

ELECTROCHEMICAL CELL HAVING "IN SITU GENERATED" COMPONENT

BACKGROUND TO THE INVENTION

[0001] This invention relates to the enhancement of the ionic conductivity of a solid electrolyte, especially for rechargeable batteries and super capacitors, obviating the need for organic solvents which are expensive and which are also flammable, and thus constitute a safety hazard in large batteries.

[0002] Solid electrolytes, particularly those based on organic polymer compositions which contain basic sites (ether, secondary or tertiary amine, imide etc.), are now gaining favour in lithium rechargeable battery technology as a viable alternative and replacement for liquid electrolytes having a high percentage of organic solvents. The ionic conductivity of these polymer electrolytes is however inferior to that of the liquid types and is not acceptable for high rate, low temperature applications. Many so called "solid electrolyte" cells have indeed a significant amount of polar organic solvents added in order to raise the conductivity to acceptable levels. Such electrolytes with added solvents typically form a viscous gel which is sticky, and this makes control of electrode assembly into cells a difficult assembly operation. This gelled electrolyte must also be added to both the anode and cathode compositions in order to achieve acceptable ionic conductivity. The control of composition and handling of these electrodes gives rise to problems in quality assurance with a resulting cost penalty.

[0003] The use of an acid anhydride as a major electrolyte constituent in non-aqueous batteries was first demonstrated by American Cyanamid in the 1960's with a succession of patents involving the use of sulphur dioxide having a dissolved lithium salt, playing the role of both electrolyte vehicle and cathode in conjunction with lithium or other alkali metal as anode. A considerable amount of research and development work was carried out over the ensuing 25 years, mainly in the USA, towards better utilisation of this liquid electrolyte and cathode chemistry for both primary and secondary batteries. Several companies were successful in the production of lithium sulphur dioxide primary cells but their use was mainly restricted to military applications. Although a viable rechargeable battery based on the same chemistry was never realized, a sulphur dioxide based liquid electrolyte used in conjunction with a lithium cobalt oxide cathode has been demonstrated for high rate applications, the ionic conductivity of the sulphur dioxide electrolyte used being an order of magnitude greater than in existing organic solvent based electrolytes. The volatility of the sulphur dioxide electrolyte has precluded its use in most consumer applications, this accounting for the virtual cessation of further research and development work on sulphur dioxide chemistry for battery applications.

[0004] In patents from Schwartz (CA 1114894A, CA 1089929A and CA 1112719A) the use of lithium dithionite is disclosed as a charge transfer agent in an organic electrolyte system, unlike the solid electrolyte system used in the present invention.

[0005] GTE Laboratories (U.S. Pat. No. 4,403,021) claim the use of an electrolyte solute consisting of the reaction products of lithium sulphite and a Lewis acid dissolved in a liquid electrolyte/cathode material. This differs from the present invention which does not use a liquid electrolyte/cathode in the cell assembly.

[0006] Previous work by Lexel Technology Ltd (WO 95/34920A) disclosed the use of lithium sulphite and dithionite in conjunction with transition metal oxides as cathode materials to be used with liquid organic solvent based electrolytes. In the present invention, lithium dithionite plays an entirely different role by acting not as a cathode material but as an "in situ" source of sulphur dioxide in the absence of organic solvents.

[0007] One of the first successful lithium battery systems to use polymers having basic functionality due to the presence of nitrogen was patented by Schneider and Moser (U.S. Pat. No. 3,674,562). In the implementation of this patent, poly(vinyl-pyridine) was used in conjunction with iodine for the cathode, and this charge transfer complex also functioned as a solid state separator. This system inherently has a low rate capability and is non-rechargeable.

[0008] Lexel Technology Ltd has disclosed the use of thermally restructured poly(acrylonitrile), in conjunction with lithium sulphite as a rechargeable electrode (GB Patent 2335073). The electrolyte specified in the invention of GB Patent 2335073 was a liquid based on organic solvents using a micro porous polymeric separator.

DETAILED DESCRIPTION OF THE INVENTION

[0009] The present invention provides an electrochemical cell which comprises the following:—

[0010] (i) a positive electrode which, in addition to the cathodic active material, contains a compound MA_xO_y , where M is an alkali or alkaline earth metal such as lithium and A is a non-metallic element such as sulphur, nitrogen, carbon or phosphorus where $0.3 \leq x \leq 2.0$ and $1.3 \leq y \leq 4.0$, such that on charging, the acid anhydride A_xO_y is generated "in situ", and

[0011] (ii) a solid composite polymer film acting as separator whose structural units contain basic functional groups containing nitrogen atoms in 5 or 6 member heterocyclic rings or in tertiary aliphatic configuration into which is incorporated an ionisable salt LiX , having a higher decomposition voltage than MA_xO_y , where X is an acid radical which may be, but not limited to, one or more of the following:—

[0012] $AlCl_4$, BF_4 , PF_6 , ClO_4 , CF_3SO_3 , $N(CF_3SO_2)_2$.

[0013] The electrochemical cell according to this invention shows a marked increase in rate capability, particularly for rechargeable non-aqueous batteries and super capacitors and by obviating the need for organic solvents, results in lower material costs and eliminates the safety hazard associated with large capacity cells.

[0014] The present invention brings together the ease of manufacturing and leak resistance advantages of solid electrolytes with the performance enhancement due to the presence of sulphur dioxide or related acidic anhydrides in the electrolyte. Sulphur dioxide is generated at the cathode on first charging the cell and at the same time, lithium metal is electroformed at the anode. The solid electrolyte chosen for the implementation of the present invention this invention has a structure with basic functional sites which associate with sulphur dioxide and sulphur trioxide to give a non-volatile network thus facilitating lithium ion conduction.

[0015] Embodiments of the invention will now be described solely by way of example and with reference to the accompanying drawings in which: