

SPECIFICATION

A lithium primary cell containing thionyl chloride

5 The present invention relates to a primary cell whose negative active material is lithium, and which contains thionyl chloride which constitutes at least a part of the solvent of the electrolyte and/or of the positive active material.

10 The use of thionyl chloride as an electrolyte solvent and as a positive active material has already been described in French patent n° 70 04 833 published under the number 2 079 744. More recently, French patent n° 72 46 158 published under

15 the number 2 166 015 has described cells whose positive active material is, *inter alia*, thionyl chloride. In cells which are to be stored for some time before use, the use of a liquid positive active material which also acts at the same time as a solvent for the electrolyte (with or without addition of a co-solvent) is only possible provided that there is some degree of passivation of the lithium negative electrode, since the liquid necessarily comes into contact therewith. This passivation phenomenon is related to the observation that the cell potential rises slowly before reaching its operational value when this type of cell is brought into use after a period of storage.

To remedy this drawback French patent n° 76 08 397 published under the n° 2 305 863, proposes 30 covering the negative electrode with a thin layer of a vinyl polymer. However, this requires special treatment of the negative electrode and precise adjustment of the thickness of the polymer layer, since it must be thick enough to protect the lithium effectively while not being so thick that it increases the internal resistance of the cell unnecessarily.

Preferred embodiments of the invention mitigate these drawbacks and provide a cell which arrives at its normal operating potential from the beginning of 40 discharge.

The present invention provides an electrochemical primary cell whose negative active material is lithium, whose positive active material includes thionyl chloride, and whose electrolyte is composed 45 of at least one solvent and at least one solute, the solvent including at least the said thionyl chloride and the solute including a complex salt resulting from the action of at least one ionisable compound on aluminium chloride, wherein the said ionisable compound comprises lithium oxide Li_2O , calcium oxide CaO , or barium oxide BaO .

According to preferred embodiments of the invention, the molar concentration of the lithium, calcium or barium oxide in the electrolyte is 55 substantially equal to half the molar concentration of the aluminium chloride.

The invention will be better understood from the following detailed description given by way of example with reference to the accompanying 60 drawings, in which:

Figure 1 is a diagrammatic cross-section of an embodiment of a cell in accordance with the invention;

Figure 2 is a graph of the variation of the 65 conductivity of a solution of aluminium chloride in

thionyl chloride while lithium oxide is added thereto;

Figure 3 is a graph of the variation of the conductivity of a solution of the $\text{Al}_2\text{Cl}_6\text{OLi}_2$ complex salt with varying temperature;

70 *Figure 4* is the discharge curve of a prior art cell and of a cell in accordance with the invention using the $\text{Al}_2\text{Cl}_6\text{OLi}_2$ complex salt;

Figure 5 is a graph showing the first few minutes of the discharge curves of cells in accordance with the prior art and in accordance with the invention using the $\text{Al}_2\text{Cl}_6\text{OLi}_2$ complex salt, in both cases after storage at 70°C;

Figure 6 is a graph showing the first few minutes of the discharge curve, J , of a cell in accordance with the invention using the $\text{Al}_2\text{Cl}_6\text{OCa}$ complex salt; and

Figure 7 is a graph showing the discharge curve, J' , of the cell of *Figure 6* as a function of time t' in hours.

An example of a primary cell in accordance with 85 the invention and illustrated in *Figure 1* is of cylindrical shape and has the following dimensions: Height: 3.73 cm; Diameter: 1.15 cm.

A stainless steel can 1 contains a carbon cathode collector mass 2. It may be obtained by mixing 90 polytetrafluoroethylene (PTFE) with acetylene black using about 15% by weight PTFE in the dry state. This mixture is dried and sintered into the shape of a ring against the walls of the can 1 and has a porosity of about 85%. A glass fibre separator 3 is interposed 95 between the collector 2 and a negative electrode 4 of lithium. The lithium electrode 4 is composed of two half-cylinders which are separated along a plane passing through the axis of the cylindrical cell. A cylindrical metal braid 5 is placed inside the half-cylinders and is acted upon via a metal distance 100 piece 6 by a spring 7 which tends both to shorten and to widen the braid. In this manner, the half-cylinders of the negative electrode 4 constantly bear against the separator 3 as is described in our 105 published French patent application No 2 388 414. The braid 5 acts as a negative collector and the current flows through the metal distance piece 6 and the spring 7 to a cap 8 of the cell. The cap 8 is separated from the can 1 by an insulating seal 9. The base of the can is isolated in a known manner by a base disc 10 and a centering cup 11. The apparent internal surface area of the collector 2 is 8.57 cm². The cell contains about 2.5 cm³ of thionyl chloride solution in accordance with the invention, which acts 115 both as an electrolyte and as a positive active material.

Figures 2 to 5 relate to an electrolyte in accordance with the invention prepared as follows: a molar solution of aluminium chloride in thionyl chloride was taken and lithium oxide Li_2O was added thereto little by little while observing the conductivity of the solution on a measuring instrument.

Figure 2 shows the conductivity, Λ , in ohms⁻¹ cm⁻¹ $\times 10^{-3}$ on the y-axis as a function of the molar concentration, C , of lithium oxide Li_2O on the x-axis. It can be seen that the conductivity does not change once the molar concentration of Li_2O reaches about 0.5. (The operation was performed at 16°C). At this concentration the solute has a composition of one 125 molecule Li_2O for every two molecules of AlCl_3 130

which gives a formula near to $\text{Al}_2\text{Cl}_6\text{OLi}_2$ which can be called lithium oxychloroaluminate.

