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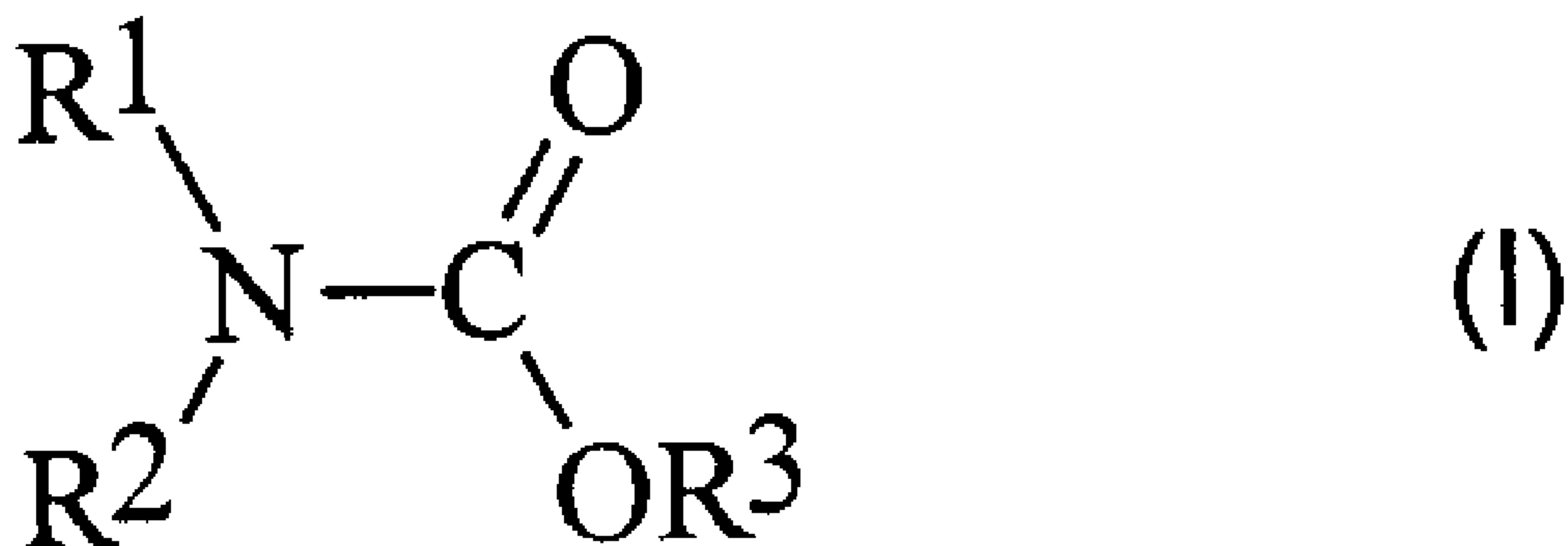
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(54) Titre : SYSTEME ELECTROLYTIQUE POUR PILES AU LITHIUM, UTILISATION DE CE SYSTEME ET METHODE  
POUR ACCROITRE LA SECURITE DES PILES AU LITHIUM

(54) Title: ELECTROLYTE SYSTEM FOR LITHIUM BATTERIES AND USE OF SAID SYSTEM, AND METHOD FOR  
INCREASING THE SAFETY OF LITHIUM BATTERIES



(57) Abrégé/Abstract:

Electrolyte systems for lithium batteries of increased safety comprise at least one lithium-containing conducting salt and at least one electrolyte fluid and, according to the invention, are defined by an effective content of at least one partially fluorinated carbamate of general formula (I) (see formula I) where R<sup>1</sup> and R<sup>2</sup> independently of one another or identical or different, linear C<sub>1</sub>-C<sub>6</sub>-alkyl, branched C<sub>3</sub>-C<sub>6</sub>-alkyl, C<sub>3</sub>-C<sub>7</sub>-cycloalkyl or R<sup>1</sup> and R<sup>2</sup> directly or via one or more additional nitrogen and/or oxygen atoms are linked to form a ring having from 3 to 7 ring members, and the additional nitrogen atoms present in the ring being saturated with C<sub>1</sub>-C<sub>3</sub>-alkyl and the ring carbon atoms possibly likewise carrying C<sub>1</sub>-C<sub>3</sub>-alkyl, with the possibility of one or more hydrogen atoms in the radicals R<sup>1</sup> and R<sup>2</sup> being replaced by fluorine atoms, R<sup>3</sup> is a partially fluorinated or perfluorinated straight-chain alkyl group having from 1 to 6 carbon atoms, is a partially fluorinated or perfluorinated branched alkyl group having from 3 to 6 carbon atoms or a partially fluorinated cycloalkyl group having from 3 to 7 carbon atoms, which may or may not be monosubstituted or polysubstituted with C<sub>1</sub>-C<sub>6</sub>-alkyl.

**Abstract**

Electrolyte systems for lithium batteries of increased safety comprise at least one lithium-containing conducting salt and at least one electrolyte fluid and, according to 5 the invention, are defined by an effective content of at least one partially fluorinated carbamate of general formula (I)



where  $\text{R}^1$  and  $\text{R}^2$  independently of one another or identical or different, linear  $\text{C}_1\text{-C}_6$ -alkyl, branched  $\text{C}_3\text{-C}_6$ -alkyl,  $\text{C}_3\text{-C}_7$ -cycloalkyl or  $\text{R}^1$  and  $\text{R}^2$  directly or via one or 10 more additional nitrogen and/or oxygen atoms are linked to form a ring having from 3 to 7 ring members, and the additional nitrogen atoms present in the ring being saturated with  $\text{C}_1\text{-C}_3$ -alkyl and the ring carbon atoms possibly likewise carrying  $\text{C}_1\text{-C}_3$ -alkyl, with the possibility of one or more hydrogen atoms in the radicals  $\text{R}^1$  and  $\text{R}^2$  being replaced by fluorine atoms,  $\text{R}^3$  is a partially fluorinated or perfluorinated 15 straight-chain alkyl group having from 1 to 6 carbon atoms, is a partially fluorinated or perfluorinated branched alkyl group having from 3 to 6 carbon atoms or a partially fluorinated cycloalkyl group having from 3 to 7 carbon atoms, which may or may not be monosubstituted or polysubstituted with  $\text{C}_1\text{-C}_6$ -alkyl.

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Dr.RB/sp

Description

5      Electrolyte system for lithium batteries and use of said system, and method for  
increasing the safety of lithium batteries

10     The invention relates to electrolyte systems for lithium batteries of increased safety,  
which comprise at least one lithium-containing conducting salt and at least one  
electrolyte fluid, to the use thereof, and to a method for enhancing the safety of  
lithium batteries.

15     Portable, sophisticated electronic equipment such as mobile phones, laptop  
computers, camcorders, etc., are enjoying a market which is growing extremely  
rapidly. An adequate electrical supply of this equipment requires low-weight, high-  
capacity and high-quality power sources. The upshot of environmental and  
economic considerations is that quite predominant use is made of secondary,  
rechargeable batteries. Essentially, three systems are competing here with one  
20    another: nickel-cadmium, nickel-metal hydride and lithium-ion batteries. Another  
interesting field for this battery system could be the use in electrically driven  
vehicles.

25     Because of its excellent performance characteristics, the lithium battery has already  
captured a large share of the market, even though, in current technology, it was  
introduced into the market as late as 1994. Despite this triumphant progress of the  
secondary lithium battery the fact should not be overlooked that in terms of safety  
aspects it does present some problems.

30     The rechargeable lithium batteries usually comprise a compound of lithium oxide  
and a metal oxide as the cathode (for example  $\text{Li}_x\text{MnO}_2$  or  $\text{Li}_x\text{CoO}_2$ ) and lithium  
metal as the anode, the lithium preferentially being used as an intercalation  
compound with graphite or with carbon fibers or graphite fibers. An overview of the

use of such batteries is given by K. Brandt (Solid state ionics 69 (1994), 173-183, Elsevier Science B.V.).

The electrolyte fluids used to achieve high conductivities in the prior art preferentially  
5 are solvent mixtures of at least two or alternatively more components. The mixture  
must comprise at least one strongly polar component which, owing to its polarity,  
has a stronger dissociative effect on salts, ethylene carbonate or propylene  
carbonate generally being employed as polar components of this type. These highly  
polar solvents are relatively viscous and usually have relatively high melting points,  
10 e.g. 35°C for ethylene carbonate. To ensure adequate conductivity even at lower  
operating temperatures, one or more low-viscosity components are generally  
additionally admixed as "thinners". Examples of typical thinners are 1,2-dimethoxy-  
ethane, dimethyl carbonate or diethyl carbonate. Usually, the thinners are admixed  
in a proportion of 40-60% of the total volume. A grave drawback of these thinner  
15 components resides in their high volatility and the low flash points: 1,2-dimethoxy-  
ethane: b.p. 85°C, flash point -6°C and explosion limit between 1.6 and 10.4 vol%;  
dimethyl carbonate: b.p. 90°C, flash point 18°C. At present, no equivalent  
substitutes exist for these "thinners"  
20 Given that the electrochemical use of electrolyte solutions always results in warming,  
and that this applies to a far greater extent in the event of faults (short-circuiting,  
overcharging, etc.), this means - particularly if the cell should burst and solvent  
should escape - the risk of ignition and corresponding serious consequences. With  
the systems currently used, this is avoided, in principle, by elaborate electronic  
25 control systems. Nevertheless, some accidents due to fires in the course of  
fabrication and use of rechargeable lithium batteries are known to have happened.  
This would constitute a far greater potential hazard in the case of electric vehicles.  
These require considerably larger quantities of electrolyte fluid per energy storage  
system, and the electronic management of numerous interconnected cells is far  
30 more difficult and involves correspondingly higher risks.

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To increase safety, cathode and anode compartments can be separated by a microporous separator membrane having the characteristic that, as a certain limit temperature is exceeded, fusion of the pores causes the current flow to be 5 interrupted. Suitable membranes of this type are found, for example, in the <sup>®</sup>Celgard line from Hoechst Celanese Corporation.

Another option to increase the safety of lithium batteries is to make use of overpressure safety devices responding to the liberation of gas in the event of 10 overcharging, and also, as already mentioned, by means of monitoring and control electronics.

Also recommended are flame-retardent phosphorous- and halogen-containing additives, although these often have an adverse effect on the performance 15 characteristics of the batteries.

All these measures, however, are unable to preclude that, in the event of malfunctions, the highly volatile and highly flammable "thinner" will ultimately still ignite, resulting, after rupture of the cell, in a fire that will be virtually uncontrollable 20 with standard extinguishing agents. Burning lithium will react very violently not only with water, but also with carbon dioxide.

