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(54) Title: ANODE FOR RECHARGEABLE LITHIUM CELL

(57) Abstract: An anode for a rechargeable lithium cell comprises carbon nanotubes that contain within them an element that can form alloys or compounds reversibly with lithium over a range of compositions. The element within the nanotubes may be aluminium or tin. These carbon nanotubes are bound together to form a coherent layer with a polymeric binder, such as a polymer of vinylidene fluoride. A cell with such an anode should have improved capacity and improved reversibility, because the nanotubes provide a stabilising framework for the alloy.

Anode for Rechargeable Lithium Cell

This invention relates to an anode for a rechargeable lithium cell, and to a cell incorporating 5 such an anode.

For many years it has been known to make cells with lithium metal anodes, and cathodes of a material into which lithium ions can be intercalated or inserted. A 10 wide variety of intercalation or insertion materials are known as cathode materials for rechargeable lithium cells, such as TiS_2 , V_6O_{13} and Li_xCoO_2 where x is less than 1; and these materials are often mixed with solid electrolyte material to form a composite cathode. To 15 avoid the problems arising from dendrite growth at lithium metal anodes during cycling, it has been proposed to use an intercalation material such as graphite as the anode material, and this also may be mixed with solid electrolyte material to form a composite anode.

20 Rechargeable cells of this type, in which both the anode and cathode contain intercalated lithium ions, are now available commercially, and may be referred to as lithium ion cells, or as swing or rocking-chair cells.

25 Another known possibility is to use, as the anode material, a metal such as aluminium that forms an alloy with lithium. However, repeated cycling of a cell with a lithium/aluminium alloy anode leads to volumetric changes and structural damage. Tin oxide has also been suggested 30 as a reversible anode material in a lithium ion cell. The lithium insertion process is believed to proceed by the initial reduction of the tin oxide, followed by reversible formation of the lithium alloy. While the

repeated insertion and removal of lithium into bulk tin metal tends to show poor reversibility due to large volumetric changes, improved stability of tin oxide anodes is observed due to the presence of an oxide 5 framework surrounding the metallic tin particles.

According to the present invention an anode for a rechargeable lithium cell comprises carbon nanotubes that 10 contain within them a metal or a metalloid that can form alloys reversibly with lithium over a range of compositions.

Preferably the metal or metalloid within the 15 nanotubes is a metallic element such as aluminium or tin, or a metallic alloy such as antimony/tin, but it may also be possible for it to be a metalloid such as silicon. The term alloy should be understood as encompassing both conventional alloys and lithium/elemental compounds of 20 the general formula MLi_x , where M represents the other element (metal or metalloid) and x may have a range of different values.

Preferably the carbon nanotubes are bound together 25 by a polymeric binder, which may for example be polyvinylidene fluoride.

The present invention also provides a rechargeable lithium cell incorporating an anode as specified above, a 30 reversible cathode, and an electrolyte. The electrolyte may be either a solid polymeric electrolyte, or a liquid electrolyte. Where the electrolyte is a liquid, an inert, liquid-permeable separator is usually provided to

separate the anode from the cathode. A variety of different intercalation materials may be used in such a cathode.

5 Such a cell can be expected to have improved capacity and improved reversibility, because the nanotubes will provide a stabilising framework for the alloy. The carbon nanotubes may also provide additional lithium intercalation capacity.

10 Carbon nanotubes are tube-like structures of diameter no more than a few nanometres, but which may be several microns in length. They can be considered as a sheet or hexagonal lattice of carbon atoms (as in a layer 15 of graphite) which has been rolled up to make a cylinder, with a hemispherical cap like half a fullerene molecule at each end. The nanotubes can be characterized by their diameter, and their helicity, which is determined by the axis about which the sheet is rolled. They have been made 20 by laser vaporisation of a carbon target in a furnace, in the presence of a cobalt/nickel catalyst; they have also been made using a carbon arc.

25 The invention will now be further and more particularly described, by way of example only. Carbon nanotubes are prepared electrolytically, by using a carbon electrode as cathode in a bath of molten salt, such as sodium chloride. It is believed that, on the application of current, sodium is forced into the 30 graphite structure and this induces the extrusion of the nanotubes. A less stable salt, such as tin chloride, is also introduced into the molten salt bath. This decomposes first, and the resulting metal (tin) is

initially deposited onto the surface of the graphite. It is found that the nanotubes resulting from this procedure contain the metal of the less stable salt inside the nanotubes. After electrolysis, the salt is dissolved in 5 water; the nanotubes remain in suspension, but will collect at the interface between the aqueous solution and an immiscible organic liquid. In this way the nanotubes can be produced with high yield.

10 The tin-filled nanotubes made as described above are thoroughly dried. The nanotubes are then used to make an anode, by mixing 90 parts by weight of the nanotubes with 10 parts of polyvinylidene fluoride homopolymer (PVdF), forming a slurry with N-methyl pyrrolidone (NMP) as 15 solvent for the PVdF, casting onto a copper foil current collector, and thoroughly drying the cast layer to remove the NMP solvent. A similar procedure is then used to make a cathode, mixing lithium cobalt oxide, carbon and PVdF with NMP as solvent to form a slurry, casting onto 20 an aluminium foil current collector, and thoroughly drying the cast layer to remove the NMP solvent. The anode and the cathode are then separated by a microporous polyethylene separator, wound up to form a coil, and inserted into a can. The can is then filled with organic 25 liquid electrolyte consisting of 1M LiPF₆ dissolved in ethylene carbonate/ethyl methyl carbonate mixture, and sealed.

