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(54) ALKALI METAL-SULPHUR SECONDARY BATTERY OR CELL WITH POLYSULFIDE WETTABLE ELECTRODE

(71) We FORD MOTOR COMPANY LIMITED., a British Company, of Eagle Way, Brentwood, Essex, CM13 3BW 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:

This invention relates to an improved alkali metal-sulfur or secondary cell or battery of the type comprising in the or each cell at least one molten alkali metal anode, at least one cathode, a liquid electrolyte electrochemically reversibly reactive with said alkali metal and in contact with said cathode, and a cation-permeable barrier to mass liquid transfer interposed between and in contact with, said anode and said liquid electrolyte.

More particularly, this invention relates to an improved alkali metal/sulfur battery or cell of increased ampere-hour capacity.

A recently developed type of secondary or rechargable electrical conversion device comprises: (A) an anodic reaction zone containing a molten alkali metal anode-reactant, e.g., sodium, in electrical contact with an external circuit; (B) a cathodic reaction zone containing: (i) a cathodic reactant comprising sulfur or a mixture of sulfur and molten polysulfide, which is electrochemically reversibly reactive with said anodic reactant, and (ii) a conductive electrode which is at least partially immersed in said cathodic reactant; and (C) a solid electrolyte comprising a cation-permeable barrier to mass liquid transfer interposed between, and in contact with, said anodic and cathodic reaction zones. As used herein, the term "reactant" is intended to mean both reactants and reaction products.

During the discharge cycle of such a device, molten alkali metal atoms such as sodium surrender an electron to an external circuit and the resulting cation passes through the solid electrolyte barrier and into the liquid electrolyte to unite with polysulfide ions. The polysulfide ions are formed by charge transfer on the surface of the electrode by reaction of the cathodic reactant with electrons conducted through the electrode from the external circuit. Because the ionic conductivity of the liquid electrolyte is less than the electronic conductivity of the electrode material, it is desirable during discharge that both electrons and sulfur be supplied to, and distributed along, the surface of the conductive material in the vicinity of the cation-permeable solid electrolyte. When the sulfur and electrons are so supplied, polysulfide ions can be formed near the solid electrolyte and the alkali metal cations can pass out of the solid electrolyte into the liquid electrolyte and combine to form alkali metal polysulfide near the solid electrolyte.

During the charge cycle of such a device, when a negative potential larger than the open circuit cell voltage is applied to the anode, the opposite process occurs. Thus, electrons are removed from the alkali metal polysulfide by charge transfer at the surface of the electrode and are conducted through the electrode material to the external circuit, and the alkali metal cation is conducted through the liquid electrolyte and the solid electrolyte barrier to the anode where it accepts an electron from the external circuit. Because of the aforementioned relative conductivities of the ionic and electronic phases, this charging process occurs preferentially in the vicinity of the solid electrolyte barrier and leaves behind molten elemental sulfur. As can be readily appreciated, the production of large amounts of sulfur near the surface of the cation-permeable membrane has a limiting effect on rechargeability. This is the case since sulfur is non-conductive and, when it covers surfaces of the electrode, charge transfer is inhibited and the charging process is greatly hindered or terminated. Thus, in order to improve the rechargeability of a cell of this type, it is necessary not only to supply polysulfide to the surface of the porous electrode in the vicinity of the cation-permeable membrane, but also to remove sulfur therefrom.

United States Patent No. 3,811,943 and our copending United Kingdom Patent Application No. 720/76 (now Serial No. 1,536,181) both disclose energy conversion device designs which allow or promote improved mass transportion of reactants and reaction products to and from the vicinity of the solid electrolyte and the electrode during both discharge and charge. In the device disclosed in U.S. Patent No. 3,811,943, an ionically conductive solid electrolyte is located between a first reactant in one container and a second reactant in another container. An electrode for one of the reactants comprises a layer of porous, electronically conductive material having one surface in contact with one side of the ionically conductive solid electrolyte and the other surface in contact with a structurally integral, electronically conductive member permeable to mass flow of its reactant and electrically connected to the external circuit. An open volume exists between the structurally integral conductive member and the container wall to promote free flow and mixing of the reactant. Reactants also flow readily through the conductive member into the layer of porous electronically conductive material. The conductive member distributes electrons to the porous, conductive material which in turn transfers electrons to or from the reactants.

The improvement disclosed in U.K. Patent Specification No. 1,536,181, comprises designing the cathodic reaction zone of the device in such manner that there are a plurality of channels and/or spaces within said zone which are free of porous conductive electrodes and which thus allow free flow of the molten cathodic reactants during operation of the device. This flow results from free convection within the channels and/or spaces, and from wicking of cathodic reactants within the conductive porous material.

Our copending United Kingdom Patent Application No. 721/76 (now Serial No. 1,536,182) discloses an improved method for recharging secondary batteries or cells of the above-described type. The process involves maintaining a temperature gradient within the cathodic reaction zone during recharging which is such that the temperature of the cathodic reactants in a first region adjacent to the solid electrolyte or cation-permeable barrier is sufficiently higher than the temperature of said reactants in a second region not adjacent the barrier for sulfur in the first region to vaporize and be transported to said second region where it condenses.

