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(54) Making active electrodes

(57) A method of making an electrical device, e.g. a lithium cell wherein protective material is removed from a sensitive material (e.g. lithium strip) during, after, or immediately before, incorporating the sensitive material in the device. The protective material (preferably polymer film) may be peeled off the sensitive material or may be dissolved in liquid, preferably a liquid with which it comes in contact in the device. Articles comprising suitably protected sensitive material and apparatus for making the electrical devices automatically are also disclosed.

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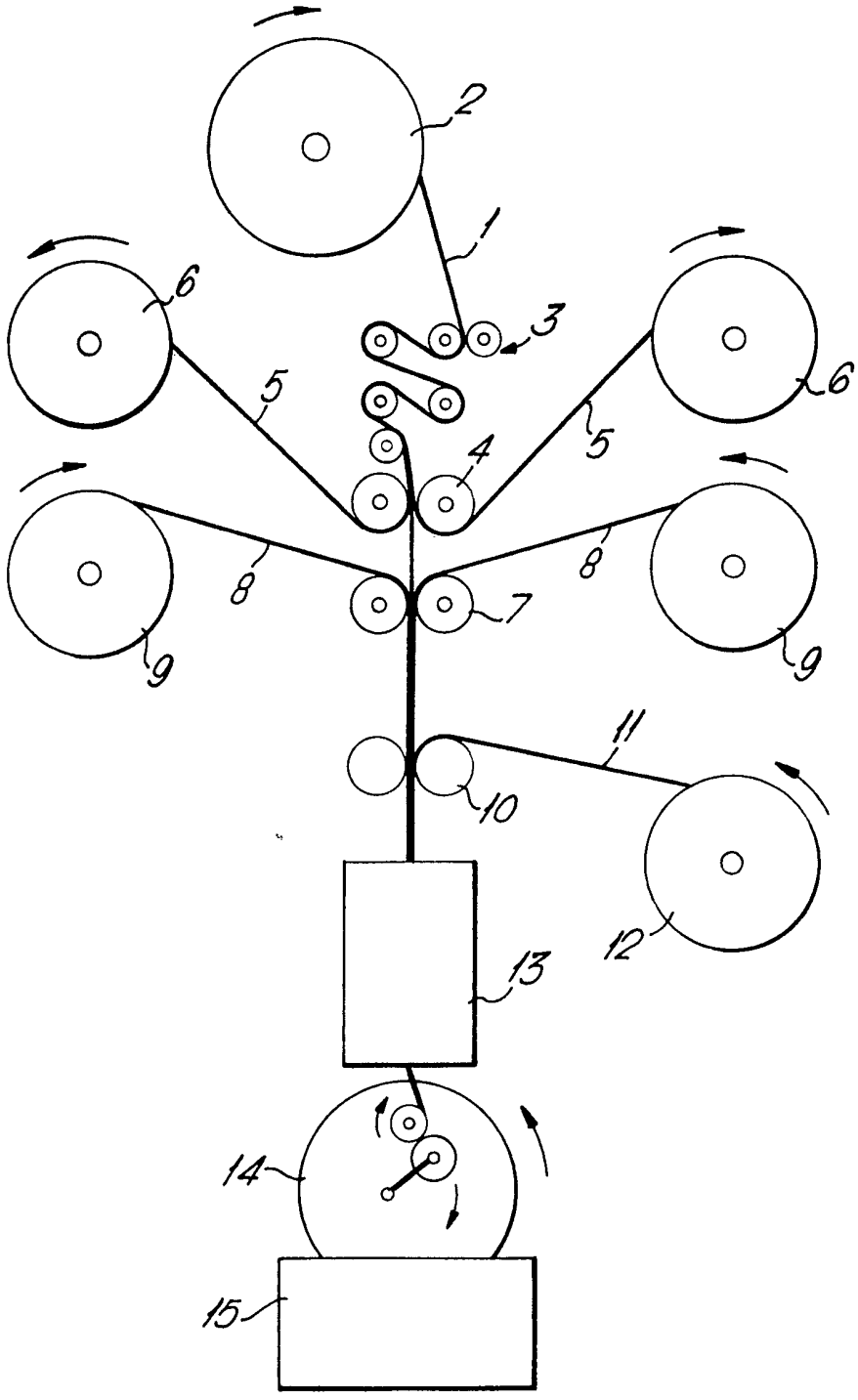
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SPECIFICATION

Method and protected material for making an electrical device

This invention relates to a method of making electrical devices incorporating sensitive materials, and articles for use in such a method.

Sensitive materials, for example some electrode materials, are sensitive insofar as they are difficult to handle during manufacture of electrical devices owing to physical weakness or high chemical reactivity, which may necessitate inconvenient handling procedures and/or special conditions such as dry room assembly. Examples of such sensitive materials include alkali metals and alkaline earth metals, notably lithium metal electrodes for lithium cells.

Lithium metal is difficult to roll into thin strips for use as an electrode, and U.S. Patent No. 3721113 describes a method of alleviating this difficulty by rolling the lithium between smooth (surface asperities less than one micron) polymeric surfaces having sufficiently low critical surface tension to prevent adhesion to the lithium. The polymer may be a coating on the surface of rolls used to roll the lithium, or may be in the form of sheeting enclosing or facing the lithium, which does not adhere to the lithium and is peeled off the lithium strip after rolling. While this method facilitates the rolling operation, which produces the thin lithium strip, it does not improve the efficiency of assembling the delicate lithium strip into electrical devices.

The present invention provides an improved method of making an electrical device, comprising the steps of (a) providing an article comprising sensitive material capable of functioning as a component of the device, the sensitive material being protected by a removable layer of protective material (b) removing the protective material during, after or immediately before incorporating the sensitive material in the device, and (c) incorporating the sensitive material in the device.

This introduction of protected sensitive material into the electrical device assembly process leads to a number of advantages, especially with regard to automation of hitherto inefficient production processes for electrical devices.

It is an advantage of the present invention that the said article may be used in a method wherein the said article is fed to apparatus which assembles portions of the sensitive material, preferably electrode material, into a plurality of the electrical devices. The protective material may be removed during the feeding of the article to the apparatus, and the apparatus receives a substantially continuous feed of the said article and automatically removes the protective material and assembles successive portions of the article into a succession of the electrical devices. The advantages of such an automated process over the piece-by-piece hand assembly methods hitherto used, especially for alkali metal or alkaline earth metal electrode materials, will be appreciated. The protective material may be non-adherent to the sensitive material, for example in the form of a tube surrounding a strip of the sensitive material. However, adherent protective material is preferred.

The method according to this invention can be used to assemble the opposing electrode materials and other components of the electrical device with fewer difficulties than are encountered in handling unprotected electrode materials, especially reactive metals such as alkali metals or alkaline earth metals. The anode or the cathode, or both, of suitable electrical devices, for example electrical cells, may be provided by way of the method according to this invention, reactive metal anodes, especially lithium anodes, for electrical cells being an important practical application of the invention. The protected articles used may include other components, for example current collector layers, or anti-passivation layers as known *per se*, adhering to part of the sensitive material, e.g. on one major surface of a flat strip electrode. Such a current collector layer, for example, may provide permanent protection to one side of the electrode, with the removable protective material giving it desired temporary protection only on the other side.

The protective material may be removed by liquid contact, for example contact with a liquid which is incorporated in the device, such as an electrolyte liquid. The protective material may be dissolved by the liquid. Alternatively, the protective material may be a coherent film which is peeled away from the sensitive material.

This invention is useful in relation to sensitive materials such as weak metals, by which is meant metal bodies having a lower tensile strangeth than an equal thickness of the protective material, especially reactive metal electrodes such as alkali metal or alkaline earth metal electrodes, especially lithium electrodes for lithium cells. Production of cells (preferably non-aqueous cells) having thin sheet electrodes of these and other materials, e.g., inherently conductive polymers, for example doped polyacetylenes or polypyrroles, or conductively filled polymers, can be facilitated by including the step of deforming the electrode material, for example by rolling, while in contact with the layer of protective material so as to decrease the thickness of the electrode material or otherwise alter its form or surface configuration. In this way, devices can be more conveniently assembled from thin sheets of lithium, for example of less than 0.25 millimetres, preferably less than 0.125 milli-

metres, especially of about 0.075 millimetres thickness, which would otherwise be difficult and expensive to make and assemble into such devices. It is preferred that the sensitive material be malleable under temperatures and pressures which do not unacceptably damage the protective layer. The protective material may also be deformed, e.g. by the rolling operation, in a manner which will assist its subsequent removal from the sensitive material.

The invention includes articles comprising the polymer-protected sensitive material in forms especially suited to the method of the invention, for example articles in elongate strip form suitable for feeding to the assembly apparatus; articles wherein cross-linked organic polymeric protective material is used; articles comprising the other components as aforementioned; articles wherein the protective material has been deformed in a manner which assists its subsequent removal; and articles wherein the sensitive material has been deformed as aforementioned. Suitable protective materials include organic materials preferably polymeric materials for example polymers of compounds with polymerizable double bonds and condensation polymers of condensable compounds.

Useful polymers of compounds with polymerizable double bonds may be selected from polymers of ethylenically unsaturated hydrocarbons having 2 to 12 carbons, such as ethylene propylene, n-hexylene, n-dodecene or 4-tert butylstyrene and of vinyl ethers such as methyl or ethyl vinyl ether. Preferred among these compounds are polyethylene and polypropylene due to their low cost.

Copolymers of the above monomeric compounds are also useful.

Useful condensation polymers may be selected from self-condensates of omega-aminofatty acids and their lactams, such as condensation polymers from caprolactam and from 11-amino-undecanoic acid.

The condensation polymers can be polyamides of diamines having 6 to 9 carbons and dicarboxylic acids having 6 to 10 carbons. Typical useful diamines include hexamethylenediamine, nonamethylenediamine and aryldiamines such a m- and p-phenylenediamine. Typical useful dicarboxylic acids include adipic acid, suberic acid, azelaic acid, terephthalic acid and isophthalic acid. The preferred polyamide is the condensate of hexamethylenediamine and adipic acid, for reasons of general availability.

The condensation polymers can also be selected from polyesters of aryldicarboxylic acids such as phthalic, terephthalic and isophthalic acids and glycols having 2 to 6 carbons, such as ethylene, butylene and hexyleneglycols.

Useful solid polymeric compositions include ethylene/chlorotrifluoroethylene copolymers, poly (2-methylpropene), polypropylene, polyethylene, poly (4-tert-butylstyrene), poly(vinyl methyl ether), poly (6-aminocaproic acid), poly(ll-aminoundecanoic acid), poly(ethyleneterephthalate), poly(decamethylene sebacamide), poly(heptamethylene pimelamide), poly(octamethylene suberamide), poly(nonamethylene azelaamide) and poly(hexamethylene adipamide).

In electrochemical cells incorporating substantially non-aqueous polar liquids, the protective material may comprise polymers which are soluble in such liquids, polyethylene oxides being preferred although other polar polymers may be chosen according to their solubility in the liquid actually used. Liquids used in such cells, for example in lithium cells, may for example include various combinations of propylene carbonate, dimethyl sulphoxide, gammabutyrolactone, dimethyl formamide, acetonitrile, tetrahydrofuran, 1,2-dimethoxyethane and dioxolane.

Polyethylene oxides and other polar polymers may also be useful in cells incorporating aqueous liquids.

The protective polymeric materials will preferably be flexible and capable of adhering temporarily to the sensitive material, which may be assisted by suitable surface roughness of the polymer, for example surface asperities greater than one micron in height.

The invention may include the steps of making the protected article by a convenient method, for example by assembling together the sensitive material and at least one layer of the protective material, either by surrounding the sensitive material with a non-adherent layer of the protective material, for example by sealing together two strips of the protective material around the sensitive material; or preferably by adhering the protective material to at least part of the surface of the sensitive material, for example by melt extrusion, pressure lamination, or solvent coating. The protective material preferably will not interact with the sensitive material, although beneficial interactions are not excluded from the invention. Cross-linked protective materials, especially polymers cross-linked by ionising radiation, may have beneficial temperature resistance and other properties, and may be easier to peel away from the electrode material than uncrosslinked material.

Examples of the preparation of electrode materials in assembly with the protective polymer layer will now be described to illustrate the invention.

EXAMPLE 1

Lithium metal (supplied by Foote Mineral Co.) 0.25 millimetres thick was encapsulated in a polymeric coating by lamination under pressure with two layers of polyethylene each approximately 0.25 millimetres thick. This laminate was then rolled to reduce the thick-

ness of the lithium to approximately 0.075 millimetres.

The polyethylene used was DYNH-3, a low density resin from Union Carbide. The coating provided protection for lithium against environmental attack until it was removed by peeling away from the underlying metal. Shiny metallic lithium suitable for the manufacture of batteries was seen on removal of the polyethylene coating immediately before incorporation as an electrode in a lithium cell.

The laminate was prepared in a dry environment and the coating removed for examination in a similar environment.

EXAMPLE 2

Lithium metal (supplied by Foote Mineral Co.) was encapsulated with polyethylene in a continuous process. Lithium tape, 0.25 millimetres thick and 37 millimetres wide was passed through a crosshead die on a single screw extruder (Baughn 32mm diam screw 25:1 L/D ratio) and a tube of polyethylene extruded around the lithium. The tube was drawn down and laminated with the lithium by passing the lithium plus polyethylene between nip rolls. The total thickness of the three layered laminate was 0.75 millimetres i.e. 0.25 millimetres polyethylene on either side of the lithium. As in example 1, the polyethylene coating provided protection for lithium against the environment during storage and during rolling to reduce the lithium thickness to 0.075 millimetres prior to use in battery manufacture. Removal of the protective polymer during assembly into a lithium cell revealed shiny unreacted lithium metal. This procedure was followed with DYNH-3, a low density polyethylene from Union Carbide and Sclair 8405 a linear medium density polyethylene from Du Pont.

The laminates were prepared in a dry environment and the cell was assembled in a similar environment.

Example 3

Automated cell assembly is demonstrated by feeding a strip of the protected lithium to apparatus illustrated schematically in the accompanying drawing.

Referring to the drawing, a strip (1) of lithium anode material protected by polymeric protective material according to the invention is fed from a supply roll (2) via feed rolls (3) to stripping rolls (4), where the protective material (5) is taken off onto collector rolls (b), and thence to lay-up rolls (7) where a strip (8) of porous electrode separator material from supply rolls 9 is aligned with each side of the lithium strip. This assembly then passes to lay-up rolls 10 where a strip of cathode material (11) from feed roll (12) is closely aligned with the lithium anode separator assembley, the separator material previously aligned with the lithium anode being between the anode and the cathode. The aligned anode/cathode assembly then proceeds to a spool threading unit (13) and thence to a spool winding unit (14) wherein the assembly is coiled or spooled to provide a coiled electrode assembly. The coiled assembly then passes to the spool casing unit (15), where the coiled assembly is sealed in a cell casing together with suitable electrolyte liquid. Suitable practical embodiments of the production equipment thus schematically described can readily be devised, and it will be understood that removal of the protective layer from only one side of the electrode strip is acceptable where the other side carries a coating such as a current collector layer which itself provides adequate protection without an overlying protective layer.

Example 4

Example 2 was repeated using polyethylene oxide (WSR N750 from Union Carbide) in place of the polyethy lene, and the encapsulating polyethylene oxide was removed from a portion of the lithium by dissolving it in a typical electrolyte solution for lithium cells, viz. 1M $LiC1O_4$ in a 50:50 mixture of 1, 2-dimethoxyethane and propylene carbonate.

Example 5

The encapsulated lithium produced in Example 4 was incorporated in a cell in a manner similar to that described in Example 3, except that the encapsulating polyethylene oxide was not removed at the stripper rolls (4) and was incorporated in the cell for subsequent removal by dissolution in the cell electrolyte liquid.

CLAIMS

1. A method of making an electrical device, comprising the steps of (a) providing an article comprising sensitive material capable of functioning as a component of the device, the sensitive material being protected by a removable layer of protective material, (b) removing the protective material during, after or immediately before incorporating the sensitive material in the device, and (c) incorporating the sensitive material in the device.

2. A method according to claim 1, wherein the sensitive material is electrode material and is incorporated as an electrode in the device.

3. A method according to claim 1 or 2, wherein the said article is fed to apparatus which assembles portions of the sensitive material into a plurality of the electrical devices.

4. A method according to claim 3, wherein the protective material is removed during the feeding of the article to the apparatus.

5. A method according to claim 4, wherein the apparatus receives a substantially continuous feed of the said article and automatically removes the protective material and assembles successive portions of the electrode material into a succession of the electrical

devices.

6. A method according to any of claims 1 to 5, wherein the protective material is removed by contact with liquid.

7. A method according to any of claims 1 to 3, wherein the protective material is removed by contact with liquid incorporated in the device.

8. A method according to claim 7, wherein the liquid is a substantially non-aqueous polar liquid and the protective material comprises polyethylene oxide.

9. A method according to any of the preceding claims, including the step of deforming the sensitive material while protected by the protective material.

10. A method according to claim 9, wherein the sensitive material is deformed so as to decrease its thickness while in contact with the protective material.

11. A method according to any of the preceding claims, wherein the said article incorporates at least one additional material in addition to the sensitive material and the removable protective material, the additional material being capable of functioning as another component of the said electrical device.

12. A method according to any of the preceding claims, wherein the sensitive material is a reactive metal, or weak metal.

13. A method according to claim 12, wherein the reactive metal is an alkali metal or an alkaline earth metal.

14. A method according to claim 13, wherein the reactive metal is lithium.

15. A method according to any of the preceding claims wherein the said electrical device is an electrochemical cell.

16. An article comprising sensitive material capable of functioning as a component of an electrical device which sensitive material is protected by a removable layer of protective material, the article being in elongate strip form suitable for feeding to apparatus capable of assembling portions of the sensitive material into a plurality of the devices.

17. An article comprising sensitive material capable of functioning as a component of an electrical device which sensitive material is protected by a removable layer of cross-linked organic polymeric material.

18. An article comprising sensitive material capable of functioning as a component of an electrical device which sensitive material is protected by a removable layer of protective material, and comprising at least one additional material capable of functioning as another component of the device.

19. An article according to claim 18, wherein the sensitive material is electrode material and the additional material is capable of functioning as a current collector or an anti-passivating layer.

20. An article according to claim 16, 17 or 18, wherein the sensitive material is electrode material.

21. An article according to any of claims 16 to 20, wherein the sensitive material has been deformed while protected by the protective material.

22. An article according to any of claims 16 to 21, wherein the protective material has been deformed in a manner which assists its subsequent removal from the sensitive material.

23. An article according to any of claims 15 to 22, wherein the sensitive material comprises a reative metal, or weak metal.

24. An article according to claim 23, wherein the metal is an alkaline earth metal.

25. An article according to claim 24, wherein the metal is lithium.

26. An article according to any of claims 16 to 25 wherein the sensitive material is in the form of a strip of less than 0.25 millimetres thickness, preferably less than 0.125 millimetres thickness.

27. An article according to any of claims 16 to 26, wherein the protective material is soluble in a liquid with which it will come into contact in the said device.

28. An article according to any of claims 13 to 24, wherein the protective material comprises polyethylene oxide.

29. A method according to claim 1 substantially as described with reference to any one of the foregoing Examples 1 to 5.

30. An article according to any one of claims 16, 17 and 18 and substantially as described with reference to any one of the foregoing Examples 1 to 5.

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