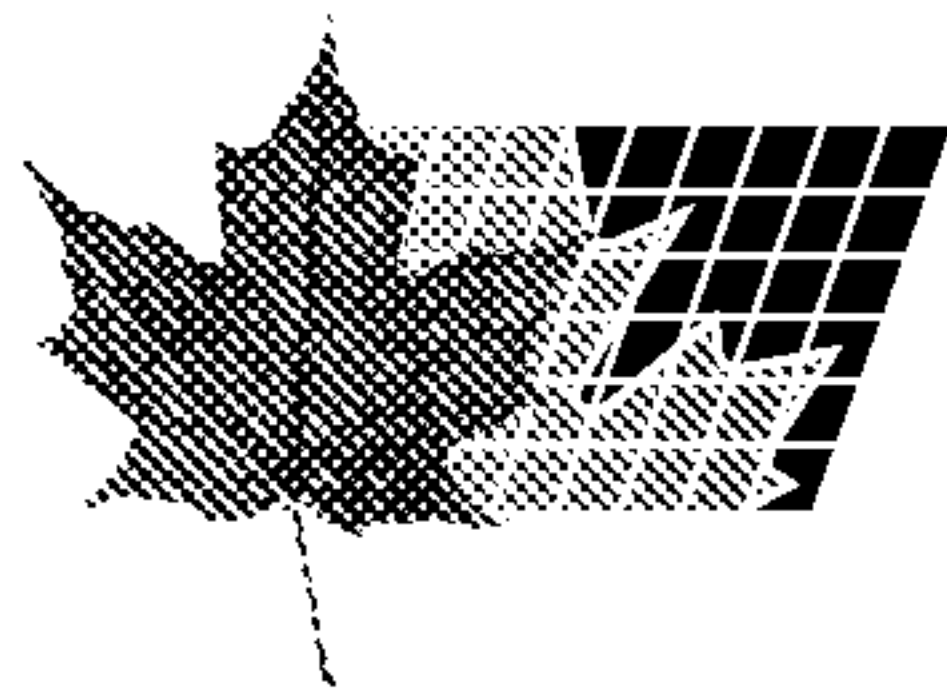




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(54) PARTICULES D'OXYDE MIXTE DE LITHIUM ENDUITES ET
LEUR UTILISATION

(54) COATED LITHIUM MIXED OXIDE PARTICLES, AND THEIR
USE II

(57) The invention relates to polymer-coated lithium mixed oxide particles for improving the properties of electrochemical cells.

Abstract

The invention relates to polymer-coated lithium mixed oxide particles for improving the properties of electrochemical cells.

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Coated lithium mixed oxide particles, and their use II

The invention relates to coated lithium mixed oxide particles for improving the properties of electro-
5 chemical cells, in particular at elevated temperatures.

The demand for rechargeable lithium batteries is high and will increase much more considerably still in the future. The reasons for this are the high energy
10 density that can be achieved and the low weight of these batteries. These batteries are used in mobile telephones, portable video cameras, laptops, etc.

As is known, the use of metallic lithium as anode
15 material results, owing to dendrite formation during dissolution and deposition of the lithium, in inadequate cycle stability of the battery and in a considerable safety risk (internal short-circuit) (J. Power Sources, 54 (1995) 151).

20 These problems have been solved by replacing the lithium-metal anode by other compounds which can reversibly intercalate lithium ions. The principle of functioning of lithium ion batteries is based on the
25 fact that both the cathode and anode materials can reversibly intercalate lithium ions, i.e. the lithium ions migrate out of the cathode during charging, diffuse through the electrolyte and are intercalated in the anode. During discharging, the same process occurs
30 in the opposite direction. Owing to this mechanism of functioning, these batteries are also referred to as "rocking-chair" or lithium ion batteries.

The resultant voltage of a cell of this type is
35 determined by the lithium intercalation potentials of the electrodes. In order to achieve the highest possible voltage, cathode materials which intercalate lithium ions at very high potentials and anode materials which intercalate lithium ions at very low

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potentials (vs. Li/Li^+) must be used. Cathode materials which satisfy these requirements are LiCoO_2 and LiNiO_2 , which have a layered structure, and LiMn_2O_4 , which has a cubic three-dimensional network structure. These compounds deintercalate lithium ions at potentials of around 4 V (vs. Li/Li^+). In the case of the anode compounds, certain carbon compounds, such as, for example, graphite, meet the requirement of low potential and high capacity.

10

At the beginning of the 1990s, Sony brought a lithium ion battery onto the market which consists of a lithium cobalt oxide cathode, a non-aqueous liquid electrolyte and a carbon anode (Progr. Batteries Solar Cells, 9 (1990) 20).

15

For 4 V cathodes, LiCoO_2 , LiNiO_2 and LiMn_2O_4 have been discussed and employed. The electrolytes used are mixtures which contain aprotic solvents in addition to a conductive salt. The most frequently used solvents are ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC) and ethyl methyl carbonate (EMC). Although a whole series of conductive salts is being discussed, LiPF_6 is used virtually without exception. The anode used is generally graphite.

20

25

A disadvantage of the state-of-the-art batteries is that the high-temperature shelf life and cycle stability are poor. The reasons for this, besides the electrolyte, are the cathode materials used, in particular lithium manganese spinel LiMn_2O_4 .

30

However, lithium manganese spinel is a very promising material as cathode for batteries in electrical equipment. The advantage over LiNiO_2 - and LiCoO_2 -based cathodes is improved safety in the charged state, the low toxicity and the lower costs of the raw materials.

35

- 3 -

The disadvantages of the spinel are its low capacity and its inadequate high-temperature shelf life and consequently poor cycle stability at high temperatures. The reason for this is thought to be the solubility of divalent manganese in the electrolyte (Solid State Ionics 69 (1994) 59; J. Power Sources 66 (1997) 129; J. Electrochem. Soc. 144 (1997) 2178). The manganese in the spinel LiMn_2O_4 exists in two oxidation states, namely trivalent and tetravalent. The LiPF_6 -containing electrolyte always also contains water impurities. This water reacts with the LiPF_6 conductive salt to form LiF and acidic components, for example HF . These acidic components react with the trivalent manganese in the spinel to form Mn^{2+} and Mn^{4+} (disproportionation: $2\text{Mn}^{3+} \rightarrow \text{Mn}^{2+} + \text{Mn}^{4+}$). This degradation does take place even at room temperature, but accelerates with increasing temperature.