Regarding the specific state of the art, reference is made to the publications  
JP-A-7-249432 = D1,  
25 EP-A-0 631339 = D2,  
EP-A-0 599534 = D3,  
EP-A-0 575191 = D4,  
US-A-5 169736 = D5,

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M. Armand, W. Gorecki and R. Andréani, Perfluorosulphonimide Salts as Solute for Polymer Electrolytes, pages 91 to 97 in B. Scrosati, Ed., 2<sup>nd</sup> International Symposium on Polymer Electrolytes, Elsevier, London and New York (1990) = D6,  
US-A-5 393621 = D7 and  
JP-A-06020719 = D8.

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D1 and D2, for example, propose highly fluorinated ethers as electrolyte solvents or as additives to other electrolytes. These are generally highly stable, both thermally and chemically, and have high flash points. However, on the one hand, they have far too low a dissolving power for the required lithium electrolyte salts to be used on 10 their own, and on the other hand are not sufficiently miscible with the customary battery solvents.

Partially fluorinated carbonates have likewise been described as electrolytes having elevated flash points (D3). The problems in this case, however, are that those 15 compounds which appear suitable owing to their low viscosity have an only moderately elevated flash point (37°C) and the electrical conductivities are distinctly below the prior art (assumption: measurements were carried out at room temperature, no temperature specified).

20 Carbamates have likewise been described as thinners for anhydrous electrolytes (D4). While their boiling points are higher than those of currently used thinners, their flash points are hardly any better.

Disclosed by D8, as electrolytes for secondary lithium batteries, are ester 25 compounds of formula  $R^1COOR^2$ , where at least one of the radicals  $R^1$  and  $R^2$  is fluorine-substituted. The preferred compound is methyl trifluoroacetate. However, this compound has a boiling point of only 43°C and a flash point of -7°C, which constitutes a high safety risk in the event of damage.

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According to the prior art, reduced flammability of the electrolyte solution is achieved, in particular, by an increase in the viscosity of the electrolyte solution by means of binders or fillers or via the use of polymer electrolytes which are virtually solid at room temperature.

5

D5, for example, describes organic or inorganic thickeners (poly(ethylene oxide),  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and others), to consolidate liquid electrolyte solutions.

10 Polymer electrolytes based on macromolecules having numerous polar groups, such as poly(ethylene oxides), as disclosed, for example, by D6, are likewise far less flammable, owing to their low volatility.

15 D7 describes polymer electrolytes whose polar macromolecules are formed by polymerization of organophosphorous compounds, which are distinguished by particularly low flammability.

20 What all these gel-like to solid electrolytes have in common is that, owing to their high viscosity, the mobility of the ions of the salts dissolved therein is far less than in liquid electrolyte solutions, so that, particularly at relatively low temperatures, the requisite conductivities are no longer achieved, at least for most technical applications. This is why, for example, alkali metal batteries comprising polymer electrolytes are continuing to fail, in spite of very intensive research spanning decades, to achieve economic significance.

25 The invention provides novel electrolyte solvents which are chemically and physically stable, are sufficiently miscible with other suitable solvents, adequately dissolve lithium conducting salts and have a distinctly higher flash point, but nevertheless exhibit viscosity and conductivity behavior that makes them suitable for practical use even at low temperatures.

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This is achieved by an electrolyte system for a lithium battery, which reduces the risk of fire, comprising at least one lithium-containing conducting salt and at least one electrolyte fluid, wherein the electrolyte fluid 5 comprises at least one partially fluorinated carbamate of the general formula (I):



wherein: R<sup>1</sup> and R<sup>2</sup> independently of one another are identical 10 or different, linear C<sub>1</sub>-C<sub>6</sub>-alkyl, branched C<sub>3</sub>-C<sub>6</sub>-alkyl or C<sub>3</sub>-C<sub>7</sub>-cycloalkyl; or R<sup>1</sup> and R<sup>2</sup> directly or via one or more additional nitrogen, oxygen or both nitrogen and oxygen atoms are linked to form a ring having from 3 to 7 ring members, wherein the additional nitrogen atom(s) present in 15 the ring are saturated with C<sub>1</sub>-C<sub>3</sub>-alkyl and optionally: (i) the ring carbon atoms are C<sub>1</sub>-C<sub>3</sub>-alkyl substituted, and (ii) one or more hydrogen atoms in the radicals R<sup>1</sup> and R<sup>2</sup> is replaced by fluorine atoms; and R<sup>3</sup> is: (i) a partially fluorinated or perfluorinated straight-chain alkyl group 20 having from 1 to 6 carbon atoms, (ii) a partially fluorinated or perfluorinated branched alkyl group having from 3 to 6 carbon atoms, or (iii) a partially fluorinated cycloalkyl group having from 3 to 7 carbon atoms, optionally monosubstituted or polysubstituted with C<sub>1</sub>-C<sub>6</sub>-alkyl.