It will be appreciated that an anode comprising only 30 nanotubes and a polymer binder (such as polyvinylidene fluoride) is suitable where the anode is to be used in a cell with a liquid electrolyte. An alternative anode incorporates plasticising solvent (such as ethylene

carbonate or propylene carbonate) along with the nanotubes and the polymer binder, and a lithium salt, and is suitable for use with a solid polymer electrolyte. A further alternative anode incorporates plasticising 5 solvent, nanotubes and polymer binder, but no lithium salt. Such an anode would be easier to handle, as an anode containing lithium salt must be kept in a totally dry environment.

10 To produce aluminium-filled nanotubes the electrolysis process is substantially the same as that described earlier, except that the less stable salt to be added to the molten salt bath is aluminium chloride.

15 Thus an alternative cell may be made as follows, using aluminium-filled nanotubes that have been thoroughly dried. Forty eight parts of the nanotubes are mixed with 24 parts of the volatile solvent tetrahydrofuran to produce a slurry (all parts are parts by 20 weight). This is then mixed with a polymer solution containing six parts of a PVdF copolymer, 30 parts of salt solution (1 M LiPF₆ in a mixture of three parts ethylene carbonate to two parts propylene carbonate), and 40 parts tetrahydrofuran. This mixture is then cast, 25 using a doctor blade over a roller with a blade gap 0.5 mm, onto a copper foil, and passed through a dryer at 70°C to ensure evaporation of the volatile solvent tetrahydrofuran. In this particular example the copolymer is of vinylidene fluoride with 2 percent by 30 weight of hexafluoropropylene, and has a sufficiently high molecular weight that its melt flow index (at a temperature of 230°C and a load of 21.6 kg) is only 3.1 g/10 min.

The resulting anode comprises the aluminium-filled nanotubes along with copolymer, plasticising solvents and lithium salt. It can be combined with a composite 5 cathode and a polymer electrolyte to form a reversible lithium ion cell.

Claims

1. An anode for a rechargeable lithium cell, the anode comprising carbon nanotubes, characterized in that the 5 nanotubes contain within them a metal or a metalloid that can form alloys reversibly with lithium over a range of compositions.
2. An anode as claimed in claim 1 wherein the metal or 10 metalloid is selected from: aluminium, tin, metallic alloys containing aluminium or tin, or silicon.
3. An anode as claimed in claim 1 or claim 2 wherein the carbon nanotubes are bound together by a polymeric 15 binder.
4. An anode as claimed in claim 3 comprising both a polymeric binder and a plasticising solvent.
- 20 5. A rechargeable lithium cell incorporating an anode as claimed in any one of the preceding claims, a reversible cathode, and an electrolyte.

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A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 H01M4/58 C01B31/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 7 H01M C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, INSPEC, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category [°]	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHE G ET AL: "CARBON NANOTUBULE MEMBRANES FOR ELECTROCHEMICAL ENERGY STORAGE AND PRODUCTION" NATURE, MACMILLAN JOURNALS LTD. LONDON, GB, vol. 393, no. 6683, 28 May 1998 (1998-05-28), pages 346-349, XP000960755 ISSN: 0028-0836 the whole document ---	1, 3-5
X	CHE G ET AL: "METAL-NANOCLUSTER-FILLED CARBON NANOTUBES: CATALYTIC PROPERTIES AND POSSIBLE APPLICATION IN ELECTROCHEMICAL ENERGY STORAGE AND PRODUCTION" LANGMUIR, vol. 15, no. 3, 1999, pages 750-758, XP000964916 the whole document ---	1, 3-5
		-/-

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Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 06, 30 June 1997 (1997-06-30) & JP 09 045312 A (MATSUSHITA ELECTRIC IND CO LTD), 14 February 1997 (1997-02-14) abstract ---	1, 3-5
A	FRACKOWIAK E ET AL: "ELECTROCHEMICAL STORAGE OF LITHIUM MULTIWALLED CARBON NANOTUBES" CARBON, vol. 37, no. 1, 1999, pages 61-69, XP000964865 the whole document ---	1-5
A	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 10, 31 August 1998 (1998-08-31) & JP 10 125321 A (SONY CORP), 15 May 1998 (1998-05-15) abstract ---	1-5
A	LOISEAU A ET AL: "Synthesis of long carbon nanotubes filled with Se, S, Sb and Ge by the arc method" CHEMICAL PHYSICS LETTERS, 1996, pages 246-252, XP000972665 abstract Section "1. Introduction" Section "4. Conclusion" ---	1, 2
A	GUERRET-PLECOURT C ET AL: "RELATION BETWEEN METAL ELECTRONIC STRUCTURE AND MORPHOLOGY OF METALCOMPOUNDS INSIDE CARBON NANOTUBES" NATURE, GB, MACMILLAN JOURNALS LTD. LONDON, vol. 372, no. 6508, 22 December 1994 (1994-12-22), pages 761-764, XP000569346 ISSN: 0028-0836 abstract -----	1, 2

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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