EUROPEAN PATENT SPECIFICATION

Covered electrode for electrochemical cells
Elektrode mit Überzug für elektrochemische Zellen
Electrode recouverte pour cellules électrochimiques

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Proprietor: WILSON GREATBATCH LTD.
Clarence New York 14031 (US)

Inventors:
- Nesselbeck, Neil N.
  Lockport, New York 14094 (US)
- Muffoletto, Barry C.
  Alden, New York 14004 (US)
- Spaulding, Joseph E.
  Buffalo, New York 14216 (US)

Representative: Colmer, Stephen Gary et al
Mathys & Squire
100 Gray's Inn Road
London WC1X 8AL (GB)

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  J. SPECHT)

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Description

Field Of The Invention

[0001] This invention relates to the art of electrochemical cells and more particularly to a new and improved electrode covering for alkali metal-halogen and alkali metal-oxyhalide cells.

Background of The Invention

[0002] The recent growth in small-sized electronic devices has required electrochemical cells having high energy density and current delivery capability. As a result of this need, alkali metal-halogen and alkali metal-oxyhalide cells have been developed wherein the anode typically is lithium and the electrolyte in operative contact with the anode and the cathode element is either solid or liquid. In the development of such cells it has been found advantageous to coat the operative electrode surfaces, and particularly the anode surface with organic electron donor material. For example, in alkali metal-oxyhalide, solid electrolyte cells, such an electrode covering beneficially results in a greater utilization of the lithium anode and a reduction in cell impedance. In alkali metal-oxyhalide, liquid electrolyte cells, an organic electron donor material electrode covering advantageously inhibits the formation of compounds on the anode surface that otherwise would cause passivation giving rise to a voltage delay after storage at elevated temperatures.

Discussion Of The Prior Art

[0003] The prior art has developed a variety of techniques for applying coatings including painting or brushing a solution of organic electron donor material dissolved in solvent onto the anode surface. Another method comprises forming a sheet of the organic electron donor material such as by hot pressing and then applying the preformed sheet onto the anode surface, often in conjunction with an adhesive. WO 92/10860 discloses the use of an ion permeable polymeric organic donor film which has been perforated for covering a lithium anode surface. The film is formed by extrusion. These methods are well known to those of ordinary skill in the art. However, they are often time consuming and do not necessarily result in a uniform layer of organic material being applied to the anode surface.

[0004] As a solution, US Patent No. 4,812,376 issued March 14 1989 to Rudolph and entitled Anode Coating For Lithium Cell, which is assigned to the assignee of the present invention and is incorporated herein by reference, discloses an improved anode coating for use in an alkali metal halogen or oxyhalide electrochemical cell comprising a thin film of synthetic open mesh fabric material having the organic electron donor material impregnated therein. The film is prepared by contacting the fabric substrate material with a solution of the organic material and solvent, followed by drying. The resulting film is flexible enough to be applied to the operative surface of the anode by pressing, thereby coating the anode. The open mesh fabric material used as the substrate can comprise a polyester open mesh fabric material, such as #3251 Hollytex-Paper polyester. This material works well, but the fabric substrate varies in its weight per unit area, i.e., large standard deviation, resulting in a non-uniform layer of organic material being contacted with the anode surface. Alternate spin-bonded nonwoven or woven fabric substrate materials are known, but they too vary widely in their unit weight.

[0005] The present invention thus provides an electrochemical cell as set out in claim 1, an anode for such an electrochemical cell as set out in claims 16 and 17, and a method of forming such anode as set out in claim 27.

[0006] The electrochemical cell is preferably an alkali metal halide or oxyhalide electrochemical cell in which an alkali metal, preferably lithium, has a surface in operative contact with a halogen-containing or oxyhalide cathode/electrolyte including a solvent if necessary.

[0007] It is preferably the anode surface that is coated. The coating is preferably a thin film. The thin film substrate material is preferably flexible, and most preferably comprises a perforated synthetic polyester film material. The film may be prepared by contacting the substrate material with a solution of the organic material and solvent, followed by drying. The resulting coated film is flexible and is applied to the operative surface of the electrode thereby covering the same, preferably adhered to the surface by pressing. The flexible film can be applied equally well to electrode surfaces which are either smooth and flat or irregular.

Objects Of The Invention

[0008] It is, therefore, a primary object of this invention to provide a new and improved electrode covering for alkali metal/halogen or oxyhalide cells and method of making the same.

[0009] It is a further object of this invention to provide such an improved covering in the nature of a preformed film which is applied to the anode surface.

[0010] It is another object of this invention to provide such a pre-formed coated film having a uniform thickness or
uniform weight per unit area when applied to the electrode surface.

[0011] It is a more particular object of this invention to provide such a preformed coating film for an electrode covering which has some flexibility.

[0012] It is a further object of this invention to provide such a preformed coated film for electrode covering which includes organic electron donor material as the coating and is flexible in nature.

[0013] It is still another object of this invention to provide such a preformed coated film for anode covering which is flexible in nature and adheres well to the surface of the metal anode.

[0014] Yet a further object of this invention is to provide such a preformed coated film comprised of a perforated thin film of polymeric substrate material provided with an organic electron donor coating material, wherein the preformed film is flexible in nature.

[0015] It is a further object of this invention to provide such an electrode covering and method that is convenient, effective and economical to practice and that is readily adapted to current manufacturing techniques.

Brief Description Of The Drawing Figures

[0016] The above and other objects, features, and advantages of the present invention will be apparent in the following detailed description of the preferred embodiments taken in conjunction with the accompanying drawings, in which:

FIG. 1 is a perspective view of an alkali metal-nalogen cell having a covered anode according to the present invention;
FIG. 2 is an enlarged sectional view taken about on line 2-2 in FIG. 1;
FIG. 3 is a sectional view taken about on line 3-3 in FIG. 2;
FIG. 4 is a sectional view similar to FIG. 2 of a cell according to another embodiment of the present invention;
FIG. 5 is a sectional view taken about on line 5-5 in FIG. 4;
FIG. 6 is a sectional view taken about on line 6-6 in FIG. 4; and
FIG. 7 is a perspective view of an electrochemical cell 200 having a covered cathode according to the present invention; and
FIG. 8 is a diagrammatic view of the apparatus used in performing the method of the present invention.

Detailed Description Of The Illustrated Embodiments

[0017] Referring now to FIGS. 1-3, there is shown an alkali metal-halogen electrochemical cell 10 including a covered anode according to one embodiment of the present invention. The covered anode and other cell components are contained within a casing 12 of metal, such as stainless steel, including spaced apart side walls 14, 16 joined by curved end walls 18, 20 and a curved bottom wall 22. The open top of casing 12 is closed by a lid 24 which can be welded to casing 12.

[0018] The covered anode of the present invention can be used with alkali metal-halogen or alkali metal-oxyhalide electrochemical cells of both solid and liquid electrolyte types. In the solid electrolyte type, for example a lithium-halogen cell, halogen-containing material such as a charge transfer complex of an organic electron donor component and halogen, is contained within casing 12 in operative contact with the anode of the present invention and with the sides, bottom and end walls of the conductive metal casing 12, which serves as a cathode current collector. External cell connection is provided by terminal leads 26 and 28 which are operatively connected to the anode and cathode, respectively, of the cell in a manner which will presently be described in detail. For a more detailed description of such a solid electrolyte cell, reference may be made to U.S. Pat. No. 4,401,736 issued Aug. 30, 1983, entitled Anode Assembly For Lithium Halogen Cell and assigned to the assignee of the present invention, the disclosure of which is hereby incorporated by reference.

[0019] In the liquid electrolyte system, for example a lithium-oxyhalide cell, liquid electrolyte fills the casing interior and is in operative contact with the anode and with either the conductive casing serving as a cathode current collector or with a cathode having a current collector embedded therein with a lead extending therefrom to the terminal lead 28. The liquid electrolyte can comprise a liquid organic electron donor material that is in operative contact with both electrodes. A separator is employed between the anode and cathode. For a more detailed description of such a liquid electrolyte cell reference may be made to U.S. Pat. No. 4,246,327 issued Jan. 20, 1981 and entitled High-Energy Density Battery System, to U.S. Pat. No. 4,440,453 issued Aug. 23, 1983 and entitled Non-Aqueous Electrochemical Cell, and to U.S. Pat. No. 4,666,799 issued May 19, 1987 and entitled Current Collectors for Batteries Having Cathode-Electrolytes And Batteries Incorporating Same.

[0020] The electrochemical cell 10 includes an anode generally designated 30 according to the present invention and comprising an anode body 32 of alkali metal, preferably lithium. The anode body 32 can comprise a pair of lithium...
plates 34,36 pressed together and bonded against an anode current collector 38, which is a portion of the anode conductor means of the cell. Current collector 38 thus is sandwiched between plates 34,36 and can be of various forms such as a length of wire, a strand or ribbon, or a mesh or screen. Current collector 38 is of metal such as nickel or nickel alloy. Each of the plates 34,36 in the cell of FIGS. 2 and 3 has generally planar, flat, oppositely directed generally parallel surfaces. The edge or periphery of each plate is shown in FIG. 2. In particular, each plate, for example place 34 shown in FIG. 2, has a curved edge 42 extending along a major portion of the periphery or border and having a curvature conforming generally to the curvature of the casing bottom wall 22. A relatively straight edge portion 44 also is provided and meets curved edge 42 through step-like portions at each end thereof. In particular, the left hand end of edge 44 meets a relatively short inclined edge portion 48, which, in turn, meets another relatively short edge portion 50 leading to one end of the curved edge 42. Edge 50 is disposed generally parallel to edge 44 and is longer than edge 48. Similarly, the right hand end of edge 44 meets a relatively short inclined edge portion 52 which, in turn, meets another relatively short edge portion 54, leading to the other end of curved edge 42. Edge 54 is disposed at an acute angle to edge 44 and is longer than edge 52. Place 36 is identical to place 34 in size and peripheral outline, the two plates being in registry or in alignment when pressed together.

[0021] A strip or band of electrical insulating material 60 is placed on and extends along edge 44 and the edge portions 48 and 50. Insulator 60 serves to insulate anode 30 from the metal lid 24 of casing 12 in a completed or assembled cell. Insulator 60 can be relatively thin and may have a width larger than the width of the anode as shown in FIG. 3. An anode lead (not shown) extends from the anode current collector 38 through an insulator and seal structure 66 and becomes the terminal lead 26 which extends through lid 24. For a more detailed description of an illustrated form of insulator and seal structure 66, reference may be made to the above-identified U.S. Pat. No. 4,401,736.

[0022] In accordance with the present invention, the surface of anode 30 in operative contact with the halogen-containing cathode/electrolyte 68 is provided with a covering comprising a coated chin film made of inert substrate material coated with organic electron donor or other suitable organic material. The electron donor material can be any organic compound having a double bond or an amino group. The electron donor functions to give the cathode/electrolyte 68 sufficient conductivity for proper cell operation.

