March 23, 1965 T. J. BUITKUS 3,174,880

DUAL ELECTROLYTE BATTERY CELLS

Filed June 26, 1962

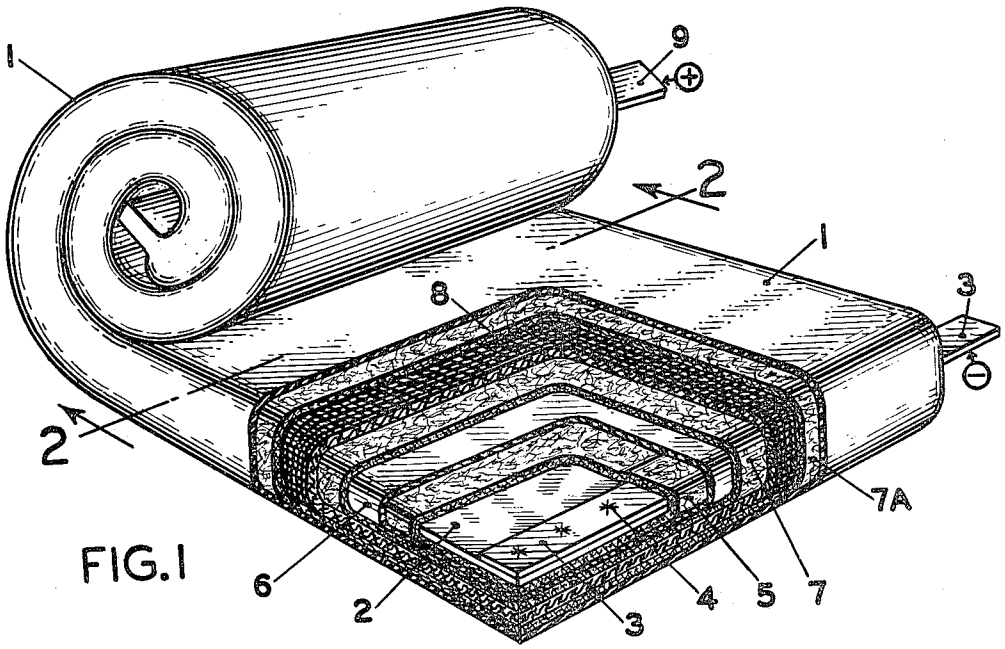


FIG. 1

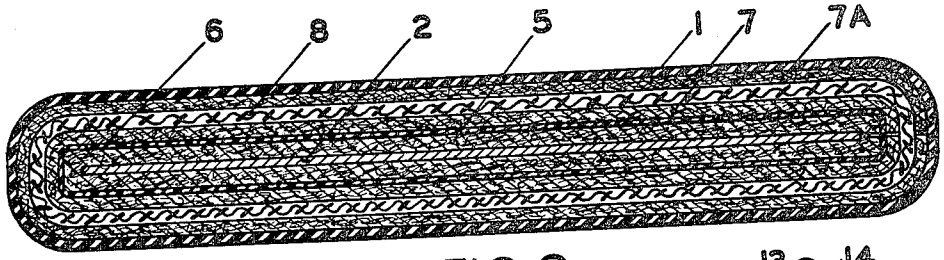


FIG. 2

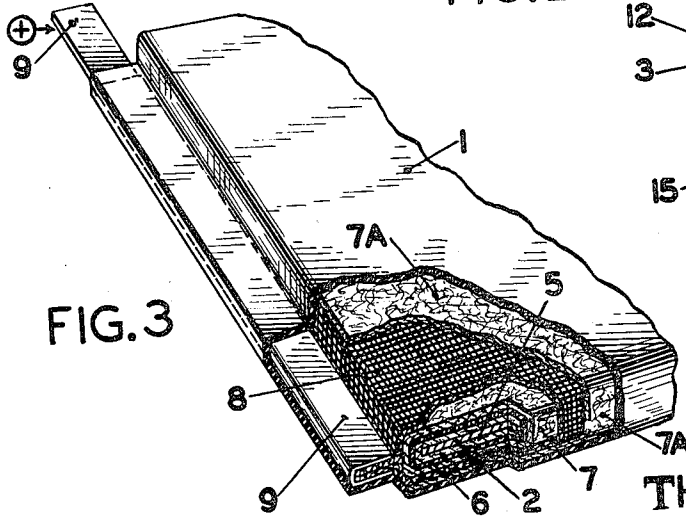


FIG. 3

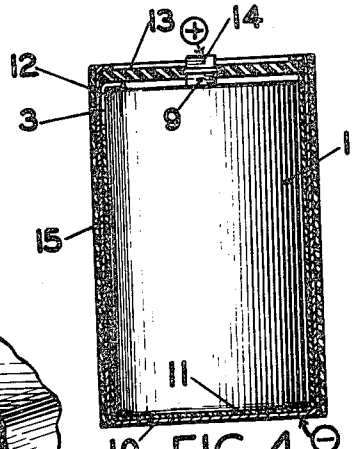


FIG. 4

INVENTOR:
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DUAL ELECTROLYTE BATTERY CELLS

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11 Claims. (Cl. 136—83)

This application is a continuation-in-part of my copending application Serial No. 155,145, filed November 27, 1961, now abandoned.

This invention relates to electric battery cells. More specifically, it relates to improvements in the construction of dual electrolyte voltaic cells.

An object of the present invention is the provision of a cell having an improved capacity-to-volume ratio with a long storage life and a reduced rate of deterioration during periods of non-use. Another object is the provision of a cell having a relatively constant ampere-hour capacity over sustained periods together with a greater operating efficiency at high current drains. The aforesaid improvements are attained by providing a cell design incorporating the increased electrode surface areas made possible by the use of a graphite fabric cathode in combination with a variety of anodes and electrolytes. In accordance with the present invention, I have discovered that cathode electrodes constructed from graphite fabrics provide a large surface area in contact with the catholyte which improves operating efficiencies at high current drains by reducing current density within the cells.

The present invention will be described with reference to the accompanying drawing in which:

FIGURE 1 is a perspective view of the cell with the outer end of the roll partly cut away to illustrate the internal construction.

FIGURE 2 is an enlarged cross-sectional view of the cell taken along the line 2—2 of FIGURE 1.

FIGURE 3 is a fragmentary perspective view of the inner end of the cell roll partly broken away to show certain parts associated therewith.

FIGURE 4 is a sectional elevational view showing the rolled cell of FIGURE 1 housed in a container.

Referring to FIGURES 1 and 2 of the drawing, the battery cell is shown to comprise a casing 1 preferably formed of a pliable insulating material such as one of the plastics polyvinyl-chloride or polyethylene. Positioned centrally within the casing 1 is a strip of metal 2 which serves as the anode electrode. A tab 3 consisting of a ribbon of heavier metal is spot welded at 4 to the outer end of the anode 2 and passes through the casing 1 to provide external electrical connection. The anolyte is held in a sheet of an absorbent material 5 such as blotting paper, glass cloth, or similar unreactive absorbing material which is wrapped around the anode 2. The anode electrode 2 and anolyte absorbent 5 are completely enclosed by an anion permeable membrane envelope 6. The catholyte is held in a sheet of an absorbent material 7, similar to 5, which is wrapped around the anion permeable membrane envelope 6. Encircling and in contact with the catholyte absorbent 7 is a sleeve of graphite fabric 8 which serves as the cathode electrode. A thinner sheet of the catholyte absorbent 7A is wrapped around the graphite fabric sleeve 8 which serves to enhance ionic transfer over the entire cathode surface area by allowing all of the graphite fabric sleeve to be saturated with the catholyte. A tab 9 consisting of a ribbon of metal is

attached to the inner end of the cathode electrode 8 (FIG. 3) and passes through the cell casing 1 at the axis of the roll to provide external electrical connection.

FIGURE 4 shows the rolled cell of FIGURE 1 housed in a metal can 10 provided with a suitable liner 11 of paper, plastic, or the like. The anode tab 3 is electrically connected at 12 to the can 10, the bottom of which serves as the negative terminal. The cathode tab 9 passes through an insulating cover 13 and is connected to a metal cap 14 affixed thereon which serves as the positive terminal. The rim of the metal can 10 is bent inwardly over the cover 13 securing it in place and sealing the cell. A cylindrical jacket 15 of a suitable non-conductive material such as cardboard or plastic provides protection and insulation to the outer side wall. The type of cell container shown is to be interpreted as illustrative only and not in a limiting sense as various types of containers and terminal arrangements may be utilized within the scope of the present invention. Since the anode is not employed as a cell container, leakage difficulties are greatly reduced.