The variation in the conductivity of a solution having 1/2 mole of lithium oxychloroaluminate per litre is shown on the graph of figure 3 in which conductivity, Λ , in $\text{ohms}^{-1} \text{cm}^{\text{VI}} \times 10^{-3}$ is plotted along the y-axis against temperature, T, in degrees centigrade plotted along the x-axis. Although much less than the conductivity of an analogous solution of lithium thiochloroaluminate at the same temperatures, the present conductivity is nonetheless sufficient for the electrolyte of a cell. It should also be noted that the conductivity is considerably improved when the overall concentration is increased while retaining the same proportion of oxide to aluminium chloride.

Figure 4 shows the discharge curve of a cell according to the prior art where the electrolyte is a molar solution of lithium tetrachloroaluminate in thionyl chloride, and of a cell in accordance with the invention using the $\text{Al}_2\text{Cl}_6\text{OLi}_2$ complex salt. The cells were fresh cells discharged through a resistance of 75 ohms. Discharge capacity, Ca, is plotted along the x-axis in mAh and discharge potential is plotted along the y-axis in volts. The curve E is the discharge curve of the prior art cell and the curve F is the discharge curve of the cell in accordance with the invention.

Other cells were stored at 70°C for 4 days, and figure 5 shows the first few minutes of their discharge. The discharge time t in minutes is plotted along the x-axis and the potential V is plotted along the y-axis in volts. The curve G corresponded to the discharge of a cell in accordance with the invention. It can be seen that the prior art cell exhibits a slow rise in potential. It does not reach three volts until after about ten minutes, while the cell in accordance with the invention operates at 3.35 volts almost immediately.

Likewise, cells in accordance with the invention and discharged at 14°C operated from the first at 3 volts whilst prior art cells did not reach their rated discharge potential and lithium-sulphur dioxide cells of the same capacity exhibited a delay of 30 to 40 seconds before their potentials rose.

Salts other than lithium salts are capable of acting on aluminium chloride to give analogous compounds with comparable effects. Thus by making calcium oxide or barium oxide act on aluminium chloride compounds having the formula $\text{Al}_2\text{Cl}_6\text{OCa}$ or $\text{Al}_2\text{Cl}_6\text{OBa}$ are obtained. Nonetheless these compounds are more difficult to dissolve in thionyl chloride than the lithium salts and it requires a lengthy process to arrive at a concentration of 0.15M. However, using a 0.5M solution as an electrolyte (i.e. 0.3M of AlCl_3) cells have been made more identical to the preceding examples. The discharge performance of such cells is shown in figures 6 and 7. The discharge is through 75 ohms as before. The cell potential V is plotted along the y-axis in volts and time is plotted along the x-axis. (For graph J time t is in minutes while for graph J' time t' is in hours). It can be seen that there is substantially no delay before the cell potential rises. These cells were previously stored for ten days at 24°C. It can be

seen that even with a fairly dilute electrolyte which is therefore of low conductivity (about $1.5 \times 10^{-3} \text{ohm}^{-1} \text{cm}^{\text{VI}}$) and even at a fairly high rate of discharge, the discharge lasts for nearly 20 hours i.e. the capacity is greater than 800 mAh.

Naturally, the invention is not limited to the above examples. Various modifications can be made to the composition of the electrolyte/positive active material of these cells without going beyond the scope of the claims. For example, the electrolyte could include a co-solvent such as phosphoryl chloride. A portion of the lithium oxide may be replaced by lithium chloride. The concentration of the electrolyte may also be modified. And finally, a cell in accordance with the invention may have a totally different geometrical configuration from that described.

CLAIMS

1. An electrochemical primary cell whose negative active material is lithium, whose positive active material includes thionyl chloride, and whose electrolyte is composed of at least one solvent and at least one solute; the solvent including at least the said thionyl chloride and the solute including a complex salt resulting from the reaction of at least one ionisable compound with aluminium chloride, wherein the said ionisable compound comprises lithium oxide Li_2O , calcium oxide CaO , or barium oxide BaO .

2. A cell according to claim 1, including lithium oxide in its electrolyte at a molar concentration substantially equal to half the molar concentration of the aluminium chloride.

3. A cell according to claim 1, including calcium oxide or barium oxide in its electrolyte at a molar concentration substantially equal to half the molar concentration of the aluminium chloride.

4. A cell according to any preceding claim, wherein the positive electrode includes a porous carbon-based collector.

5. A cell according to claim 4, wherein said collector is constituted by a mixture of acetylene soot and polytetrafluoroethylene with about 15% by weight polytetrafluoroethylene, and having a porosity of about 82%.

6. A cell according to any preceding claim, wherein the electrolyte further includes phosphoryl chloride as a solvent.

7. A cell according to any preceding claim, wherein the ionisable compound further comprises lithium chloride.

8. An electrochemical cell including, as a solute in its electrolyte, a complex salt derived from lithium oxide Li_2O and substantially as herein described with reference to figures 2 to 5 of the accompanying drawings.

which gives a formula near to $\text{Al}_2\text{Cl}_6\text{OLi}_2$ which can be called lithium oxychloroaluminate.

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7. A cell according to any preceding claim, wherein the ionisable compound further comprises lithium chloride.

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9. An electrochemical cell including, as a solute in its electrolyte, a complex salt derived from calcium oxide CaO or barium oxide BaO and substantially as herein described with reference to figures 6 and 7 of the accompanying drawings.

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