25 As a result of the electrolyte system for lithium batteries having an effective content of at least one partially fluorinated carbamate of general formula (I)



30 where

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$R^1$  and  $R^2$  independently of one another are identical or different, linear  $C_1$ - $C_6$ -alkyl, branched  $C_3$ - $C_6$ -alkyl,  $C_3$ - $C_7$ -cycloalkyl or

$R^1$  and  $R^2$  directly or via one or more additional 5 nitrogen and/or oxygen atoms are linked to form a ring having from 3 to 7 ring members, and the additional nitrogen atoms present in the ring being saturated with  $C_1$ - $C_3$ -alkyl and the ring carbon atoms possibly likewise carrying  $C_1$ - $C_3$ -alkyl, with the possibility of one or more hydrogen 10 atoms in the radicals  $R^1$  and  $R^2$  being replaced by fluorine atoms,

$R^3$  is a partially fluorinated or perfluorinated straight-chain alkyl group having from 1 to 6 carbon atoms, is a partially fluorinated or perfluorinated branched alkyl

group having from 3 to 6 carbon atoms or a partially fluorinated cycloalkyl group having from 3 to 7 carbon atoms, which may or may not be monosubstituted or polysubstituted with C<sub>1</sub>-C<sub>6</sub>-alkyl, and

5 it becomes possible, in a particularly advantageous and not readily foreseeable manner, to provide an electrolyte which is superior or at least equivalent to the known electrolyte systems for lithium batteries with respect to the customary requirement spectrum and at the same time provides for increased safety compared with the previously known systems.

10

In particular it was found, surprisingly, that electrolyte systems for lithium batteries comprising an addition of partially fluorinated carbamate of general Formula I show very good to excellent compliance with the following requirements:

15 1. High thermal stability;

2. High flash point;

3. Low vapor pressure;

4. High boiling point;

5. Low viscosity;

20 6. Good miscibility with solvents customary in batteries, especially with ethylene carbonate, propylene carbonate or  $\alpha,\omega$  dialkyl glycol ethers;

7. Good dissolving power for lithium conducting salts, for example LiClO<sub>4</sub>;

8. Good dissolving power for fluorine-containing lithium conducting salts, for example LiPF<sub>6</sub>, LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> or LiC(SO<sub>2</sub>CF<sub>3</sub>)<sub>3</sub>;

25 9. Good electrical conductivity of their solutions of electrolyte salts over a wide temperature range;

10. High stability with respect to metallic lithium;

11. High decomposition voltage;

12. Good dissolving power for carbon dioxide: CO<sub>2</sub> accelerates the build-up of protective films on lithium and LiC<sub>n</sub> anodes;
13. Good dissolving power for SO<sub>2</sub>: this improves the conductivity over the entire temperature range and the build-up of protective films on the electrodes;
- 5 14. Unusual tolerance to initial moisture content. Thus, even with water contents of the electrolyte up to 10,000 ppm, good electrode protective films still built up, and stable electrolyte systems were obtained.

The designation "linear C<sub>1</sub>-C<sub>6</sub>-alkyl" or "straight-chain alkyl group having from 1 to 6 carbon atoms" comprises the radicals methyl, ethyl, n-propyl, n-butyl and n-hexyl;

The designation "branched C<sub>3</sub>-C<sub>6</sub>-alkyl" or "branched alkyl group having from 1 to 6 carbon atoms" comprises the radicals isopropyl, isobutyl (2-methylpropyl), sec-butyl (1-methylpropyl), t-butyl (1,1-dimethylethyl), 1-methylbutyl, 2-methylbutyl, isopentyl (3-methylbutyl), 1,2-dimethylpropyl, t-pentyl (1,1-dimethylpropyl), 2,2-dimethylpropyl, 3,3-dimethylpropyl, 1-ethylpropyl, 2-ethylpropyl, and the branched hexyls, in particular inter alia 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 1,1-dimethylbutyl, 2,2-dimethylbutyl, 3,3-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 2,3-dimethylbutyl, 1-ethylbutyl, 2-ethylbutyl, 3-ethylbutyl, 1,1,2-trimethylpropyl, 1,2,2-trimethylpropyl, 1-methyl-1-ethylpropyl, 1-ethyl-2-methylpropyl;

The designation "C<sub>3</sub>-C<sub>7</sub>-cycloalkyl" comprises cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl;

25 "C<sub>1</sub>-C<sub>6</sub>-alkyl", without the specification linear or branched, as a matter of principle comprises both linear and branched radicals, preferentially the linear radical;

"Radicals R<sup>1</sup> and R<sup>2</sup> linked directly to form a ring having from 3 to 7 ring members"

especially mean aziridinyl, azetidinyl, pyrrolidinyl, piperidinyl, azepanyl;

"Radicals R<sup>1</sup> and R<sup>2</sup> linked, via one or more additional nitrogen and/or oxygen atoms

5 to form a ring having from 3 to 7 ring members" mean, for example, oxaziridinyl, diaziridinyl, 1,3-oxazetidinyl, 1,3-diazetidinyl, oxazolidinyl, diazolidinyl, morpholinyl (tetrahydro-1,4-oxazinyl), tetrahydro-1,4-diazinyl.

Partially fluorinated compounds or radicals within the scope of the invention mean

10 compounds or radicals in which at least one, but not all, of the carbon-bound hydrogen atoms of the compound in question or the radical in question is replaced by fluorine.

Perfluorinated compounds or radicals, within the scope of the invention, are

15 compounds or radicals in which all carbon-bound hydrogen atoms of the compound or the radical have been substituted by fluorine.

The novel electrolyte systems for lithium batteries of increased safety, which comprise at least one lithium-containing conducting salt and at least one electrolyte 20 fluid, comprise "an effective content" of one or more compounds of the general Formula I. Within the scope of the invention, this is understood to be such an amount of partially fluorinated or perfluorinated carbamate of Formula I as to be sufficient to fabricate a useable and functional secondary lithium battery.

25 In principle, the invention relates to compounds which are distinguished in that a trialkylated carbamate is present, in which especially the radical located on the oxygen comprises one or more fluorine atoms.

Of particular interest among the compounds of the general Formula I are inter alia

30 those compounds in which, in Formula I, R<sup>1</sup> and R<sup>2</sup> represent linear C<sub>1</sub>-C<sub>4</sub>-alkyl,

branched C<sub>3</sub>-C<sub>4</sub>-alkyl, cyclopropyl, cyclobutyl, where one or more hydrogen atoms may be substituted by fluorine atoms.

Where the radicals R<sup>1</sup> and R<sup>2</sup> are linked together to form a ring, this ring contains at 5 least one nitrogen atom and is fully saturated, R<sup>1</sup>, R<sup>2</sup> therefore being linked via methylene groups -(CH<sub>2</sub>)<sub>n</sub>- to form a ring, n being an integer between 2 and 5. At the same time, C<sub>1</sub>-C<sub>3</sub>-alkyl substituents may be present on the ring, the ring may 10 contain oxygen or C<sub>1</sub>-C<sub>3</sub>-alkyl-substituted nitrogen atoms, as for example in - (CH<sub>2</sub>)<sub>m</sub>-O-(CH<sub>2</sub>)<sub>p</sub>- or in -(CH<sub>2</sub>)<sub>m</sub>-N(alkyl)-(CH<sub>2</sub>)<sub>p</sub>- where m,p = 1, 2 or 3. In addition, one or more hydrogen atoms may be replaced by fluorine.

Particularly expedient electrolyte systems result if the system comprises compounds of Formula I, in which the radicals R<sup>1</sup> and R<sup>2</sup> are linked directly or via an additional nitrogen or oxygen atom to form a ring having 5 or 6 ring members.

15 An electrolyte system with excellent performance characteristics also results if one or more of compounds I are present, in which R<sup>3</sup> is a partially fluorinated or perfluorinated straight-chain alkyl group having from 1 to 4 carbon atoms or a partially fluorinated or perfluorinated branched alkyl group having 3 or 4 carbon 20 atoms.

In another advantageous embodiment an electrolyte system is defined by the presence therein of compounds of Formula I, in which the radical R<sup>3</sup> has the composition C<sub>n</sub>H<sub>2n+1-m</sub>F<sub>m</sub>, where n = 1 to 6 and m = 1 to 13.

25 The inventive solution of the safety problem of secondary lithium batteries is achieved by the use of compounds of Formula I as an essential component of the

electrolyte system, one of the aspects being utilized being their comparatively favorable viscosity.

The substances of general formula I can be used as thinners for low-flammability 5 high-viscosity components, for example ethylene carbonate and propylene carbonate. Thus it is possible to prepare aprotic electrolyte systems which are virtually non-flammable.

In a particular embodiment of the invention, the content of carbamates of formula (I) 10 is from 5 to 100, preferably from 20 to 70, vol%, based on the total volume of the electrolyte system. This means that it is possible for carbamates of formula (I) to be the sole solvent and thinner of a secondary lithium battery.

The compounds according to formula I in the pure form, however, can serve not 15 only, on their own, as safety electrolyte fluids for nonaqueous battery systems, they can also be used in conjunction with known electrolyte fluids such as carbonates, esters, lactones, nitriles and the like, as electrolyte fluid systems or electrolyte fluid combinations or, for the purpose of an additional increase in the conductivity over the entire temperature range and yet a further improvement of the protective-film 20 formation at the electrodes, comprise certain additives (for example certain gases).

If the proportion of the carbamates of formula I to be used according to the invention in the electrolyte system of a secondary lithium battery is below 5 vol%, the hereinabove mentioned advantages 1 to 14 do not manifest themselves as 25 markedly. Customarily the content is from 5 to 70 vol%, preferably from 20 to 50 vol%, based on the total volume of the electrolyte system.

Given the above explanations, very expedient modifications of the electrolyte systems according to the invention also result if, in addition to the content of at least 30 one carbamate of general formula (I), an additional content of ethylene carbonate

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and/or propylene carbonate is present. In that case, preferably, no further component in addition to the conducting salt is present in the electrolyte system.

The partially fluorinated or perfluorinated carbamates according to formula I also

5 improve the dissolving power for nonpolar or low-polarity gases, in particular CO<sub>2</sub>, N<sub>2</sub>, N<sub>2</sub>O, SF<sub>6</sub>, SO<sub>2</sub>FCI or SO<sub>2</sub>F<sub>2</sub>. These gases may advantageously be used as a protective gas in lithium batteries, since they have a positive effect on the reactions proceeding at the interface electrode/electrolyte [compare J.O. Besenhard et. al., J. Power Sources, 44 (1993), 413].

10

Of particular interest are electrolyte systems according to the invention for secondary lithium batteries in which SO<sub>2</sub> or CO<sub>2</sub> are used as a protective gas, and such systems, respectively, which are saturated with SO<sub>2</sub> or CO<sub>2</sub>. This promotes a decidedly advantageous formation of protective films at the electrodes.

15

Particularly expedient systems also result if they comprise the components conducting salt, partially fluorinated or perfluorinated carbamate of general formula I, ethylene carbonate and/or propylene carbonate and SO<sub>2</sub> or CO<sub>2</sub>.

20 The electrolyte systems may have an initial water content of up to 10,000 ppm.

The compounds of formula I in some cases are commercially available, can in some instances be synthesized in accordance with methods known from the literature or sometimes also be prepared in accordance with modified methods from the literature 25 and are thus available. As part of the invention, a route to specific compounds of formula I is also specified.

Carbamates can generally be prepared in a two-stage synthesis, one way being the initial reaction of an alcohol with phosgene to give the corresponding chloroformate, which then, in a second step, reacts with a primary or secondary amine to form the carbamate (Method A).

Equally possible is the inverse procedure, in which the carbamoyl chloride is initially formed from phosgene and the amine and then, in the next stage, reacts with the alcohol to give the end product (Method B).

5 A particular variant of the preparation relates to carbamates perfluorinated in the alcohol moiety. To this end, the carbamoyl chloride synthesized in accordance with Method B is reacted, in the presence of cesium chloride, with the corresponding perfluoroalkanoyl fluoride, e.g. trifluoroacetyl fluoride, in an inert solvent.

10 Table 1 summarizes a few examples of preparation methods and physical characteristics of carbamates.

15 The invention also relates to secondary lithium batteries of increased safety, which are defined by comprising an electrolyte system according to the invention.

It is also known that reactive impurities (for example water) even in very low concentrations have drastic adverse effects on the functioning of the lithium batteries. In practice, the sum of such impurities should not exceed 50 ppm if 20 possible. A major advantage of the compounds defined by formula I is that their boiling points are usually so high that complete removal of water and other reactive impurities by distillation is readily achievable.

25 The invention also provides a method for increasing the safety of a secondary lithium battery, the method being distinguished in that the electrolyte used is an electrolyte system according to the invention.

Finally, the invention also relates to the use of compounds of general formula (I) in safety electrolyte systems for lithium batteries.

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The following examples illustrate the subject matter of the invention.

To prepare the electrolyte, the solvent components used are first prepared as follows:

- 5 Ethylene carbonate (> 99%, from Merck) is distilled in an oil pump vacuum (boiling point 85 to 95°C) and dehydrated for 3 days at 150°C on an activated molecular sieve (from Roth, pore size 4 angstrom) and stored at 60°C under a dried argon atmosphere (argon, 99.996%, from AGA, was first, to remove traces of oxygen, passed at 150°C over copper(I)oxide [from BASF] which had been reduced with
- 10 argon W5 [mixture of 95% argon and 5% hydrogen, industrial grade, from AGA] then dried over activated molecular sieve).

Propylene carbonate (purum<sup>TM</sup>, from Aldrich) is distilled in an oil pump vacuum over a 1.5 m metallized packed column (boiling point 64 to 66°C) and stored over activated

- 15 molecular sieve under a dried argon atmosphere to room temperature. After purification and drying, the residual water content of the solvents is determined according to the Karl Fischer method (for example with the automatic titration apparatus Mitsubishi CA 05). The water content should be below 10 ppm.
- 20 The fluorinated solvent component is dried for a few days over activated molecular sieve under a dried argon atmosphere at room temperature.

The preparation of the electrolyte solutions is effected via the so-called Schlenk technique in a dried argon stream, removing any moisture clinging to the glassware

- 25 employed with a protective gas connection, before it is used, in a nonluminous bunsen burner flame, repeatedly alternating between argon purging and oil pump vacuum suction.

**Example 1**

Preparation of a safety battery electrolyte based on 2,2,2-trifluoroethyl N,N-dimethylcarbamate.

28.7 g of lithium bis(trifluoromethanesulfon)imide (0.01 mol) ("imide") are introduced  
5 into 70 ml of 2,2,2-trifluoroethyl N,N-dimethylcarbamate and, after a clear solution is obtained, made up to 100 ml by addition of the same solvent. The conductivity of the electrolyte thus prepared was measured from -60 to +60°C.

For results see Table 2.

**10 Example 2**

Preparation of a safety battery electrolyte based on 2,2,2-trifluoroethyl N,N-dimethylcarbamate/propylene carbonate (1:1).

In a 1:1 (v/v) mixture of 2,2,2-trifluoroethyl N,N-dimethylcarbamate and propylene  
15 carbonate (PC), 28.7 g of imide (0.1 mol) were dissolved, the solution then being made up to 100 ml by addition of the same mixture. The conductivity of this electrolyte was measured from -60 to +60°C.

The results can be seen in Table 2.

**20 Example 3**

Preparation of a safety battery electrolyte based on 2,2,2-trifluoroethyl N,N-dimethylcarbamate with lithium hexafluorophosphate.

The preparation of the electrolyte was carried out as in Example 1, except that the  
25 electrolyte salt used was LiPF<sub>6</sub>. The conductivity of this electrolyte was determined from -60 to +60°C.

The results are shown in Table 2.

**Example 4**

Preparation of a safety battery electrolyte based on 2,2,2-trifluoroethyl N,N-dimethylcarbamate/propylene carbonate with lithium hexafluorophosphate.

5 The preparation of the electrolyte was carried out as in Example 2, except that the electrolyte salt used was 0.1 mol LiPF<sub>6</sub>. The conductivity of this electrolyte was determined from -60 to +60°C.

The results can be seen in Table 2.

10 **Example 5**

Preparation of a safety battery electrolyte based on 2,2,2-trifluoroethyl N,N-dimethylcarbamate with the addition of sulfur dioxide gas and lithium bis(trifluoromethanesulfon)imide.

15 28.7 g (0.1 mol) of the imide were dissolved in 80 ml of the carbamate saturated with SO<sub>2</sub> gas, this then being made up to 100 ml with further SO<sub>2</sub>-saturated carbamate. The conductivity of the electrolyte thus obtained was determined from -60 to +60°C.

The results can be seen in Table 2.

20 **Example 6**

Preparation of a safety battery electrolyte based on 2,2,2-trifluoroethyl N,N-dimethylcarbamate/ethylene carbonate and lithium hexafluorophosphate.

25 The preparation was carried out as in Example 4, except that ethylene carbonate was used instead of PC. The conductivity of the electrolyte mixture thus obtained was studied from -60 to +60°C.

The results can be seen in Table 2.

Table 2

Example No.	Conductivity [mS/cm]			
	-10 [°C]	0 [°C]	25 [°C]	40 [°C]
1	1.2	1.8	2.9	3.6
2	1.9	2.7	5.1	7.1
3	1.2	1.7	2.8	3.5
4	2.0	2.8	5.6	8.0
5	2.3	2.8	4.1	4.7
6	-	3.1	6.7	9.4

Further advantages and embodiments of the invention can be deduced from the  
5 following claims.

Table 1

Compound	Method	Boiling point °C	Flash point °C	Miscibility <sup>1)</sup> (1:1)		Stability with respect to lithium <sup>2)</sup>	Viscosity <sup>3)</sup> mm <sup>2</sup> /s (20°C)
				PC	EC		
2,2,2-trifluoroethyl N,N-dimethylcarbamate	B	138	85	+	+	+	1.0
2,2,2-trifluoroethyl N,N-diethylcarbamate	A, B	140	76	+	+	+	1.4
2,2,2-trifluoroethyl N-piperidinecarbamate	B	181	107	+	+	+	2.3
2,2,2-trifluoroethyl N-morpholinecarbamate	B	220	> 110	+	+	+	6.8

1) Miscibility at room temperature with propylene carbonate (PC) and ethylene carbonate (EC), respectively;  
 2) Metallic lithium remains bright, no reaction takes place;(20°C: 72h, 80°C: 8h)  
 3) Automatic capillary viscometer, AVS 310,<sup>TM</sup> from Schott Geräte.

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CLAIMS:

1. An electrolyte system for a lithium battery, which reduces the risk of fire, comprising at least one lithium-containing conducting salt and at least one electrolyte fluid, wherein the electrolyte fluid comprises at least one partially fluorinated carbamate of the general formula (I):



wherein:

10  $\text{R}^1$  and  $\text{R}^2$  independently of one another are identical or different, linear  $\text{C}_1\text{-C}_6$ -alkyl, branched  $\text{C}_3\text{-C}_6$ -alkyl or  $\text{C}_3\text{-C}_7$ -cycloalkyl; or

15  $\text{R}^1$  and  $\text{R}^2$  directly or via one or more additional nitrogen, oxygen or both nitrogen and oxygen atoms are linked to form a ring having from 3 to 7 ring members, wherein the additional nitrogen atom present in the ring is saturated with  $\text{C}_1\text{-C}_3$ -alkyl and optionally: (i) the ring carbon atoms are  $\text{C}_1\text{-C}_3$ -alkyl substituted, and (ii) one or more hydrogen atoms in the radicals  $\text{R}^1$  and  $\text{R}^2$  is replaced by 20 fluorine atoms; and

25  $\text{R}^3$  is: (i) a partially fluorinated or perfluorinated straight-chain alkyl group having from 1 to 6 carbon atoms, (ii) a partially fluorinated or perfluorinated branched alkyl group having from 3 to 6 carbon atoms, or (iii) a partially fluorinated cycloalkyl group having from 3 to 7 carbon atoms, optionally monosubstituted or polysubstituted with  $\text{C}_1\text{-C}_6$ -alkyl.

2. An electrolyte system as claimed in claim 1, wherein  $\text{R}^1$  and  $\text{R}^2$  represent linear  $\text{C}_1\text{-C}_4$ -alkyl, branched

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$C_3$ - $C_4$ -alkyl, cyclopropyl or cyclobutyl, optionally with one or more hydrogen atoms having been replaced by fluorine atoms.

3. An electrolyte system as claimed in claim 1,  
5 wherein  $R^1$  and  $R^2$  are linked, directly or via an additional nitrogen atom or oxygen atom, to form a ring having 5 or 6 ring members.

4. An electrolyte system as claimed in any one of claims 1 to 3, wherein  $R^3$  is: (i) a partially fluorinated or  
10 perfluorinated straight-chain alkyl group having from 1 to 4 carbon atoms, or (ii) a partially fluorinated or perfluorinated branched alkyl group having 3 or 4 carbon atoms.

5. An electrolyte system as claimed in any one of claims 1 to 3, wherein  $R^3$  is:  $C_nH_{2n+1-m}F_m$ , wherein  $n = 1$  to 6  
15 and  $m = 1$  to 13.

6. An electrolyte system as claimed in any one of claims 1 to 5, wherein the content of the carbamate of the general formula (I) is from 5 to 100 vol% of the total  
20 electrolyte fluid.

7. An electrolyte system as claimed in claim 6,  
wherein the content of the carbamate of the general formula (I) is from 20 to 70 vol% of the total electrolyte fluid.

8. An electrolyte system as claimed in any one of  
25 claims 1 to 7, which further comprises, in addition to the at least one carbamate of the general formula (I), a carbonate, an ester, a lactone, a nitrile or a mixture thereof.

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9. An electrolyte system as claimed in claim 8, wherein the carbonate is ethylene carbonate, propylene carbonate or a mixture thereof.

10. An electrolyte system as claimed in any one of 5 claims 1 to 9, which is saturated with SO<sub>2</sub> or CO<sub>2</sub>.

11. An electrolyte system as claimed in any one of claims 1 to 10, wherein an initial water content is up to 10,000 ppm.

12. A secondary lithium battery having reduced fire 10 risk, comprising the electrolyte system as claimed in any one of claims 1 to 10.

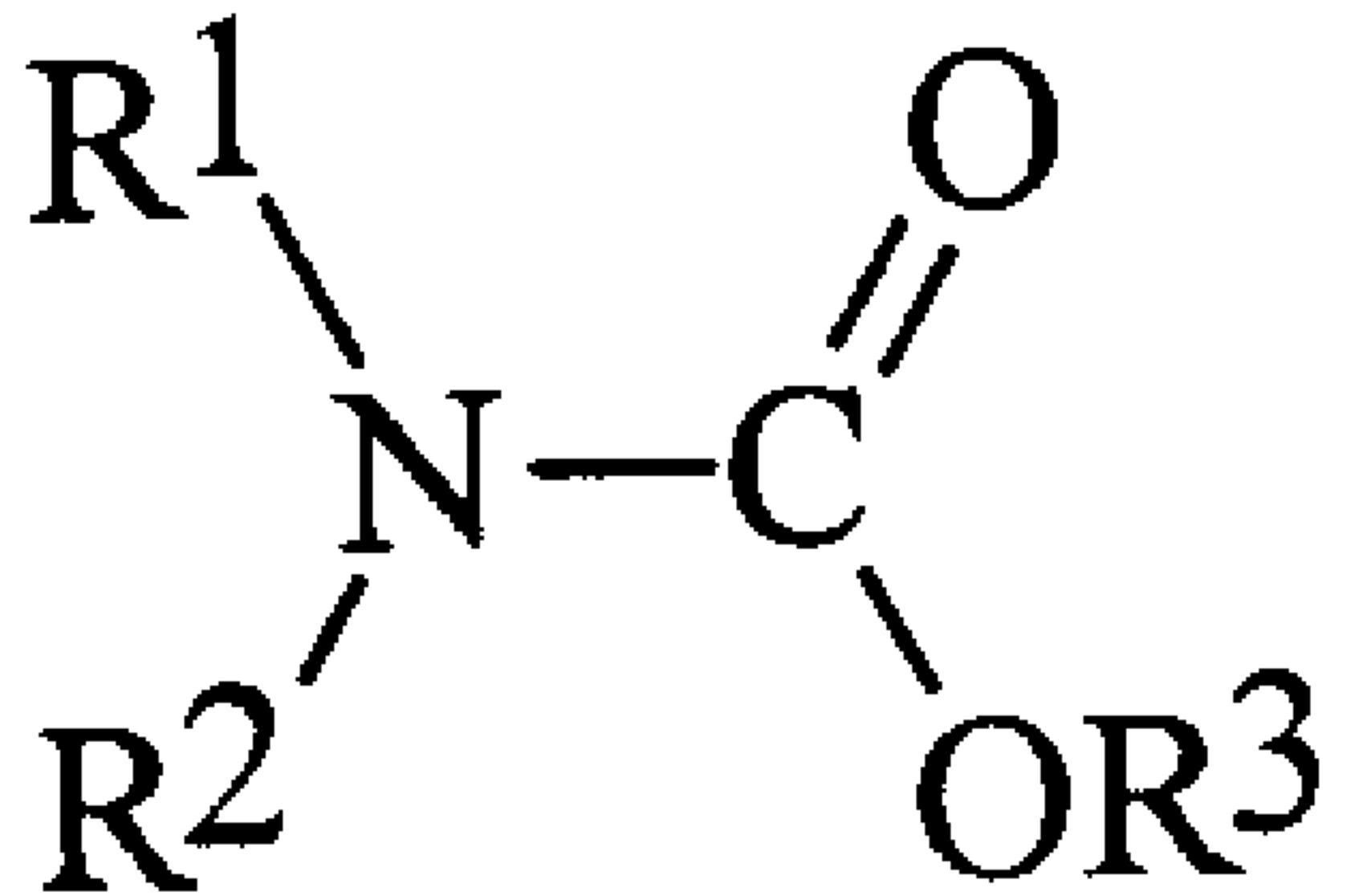
13. A method for decreasing the fire risk of a secondary lithium battery by using as an electrolyte thereof the electrolyte system as claimed in any one of claims 1 15 to 10.

14. Use of a compound of the general formula (I) as defined in any one of claims 1 to 5, in an electrolyte system for reducing the risk of fire in a lithium battery.

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PATENT AGENTS



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