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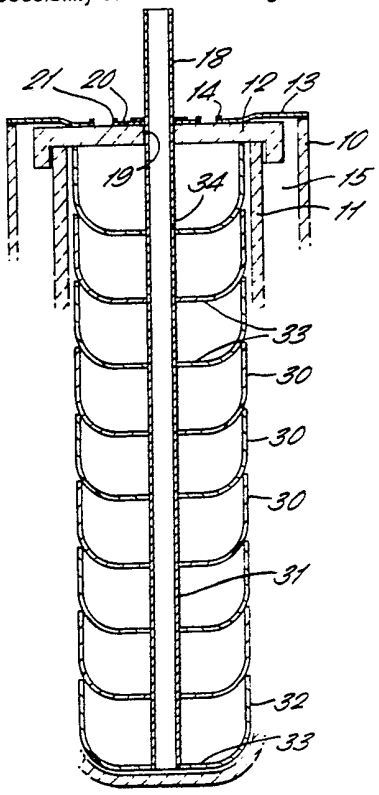
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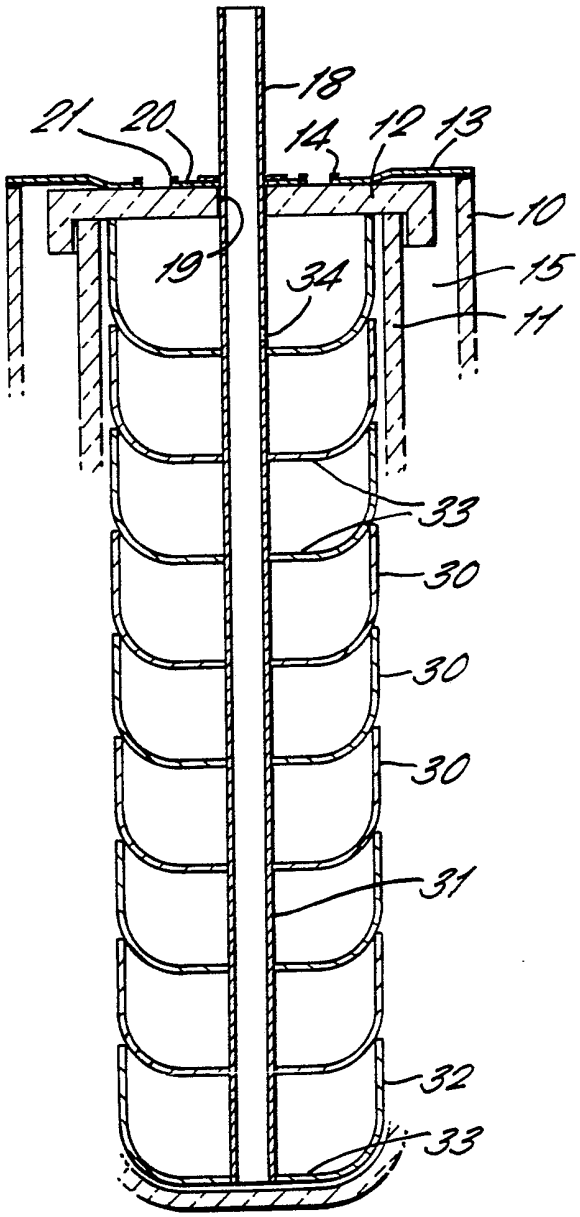
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(54) Improved alkali metal cell

(57) Failure of the electrolyte of a sodium sulphur cell may seriously damage that cell. This specification discloses a metal reservoir, inside the electrolyte, which comprises at least one internal baffle 30 providing a restricted flow of molten alkali across the baffle. This limits the amount of sodium with which cathodic reactants can mix in the event of a breach of the electrolyte, thus considerably reducing the possibility of serious damage.



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IMPROVED ALKALI METAL CELL

The present invention is concerned with alkali metal cells of the kind comprising an outer container with a solid electrolyte member dividing the interior of the container into anodic and cathodic regions. The anodic region will contain a molten alkali metal, typically sodium, and the cathodic region will contain a suitable cathodic reactant

It is known to form such alkali metal cells with the solid electrolyte member shaped as a cup located inside the outer container, and with the alkali metal forming the anode contained within the electrolyte cup and the cathodic reactant contained in the outer region between the cup and the outer container. The outer container is typically made of metal and forms a current collector for the cathode. Current may be collected from the alkali metal anode within the electrolyte cup by an electronically conductive current collecting member located within the cup so as normally to be in contact with any alkali metal remaining in the cup, and extending out through a closure member for the electrolyte cup so as to provide a current lead-out.

An example of such an alkali metal cell, taking the form of a sodium/sulphur cell is illustrated in GB-A-2161017.

The solid electrolyte employed in alkali metal cells is typically made of a ceramic material which though electronically insulating is conductive to cations of the alkali metal. Beta alumina is the usual material for sodium sulphur cells. A problem which arises with such cells is the possibility of the electrolyte failing, e.g. cracking, and so allowing direct contact and mixing of the anodic and cathodic materials. Any direct mixing results in a

highly exothermic reaction which, if not checked, can result in the temperature of the cell rising so high that the outer cell container is breached. This in turn can result in the highly corrosive reaction products leaking into the battery cavity containing the cells.

Whilst substantial effort is directed to the preparation of electrolyte members which have a very high integrity, thereby reducing the risk of a damaging failure of the cell to a very low level, some risk may still remain and efforts have been directed at substantially eliminating this remaining risk of damaging failure.

As one example, GB-A-1517287 describes a sodium sulphur cell having a molybdenum tube located inside a tubular solid electrolyte to act as a sodium reservoir. The molybdenum tube defines with the electrolyte a shallow wicking space through which the sodium flows by capillary action. A small hole at the otherwise closed end of the molybdenum tube allows sodium to enter the wicking space from the reservoir and the hole is dimensioned to permit a rate of flow of sodium adequate to meet the designed discharge and charge requirements of the cell. However, in the event of a crack occurring in the electrolyte, the corrosive reaction at that portion of the wicking space could result in penetration of the reservoir and access to a large quantity of sodium.

According to the present invention, an alkali metal cell comprises an outer container, a solid electrolyte cup within the container dividing the container into an anode region inside the cup and a cathode region outside the cup, and an alkali metal reservoir fitting inside the electrolyte cup, the reservoir having flow means providing a maximum rate

of flow of alkali metal from within the reservoir which maximum rate corresponds to the maximum rate of discharge of the cell, characterised by the alkali metal reservoir comprising at least one internal baffle providing a restricted flow of molten alkali metal across the baffle. Preferably, the reservoir is formed as a stack of two or more cups. By dividing the reservoir into a number of cups, should the highly corrosive cathodic reactant material corrode through the wall of the reservoir at one point, access will only be gained to the interior of a single cup. The total amount of sodium which is accesible for reaction with incoming sulphur/sodium polysulphides in the event of a breach of the electrolyte is therefore limited. During filling of the reservoir with the molten alkali metal, or when this is completed, a vacuum or reduced pressure can be produced inside the reservoir, so that alkali metal passes through the flow means to fill, and fully wets the surfaces of the active region between the electrolyte cup and the reservoir. If no such vacuum or reduced pressure is produced in the reservoir the surfaces of the active region, particularly the exposed surface of the solid electrolyte, will not readily be wetted with molten alkali metal through the flow means from the reservoir.

In one embodiment, the reservoir cups have cylindrical symmetry and are mounted co-axially on a vertically extending axially located rod. The rod may be tubular and provide a filling tube arranged to allow filling of the cups with alkali metal.

The assembly comprising the stack of cups mounted on the filling tube can be used to mutually locate the electrolyte cup and the insulating ceramic closure for these two to be sealed together. The

stack of cups of the reservoir fits closely inside the electrolyte cup, and the filling tube extends through and locates the insulating ceramic closure, so that the cup and closure are held in appropriate positions for sealing together, e.g. by glazing. Since the firing process used to make the electrolyte cups does not produce precisely reproducible dimensions for the cups, it has been necessary to machine the outer periphery of each electrolyte cup near its open end for self-jigging with a closure. The electrolyte material is hard and brittle, so that machining is difficult and expensive. With the arrangement described, this machining can be avoided.

Normally, the reservoir is made of a material which is impervious to the alkali metal and said means providing a maximum rate of flow comprises one or more apertures through the reservoir. Then, when the cell is adapted for operation normally in a predetermined orientation relative to the vertical, the reservoir may have at least one said aperture at a lower end of the lower most cup.

In a further aspect the invention provides a method of making an alkali metal cell of the type having an outer container and a solid electrolyte cup within the container dividing the container into an anode region inside the cup and a cathode region outside the cup, the method including the steps of fitting an alkali metal reservoir inside the electrolyte cup, the reservoir comprising at least one internal baffle providing a restricted flow of molten alkali metal across the baffle and further comprising flow means for providing a maximum rate of low of alkali metal from within the reservoir which maximum rate corresponds to the maximum rate of discharge of the cell, closing the electrolyte cup with the reservoir contained therein by sealing to

the cup an electrically insulating ceramic closure having an aperture therein, providing a filling tube extending through the aperture in the ceramic closure, introducing molten alkali metal into the reservoir thorough said filling tube, providing a reduced pressure within the reservoir to provide for molten alkali metal to flow through said flow means to fill and fully wet the region between the reservoir and the electrolyte cup, so that during discharge of the completed cell alkali metal will be drawn into said active region through the flow means and subsequently sealing off the filling tube and the anode region.

Examples of the invention will now be described with reference to the accompanying drawing which shows a cross-sectional view of a sodium sulphur cell embodying the present invention.

Referring to the drawing, the sodium sulphur cell has a generally cylindrical shape and is illustrated in the drawing with the cylindrical axis vertical. The cell has an outer container 10 of metal, typically mild steel internally coated to make it resistant to the cathodic reactant of the cell, sulphur/sodium polysulphide. The cell incorporates an inner tube 11 of beta alumina forming the electrolyte cup. The electrolyte cup 11 is closed at the upper end by a cap 12 of insulating material, typically alpha alumina. The cap 12 is sealed to the electrolyte cup 11 by glazing. A cathode seal 13 is formed of an annular metal foil element, typically of Fecralloy or Inconel which are resistant to attack by the cathodic reactant materials in the cathode region, between the electrolyte 11 and the container 10. The outer periphery of the seal 13 is welded to the open end of the container 10 and the inner edge is sealed to the upper surface of the lid 12 by

thermo-compression bonding at 14.

The annular space 15 defining the cathode region of the cell is filled with an electrically conducting felt (not shown) impregnated, in the fully charged cell, with sulphur which is liquid at the operating temperature of the cell, about 350°C.

The inside of the electrolyte cup 11 forms an anode region 16 and, in this embodiment of the invention, contains a reservoir 17 which may be made of mild steel. The reservoir 17 comprises a stack of 9 cups 30 each sized to fit snugly within the cup 11 leaving only a narrow space or active region between the reservoir 17 and the inner faces of the cup 11 sufficient to cause a film of molten sodium to be drawn up to fill this narrow space by capillary attraction.

Conveniently, the narrow space 45 between the wall of the reservoir 17 and the solid electrolyte 11 is packed with nickel mesh. This mesh packing provides a wicking effect to ensure that sodium from the reservoir is fully distributed to wet the entire inner cylindrical surface of the electrolyte cup.

The anode region of the cell is sealed by an annular foil member 20, also of Fecralloy or Inconel, which is thermocompression bonded at 21 to the lid 12 just inside but spaced from the sealing point 14 of the cathode region seal 13. A metal washer 22 is welded to the upper face of the annular member 20 and is in turn welded around its inner periphery to the portion of the filling tube 18 extending out through the lid 12. The filler tube 18 is shown prior to pinching off and filling with sodium.

The cups 30 are each mounted axially on an axially extending tube 31 which continues through the aperture 19 in the lid 12 to form the filling tube 18. On assembly at room temperature, the cups 30 are

made a sliding fit over the tube 31 so that only the lower most cup 32 of the stack need be fastened to the bottom end of the tube 31 to retain the stack in place as it is inserted into the electrolyte cup 11. At this stage, each of the cups 30 are loosely stacked on the tube 31 prior to closing of the electrolyte cup 11 by glazing on the lid 12.

Apertures 33 are provided in the bases of each of the cups 30 and a further aperture 34 is provided from the top most cup into the tube 31 so that, on filling with sodium, molten sodium can flow into the cups 30 through the aperture 34 and then down through the cups in turn via the apertures 33. At the same time, since the lower end of the tube 31 may be left open, sodium can percolate upwards into the cups from the apertures 33 in the lower most cup of the stack.

In one arrangement (not shown), the lower end of the tube 31 may be closed, whereupon filling of the cups 30 is by aperture 34 which is provided at the desired maximum level of sodium in the reservoir.

In another arrangement, the lower end of the tube is left open, in which case the aperture 34 is not required. However it is then desirable, after the cell has been filled with sodium, to insert a tight fitting rod of metal, preferably aluminium or copper, into the tube 31, to reduce and keep constant its electrical resistance.

The stack of cups 30 form between them a reservoir for the sodium which has an outer cylindrical wall providing a snug fit within the electrolyte cup 11. In this case, however, the bases of the cups 30 provide in effect horizontally extending baffles vertically spaced along the length of the reservoir so as to limit flow of molten sodium, via the apertures 33, from one side of each baffle to the other.

Furthermore, the described structure of the Figure 2 can facillitate production. It is difficult to form the electrolyte cups 11 sized and shaped accurately to a very high tolerance. As the cups 30 are a loose fit on the tube 31 when first inserted into the electrolyte, greater variations in the tolerance of the electrolyte cup can be tolerated.

It can be seen that the filler tube 18 and reservoir 17 effectively locates the cap 12 in position over the open end of the cup 11 so that these can then be sealed together by glazing, without requiring the cup to be machined.

Very conveniently, the tube 31 is made of stainless steel, whereas the cups 30 are made of mild steel which has a somewhat lower coefficient of thermal expansion. As a result, when the cell is brought up to the operating temperature, relative expansion of tube 31 causes it to grip the surrounding cups 30 subsequently holding them rigidly in place but only after they have adopted positions appropriate to accommodate any slight distortion in the shape of the electrolyte cup 11.

CLAIMS

1. An alkali metal cell comprising an outer container, a solid electrolyte cup within the container dividing the container into an anode region inside the cup and a cathode region outside the cup, and an alkali metal reservoir inside the electrolyte cup, the reservoir having flow means providing a maximum rate of flow of alkali metal from within the reservoir which maximum rate corresponds to the maximum rate of discharge of the cell, wherein the alkali metal reservoir comprises at least one internal baffle providing a restricted flow of molten alkali metal across the baffle.

2. An alkali metal cell as claimed in Claim 1, wherein the cell is adapted for operation normally in a predetermined orientation relative to the vertical and the reservoir has at least one said flow means at a lower end of the reservoir, the internal baffle being substantially horizontal and providing a restricted flow of molten alkali metal from above to below the baffle.

3. An alkali metal cell as claimed in Claim 2, wherein the reservoir is formed as a stack of two or more cups.

4. An alkali metal cell as claimed in Claim 3, wherein the reservoir cups have cylindrical symmetry and are mounted coaxially on a vertically extending axially located rod.

5. An alkali metal cell as claimed in Claim 4, wherein said rod is tubular and provides a filling tube.

6. An alkali metal cell as claimed in Claim 5, wherein the reservoir and the filling tube are metallic.

7. An alkali metal cell as claimed in any preceding claim, wherein the reservoir is made of a material which is impervious to the alkali metal and said flow means comprises one or more apertures through the reservoir.

8. An alkali metal cell as claimed in Claim 5, wherein the filling tube extends down into the reservoir below a desired maximum level of alkali metal in the reservoir, the tube being closed below said level and having a lateral aperture to the reservoir at said level.

9. An alkali metal cell as claimed in Claim 8, wherein the filling tube is closed off at its lower end.

10. An alkali metal cell as claimed Claim 5, wherein the filling tube extends down into the reservoir close to the bottom, and is filled over its length with a solid electrically conductive material.

11. An alkali metal cell as claimed in Claim 5, wherein the filling tube is filled with a close fitting rod of metal of high electrical conductivity.

12. An alkali metal cell as claimed in Claim 1 wherein the alkali metal reservoir fits closely inside the electrolyte cup so as to limit the amount of the alkali metal directly exposed to the inner surface of the electrolyte cup to a film of the

alkali metal extending by capillary action in an active region between the electrolyte cup and the reservoir.

13. An alkali metal cell as claimed in Claim 12 wherein the active region between the reservoir and the electrolyte cup contains nickel mesh material providing a wick to assist capillary action.

14. A method of making an alkali metal cell of the type having an outer container and a solid electrolyte cup within the container dividing the container into an anode region inside the cup and a cathode region outside the cup, the method including the steps of fitting an alkali metal reservoir inside the electrolyte cup, the reservoir comprising at least one internal baffle providing a restricted flow of molten alkali across the baffle and further comprising flow means for providing a maximum rate of flow of alkali metal from within the reservoir which maximum rate corresponds to the maximum rate of discharge of the cell, providing a filling tube extending through the aperture in the ceramic closure, closing the electrolyte cup with the reservoir contained therein by sealing to the cup an electrically insulating ceramic closure having an aperture therein, introducing molten alkali metal into the reservoir through said filling tube, providing an overpressure within the reservoir to provide for molten alkali metal to flow through said flow means to fill and fully wet the region between the reservoir and the electrolyte cup, so that during discharge of the completed cell alkali metal will be drawn into the region between the reservoir and the electrolyte cup through the flow means, and subsequently sealing off the filling tube and the

anode region.

15. A method as claimed in Claim 14 wherein the reservoir is fitted inside the electrolyte cup to form an active region between the electrolyte cup and the reservoir for a film of alkali metal to extend therein by capillary action and wherein during the step of providing the reduced pressure, alkali metal is drawn into the active region through the flow means by capillary action.

16. A method as claimed in Claim 14 wherein the filling tube extends right through the aperture in the ceramic closure

17. A method as claimed in Claim 16 wherein the filling tube is sealed in the aperture of the ceramic closure, and the filling tube and the anode region are finally sealed off by crimping the filling tube where it extends out from the aperture of the closure.

18. A method as claimed in any of Claims 14 to 17, wherein the filling tube is provided connected to the reservoir before the electrolyte cup is closed with the ceramic closure.

19. A method as claimed in Claim 18 wherein the reservoir with the filling tube connected thereto are used to locate the electrolyte cup and the ceramic closure for sealing together.

20. An alkali metal cell substantially as hereinbefore described with reference to the accompanying drawing.

21. A method of making an alkali metal cell substantially as hereinbefore described.

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