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(54) **Safe non-venting electrolyte for non-aqueous electrochemical cells**

(57) A safe non-venting electrolyte for use in non-aqueous cells such as Li/SO_2 cells comprises LiCl in propylene carbonate.

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SPECIFICATION

Safe non-venting electrolyte for non-aqueous electrochemical cells

This invention relates to non-aqueous electrolytes and particularly to non-aqueous electrolytes used in Li/SO_2 cells.

Non-aqueous electrochemical cell such as the Li/SO_2 cells have very high energy densities and are capable of being discharged at very high rates. However, because of these very advantages, such cells, in general consumer applications, may present certain hazards when subject to abusive conditions such as short circuiting and cell reversal. In order to alleviate such hazardous conditions, particularly with respect to pressurized cell systems such as the aforementioned Li/SO_2 system, safety vents have been utilized. Such vents function by relieving the internal cell pressure, built up under the abusive condition, prior to possible violent rupture of the cell containers. While such expedient provides a measure of safety there is an additional problem with their very use i.e. that a noxious irritant such as SO_2 is released by the venting action.

It is an object of the present invention to provide an electrolyte particularly for use with the SO_2 containing cells which alleviates and substantially eliminates vent-causing conditions even under abusive conditions.

This and other objects, features and advantages of the present invention will become more evident from the following discussion.

Generally the present invention comprises an abuse resistant non-aqueous electrochemical cell containing a LiCl-propylene carbonate (PC) electrolyte particularly an SO_2 containing non-aqueous cell. In commercially available Li/SO_2 cells the electrolyte is generally comprised of the SO_2 (which functions as an electrolyte cosolvent and cathode depolarizer) and an acetonitrile (AN) cosolvent with LiBr dissolved therein as the electrolyte salt. Such cells are usually provided with pressure release vents since abuse thereof particularly short circuiting causes a heat build up therein with excessive pressurization of the contained SO_2. Such heat build up results from the high current capability of the cell which on short circuiting may result in current spikes of up to 80 amperes in a "D" size cell with cell wall temperatures approaching 90°C.

Another possible hazardous condition of the common Li/SO_2 cells is cell reversal wherein under sufficiently severe conditions dendritically plated lithium tends to react with the acetonitrile cosolvent in an untoward fashion.

The utilization of the LiCl-PC electrolyte of the present invention in an Li/SO_2 cell unexpectedly alleviates the aforementioned hazardous conditions by eliminating the venting condition of such cell even under abusive short circuiting for extended periods of time. Additionally, the LiCl-PC electrolyte of the present invention permits the elimination of or substantial elimination of acetonitrile as a cosolvent for the Li/SO_2 whereby reaction thereof under abusive cell reversal is obviated.

The LiCl-PC electrolyte of the present invention is utilized in a Li/SO_2 cell in place of the common LiBr-AN electrolyte and in generally similar amounts. In a typical Li/SO_2 cell the electrolyte is comprised of about 70% SO_2, 24% AN and 6% LiBr (0.9 *M*). Such cell when short circuited vents within 90 seconds. The amount of SO_2 in cells having the electrolyte of the present invention is between about 30—80% with a preferred amount of SO_2 being between 60 to 70% by weight of the total electrolyte. The concentration of the LiCl electrolyte salt of the present invention is between 0.1 to 2.0 *M* and preferably between about 0.5 to 1.0 *M* with the remainder of the electrolyte being substantially comprises of PC. Small amounts of solvents (up to about 10% of the PC weight) such as AN may be added to the PC for conductivity enhancement without detrimentally affecting the safety of the cell of the present invention.

The LiCl-PC electrolyte of the present invention unexpectedly reduces short circuit current spikes to about 18 amperes and sustained short circuit currents to only about 2 amperes and cell wall temperatures to only about 65°C while maintaining satisfactory discharge performances at normal consumer rate applications of up to about 0.6 amperes. It was additionally discovered that similar reduction of short circuit currents in prior art cells by reduction of the LiBr electrolyte salt concentrations did not in fact alleviate such venting conditions. The electrolyte of the present invention is accordingly unique in such safety function.