A voltaic cell depends upon an oxidation-reduction reaction to produce a flow of electrons through an external circuit. In order that such an oxidation-reduction reaction may be effectively utilized in the generation of an electrical current, the two half reactions must be separated so that the exchange of electrons occurs only when the anode and cathode electrodes are externally connected by a conductor. In the present invention, the reaction that occurs at the anode is oxidation of a metal thereby yielding valence electrons which return to the cell at the cathode causing a concommitant reduction of the catholyte.

In accordance with the present invention, the anodic and cathodic reactants are separated one from the other by an anion permeable membrane. Such membranes contain dissociable ionizable radicals in their structure, the cationic component being fixed into and retained by the polymeric matrix with the anionic component being a mobile and replaceable ion electrostatically associated with the fixed component. The ability of the membrane to permit passage of anions imparts ion exchange characteristics to these materials known as permselectivity. An anion permeable membrane found suitable for use in the present invention is sold under the trade name AMFion, Chemically Resistant 300 Series. This product consists of a thin film of non-hydrolysable polymers incorporating a quaternary ammonium type of structure. Membranes suitable for use in the present invention are not limited to any particular organic type of resin as any substance capable of acting as a selective electrolyte barrier is suitable for this purpose including inorganic materials and compositions of same having proper ion exchange characteristics.

The present invention comprises essentially a voltaic cell having a metal anode, an anolyte comprising an aqueous solution of a compound of said anode metal, a graphite fabric cathode electrode, and a catholyte comprising an aqueous solution of an electrolytically reducible anion yielding compound of one of the metals copper, manganese, mercury and silver, said anolyte and catholyte being separated by and making electrolytic contact through an anion permeable membrane.

Examples of suitable combinations of anodes, anolytes, and catholytes for the present invention are listed in the following table:

Table 1

Example	Anode	Anolyte	Catholyte
1	Zinc	$ZnCl_2$-Zinc Chloride	$CuCl_2$-Cupric Chloride.
2	do	$Zn(BF_4)_2$-Zinc Fluoborate	$Cu(BF_4)_2$-Cupric Fluoborate.
3	do	$ZnCl_2$-Zinc Chloride	HgCl-Mercurous Chloride.
4	do	do	Do.
5	do	$Zn(ClO_3)_2$-Zinc Chlorate	$HgClO_3$-Mercurous Chlorate.
6	do	do	$Hg(ClO_3)_2$-Mercuric Chlorate.
7	do	ZnF_2-Zinc Fluoride	HgF-Mercurous Fluoride.
8	do	do	HgF_2-Mercuric Fluoride.
9	do	do	MnF_3-Manganese Trifluoride.
10	do	$Zn(BF_4)_2$-Zinc Fluoborate	$HgBF_4$-Mercurous Fluoborate.
11	do	do	$Hg(BF_4)_2$-Mercuric Fluoborate.
12	do	$ZnSO_4$-Zinc Sulfate	Hg_2SO_4-Mercurous Sulfate.
13	do	do	$HgSO_4$-Mercuric Sulfate.
14	do	$Zn(NO_3)_2$-Zinc Nitrate	$HgNO_3$-Mercurous Nitrate.
15	do	do	$Hg(NO_3)_2$-Mercuric Nitrate.
16	do	$Zn(ClO_3)_2$-Zinc Chlorate	$AgClO_3$-Silver Chlorate.
17	do	$Zn(ClO_4)_2$-Zinc Perchlorate	$AgClO_4$-Silver Perchlorate.
18	do	ZnF_2-Zinc Fluoride	AgF-Silver Fluoride.
19	do	$Zn(BF_4)_2$-Zinc Fluoborate	$AgBF_4$-Silver Fluoborate.
20	do	$Zn(NO_3)_2$-Zinc Nitrate	$AgNO_3$-Silver Nitrate.
21	do	$ZnSO_4$-Zinc Sulfate	Ag_2SO_4-Silver Sulfate.
22	do	$Zn(CN)_2$-Zinc Cyanide	CuCN-Cuprous Cyanide.
23	do	do	$Hg(CN)_2$-Mercuric Cyanide.
24	do	do	AgCN-Silver Cyanide.
25	Cadmium	$Cd(CN)_2$-Cadmium Cyanide	CuCN-Cuprous Cyanide.
26	do	do	$Hg(CN)_2$-Mercuric Cyanide.
27	do	do	AgCN-Silver Cyanide.
28	Magnesium	$MgCrO_4$-Magnesium Chromate	Ag_2CrO_4-Silver Chromate.
29	do	$Mg(NH_4)_2(CrO_4)_2$-Magnesium Ammonium Chromate.	$Ag_2CrO_4,4NH_3$-Silver Tetrammino Chromate.
30	Aluminum	$Al_2(SO_4)_3$-Aluminum Sulfate	Hg_2SO_4-Mercurous Sulfate.
31	do	do	$HgSO_4$-Mercuric Sulfate.

