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(54) IODINE-CONTAINING CATHODE FOR PRIMARY CELL

(71) We, CATALYST RESEARCH CORPORATION, a Maryland corporation of 6101 Falls Road, Baltimore, Maryland 21209, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to a cathode for use in a solid state primary cell.

According to the invention there is provided a plastic cathode consisting of a mixture of iodine and a charge transfer complex of an iodine electron acceptor component and an organic electron donor component selected from the group consisting of poly-2-vinylquinoline and poly-2-vinylpyridine, the mixture containing between 2 and 15 molecules of iodine for each atom of nitrogen.

20 The cathode may contain between about 2 and 6 molecules of iodine for each atom of nitrogen but the preferred content is 6 molecules of iodine for each atom of nitrogen.

25 The cathode of the invention may be fitted into a solid state primary cell having an anode of lithium or silver or magnesium.

30 In order that the invention may be more clearly understood, a cell incorporating a cathode in accordance with the invention will now be described, by way of example, with reference to the accompanying diagrammatic drawings, in which:

35 Fig. 1 is a cross section through the cell; and

Fig. 2 is a chart showing the discharge characteristics of the cell of Fig. 1.

40 The cell of Fig. 1 may be made in the form of a thin sheet, as little as 20 mils thick, of any desired area. The cell is enclosed in a plastics envelope 16, suitably polyvinyl chloride or polytetrafluoroethylene, or a potted housing of polyester or epoxy, or other hermetically sealed housing that is impervious to iodine and ordinary atmospheres; that is, oxygen, nitrogen and water

vapour. A thin metallic anode current collector 18, suitably nickel foil or nickel plate deposited on the plastics envelope by vacuum deposition or electroless plating, abuts a thin lithium electrode 19, suitably 1 to 10 mils thick. The lithium is most conveniently in the form of a foil, but it may also be deposited on the current collector by vacuum deposition, electroplating or other conventional methods. An initial thin film of lithium iodide electrolyte 20, may be preformed on the lithium surface before assembling the cell or formed spontaneously when the clean lithium anode surface is brought into contact with the cathode. The new plastic cathode material 22 is preferably directly applied to the cathode current collector 24, which laminate is then brought into contact with the anode. The new plastic cathode material may be also heated to melting and be applied by brushing or spraying, or be applied as a solution in tetrahydrofuran and then evaporating the solvent. The cathode current collector 24 may be a thin metal foil or, as in the case of the anode current collector, a metal coating deposited on the plastics envelope. We have discovered that zirconium, platinum or alloys thereof are the most desirable materials for cathode collectors as they exhibit no apparent reaction or deterioration. The alloy known under the Registered Trade Mark Nichrome, nickel and other high nickel alloys are suitable for shorter life batteries, e.g. 4—6 months. Metal leads 26 and 28, for external circuit connections, are connected to the anode and cathode current collectors respectively and tightly sealed through openings in the plastics envelope. The stacked cell components may be compressed to provide good adhesion and contact between the layers; only small pressures of the order of 25 lb/in² are needed with the new plastic cathode materials to ensure that adhesion between layers is maintained during storage and discharge without external force.

The cells may be made in a variety of

forms, and completely encapsulated flexible cells have been made as thin as 0.020 inches, allowing batteries to be formed in almost any configuration; for example, a battery can be wrapped around electronic circuitry for efficient use of available space. When flexibility is not needed, cells can be encapsulated in rigid plastics or sealed in metal cans. Larger capacities per unit electrode area can be obtained by increasing the thickness of the anode and cathode, suitably to give cells having a thickness as much as 0.5 inches, or more. Batteries of low internal impedance are formed by stacking cells in series and parallel.

Prior to encapsulation the cells are adversely affected by atmospheric moisture, so cells are assembled and encapsulated in a dry atmosphere, suitably in dry rooms or enclosures having a relative humidity less than about 2%, using substantially anhydrous and/or dried components. All of the cell assemblies and tests of non-encapsulated cells described herein were performed in such a dry room or in dry boxes having even dried air or argon atmospheres.

The herein described charge transfer complexes of an organic material and iodine are suitable cathode materials particularly for use in lithium anode cells as described in our Application No. 16067/71, (Serial No. 1,358,998), although other anode materials may also be used.

In the cathode materials of this invention, which are pliable putty-like solids containing an iodine electron acceptor component and an organic electron donor component selected from the group poly-2-vinyl quinoline and poly-2-vinyl pyridine, the proportions of iodine to organic component can be varied within the hereinbefore stated range, although when the proportion of uncomplexed iodine in the cathode is increased beyond a certain limit the internal cell resistance becomes unacceptable for certain applications.