One way of increasing the stability of the spinel at high temperatures is to dope it. For example, some of the manganese ions can be replaced by other, for example trivalent, metal cations. Antonini et al. report that spinels which have been doped with gallium and chromium (for example $\text{Li}_{1.02}\text{Ga}_{0.025}\text{Cr}_{0.025}\text{Mn}_{1.95}\text{O}_4$) exhibit a satisfactory shelf life and cycle stability at 55°C (J. Electrochem. Soc., 145 (1998) 2726).

A similar path is being trodden by the researchers at Bellcore Inc. They are replacing some of the manganese by aluminium and in addition some of the oxygen ions by fluoride ions ($(\text{Li}_{1+x}\text{Al}_y\text{Mn}_{2-x-y})\text{O}_{4-z}\text{F}_z$). This doping likewise results in an improvement in the cycle stability at 55°C (WO 9856057).

A further topic of discussion is the use of appropriate binder materials. US 5468571 proposes a polyimide as binder, US 5888672 a battery comprising amorphous thermoplastic polyimides.

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Another approach is to modify, i.e. coat, the surface of the cathode material. Coating may be carried out both with organic and with inorganic materials. This coating of the electrodes results in the improvement of various properties of lithium ion batteries.

It is possible to cover the cathode particles for example with a lithium borate glass coating (Solid State Ionics 104 (1997) 13). For this purpose, a spinel is introduced into a methanolic solution of H_3BO_3 , $LiBO_2 \cdot 8H_2O$ and $LiOH \cdot H_2O$ and the mixture is stirred at 50-80°C until the solvent has completely evaporated. The powder is subsequently heated to 600-800°C in order to ensure conversion into the borate. The shelf life at high temperatures is thereby improved. However, an improved cycle stability has not been found.

It is also possible to coat the cathode and/or anode by pasting the active material together with binder and a conductive material onto the collector. A paste consisting of the coating material, binder and/or solvent is subsequently applied to the electrode. The coating materials mentioned are inorganic and/or organic materials, which may be conductive, for example Al_2O_3 , nickel, graphite, LiF, PVDF, etc. Lithium ion batteries which contain electrodes coated in this way exhibit high voltages and capacities and improved safety characteristics (EP 836238).

In the case of coating with organic materials, polymers are frequently used.

For example, JP 07296847 coats the cathode and/or anode with fluoropolymers. Coating takes place by immersing the finished electrodes in a 1% fluoropolymer solution. The electrodes coated in this way prevent short circuits in the battery and therefore improve safety.

- 5 -

In JP 08138649, the cathodes are partly coated with an electrolytically oxidized film. The film comprises a polymer, examples being polyaniline, polypyrrole, polythiophene and derived compounds.

5

In JP 08064203, the electrodes are coated with a conductive polymer, for example polyaniline. In JP 08148183, the electrode strips are likewise coated with a conductive polymer.

10

In EP 517070, the cathodes are coated with a conductive polymer, for example polyacetylene, polyaniline or polypyrrole doped with X anions.

15 However, coatings are not only produced using polymers. For example, in US 5869208 an electrode paste (cathode material: lithium manganese spinel) is prepared and applied to the collector. The protective coating, consisting of a metal oxide and binder, is then pasted
20 onto the electrode. Examples of metal oxides used are aluminium oxide, titanium oxide and zirconium oxide.

In JP 08250120, the coating is carried out with sulfides, selenides and tellurides for improving the
25 cycle performance, and in JP 08264183 with fluorides for improving the cycle life.

The object of the present invention is to provide electrode materials which do not have the disadvantages
30 of the prior art and have an improved shelf life and cycle stability at high temperatures, in particular at temperatures above room temperature.

The object according to the invention is achieved by
35 lithium mixed oxide particles which have been coated with a polymer.

The invention also relates to a process for coating the lithium mixed oxide particles and to their use in

- 6 -

electrochemical cells, batteries, secondary lithium batteries and supercapacitors.

The present invention relates to undoped and doped mixed oxides as cathode materials, selected from the group consisting of $\text{Li}(\text{MnMe}_z)_2\text{O}_4$, $\text{Li}(\text{CoMe}_z)\text{O}_2$ and $\text{Li}(\text{Ni}_{1-x-y}\text{Co}_x\text{Me}_y)\text{O}_2$, where Me is at least one metal cation from Groups IIa, IIIa, IVa, IIb, IIIb, IVb, VIb, VIIb and VIII of the Periodic Table of the Elements. Particularly suitable metal cations are copper, silver, nickel, magnesium, zinc, aluminium, iron, cobalt, chromium, titanium and zirconium, and also lithium for the spinel compounds. The present invention likewise relates to other lithium intercalation and insertion compounds which are suitable for 4 V cathodes, having improved high-temperature properties, in particular at temperatures above room temperature, and to their production and use, in particular as cathode material in electrochemical cells.

In the present invention, the lithium mixed oxide particles are coated with polymers in order to achieve an improved shelf life and cycle stability, in particular at high temperatures (above room temperature).

Suitable polymers for the coating are compounds which meet at least one of the following criteria:

- acid stable
- electrochemically stable
- polar
- ideally basic, at least neutral
- aprotic

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Consequently, examples of suitable polymers are polyimide, polyaniline, polypyrrole, polythiophene, polyacetylene, polyacrylonitrile, carbonized polyacrylonitrile, poly-p-phenylene, polyphenylenevinylene, polyquinoline, polyquinoxalines, polyphthalocyanine-siloxane, polyvinylidene fluoride, polytetrafluoroethylene, polyethyl methacrylate, polymethyl methacrylate, polyamides, vinyl ether copolymers, cellulose, polyfluoroethylene, polyvinyl alcohol and polyvinylpyridine, and derivatives thereof.

It has been found that the coating of the lithium mixed oxide particles results in a significant improvement in the high-temperature cycle stability of the cathodes produced therefrom. This results in a reduction of the capacity loss per cycle of the coated cathode material compared with uncoated cathode materials.

It has furthermore been found that the coating of the individual particles has some advantages over coating of the electrode bands. In the case of damage to the electrode material, the electrolyte can attack the majority of the active material in the case of coated bands, whereas these undesired reactions remain highly localized in the case of coating of the individual particles.

The coating process allows layer thicknesses of from 0.01 μm to 50 μm to be achieved. Preferred layer thicknesses are from 0.05 μm to 3 μm . The lithium mixed oxide particles can have one or more coatings.

The coated lithium mixed oxide particles can be converted into 3 V and 4 V cathodes for electrochemical cells, such as lithium ion batteries, and supercapacitors using the usual support materials and auxiliaries.