[0023] In the cell of the present invention, anode body 32 has two oppositely directed operative surfaces which are the exposed surfaces of plates 34,36, and these surfaces are provided with coverings 70 and 72, according to the present invention. Each covering, for example covering 70, comprises a thin film of inert substrate material preferably in the form of perforated synthetic polymeric film material. The perforated characteristic of the film material, i.e., allowing a significant flow of air therethrough, is important to insure that the substrate material does not act as a complete barrier to ion flow therethrough. By way of example, in an illustrative cell, the substrate can be made of perforated polyester film material, preferably a polyethylene terephthalate material. The thin film or substrate is coated with organic electron donor material. In particular, the film or substrate is coated - such as by drawing the film through a solution of organic electron donor material and solvent for a suitable time whereupon it is removed from the solution and allowed to dry. By way of example, in an illustrative cell, a preferred form of the organic electron donor material is polyvinyl pyridine polymer, and in particular poly-2-vinylpyridine (PVP) and more particularly cross-linked poly-2-vinylpyridine. The solvent can be dimethylformamide/tetrahydrofuran (DMF/THF). The resulting coated thin film or substrate, which is a perforated polymeric film is cut out or otherwise formed to have a peripheral outline or border matching that of the anode plate or element that is intended to be covered. Then the coated film is applied to the operative surface of the anode element by pressing with suitable force to pressure bond the film to the anode place. One method of pressing a chin film covering to a lithium anode element is described in U.S. Pat. No. 4,359,818 issued Nov. 23, 1982, the disclosure of which is hereby incorporated by reference. In the cell of the present invention, each lithium anode element 34, 36 is covered in the same way, and the resulting anode 30 with coverings 70,72 adhered to the relatively flat-oppositely directed anode surfaces is shown in FIGS. 2 and 3.

[0024] Applying the coated film by pressure bonding requires only the mechanical energy of pressing, in contrast to some other methods such as hot pressing a preformed sheet of organic material onto the anode surface, often in conjunction with adhesives. This method has energy requirements as well as handling requirements that detract from its usefulness. A further advantage is that the resulting coating of active organic electron donor material is more uniform as compared to a coating which is painted or brushed on the electrode surface or as compared to a coating that is impregnated into an open mesh or open weave fabric material. Furthermore, the present invention enables the thickness of the coating, which affects battery performance and characteristics, to be controlled precisely. A uniform coating thickness on the inert substrate material provides improvements in reducing self-discharge of the cell due to the partial masking of the electrode surface, and in particular the anode surface. In addition, a significant advantage of the present invention is a covering having a desirable degree of flexibility that is retained under dry room conditions. Such flexibility is important for example, in facilitating handling and pressure bonding of the film to the electrode element to provide proper conformance and adherence to the electrode surface. While this is important even in situations where the anode surfaces are flat as in FIGS. 2 and 3, flexibility becomes particularly important when the preformed film is to be applied to an electrode surface which is not flat but instead has surface formations for the purpose of increasing the available...
active material surface for operative contact with the other electrode material. This now will be described.

[0025] FIGS. 4-6 illustrate an alkali metal-halogen electrochemical cell 80 including a covered anode according to
another embodiment of the present invention. In FIGS. 4-6, components of cell 80 which are identical to components
of cell 10 in FIGS. 1-3 are identified by the same reference numeral with a prime designation. Thus, the covered anode
and other cell components are contained within a casing 12' of metal such as stainless steel including spaced apart
side walls 14',16' joined by curved end walls 18',20' and a curved bottom wall 22'.

[0026] The open top of casing 12' is closed by a lid 24'. Terminal leads 26',28' extend from lid 24', which lid is of
conductive metal and welded to casing 12'.

[0027] Electrochemical cell 80 includes an anode, generally designated 90 according to this embodiment of the
present invention and comprising an anode body 92 of alkali metal, preferably lithium. The body 92 can comprise a
pair of lithium plates 94,96 pressed together and bonded against an anode conductor 38', which is a portion of the
anode conductor means of the cell. Conductor 38' thus is sandwiched between plates 94,96 and can be of various
forms such as a length of wire, a strand or ribbon or a mesh screen and of metal such as nickel or nickel/alloy.

[0028] In the anode 90 of this embodiment of the present invention, at least one and preferably both of the oppositely
directed lithium surfaces of plates 94,96 are shaped to include formations which increase the surface area thereof.
The formations are designated 100 and each formation is elongated and has terminations at both ends thereof. The
terminations are spaced inwardly a short distance from the peripheral edge of the anode assembly thereby defining a
marginal border region between a peripheral edge and the terminations of the formations. The formations 100 are
generally mutually parallel and also are generally parallel to the longitudinal axis of leads 26',28'. The formations 100,
which are in the shape of ribs or corrugations, have generally smooth outer surfaces and preferably are generally semi-
circular in cross-section. In the anode structure shown, the ribs 100 occupy a major portion of the outer surface of each
lithium element. The remaining surface portions are generally planar and mutually generally parallel except around
conductor 38' where they are curved or outwardly bulged slightly.

[0029] The edge or periphery of each anode plate is shown in FIG. 4 and is similar to that of anode plates 34,36 in
FIGS. 2 and 3. In particular, each place, for example, place 94 shown in FIG. 4, has curved edge 102 extending along
a major portion of the periphery or border and having a curvature conforming generally to curvature of casing bottom
wall 22'. A relatively straight edge portion 104 also is provided and meets curved edge 102 through step-like portions
at each end thereof. In particular, the left-hand end of edge 104 meets a relatively short inclined edge portion 108 which,
in turn, meets another relatively short edge portion 110 leading to one end of curved edge 102. Edge 110 is
disposed generally parallel to edge 104 and is longer than edge 108. Similarly, the right-hand end of edge 104 meets
a relatively short inclined edge portion 112 which, in turn, meets another relatively short edge portion 114 leading to
the other end of curved edge 102. Edge 114 is disposed at an acute angle to edge 104 and is longer than edge 112.
Plate 96 is identical to plate 94 in size and peripheral outline, the two places being in registry or alignment when pressed
together.