Our copending United Kingdom Patent Application No. 20647/76 (Serial No. 1555133) discloses an improved secondary battery or cell of the type described above which exhibits an increased ampere-hour capacity as the result of an improvement which comprises: (a) employing a porous conductive material which will wick both sulfur and alkali metal polysulfides and which, in different regions of said cathodic reaction zone, exhibits different degrees of wettability by said alkali metal polysulfides, said material in a region adjacent to said cation-permeable barrier being more readily wetted by said polysulfides than is said material in a region further removed from said barrier to an extent such that sulfur will boil near said barrier and condense away from it; (b) disposing said porous conductive material within said cathodic reaction zone so that it forms and encloses one or more channels which extend from said region adjacent said cation-permeable barrier outwardly into said region of said cathodic reaction zone which is further removed from said barrier; and (c) maintaining the amount of molten cathodic reactant within said cathodic reaction zone such that said channels remain free of said molten reactant and are thus adapted to transport sulfur vapour.

Our copending United Kingdom Patent Application No. 20645/76 (Serial No. 1555131) discloses still another improved secondary battery or cell of the type described above which exhibits an increased ampere-hour capacity as the result of an improvement which comprises: causing the cathodic reaction zone to operate as a gas fuel cell electrode by employing a sulfur storage chamber containing molten sulfur connected with said cathodic reaction zone so as to allow sulfur vapours to pass therebetween, the storage chamber being adapted to be maintained at a temperature (i) above the temperature of said cathodic reaction zone when said cell is being discharged such that sulfur distills into said cathodic reaction zone and (ii) below the temperature of said storage chamber.

The devices of the latter U.K. Patent Applications Nos. 20647/76 and 20645/76 each employ electrode materials which are preferentialy wetted by polysulfide salts as is the case in the invention covered by this application. However, in the latter cases (Nos. 20647/76 (Serial No. 1555133) and 20645/76 (Serial No. 155513) the electrode material is used in conjunction with an electrode material which is preferentially wetted by sulfur. Also, each of those devices, unlike the device of this application, relies on vapour transport for the removal of objectionable sulfur from the region of the electrode near the cation-permeable barrier. The process of U.K. Patent Specification Serial No. 1,536,182 also relies on vapour transfer of sulfur and requires the maintaining of a temperature gradient using external heating elements.

Our copending U.K. Patent Application No. 20646/76 (Serial No. 1555132) teaches increasing the ampere-hour capacity of a secondary battery or cell of the type described by including certain metals, metal salts and other metal compounds in the cathodic reactant. The mechanism by which these materials increase the ampere-hour capacity of the device is not known. One of several theories mentioned in the latter U.K. Application No. 20646/76 is that the materials may to an extent coat the graphite felt, thereby rendering it preferentially wettable by polysulfide and, thus, increasing charge efficiency. Such a mechanism, as stated therein, is only one of several possibilities, and is not certain. It is just as likely that, when these materials are dissolved in, or mixed with, the polysulfide melt, they impart general or localized electronic conductivity to the melt, thereby extending the effective electrode area, altering the electrode kinetics and improving charge capacity. A still further theory suggests that the materials disperse in the melt as a solid phase and thereby increase effective electrode area so as to increase capacity. In any event, the battery or cell disclosed in U.K. Patent Application No. 20646/76 (Serial No. 1555132), unlike the battery or cell made in accordance with the improvement of this invention, requires the addition of materials to the cathodic reactant.

The prior art designs of the aforementioned U.S. Patent No. 3,811,943 and U.K. Patent Specification Serial No. 1,536,181 are effective in promoting distribution of reactants during both discharge and charge. However, even with these improved designs, it is difficult to recharge the batteries or cells at high rates.

We have found that, by employing the improvement of this invention, it is possible to obtain a secondary battery or cell which, without the necessity of external heating or cooling or other modifications, exhibits a high efficiency on charging, thus increasing the ampere-hour capacity of the secondary cell or battery.

The improvement of this invention comprises employing as the electrode in the secondary cell or battery a material which consists essentially of a porous electrically conductive material which during the operation of the device, is preferentially wetted by polysulfide salts as opposed to sulfur, i.e., molten polysulfide salts exhibit a contact angle with the electrode material which is smaller than the contact angle which is exhibited by molten sulfur with the electrode material.

The invention will be more fully understood after reading the following detailed description thereof in conjunction with the drawings in which:

Figure 1 is a vertical sectional view of a cell design suitable for use with the improvement of this invention;

Figure 2 is a cross-sectional view of the cell shown in Figure 1;

Figures 3, 4 and *6* are cut-away vertical sections of a portion of the cell showing other designs incorporating the improvement of the invention; and

Figure 5 is a graph showing performance data for a cell including the improvement of this invention.

The type of secondary or rechargeable electrical conversion devices to which the improvement of this invention applies and various components thereof are disclosed in the following United States Patents, the disclosures of which are incorporated herein by reference: Nos. 3,404,035; 3,404,036; 3,446,677; 3,458,356; 3,468,709; 3,468,719; 3,475,220; 3,475,223; 3,475,225; 3,535,163; 3,719,531 and 3,811,943.

As mentioned above, the secondary cells or batteries to which the improvement of this invention applies comprise generally in the or each cell: (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) a cathodic reactant comprising a liquid electrolyte consisting of sulfur or a mixture of sulfur and sulfur-saturated polysulfide of said molten alkali metal reactant which is electrochemically reversibly reactive with said anodic reactant, and (b) an electrode which is at least partially immersed in 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 electrode being in electrical contact with both said cation-permeable barrier and said external circuit.

The anodic reactant employed in such devices is an alkali metal which is maintained above its melting point when the device is in operation. The anodic reactant is heated by one of the various conventional means including, not by way of limitation, Joule heating, induction heating, and heat-exchange with a suitable fluid. The anodic reactant may also be viewed as the anode proper or conductor through which the electron flow to the external circuit is achieved. A cell component of this type is conventionally referred to in the art as a sacrifical electrode in that, while it is serving the role of a conductor, it is also undergoing electrochemical reaction. Molten sodium is employed as the anodic reactant in most preferred embodiments of such devices. However, potassium, lithium, other alkali metals, mixtures of such alkali metals, or alloys containing such alkali metals can be used.

The cathodic reactant of the fully charged battery or cell is molten sulfur, which is electrochemically reversibly reactive with the anodic reactant. As the device begins to discharge, the mole fraction of elemental sulfur drops whilst the open circuit voltage remains constant. During this portion of the discharge cycle, as the mole fraction of sulfur drops from 1.0 to approximately 0.72, the cathodic reactant displays two phases, one being essentially pure sulfur and the other being sulfur-saturated alkali metal polysulfide in which the molar ratio of sulfur to alkali metal is substantially 5.2:2. When the device is discharged to the point where the mole fraction of sulfur is substantially 0.72, the cathodic reactant becomes single-phase in nature since all elemental sulfur has formed polysulfide salts. As the device is discharged further, the cathodic reactant remains single-phase in nature, and as the mole fraction of sulfur drops so does the open-circuit voltage corresponding to the change in the potential-determining reaction. Thus, the device continues to discharge from a point where polysulfide salts contain sulfur and alkali metal in a molar ratio of approximately 5.2:2 to the point where polysulfide salts contain sulfur and alkali metal in a ratio of substantially 3:2. At this point the device is fully discharged.

Since, in the fully discharged state, the polysulfide melt is single-phase in nature, the activity of sulfur in the melt is substantially less than unity when the mole fraction of sulfur is 0.60 and approaches unity as the mole fraction approaches 0.72, the point at which the polysulfide is sulfur-saturated. As the cell is recharged, elemental sulfur is formed momentarily on the surfaces of the electrode in the vicinity of the solid ceramic electrolyte. Since sulfur is non-conductive, the presence of elemental sulfur on the electrode could cause difficulty in continuing the recharging process. However, when the mole fraction of sulfur in the melt is between 0.60 and 0.72, i.e., the single-phase region, the sulfur which forms on the surface of the electrode tends to react immediately with the polysulfide melt in the vicinity thereof to form a second polysulfide in which the molar ratio of sulfur to alkali metal is greater than 3:2. This process occurs until the molar ratio of sulfur to alkali metal is approximately 5.2:2. This is the point where the mole fraction of sulfur is approximately 0.72 and the open circuit voltage becomes constant.

As charging of the cell or battery continues, the sulfur saturated polysulfide will no longer react with elemental sulfur deposited on the electrode to form polysulfide having a greater mole ratio of sulfur to alkali metal. Thus, as the charging cycle continues the cathodic reactant becomes two-phase in nature. One phase is elemental sulfur and the other is sulfur-saturated alkali metal polysulfide in which the molar ratio of sulfur to alkali metal is substantially 5.2:2, with the mole fraction of sulfur in the cathodic reaction zone continually increasing as the recharging cycle progresses. It is in this region of the recharging cycle that substantial difficulties are confronted because of the formation of large amounts of non-conductive elemental sulfur on porous electrode surfaces. In fact, it is extremely difficult to recharge such secondary cells or batteries to any great extent past the point at which the polysulfide becomes saturated with sulfur and thus the deposition of elemental sulfur has a limiting effect on rechargeability.

The anodic reactant is separated from the cathodic reactant by a solid barrier to mass liquid transfer that is selectively ionically conductive with respect to cations of the anodic reactant and substantially impermeable to other ions which may be stored in the cathodic reactant. Thus, the reaction zone separator or solid electrolyte is a material which will permit the transfer of the ions of the anodic reactant through the separator and into the cathodic reactant during operation of the device. The cathodic reactant together with the separator provides a sufficient barrier to free electron flow in the internal portion of the electrical circuit to permit a difference of potential to develop at the respective electrodes of the devices in operation. It is preferred that the separator should be as thin as possible without unduly sacrificing strength. Although optimum thickness may vary with intended use, separators having a thickness in the range of from 20 to 2,000, preferably from 100 to 1,000, microns have been found to be effective.

Both glasses and polycrystalline ceramic materials have been found suitable for use in such devices as the solid electrolyte or reaction zone separators. Among the glasses which may be used with such devices and which demonstrate an unusually high resistance to attack by molten alkali metal are those having the following composition: (1) from 47 to 58 mole percent sodium oxide, from 0 to 15, preferably from 3 to 12, mole percent of aluminium oxide and 34 to 50 mole percent of silicon dioxide; and (2) 35 to 65, preferably 47 to 58, mole percent sodium oxide, from 0 to 30, preferably from 20 to 30, mole percent of aluminium oxide, and from 20 to 50, preferably from 20 to 30, mole percent boron oxide. These glasses may be prepared by conventional glass-making procedures using the listed ingredients and firing at temperatures of substantially 2700°F.

The polycrystalline ceramic materials useful as reaction zone separators of solid electrolytes are bi- or multi-metal oxides. Among the polycrystalline bi- or multi-metal oxides most useful in the devices to which the process of this invention applies are those in the family of Beta-alumina all of which exhibit a generic crystalline structure which is readily identifiable by X-ray diffraction. Thus, Beta-type alumina or sodium Beta-type-alumina is a material which may be thought of as a series of layers of aluminium oxide held apart by columns of linear Al-O bond chains with sodium ions occupying sites between the aforementioned layers and columns. Among the numerous polycrystalline Beta-type-alumina materials useful as reaction zone separators or solid electrolytes are the following:

(1) Standard Beta-type-alumina which exhibits the above-discussed crystalline structure comprising a series of layers of aluminium oxide held apart by layers of linear Al-O bond chains with sodium occupying sites between the aforementioned layers and columns. Beta-type-alumina is formed from compositions comprising at least 80% by weight, preferably at least 85% by weight, of aluminium oxide and between 5 and 15 weight percent, preferably between 8 and 11 weight percent, of sodium oxide. There are two well-known crystalline forms of Beta-type-alumina, both of which demonstrate the generic Beta-type-alumina crystalline structure discussed hereinbefore and both of which can easily be identified by their own characteristic X-ray diffraction pattern. Beta-alumina is one crystalline form which may be represented by the formula $Na_2O{\cdot}11Al_2O_3$. The second crystalline form is β″-alumina which may be represented by the formula: $Na_2Om6Al_2O_3$. It will be noted that the β″ crystalline form of Beta-type-alumina contains approximately twice as much soda (sodium oxide) per unit weight of material as does the Beta-alumina. It is the β″-alumina crystalline structure which is preferred for the formation of solid electrolyte or reaction zone separators for the device to which the process of this invention is applicable. In fact, if the less desirable beta form is present in appreciable quantities in the final ceramic, certain electrical properties of the body will be impaired.

(2) Boron oxide (B_2O_3) modified Beta-type-alumina wherein from 0.1 to 1 weight percent of boron oxide is added to the composition.

(3) Substituted Beta-type alumina wherein the sodium ions of the composition are replaced in part or in whole with other positive ions which are preferably metal ions.

(4) Beta-type-alumina which is modified by the addition of a minor proportion by weight of metal ions having a valence not greater than 2 such that the modified Beta-type-alumina composition comprises a major proportion by weight of ions of aluminium and oxygen, and a minor proportion by weight of a metal ion in crystal lattice combination with cations which migrate in relation to the crystal lattice as a result of an electric field, the preferred embodiment for use in such electrical conversion devices being that wherein the metal ion having a valence not greater than 2 is lithium or magnesium, or a combination of lithium and magnesium. These metals may be included in the composition in the form of lithium oxide or magnesium oxide, or mixtures thereof, in amounts ranging from 0.1 to substantially 5 weight percent.

The cathodic electrode is in electrical contact with the cation-permeable barrier and an external circuit. The conductive material is of significantly greater surface area than a solid cathode and may comprise any porous material which is electronically conductive and which is resistant to attack by reactants within the cathodic reaction zone.

While the secondary cells or batteries to which the improvement of this invention is applicable may have a number of different configurations, several of which are disclosed in the above-incorporated Patents, a preferred configuration comprises: (1) a container, preferably tubular; (2) a cation-permeable barrier to mass liquid transfer, preferably tubular, which is disposed within said container so as to create an anodic reaction zone within said barrier and a cathodic reaction zone between said barrier and said container; (3) a molten alkali metal anodic reactant within said anodic reaction zone in electrical contact with an external electrical circuit; (4) a cathodic reactant comprising a liquid electrolyte which is electrochemically reversibly reactive with said anodic reactant and which, in at least the partially discharged state, consists of (a) a single-phase composition comprising at least one molten polysulfide salt of said anodic reactant and (b) a two-phase composition comprising molten sulfur and at least one molten sulfur-saturated polysulfide salts of said anodic reactant; and (5) an electrode composed of electrically conductive, porous material which is disposed within said cathodic reaction zone, is at least partially immersed in said cathodic reactant and is in electrical contact with both said barrier and said external circuit. Such secondary cells which are preferably tubular or cylindrical, thus comprise cathodic reaction zones which completely surround the solid electrolyte or reaction zone separator.

The improved batteries or cells in accordance with this invention serve to overcome difficulties caused by formation of elemental sulfur on the electrode surface near the cation-permeable barrier. The improvement comprises employing as the electrode of the battery or cell a porous conductive material which, during operation of the device, is preferentially wet by polysulfide salts as opposed to sulfur. The measure of wettability of a substrate by a liquid material is the contact angle formed between the liquid and the substrate. If the liquid completely wets the substrate, the contact angle will be 0°. If the liquid beads up completely on the substrate surface, the contact angle will be 180°. Thus, the lower the contact angle between the liquid and the substrate, the greater the wettability of the substrate by the liquid. For example, in helium at 318°C the contact angle formed by molten Na_2S_4 on graphite is approximately 100° while the contact angle formed by molten sulfur on graphite is approximately 25°. Thus, graphite is preferentially wetted by sulfur as opposed to polysulfide salt and, as such, is unacceptable for use in the improvement of this invention unless modified to make it preferentially wettable by polysulfide.

We have found that, by employing conductive materials which are preferentially wetted by polysulfide salts, it is possible substantially to reduce or to eliminate electrode polarization while charging in the two-phase region (sulfur and $Na_2S_{5.2}$) at current densities as high as 545 ma/cm^2. This is in contrast to materials which are preferentially wet by sulfur, such as graphite felt electrodes which during charge become blocked by sulfur at temperatures between 300° and 350°C at high current densities.

While the polysulfide-wettable materials useful as the conductive materials in the improvements of the invention may result in appreciable electrode polarization during discharge it is not so significant as seriously to affect the operation of the device. Secondary batteries or cells incorporating the improvement of the invention are particularly suitable for use in electric utility load levelling applications since such applications require charging in about one-half (1/2) the time avilable for discharging and thus require twice the current on charge as on discharge.

Among the numerous materials which are preferentially wettable by polysulfide salts and which will be apparent to those skilled in the art are:

(1) Metals, which term as used herein include alloys as well as metals or alloys having an oxidized surface(s). A preferred metal for use in the invention is stainless steel. We have found, for example, that no electrode polarization occurs at a stainless steel AISI #446 electrode at 330°C while charging in the two-phase region. The contact angle in helium at 318°C formed by molten Na_2S_4 on AISI #446 stainless steel in 0-5°, while the contact angle formed by sulfur on stainless steel is approximately 25°C. These contact angles remain the same independently of the thickness of the oxide layer on the stainless steel (i.e., the virgin stainless steel can be abraded so as to remove old oxide, can be oxidized in hot nitric acid, etched in HCl, oxidized in air at 800°C, or used untreated). Thus, in all cases, the stainless steel is preferentially wetted by sodium polysulfide. All metals which have been exposed to air are covered to a greater or lesser extent, depending on the particular metal, with an oxide coating. Since oxides are particularly stable to molten sulfur and molten alkali metal polysulfides, such as sodium polysulfides, it becomes advantageous further to oxidize the metal surfaces, either by oxidation at elevated temperatures or by attack by oxidizing acids. It is understood that metals and alloys, as used herein, can be coated with oxide due to normal exposure to an ambient atmosphere or specially treated to thicken their oxide coatings.

(2) Materials having a surface comprising, and including materials formed completely of, a composition of a polar or ionic character or materials with unfilled *d*-orbitals. Such compositions include oxides or sulfides of metals consisting of a) Metals of Group I, II or III of the Periodic Table of Elements, b) Transition Series Metals or c) tin, lead, antimony or bismuth. Preferentially, the metal salts or oxides are highly insoluble in the sulfur and polysulfide phases. Preferred materials are: aluminium oxide (Al_2O_3), molybdenum disulfide (MoS_2), chromium trioxide (Cr_2O_3), lanthanum chromite ($LaCrO_3$), calcium-doped lanthanum chromite ($La_{1-x}Ca_xCrO_3$), antimony pentoxide-doped tin oxide (Sb_2O_5-SnO_2), lithium-doped nickel oxide ($Li_xNi_{1-x}O$), titanium-doped iron oxide ($Ti_xFe_{2-x}O_3$), or tantalum-doped titanium oxide (Ta_2O_5-TiO_2). Most of these materials are electronic conductors and can therefore serve as the electrode or completely coat the electrode. Others of these materials, such as aluminium oxide or chromium trioxide, are insulators and must, therefore, only partially cover the electrode surface.

(3) Surface-oxidized graphite. Graphite oxide can be prepared by the standard methods (e.g., graphite in a 1:2 v/v mixture of concentrated nitric and sulfuric acids with solid potassium chlorate added or graphite in sulfuric acid containing sodium nitrate and potassium permanganate). Treatment of the graphite must be brief so that only the surface is oxidized. When this material is used as an electrode in an alkali metal/sulfur cell and heated in the presence of the cathodic reactant to operating temperatures, the graphitic oxide surface converts to graphite sulfide which is preferentially wet by the polysulfide.

(4) Electrically conducting intercalated graphite. Graphite bromide is formed by exposure of graphite felt electrodes to either liquid bromine or bromine vapour. Considerable bromine is retained in the graphite at the operating temperature of the cell. The graphite bromide surface is more wettable by polysulfides than the untreated graphite.

Many materials can be reversibly intercalated in graphite. These materials all tend to make graphite more wettable by polysulfides. The intercalated graphite is prepared by heating the materials with the graphite. Some of the more desirable intercalating materials are: FeCL⅜, CrO_3, V_2S_3, MoO_3, Sb_2S_5, $FeCl_3/AlCl_3$ and $CoCl_3$.

5. Graphite which bears a continuous or discontinuous coating of one or more of the materials of (1), (2), (3) or (4). Thermal decomposition and oxidation methods for coating substrates, such as graphite with metal oxides, are described in U.S. Patents Nos. 2,615,932, 2,669,598 and 3,077,507. Other methods, such as flame-spraying or chemical vapour deposition are well-known in the art. It will be appreciated that, as mentioned above, when the coating to be applied is insulating in nature, it must be applied discontinuously.

(6) A combination or mixture of the materials of (1), (2), (3), (4) or (5). Particularly preferred members of this category are metals of (1) which have been further oxidized and doped by the class of materials given in (2). For example, a nickel metal electrode can be oxidized at high temperature in the presence of nickel nitrate and lithium nitrate, resulting in a lithium-doped nickel oxide-nickel electrode.

Any of the conductive materials chosen for use as an electrode may be disposed within said cathodic reaction zone in a variety of patterns and forms. Exemplary of these many patterns and forms are those consisting of:

(1) Porous conductive material which is disposed within the cathodic reaction zone in the manner disclosed in U.K. Patent Specification Serial No. 1,536,181 mentioned previously so that the cathodic reaction zone contains a plurality of channels or spaces which are free of said porous conductive material and which, in combination with said porous conductive material, allow flow within said cathodic reaction zone of said cathodic reactant during operation of the battery or cell. The term "porous electrically conductive material" as used in this application is intended to mean any of the compositions within the purview of the invention which is in the form of a perforated material, an expanded material; a felt; a woven or nonwoven fabric; a sintered material, a foam, a flame-sprayed material or other forms which will be apparent to those skilled in the art to which this invention relates.

(2) Porous electrically conductive material which is disposed within said cathodic reaction zone such that it is confined to an area of the cathodic reaction zone which is adjacent to the cation-permeable barrier. For example, a perforated or expanded metal sheet, such as stainless steel, may be disposed so as to be contiguous with said barrier, but not with the outer container wall. Thus, in the preferred tubular configuration for cells of the type to which the improvement relates, the perforated or expanded metal sheet may be wrapped around the cation-permeable barrier. An advance which is achieved by positioning the electrode adjacent to, or contiguous with the cation-permeable barrier is that wetting by polysulfide is enhanced by the capillarity between the electrode material and the barrier.

(3) Electrically conductive material which is disposed in such manner that there are two major electrode portions, the first portion being porous electrically conductive material which is confined to an area of said cathodic reaction zone adjacent to said cation-permeable barrier and the second being conductive material which is electrically connected to said first portion, but which is spaced from said first portion so as to create a channel therebetween. In a preferred embodiment, both portions may be formed of a metal such as stainless steel. Thus, in the preferred tubular configuration discussed previously, a perforated or expanded metal sheet is wrapped around the cation-permeable barrier, and a metal cylinder, which may or may not be perforated, is disposed concentrically about, and spaced from, the wrapped barrier.

All of the aforementioned preferred designs and others will be better understood from the following detailed description of the drawings.

Figure 1 shows a full vertical cross-section of a preferred tubular type cell to which the improvement of this invention may relate. Figures 3, 4 and 6 are merely broken-away vertical sections of the lower portion of the cell which show several examples of suitable designs for the porous conductive material. Figure 2 is a cross-section of Figure 1 taken along the line 2-2. To the extent that the part or material described is shown in each of the figures it will be designated by the same numeral used to describe Figure 1.

The cell shown in Figure 1 comprises: a tubular container 4 which may be in electrical contact with an external circuit *via* a lead 2; a tubular cation-permeable barrier to mass liquid transfer 6 which is disposed within said tubular container 4 so as to create an anodic reaction zone within the tubular barrier containing a molten alkali metal reactant-anode 8, which is in electrical contact *via* a lead 10 with an external circuit; a cathodic reaction zone between the tubular barrier 6 and the tubular container 4; a molten cathodic reactant 12 and a porous electrode 14 which is disposed within the cathodic reaction zone.

Figure 1 and its cross-section (Figure 2) are representative of the type of cell design disclosed in U.K. Specification Serial No. 1,536,181 discussed above wherein porous conductive material 14 is disposed within the cathodic reaction zone in such manner that said zone contains a plurality of channels or spaces 16 which are free of said porous conductive material and which, in combination with said porous conductive material, allow flow within said cathodic reaction zone of said cathodic reactant during operation of the battery or cell.

Figures 3 and 4 show designs where porous conductive material 14 is confined to an area adjacent the cation-permeable barrier 6. The material 14 is illustrated as a felt in Figure 3 and as a perforated metal sheet with openings 18 in Figure 4.

Figure 6 shows a cell design where, in addition to a first portion of porous conductive material 14 confined to the area adjacent the barrier 6, there is a second conductive material 20 which may or may not be porous. In the embodiment illustrated, the material 14 is a perforated metal sheet and the material 20 is a solid cylinder of metal which is disposed in such manner that a cathodic reactant can flow around it at the top and bottom of the cathodic reaction zone. The material 20 may also be porous or perforated to allow flow of reactant therethrough. In any event, however, the disposition of materials 14 and 20 as illustrated does create a vertical channel in the cell such that a chimney effect is created, thus increasing free convective flow of reactants. Electrode material 20 and electrode material 14, of course, are electrically connected, e.g. by wires 22.

In order still further to illustrate the improvement of the invention, a specific example is set forth below. However, it will be appreciated that the device design discussed in the Example is merely for illustration and should not be considered limiting in any way.

Example

A sodium/sulfur cell as described, was constructed with an electrode of stainless steel AISI #446 perforated sheet, 0.025 inch thick. The perforation removed 40% of the sheet area. The sheet was formed into a cylinder and fitted snugly about a 1.0 cm O. D. β"-alumina tube. An AISI stainless steel cylinder with a 2cm I.D. was disposed concentrically about said β"-alumina tube. The cell is essentially that shown in part in Figure 6. The performance data for the cell are set forth in Figure 5, where the open cell voltage (O.C.V.) is shown as a broken line. An analysis of internal cell losses is given in the table below which shows that, on charging in the two-phase region, all internal losses are voltage drops (IR) due to ceramic resistance, stainless steel #446 electrode resistance, and melt resistance between the ceramic and the electrode. These losses can be decreased only by improving ceramic conductance or metal electrode conductivity, or by bringing the electrode surface even closer to the ceramic so that the average path length of melt between ceramic and metal is reduced. Since the metal is already in close contact with the ceramic, improvement can come only from the use of porous metal or metal felt, by means of which more metal surface can be brought close to the ceramic. The important feature is that the electrode polarization, which decreases the efficiency of most batteries, is reduced.

TABLE

Electrode polarization and voltage drop (iR) in metal cell at 330°C (theoretical capacity - 5.11 Ah)

Amp-hrs. charged at 125 ma/cm^2 starting from full discharge	iR* (volts)	Electrode polarization (volts)	Terminal cell voltage
One phase region and polarization data not yet available			
0.50	–	–	2.150
Two phase region			
2.10	.183	0	2.260
4.80	.213	0	2.290
Amp-hrs. discharged at 78 ma/cm^2 starting from full charge			
Two phase region			
0.88	.103	.149	1.825
One phase region			
4.03	.118	.216	1.586
4.34	.118	.634	1.118

* Includes melt, metal electrode and ceramic resistance.
During charge at 125 ma/cm^2, about 0.090 V is due to the ceramic. During discharge at 78 ma/cm^2 about 0.056 V. is due to the ceramic.

WHAT WE CLAIM IS

1. A secondary cell or battery comprising, in the or each cell:

(A) one or more anodic reaction zones containing a molten alkali metal reactant-anode in electrical contact with an external circuit;

(B) one or more cathodic reaction zones containing (1) a cathodic reactant which when said battery or cell is at least partially discharged, consists of (i) a single-phase composition comprising at least one molten polysulfide salt of said anodic reactant or (ii) a two-phase composition comprising at least one molten sulfur saturated polysulfide salt of said anodic reactant, and (2) an electrode which is at least partially immersed in said cathodic reactant; and

(C) a cation-permeable barrier to mass liquid transfer interposed between, and in contact with, said anodic and cathodic reaction zones, said electrode being in electrical contact with said cation-permeable barrier and said external circuit, and consisting essentially of a porous electrically conductive material (as herein defined), said molten polysulfide salt exhibiting during the operation of said cell or secondary battery a contact angle with said electrode which is smaller than the contact angle which is exhibited by said molten sulfur with said electrode.

2. A secondary cell or battery comprising, in the or each cell:

(A) a container;

(B) a cation-permeable barrier to mass liquid transfer which is disposed within said container so as to create an anodic reaction zone within said barrier and a cathodic reaction zone between said barrier and said container;

(C) a molten alkali metal anodic reactant within said anodic reaction zone in electrical contact with an external circuit;

(D) a cathodic reactant comprising a liquid electrolyte which is electrochemically reversibly reactive with said anodic reactant and which, when said cell or battery is in at least a partially discharged state, consists of (a) a single-phase composition comprising at least one molten polysulfide salt of said anodic reactant or (b) a two-phase composition comprising molten sulfur and at least one molten sulfur-saturated polysulfide salt of said anodic reactant; and

(E) an electrode disposed within said cathodic reaction zone, at least partially immersed in said cathodic reactant and in electrical contact with said barrier and with said external circuit said electrode consisting essentially of a porous electrically conductive material (as herein defined), said molten polysulfide exhibiting during operation of said cell or battery a contact angle with said electrode which is smaller than the contact angle which is exhibited by said molten sulfur with said electrode.

3. A secondary cell or battery in accordance with claim 1 or 2 wherein said electrode material consists of:

(A) a "porous electrically conductive material" (as herein defined) which is disposed within said cathodic reaction zone in such manner that said zone contains a plurality of channels or spaces which are free of said porous conductive material, and allow flow within said zone of said cathodic reactant during the operation of said battery or cell;

(B) a "porous electrically conductive material" (as herein defined) which is confined to an area of said cathodic reaction zone adjacent to said cation-permeable barrier; and

(C) two major electrode portions, the first being composed of "porous electrically conductive material" (as herein defined) which is confined to an area of said cathodic reaction zone adjacent to said cation-permeable barrier, and the second being composed of a "porous electrically conductive material" (as herein defined) which is electrically connected to said first portion, but which is spaced from said first portion so as to create a channel therebetween.

4. A secondary battery or cell in accordance with any of claims 1 to 3, wherein said "porous electrically conductive material" consists of:

(1) a metal or alloy;

(2) a material having a surface consisting of an oxide or sulfide of at least one metal consisting of (i) a metal of Groups I, II or III of the Periodical Table of the Elements, (ii) a Transition Series Metal or (iii) tin, lead, antimony or bismuth;

(3) suface oxidized graphite;

(4) intercalated graphite;

(5) graphite coated with a material of (1), (2), (3) or (4), or

(6) a mixture of any of the materials of (1), (2), (3), (4), and (5).

5. A secondary cell or battery in accordance with claim 4, wherein said conductive material comprises a material having a surface consisting of: aluminium oxide (Al_2O_3), molybdenum disulfide (MoS_2), chromic oxide (CrO_3), lanthanum chromite ($La_{1-x}Ca_xCrO_3$), antimony pentoxide-doped tin oxide (Sb_2O_5-SnO_2), lithium-doped nickel oxide ($Li_xNi_{1-x}O$); titanium-doped iron oxide ($Ti_xFe_{2-x}O_3$) or tantalum-doped titanium oxide (Ta_2O_5-TiO_2).

6. A secondary cell or battery in accordance with any of claims 1 to 3, wherein said "porous electrically conductive material" is a perforated metal sheet which is confined to an area adjacent said cation-permeable barrier.

7. A secondary cell or battery in accordance with claim 6, wherein said perforated metal sheet is composed of stainless steel.

8. A secondary cell or battery in accordance with claim 3, wherein said "porous electrically conductive material" comprises said two major electrode portions, both of which are composed of metal.

9. A secondary cell or battery in accordance with any of claims 1 to 3, wherein said conductive material is a perforated metal sheet which is in contact with, and wrapped around, said cation-permeable barrier.

10. A secondary cell or battery in accordance with claim 9, wherein said cation-permeable barrier is tubular, and said perforated metal sheet is stainless steel.

11. A secondary cell or battery in accordance with claim 3, wherein said conductive material comprises said first and second portions, with said first portion being in contact with, and wrapped around, said cation-permeable barrier, and said second portion being a cylinder surrounding said first portion.

12. A secondary cell or battery in accordance with any of claim 2 and claims 3 to 11, wherein said cation-permeable barrier and said container are tubular.

13. A secondary cell or battery substantially as herein described with reference to Figures 1 to 4 and 6 of the accompanying drawings.

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1569116 COMPLETE SPECIFICATION

2 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 1

FIG.1

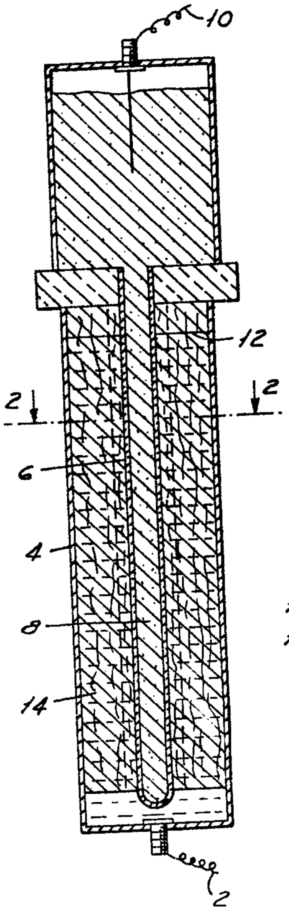


FIG.2

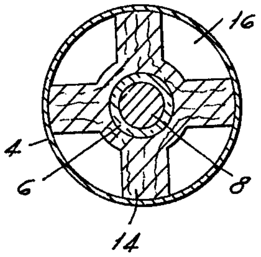


FIG.3

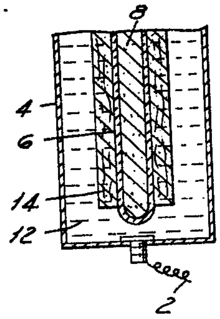


FIG.4

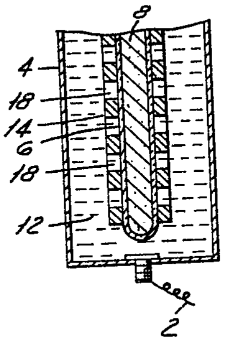
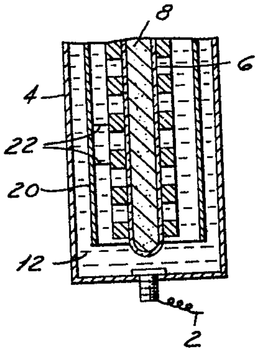


FIG.6



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Sheet 2

FIG. 5