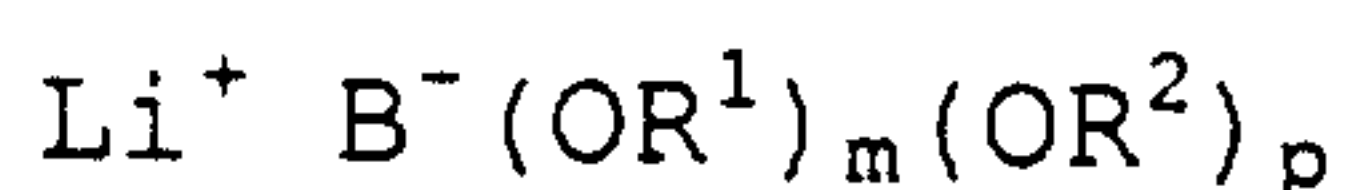
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Owing to the coating of the materials, an improvement in the safety aspects can also be expected.

5 The coating of the cathode material with organic materials (polymers) greatly inhibits the undesired reactions of the electrode material with the electrolyte and thus enables an improvement in the shelf life and cycle stability at elevated temperatures.

10

The compounds according to the invention can be used in electrolytes with conventional conductive salts. Examples of suitable electrolytes are those with conductive salts selected from the group consisting of
 15 LiPF_6 , LiBF_4 , LiClO_4 , LiAsF_6 , LiCF_3SO_3 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ and $\text{LiC}(\text{CF}_3\text{SO}_2)_3$, and mixtures thereof. The electrolytes can also contain organic isocyanates (DE 199 44 603) for reducing the water content. The electrolytes may also contain organic alkali metal salts (DE 199 10 968) as
 20 additive. Suitable alkali metal salts are alkali metal borates of the general formula



in which

25 m and p are 0, 1, 2, 3 or 4, where $m + p = 4$, and R^1 and R^2 are identical or different,

are optionally bonded directly to one another via a single or double bond,

30

are each, individually or together, an aromatic or aliphatic carboxylic, dicarboxylic or sulfonic acid radical, or

35 are each, individually or together, an aromatic ring from the group consisting of phenyl, naphthyl, anthracenyl and phenanthrenyl, which may be unsubstituted or mono- to tetrasubstituted by A or Hal, or

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are each, individually or together, a heterocyclic aromatic ring from the group consisting of pyridyl, pyrazyl and bipyridyl, which may be unsubstituted or mono- to trisubstituted by A or Hal, or

5

are each, individually or together, an aromatic hydroxy acid from the group consisting of aromatic hydroxycarboxylic acids and aromatic hydroxysulfonic acids, which may be unsubstituted or mono- to tetrasubstituted by A or Hal,

10

and

Hal is F, Cl or Br

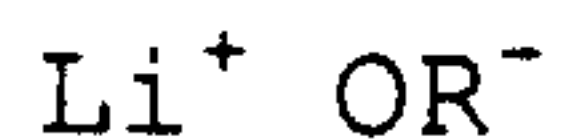
15

and

A is alkyl having 1 to 6 carbon atoms, which may be mono- to trihalogenated.

20

Likewise suitable are alkali metal alkoxides (DE 9910968) of the general formula



25

in which R

is an aromatic or aliphatic carboxylic, dicarboxylic or sulfonic acid radical, or

30

is an aromatic ring from the group consisting of phenyl, naphthyl, anthracenyl and phenanthrenyl, which may be unsubstituted or mono- to tetrasubstituted by A or Hal, or

35

is a heterocyclic aromatic ring from the group consisting of pyridyl, pyrazyl and bipyridyl, which may be unsubstituted or mono- to trisubstituted by A or Hal, or

- 10 -

is an aromatic hydroxy acid from the group consisting of aromatic hydroxycarboxylic acids and aromatic hydroxysulfonic acids, which may be unsubstituted or mono- to tetrasubstituted by A or Hal,

5

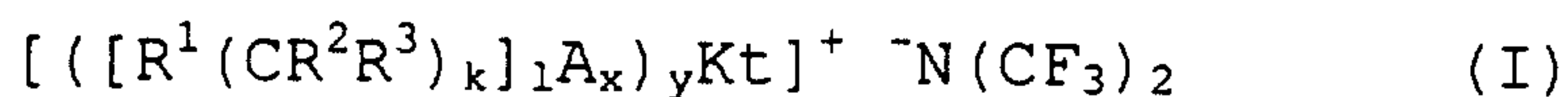
and

Hal is F, Cl or Br

10 and

A is alkyl having 1 to 6 carbon atoms, which may be mono- to trihalogenated.

15 Compounds of the general formula



where

20 Kt is N, P, As, Sb, S or Se,

A is N, P, P(O), O, S, S(O), SO₂, As, As(O), Sb or Sb(O),

25 R¹, R² and R³

are identical or different

and are H, halogen, substituted and/or unsubstituted alkyl C_nH_{2n+1}, substituted and/or unsubstituted alkenyl having 1-18 carbon atoms and one or more double bonds, substituted and/or unsubstituted alkynyl having 1-18 carbon atoms and one or more triple bonds, substituted and/or unsubstituted cycloalkyl C_mH_{2m-1}, mono- or polysubstituted and/or unsubstituted phenyl, substituted and/or unsubstituted heteroaryl,

35

- 11 -

A can be included in R^1 , R^2 and/or R^3 in various positions,

5 Kt can be included in a cyclic or heterocyclic ring,

the groups bonded to Kt may be identical or different,

10 where

n is 1-18

m is 3-7

15

k is 0 or 1-6

l is 1 or 2 in the case where $x = 1$ and 1 in the case where $x = 0$

20

x is 0 or 1

y is 1-4.

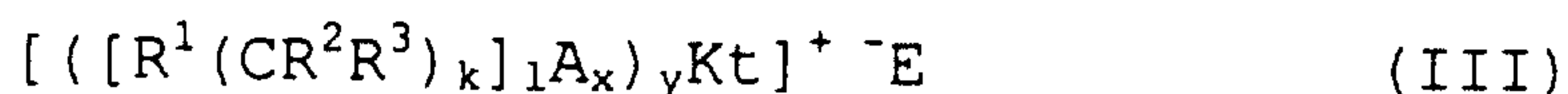
25 may also be present (DE 9941566). The process for the preparation of the compounds is characterized in that an alkali metal salt of the general formula

30



where D^+ is selected from the group consisting of alkali metals, is reacted, in a polar organic solvent, with a salt of the general formula

35



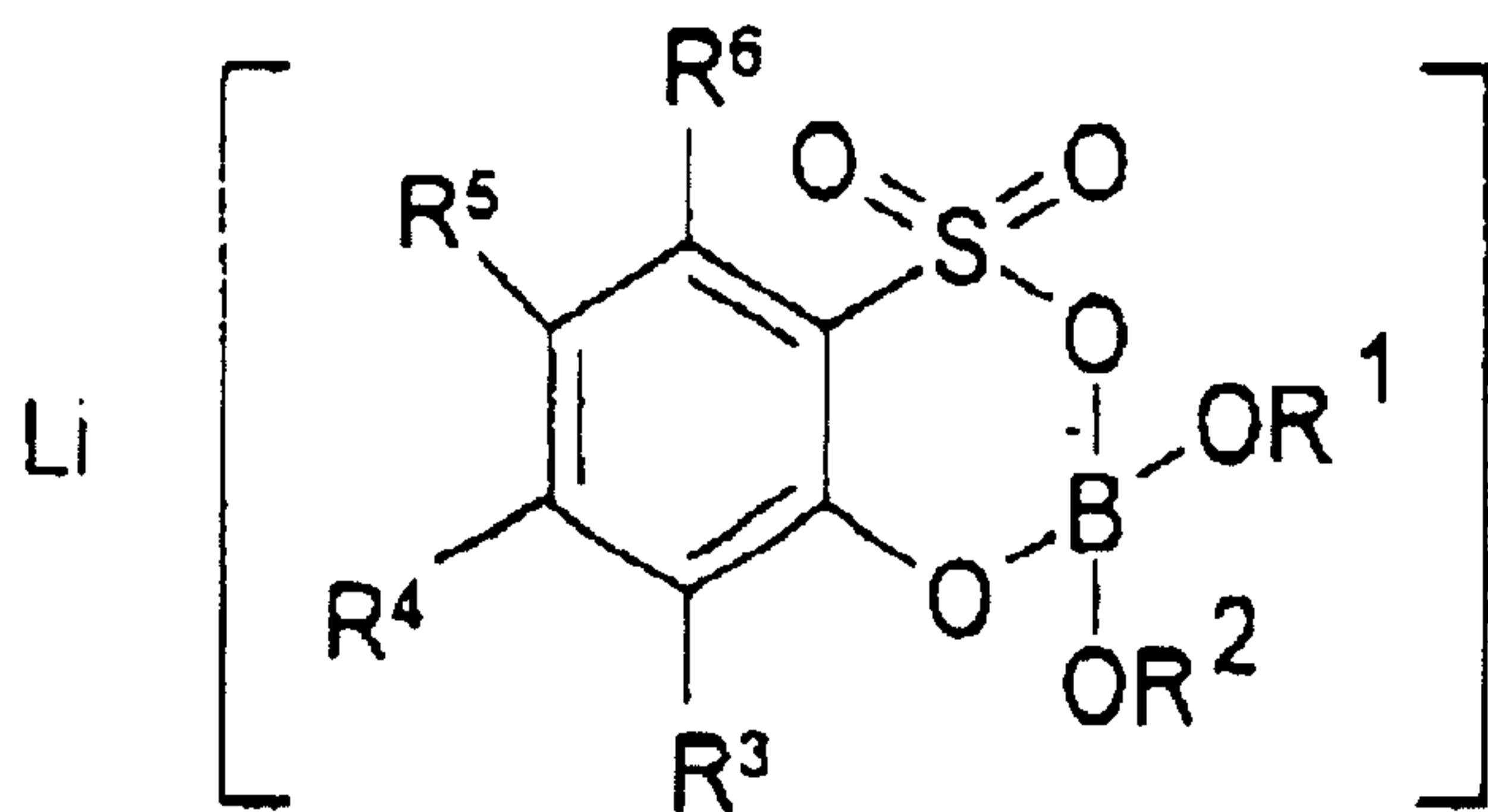
where

- 12 -

Kt, A, R¹, R², R³, k, l, x and y are as defined above, and

5 ⁻E is F⁻, Cl⁻, Br⁻, I⁻, BF₄⁻, ClO₄⁻, AsF₆⁻, SbF₆⁻ or PF₆⁻.

Lithium complex salts of the formula



where

10

R¹ and R² are identical or different, are optionally directly bonded to one another via a single or double bond, and are each, individually or together, an aromatic ring from the group consisting of phenyl, naphthyl, anthracenyl and phenanthrenyl, which may be
15 unsubstituted or mono- to hexasubstituted by alkyl (C₁ to C₆), alkoxy groups (C₁ to C₆) or halogen (F, Cl or Br),

20

or are each, individually or together, an aromatic heterocyclic ring from the group consisting of pyridyl, pyrazyl and pyrimidyl, which may be unsubstituted or mono- to tetrasubstituted by alkyl (C₁ to C₆), alkoxy groups (C₁ to C₆) or halogen (F, Cl or Br),

25

or are each, individually or together, an aromatic ring from the group consisting of hydroxybenzocarboxyl, hydroxynaphthalenecarboxyl, hydroxybenzosulfonyl and hydroxynaphthalenesulfonyl, which may be unsubstituted
30 or mono- to tetrasubstituted by alkyl (C₁ to C₆), alkoxy groups (C₁ to C₆) or halogen (F, Cl or Br),

- 13 -

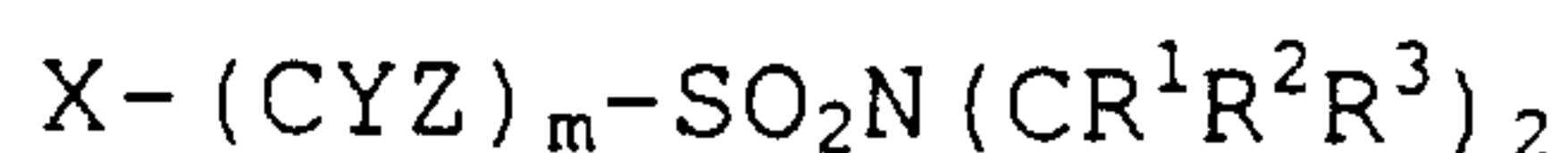
R^3-R^6 may each, individually or in pairs and optionally bonded directly to one another via a single or double bond, have the following meanings:

- 5 1. alkyl (C_1 to C_6), alkoxy (C_1 to C_6) or halogen (F, Cl or Br)
2. an aromatic ring from the groups consisting of
- 10 phenyl, naphthyl, anthracenyl and phenanthrenyl, which may be unsubstituted or mono- to hexasubstituted by alkyl (C_1 to C_6), alkoxy groups (C_1 to C_6) or halogen (F, Cl or Br),
- 15 pyridyl, pyrazyl and pyrimidyl, which may be unsubstituted or mono- to tetrasubstituted by alkyl (C_1 to C_6), alkoxy groups (C_1 to C_6) or halogen (F, Cl or Br),
- 20 which are prepared by the following process (DE 199 32 317):
- a) chlorosulfonic acid is added to 3-, 4-, 5- or 6-substituted phenol in a suitable solvent,
- 25 b) the intermediate from a) is reacted with chlorotrimethylsilane, and the product is filtered and subjected to fractional distillation,
- 30 c) the intermediate from b) is reacted with lithium tetramethoxyborate(1-) in a suitable solvent, and the end product is isolated therefrom,

may also be present in the electrolyte.

35

However, use can also be made of electrolytes comprising compounds of the general formula (DE 199 53 638)



- 14 -

where

X is H, F, Cl, C_nF_{2n+1} , C_nF_{2n-1} or $(SO_2)_kN(CR^1R^2R^3)_2$,

5 Y is H, F or Cl

Z is H, F or Cl

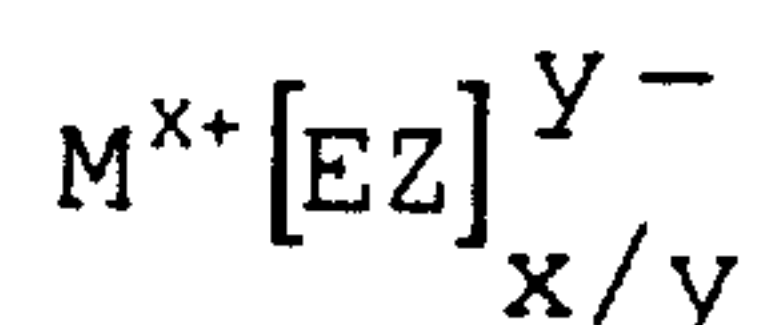
10 R^1 , R^2 and R^3 are H and/or alkyl, fluoroalkyl or cyclo-alkyl

m is 0-9 and, if $X = H$, $m \neq 0$

15 n is 1-9

k is 0 if $m = 0$ and $k = 1$ if $m = 1-9$,

20 prepared by reacting partially or perfluorinated alkylsulfonyl fluorides with dimethylamine in organic solvents, and complex salts of the general formula (DE 199 51 804)



25 in which

x and y are 1, 2, 3, 4, 5 or 6

30 M^{x+} is a metal ion

E is a Lewis acid selected from the group consisting of $BR^1R^2R^3$, $AlR^1R^2R^3$, $PR^1R^2R^3R^4R^5$, $AsR^1R^2R^3R^4R^5$ and $VR^1R^2R^3R^4R^5$,

35 R^1 to R^5 are identical or different, are optionally bonded directly to one another via a single or double bond, and each, individually or together, have the following meanings:

- 15 -

a halogen (F, Cl or Br),

an alkyl or alkoxy radical (C_1 to C_8), which can be partially or fully substituted by F, Cl or Br,

5

an aromatic ring, optionally bonded via oxygen, from the group consisting of phenyl, naphthyl, anthracenyl and phenanthrenyl, which may be unsubstituted or mono- to hexasubstituted by alkyl (C_1 to C_8) or F, Cl or Br,

10

an aromatic heterocyclic ring, optionally bonded via oxygen, from the group consisting of pyridyl, pyrazyl and pyrimidyl, which may be unsubstituted or mono- to tetrasubstituted by alkyl (C_1 to C_8) or F, Cl or Br, and

15

Z is OR^6 , NR^6R^7 , $CR^6R^7R^8$, OSO_2R^6 , $N(SO_2R^6)(SO_2R^7)$, $C(SO_2R^6)(SO_2R^7)(SO_2R^8)$ or $OCOR^6$, where

R^6 to R^8 are identical or different, are optionally bonded directly to one another via a single or double bond and are each, individually or together,

20

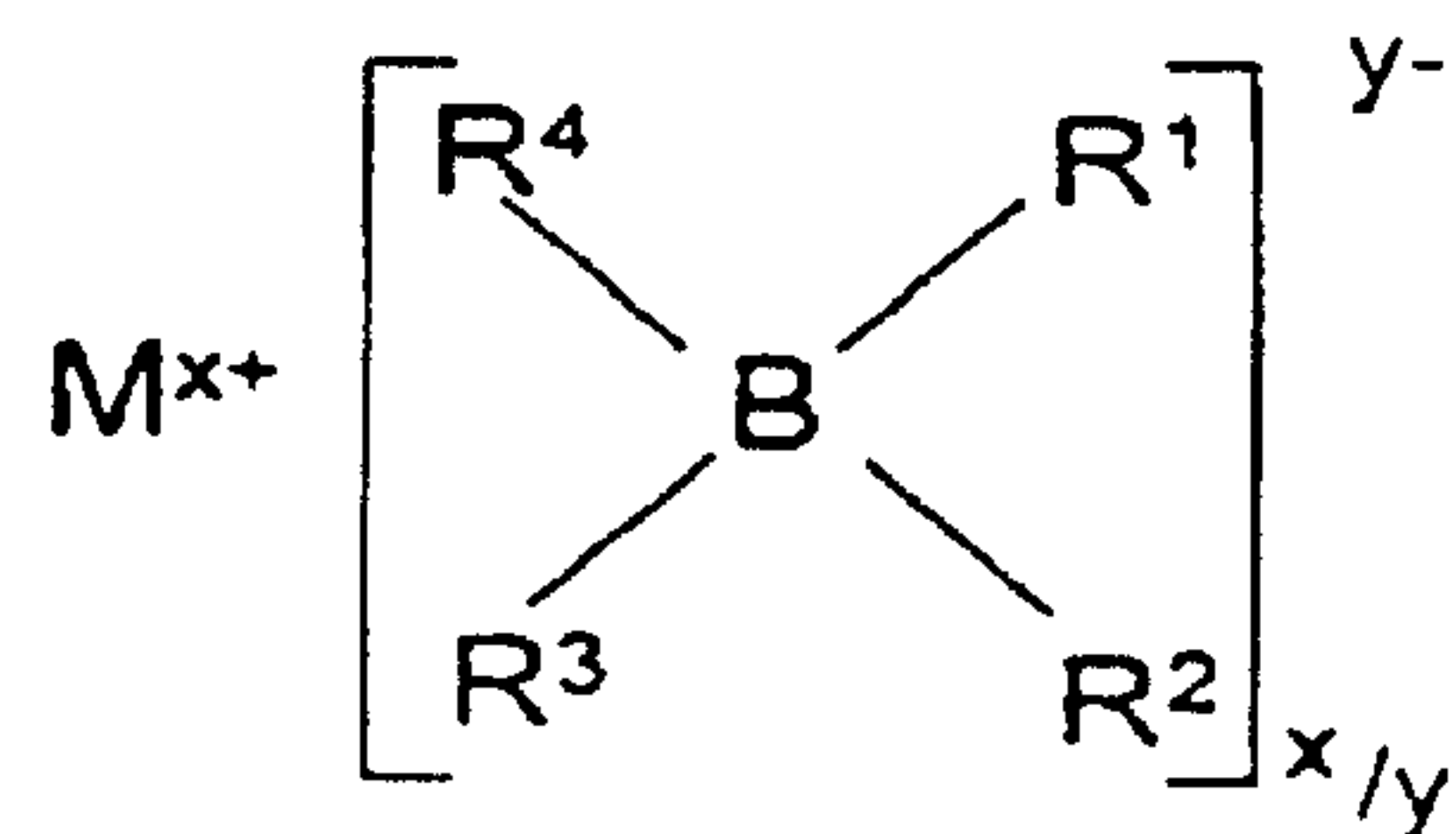
hydrogen or as defined for R^1 to R^5 ,

prepared by reacting a corresponding boron or phosphorus Lewis acid/solvent adduct with a lithium or tetraalkylammonium imide, methanide or triflate.

25

It is also possible for borate salts (DE 199 59 722) of the general formula

30



in which

M is a metal ion or tetraalkylammonium,

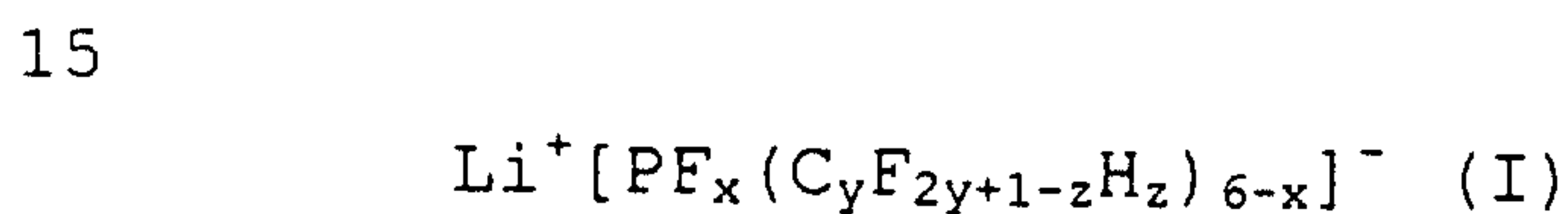
35

- 16 -

x and y are 1, 2, 3, 4, 5 or 6,

R¹ to R⁴ are identical or different and are alkoxy or carboxyl radicals (C₁-C₈), which are optionally bonded
 5 directly to one another via a single or double bond, to be present. These borate salts are prepared by reacting a lithium tetraalkoxyborate or a 1:1 mixture of lithium alkoxide with a borate in an aprotic solvent with a
 10 suitable hydroxyl or carboxyl compound in the ratio 2:1 or 4:1.

The compounds of the invention may also be used in electrolytes comprising lithium fluoroalkyl phosphates of the general formula (I)



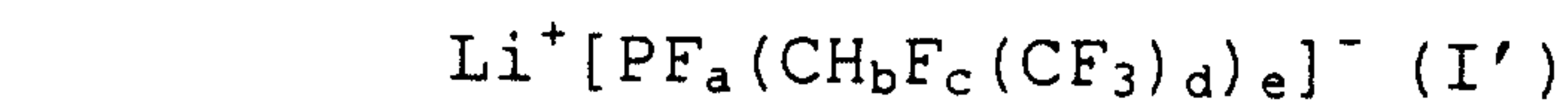
in which

20 $1 \leq x \leq 5$

$3 \leq y \leq 8$

$0 \leq z \leq 2y + 1$

25 and the ligands (C_yF_{2y+1-z}H_z) may be identical or different, with the exception of the compounds of the general formula (I'),