In order to further illustrate the efficacy and performance of the electrolyte of the present invention particularly as compared to the prior art the following examples are presented. It is understood that such examples are illustrative in nature and are not to be construed as limitations on the present invention. Unless otherwise indicated in the examples and elsewhere herein all parts are parts by weight.

EXAMPLE 1 (PRIOR ART)

A "D" size cell is made with 2.4 gms Li foil convolutely wound with microporous polypropylene separators and a 9 gm. carbonaceous cathode on an aluminium grid substrate. The cell is filled with grams of 70% SO_2, 24% AN and 6% LiBr (0.90 *M*). The cell is short circuited and vents within 90 seconds.

EXAMPLE 2 (MODIFIED PRIOR ART)

A cell made in accordance with example 1 but with a 0.1 *M* LiBr electrolyte is short circuited and vents within several minutes.

EXAMPLE 3 (MODIFIED PRIOR ART)

A cell made in accordance with Example 1 but with a 0.1 *M* LiBr in PC electrolyte, is short circuited and vents within several minutes.

EXAMPLE 4

A cell made in accordance with Example 1 but with an equal volume of PC replacing the AN and a 0.5 *M* LiCl electrolyte salt in place of the LiBr. The weight proportions of the materials of the electrolyte are 66% SO_2 (equal to the volume in the cell of Example 1), about 32.5% PC and 1.5% LiCl with a total weight of electrolyte being about 38 grams. The cell does not vent even under prolonged short circuit conditions.

EXAMPLE 5

A cell made in accordance with Example 4 but with 0.87 *M* LiCl does not vent on short circuiting.

EXAMPLE 6

Cells made in accordance with Examples 4 and 5 are short circuited at 45°C with thermal insulation without venting.

EXAMPLE 7

Two cells made in accordance with Example 4 are discharged at 3.39Ω (0.79A) and 5.05Ω (0.54A) and provide 5.75 and 11.4 hours respectively to a 1.8 volt cutoff.

It is evident from the examples that the cells containing the electrolyte of the present invention provide a reasonable capacity in consumer rate conditions and are substantially safer than cells of the prior art (even when modified).

The LiCl-PC electrolyte of the present invention is generally useful for providing abuse resistant non-aqueous cells having alkali or alkaline earth metal anodes such as lithium and both solid and fluid cathode depolarizers. However, it is most effectively utilized in cells wherein the problem of cell pressurization and venting might present some hazardous conditions such as in the above described pressurized SO_2 containing cells.

It is understood that the above examples were presented for illustrative purposes and that changes may be made to cell components, cell structure and the like without departing from the scope of the present invention as defined in the following claims.

CLAIMS

1. An abuse resistant non-aqueous electrochemical cell comprising an anode comprised of an alkali or alkaline earth metal, a cathode depolarizer and a non-aqueous electrolyte comprised of lithium chloride dissolved in propylene carbonate.

2. The cell of claim 1 wherein said anode comprises lithium.

3. The cell of claim 1 or 2 wherein said cathode depolarizer comprises sulfur dioxide.

4. The cell of claim 1, 2 or 3 wherein said lithium chloride is in a concentration between 0.1 to 2.0 molar in said electrolyte.

5. The cell of claim 1, 2, 3 or 4 wherein said non-aqueous electrolyte contains acetonitrile in an amount up to 10% by weight of said propylene carbonate.

6. An abuse resistant non-aqueous electrochemical cell comprising a lithium anode, a sulfur dioxide cathode depolarizer, and a non-aqueous electrolyte comprising LiCl dissolved in propylene carbonate and said sulfur dioxide.

7. The cell of claim 6 wherein the concentration of LiCl in said electrolyte is 0.5 to 1.0 molar.

8. The cell of claim 6 or 7 wherein said sulfur dioxide comprises 60—70% of said electrolyte by weight.

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