Cadmium metal and its corresponding cadmium compounds may be substituted for the zinc anode and anolytes in Examples 1 through 21, although it produces a cell of lower voltage and therefore is not so desirable. The double salts of zinc and cadmium may also be substituted for the single salts cited. For example, in Example 7 the zinc fluoride anolyte may be replaced by potassium zinc fluoride. Examples 22 through 26 disclose cell systems in which the electrolyte comprises aqueous alkaline solutions of the metallic cyanides. Suitable electrolytes may be prepared by dissolving the cited cyanides in aqueous solutions of alkali metal cyanides such as sodium or potassium cyanide. The anolytes and catholytes cited are preferably saturated aqueous solutions although the concentration of the electrolytes may be varied to obtain optimum cell performance under various conditions. The catholytes cited in Examples 1 through 21 have a tendency to hydrolyse in aqueous solution. Hydrolysis of these salts may be suppressed by adding sufficient acid to their aqueous solutions. Where cost is not a prohibiting factor, electrolytically reducible anion yielding compounds of gold and platinum may be utilized as catholytes to produce higher cell voltages.

The zinc and cadmium anodes may be amalgamated to reduce local action. Since amalgamated zinc is brittle, anodes constructed from same are preferably amalgamated after assembly of the cell. This may be accomplished in certain instances by adding a quantity of a soluble mercury salt to the anolyte prior to filling of the cell which will cause a displacement coating of mercury to form on the anode. For example, mercuric fluoride added to an anolyte of zinc fluoride will result in the deposition of mercury metal on the zinc anode, the mercuric fluoride being changed into zinc fluoride. Other means of inhibiting spontaneous corrosion of the anode may be employed within the scope of the present invention. The battery cells may be filled by any suitable means such as vacuum impregnation and are preferably heat-sealed.

In the present invention, the cathode 8 does not take part in the chemical reaction but only serves as a site for the electrochemical reduction of the catholyte. To perform the above function satisfactorily, the cathode must be a good conductor of electrons, relatively inert to the catholyte and porous or otherwise permeable so as to provide a large surface area in contact with the catholyte.

I have discovered that suitable cathodes satisfying the foregoing requirements may be constructed from graphite fabrics. Graphite fabrics are manufactured from conditioned organic fibers that have been graphitized at temperatures up to 5400° F. The resultant product consists entirely of high purity graphite fibers which assay over 99% graphitic carbon. The good electrical conductivity of graphite together with its relative chemical inertness in combination with the inherently porous nature of graphite fabrics provides the essential requisites of an ideal cathode. Graphite felt is available with a surface area of approximately 2 square meters per gram weight and graphite cloth with a surface area of approximately 3 square meters per gram weight. Grades WCB and WCC graphite cloth and Grades WDD and WDF graphite felt have been found to be satisfactory. It should be understood, however, that other textile forms of graphite may be utilized for constructing cathodes of the character described within the scope of the present invention.

The thickness of the cathode employed in the practice of the present invention is governed by its total available surface area which should be sufficient to accommodate all the metal resulting from the reduction of the catholyte.

The primary reaction of the cell is explained as follows: The anode 2 in contact with the anolytic held in 5 assumes a relatively passive state when no current is being drawn from the cell. The interleaved absorbent 5 retains the anolyte and facilitates ionic transfer over the entire anode surface area. When the external circuit between the positive and negative terminals is completed, the anode reacts with the anolyte forming positive metal ions (cations) yielding electrons which travel through the external circuit and return to the cell via the cathode reducing the anion yielding catholyte held in the absorbent 7 and 7A and in contact with the graphite sleeve 8. Neutralized copper, mercury and silver cations are deposited upon the cathode 8 in the form of a metallic coating. Trivalent manganese is reduced to the bivalent state only and no metal is deposited. Reduction of the catholyte releases negative ions (anions) which migrate through the anion permeable membrane envelope 6 to replenish the anions being consumed at the anode 2. An excess of the catholyte compound may be added to the saturated catholyte so that as the catholyte is consumed, the undissolved excess will gradually dissolve and thus replenish the catholyte.

From the foregoing, it can be seen that the primary reaction proceeds only when current is being drawn from the cell. The inherent porosity of the fibrous graphite

sleeve utilized as the cathode 8 provides a large surface area upon which the metal resulting from the reduced catholyte is deposited. As the cell is discharged, the increasing accumulation of deposited metal has the beneficial effect of reducing the ohmic resistance of the cathode which compensates in part for reduced cell output as the reactants become exhausted. The amount of metal deposited upon the cathode during discharge of the cell corresponds to the electrochemical equivalent of the anode metal consumed. Cells constructed in accordance with the present invention may be balanced by limiting the amount of metal in the anode to less than that corresponding to the electrochemical equivalent of the catholyte in order that the anode will be consumed before the catholyte is depleted. This would serve to prevent residual gassing which might create excessive pressure within the cells.

Battery cells utilizing the combination of anode, anolytes, and catholytes cited in Examples 1 through 27 have reactions which are electrochemically reversible. Such cells are rechargeable and may be classified as both primary and secondary type batteries.

While this invention has been described with particular reference to the construction shown in the drawing and while various changes may be made in the detail construction and selection of reactants, it shall be understood that such changes shall be within the scope of the present invention as defined by the appended claims.

What is claimed as new and desired to be protected by Letters Patent is:

1. A voltaic cell comprising, in combination, a metal anode, an aqueous anolyte, a cathode electrode formed substantially of graphite fibers in fabric form and a catholyte comprising essentially an aqueous solution of an electrolytically reducible anion yielding compound, said anolyte and catholyte being separated by and making electrolytic contact through an anion permeable membrane.

2. The voltaic cell of claim 1 in which the anode is formed of zinc.

3. The voltaic cell of claim 1 in which the catholyte is selected from the group of compounds consisting of a halide of one of the metals copper, mercury, and silver.

4. The voltaic cell of claim 1 in which the catholyte is selected from the group of compounds consisting of a fluoborate of one of the metals copper, mercury, and silver.

5. The voltaic cell of claim 1 in which the catholyte is selected from the group of compounds consisting of a cyanide of one of the metals copper, mercury, and silver.

6. The voltaic cell of claim 1 in which the catholyte is an aqueous solution of manganese trifluoride.

7. The voltaic cell of claim 1 in which the anode is magnesium, the anolyte an aqueous solution of magnesium chromate, and the catholyte an aqueous solution of silver chromate.

8. The voltaic cell of claim 1 in which the anode is magnesium, the anolyte an aqueous solution of magnesium ammonium chromate and the catholyte an aqueous solution of silver tetrammino chromate.

9. The voltaic cell of claim 1 in which the anode is aluminum, the anolyte an aqueous solution of aluminum sulfate and the catholyte an aqueous solution of a sulfate of one of the metals mercury and silver.

10. A voltaic cell comprising a casing containing a zinc anode surrounded by an anion permeable membrane envelope, an anolyte comprising an aqueous solution of a compound of zinc, a cathode formed substantially of graphite fibers in fabric form surrounding said anion permeable membrane envelope, a catholyte comprising an aqueous solution of an electrolytically reducible anion yielding compound of one of the metals copper, mercury and silver, said anolyte and catholyte being separated by and making electrolytic contact through said anion permeable membrane envelope.

11. A voltaic cell comprising a spirally enrolled casing containing a zinc anode and anolyte surrounded by an anion permeable membrane envelope, said anolyte comprising an aqueous solution of a compound of zinc, a graphic fabric sleeve cathode electrode surrounding said anion permeable membrane envelope, a catholyte comprising an aqueous solution of an electrolytically reducible anion yielding compound of one of the metals copper, mercury and silver, said anolyte and catholyte being separated by and making electrolytic contact through said anion permeable membrane envelope, together with electrical conducting means for withdrawing electrical current.

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JOHN H. MACK, *Primary Examiner.*

MURRAY TILLMAN, *Examiner.*

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

March 23, 1965

Patent No. 3,174,880

Thomas J. Buitkus

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Columns 3 and 4, Table 1, under the heading Catholyte, opposite Example 4, for "Do" read -- $HgCl_2$-Mercuric Chloride --; same table, same heading, opposite Example 12, for "Hg_3SO_4-Mercurous Sulfate" read -- Hg_2SO_4-Mercurous Sulfate --; column 4, line 52, for "anolytic" read -- anolyte --; column 6, line 26, for "graphic" read -- graphite --.

Signed and sealed this 24th day of August 1965.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents