High contact resistance between metallic or semiconducting cladding materials resulting from poor surface preparation may be eliminated by preheating the ceramic in vacuum or reducing atmospheres before conventionally applying the metallic coating. 20

The following metal-ceramic combinations have demonstrated the necessary characteristics: 25

- 1) Tantalum doped rutile ( $\text{TiO}_2$ ) covered with a metal cladding of (either sputtered, electrolytically or chemically deposited) nickel.
- 2) Tantalum doped rutile ( $\text{TiO}_2$ ) covered with a metal cladding of aluminum.
- 3) Tantalum doped rutile ( $\text{TiO}_2$ ) covered with a metal cladding of chromium.
- 30 4) Tantalum doped rutile ( $\text{TiO}_2$ ) covered with a thin cladding of silicon (overcoated with metallic platinum).
- 5) Niobium doped rutile covered with a metal cladding of platinum.
- 6) Iron doped calcium titanate covered with a coating of gold.
- 7) Reduced strontium titanate covered with a coating of gold.
- 35 8) Lanthanum strontium chromite ( $\text{La}_{0.84}\text{Sr}_{0.16}\text{CrO}_3$ ) covered with a metal cladding of platinum.

Samples of several of the above materials were prepared and tested. For  $\text{TiO}_2$ , sputtered nickel, sputtered aluminum and sputtered silicon overcoated with platinum exhibit no apparent electrical resistance increase or degradation when applied with a thickness of about 2000Å and cycled to 500°C for 10 hours. Titanium dioxide in the rutile crystallographic form and containing either tantalum electrolytically plated with nickel, or chromium also exhibits no degradation as measured by changes in apparent electrical resistance after cycling to 500°C for 10 hours and remeasuring the composite conductance at room temperature, a temperature condition where contact resistance is larger than at the higher temperatures of expected application. Similar behavior is noted for vapor deposited gold on the surface of rutile doped with niobium, vapor deposited gold on the surface of calcium titanate, vapor deposited platinum on the surface of lanthanum strontium chromite ( $\text{La}_{0.84}\text{Cr}_{0.16}\text{CrO}_3$ ). The electrical resistance change is monitored by the common two probe method of measurement. 40

Each of the aforementioned materials in nearly pure form is easily processed by the common arts of ceramics, whereby powders are compacted to form a green shape and sintered at elevated temperatures where densification occurs. Densities of above 98 percent of the theoretical values are easily obtained for all materials. The total time the sample is maintained at the temperature of sintering as well as the temperature of sintering can be varied to suit the needs of the processor and to vary the subsequent properties of the material. The addition of impurities to the nearly pure materials normally causes required changes in the processing technique especially in so far as the homogeneous distribution of impurities is desired. 45

As mentioned previously the ideal high strength, noncorrosive, electronically conductive polycrystalline ceramic for use in preparing the current collectors of the invention are prepared in accordance with either one of two novel and unobvious methods. The ceramics are titanium dioxide in the rutile crystallographic form which is doped with a homogeneously distributed ionic metal species selected from tantalum and niobium. This homogeneous distribution of dopant is a result of the processes employed and results in ceramics having excellent properties including high resistance to thermal shock, uniform grain size and an 60

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average grain size of less than about 25 micrometers.

The first of the two processes comprises:

5 A) The formation of a slurry of titanium dioxide in either the rutile or anatase  
crystallographic forms in water solution (or aliphatic alcohol solution) of tantalum or  
niobium pentafluoride. The weights of titanium and the pentafluoride salt constituent will  
be determined by the desired final concentration of dopant in the titanium dioxide. In  
10 general, it is desirable to provide from about .01 to about 8 atomic percent of the ionic  
metal species in the sintered ceramic. It will be appreciated that the amount of dopant  
which may be added with continuous electrical property enhancement of the  $\text{TiO}_2$  due to  
homogeneous tantalum or niobium distribution is ultimately limited by the solubility of  
15 tantalum or niobium in  $\text{TiO}_2$ , but certainly quantities of up to 3 percent Ta or Nb on a  
titanium ion basis is possible. For no tantalum or niobium percentage should the sum of all  
percentages of cationic impurities of normal ionic charge less than +4 or greater than +5 be  
greater than about 0.10 percent and concurrent with this restriction, the sum of all  
percentages of cationic impurities of ionic charge less than +4 or greater than +5 should not  
20 exceed 10 percent of the added tantalum concentration. Impurity levels greater than these  
mentioned serve to drastically limit the attainable conductivity resulting in a highly  
inefficient use of the tantalum pentafluoride additions.

20 B) The slurry is next dried to powder at a temperature adapted to avoid evaporation of  
the metal species. The drying of the slurry is generally accomplished by slowly heating to a  
temperature of not more than  $110^\circ\text{C}$  and should be accomplished in a time of not more than  
10 hours. Stirring of the slurry enhances the rate of drying. During this process addition of a  
suitable binder useful in green forming of the ceramic body may be accomplished.  
25 Pentafluoride salts of the metal ion which remains after drying, melts at temperatures less  
than  $100^\circ\text{C}$  and the vapor pressure of the substance rises to an unreasonably high value  
before the drying slurry reaches  $130^\circ\text{C}$ . Long term heating at temperatures above  $120^\circ\text{C}$   
results in the evaporation loss of the pentafluoride when experimental conditions are  
equivalent to open container heating.

30 C) The powder with water removed is pressed into a suitable or desired form and sintered  
at elevated temperatures in air or oxygen with critical heating rate of at least  $10^\circ\text{C}$  per  
minute maintained between ambient and  $350^\circ\text{C}$  to prevent loss of tantalum or niobium via a  
vaporization process. Above  $350^\circ\text{C}$  oxidation of tantalum or niobium and fluorine to  
succeedingly more stable oxides occurs, each succeeding form being less susceptible to  
35 vaporization loss until the final form of tantalum or niobium pentoxide is reached and which  
is stable to vaporization loss throughout common sintering temperature ranges. A wide  
range of final sintering temperatures and holding times at the sintering temperature may be  
useful to those skilled in the arts of ceramic processing. A temperature of at least about  
 $1330^\circ\text{C}$  and more preferably a range of about  $1380^\circ\text{C}$  to about  $1440^\circ\text{C}$  may be used.  
40 However, the preferred conditions for optimal densification, homogenization of the  
tantalum or niobium ion by diffusion into the rutile powders and minimization of uniform  
grain size is about  $1400^\circ\text{C}$  for approximately 3 hours. A minimum temperature of  $1330^\circ\text{C}$  is  
required for reasonable rates of homogenization. These above stated conditions apply to  
the processing regardless of the quantity of tantalum or niobium fluoride added to the  
45 rutile. The resulting dense material may be cooled to room temperature from  $1400^\circ\text{C}$  in as  
little as 10 minutes for samples containing 1 percent tantalum or niobium. Cooling rates  
must decrease for samples with decreasing percentages of tantalum additive.

The above stated method is conducive to the fabrication of highly conductive tantalum  
or niobium doped rutile in a batch sintering mode and may be subjected to many minor  
50 modifications to suit available processing apparatus. Samples of dried  $\text{TiO}_2$  powders in both  
the rutile and anatase forms and under several forming conditions may be processed with  
the method described including about 1 atom percent of Ta and produce very nearly  
identical values for properties of electrical conductivity (i.e. about 1 mho/cm), uniform  
grain size less than 25 micrometers, fracture strength of 18,000 psi or greater and density  
55 greater than 98 percent of the theoretical density of  $\text{TiO}_2$  in the rutile form. Some variations  
of processing methods, starting  $\text{TiO}_2$  powders and green forming methods are discussed in  
specific examples will make this point clear.

The second method of processing  $\text{TiO}_2$  and small percentages of tantalum or niobium  
additive into a highly conducting, thermally shock resistant ceramic with uniform grain size  
60 of less than 5 micrometers and fracture strength of 18,000 psi or greater comprises:

60 A) The addition of tantalum or niobium pentachloride to diethyl ether to form the  
molecular complex tantalum or niobium pentachloride diethyletherate, with any excess  
ether to serve as a liquid into which  $\text{TiO}_2$  powder in either the rutile or anatase form may be  
stirred to form a slurry. Constant stirring causes the ether to evaporate rapidly at room  
65 temperature leaving essentially dry, mixed powders to which a binder may be added. This  
simple method is ideally suited for rapid, continuous raw material preparation. At this stage

of processing, the concentration of tantalum or niobium is adjusted by varying the amount of tantalum or niobium pentachloride used to react with the diethyl ether. As in the first method, it will be appreciated that the amount of tantalum or niobium which may be added with continuous electrical conductivity enhancement of the rutile due to homogeneously distributed tantalum or niobium is ultimately limited by the solubility of the metal species in  $\text{TiO}_2$ , but certainly quantities of up to 3 atomic percent are possible. For no tantalum or niobium percentages should the sum of all percentages of cationic impurities of normal ionic charge less than +4 or greater than +5 exceed 10 percent of the added tantalum or niobium concentration. Impurity levels greater than these mentioned serve to drastically limit the attainable conductivity resulting in a highly inefficient use of the tantalum or niobium pentachloride additions. The resulting mixed powders may not be dried at temperatures exceeding  $65^\circ\text{C}$  for times exceeding a few minutes due to the loss of tantalum or niobium by vaporization of  $\text{TaOCl}_3$ , a product of the tantalum chloride diethyletherate decomposition at  $65^\circ\text{C}$  or the comparable niobium compound.

B) The powder with a suitable binder is pressed into a suitable form and sintered at elevated temperatures in air or oxygen with a critical heating rate of at least  $40^\circ\text{C}$  per minute maintained between ambient and  $500^\circ\text{C}$  to prevent loss of tantalum or niobium via vaporization processes. Above  $500^\circ\text{C}$ , more stable oxides of tantalum or niobium and chlorine form and are less susceptible to vaporization, the final form being tantalum or niobium pentoxide which is stable to vaporization loss throughout the common sintering temperature ranges. The methods, ranges of sintering conditions, cooling rates and properties are very similar to the first method of preparation except that the grain size is uniform at 5 micrometers or less and has fracture strength of greater than 18,000 psi.

For either of the above methods, in order to produce rutile doped with tantalum or niobium of repeatable electrical characteristics an anneal of the ceramic in a relatively low oxygen pressure environment is useful. Such a reducing treatment serves to increase the conductivity of the sample to values as high as  $5 (\text{ohm-cm})^{-1}$  at room temperature for material containing about 0.5% tantalum and  $9 (\text{ohm-cm})^{-1}$  at room temperature for material containing 1 atom percent tantalum. The approximate range of useful oxygen partial pressure is from  $10^{-5}$  to  $10^{-25}$  atmospheres (optimum being  $10^{-10}$  to  $10^{-20}$  atmospheres) with the annealing temperature ranging from about  $850^\circ\text{C}$  to about  $1400^\circ\text{C}$ . At the lower temperature of  $850^\circ\text{C}$ , the anneal should be carried out for approximately 3 hours while at  $1400^\circ\text{C}$  approximately 1/2 hour should be adequate. Those skilled in the art can easily determine optimum times for anneals carried out in the middle of the above temperature range. After such an anneal, the conductivity of the ceramic containing from 0.1 to 3.0 atomic percent of tantalum or niobium in the temperature range of ambient to  $350^\circ\text{C}$  is relatively independent of temperature. Figure 5 is a graph showing the relationship between the resistivity of the ceramic and the annealing step.

As mentioned above, the current collector prepared in accordance with this invention are useful as current collectors or as current collector/containers in energy conversion devices of the type comprising: (1) an anodic reaction zone containing a molten alkali metal reactant-anode in electrical contact with an external circuit; (2) a cathodic reaction zone containing a cathodic reactant comprising a molten liquid electrolyte which is electrochemically reactive with said anodic reactant and a current collector at least one surface of which is exposed to said cathodic reactant; and (3) a cation permeable barrier to mass liquid transfer interposed between and in contact with said anodic and cathodic reaction zones, said current collector being in electrical contact with both said cation-permeable barrier and said external circuit. Such devices, the most common of which is the sodium/sulfur electrical storage cell are well known to those skilled in the art and are disclosed in the following U.S. Patents: 3,404,035; 3,404,036; 3,413,150; 3,446,677; 3,458,356; 3,468,709; 3,468,719; 3,475,220; 3,475,223; 3,475,225; 3,535,163 and 3,719,531.

Figure 2 shows a typical electrical conversion device of the above type wherein the current collector of this invention also serves as the container for the cathodic reactant and, in fact, for the entire cell. In the Figure a cell is generally indicated at 14. Such a cell may, of course, be one unit of a plurality of cells in series and/or parallel forming a battery. In the embodiment sodium 16, is shown within a tubular cation permeable barrier 20. In contact with the exterior of tube 20 is a porous conductor 22 immersed in the molten cathodic reactant-electrolyte. Encasing both 20 and 22 is an electronically conducting metal clad cylindrical container 24 which be formed of the current collector material of this invention such that the interior surface thereof is conductive ceramic and the outside surface is metal cladding. In contact with the molten sodium 16, is a conductor 26, e.g., platinum wire, which serves as the negative lead to an external circuit, not shown, which includes a resistance, e.g., a light bulb, D.C. motor, etc. and is in electrical connection with a positive lead, conductor 30. Lead 30 is in electrical contact with current collector/container. The sodium atoms of the anode-reactant 16 yield electrons to the conductor 26 and the ions pass

through tube 20 to the cathodic reactant. Sulphur atoms within 22 accept electrons from the external circuit by cathode 24 and the porous conductor 22. In this particular embodiment, the porous conductor is shown as a fibrous sheet material fabricated from graphite or carbon fibers.

5 In another configuration of the above type of energy conversion device the current collector of the invention could be tubular or cylindrical in configuration with the exterior of said tubes or cylinder comprising the ceramic member and the interior of the tube or cylinder bearing the metal cladding. Such a current collector is then immersed in the cathodic reactant such that said ceramic member, but not the metal cladding is exposed to the cathodic reactant. The design shown in Figure 2 could be modified to this type of design by inserting such a current collector directly into molten cathodic reactant within the cathodic reaction zone and employing a container which is not a current collector. Such a current collector design as would be suitable for such a use is shown in Figure 4 wherein 2 is the electronically conductive tubular ceramic primary load bearing element and 4 is a thin layer of metal cladding substantially covering the interior of the ceramic tube. The current collector is shown adapted for making electrically contact with an external circuit. Conductive metal rod 6 (e.g., aluminum or copper) is disposed internally of said tube and extends through the open end thereof held in sealed relationship by seal 8. Contact is made complete between the current collector and rod 6 by a conductive powder 10 which fills the space between the rod 6 and metal cladding 4.

20 Figure 3 shows still another design of the type of electrical conversion device described above and employing the current collector of the design shown in Figure 4 and discussed above. In the design shown a cylindrical or tubular container 32 has a tubular cation permeable barrier 34 disposed internally thereof such that, as was the case in the design of Figure 2, a first reaction zone is located internally of the cation permeable barrier 34 and a second reaction zone is located between the container 32 and the cation permeable barrier 34. However, in contrast to the cell of Figure 2 in the cell of Figure 3 the first reaction zone is the cathodic reaction zone, not the anodic reaction zone and contains cathodic reactant 36 rather than alkali metal. Alkali metal 38 is contained in the second reaction zone which is the anodic reaction zone rather than the cathodic as in Figure 2.

30 The following specific examples will more fully illustrate the details of the design and construction methods of this invention.

#### *Example I*

35 In order to produce 102.28 grams of  $\text{TiO}_2$  powder containing 1 percent Ta cations, 3.49 grams of tantalum pentafluoride of 99+ % purity on a metals basis is dissolved in 20 ml of water at about 25°C in a polyethylene beaker. The solution is added to an ethyl alcohol slurry containing 100.0 grams of reagent  $\text{TiO}_2$  powder in the anatase form while constantly stirring until the slurry becomes very viscous and nearly dry. The powder, still slightly wet, is placed in an oven at 100°C for overnight drying.

40 To the dried powders is added 1 ml. of a binder composed of a solution of polyvinyl alcohol (PVA) in water. The PVA-powder combination is ground in a mortar and pestle until apparently well mixed. The combination is then screened into nearly round pellet form by forcing the powder-binder combination through a screen of 20 wires per lineal inch. Subsequently, the powders are poured into molds and pressed at about 20,000 psi after which they are prefired to a temperature of 950°C. During prefiring the elapsed time between ambient and 350°C is less than about 35 minutes. The heating rate is this temperature range is approximately constant; the average heating rate is about 10°C per minute. The green ceramic bodies are held at 950°C for approximately 3 hours and then cooled in about 4 hours to room temperature.

50 The prefired ceramic bodies are placed on a small brick slab which has been coated with unpressed powders of the ceramic body composition and placed in a sintering furnace at 1000°C. The sintering furnace is composed of a tubular, nonporous aluminum oxide tube and aluminum oxide flat shelf and electrically heated by silicon carbide rods. The sample is introduced into the highest temperature zone of the furnace over a period of 5 to 10 minutes, after which the furnace is heated to a sintering temperature of 1400°C in about 2 to 3 hours in air. The ceramic body is held at the sintering temperature for 3 hours and immediately removed by pushing the brick sample slab to the end of the furnace tube and placing in ambient air to cool.

60 The ceramic bodies are placed upon powders of Ta doped rutile within a tubular furnace, the ends of which are sealed with water-cooled rubber rings. The furnace is evacuated with a mechanical pump after which nitrogen gas with less than 8 ppm oxygen is passed over metallic titanium powder and through the furnace. The furnace temperature is raised to 1200°C at the point of placement of the ceramic body and at 1050°C at the point of placement of the metallic titanium powder. The temperatures are maintained for



approximately 3 hours before slowly cooling over 8 hours to ambient.

The ceramic body is sectioned for density measurement by hydrostatic weighing and a section is removed for the addition of metal electrodes required for a determination of electrical resistivity and degradation of the metal-ceramic interface upon exposure to oxygen at various (higher than ambient) temperatures.

The conductivity of a sample treated by this method will be approximately 9 mho per centimeter at room temperature, increasing to 16 mho per centimeter or greater above 300°C. The fracture strength of ceramics prepared in this fashion, as measured by the 4 point bending test is greater than 18,000 psi.

It is speculated that uniform grain size and high electrical conductivity is largely due to the homogeneous distribution of tantalum in the rutile phase of  $\text{TiO}_2$ . Apparently the most critical step is the addition of a volatile fluoride and rapid prefiring to prevent its loss through vaporization.

### Example II

In order to produce 102.29 grams of  $\text{TiO}_2$  powder containing, 4.5284 grams of tantalum pentachloride ( $\text{TaCl}_5$ ) of 99.5+% purity on a metals basis is dissolved in 20 ml of diethyl ether in a pyrex beaker. This solution is added to a diethyl ether slurry of 100.0 grams of reagent grade  $\text{TiO}_2$  powder in the anatase form. The combination slurry is then stirred for several minutes to assure mixing. Subsequently the slurry is poured into 5 inch diameter watch glasses from which the excess diethyl ether is allowed to evaporate. At no time is the temperature of the chemical system raised above ambient.

To the dried powders is added about 2 ml of fine carbon powder which is mixed with a mortar and pestle. Following this procedure about 2 ml of ethyl alcohol is added and mixed with a plastic spoon. The powders with the carbon and ethyl alcohol binder are screended into nearly round pellet form by forcing the powder binder combination through a screen of 20 wires per lineal inch. The powders are then poured into molds and pressed at pressures of about 20,000 psi after which they are prefired to a temperature of 950°C. During prefiring the elapsed time between ambient and 950°C is less than about 25 minutes. The average heating rate in this temperature range is about 38°C per minute and greater than 40°C per minute between ambient and 500°C. The green ceramic bodies are held at 950°C for approximately 3 hours and then cooled in about 4 hours to room temperature.

The prefired ceramic bodies are placed in a small brick slab which has been coated with unpressed powders of the ceramic body composition and placed in a sintering furnace at 1000°C. The sintering furnace is composed of a tubular, nonporous aluminum oxide tube and aluminum oxide flat shelf and electrically heated by silicon carbide rods. The sample is introduced into the highest temperature zone of the furnace over a period of 5 to 10 minutes, after which the furnace is heated to the sintering temperature of 1400°C in about 2 to 3 hours in air. The ceramic body is held at the sintering temperature for 3 hours and immediately removed by pushing the brick sample slab to the end of the furnace tube and placing in ambient air to cool.

The ceramic bodies are placed upon powders of Ta doped rutile within a tubular furnace, the ends of which are sealed with water-cooled rubber rings. The furnace is evacuated with a mechanical pump after which nitrogen gas with less than 8 ppm oxygen is passed over metallic titanium powder and through the furnace. The furnace temperature is raised to 1200°C at the point of placement of the ceramic body and at 1050°C at the point of placement of the metallic titanium powder. The temperatures are maintained for approximately 3 hours before slowly cooling over 8 hours to ambient.

The ceramic body is sectioned for density measurement by hydrostatic weighing and microscopic examination and a section is removed for the addition of metal electrodes required for a determination of electrical conductivity.

The density of the ceramic body prepared in this way is greater than 4.10 grams per cubic centimeter, the electronic conductivity is greater than or about 9 mho per centimeter at 25°C. The very uniform grain size in a ceramic prepared in this fashion will be less than or about 5 micrometers and the corresponding fracture strength as measured by the 4 point bending method is greater than 18,000 psi.

It is speculated that small uniform grain size and relatively high electrical conductivity is largely due to the homogeneous distribution of tantalum in the rutile phase of  $\text{TiO}_2$ . Apparently the most critical processing step in the formation of  $\text{TaOCl}_3$  upon decomposition of tantalum pentachloride diethyl operate 65°C and the very rapid prefiring to prevent its loss through vaporization.

### Example III

A small bar shaped sample of electrically conductive ceramic, prepared as described in Example I or II, is coated with aluminum by conventional r.f. sputtering techniques, using

argon gas at a pressure of 10 to 20 millitorr as a sputtering agent. At a power level of 100 watts, with a 2 inch diameter aluminum cathode, and a cathode-to-target spacing of 1 to 2 inches, the sputtering is continued for 5 to 10 minutes, producing a uniform adherent layer of aluminum of approximately 2000Å thickness. All aluminum on the specimen except for four parallel grooves on one surface is mechanically removed from the specimen. Electrical contact with each of these aluminum coated grooves is then established with four conducting probes. Standard four terminal resistance measurement is then made permitting accurate determination of that part of the resistance between the two middle terminals due only to bulk resistance of the conductive ceramic,  $R_B$ . Standard two terminal measurement of resistance between the two middle terminals is then made. This resistance,  $R_T$ , (after well-known geometrical corrections) is then compared with the four terminal resistance,  $R_B$ , previously determined. The difference between these two values of resistance is the total contact resistance of the two middle terminals. With a specimen prepared as described, this contact resistance will be negligible (less than 10% of  $R_B$ ). The sample may be heated to 500°C in air for periods of at least 10 hours with no measurable change in contact resistance determined as described above.

This experiment, one should note, is performed under conditions whereby contact resistance increases are most easily observed. By applying only a thin metal cladding of 2000 angstroms instead of the relatively thick cladding required by the design, mass transport of material which degrades the contact to the metal-ceramic interface is enhanced. Further, by cycling the samples to high temperatures and measuring the contact resistance at ambient, one observes the degradation effect at its worst. Contact resistances are generally known to decrease as the temperature of the contact is increased. Thus a container operating at temperatures above ambient will show improved behavior over that observed in the manner of this experiment.

#### Example IV

A specimen of electrically conductive ceramic is prepared and treated as described in Example III, (except that the sputter-deposited layer is silicon rather than aluminum). Contact resistance, as described in Example III, is negligible both before and after heat treatment in air at 500°C for periods up to at least 10 hours.

#### Example V

A specimen of electrically conductive ceramic is prepared and treated as described in Example III, except that the cladding material is nickel, deposited electrolytically according to standard electroplating processes. Contact resistance, as described in Example III, is negligible both before and after heat treatment in air at 500°C for periods up to at least 10 hours.

#### Example VI

A small bar shaped sample of dimensions approximately 1.5 mm by 3.0 mm x 20 mm prepared as an Example I is electroplated at ambient via standard methods at a current density of 50 milliamperes per square centimeter with nickel to a thickness of approximately 1000Å on the ends and in two parallel strips on one side of the sample. The two metallic strips have a width of approximately 0.5 mm and are positioned to be approximately 5 mm from either end. Standard two and four terminal direct current resistance measurements are made at ambient. The four probe resistance measurements allows accurate determination of the contribution of the bulk resistivity to the sample resistance between the two metallic strips. The two probe resistance measurement allows accurate determination of the contribution of the bulk resistivity to the sample resistance between the ends and the contribution of the metal-ceramic contact resistance to the total sample resistance. The difference between the apparent resistivity measured with the two terminal method and that from a measurement with the four terminal method is the total contact resistance of the contacts at the 1.5 mm by 3.0 mm ends of the sample. Such a sample is prepared as described and the contact resistance is found to be negligible (less than 10% of the apparent sample resistivity). The sample with electrodes is heated in air at 400°C for 15 hours and cooled to ambient whereupon a second measurement of the contact resistance is made and again found to be negligible. Reheating the sample and electrodes to 500°C for 15 hours with subsequent remeasurement of the contact resistance at ambient shows negligible contribution. A third heat treatment in air at 600°C for 15 hours with subsequent remeasurement of the contact resistance at ambient shows a measureable but still negligible contact resistance of approximately 0.02 (ohm-cm<sup>2</sup>).

#### Example VII

A specimen of electrically conductive ceramic is prepared and treated as described in

Example VI except that the electrode contacting material is chromium, deposited electrolytically according to standard electroplating processes. Contact resistance, as described in Example VI, is negligible both before and after heat treatment in air at 500°C for periods greater than 10 hours.

#### Example VIII

A specimen of electrically conductive ceramic is prepared and treated as described in Example III, except that the specimen is heated in air to 600°C for 1 hour before deposition of cladding material, and that the cladding material is gold, deposited by vacuum evaporation, according to standard vacuum deposition techniques. The contact resistance, determined as described in Example III is not negligible, but is at least 10  $\Omega$ . The specimen is now heated to a temperature of 700°C for 10 minutes in an atmosphere consisting of 1 Torr of dry H<sub>2</sub>, and the contact resistance upon cooling is reduced to negligible values (less than 10% of R<sub>B</sub>, as defined in Example III).

#### Example IX

Dried TiO<sub>2</sub> powders containing 1 percent Ta cations are prepared as described in either Example I or II and binders are added as described in Example I or II respectively and screened in a standard 20 mesh screen into nearly spherical pellet form.

The pelletized powder-binder mixtures are poured into a mold consisting of a Hysol coated central stainless steel mandrel and cast polyurethane outer boot, of hardness durometer 90. Holding the polyurethane boot in a rigid position with respect to the mandrel is a stainless steel outer casting with perforations through which fluids may flow. Enough powder is added over the exposed end of the mandrel to produce a closed end and ceramic container and a rubber stopper with stainless steel core is placed on the assembly for sealing.

The powder is compressed at a pressure of 30,000 pounds per square inch in a commercial isostatic press. After removal from the assembly, the green formed closed end tube body is prefired in a manner described in Example I and II respectively and sintered at 1400°C for 3 hours.

Subsequently a coating of nickel of the thickness 200 micrometers is added by electrolytic deposition as described in Example V producing a container of total resistance less than 1 milliohm at 350°C as measured between the total internal surface area and a banded contact on the center of the outer metallic cladding.

#### Example X

Ceramic prepared as in Example I or II pressed into closed end tube form as in Example VII but of dimensions after sintering of 1 cm outside diameter, 0.1 cm wall thickness and 20 cm length is nickel coated by the method of electroplating on the inner surface of the tube as given in example V. The closed end tube with inner coating of nickel is contacted by a high conductivity metal rod to produce a contacting electrode for a device an example of which is shown in Figure 3.

Patent Application 2831/78 (Serial No. 1577364) describes and claims a method of manufacturing a polycrystalline titanium dioxide ceramic member.

#### WHAT WE CLAIM IS:-

1. An electrically conductive current collector suitable for use in high temperature applications in the presence of currosive environments, comprising:

(A). A high strength, noncorresive electronically conductive, polycrystalline ceramic member of rutile which is doped with ionic metal species having a stablevalence in said polycrystalline ceramic of at least +5 which serves as the primary load bearing member of said current collector, said ceramic being substantially impervious to materials constituting said corrosive environments; and

(B). A highly electronically conductive metal cladding intimately attached to a substantial portion of one surface of said ceramic member, said metal cladding having a thickness sufficiently thin to be plastically deformable in relation to said ceramic which preserves the function of said ceramic member as the primary load bearing element of said current collector and being based on the relative elastic modulus of the metal of said metal compared to that of the ceramic member, said metal cladding being arranged to direct current flow through said ceramic member and to shunt said current between said member and an external contact.

2. A current collector in accordance with Claim 1, wherein at the temperature of the environment in which said current collector is employed said ceramic member has an electrical resistivity of less than 1000 ohm-cm and said metal has an electrical resistivity of less than .001 ohm-cm.

3. A current collector in accordance with Claim 1, wherein at the temperature of the

environment in which said current collector is employed said ceramic member has an electrical resistivity of less than 50 ohm-cm and said metal has an electrical resistivity of less than .0003 ohm-cm.

4. A current collector in accordance with Claim 1, wherein at the temperature of the environment in which said current collector is employed said ceramic member has an electrical resistivity of less than 10 ohm-cm and said metal has an electrical resistivity of less than .0001 ohm-cm.

5. A current collector in accordance with any one of the preceding claims, wherein said ceramic member is selected from the group consisting of polycrystalline, electronically conductive forms of ceramics selected from the group consisting of calcium titanate, strontium titanate, lanthanum strontium chromite and titanium dioxide.

6. A current collector in accordance with claim 5, wherein said titanium dioxide is in the rutile crystallographic form which is doped with ionic metal species having a stable valence in said polycrystalline ceramic of at least +5.

7. A current collector in accordance with claim 6, where the dopant is selected from tantalum and niobium.

8. A current collector in accordance with any one of the preceding claims, wherein said metal cladding has the additional chemical properties of strong adherence to said ceramic member and resistance to degradation of electrical conductance at the ceramic-metal interface.

9. A current collector in accordance with claim 8, wherein said metal cladding is selected from the class of highly conductive metals which are impermeable to oxidizing species in the environment in which said current collector is to be employed.

10. A current collector in accordance with claim 9, wherein said metal cladding is selected from the class of highly conductive metals which form a protective surface coating from said oxidizing species.

11. A current collector in accordance with claim 10, wherein said metal cladding is selected from the group consisting of aluminum, and nickel.

12. A current collector in accordance with claim 10, wherein said metal cladding is chromium.

13. A current collector in accordance with claim 9, wherein said metal cladding is a dual metal consisting of a first layer of silicon covered with a second layer of platinum.

14. A current collector according to any one of the preceding claims, wherein said ceramic member is an electronically conductive polycrystalline titanium dioxide ceramic member exhibiting high resistance to thermal shock and uniform grain size with an average size of less than 25 micrometers and consisting of titanium dioxide in the rutile crystallographic form doped with a homogeneously distributed ionic metal species selected from tantalum and niobium, which has been prepared by

(A) dissolving in a solvent selected from water and aliphatic alcohols the pentafluoride salt of said metal species in an amount adapted to provide from .01 to 8 atomic per cent of said metal species in said ceramic member;

(B) adding titanium dioxide powder in either the rutile or anatase form to the solution of (A) to produce a mixed slurry;

(C) drying said slurry to powder form at a temperature adapted to avoid evaporation of said metal species;

(D) green forming said powder to the desired shape;

(E) heating the shaped green body to about 350°C. at a rate of at least about 10°C. per minute;

(F) sintering said shaped green body at a temperature of at least about 1330°C; and

(G) annealing said sintered shaped body in a reducing atmosphere having an oxygen partial pressure of  $10^{-5}$  to  $10^{-25}$  atmospheres at a temperature of from 850°C. to 1400°C. to increase the conductivity of said ceramic member.

15. A current collector in accordance with claim 14, wherein said pentafluoride salt is employed in amounts sufficient to provide from .1 to 3 atomic percent of said metal species in said ceramic body.

16. A current collector in accordance with either of claims 14 and 15, wherein said shaped green body is sintered at a temperature in the range of 1380°C. to 1440°C.

17. A current collector in accordance with claim 14, wherein (i) said pentafluoride salt is employed in amounts sufficient to provide from .1 to 3 atomic percent of said metal species in said ceramic body, (ii) said shaped green body is sintered at a temperature of 1400°C., and (iii) said oxygen partial pressure during annealing is from  $10^{-10}$  to  $10^{-20}$  atmospheres.

18. A current collector according to any one of claims 1 to 13, wherein said ceramic member is an electronically conductive polycrystalline titanium dioxide ceramic member exhibiting high resistance to thermal shock and uniform grain size with an average size of

less than 25 micrometers and consisting of titanium dioxide in the rutile crystallographic form doped with a homogeneously distributed ionic metal species selected from tantalum and niobium, which has been prepared by

- 5 (A) dispersing a mixture of a pentachloride-diethyletherate complex of said metal species and titanium dioxide powder in either the rutile or anatase form to form a slurry, said slurry components being included in amounts adapted to provide from .01 to 8 atomic percent of said metal species in said ceramic member; 5
- (B) drying said slurry to powder form at a temperature adapted to avoid evaporation of said metal species, 10
- 10 (C) green forming said powder to the desired shape; 10
- (D) heating the shaped green body to about 500°C. at a rate of at least 40°C. per minute; 10
- (E) sintering said shaped green body at a temperature of at least 1330°C., and 10
- (F) annealing said sintered shaped body in a reducing atmosphere having an oxygen partial pressure of  $10^{-5}$  to  $10^{-25}$  atmospheres at a temperature of from 850°C. to 1400°C. to 15
- 15 increase the conductivity of said ceramic member. 15
19. A current collector in accordance with claim 18, wherein said pentachloride-diethyletherate complex of said metal species is prepared by adding a pentachloride salt of said metal species to an excess of diethylether.
20. A current collector in accordance with either of claims 18 and 19, wherein the components of said slurry are included in amounts adapted to provide from .1 to 3 atomic percent of said metal species in said ceramic body. 20
21. A current collector in accordance with any one of claims 18 to 20, wherein said shaped green body is sintered at a temperature in the range of 1380°C. to 1440°C.
22. A current collector in accordance with any one of claims 18 to 21, wherein (i) said slurry components are employed in amounts sufficient to provide from .1 to 3 atomic percent of said metal species in said ceramic body, (ii) said shaped green body is sintered at a temperature of 1400°C., and (iii) said oxygen partial pressure during annealing is from  $10^{-10}$  to  $10^{-20}$  atmospheres. 25
23. A current collector according to any one of claims 1 to 13, wherein said ceramic member is an electronically conductive polycrystalline titanium dioxide ceramic member exhibiting high resistance to thermal shock and uniform grain size with an average size of 25 micrometers and consisting of titanium dioxide in rutile crystallographic form doped with a homogeneously distributed ionic metal species selected from tantalum and niobium which has been prepared by: 30
- 35 (a) dissolving the desired amount of a pentafluoride compound of the doping material in water; 35
- (b) adding titanium dioxide powders to form a slurry;
- (c) drying the slurry to powder form by procedures which preclude critical evaporation of the pentafluoride, 40
- (d) forming said powder form into a suitable green body, 40
- (e) heating the green body to a temperature above 340°C. at a rate of 10°C. per minute or greater, and
- (f) sintering at temperatures above 1300°C. until appropriate homogenization has occurred. 45
24. A current collector according to any one of claims 1 to 13, wherein said ceramic member is an electronically conductive polycrystalline titanium dioxide ceramic member exhibiting high resistance to thermal shock and uniform grain size with an average size of 25 micrometers and consisting of titanium dioxide in rutile crystallographic form doped with a homogeneously distributed ionic metal species selected from tantalum and niobium which has been prepared by: 50
- (a) preparing a pentachloride-diethyletherate complex of the doping material by the addition of its pentachloride compound to diethylether; 55
- (b) adding titanium dioxide powders to form a slurry,
- (c) drying the slurry to powder form by procedures which preclude critical evaporation of the pentafluoride, 55
- (d) forming said powder form into a suitable green body,
- (e) heating the green body to a temperature above 500°C. at a rate of 10°C. per minute or greater, and
- (f) sintering at temperatures above 1300°C. until appropriate homogenization has occurred. 60
25. A current collector substantially as hereinbefore described with reference to either of Figures 1 and 4 of the accompanying drawings.
26. In an electrical conversion device of the type comprising:
- (1) an anodic reaction zone containing a molten alkali metal reactant - anode in electrical contact with an external circuit; 65

(2) a cathodic reaction zone containing a cathodic reactant comprising a molten liquid electrolyte which is electro-chemically reactive with said anodic reactant and a current collector at least one surface of which is exposed to said cathodic reactant; and

5 (3) a cation permeable barrier to mass liquid transfer interposed between and in contact with said anodic and cathodic reaction zones, said current collector being in electrical contact with both said cation-permeable barrier and said external circuit, wherein the improvement comprises:

10 employing as said current collector in said device the current collector in accordance with any one of claims 1 to 22, said current collector being disposed within said cathodic reaction zones such that said ceramic member but not said metal cladding is exposed to said molten cathodic reactant. 10

27. An electrical conversion device in accordance with claim 26, wherein said current collector also serves as a container for said cathodic reactant.

15 28. An electrical conversion device in accordance with claim 24, wherein said container is a cylinder, the inside surface of which is said ceramic member and the outside surface of which bears said metal cladding. 15

29. An electrical conversion device in accordance with claim 23, wherein said current collector is tubular or cylindrical in configuration with the exterior of said tube or cylinder comprising said ceramic member and the interior of said tube or cylinder bearing said metal cladding, said current collector being immersed in said cathodic reactant such that said ceramic member but not said metal cladding is exposed to said cathodic reactant. 20

30. An electrical conversion device in accordance with claim 23, wherein a cylindrical or tubular container has disposed internally thereof a tubular or cylindrical cation permeable barrier such that a first reaction zone is located internally of said cation permeable barrier and the second reaction zone is located between the inside wall of said cylindrical or tubular container and the outer wall of said tubular or cylindrical cation permeable barrier. 25

31. An electrical conversion device in accordance with claim 30, wherein said first reaction is the anodic reaction zone, the second reaction zone is the cathodic reaction zone and said container is said current collector.

30 32. An electrical conversion device in accordance with claim 30, wherein said first reaction zone is said cathodic reaction zone, said second reaction zone is said anodic reaction zone and said current collector is tubular or cylindrical in configuration with the exterior of said tube or cylinder comprising said ceramic member and the interior of said tube or cylinder bearing said metal cladding, said current collector being immersed in said cathodic reactant such that said ceramic member but not said metal cladding is exposed to said cathodic reactant. 35

33. An electrical conversion device in accordance with any one of claims 23 to 32, wherein said anodic reactant is sodium and said cathodic reactant comprises molten polysulfide salts or a mixture of sulfur and sulfur saturated molten polysulfide salts.

40 34. An electrical conversion device substantially as hereinbefore described with reference to either of Figures 2 and 3 of the accompanying drawings. 40

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COMPLETE SPECIFICATION

5 SHEETS

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Sheet 1

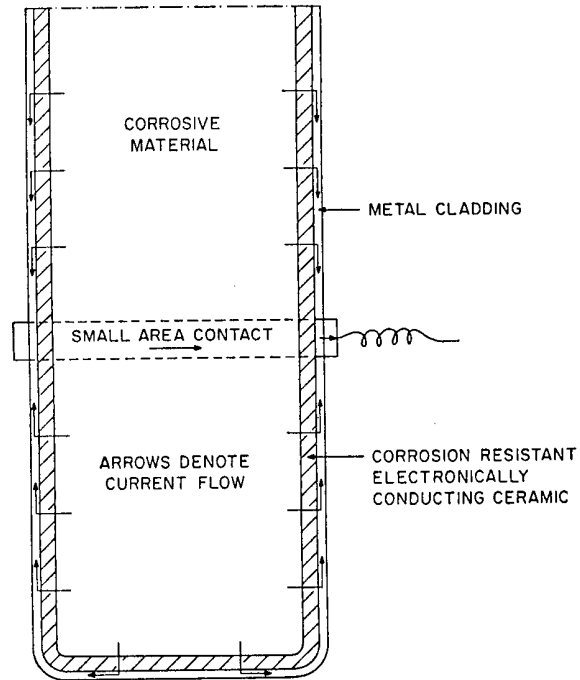


FIG. 1

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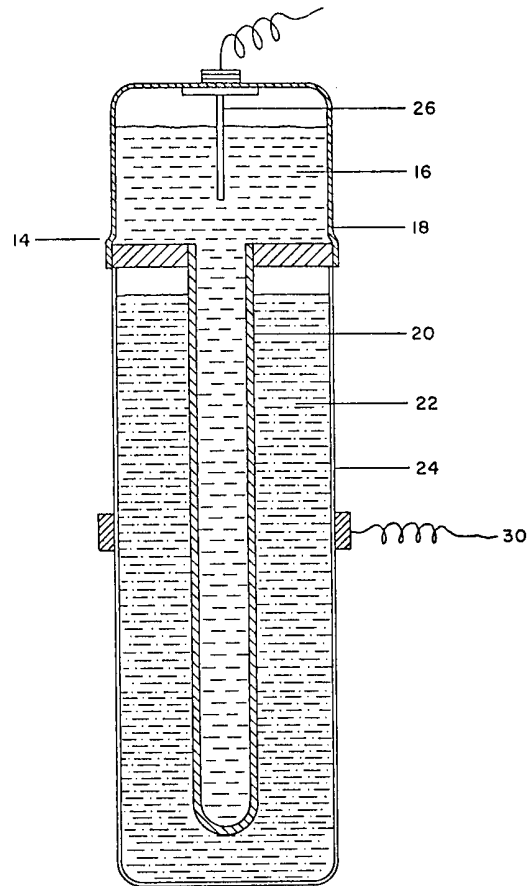


FIG. 2



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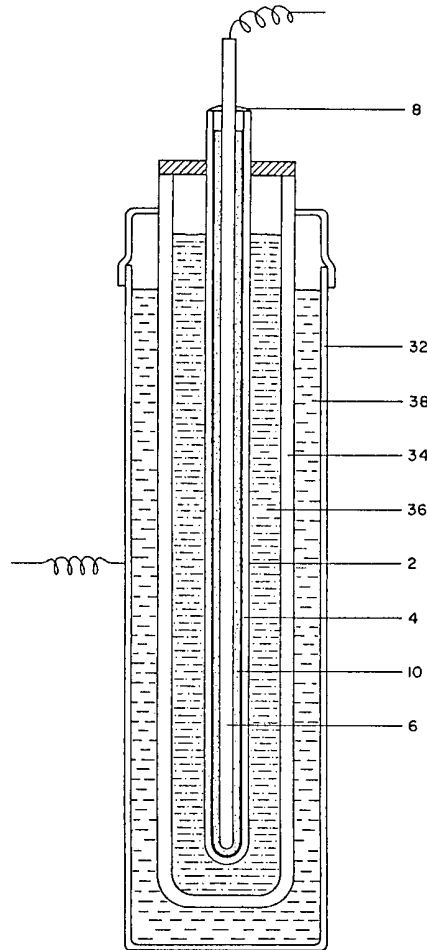


FIG. 3

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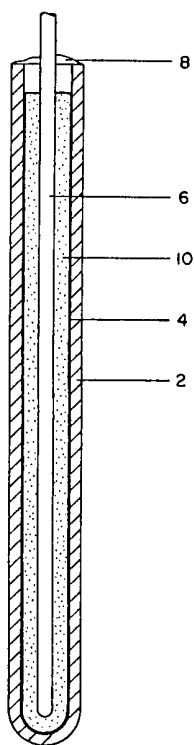


FIG. 4

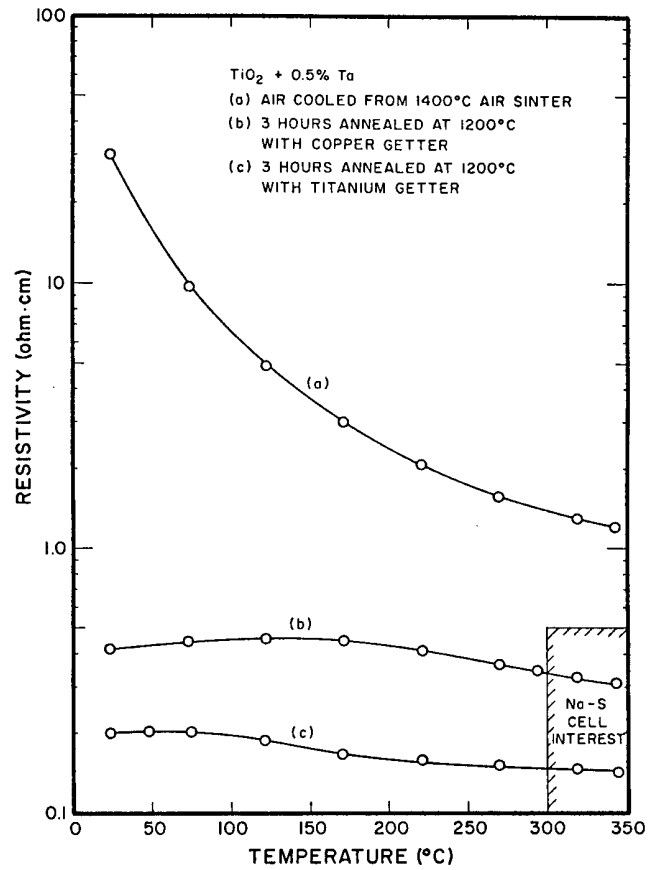


FIG. 5