In the preparation of charge transfer complexes of iodine with poly-2-vinyl pyridine or poly-2-vinyl quinoline one molecular of I_2 coordinates with each N atom resulting in a solid having an iodine content of about 71% by weight in the case of the poly-2-vinyl pyridine complex and about 62% in the case of the poly-2-vinyl quinoline complex. The cathode compositions of the invention are a mixture of iodine and the solid poly-2-vinyl pyridine $\cdot I_2$ or poly-2-vinyl quinoline $\cdot I_2$ charge transfer complex in the desired proportions within the stated range. The cathode compositions may be designated by the formulas $P2VP \cdot nI_2$ and $P2VQ \cdot nI_2$, where P2VP is poly-2-vinyl pyridine, P2VQ is poly-2-vinyl quinoline and n is the number of moles of I_2 for each atom of N. For example, the charge transfer complex of

iodine with PV2, having one mole of I_2 per N atom, is designated as P2VP $\cdot I_2$; when four moles of I_2 per N atom are added to form a cathode material, the mixture is designated P2VP $\cdot 5I_2$. The mixture is at ordinary ambient room temperatures a putty-like, pliable solid that is sufficiently plastic to be spread on a solid substrate, such as a sheet of anode metal. The materials are useable as cathodes in solid state cells at temperatures up to the point where softening causes loss of dimensional stability; this point may range from 20° to 75°C, or higher, depending on the degree of polymerization of the organic component of the charge transfer complex. It is believed that the plastic state of the cathode materials permits excellent atomic bonding of the cathode materials to the anode and to the cathode current collector resulting in greater outputs from a cell.

The following examples are illustrative of the preparation of the new cathode compositions, it being recognized that any methods of preparing the charge transfer complex may be used, variations in which may modify the molecular weight of the polymer component of the complex. In general, the most satisfactory cathode materials are obtained using a charge transfer complex precipitated from organic solution.

EXAMPLE I

Poly-2-vinylquinoline is prepared by the conventional method of polymerizing a benzene solution of 2-vinylquinoline using n-butyllithium polymerization initiator, suitably by adding 11.3 g. of initiator (15—22% by weight in hexane) to a solution of 100 g. of 2-vinylquinoline in 1500 cc. of benzene (the solution at 45°C) and stirring for about 10 minutes. A solution of iodine in benzene, is added in excess of stoichiometric to the poly-2-vinylquinoline solution to precipitate P2VQ $\cdot I_2$ charge transfer complex. The presence of an excess of iodine is readily determinable by a red coloration of the mixed solutions. The precipitate is filtered, vacuum dried and mixed with iodine in such amount that in the final product there are between 2 and 15 molecular weights of I_2 for each atomic weight of N in the plastic, pliable solid.

EXAMPLE II

Example I is repeated except that 2-vinylpyridine is used in place of the 2-vinylquinoline. The resultant materials having the formula P2VP $\cdot nI_2$ when n is between about 2 and 7, are plastic.

It will be recognized that solutions of poly-2-vinylquinoline and poly-2-vinylpyridine may be prepared using a variety of organic solvents or conventional catalysts, such as for example the solvents toluene and hexane and the catalysts sodium metal and potassium

metal. The polymers may also be prepared from aqueous solution using catalysts such as acetyl peroxide, lauroyl peroxide or methyl ethyl ketone peroxide with a cobalt naphthenate accelerator.

EXAMPLE III

2-vinylpyridine was thermally polymerized by heating to about 80° to 8 hours. The resultant red thermoplastic material was cooled, ground to a powder, and mixed with from 20 to 40 parts of iodine to form a plastic, pliable solid.

The new compositions of the invention are particularly suitable as iodine-containing cathode materials because, in addition to their putty-like physical state, they exhibit a low and relatively constant electronic resistance over a wide range of iodine content and have a comparatively low electronic resistance even at extremely high iodine contents.

