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(54) ALKALI-METAL SULPHUR SECONDARY BATTERY OR CELL WITH COMPOSITE 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 secondary cell or battery of the type comprising 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 which exhibits increased energy efficient on both charge and discharge, and which as a result is especially useful for but not limited to, use in electric utility load levelling applications. Still more particularly, this invention relates to an improved alkali metal/sulfur battery which includes a composite electrode with portions thereof being optimized for charging and portions thereof being optimized for discharging.

A recently developed secondary or rechargeable electrical conversion device, e.g. secondary cell or battery, comprises in the or each cell: (1) an anodic reaction zone containing a molten alkali metal anode-reactant, e.g. sodium, in electrical contact with an external circuit; (2) a cathodic reaction zone containing (a) a cathodic reactant comprising sulfur or a mixture of sulfur and molten polysulfide, which is electrochemically reversibly reactive with said anodic reactant; (b) a solid electrolyte comprising a cation-permeable barrier to mass liquid transfer interposed between, and in contact with, said anodic and cathodic reaction zones; and (c) electrode means within said cathodic reaction zone for transporting electrons to and from the vicinity of said cation- permeable barrier. As used herein, the term "reactant" is intended to mean both reactants and reaction products.

During the discharge cycle of such a device, e.g. the secondary cell or battery, 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 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 electrode 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 the secondary cell or battery, for example, 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 solid electrolyte to the anode where it accepts an electron from the external circuit. Because of the aforementioned relative conductivities of the liquid electrolyte and electrode material, respectively, this charging process occurs preferentially in the vicinity of the solid electrolyte barrier and leaves behind molten elemental sulfur. As can readily be 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 electrode in the vicinity of the cation-permeable membrane, but also to remove sulfur therefrom.

Numerous suggestions have been made for improving the mass transportation of cathodic reactants so as to improve charge and discharge efficiency as well as to increase the ampere-hour capacity of the battery or cell.

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 transportation of reactants and charge, thus increasing both energy efficiency and the ampere-hour capacity of the device. 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 Application 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 Applications 721/76 (now Serial No. 1,536,182) and Nos. 20647/76 (Serial No. 1,555,133) and 20645/76 (Serial No. 1,555,131) all teach ways of increasing mass transportation of reactants in such a device, thus increasing the ampere-hour capacity of the battery or cell and, to an extent, the charge/discharge energy efficiency. However, each of these modifications relies on vapour transport of sulfur to accomplish its purpose and, as such, involves either external heating or a special cell design.

The various designs or methods of the aforementioned U.S. Patent No. 3,811,943 and U.K. Patent Specifications Nos. 1,536,181 and U.K. Patent Application Nos. 20647/76 (Serial No. 1,555,133) and 20645/76 (Serial No. 1,555,131) are all effective in promoting the distribution of reactants during both discharge and charge. However, even with these improved designs or methods it is difficult to recharge the batteries or cells at high rates.

Our copending Application No. 45056/76 (Serial No. 1,569,116), entitled "Alkali Metal-Sulphur Secondary Battery or Cell with Polysulfide Wettable Electrode", filed concurrently herewith, teaches a secondary battery or cell employing an electrode which is preferentially wetted by polysulfide. As a result, the cell exhibits a high energy efficiency on charge. The use of such a polysulphide-wettable, electrode, however, while increasing charge efficiency, results in appreciable electrode polarization and somewhat decreased efficiency on discharge.

Our copending Application No. 45054/76 (Serial No. 1,569,114), entitled "Alkali Metal-Sulphur Secondary Battery or Cell with Dual Electrode", also filed concurrently herewith, teaches a secondary cell or battery in which the or each cell contains two separate electrodes, one being preferentially wetted by polysulfide and operating on charge and the other being preferentially wetted by sulfur and operating on discharge. While such cells or batteries are effective in creasing energy efficiency on both charge and discharge, the cell construction is complicated by the use of two separate electrodes.

Our copending Application No. 45053/76 (Serial No. 1,569,113) filed concurrently herewith, and entitled "Alkali Metal-Sulfur Secondary Battery with Separate Charge and Discharge Zones", teaches a battery which exhibits excellent energy efficiency on charge and discharge. However, that device comprises separate storage, charge and discharge zones and, thus, is somewhat complicated.

The secondary cell or battery of this invention, like that of the dual electrode device and the device comprising storage zones, has an increased energy efficiency on both charge and discharge. In addition, the device provides a greater power and energy density than those devices.

According to one aspect of this invention, we provide a secondary battery or cell comprising in the or each cell:

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

(B) one or more cathodic reaction zones containing (1) a cathodic reactant which, when said cell or battery 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 molten sulfur and at least one molten sulfur-saturated polysulfide salt of said anodic reactant, and (2) a composite 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, the composite electrode being in electrical contact with both said cation-permeable barirer and said external circuit, and comprising:

(a) at least one first portion of "porous electrically conductive material" (as herein defined, which: (i) is disposed adjacent to said cation-permeable barrier and is in electrical contact therewith, (ii) is in physical contact at least in part with said cation-permeable barrier, and (iii) is composed of a material which is such that, during operation of said cell or battery, said polysulfide exhibits a contact angle with said electrode which is smaller than the contact angle exhibited by said molten sulfur with said electrode, and (b) at least one second portion of porous electrically conductive material (as herein defined) which: (i) is disposed adjacent to said at least one first portion and in physical contact at least in part therewith, (ii) is in electrical contact with said cation-permeable barrier, and (iii) is composed of a material which, is such that, during operation of said battery said molten sulfur exhibits a contact angle with said electrode which is smaller than the contact angle exhibited by said molten polysulfide with said electrode,

said at least one first portion serving primarily as the electrode during charge of said cell or battery and serving primarily to wick molten polysulfide away from said at least one second portion during discharge, and said at least one second portion serving primarily as the electrode during discharge of said cell or battery and serving primarily to wick molten sulfur away from said at least one first portion during charge.

According to another aspect of this invention, we provide a secondary cell or battery comprising:

(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 provided with means for establishing 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 at least one molten sulfur saturated polysulfide salt of said anodic reactant; and

(E) an electrode disposed within said cathodic reaction zone, filled at least in and part with said cathodic reactant and provided with means for establishing electrical contact with both said barrier and said external circuit, said electrode comprising: (a) at least one first portion of "porous electrically conductive material" (as herein defined), which (i) is disposed adjacent to said cation-permeable barrier and is in electrical contact therewith, (ii) is in physical contact at least in part with said cation-permeable barrier, and (iii) is composed of a material which is such that, during operation of said cell or battery, said molten polysulfide exhibits a contact angle with said first portion which is smaller than the contact angle exhibited by said molten sulfur with said first portion, and (b) at least one second portion of "porous electrically conductive material" (as herein defined), which (i) is disposed adjacent to said at least one first portion and in physical contact at least in part therewith, (ii) is in electrical contact with said cation-permeable barrier, and (iii) is composed of a material which is such that during operation of said battery said molten sulfur exhibits a contact angle with said second portion which is smaller than the contact angle exhibited by said molten polysulfide with said second portion, said at least one first portion serving primarily as the electrode during charge of said battery, and serving primarily to wick molten polysulfide away from said at least one second portion during discharge, and said at least one second portion serving primarily as the electrode during discharge of said cell or battery, and serving primarily to wick molten sulfur away from said at least one first portion during charge.

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 showing one embodiment of the invention;

Figures 2 and 3 are illustrations of cross-sections suitable for the design shown in Figure 1;

Figure 4 is a broken-away lower vertical section of a cell similar to that of Figure 1, but with a different electrode design;

Figure 5 is a cross-section of a suitable electrode design such as is illustrated in Figure 4; and

Figure 6 is a sectional view of a third type of cell design embodying the improvement of the invention.

Figure 1 shows a full vertical section of a cell which embodies the improvement of the invention. The device shown is the preferred tubular design discussed hereinbefore. Figures 2 and 3 are examples of several types of preferred cross-sections for a cell such as that shown in Figure 1. Figure 4 shows a broken-away lower section of a similar cell embodying another type of electrode design in accordance with the invention and Figure 5 shows a suitable cross-sectional design for such a cell. Figure 6 shows still another cell embodying another type of electrode design. To the extent that the part or material described is shown in each of the figures, it will be designated by the same reference numeral used to describe Figure 1.

The type of secondary or rechargeable electrical conversion devices, e.g. secondary cells or batteries 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: 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; 3,535,162; 3,719,531 and 3,811,943.

As mentioned above, the secondary cells or batteries to which the improvement of this invention applies comprises 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 may be heated by 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 sacrificial 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 instead.

The cathodic reactant of the fully charged batetry 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 while the open circuit voltage remains constant. During this portion of the discharge cycle, as the mole fraction of sulfur drops from 1·0 to aproximately 0·72, the cathodic reactant displays two phases, one being essentially pure sulfur and theo ther 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 he 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 substantially 0·60 and approaches unity as the mole fraction approaches 0·72, the point at which the polysulphide is sulfur-saturated. As the cell is recharged, elemental sulfur is momentarily formed 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 may cause difficulty in continuing the recharging process. However, when the mole fraction of sulfur in the melt is within the range of from 0·60 to 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 at which the mole fraction of sulfur is approximately 0·72 and the open-circuit voltage becomes substantially 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 microns, 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 from 34 to 50 mole percent of silicon dioxide; and (2) from 35 to 65, preferably from 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 from 5 to 15 weight percent, preferably from 8 to 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: $Na_2O.11Al_2O_3$. The second crystalline form is β''-alumina which may be represented by the formula: $Na_2O.6Al_2O_3$. 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 in which the metal ion having a valence not greater than 2 is either 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 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, or (b) a two-phase composition comprising molten sulfur and at least one molten sulfur-saturated polysulfide salt of said anodic reactant; and (5) an electrode which is disposed within said cathodic reaction zone, at least partially immersed in said cathodic reactant and 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 improvement of this invention comprises employing as the electrode in the aforementioned devices a composite electrode which comprises:

(A) at least one first portion of porous conductive material which (i) is disposed adjacent to the cation- permeable barrier and in electrical contact therewith, (ii) is in physical contact, at least in part, with the barrier, and (iii) is composed of a material which, during the operation of the device, is more readily wettable by molten polysulfide salts than it is by molten sulfur; and

(B) at least one second portion of porous conductive material which (i) is disposed adjacent to the first portion or portions and in contact therewith, (ii) is in electrical contact with the cation-permeable barrier, and (iii) is composed of a material which is more readily wettable by molten sulfur than by molten polysulfide.

During the operation of the battery or cell embodying this improved composite electrode, the one or more first portions serve primarily as the electrode during charge and serve primarily to wick molten polysulfide away from the second portion or portions during discharge. The one or more second portions, on the other hand, serve primarily as the electrode during discharge and serve primarily to wick sulfur away from the one or more first portions during charge. The result is a secondary cell or battery which exhibits increased energy efficiency on both charge and discharge as well as an increased power and energy density as compared with prior art devices of this type.

The measure of wettability of substrate by a liquid material is the contact angle formed between the liquid and the substrate. If the liquid wets the substrate completely, the contact angle will be 0°. If the liquid beads up completely on the substrate, 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 wet by sulfur as opposed to polysulfide salts. As such a graphite material such as a graphite felt is ideal for use as the second or discharging portion of the electrode and unsuitable unless modified to make it preferentially wettable by polysulfide, as the first or charging portion(s) of the electrode in the improvement of this invention.

We have found that, by employing conductive materials which are preferentially wettable by polysulfide salts and by sulfur as the first or charging and second or discharging portion(s) of the electrode, respectively, it is possible substantially to reduce or to eliminate electrode polarization while etiher charging or discharging. As a result, the batteries or cells made in accordance with the improvement of this invention demonstrate good electrical efficiency on both charge and discharge, and, as such, are ideal for a number of uses such as for electric utility load levelling.

The term "porous electrically conductive material" as used in this application is intended to mean any composition 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 one of a number of other forms which will be apparent to those skilled in the art to which this invention relates.

Among the numerous materials which are preferentially wettable by polysulfide salts, and which are therefore preferred materials for use as the first or charging portion(s) of the electrode discussed above are: (1) metals, which as used herein shall include alloys as well as such 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 Na_2S_4 on AISI # 446 stainless steel is 0–5°, while the contact angle formed by sulfur on stainless steel is approximately 25°. 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 polysulfide, it becomes advantageous further to oxidize the metal surfaces, either by oxidation at elevated temperatures or by attack by oxidizing acids. It will be understood that metals and alloys, as used herein can be either coated with oxide due to normal exposure to an ambient atmosphere or specially treated to thicken their oxide coatings; (2) materials having a surface consisting of and including materials formed completely of a composition of a polar or ionic character or with unfilled *d*-orbitals. Such compositions include oxides or sulfides of metal consisting of (a) metals of Group I, II or III of the Periodic Table of Eelements, (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 Ca CrO_3); antimony pentoxide-doped tin oxide (Sb_2O_5–SnO_2); lithium-doped nickel oxide (Li N_1 O); titanium-doped iron oxide (Ti Fe_2 O_3); on tantalum-doped titanium oxide (Ta_2O_5-TiO_2). Most of these material are electronic conductors and can therefore serve as the electrode or can 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 graphite oxide surface converts to graphite sulfide which is preferentially wet by the polysulfide.

(4) Electrically conductive 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 materails with the graphite.

(5) Graphite which bears a continuous or discontinuous coating of one or more of the materials of (1), (2), (3) or (4); and

(6) A combination or mixture of the material of (1), (2), (3), (4) or (5).

The various material which will exhibit the required preferential wettability by sulfur and which, therefore, are suitable as the second or discharging portion(s) of the electrode will be apparent to those skilled in the art. However, some preferred materials include graphite felt or foam, porous graphite, vitreous carbon foam pyrolytic graphite felt or foam, rigidized graphite felt or foam, or materials which have been covered or coated with the above carbon materials.

The cell shown in Figure 1 comprises: a tubular container 4; 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 composite porous electrode generally indicated at 14. As shown in Figure 1, the composite electrode comprises a first or charging portion 14′ which is preferentially wetted by molten polysulfide and a second or discharging portion 14″ which is preferentially wetted by sulfur. It will be noted that the first portion 14′ is adjacent to the cation-permeable barrier 6 and in contact therewith. The second portion 14″ is disposed adjacent to the first portion 14′ and in contact therewith. In the particular electrode design shown in Figure 1, the first portion 14′ substantially covers the cation-permeable barrier 6 and the second portion 14″ substantially covers the portion 14′. When such a design is used, it is necessary that the first portion 14′ should be sufficiently thin and porous to allow ions to pass therethrough. The optimal thickness of the portion 14′ will depend on the material chosen and the degree of porosity thereof. Generally, however, it is desirable to employ a first portion 14′ which is 3mm or less in thickness and preferably 1mm or less. These thicknesses are particularly suitable for the case where the first portion 14′ is a perforated or expanded metal sheet. As shown, the composite electrode of Figure 1 makes electrical contact with the external circuit *via* a lead 16 which contacts the first portion 14′.

The cross-sectional view of Figure 2 shows an embodiment wherein the first portion 14′ is wrapped around the cation-permeable barrier 6 so as substantially to cover it and the second portion 14″ substantially covers the first portion 14′. The first portion 14′ is sufficiently porous to allow the second portion 14″ to be in partial contact with the barrier 6. The porous screen shown in the cross-section is merely representative of porous materials which may be used.

The cross-sectional view of Figure 3 shows an embodiment similar to that of Figure 1, in which a porous cloth serves to that of Figure 1, in which a porous cloth serves as the portion 14′ and the second portion 14″ substantially covers the first portion 14′ but does not contact the barrier 6.

The sectional view of Figure 4 shows a design which, unlike those shown in Figures 1 to 3, employs a second portion which substantially fills the area of the cathodic reaction zone between the first portion 14′ and the container 4. In the design shown in Figure 4, the first portion 14′ substantially covers the barrier 6 and the second portion 14″ does not partially cover the barrier 6. However, we may also use a design comprising a porous portion 14′ as shown in Figure 2, in which a second portion 14″ contacts the barrier 6.

Figure 5 shows a cross-section of a design similar to that of Figure 4. This design is representative of those in which the porous conductive material of section portion 14″ is disposed within the cathodic reaction zone in such manner that the zone contains a plurality of channels or spaces 18 which are free of the porous conductive material, and which, in combination with the porous conductive material, are adapted to allow flow within the zone of the cathodic reactant 12 during operation of the battery or cell. The design shown in Figure 5 is merely representative of a number of designs which are suitable. Other designs for this type of electrode structure are shown in our aforementioned U.K. Patent Specification Serial No. 1,536,181.

Figure 6 shows still another design of an embodiment which is representative of another type of design in accordance with the invention. The electrode of this device comprises a plurality of first portions 14′ and second portions 14″. The portions 14′ and 14″ are disposed alternately along the length of and adjacent to the cation-permeable barrier 6. Each of the portions 14′ and 14″ shown in Figure 6 is a toroid which is disposed about the tubular barrier 6. Open spaces 20 to allow flow of cathodic reactant are shown within the cathodic reaction zone between the first portions 14′ and the container 4. In the preferred design shown in Figure 6, the cell is disposed horizontally with the tubular barrier 6 extending in a lateral direction. As shown, the electrical contact with the electrode 14 and the cation-permeable barrier 6 may be *via* an electrode lead 22 which is attached to conductive container 4. In a preferred embodiment of the type shown, first portions 14′ are formed of perforated or porous metal.

WHAT WE CLAIM IS:—

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

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

(B) one or more cathodic reaction zones containing (1) a cathodic reactant which, when said cell or battery 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 molten sulfur and at least one molten sulfur-saturated polysulfide salt of said anodic reactant, and (2) a composite 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, the composite electrode being in electrical contact with both said cation-permeable barrier and in said external circuit, and comprising:

(a) at least one first portion of "porous electrically conductive material" (as herein defined) which:

(i) is disposed adjacent to said cation-permeable barrier and is in electrical contact therewith,

(ii) is in physical contact at least in part with said cation-permeable barrier, and

(iii) is composed of a material which is such that, during operation of said cell or battery, said molten polysulfide exhibits a contact angle with said electrode which is smaller than the contact angle exhibited by said molten sulfur with said electrode, and

(b) at least one second portion of porous electrically conductive material (as herein defined) which:

(i) is disposed adjacent to said at least one first portion and in physical contact at least in part therewith;

(ii) is in electrical contact with said cation-permeable barrier, and

(iii) is composed of a material which is such that, during operation of said battery said molten sulfur exhibits a contact angle with said electrode which is smaller than the contact angle exhibited by said molten polysulfide with said electrode,

said at least one first portion serving primarily as the electrode during charge of said cell or battery and serving primarily to wick molten polysulfide away from said at least one second portion during discharge, and said at least one second portion serving primarily as the electrode during discharge of said cell or battery and serving primarily to wick molten sulfur away from said at least one first portion during charge.

2. A secondary cell or battery comprising:

(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 provided with means for establishing 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 of (b) a two-phase composition comprising at least one molten sulfur saturated polysulfide salt of said anodic reactant; and

(E) an electrode disposed within said cathodic reaction zone, filled at least in part with said cathodic reactant and provided with means for establishing electrical contact with both said barrier and said external circuit, said electrode comprising:

(a) at least one first portion of "porous electrically conductive material" (as herein defined), which:

(i) is disposed adjacent to said cation-permeable barrier and is in electrical contact therewith,

(ii) is is physical contact at least in part with said cation-permeable barrier, and

(iii) is composed of a material which is such that, during operation of said cell or battery said molten polysulfide exhibits a contact angle with said first portion which is smaller than the contact angle exhibited by said molten sulfur with said first portion, and

(b) at least one second portion of "porous conductive material" (as herein defined), which:

(i) is disposed adjacent to said at least one first portion and in physical contact at least in part therewith;

(ii) is in electrical contact with said cation-permeable barrier, and

(iii) is composed of a material which is such that, during operation of said battery, said molten sulfur exhibits a contact angle exhibited by said molten polysulfide with said second portion,

said at least one first portion serving primarily as the electrode during charge of said battery and serving primarily to wick molten polysulfide away from said at least one second portion during discharge, and said at least one second portion serving primarily as the electrode during discharge of said cell or battery and serving primarily to wick molten sulfur away from said at least one first portion during charge.

3. A battery or cell in accordance with claim 1 or 2, wherein said at least one second portion is contiguous in part with said cation-permeable barrier.

4. A battery or cell in accordance with claim 3, wherein said first and second portions are disposed alternately along the length of and adjacent to said cation-permeable barrier.

5. A battery or cell in accordance with claim 3, wherein said first portion substantially covers said cation-permeable barrier and said second portion substantially covers said first portion, sáid first portion being sufficiently porous to allow said second portion to be in partial contact with said cation-permeable barrier.

6. A battery or cell in accordance with claim 3, wherein said at least one first portion is formed from a material consisting of:

(1) a metal or alloy;

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

(3) surface 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).

7. A battery or cell in accordance with claim 6, wherein said at least one first portion comprises a material having a surface consisting of: aluminium oxide (Al_2O_3), molybdenum disulfide (M_0S_2), chromic oxide (CrO_3), lanthanum chomite (La_1 Ca CrO_3), antimony pentoxide-doped tin oxide (Sb_2O_5-SnO_2), lithium-doped nickel oxide (li Ni_1 O); titanium-doped iron oxide (Ti Fe_2 O_3), or tantalum doped titanium oxide (Ta_2O_5-TiO_2).

8. A battery or cell in accordance with Claim 3, wherein said at least one second portion consists of: graphite felt, graphite foam, porous graphite, vitreous carbon foam, pyrolytic graphite felt, pyrolytic graphite foam, or a material coated with such felt or foam.

9. A battery or cell in accordance with Claim 1 or 2, wherein said at least one first portion covers said cation-permeable barrier, but is sufficeintly thin and porous to allow ions to pass therethrough, and said at least one second portion substantially covers said at least one first portion but does not physically contact said cation-permeable barrier.

10. A battery or device in accordance with Claim 9, wherein said at least one first portion is 3mm or less in thickness.

11. A battery or cell in accordance with any of Claims 1 to 10, wherein said cation-permeable barrier is tubular and said first and second portions are toroids disposed around said tube.

12. A battery or cell in accordance with Claim 11, wherein said first portions are formed of perforated or porous metal.

13. A battery or cell in accordance with Claims 2 and 11, wherein there exists an open volume between said first portions and said container.

14. A battery or cell in accordance with any of Claims 1 to 10, wherein the or each cell is disposed horizontally with said cation-permeable barrier extending in a lateral direction.

15. A battery or cell in accordance with Claim 5, wherein said porous electrically conductive material of said second portion 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 which, in combination with said porous conductive material, allow flow within said zone of said cathodic reactant during operation of said battery or cell.

16. A battery or cell in accordance with Claim 5, wherein said first portion comprises a perforated or expanded metal sheet.

17. A battery or cell in accordance with Claim 3, wherein:

(a) said at least one first portion consists of:

(1) a metal or alloy;

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

(3) surface oxidized graphite;

(4) intercalated graphite;

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

(6) a mixture of any of (1), (2), (3), (4) (5); and

(b) said at least one second portion consists of:

(1) graphite felt;

(2) porous graphite;

(3) graphite foam;

(4) vitreous carbon foam;

(5) pyrolytic graphite felt;

(6) pyrolytic graphite foam; or

(7) a material coated with any of (1) to (6).

18. A battery or cell in accordance with Claim 9, wherein said first portion comprises a perforated or expanded metal sheet.

19. A battery or cell in accordance with Claim 9, wherein said first portion is 3mm or less in thickness.

20. A battery or cell in accordance with Claim 9, wherein said first portion is 1mm or less in thickness.

21. A battery or cell in accordance with any of Claims 1 to 20, wherein said electrode is in direct electrical contact with said external circuit through said first portion.

22. A secondary battery or cell as claimed in Claim 1 or 2, substantially as herein described with reference to any of the accompanying drawings.

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1569115 COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of the Original on a reduced scale

FIG.1

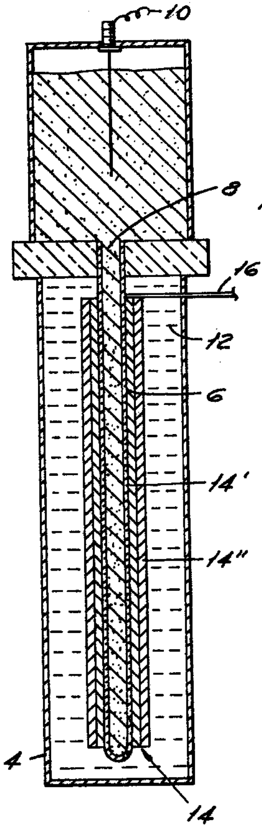

FIG.2

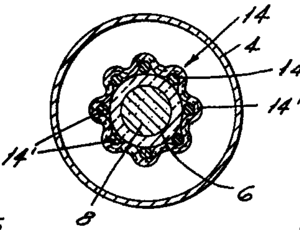

FIG.3

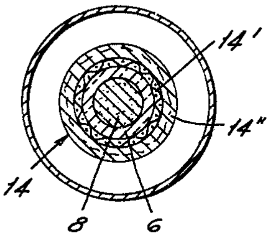

FIG.4

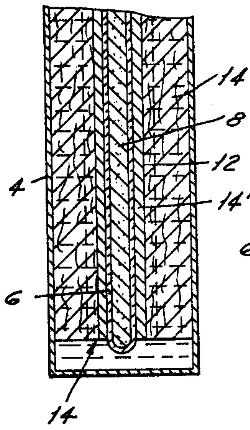

FIG.5

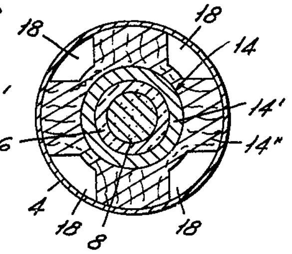

FIG.6