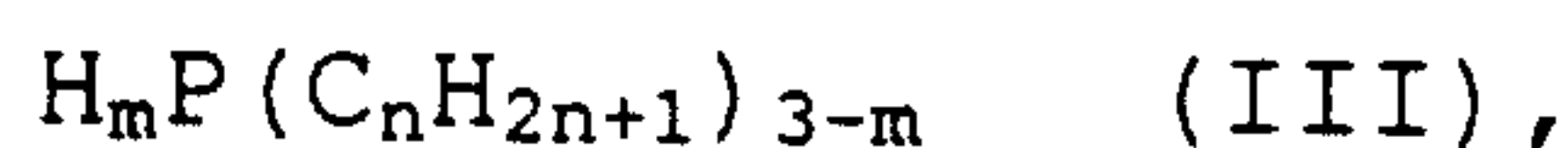


30 in which a is an integer from 2 to 5, b = 0 or 1, c = 0 or 1, d = 2 and

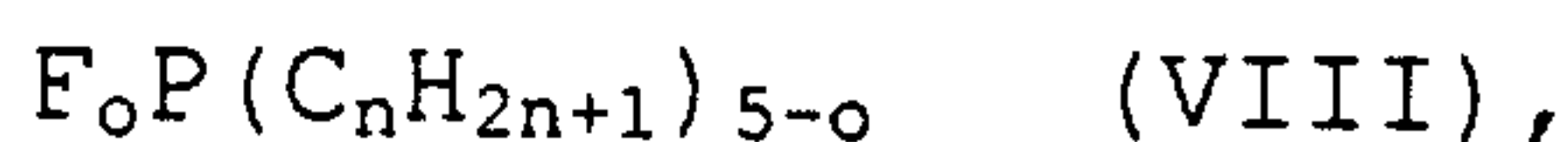
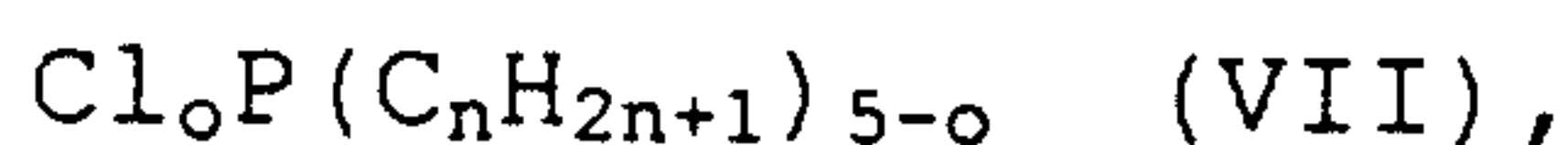
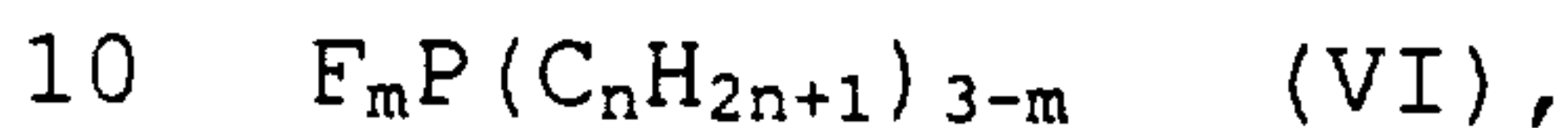
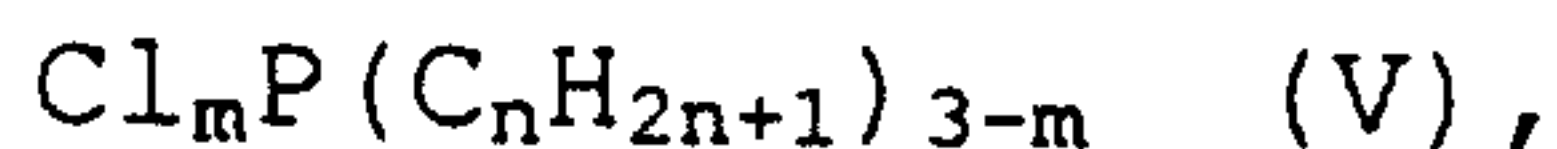
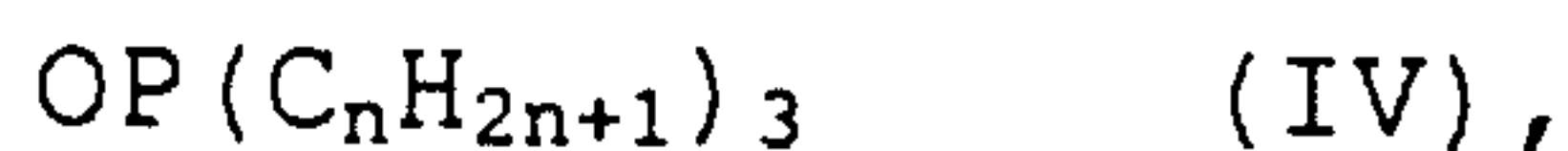
e is an integer from 1 to 4, subject to the conditions
 35 that b and c are not simultaneously each 0 and the sum of a + e is 6 and the ligands (CH_bF_c(CF₃)_d) may be identical or different (DE 100 089 55). The process for preparing lithium fluoroalkyl phosphates of the general

- 17 -

formula (I) is characterized in that at least one compound of the general formula



5



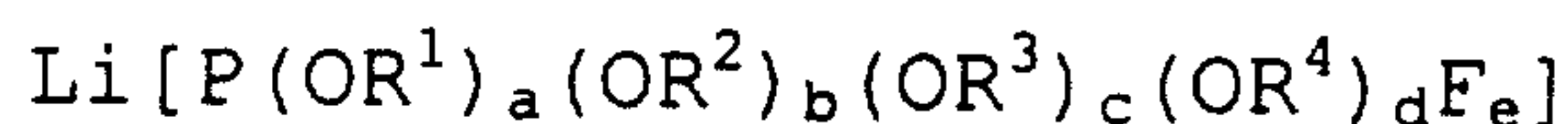
15

in each of which

$$0 < m < 2, \quad 3 < n < 8 \text{ and } 0 < o < 4,$$

20 is fluorinated by electrolysis in hydrogen fluoride, the mixture of fluorination products thus obtained is separated by extraction, phase separation and/or distillation, and the fluorinated alkylphosphorane thus obtained is reacted with lithium fluoride in an aprotic
25 solvent or solvent mixture in the absence of moisture, and the salt of the general formula (I) thus obtained is purified and isolated in accordance with the standard methods.

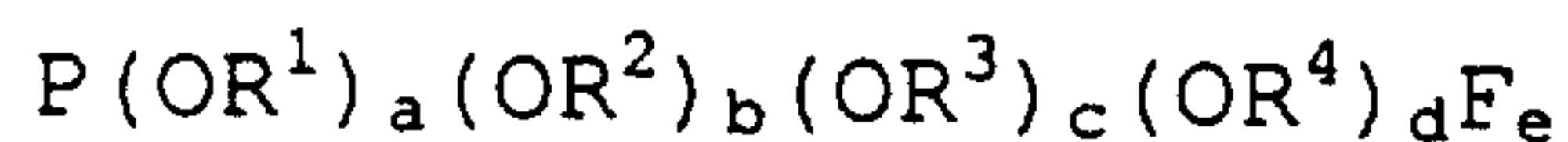
30 The compounds of the invention may also be used in electrolytes comprising salts of the formula



35 in which $0 < a+b+c+d \leq 5$ and $a+b+c+d+e = 6$, and R^1 to R^4 independently of one another are alkyl, aryl or heteroaryl radicals, it being possible for at least two of R^1 to R^4 to be connected to one another directly by a single or double bond (DE 100 16801). The compounds are

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prepared by reacting phosphorus(V) compounds of the general formula



5

in which $0 < a+b+c+d \leq 5$ and $a+b+c+d+e = 5$, and R^1 to R^4 are as defined above, with lithium fluoride in the presence of an organic solvent.

10 The compounds of the invention may be used in electrolytes for electrochemical cells comprising anode material comprising coated metal cores selected from the group consisting of Sb, Bi, Cd, In, Pb, Ga and tin or alloys thereof (DE 100 16 024). The process for
15 producing this anode material is characterized in that

a) a suspension or a sol of the metal or alloy core in urotropine is prepared,

20 b) the suspension is emulsified with C_5 - C_{12} hydrocarbons,

c) the emulsion is precipitated onto the metal or alloy cores, and

25

d) the metal hydroxides or oxyhydroxides are converted into the corresponding oxide by heat-treating the system. A general example of the invention is elucidated below.

30

Process for coating cathode materials

4 V cathode materials, especially materials with a layer structure (e.g. $Li(CoMe_2)O_2$ or $Li(Ni_{1-x-y}Co_xMe_y)O_2$)
35 and spinels (e.g. $Li(MnMe_2)_2O_4$), are placed in a vessel containing the polymer dissolved in an appropriate solvent. This suspension is stirred at temperatures of 10 - $100^\circ C$ for 1-10 hours. Subsequently, the solution is

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removed and the powder is dried at temperatures of 60-200°C.

Suitable polymers are the following: polyimide,
5 polyaniline, polypyrrole, polythiophene, polyacetylene,
polyacrylonitrile, carbonized polyacrylonitrile, poly-
p-phenylene, polyphenylenevinylene, polyquinoline,
polyquinoxalines, polyphthalocyaninesiloxane, poly-
vinylidene fluoride, polytetrafluoroethylene, polyethyl
10 methacrylate, polymethyl methacrylate, polyamides,
vinyl ether copolymers, cellulose, polyfluoroethylene,
polyvinyl alcohol and polyvinylpyridine, and
derivatives thereof.

15 Solvents used are in principle all solvents which
dissolve the polymers, preferably non-aqueous solvents.
Suitable solvents are, for example, methylene chloride,
ethylene chloride, chloroform, tetrachloroethane,
tetrahydrofuran, dioxane, acetophenone, cyclohexanone,
20 γ -butyrolactone, dimethylformamide, dimethylacetamide,
N-methylpyrrolidone and carbonates.

In order to ensure that the polymer in the solution is
adsorbed by the surface of the powder particles, the
25 suspension is stirred at a temperature of 10-100°C for
a period, preferably 1-10 hours. Subsequently, the
solution is removed and the powder obtained is dried
(evaporation of the solvent).

30 The particles can be given one or more coats. If
desired, the first coating can be carried out with a
polymer and the next coating with another polymer.

The examples below are intended to illustrate the
35 invention in greater detail, but without representing a
limitation.

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ExamplesExample 1

- 5 Process for coating cathode materials with polymers.

50 ml of NMP are placed in a 100 ml round-bottomed flask. Subsequently, 1 g of Matrimid 5218[®] is added and dissolved with stirring. Then 10 g of lithium manganese spinel, SP30 Selectipur[®] from Merck, are added. The
10 resulting suspension is stirred at room temperature for about 1.5 hours. The suspension is filtered off through a white ribbon filter and dried to constant mass in a drying oven at temperatures of 60°C - 150°C.

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Example 2

Cycling at high temperatures

- 20 The coated cathode powder prepared as described in Example 1 and, as comparison, an uncoated material SP30 Selectipur[®] from Merck are cycled at 60°C.

In order to produce the electrodes, the cathode powder
25 is mixed well with 15% of conductive black and 5% of PVDF (binder material) and NMP. The paste prepared in this way is applied to a VA steel mesh serving as collector and dried overnight at 175°C under an argon atmosphere and under reduced pressure. The dried
30 electrode is introduced into the argon-flushed glove box via the lock and installed in the measurement cell. The counterelectrode and reference electrode are lithium metal. The electrolyte used is LP 30 Selectipur[®] from Merck (1M LiPF₆ in EC:EMC 50:50% by
35 weight). The measurement cell with the electrodes and the electrolyte is placed in a steel container, which is sealed in a gas-tight manner. The cell produced in this way is removed from the glove box via the lock and placed in a climate-controlled cabinet set to 60°C.

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After the measurement cell has been connected to a potentiostat/galvanostat, the electrode is cycled (charging for 5 hours, discharging for 5 hours).

- 5 The result is that the cycle stability of the uncoated spinel is lower than that of the coated spinel.

10 In the first 5 cycles, irreversible reactions take place, such as, for example, film formation on the negative and anodes, meaning that they cannot be employed for the calculation. The loss in capacity per cycle of the uncoated spinel is then 0.78 mAh/g, while the polymer-coated spinel only loses 0.55 mAh/g per cycle. The loss in capacity per cycle is reduced by
15 about one third. This shows that the high-temperature cycle stability of the cathode powder is significantly improved by coating with polymers.

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Patent Claims

1. Lithium mixed oxide particles, characterized in that they are coated with one or more polymers.
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2. Lithium mixed oxide particles according to Claim 1, characterized in that the particles are selected from the group consisting of $\text{Li}(\text{MnMe}_z)_2\text{O}_4$, $\text{Li}(\text{CoMe}_z)\text{O}_2$, $\text{Li}(\text{Ni}_{1-x-y}\text{Co}_x\text{Me}_y)\text{O}_2$ and other lithium intercalation and
10 insertion compounds.
3. Lithium mixed oxide particles according to Claim 1 or 2, characterized in that the polymers are acid stable, electrochemically stable, polar, ideally basic,
15 at least neutral, and/or aprotic.
4. Lithium mixed oxide particles according to one of Claims 1 to 3, characterized in that the layer thicknesses of the polymers are 0.01-50 μm .
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5. Lithium mixed oxide particles according to one of Claims 1 to 4, characterized in that the layer thicknesses of the polymers are 0.05-3 μm .
- 25 6. Cathodes essentially consisting of lithium mixed oxide particles according to one of Claims 1 to 5 and conventional support materials and auxiliaries.
7. Process for the preparation of lithium mixed oxide
30 particles coated with one or more polymers, characterized in that the particles are suspended in a solvent, and the coated particles are then filtered off, dried and optionally calcined.
- 35 8. Process for the preparation of lithium mixed oxide particles coated with one or more polymers, characterized in that the polymers are selected from the group consisting of polyimides, polyanilines,

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polypyrroles, polythiophenes, polyacetylenes, polyacrylonitriles, carbonized polyacrylonitriles, poly-p-phenylenes, polyphenylenevinylenes, polyquinolines, polyquinoxalines, polyphthalocyaninesiloxanes, polyvinylidene fluorides, polytetrafluoroethylenes, polyethyl methacrylates, polymethyl methacrylates, polyamides, vinyl ether copolymers, cellulose, polyfluoroethylenes, polyvinyl alcohols and polyvinylpyridines, and derivatives thereof.

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9. Process for the preparation of lithium mixed oxide particles coated with one or more polymers, characterized in that the polymer is 5-(6)-amino-1-(4'-aminophenyl)-1,3-trimethylindane.

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10. Process for the preparation of lithium mixed oxide particles coated with one or more polymers, characterized in that the solvents are methylene chloride, ethylene chloride, chloroform, tetrachloroethane, tetrahydrofuran, dioxane, acetophenone, cyclohexanone, γ -butyrolactone, dimethylformamide, dimethylacetamide, N-methylpyrrolidone and/or carbonates.

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11. Use of coated lithium mixed oxide particles according to one of Claims 1 to 5 for the production of cathodes having an improved shelf life and cycle stability, in particular at temperatures above room temperature.

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12. Use of coated lithium mixed oxide particles according to one of Claims 1 to 5 for the production of 3 V and 4 V cathodes.

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13. Use of coated lithium mixed oxide particles according to one of Claims 1 to 4 in electrodes for electrochemical cells, supercapacitors, batteries and secondary lithium batteries.

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