With proportions of between about 3 and 7 moles of I₂ per atom of nitrogen (or monomer unit) the electrical resistance of the new cathode material is low and substantially constant. For example, the specific resistance of P2VP . 3I₂ prepared by the method of Example I is about 1400 ohm-cm; P2VP . 4I₂ is 1000 ohm-cm; P2VP . 5I₂ is 1000 ohm-cm; P2VP . 6I₂ is 930 ohm-cm; and P2VP . 7I₂ is 1400 ohm-cm. With lower iodine content, the resistance rapidly increases; for example, P2VP . 2I₂ has a specific resistance of about 40,000 ohm-cm. With increasing iodine content above about 7 moles of I₂ per monomer unit, the resistance also increases; for example, the specific resistance of P2VP . 8I₂ is 2600 ohm-cm. Thus the new cathode materials are especially advantageous in that they can provide a large amount of iodine for electrochemical reaction without greatly increasing the cell resistance because of change in the cathode composition resulting from consumption of iodine; this results in longer lived cells with higher power and energy outputs. For high current drain batteries it is preferred to use cathodes containing about 6 moles of iodine per monomer unit, as about 4 moles of iodine are available for reaction at the lowest resistance level. Higher proportions of iodine, up to 15 moles or iodine per monomer unit, are advantageously used in low current drain batteries, as a much higher energy capacity is obtained and at low current drains the polarization (IR drop) is not objectionably large.

Solid state cells having a lithium anode and utilizing new plastic cathode materials above described are disclosed in our co-pending Application No. 16067/71 (Serial No. 1,358,998). The cells exhibit unexpected superior performance, have exceptional storage stability, long life, high voltage output and high energy density making them especially

suitable for long life, low current drain applications, such as power supplies for implanted prosthetic devices like heart pacers. The cell has a theoretical energy density of 213 wh/lb. or 19.2 wh/in³; actual energy densities of 136 wh/lb. and 11.5 wh/in³ have been measured during discharge of cells at room temperature.

Open circuit voltage for the cell is 2.87 volts. Since impedance is a function of electrolyte conductivity, a plot of cell voltage vs. current shows a linear decrease in voltage with increasing current until short circuit current is reached. Short circuit current densities as high as 20 ma/cm² have been measured immediately after construction. At room temperature, after 20 days the short circuit current decreases to 1 ma/cm² and to 0.5 ma/cm² after 110 days.

Under constant current discharge at relatively high current densities, voltage decay is linear with time. This behavior is illustrated in Figure 2 for cells made in accordance with Fig. 1 having a lithium anode, a P2VP . 5I₂ cathode and zirconium cathode collector which cell has been stored at room temperature for one week. In Fig. 2, the cell voltage is plotted against time of discharge at the indicated constant current density and various temperatures for several cells of different thickness, which is selected to provide the desired cell capacity. The cell thicknesses range from 0.03 cm. to 0.25 cm., the anode being about 20% and the cathode being about 80% of the cell thickness. The discharge curves generally obey the equation

$$\eta = -C \cdot (i/A)^2 \cdot t \cdot \exp(8650/RT)$$

where η is polarization, C is a constant dependent on cell construction, i/A is the current density, and t is time of discharge. The value 8650 calories/mole agrees with published data for the activation energy of ionic conduction in LiI. The constant C is typically 1.25×10^{-4} ohm . cm⁴/amp.sec. using our new cathode material.

Discharging cells at smaller current densities results in a marked decrease in polarization. For example, if the 0.13 cm. cell in Fig. 2 was discharged (at 25°C) at 25 μ A/cm² rather than 50 μ A/cm², cell voltage at 1000 hours would be increased from 0.24 to 2.16 volts. At 10 μ A/cm², polarization increase per thousand hours amounts to less than 100 mv and cell life is increased by about a factor of five.

As current density is decreased, allowing cells to run for longer periods, small deviations from linearity are evident in the discharge curves, especially at higher temperatures, which are the result of self discharge.

Self discharge for the cells involves diffusion of iodine from the cathode through the

electrolyte to the anode where additional electrolyte is then generated. Resistance increase resulting from this accumulation has been found to be governed by the relationship.

$$\Omega/A = K \cdot t^{1/2} \cdot \exp(E/RT)$$

where Ω is resistance increase per unit area and t is time. Both the pre-exponential constant K and the exponential term E have been determined for cells over a one-year storage period at temperatures between -55°C and $+75^\circ\text{C}$. For lithium anode cells using P2VP . 6I_2 cathodes, the value of K is typically $1.6 \times 10^5 \text{ coul./cm}^2 \cdot \text{sec}^{1/2}$ and the value of E -9950 cal/mole . After one year storage at 75°C , a typical cell having an initial impedance of 30 ohms exhibits an internal impedance of about 16,000 ohms (both values measured at this temperature). The same cell stored at 25°C shows an internal impedance of about 11,000 ohms, having increased from 150 ohms initially.