[0030] A strip or band of insulating material 60' is placed on and extends along edge 104 and the edge portions 108
and 110. Insulator 60' serves to insulate anode 90 from the metal lid 24' of casing 12' in a completed or assembled
cell. An anode lead 26' extends from anode conductor 38' through an insulator and seal structure 66' and through lid
24' to serve as one terminal for providing electrical connection to the cell. Lead 28' provides the other cell terminal.

[0031] In accordance with the present invention, the surface of anode 90 in operative contact with the halogen-
containing cathode/electrolyte 68' is provided with a covering comprising a thin film of perforated substrate material
coated with organic electron donor material. In the cell of this embodiment, anode body 92 has two oppositely directed
operative surfaces which are the exposed surfaces of plates 94,96 each having the formations 100 and the surfaces
are provided with coverings 120,122, respectively, according to the present invention. Each covering, for example
covering 120, comprises a thin film of substrate material preferably in the form of perforated synthetic polymeric ma-
terial. As in the embodiment of FIGS. 1-3, substrate can be made of a thin film of polyester material, preferably a
polyethylene terephthalate material. The thin film or substrate is coated with organic electron donor material. As in the
previous embodiment, the film or substrate is drawn through a solution of the organic material and solvent for a suitable
time whereupon it is removed from the solution and dried. The organic electron donor material can be poly-2-vinylpy-
ridine (PVP) and the solvent can be dimethylformamide/ tetrahydrofuran (DMF/THF) as in the previous embodiment.
The thin film of substrate is cut out or otherwise formed to have a peripheral outline matching that of the anode plate
or element which is intended to be covered. Then the film is applied to the operative surface of the anode element by
pressing with suitable force to pressure bond the film to the anode plate. In pressing the coated film on the anode
surface, the film is conformed to the surfaces of the formations 100 as well as to the remaining surface of the anode
element. The pressing can be performed in the manner illustrated in U.S. Pat. No. 4,359,919, referenced hereinafore.
Each lithium anode element 94,96 is covered in the same way, and the resulting anode 90 with coverings 120,122
adhered to the oppositely directed surfaces including formations is shown in FIGS. 4 and 5. The electrode covering
according to this embodiment of the present invention has all the advantages provided by the covering shown and
described in connection with FIGS. 1-3.
As shown in FIG. 7, the electrode covering of the present invention can also be used in an electrochemical cell 200 having an anode body 202 of alkali metal, preferably lithium, a cathode matrix 204 and a liquid electrolyte 206. The anode 202 and cathode 204 are provided with respective current collectors 208 and 210. The electrolyte is in operative contact with the electrodes and serves as a medium for migration of ions between the anode 202 and cathode 204 during the electrochemical reactions as is well known to those of skill in the art.

In accordance with the present invention, the surface of cathode 204 in operative contact with the electrolyte 206 is provided with covering 212 comprising a thin film of inert substrate material coated with organic electron donor or other suitable organic material. The electron donor material can be any organic compound having a double bond or an amino group that functions to give the cathode 204 sufficient conductivity for proper cell operation. Thus, the organic electron donor material can be a polyvinyl pyridine polymer, and preferably poly-2-vinylpyridine (PVP) and more preferably cross-linked poly-2-vinylpyridine.

FIG. 8 illustrates diagrammatically the apparatus and method for coating the thin film of substrate material with organic electron donor material according to the present invention. The substrate material designated 150 in FIG. 8 is in tape form provided with an adequate perforation pattern to insure that the substrate material does not act as a complete barrier to ion flow therethrough. The substrate 150 is withdrawn from a supply reel and guided by rollers 154, 156 and 158 into and out of a vessel or tank 160 containing a solution of an organic electron donor material or other suitable organic coating material 162. The substrate cape 150 leaving container 160 is coated with the liquid and is drawn through a hot air dryer 164 associated with a fan 166 whereupon the tape 150 is guided by an arrangement including a single roller 168 and a pair of rollers 170,172 and wound up on a take-up reel 174. Various drying methods and apparatus can of course be employed. A motor (not shown) drivingly coupled to reel 174 controls the speed of the immersion process and subsequent drying.

A parting sheet 176 wound on a reel 178 is applied to cape 150 by rollers 170,172 for the purpose of preventing cape 150 from sticking together when wound on take-up reel 174. Parting sheet 176 can be of polypropylene material, and the use of parting sheet 175 may not be necessary in all cases depending on the nature of the substrate material and the solvent. The depth of roller 156 below the level of liquid 162 controls the exposure time of tape 150 to the solution of organic material. The thickness of the organic material which coats tape 150 is thereby controlled by roller 158 and the angle over which tape 150 is drawn on roller 158. For example, at one extreme, if tape 150 is drawn along roller 158 in a straight up or vertical direction as viewed in FIG. 8, roller 158 has no effect on the thickness of the organic material coating.

Air currents from dryer 164 are designated 180 in FIG. 8. Upon leaving dryer 164, the tape 150 must be dry enough to avoid sticking to roller 168 but not excessively dry that the tape 150 is brittle and cracks upon travelling through rollers 170,172. Operating dryer 164 at a temperature in the range of between about 50°C to 150°C, preferably about 85°C, has been found to be satisfactory. The coated substrate material 150 subsequently can be withdrawn from reel 174 and cut to desired shapes for pressing onto electrode components, such as the lithium anodes described in FIGS. 1 to 6 and the cathode described in FIG. 7. For a more detailed method and apparatus for coating the thin film of substrate material 150 with organic electron donor material according to the present invention, reference may be made to the above identified U.S. Pat. No. 4,812,376.

The following examples further illustrate the covered anode of the present invention employed in an alkali metal-oxyhalide electrochemical cell:

EXAMPLE I

Samples were cut from a 1 mil commercially available polyethylene terephthalate (PET) film material to provide circular samples having an area of 1.0 square inch. Thirty-seven samples were obtained and weighed to determine the weight distribution. The mean weight density was determined to be 12.9 mg/square inch, with a standard deviation of 0.20 mg/square inch. For comparison purposes, seventy-five similarly sized samples of Hollytex #3251 were weighed and determined to have a mean weight of 13.0 mg/square inch, with a standard deviation of 2.4 mg/square inch. PET thus has approximately the same weight as the similarly sized Hollytex with a standard deviation on the order of a magnitude less.

EXAMPLE II

One hundred feet of perforated commercially available PET tape was coated using a technique similar to that described with respect to FIG. 8 by drawing the tape through a 18.6% concentration of PVP in a DMF/THF solvent, followed by air drying. Thirty-five anode blanks were cut from the tape and determined to weigh an average of 17.3 mg/blank with a standard deviation of 0.5 mg. The range in weights was slightly less (approx. 0.2 mg/blank) than that observed for similar weight density Hollytex blanks, however, the amount of PVP coating/blank was observed to be more uniform. The range in observed weights for the blanks was believed to occur partially because of the ragged
edges obtained at the tear tab because PET film is much stronger than Hollytex fabric, and thus it is more difficult to obtain a clean tear. The weight of PVP was determined to be about 21.6 mg/ pair of blanks.

[0040] Twelve (12) alkali metal-oxyhalide, solid electrolyte test cells, indicated as cell Nos. 1865 to 1876, where fabricated with the PVP coated perforated PET substrate pressed onto the lithium anode surface. The twelve test cells then were subjected to a 35 day burn-in test. The results of the mean and standard deviations of the voltages and the impedances at 1000 Hz are indicated in Table I.

<table>
<thead>
<tr>
<th>Serial Number</th>
<th>Voltage millivolts Day 35</th>
<th>Impedance @ 1000 Hz ohms Day 35</th>
</tr>
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<tbody>
<tr>
<td>1865</td>
<td>2780</td>
<td>106</td>
</tr>
<tr>
<td>1866</td>
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<tr>
<td>1876</td>
<td>2778</td>
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</tr>
<tr>
<td>mean</td>
<td>2778.8</td>
<td>98.2</td>
</tr>
<tr>
<td>st dev.</td>
<td>0.9</td>
<td>8.4</td>
</tr>
</tbody>
</table>

[0041] Two of the cells, indicated as cell No. 1875 (highest impedance) and No. 1873 (close to average impedance) were subjected to destructive analysis. There were no observable differences between the two cells. The PET substrate remained intact and was able to be peeled away from the anode with the PVP remaining on the lithium anode. The lithium anode appeared the same under the PET substrate and in the perforated areas.

EXAMPLE III

[0042] Thin, perforated PET film was coated with a 23.0% concentration of PVP in a DMF/THF solvent solution, followed by air drying to provide a coated substrate having a PVP weight of about 46.0 mg per pair of blanks. Twelve (12) alkali metal-oxyhalide, solid electrolyte test cells, indicated as Cell Nos. 2247 to 2258, were fabricated in a manner similar to that as described in EXAMPLE II. The substrate readily pressed onto the lithium anode, the test cells were then subjected to a 35 day burn-in test. The results of this test are indicated in Table II. This table also shows a burn-in test for twelve (12) standard production alkali metal/oxyhalide, solid electrolyte test cells routinely selected for testing. The latter cells were fabricated using a PVP impregnated Hollytex fabric pressed onto the lithium anode.

<table>
<thead>
<tr>
<th>PVP Coated Perforated PET Serial Number</th>
<th>Voltage millivolts Day 35</th>
<th>Impedance @1000 Hz ohms Day 35</th>
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<tr>
<td>2247</td>
<td>2780</td>
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<td>58</td>
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<td>2249</td>
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<td>2250</td>
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<tr>
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</tbody>
</table>
Those cells having the electrode covering applied to the anode according to the present invention have standard deviations for voltages and DC resistance at 1000 Hz that are roughly half of the corresponding prior art values. In addition, the electrode covering made according to the present invention has a more uniform cross-sectional thickness than those made according to the prior art. Thus, electrochemical cells having the present electrode covering have voltages that are higher on average by 2.0 millivolts and impedances at 1000 Hz that are lower on average by more than 5 ohms than previously known anode coatings.

It is therefore apparent that the present invention accomplishes its intended objects. While embodiments of the present invention have been described in detail, that is for the purpose of illustration, not limitation.

Claims

1. An electrochemical cell comprising anode and cathode electrodes and an operatively associated electrolyte and including an electrode covering at one or more interfaces of the electrodes and the electrolyte characterised in that the covering is obtainable by perforating a film of ion impermeable, synthetic polymeric substrate material to provide for ion flow therethrough and coating the resultant perforated substrate material with an organic electron donor material.

2. An electrochemical cell as claimed in claim 1 in the form of an alkali metal-halogen electrochemical cell.

3. An alkali metal-halogen electrochemical cell as claimed in claim 2 including an alkali metal anode with a surface in contact with a solid electrolyte and a said covering on said anode surface.

4. An electrochemical cell as claimed in claim 3 further including a cathode comprising a charge transfer complex formed from iodine and poly-2-vinylpyridine.

5. An electrochemical cell as claimed in claim 1 in the form of an alkali metal-oxyhalide electrochemical cell.

6. An electrochemical cell as claimed in claim 5 including an alkali metal anode having a surface in operative contact with a liquid cathode/electrolyte and a said covering on said anode surface.

7. An electrochemical cell as claimed in any one of claims 3, 4 and 6 characterised in that the covering is pressure-bonded to the anode surface.

8. An electrochemical cell as claimed in any one of claims 3, 4, 6 and 7 characterised in that the anode surface is relatively flat and the covering is adhered to the surface.

TABLE II (continued)

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9. An electrochemical cell as claimed in any one of claims 3, 4, 6 and 7 characterised in that the anode surface is provided with formations to increase the surface area thereof and the covering is adhered to the surface.

10. An electrochemical cell as claimed in any one of claims 1 to 9 wherein said anode is a lithium anode.

11. An electrochemical cell as claimed in any one of claims 1 to 10 characterised in that the organic electron donor material comprises poly-2-vinylpyridine.

12. An electrochemical cell as claimed in any one of claims 1 to 11 characterised in that the substrate material is a flexible material.

13. An electrochemical cell as claimed in claim 12 characterised in that the substrate is a polyester material.

14. An electrochemical cell as claimed in claim 13 characterised in that the polyester material is polyethylene terephthalate.

15. An electrochemical cell as claimed in any one of claims 1 to 14 wherein the covering is in the form of a unitary body.

16. An anode for an alkali metal-halogen electrochemical cell comprising:

   a) an anode body of alkali metal having a surface for operative contact with a solid electrolyte of the cell;
   b) an electrical conductor means operatively associated with the anode body; and
   c) a covering on the anode surface wherein the covering is obtainable by perforating a film of ion impermeable, synthetic polymeric substrate material to provide for ion flow therethrough and coating the resultant perforated substrate material with an organic electron donor material.

17. An anode for an alkali metal-oxyhalide electrochemical cell comprising:

   a) an anode body of alkali metal having a surface for operative contact with a liquid electrolyte of the cell;
   b) anode electrical conductor means operatively associated with the anode body; and
   c) a covering on the anode surface wherein the covering is obtainable by perforating a film of ion impermeable, synthetic polymeric substrate material to provide for ion flow therethrough and coating the resultant perforated substrate material with an organic electron donor material.

18. An anode as claimed in claim 16 or claim 17 characterised in that the body is of lithium.

19. An anode as claimed in any one of claims 16 to 18 characterised in that the substrate material is flexible.

20. An anode as claimed in any one of claims 16 to 19 characterised in that the substrate material is a polyester material.

21. An anode as claimed in claim 20 characterised in that the polyester material is polyethylene terephthalate.

22. An anode as claimed in any one of claims 16 to 21 characterised in that the organic electron donor material comprises poly-2-vinylpyridine,

23. An anode as claimed in any one of claims 16 to 22 characterised in that the covering is pressure-bonded to the anode surface.

24. An anode as claimed in any one of claims 16 to 23 characterised in that the anode surface is relatively flat and the covering is adhered to the surface.

25. An anode as claimed in any one of claims 16 to 23 characterised in that the anode surface is provided with formations to increase the surface area thereof and the covering is adhered to the surface.

26. An anode as claimed in any one of claims 16 to 25 characterised in that the covering is in the form of a unitary body.

27. A method of forming an anode as claimed in any one of claims 16 to 26 comprising the steps of:
a) perforating a film of ion impermeable, synthetic polymeric substrate material to provide for ion flow there-
through;
b) coating the film with an organic electron donor material; and
c) applying the coated film to the anode operative surface.

28. A method as claimed in claim 27 characterized in that the step of coating the film of perforated substrate material,
comprises dipping the film into a solution of the organic material and solvent, removing the film from the solution,
and drying the film.

29. A method as claimed in claim 27 or claim 28 characterized in that
the step of applying the coated film to the
anode operative surface is done by pressing.

Patentansprüche

1. Elektrochemische Zelle, umfassend Anoden- und Kathoden-elektroden und einen arbeitend verbundenen Elek-
trolyten und einschließlich eine Elektrodenabdeckung an einer oder mehreren Grenzflächen der Elektroden mit
dem Elektrolyten, dadurch gekennzeichnet, dass die Abdeckung durch Perforieren eines Films eines ionenim-
permeablen synthetischen polymerischen Substratmaterials erhältlich ist, um einen Ionenfluss dadurch bereitzu-
stellen, und Beschichten des erhaltenen perforierten Substratmaterials mit einem organischen Elektronendonorm-
material.

2. Elektrochemische Zelle gemäß Anspruch 1, in Form einer alkalimetallhalogen-elektrochemischen Zelle.

3. Alkalimetallhalogen-elektrochemische Zelle gemäß Anspruch 2, umfassend eine Alkalimetallanode mit einer Ober-
fläche in Kontakt mit einem Festelektrolyten und der Bedeckung auf der Anodenoberfläche.

4. Elektrochemische Zelle gemäß Anspruch 3, zusätzlich umfassend eine Kathode, umfassend einen Ladungstrans-
ferkomplex, gebildet aus Jod und Poly-2-vinylpyridin.

5. Elektrochemische Zelle gemäß Anspruch 1, in Form einer alkalimetalloxyhalid-elektrochemischen Zelle.

6. Elektrochemische Zelle gemäß Anspruch 5, umfassend eine Alkalimetallanode mit einer Oberfläche in arbeiten-
dem Kontakt mit einer flüssigen Kathode/einem Elektrolyten und der Bedeckung auf der Anodenoberfläche.

7. Elektrochemische Zelle gemäß einem der Ansprüche 3, 4 und 6, dadurch gekennzeichnet, dass die Abdeckung
an die Anodenoberfläche druckgebunden ist.

8. Elektrochemische Zelle gemäß einem der Ansprüche 3, 4, 6 und 7, dadurch gekennzeichnet, dass die Anoden-
oberfläche relativ eben ist und die Abdeckung an der Oberfläche haftet.

9. Elektrochemische Zelle gemäß einem der Ansprüche 3, 4, 6 und 7, dadurch gekennzeichnet, dass die Anoden-
obrfläche mit Formationen zum Erhöhen der Oberfläche derselben versehen ist und die Abdeckung an der Ober-
fläche haftet.

10. Elektrochemische Zelle gemäß einem der Ansprüche 1 bis 9, worin die Anode eine Lithiumanode ist.

11. Elektrochemische Zelle gemäß einem der Ansprüche 1 bis 10, dadurch gekennzeichnet, dass das organische
Elektronendonormaterial Poly-2-vinylpyridin umfasst.

12. Elektrochemische Zelle gemäß einem der Ansprüche 1 bis 11, dadurch gekennzeichnet, dass das Substratma-
terial ein flexibles Material ist.

13. Elektrochemische Zelle gemäß Anspruch 12, dadurch gekennzeichnet, dass das Substrat ein Polyestermaterial
ist.

14. Elektrochemische Zelle gemäß Anspruch 13, dadurch gekennzeichnet, dass das Polyestermaterial Polyethy-
lenterephthalat ist.
15. Elektrochemische Zelle gemäß einem der Ansprüche 1 bis 14, worin die Abdeckung in Form eines einheitlichen Körpers vorliegt.

16. Anode für eine alkalimetallhalogen-elektrochemische Zelle, umfassend:
   a) einen Anodenkörper aus Alkalimetall mit einer Oberfläche für Arbeitskontakt mit einem Festelektrolyt der Zelle;
   b) eine elektrische Leitvorrichtung, arbeitend verbunden mit dem Anodenkörper; und
   c) eine Abdeckung auf der Anodenoberfläche, worin die Abdeckung erhältlich ist durch Perforieren eines Films eines ionenimpermeablen synthetischen polymerischen Substratmaterials, um einen Ionenstrom dadurch bereitzustellen, und Beschichten des erhaltenen perforierten Substratmaterials mit einem organischen Elektronendonormaterial.

17. Anode für eine alkalimetalloxyhalid-elektrochemische Zelle, umfassend:
   a) einen Anodenkörper aus Alkalimetall mit einer Oberfläche für Arbeitskontakt mit einem flüssigen Elektrolyt der Zelle;
   b) elektrische Anodenleitvorrichtung, arbeitend verbunden mit dem Anodenkörper; und
   c) eine Bedeckung auf der Anodenoberfläche, worin die Bedeckung erhältlich ist durch Perforieren eines Films aus ionenimpermeablen synthetischem polymerischen Substratmaterial, um einen Ionenstrom dadurch bereitzustellen, und Beschichten des resultierenden perforierten Substratmaterials mit einem organischen Elektronendonormaterial.

18. Anode gemäß Anspruch 16 oder Anspruch 17, **dadurch gekennzeichnet, dass** der Körper aus Lithium ist.

19. Anode gemäß einem der Ansprüche 16 bis 18, **dadurch gekennzeichnet, dass** das Substratmaterial flexibel ist.

20. Anode gemäß einem der Ansprüche 16 bis 19, **dadurch gekennzeichnet, dass** das Substratmaterial ein Polyestermaterial ist.

21. Anode gemäß Anspruch 20, **dadurch gekennzeichnet, dass** das Polyestermaterial Polyethylenterephthalat ist.

22. Anode gemäß einem der Ansprüche 16 bis 21, **dadurch gekennzeichnet, dass** das organische Elektronendonormaterial Poly-2-vinylpyridin umfasst.

23. Anode gemäß einem der Ansprüche 16 bis 22, **dadurch gekennzeichnet, dass** die Bedeckung an die Anodenoberfläche druckgebunden ist.

24. Anode gemäß einem der Ansprüche 16 bis 23, **dadurch gekennzeichnet, dass** die Anodenoberfläche relativ eben ist und die Bedeckung an der Oberfläche haftet.

25. Anode gemäß einem der Ansprüche 16 bis 23, **dadurch gekennzeichnet, dass** die Anodenoberfläche mit Formationen zum Erhöhen der Oberfläche derselben versehen ist und dass die Bedeckung an der Oberfläche haftet.

26. Anode gemäß einem der Ansprüche 16 bis 25, **dadurch gekennzeichnet, dass** die Bedeckung in Form eines einheitlichen Körpers vorliegt.

27. Verfahren zum Ausbilden einer Anode gemäß einem der Ansprüche 16 bis 26, umfassend die Schritte:
   a) Perforieren eines Films aus ionenimpermeablem synthetischem polymerischen Substratmaterial, um einen Ionenstrom dadurch bereitzustellen;
   b) Beschichten des Films mit einem organischen Elektronendonormaterial; und
   c) Aufbringen des beschichteten Films auf die Anodenarbeitsoberfläche.

29. Verfahren gemäß Anspruch 27 oder Anspruch 28, **dadurch gekennzeichnet, dass** der Schritt des Aufbringens des beschichteten Films auf die Anodenarbeitsoberfläche mittels Pressen erfolgt.

**Revendications**

1. Cellule électrochimique comprenant des électrodes anode et cathode et un électrolyte associé de façon opérante et comportant un revêtement electrode sur une ou plusieurs interfaces des électrodes et de l’électrolyte, **caractérisée en ce que** le revêtement peut être obtenu en perforant un film de matériau de substrat polymère synthétique, imperméable à l’ion pour assurer un flux ionique à travers celui-ci et en revêtant le matériau de substrat perforé résultant d’un matériau donneur d’électrons organiques.

2. Cellule électrochimique selon la revendication 1, sous forme d’une cellule électrochimique halogène - métaux alcalins.

3. Cellule électrochimique halogène - métaux alcalins selon la revendication 2, comprenant une anode de métaux alcalins avec une surface en contact avec un électrolyte solide et un dit revêtement sur ladite surface d’anode.

4. Cellule électrochimique selon la revendication 3, comprenant de plus une cathode comportant un complexe de transfert de charge formé à partir d’iode et de poly-2-vinylpyridine.

5. Cellule électrochimique selon la revendication 1 sous forme d’une cellule électrochimique oxyhalogène - métaux alcalins.

6. Cellule électrochimique selon la revendication 5 comprenant une anode des métaux alcalins ayant une surface en contact opérant avec un électrolyte/cathode liquide et un dit revêtement sur ladite surface d’anode.

7. Cellule électrochimique selon l’une quelconque des revendications 3,4 et 6, **caractérisée en ce que** le revêtement est fixé par pression sur la surface de l’anode.

8. Cellule électrochimique selon l’une quelconque des revendications 3,4,6 et 7, **caractérisée en ce que** la surface d’anode est relativement plate et en ce que le revêtement est collé sur la surface.

9. Cellule électrochimique selon l’une quelconque des revendications 3,4,6 et 7, **caractérisée en ce que** la surface anode est dotée de formations pour augmenter sa superficie et en ce que le revêtement est collé sur la surface.

10. Cellule électrochimique selon l’une quelconque des revendications 1 à 9, dans laquelle ladite anode est une anode de lithium.

11. Cellule électrochimique selon l’une quelconque des revendications 1 à 10, **caractérisée en ce que** le matériau donneur d’électrons organiques comprend une poly-2-vinylpyridine.

12. Cellule électrochimique selon l’une quelconque des revendications 1 à 11, **caractérisée en ce que** le matériau de substrat est un matériau souple.

13. Cellule électrochimique selon la revendication 12, **caractérisée en ce que** le substrat est un matériau polyester.

14. Cellule électrochimique selon la revendication 13, **caractérisée en ce que** le matériau polyester est un téréphtalate de polyéthylène.

15. Cellule électrochimique selon l’une quelconque des revendications 1 à 14, dans laquelle le revêtement se présente sous la forme d’un corps unitaire.

16. Anode pour cellule électrochimique halogène - métaux alcalins, comprenant :

   a) un corps d’anode de métaux alcalins ayant une surface pour le contact opérant avec un électrolyte solide de la cellule;
   b) des moyens conducteurs électriques associés de façon opérante avec le corps d’anode
et

c) un revêtement sur la surface anode, le revêtement pouvant être obtenu en perforant un film de matériau de substrat polymère synthétique, imperméable aux ions pour assurer un flux ionique à travers celui-ci et en revêtant le matériau de substrat perforé résultant d'un matériau donneur d'électrons organiques.

17. Anode pour une cellule électrochimique oxyhalogénure - métaux alcalins, comprenant :

a) un corps d'anode de métaux alcalins ayant une surface pour le contact opérant avec un électrolyte liquide de la cellule;

b) des moyens conducteurs électriques d'anode associés de façon opérante avec le corps d'anode; et

c) un revêtement sur la surface anode, le revêtement pouvant être obtenu en perforant un film de matériau de substrat polymère synthétique pour assurer un flux ionique à travers celui-ci et en revêtant le matériau de substrat perforé résultant avec un matériau donneur d'électrons organiques.

18. Anode selon la revendication 16 ou la revendication 17, **caractérisée en ce que** le corps est en lithium.

19. Anode selon l'une quelconque des revendications 16 à 18, **caractérisée en ce que** le matériau de substrat est souple.

20. Anode selon l'une quelconque des revendications 16 à 19, **caractérisée en ce que** le matériau de substrat est un matériau polyester.

21. Anode selon la revendication 20, **caractérisée en ce que** le matériau polyester est du téréphtalate de polyéthylène.

22. Anode selon l'une quelconque des revendications 16 à 21, **caractérisée en ce que** le donneur d'électrons organiques comprend la poly-2-vinylpyridine.

23. Anode selon l'une quelconque des revendications 16 à 22, **caractérisée en ce que** le revêtement est fixé par pression sur la surface de l'anode.

24. Anode selon l'une quelconque des revendications 16 à 23, **caractérisée en ce que** la surface d'anode est relativement plate et en ce que le revêtement est collé sur la surface.

25. Anode selon l'une quelconque des revendications 16 à 23, **caractérisée en ce que** la surface d'anode est dotée de formations pour augmenter sa superficie et en ce que le revêtement est collé sur la surface.

26. Anode selon l'une quelconque des revendications 16 à 25, **caractérisée en ce que** le revêtement se présente sous la forme d'un corps unitaire.

27. Procédé pour la formation d'une anode selon l'une quelconque des revendications 16 à 26, comprenant les étapes consistant à :

a) perforer un film de matériau de substrat polymère synthétique, imperméable aux ions pour assurer un flux ionique à travers celui-ci;

b) revêtir le film d'un matériau donneur d'électrons organiques; et

c) appliquer le film revêtu sur la surface opérante d'anode.

28. Procédé selon la revendication 27, **caractérisé en ce que** l'étape de revêtement du film de matériau de substrat, comprend l'immersion du film dans une solution du matériau organique et solvant, l'enlèvement du film de la solution, et le séchage du film.

29. Procédé selon la revendication 27 ou la revendication 28, **caractérisé en ce que** l'étape d'application du film revêtu sur la surface opérante d'anode s'effectue par pressage.