Thus, for example, a cell only $4.45 \text{ cm} \times 3.50 \text{ cm} \times 0.93 \text{ cm}$, to be discharged at $30 \mu\text{A}$ with a voltage of at least 2.3 volts at 37°C for use in a prosthetic device has a projected life of at least 10 years. Even after long periods of storage, cells can be operated at microampere drains for many years over a wide temperature range. In designing for very long storage period, e.g. 10 years, cell thickness is increased to accommodate increased self discharge. Similar performance is obtained when using either P2VP . nl_2 or P2VQ . nl_2 .

It will be recognized that the new cathode materials can be used to advantage with anodes of other metals that are reactive with iodine, for example silver or magnesium. To illustrate, a sintered silver anode $1-1/2'' \times 1-1/2'' \times 0.020''$ (about 50% porous) was filled with .036 in³ of P2VP . 5I_2 to form a cell 0.026" thick. Contact with the cathode was effected using a zirconium cathode collector. The cell had an open circuit voltage of 0.67 volts. After 170 hours of discharge at $1450 \mu\text{A}$ (at 24°V) the cell voltage had dropped only to about 0.52 volts; on further discharge at the same current, the voltage dropped to zero at about 200 hours. The silver anode in this instance was a sintered mat of $0.005'' \times 0.009'' \times 0.125''$ silver needles weighing 3.7 grams. Other forms of electrodes may be used, e.g. foil, screen or electroplates, but best performance is obtained from sinters. A group of 6 cells having a silver foil anode and a P2VP . 5I_2 cathode had when freshly prepared, an average life of 987 hours when discharged at $10 \mu\text{A/cm}^2$ and 25°C ; 6 identical cells after thirty (30) days storage had an average life of 841

hours under the same discharge conditions. In contrast to the lithium cells, only about one third of the theoretical electrochemical capacity is realized in silver batteries; this is the result of the inability of the silver to conform to the growing silver iodide electrolyte causing a loss of physical contact between the anode and electrolyte.

In another example, a cell having stacked laminae of magnesium anode, P2VP . 5I_2 cathode and zirconium cathode collector has an open circuit voltage of 0.95 volts and a short circuit current of 2 mA/cm^2 . When discharged at a current density of $10 \mu\text{A/cm}^2$ the cells have a life of about 50 hours.

Patent No. 1,162,747 claims an electrochemical cell having positive and negative electrodes in electrical contact with an electrolyte, in which the positive electrode comprises a charge transfer complex containing as acceptor component a halogen and as donor component a polycyclic aromatic substance capable of forming with the halogen a solid charge transfer complex having an electrical resistivity less than 10^6 ohm cm , said negative electrode being a metal capable of reacting chemically with ions of the halogen with transfer of electrons to the electrode, and said electrolyte being a layer of solid material that includes the product of said reaction and is permeable to ions of the halogen.

WHAT WE CLAIM IS:—

1. A plastic cathode consisting of a mixture of iodine and a charge transfer complex of an iodine electron acceptor component and an organic electron donor component selected from the group consisting of poly-2-vinylquinoline and poly-2-vinylpyridine, the mixture containing between 2 and 15 molecules of iodine for each atom of nitrogen.
2. A cathode as claimed in claim 1, containing between 2 and 6 molecules of iodine for each atom of nitrogen.
3. A cathode as claimed in claim 1 containing 6 molecules of iodine for each atom of nitrogen.
4. A cathode as claimed in claim 1, wherein the proportions of iodine to nitrogen in the cathode material are such that when in use the change in the cathode composition resulting from consumption of iodine initially causes a reduction in the specific resistance of the cathode until said resistance reaches a minimum for the particular discharge rate employed, whereafter the specific resistance again increases.
5. A cathode as claimed in any one of claims 1 to 4 when used in a cell having a silver anode.
6. A cathode as claimed in any one of claims 1 to 4 when used in a cell having a magnesium anode.



electrolyte to the anode where additional electrolyte is then generated. Resistance increase resulting from this accumulation has been found to be governed by the relationship.

$$\Omega/A = K \cdot t^{1/2} \cdot \exp(E/RT)$$

where Ω is resistance increase per unit area and t is time. Both the pre-exponential constant K and the exponential term E have been determined for cells over a one-year storage period at temperatures between -55°C and $+75^\circ\text{C}$. For lithium anode cells using P2VP . 6I_2 cathodes, the value of K is typically $1.6 \times 10^5 \text{ coul./cm}^2 \cdot \text{sec}^{1/2}$ and the value of E -9950 cal/mole . After one year storage at 75°C , a typical cell having an initial impedance of 30 ohms exhibits an internal impedance of about 16,000 ohms (both values measured at this temperature). The same cell stored at 25°C shows an internal impedance of about 11,000 ohms, having increased from 150 ohms initially.

Thus, for example, a cell only $4.45 \text{ cm} \times 3.50 \text{ cm} \times 0.93 \text{ cm}$, to be discharged at $30 \mu\text{A}$ with a voltage of at least 2.3 volts at 37°C for use in a prosthetic device has a projected life of at least 10 years. Even after long periods of storage, cells can be operated at microampere drains for many years over a wide temperature range. In designing for very long storage period, e.g. 10 years, cell thickness is increased to accommodate increased self discharge. Similar performance is obtained when using either P2VP . nI_2 or P2VQ . nI_2 .

It will be recognized that the new cathode materials can be used to advantage with anodes of other metals that are reactive with iodine, for example silver or magnesium. To illustrate, a sintered silver anode $1\frac{1}{2}'' \times 1\frac{1}{2}'' \times 0.020''$ (about 50% porous) was filled with .036 in³ of P2VP . 5I_2 to form a cell 0.026" thick. Contact with the cathode was effected using a zirconium cathode collector. The cell had an open circuit voltage of 0.67 volts. After 170 hours of discharge at $1450 \mu\text{A}$ (at 24°C) the cell voltage had dropped only to about 0.52 volts; on further discharge at the same current, the voltage dropped to zero at about 200 hours. The silver anode in this instance was a sintered mat of $0.005'' \times 0.009'' \times 0.125''$ silver needles weighing 3.7 grams. Other forms of electrodes may be used, e.g. foil, screen or electroplates, but best performance is obtained from sinters. A group of 6 cells having a silver foil anode and a P2VP . 5I_2 cathode had when freshly prepared, and average life of 987 hours when discharged at $10 \mu\text{A/cm}^2$ and 25°C ; 6 identical cells after thirty (30) days storage had an average life of 841

hours under the same discharge conditions. In contrast to the lithium cells, only about one third of the theoretical electrochemical capacity is realized in silver batteries; this is the result of the inability of the silver to conform to the growing silver iodide electrolyte causing a loss of physical contact between the anode and electrolyte.

In another example, a cell having stacked laminae of magnesium anode, P2VP . 5I_2 cathode and zirconium cathode collector has an open circuit voltage of 0.95 volts and a short circuit current of 2mA/cm^2 . When discharged at a current density of $10 \mu\text{A/cm}^2$ the cells have a life of about 50 hours.

Patent No. 1,162,747 claims an electrochemical cell having positive and negative electrodes in electrical contact with an electrolyte, in which the positive electrode comprises a charge transfer complex containing as acceptor component a halogen and as donor component a polycyclic aromatic substance capable of forming with the halogen a solid charge transfer complex having an electrical resistivity less than 10^6 ohm cm , said negative electrode being a metal capable of reacting chemically with ions of the halogen with transfer of electrons to the electrode, and said electrolyte being a layer of solid material that includes the product of said reaction and is permeable to ions of the halogen.

WHAT WE CLAIM IS:—

1. A plastic cathode consisting of a mixture of iodine and a charge transfer complex of an iodine electron acceptor component and an organic electron donor component selected from the group consisting of poly-2-vinylquinoline and poly-2-vinylpyridine, the mixture containing between 2 and 15 molecules of iodine for each atom of nitrogen.

2. A cathode as claimed in claim 1, containing between 2 and 6 molecules of iodine for each atom of nitrogen.

3. A cathode as claimed in claim 1 containing 6 molecules of iodine for each atom of nitrogen.

4. A cathode as claimed in claim 1, where in the proportions of iodine to nitrogen in the cathode material are such that when in use the change in the cathode composition resulting from consumption of iodine initially causes a reduction in the specific resistance of the cathode until said resistance reaches a minimum for the particular discharge rate employed, whereafter the specific resistance again increases.

5. A cathode as claimed in any one of claims 1 to 4 when used in a cell having a silver anode.

6. A cathode as claimed in any one of claims 1 to 4 when used in a cell having a magnesium anode.



7. A cathode as claimed in claim 1 prepared substantially as hereinbefore described with reference to Example I.

5 8. A cathode as claimed in claim 1 prepared substantially as hereinbefore described with reference to Example II.

9. A cathode as claimed in claim 1 prepared substantially as hereinbefore described with reference to Example III.

10 10. A cathode as claimed in claim 1 and

substantially as herein described with reference to Fig. 1 of the accompanying drawings.

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